POLYELECTROLYTES

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PREFACE

The main purpose of this monograph is to present a theoretical analysis of the property of polyelectrolytes. Polyelectrolytes exhibit various interesting phenomena because of their dual character as highly charged electrolytes and flexible chain molecules. Very low ionic activity and extreme sensitivity of molecular conformation to the ionic condition, for example, have strongly attracted people in the field of physical chemistry of electrolytes and polymers.

In the past twenty years, most of those phenomena have become theoretically understandable. Idealized treatment based on the simplest model has been found to be very useful to extract essential features of polyelectrolytes. In this sense, the theory of polyelectrolytes yields an excellent example in which the theory is highly evaluated in its intrinsic function.

Therefore, in this monograph I have tried to draw a unified picture of "the polyelectrolytes" on the basis of fundamental laws of statistical thermodynamics without complex mathematics and detailed chemistry. Experimental data are chosen only for this purpose and efforts are made for visualizing the theoretical results. Great care is given to making up a consistent framework of the theory for comprehending polyelectrolytes as a whole.

Accordingly, this monograph is far from a full description of past experimental and theoretical works on polyelectrolytes. As shown in the Contents, the problems treated are very limited. Emphasis is placed on thermodynamic equilibrium properties. Dynamic behaviors of polyelectrolytes are not much discussed except in a few sections. Nevertheless, it is hoped that this monograph can give enough basic knowledge on the possible sources of various characteristics of polyelectrolytes.

Biological systems such as muscle, membranes, and protoplasm in general may be regarded as organized polyelectrolytes. Some of their properties can be understood from this standpoint, and others can not. The theory of polyelectrolytes must be extended in this direction. This monograph is expected to present a base for such extension.

Description of this monograph is made mainly along the line of the study developed in the group of polymer physics and molecular biology in Faculty of Science of Nagoya University. I wish to express sincere thanks to all colleagues in this group, particularly to Dr. N. Imai for his long collaboration. Stimulating discussions with him have enabled me to continue the work on polyelectrolytes. Drs. S. Asakura, A. Ikegami, and A. Minakata in this group also have made fine contributions in this field and given me useful suggestions.

I was originally initiated into the field of polyelectrolytes by Professor I. Kagawa in Faculty of Engineering of this University, who made pioneering works on polyelectrolytes in Japan and proposed very early the idea of the counter ion condensation. Professor M. Nagasawa in the same Faculty has led me to theoretical analyses by giving beautiful experimental results. To these researchers I wish to express sincere thanks.

Publication of this monograph was made possible by critical reading of the manuscript by Professor J. Marinsky. I am very grateful to him.

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Chapter 1

INTRODUCTION

I. CHARACTERIZATION OF POLYELECTROLYTES

Polyelectrolytes are macromolecules having many ionizable groups. In solution they are dissociated into polyvalent macroions (polyions) and a large number of small ions of opposite charge (counter ions). The high charge of the macroion produces a strong electric field which attracts these counter ions. This strong electric interaction between the polyvalent macroion and counter ions is a source of the characteristic properties of polyelectrolytes. The activity coefficient of counter ions is very low even at low concentrations of polyelectrolytes, and the dielectric constant of polyelectrolyte solutions is extremely large.

The electrical effect of the highly charged macroion is expected to be screened when an increasing concentration of small ions is introduced, e.g., by the addition of simple electrolytes. Experiments, however, lead to a simple empirical law which describes the thermodynamic and transference properties of polyelectrolyte—simple electrolytes mixtures as a superposition of the contributions of ions from polyelectrolyte and the simple electrolytes. This result is also attributable to the characteristic interaction between the polyvalent macroion and small ions.

As in the case of nonelectrolytic macromolecules, the morphology of polyvalent macroions is one of the central problems of polyelectrolytes. Most of the macroions are long flexible chains having a large extension in solution. Their size and shape depend on the charge and the interaction with counter ions. With increasing charge, the flexible chain changes its shape from a contracted random coil to a fully extended one. This correlation between the shape or the conformation and the electric state is another source of the characteristic properties of polyelectrolytes. Some of the macroions can form regular sstructures, for example, helical ones, by specific intrachain and/or interchain binding. In this case, the idea of the discrete states of macroions is introduced and the transition between them can be analyzed as another example of the morphology of polyelectrolytes.

The coupling between the conformation and the electric state at the molecular level is organized into typical systems of energy transformation or information transduction when polyelectrolytes make higher order structures. The polyelectrolyte gel, as is well known, can be a transformer of chemical energy to mechanical work.

The effect of interactions among ionized groups, counter ions, and solvent molecules is amplified by the high charge density of the macroion. A small difference in the interaction may have great influence on the properties of polyelectrolytes. Therefore, polyelectrolytes are most sensitive to structure and environment. The complete selective binding of polyvalent counter ions by the macroion and the sensitive insolubilization of the macroion by specific small ions are examples of the result of such amplification. The analysis of structure- and enviro-sensitive properties from this standpoint is a method of approaching the complicated problem of the origin of polyelectrolyte specificity.

Systematic studies of synthetic polyelectrolytes, whose chemical structures are well defined through their controlled construction from repeating units, have been made. A simplified model, a flexible chain with many charges, is in most cases an appropriate base for the theoretical interpretation of properties common to various polyelectrolytes. The main purpose of this monograph is to develop the theory by using a simplified model to which idealization and approximation will be freely applied, if they appear to be useful, in order to reach an understanding of the fundamental nature of polyelectrolytes. It is intended here to treat the electrostatics, thermodynamics, and morphology of polyelectrolytes systematically. A consistent picture of polyelectrolytes will be obtained by elucidating the interrelation among various characteristic properties. Limited reference to experimental and theoretical results obtained with different polyelectrolytes by various researchers will be made only to facilitate this objective.

Another aim of this monograph is to provide insight with regard to the biological functions of natural polyelectrolytes such as proteins and nucleic acids (biopolymers). The polyelectrolyte properties of biopolymers are expected to be in the background of various biological phenomena.

II. CHEMICAL STRUCTURE

Several examples of the chemical structure of the simplest polyelectrolytes are given in Fig. 1. The first of these, polyvinyl sulfonic acid, is shown to be completely dissociated into macroions having many negative charges and hydrogen ions when dissolved in water. In the second example, polyacrylic acid, a macromolecule most frequently used in experimental investigations of polyelectrolytes, the degree of dissociation of the carboxyl groups is small in pure water. On the addition of alkali, e.g., sodium hydroxide, the carboxyl groups are dissociated and the macroion gains an increasing number of negative charges, producing sodium counter ions. The number of dissociated groups or charges depends on the amount of added alkali and is reflected in the pH value of the solution. Accordingly, the chemical structure of the macroion in the solution may be expressed as a copolymer of monomers having COOH groups and COO^- groups. At a given pH value and concentration of macroions, only the average proportion of these groups is determined and the solution is a mixture of macroions that have different distributions of two thermally fluctuating groups. When alkali equimolar to the acidic groups is added, the sodium polyacrylate macroions in the resulting solution are almost fully dissociated.

The third example in Fig. 1 is a copolymer of two kinds of monomers, vinyl alcohol and acrylic acid. The latter monomer is charged by the addition of a sufficient amount of alkali. The number of charges per macroion is regulated by the ratio of the two kinds of monomer in the copolymer. In this case the distribution of charged groups in each copolymer is determined by its original chemical structure.

The stereoregularity coming from the arrangement of neighboring monomers is also a factor in polyelectrolytes; e.g., in the case of polymethacrylic acid, isotactic, syndiotactic, and atactic polyacids are distinguished by their structure and properties.

The fourth example of chemical structure presented in Fig. 1 is the polybase, polyvinyl-*N*-*n*-butylpyridiniumhydroxide, which is positively charged by the addition of acid

The next two examples in Fig. 1 are the polypeptides, polyglutamic acid and polylysine. They contain optically active carbon and can be composed of two kinds of monomer, *l*-amino acid and *d*-amino acid. As a consequence, poly-*l*-amino acid must be distinguished from the copolymer poly-*d*-*l*-amino acid. Proteins are generally copolymers of various kinds of *l*-amino acids. They have both positive and negative charges on side chains.

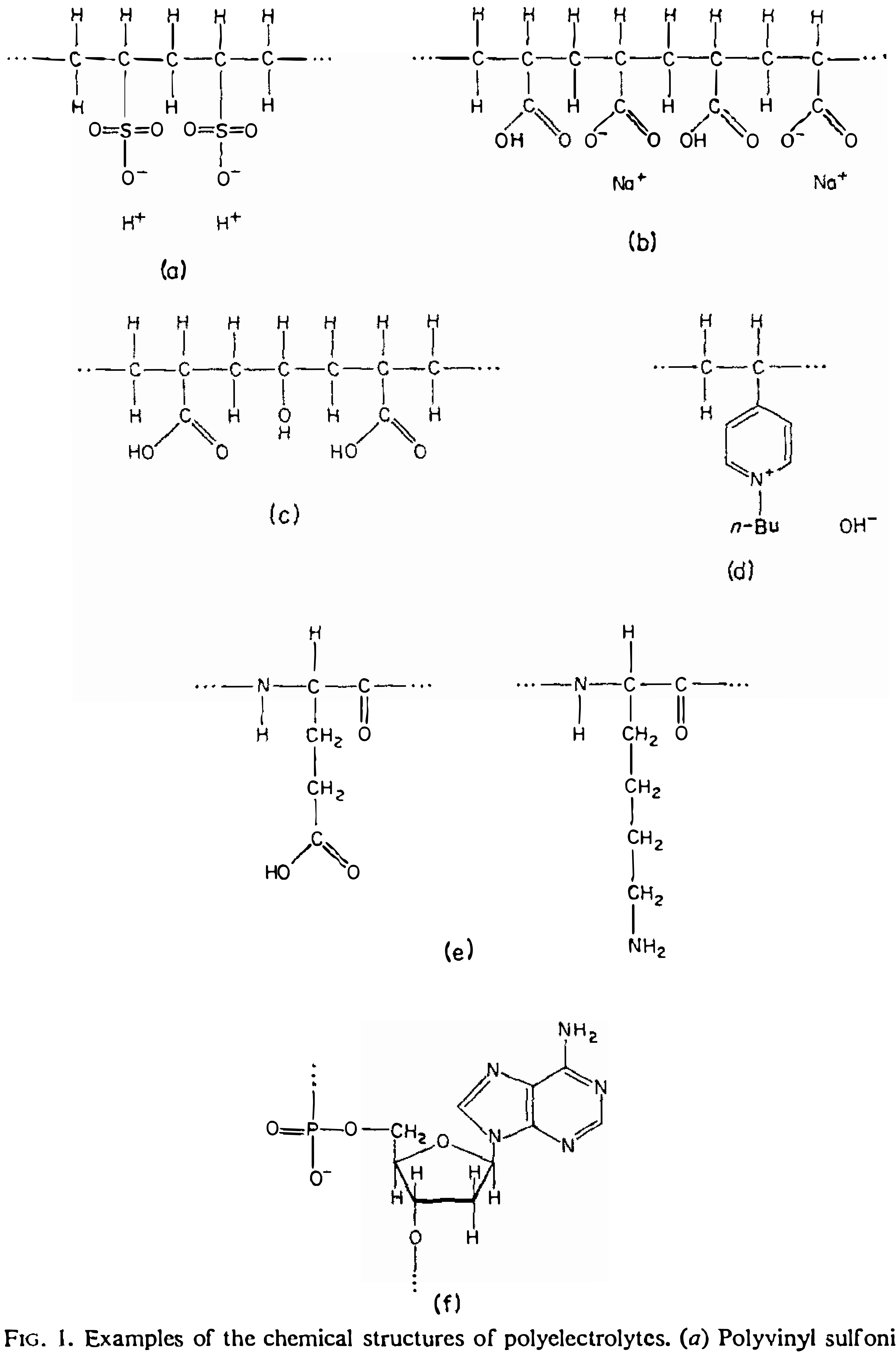


FIG. 1. Examples of the chemical structures of polyelectrolytes. (*a*) Polyvinyl sulfonic acid; (*b*) Polyacrylic acid partially neutralized by sodium hydroxide; (*c*) Copolymer of acrylic acid and vinyl alcohol; (*d*) Poly-*N*-*n*-butyl pyridinium hydroxide; (*e*) Polyglutamic acid and polylysine; (*f*) Deoxyribonucleic acid neutralized.

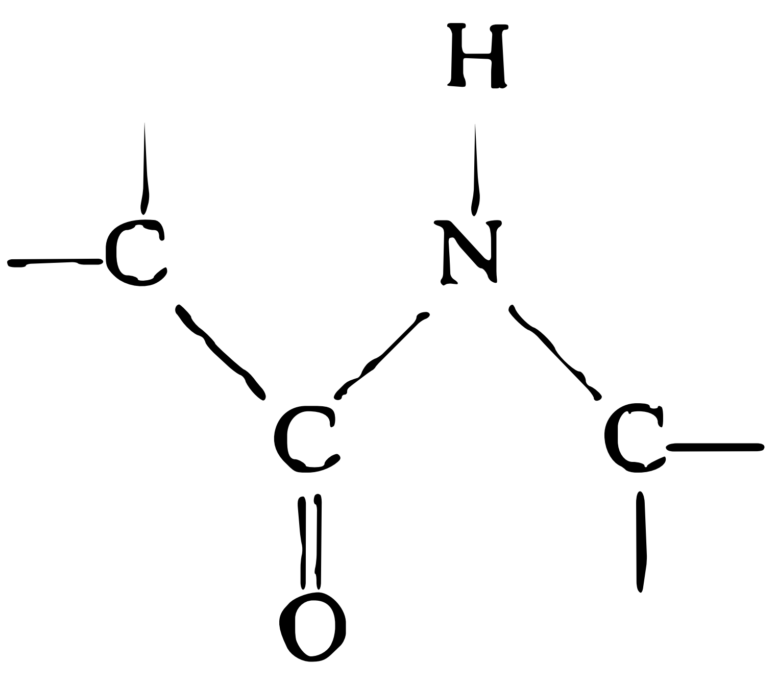
The last example in Fig. 1 presents the chemical structure of a natural polyelectrolyte, deoxyribonucleic acid (DNA), a polynucleotide in which the main chain is formed from the repetition of a definite unit and each side chain has one of four kinds of base.

The degree of polymerization, i.e., the number of monomers in a polyelectrolyte molecule, is usually 10^2 to 10^4 but may be more. In some cases the degree of polymerization is continuously controlled from the monomer limit to almost infinity. With synthetic polyelectrolytes, however, it is almost impossible to obtain a solution of polyelectrolyte in which all macroions have the same degree of polymerization and the same chemical structure. On the other hand, with natural polyelectrolytes, such as purified protein, all solute macroions may have the same chemical structure.

The length of each monomer along the chain is about 2.5 Å in the first example of Fig. 1. Since the radius of each atom in the main chain is of the order of 1 Å, the main chain is apparently a flexible cylinder as shown in Fig. 2 for models of polyacrylic acid and DNA. When the side chain of ionizable groups is short, the macroion looks like a cylinder having many charges on its surface. When it is long, the macroion looks like a cylinder having short branches from the surface, the ends of which are charged.

III. Physical Model

The flexibility of the macroion comes from the freedom of the internal rotation of bonds in the main chain. In the first example of Fig. 1 each bond, as is well known, can rotate around the neighboring bond, keeping the bond angle constant. The intrinsic free energy of the rotation is a function of the relative position of three neighboring bonds. Usually there are three energy minima, one at the *trans* (T) position and two at the *gauche* (G) positions. The difference in energy between the *trans* position, corresponding to the stretched form of the chain, and the *gauche* positions, corresponding to the contracted form, is a most important factor on determining the flexibility of the chain.



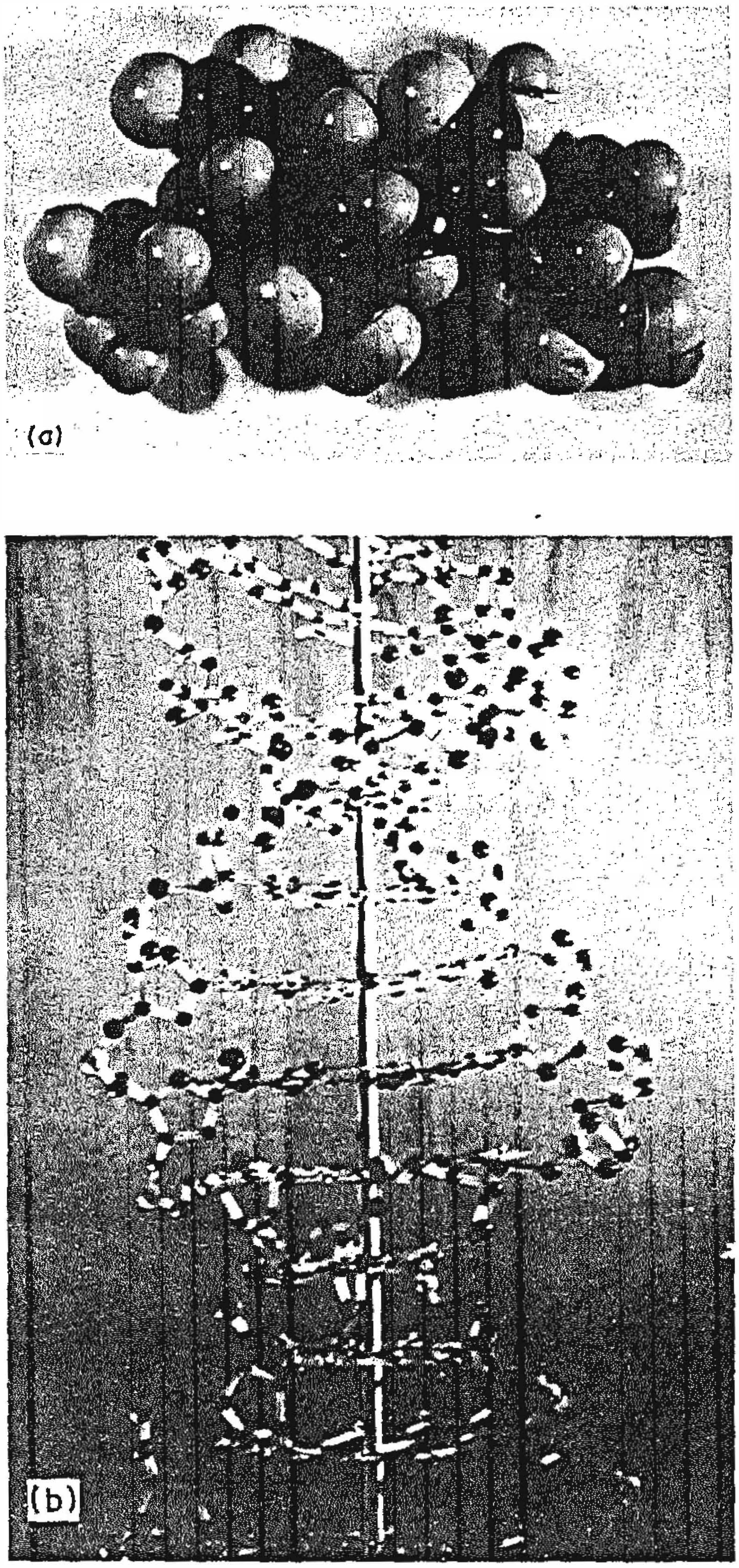


FIG. 2. Examples of three-dimensional structures of polyelectrolytes. (*a*) Polyacrylic acid; (*b*) Deoxyribonucleic acid.

In polypeptides the four neighboring atoms along the main chain must lie in the same plane. Rotation is possible only around the two kinds of bonds. The polypeptides are regarded as a series of planes linearly connected with two freedoms of rotation.

The macroion as a flexible chain thus has an extremely large number of possible conformations that are specified by a series of variables designating the rotation angles of neighboring bonds. The free energy of each conformation is determined not only by the intrinsic free energy of the rotation but also by the interaction among side chains, main chains, and solvent molecules or ions. The conformation of such a chain has two classifications, random coil and helix. In the random coil the series of rotation angles of successive bonds specifying the conformation has no long range regularity, i.e., there is no regular repetition of a certain angle or angles. The mean square of the end-to-end distance of the chain is proportional to the number of monomers if the number is sufficiently large, independent of the flexibility of the chain. In the helix, the series of rotation angles has a long range regularity; there is a repetition of an angle or angles. The mean end-to-end distance is directly proportional to the number of monomers.

In the case of the random coil, there are usually a number of conformations having equal or approximately equal free energies. Each chain assumes these conformations from time to time. The two kinds of conformation, random coil and helix, are illustrated in Fig. 3*a*, *b*, and *c*. The random coil in Fig. 3*a* is only one of the many equally possible conformations. The rapid transformation among these conformations is an essential property of the random coil. The number of equally possible conformations and the rate of the transformation are determined by the structure of the chain and the environmental condition.

The random coil conformation does not necessarily refer to a spherically contracted state of the chain. Extended and contracted states fit in the random coil category if there are no regularly repeated structures. Actually charged macroions can assume various random coil conformations over a wide range of extension, depending on the charge and the environment. At extremely high charges they may take a rodlike or cylindrical conformation. At low charge or in the absence of charge, they take a spherical conformation. The spherical random coil can have a wide range of the apparent radius. For example, polyacrylic acid, whose degree of polymerization is 1000, takes a spherical random coil form with a radius of about 200 Å at low pH. With increasing pH, the macroion extends first spherically and then becomes rodlike. Its eventual length is 2500 Å in its most stretched form. The average local curvature of the chain decreases gradually, as shown in Fig. 3*d*.

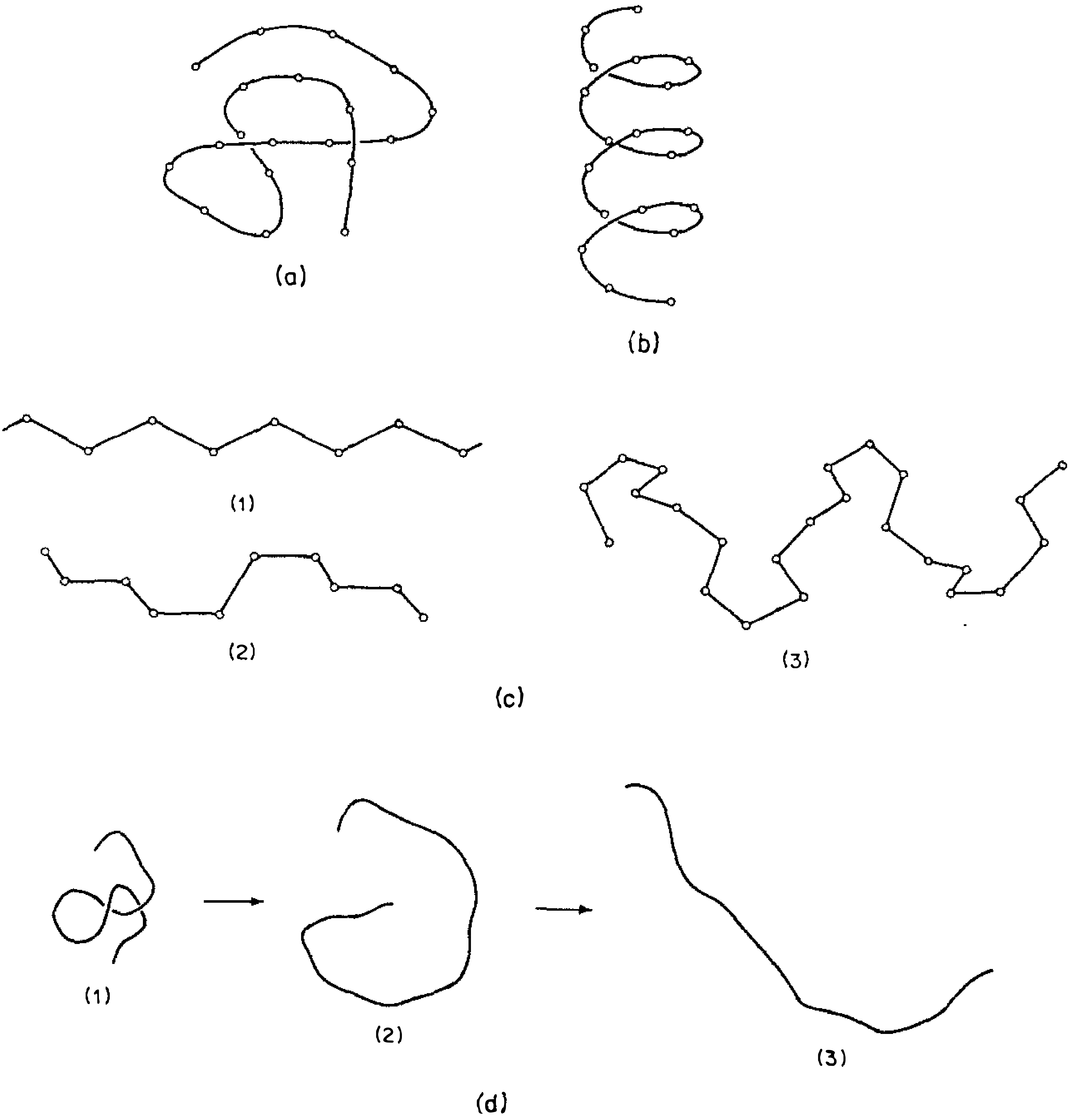


FIG. 3. Different conformations of linear chainlike macroions. (*a*) Random coil; (*b*) Helix; (*c*) Different helical conformations expressed by sequences of internal rotation angles; (1) TTT..., (2) TGTG..., (3) TGGTGG...; (*d*) deformation of contracted random coil to extended one.

IV. Electrical Potential around the Macroion

Let us consider a macroion in the spherical random coil conformation. Many discrete charges are distributed on the macroion as shown in Fig. 4a. Each of them is the source of an electric field. The resultant field in and around the macroion is given by the superposition of contributions from these charges, if the contribution from counter ions is neglected.

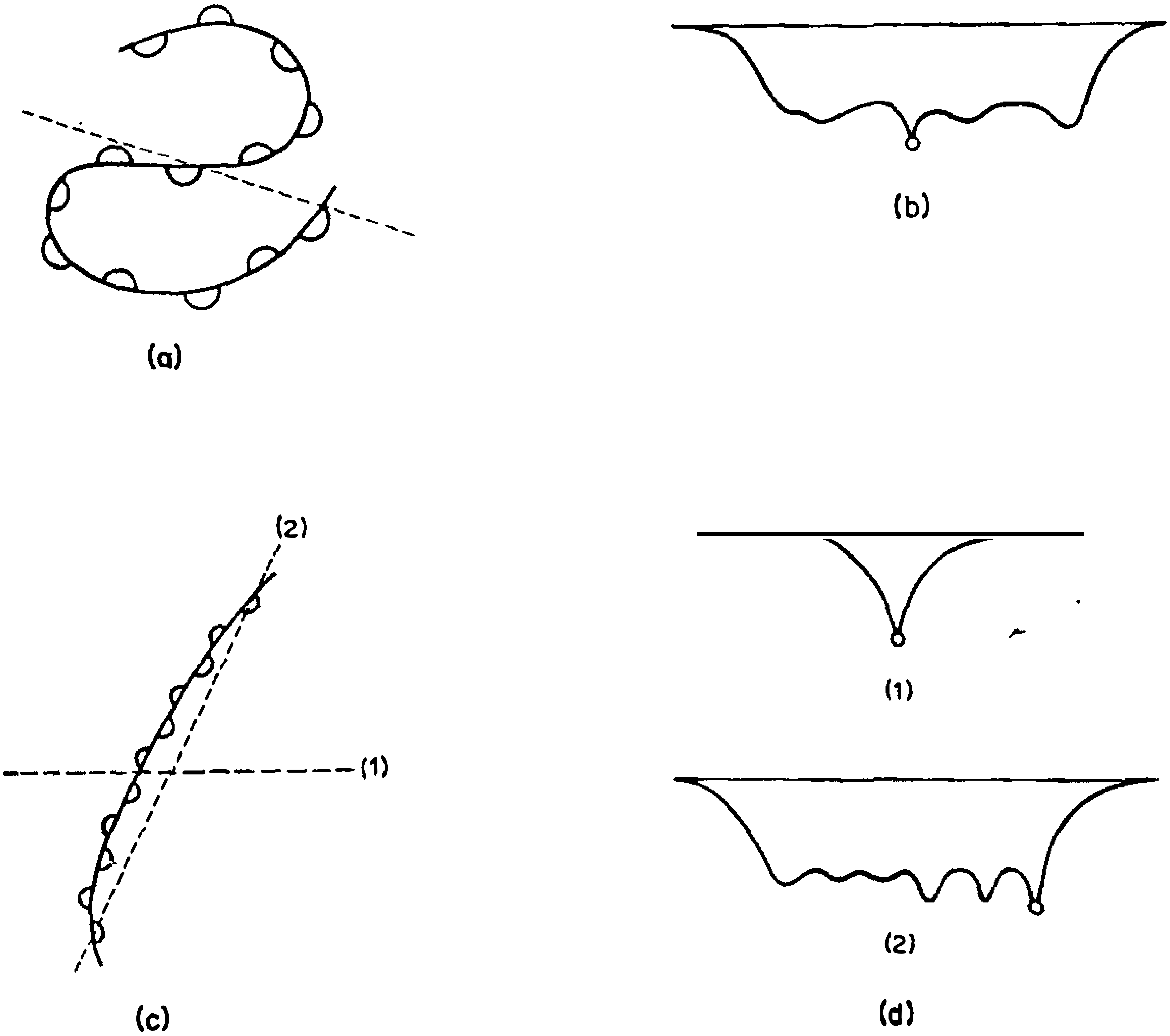


Fig. 4. (*a*) A spherical macroion with charged groups. (*b*) The potential profile along a line crossing the volume occupied by the spherical macroion. (*c*) A cylindrical macroion with charged groups. (*d*) The potential profiles along the lines crossing the volume occupied by the cylindrical macroion; (1) perpendicular to the cylinder, (2) along the cylinder.

The profile of the potential along a line passing through the macroion is shown in Fig. 4*b*. At a point where the line passes a charge, the potential curve has a deep and sharp hole. The potential curve in and near the region occupied by the random coil has the form of a trough as a result of the superposition of many such holes. The slope of the curve in the trough is rather gradual. Beyond the region occupied by the random coil there is a sharp rise in the potential. The potential profile is well represented by a trough with many holes.

The potential profile of an extended rodlike macroion of Fig. 4*c* is shown in Fig. 4*d*. Along a line parallel to the rod, the potential takes the form of a trough with sharp holes; along a line perpendicular to the rod it has a deep valley at the position of the rod.

Let us suppose that a random coil occupies a spherical volume v of radius a. If n ionized groups of the charge $-e_0$ are uniformly distributed in this volume, the potential drop at the edge is given by $ne_0/\varepsilon_0 a$, where ε_0 is the dielectric constant of the solvent. The ratio of the potential energy of a charge $+e_0$ at the edge to the kinetic energy kT is $ne_0{}^2/\varepsilon_0 akT$. If the fully neutralized polyacrylic acid ion with a degree of polymerization of 1000, the length of which is about 2500 Å in the most stretched state, is coiled into a sphere with a radius of 200 Å, the value of the above ratio is of the order of 35 in water at room temperature. Many counter ions are consequently forced to enter into the spherical region of the potential trough. As counter ions enter into the sphere, the potential drop is decreased by the cancellation of the charge. However, even with 90% of the counter ions in the sphere and 10% of the charge remaining uncancelled, the potential drop is still larger than the kinetic energy, the value of the ratio being about 3.5. The number of counter ions in the central region of the spherical trough is larger than the number at the peripheral region. The base of the potential trough thus becomes flatter and the potential drop at the edge becomes better defined when the presence of counter ions is taken into account.

A similar examination can be made of the rodlike macroion. If n charged groups are uniformly distributed on a rod of length l and radius a, the potential drop from the distance R to the surface a of the rod is given by $2(ne_0/\varepsilon_0 l) \ln (R/a)$, if $l > R \gg a$. The ratio of the potential energy to the kinetic energy is equal to $2(ne_0{}^2/\varepsilon_0 kTl) \ln (R/a)$. If $n = 1000$, $l = 2500$ Å, and $R/a = 100$, this ratio is about 26 in water at room temperature. Most of the counter ions must be bound to the rod.

For a macroion in the coiled conformation, the most realistic features of the potential which is derived from the model are as follows. Each charged group makes a sharp and deep potential hole at its position. Each linear part of the chain makes a sharp and deep potential valley along its length, as shown in Fig. 5. The coiled chain as a whole makes a (spherical) potential trough in its apparent volume. The whole volume of the solution is divided into four potential regions; holes at charged groups, the cylindrical valley along the chain of the macroion, the spherical trough in the apparent volume occupied by the macroion, and the region outside the macroion. A macroion in the extended conformation has no spherical potential trough.

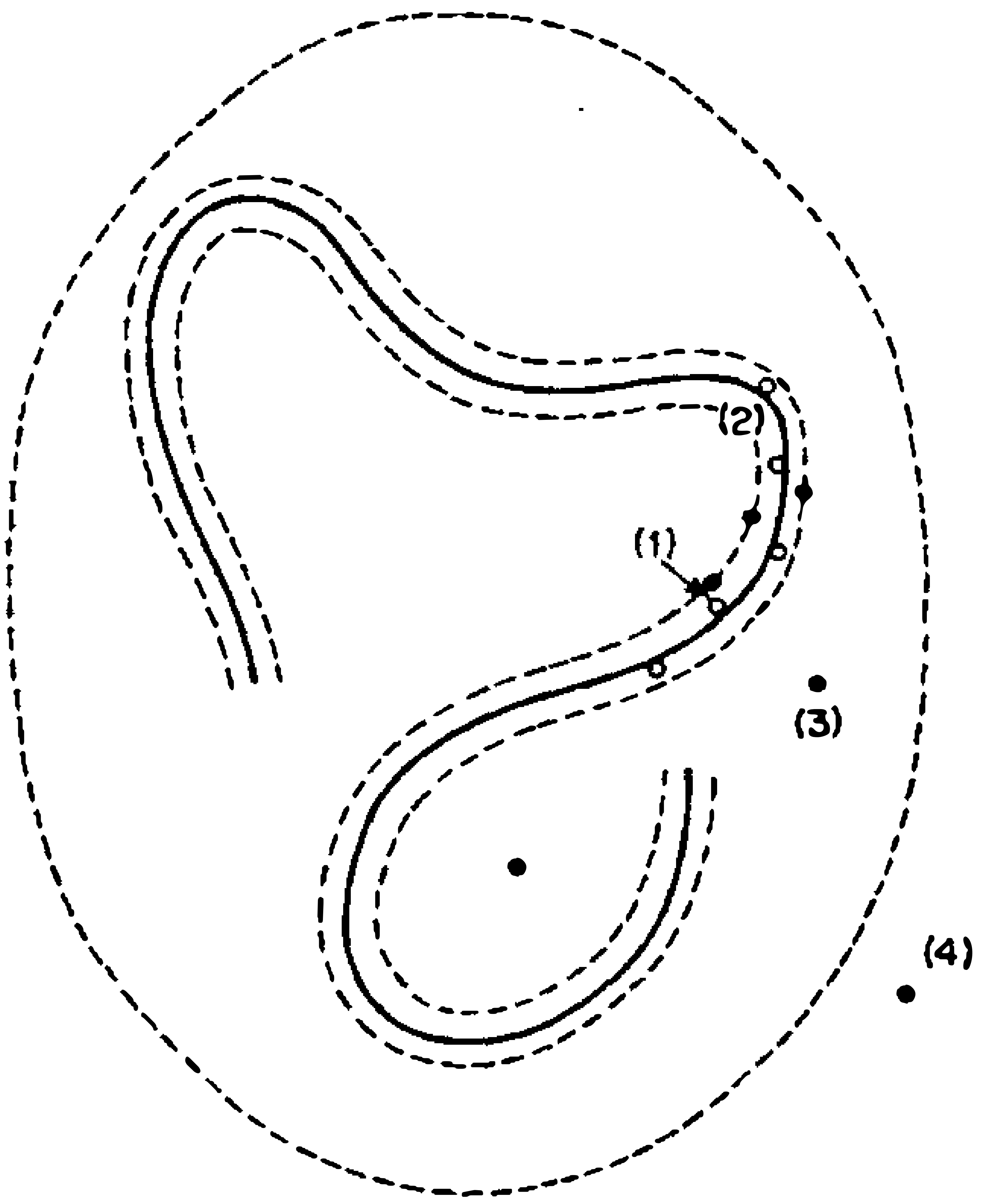


FIG. 5. Three regions for counter ions bound in and around the macroion. (1) The potential hole at charged groups; (2) the potential valley along the cylindrical region occupied by the chain of the macroion; (3) the potential trough in the region apparently occupied by the macroion as a whole. The area marked by (4) is the outside region for free counter ions.

Counter ions are distributed in these four regions. Counter ions in the first three regions can be defined as bound to the macroion. However, they are mobile in the cylindrical potential valley and in the spherical potential trough. When trapped by the sharp potential holes, they are localized at charged groups, forming ion pairs. The binding of counter ions to the macroion may be classified as localized and mobile as shown in Fig. 5.

If the assembly of charged groups and counter ions in the potential valley or trough is regarded as a closed system of an electrolyte solution, the relation between the two kinds of bound counter ions, localized and mobile, is analogous to that between free ions and ion pairs in simple electrolyte solutions. In the case of n charged groups uniformly distributed in a spherical volume v, the concentration of charged groups is given by n/v which, in the previous numerical example, is equal to 0.06 mole/liter. At this concentration the degree of ion pair formation, i.e., localized binding, is small in the case of strongly dissociative groups. In the potential valley along the chain, however, the concentration of counter ions is much higher than the above value, 0.06 mole/liter, for the uniform spherical distribution. Some of counter ions in the potential valley are then localized at holes.

Chapter 2

DISTRIBUTION OF COUNTER IONS

I. EQUILIBRIUM BETWEEN BOUND AND FREE COUNTER IONS

According to the previous discussion, counter ions in a polyelectrolyte solution are classified into three categories: counter ions freely moving outside the region occupied by macroions, those bound but mobile in this region, and those bound to individual charged groups of the macroion. The second category may be further divided to distinguish counter ions bound but mobile in the potential valley along the chain and those in the potential trough made by the coiled macroion as a whole. The equilibrium between free counter ions and bound but mobile ones is most important in determining the thermodynamic properties of polyelectrolytes. The essential feature of this equilibrium can be extracted by using the following two-phase approximation proposed by the author (*1*).

In a polyelectrolyte solution each macroion has a large charge. The repulsive force acting between them, as long as the charge is not completely cancelled by bound counter ions, tends to prevent their overlap during their movement. The whole solution can be divided into two regions. One region is occupied by macroions, the total volume of which is equal to Nv, where N is the total number of macroions and v is the apparent (effective) average volume occupied by each macroion, as shown in Fig. 6. The other region is the space free of macroions; its volume is equal to $V-Nv$, where V is the total volume of the solution.

In the absence of simple electrolytes the total number of counter ions of charge e_0 in the solution is equal to the total number of charges of the macroions. Some of the counter ions, the number of which is denoted by

n', move in each volume v and the remaining counter ions, the number of which is $nN-n'N$, move in the volume $V-Nv$. If the average potential difference between the two regions is denoted by $\delta\psi$, the distribution equilibrium between bound counter ions and free counter ions is given by the equation

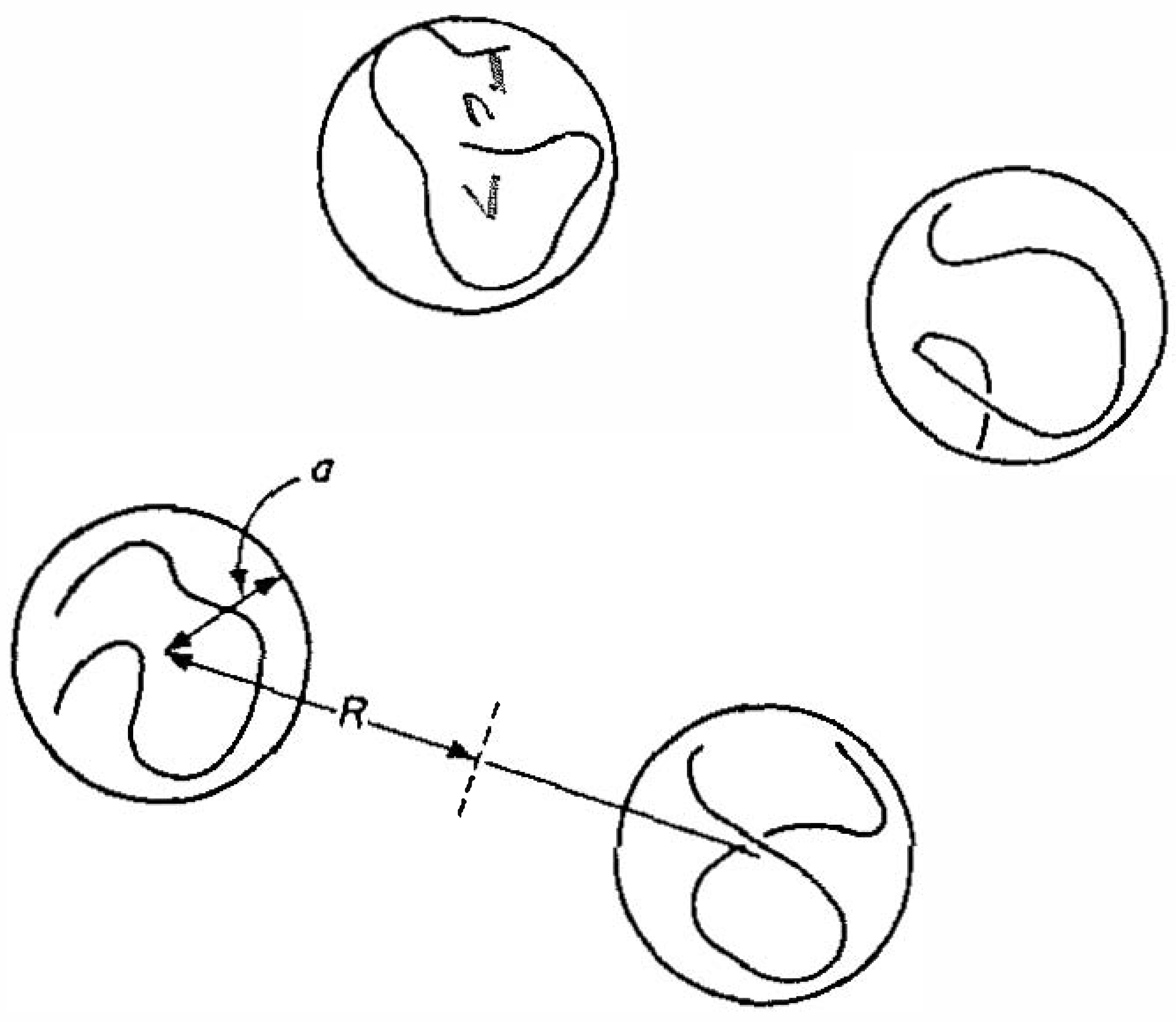


FIG. 6. Spherical macroions in a solution.

$$(n-n^*)/v = n^*N/(V-Nv)\exp(-e_0\delta\psi/kT) \tag{1}$$

or

$$\ln(1-\beta)/\beta = \ln\phi/(1-\phi)-e_0\delta\psi/kT \tag{2}$$

where $n^*=n-n'$, $\beta=n^*/n$, and the apparent volume concentration Nv/V is denoted by ϕ. The quantity $-n^*e_0$ defines the apparent charge of each macroion, and β is the apparent degree of dissociation of the macroion. The average potential difference $\delta\psi$ is a function of n^* and the size and shape of the macroion.

On the basis of this two-phase approximation, two typical cases are analysed below.

II. SPHERICAL MACROIONS

Let us consider macroions occupying spherical volume v of radius a in a solution, the dielectric constant of which is ε_0 (Fig. 6). If the average distance between centers of two neighboring macroions is denoted by

$2R$, the average potential difference between the inside and the outside of the macroion is approximately given by

$$\delta\psi = -(n^*e_0/\varepsilon_0)\,(1/a-1/R) \tag{3}$$

Since R is equal to the radius of the volume of the solution per macroion, namely $(4\pi/3)\ R^3 = V/N$ or $(a/R)^3 = Nv/V = \phi$, the equation for the distribution equilibrium may be rewritten as

$$\ln(1-\beta)/\beta = \ln \phi/(1-\phi)+\beta P(1-\phi^{1/3}) \tag{4}$$

where $P = ne_0{}^2/\varepsilon_0 kTa$, which is a nondimensional quantity giving a measure of the intensity of the potential of the macroion. The product βP is proportional to the apparent macroion charge n^*e_0. At low concentrations, the above equation is reduced to

$$\ln(1-\beta)/\beta = \ln \phi+\beta P \tag{5}$$

The relation between the apparent degree of dissociation β and the apparent volume concentration ϕ for $a = 200$ Å at different values of the number of charges (200 and 450) or of P (8 and 16) is shown in Fig. 7*a*. The apparent degree of dissociation increases with decreasing concentration, tending to unity at zero concentration. The value of β is smaller for larger values of n or P. The number of free counter ions increases very slowly with n, as shown in Fig. 7*b*. Equation (4) shows that for large values of P, the value of βP or n^* is insensitive to the increase of P or n.

In this approximation of the distribution equilibrium, the activity of counter ions must be proportional to the molar concentration of free counter ions $n^*N/(V-Nv)$ in the volume outside of the macroions. Since the total molar concentration of charged groups or counter ions in the solution c_p is equal to nN/V, the activity coefficient γ is given by

$$\gamma = (n^*N/nN)(V/(V-Nv)) = \beta/(1-\phi) \tag{6}$$

This approximation also requires that the osmotic pressure of the solution against the solvent (water) be proportional to the concentration of free counter ions outside of the macroion, and the osmotic coefficient g be equal to the activity coefficient β. The quantity $\beta/(1-\phi)$ is obtained from Eq. (4) as a function of the volume concentration ϕ and the charge P. This result is included in Fig. 7*a*. With decreasing concentration of macroion the activity coefficient slowly decreases at high concentrations, reaching a minimum at about $\phi = 0.05$, and then increases at low concentrations, approaching unity at zero concentration.

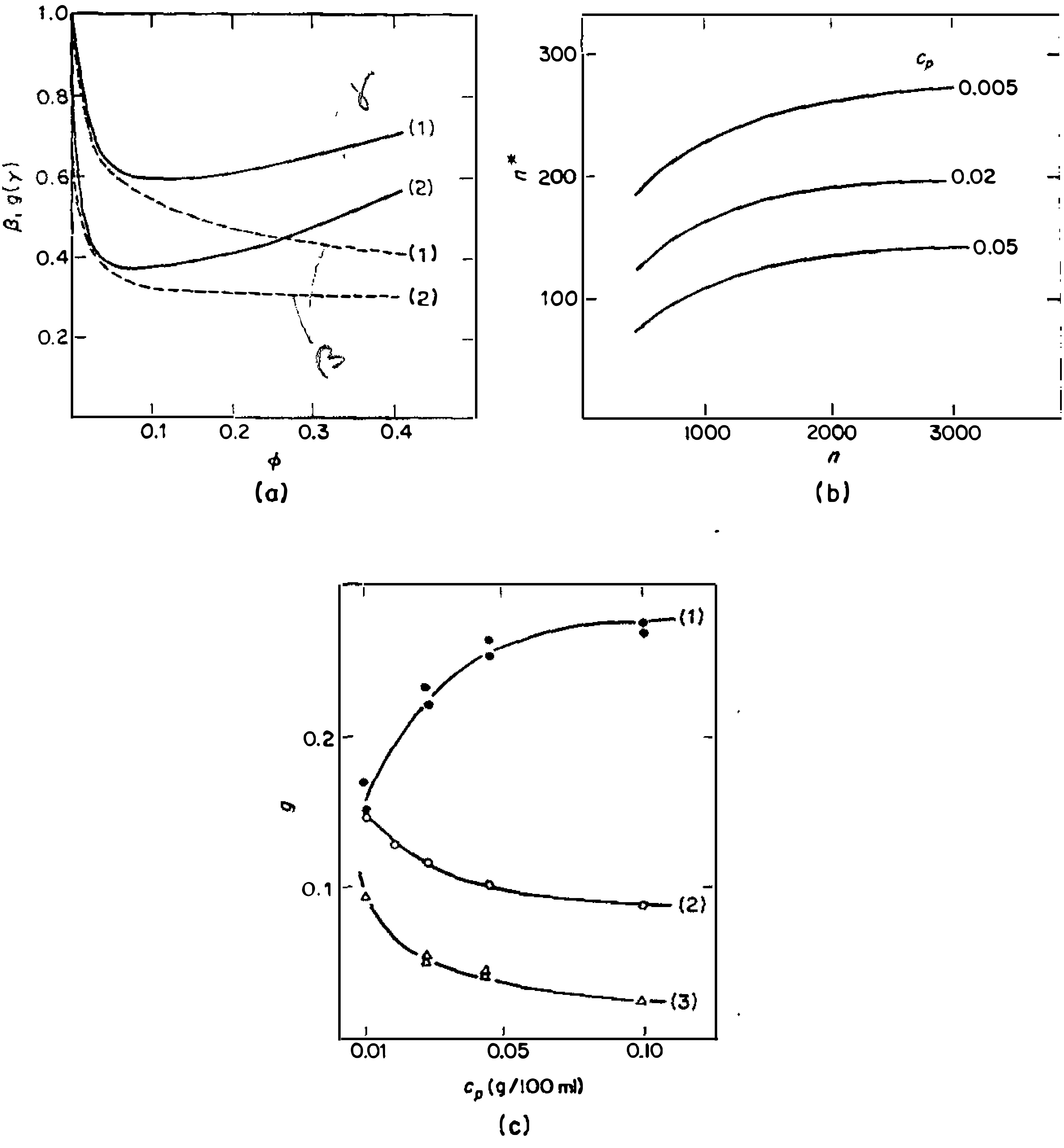


FIG. 7. (*a*) Relations of the apparent degree of dissociation of counter ions β and the activity coefficient of counter ions γ to the apparent volume concentration ϕ at various values of the charge density P in solutions of spherical macroions. (1) $P = 8$ and (2) $P = 16$. (——): The activity coefficient γ; (— —): the degree of dissociation β (*1*). (*b*) Relations of the apparent degree of dissociation β or the number of the effective charge n^* to the charge density P or the total number of charged groups n at various concentrations c_p of macroions in solutions of spherical macroions. The radius of the macroion $a = 350$ Å, $\varepsilon_0 kT/e_0^2 = 1.4 \times 10^7$ cm^{-1} and the concentration of macroions c_p is expressed in monomer-mole/liter (*4*). (*c*) The experimental relation between the osmotic coefficient, g, and the concentration of macroions, c_p (*2*). (1) Sodium carboxymethyl amylose (linear polymer); (2) sodium carboxymethyl amylopectin [branched (spherical) polymer]; (3) sodium carboxymethyl glycogen.

It is generally expected that the activity coefficient of the solute should become unity at extreme dilution and should decrease with increasing concentration. The above change of the activity of counter ions with dilution that is predicted by the present approximation is thus reasonable. As is shown in Fig. 7*c* (*2*), this behavior of γ has indeed been observed in the case of a kind of branched chain macroion, which probably takes a spherical form in the solution over a wide range of concentration.

It must be pointed out, however, that small values of the molar (weight) concentration of polyelectrolytes correspond to fairly large values of the apparent volume concentration because of the extension of the macroion. The radius of the free volume R is related to the concentration c_p (mole/liter) of charged groups or counter ions in the solution through the equation

$$(4\pi/3)\,R^3 = n/(6\times 10^{20})\cdot c_p \tag{7}$$

For example, when $n = 1000$, the concentration $c_p = 0.1$ mole/liter corresponds to $R = 150$ Å and $c_p = 0.001$ mole/liter to $R = 700$ Å. If the macroion is sufficiently coiled, its radius a can be considerably smaller than the above values of R and the apparent volume concentration will be small. However, if it is somewhat extended and the radius a is as large as 230 Å, about 1/10 the length of the most stretched form of the macroion of $n = 1000$, the apparent volume concentration is 0.04 at $c_p = 0.001$ mole/liter and attains a value of unity at $c_p = 0.03$ mole/liter. The correspondence of such low values of c_p to large values of ϕ suggests that the isolated spherical random coil model for chainlike macroions is applicable only in a very limited condition, because at large ϕ it is not reasonable to divide the solution into spherical volumes occupied by macroions and outside volumes unless the macroions are compact spheres of a fixed radius. Moreover, the highly charged macroions at low concentrations are in a more stretched conformation. In other words, at such low concentrations of macroions and counter ions where the spherical free volume model may be applied, most real chainlike macroions can not be in the spherical form.

III. RODLIKE OR CYLINDRICAL MACROIONS

Macroions as flexible chains having many charges are usually in the extended conformation. The end-to-end distance of each chain is longer than the average distance between neighboring chains, except in the extremely dilute solution. In such circumstances the rodlike or cylindrical model of macroions is preferable to the spherical model (Fig. 8). Let us suppose that each macroion is stretched to a cylindrical shape and the charged groups are distributed in a cylindrical region of volume v and radius a in which the potential profile is of the form shown in Fig. 4*d*. The average potential difference $\delta\psi$ between the inside and the outside of this volume is given approximately by

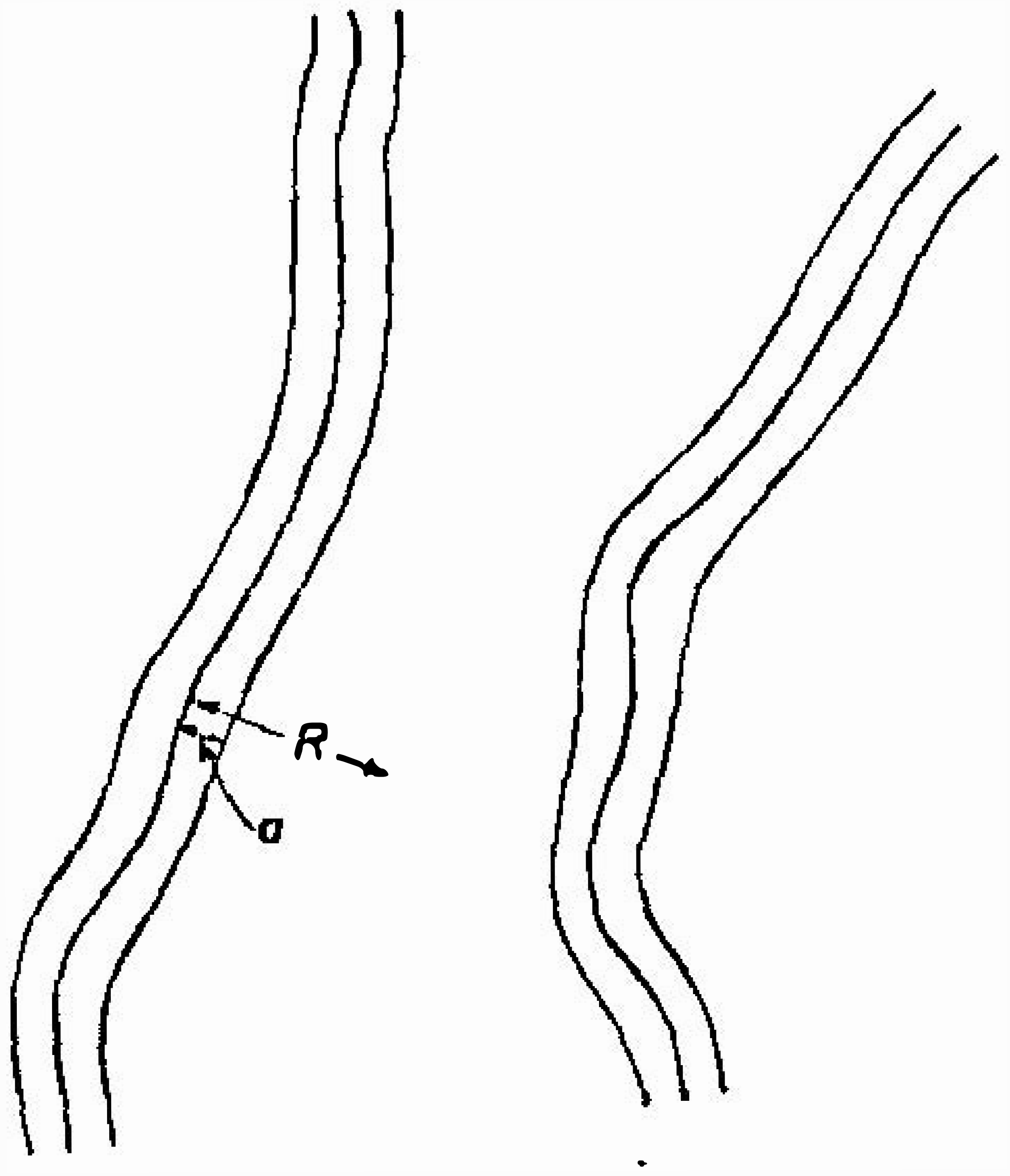


FIG. 8. Cylindrical macroions in a solution.

$$\delta\psi = -2(n^*e_0/\varepsilon_0 l)\ln(R/a) \tag{8}$$

where $2R$ is the average distance of two neighboring rodlike macroions or R is the radius of the cylindrical free volume of each macroion, and l is the end-to-end distance of the macroion. Accordingly, $\pi R^2 l = V/N$ and $\pi a^2 l = v$; therefore $a^2/R^2 = Nv/V = \phi$. If the average distance between neighboring charges on the macroion along the cylinder is denoted by $d = l/n$, the potential difference is expressed as

$$\delta\psi = -(\beta e_0/\varepsilon_0 d)\ln(1/\phi) \tag{9}$$

Strictly speaking, this expression is valid only for a rod of infinite length in a cylindrical free volume. For rods of finite length l, a term of the order of $(\beta e_0/\varepsilon_0 d)(2/l^2)(R^2-a^2)$ must be added. However, the influence of such a correction is small enough to be neglected if the condition $2(R^2/l^2)(1-\phi) < (1/\phi)$ is satisfied. For example, at $\phi = 0.1$, if $l > 3R$, the error does not exceed 10%. If $a/l = 1/1000$, Eq. (9) is applicable when ϕ is larger than 2×10^{-4}.

By employing Eq. (2), the distribution equilibrium between bound and free counter ions may be written as

$$\ln(1-\beta)/\beta = \ln\phi/(1-\phi) + \beta Q\ln(1/\phi) \tag{10}$$

where $Q = e_0^2/\varepsilon_0 kTd$. For the cylindrical model, this nondimensional quantity Q is the most important parameter determining the intensity of the binding of counter ions. It should be noted that the right-hand side of the above equation is reduced to the form

$$(1-\beta Q)\ln\phi \tag{11}$$

for sufficiently small values of ϕ.

Results of some numerical calculation, shown in Figs. 9*a* and 9*b*, reveal one of the most characteristic properties of polyelectrolytes. At a constant length l of the macroion, the value of Q increases with increasing number of charges per macroion. The relation between β and ϕ expressed by Eq. (10) depends on the value of Q. For values of Q smaller than unity, the apparent degree of dissociation β increases with decreasing ϕ; approaching unity at zero concentration, just as in the case of the spherical macroion. On the other hand, for values of Q larger than unity, β does not tend to unity, but approaches $1/Q$ at zero concentration. The activity coefficient, γ, of the counter ions, $\beta/(1-\phi)$, also approaches $1/Q$ when Q is larger than unity. Thus, at infinite dilution

$$\begin{aligned} \gamma &\to 1 &\quad &\text{for} \quad 0 \le Q \le 1 \\ \gamma &\to 1/Q &\quad &\text{for} \quad 1 \le Q \end{aligned} \tag{12}$$

For large values of Q, with increasing concentration the activity coefficient γ does not decrease but increases slightly. From Eq. (10) it is found that $(d\beta/d\phi)_{\phi\to 0} > 0$ when Q becomes larger than 2.

Such behavior of the activity of solute molecules or ions has not been observed in ordinary solutions of nonelectrolytes or electrolytes. In the case of polyelectrolytes, however, experiments give results in good agreement with the theoretical predictions of Figs. 9*a* and 9*b*. The data of Nagasawa and Kagawa (*3*) that are presented in Fig. 9*c* show that the activity coefficient of counter ions is very low even at low concentrations of polyelectrolyte and is almost constant over a wide range of concentration. When the number of charges n is increased with the degree of esterification of the polymer, the activity of counter ions changes as expected. At high values of Q, the activity is not increased with n, γ being nearly proportional to $1/Q$ or l/n, as shown in Fig. 9*d* (*3*). Similar results have been obtained in a number of experiments (*4*). The experimental data in Fig. 7*c* that were obtained by Inoue (*2*) also provide a valuable test of the present models because two kinds of macroions, spherical and linear, are compared. Both macroions show the behavior predicted by the above theory.

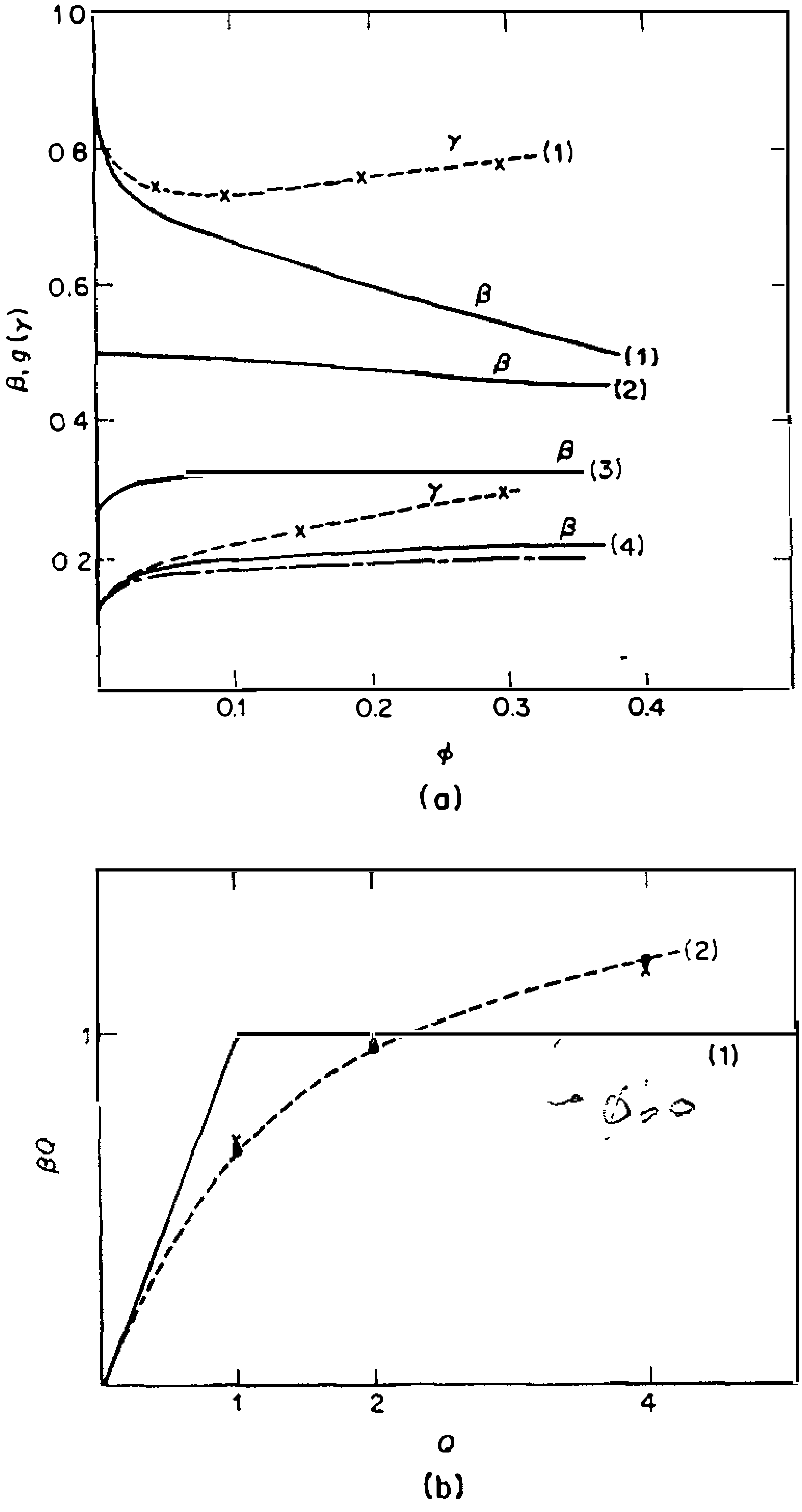


FIG. 9. (*a*) Relations of the apparent degree of dissociation of counter ions, β, and the activity coefficient of counter ions, γ, to the apparent volume concentration at various values of the charge density Q in solutions of cylindrical macroions; (1) $Q = 1$, (2) $Q = 2$, (3) $Q = 4$, and (4) $Q = 8$. (——): The degree of dissociation β; (— —): the activity coefficient γ; and (—·): the activity coefficient under the condition that $\gamma^* = 0.6$ (*1*). (See Section IV). (*b*) Relations of the number of free counter ions, βQ, to the charge density, Q, at various concentrations of macroions in solutions of cylindrical macroions; (1) in the limit of dilution, (2) the apparent volume concentration $\phi = 0.05$ and 0.1. (*c*) The experimental relation between the activity coefficient of counter ions and the concentration of macroions. Sodium polyvinyl sulfate in pure water. The degree of esterification (the charge density); (1) 0.725, (2) 0.692, (3) 0.740, (4) 0.711, (5) 0.494, (6) 0.431, and (7) 0.301 (*3*). (*d*) The relation of the activity coefficient γ (○) and the activity γQ (×) or the concentration of free counter ions to the degree of esterification (the charge density) derived from the data in Fig. 9(*c*).

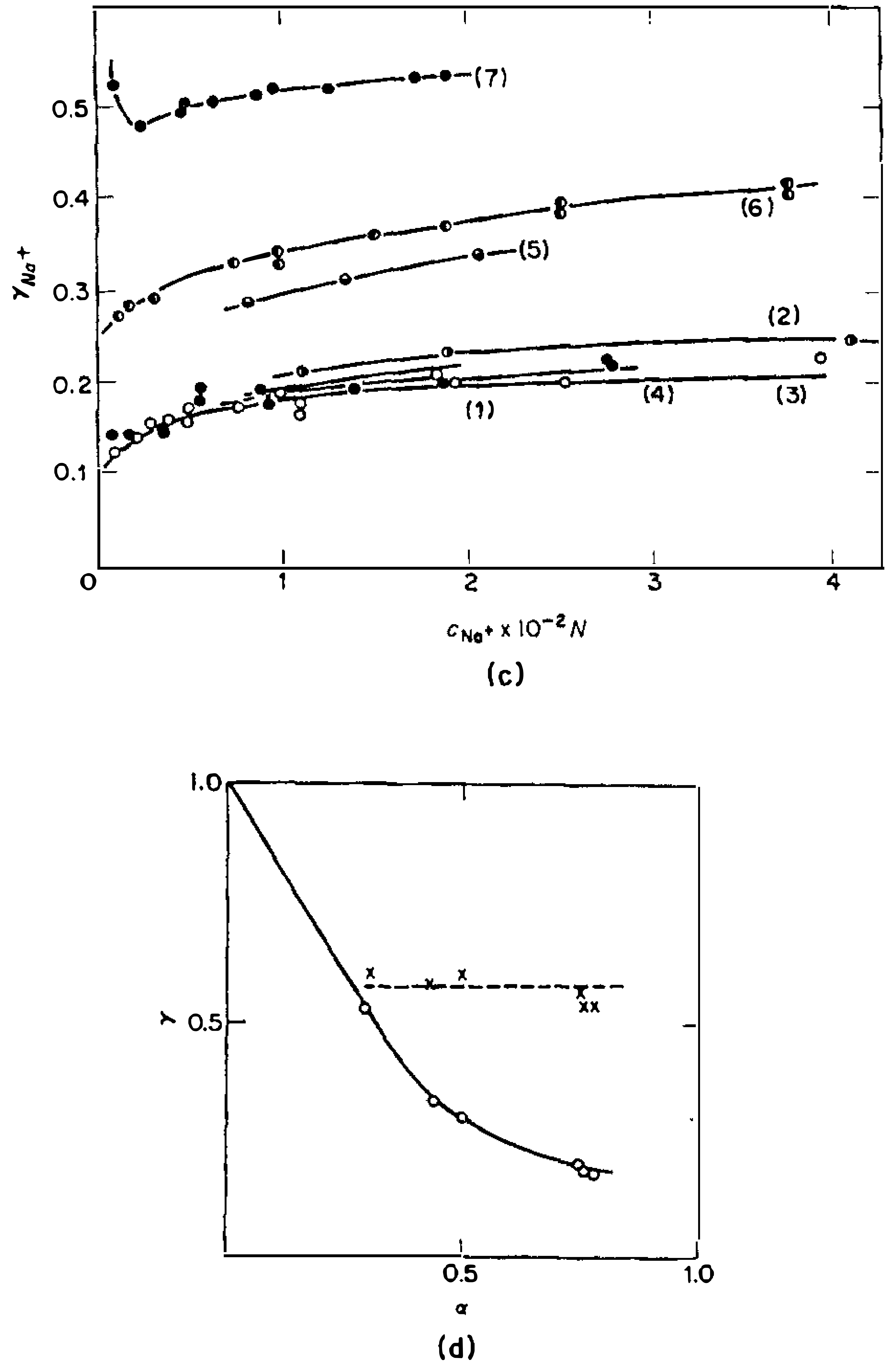

γ_{Na^+}
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
(7)
(6)
(5)
(2)
(1)
(4)
(3)
$c_{Na^+} \times 10^{-2} N$
(c)
γ
1.0
0.5
0.5
1.0
α
(d)

FIG. 9 (cont.)

In water ($\varepsilon_0 = 80$) and at room temperature, the condition $Q = 1$ corresponds to $d = 7$ Å for monovalent charged groups and counter ions. The theory suggests that when the average distance between neighboring charges on the macroion becomes less than about 7 Å with the increase of the number of charges, a further increase of charge does not result in an increase of the apparent charge of the macroion even at low concentrations of macroions. The excess number of counter ions are retained in the cylindrical region along the macroion.

In the above model the degree of dissociation and the activity are determined by the quantity Q or d, the charge density on the macroion, and are independent of the total number of charges, i.e., the degree of polymerization of the polyelectrolyte. This estimate of the situation is supported by experiments.

Of course, in actual cases each macroion is not fully stretched to a straight rod even in the extended conformation. It has curvature and takes a wavy form. The cylindrical model, however, may be applied to each nearly cylindrical part of the macroion which is long enough to satisfy the condition that the potential difference is given approximately by Eq. (9). The length of the cylindrical part is required to be longer than the distance between neighboring cylinders as shown in Fig. 8. For instance, when $\phi = 0.01$ ($a = 10$ Å and $R = 100$ Å) and the length of the cylindrical part is 200 Å, the error in the average potential difference given by Eq. (9) is less than 10%. This estimate suggests that the cylindrical model has a wide applicability, even when the macroion is coiled to a certain extent.

An isolated macroion in a more or less coiled conformation makes two regions for bound but mobile counter ions; the cylindrical volume (the potential valley) along the chain and the spherical volume (the potential trough) apparently occupied by the macroion as a whole. Therefore, equilibria must be established among these regions and the outside. The equilibrium between counter ions in the cylinder (the potential valley) and in the sphere (the potential trough) may be described by an equation analogous to Eq. (10), and the equilibrium between counter ions in the sphere and the outside may be described by an equation analogous to Eq. (4). At high values of the charge density of the macroion along the chain, most of the counter ions are retained in the cylinder and the apparent charge of the chain can not exceed a limit defined by Equation (10). Consequently, the concentration of counter ions that are mobile in the sphere is relatively low and not very different from the concentration of free counter ions in the outside region. In this case the spherical region assumed above is not important in determining the equilibrium concentration of free counter ions, and the simple cylindrical model can adequately explain the experimental facts.

The theoretical calculation show that the activity coefficient of the counter ions does not tend to unity but approaches $1/Q$ at infinite dilution. This result, which seems to contradict the requirement of the general theory of solutions that γ approaches unity, is due to the assumption that the length l of the macroion is infinite. Since the length l of real macroions is finite, R must exceed l at infinite dilution. In most cases, however, such an extreme dilution is not realized in practice before the measurement of the activity or the osmotic pressure becomes impossible, or before the number of hydrogen ions and hydroxyl ions in water becomes significant.

IV. COUNTER ION CONDENSATION

The previous section has made clear one of the characteristic properties of polyelectrolytes. Let us now increase the number of charges of each macroion at a constant total concentration of macroions in the solution. An increasing number of counter ions are distributed inside and outside of volumes occupied by macroions. When the number of charges and counter ions is small, counter ions are equally distributed in the solution. With the increase of the number of charges, the electric field becomes strong and relatively more counter ions are retained in the volume of the macroions. At infinite dilution, however, the counter ions are free from macroions if the number of charges is smaller than a certain critical value. Assuming that the cylindrical model can be applied to the macroion or at least to parts of the macroion, this critical value is given by the condition that the charge density along the cylinder n/l or $1/d$ is equal to $\varepsilon_0 kT/e_0^2$, or the average distance between neighboring (monovalent) charges d is equal to $e_0^2/\varepsilon_0 kT$, which is about 7 Å in water at room temperature.

When the number of charges increases beyond this critical value, the apparent degree of dissociation β decreases, becoming equal to $1/Q = \varepsilon_0 kTd/e_0^2$ at low concentrations of macroions. Then the concentration of free counter ions outside of the macroion is proportional to c_p/Q or nd, which becomes independent of n. In spite of the increase of the number of charged groups and counter ions in the solution, the concentration of free counter ions is kept constant and only the number of bound ones is increased, as shown in Fig. 10.

This phenomenon is a kind of condensation. Let us consider a gas composed of a large number of molecules among which attractive force acts. When the number of molecules is increased at a constant total volume of the gas, the condensation to liquid takes place at a certain critical value of the number or the density of gas molecules. Above this critical point the increase of the number of molecules does not increase the number or the density in the gas phase. Only the amount of the liquid phase is increased (Fig. 10).

In analogy to this gas–liquid condensation, the concentration of free counter ions above the critical value of the charge density corresponds to the saturated vapor pressure coexisting with the liquid. The counter ions in the volume of macroions correspond to the molecules in the liquid phase. *Counter ion condensation* is a characteristic phenomenon in polyelectrolytes. In comparison with the usual condensation caused by the increase of the density in the gas phase, it is to be noted that, in the system of counter ions and macroions, the number of charged groups of the macroion is increased in parallel with the increase of the number of counter ions. In other words, the source of the attractive force in the liquid phase is increased. The quantity kept constant above the critical condition is the *number* of free counter ions or the *apparent charge density* of macroions.

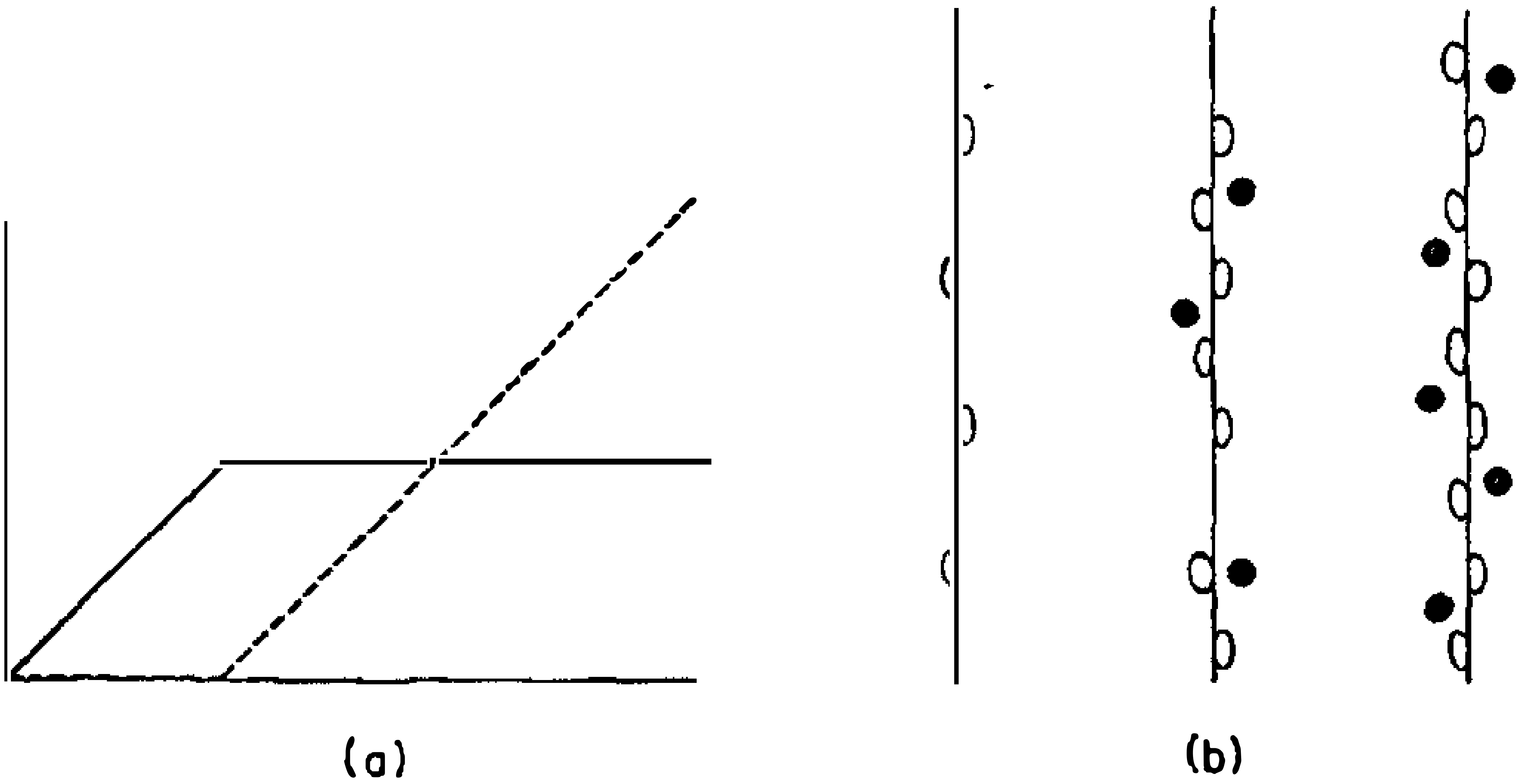


Fig. 10. (*a*) The counter ion condensation in comparison with the gas–liquid condensation. The abscissa is the charge density of macroions, or the total number of counter ions, or the total number of molecules. (——): The number of free counter ions or the density of the gas phase; (— —): the number of bound counter ions or the amount of the condensed liquid. (*b*) Illustration of counter ion condensation with increasing charge density.

What is the cause of this phenomenon of "counter ion condensation"? The distribution equilibrium represented by Eq. (2) denotes the equality of the chemical potential of counter ions in the two phases, the region occupied by the apparent volume of the macroions and the region outside of this volume. The chemical potential is the sum of energy and entropy terms. The contribution of the entropy is expressed as $kT\times\ln$ (concentration), and the difference in the entropy between the two phases contains the term $kT\times\ln$ (volume ratio). For a long cylinder having a uniform charge density, the coulomb potential around the cylinder is expressed as a logarithmic function of the distance. Therefore, the energy difference between two phases is also proportional to ln (volume ratio). If the volume outside the cylinder is increased, the entropy difference and the energy difference are both increased according to the logarithmic form of the volume. Infinite dilution does not result in the predominance of the contribution of entropy to the chemical potential, and counter ions can not leave the volume of the macroion.

On the other hand, in the usual systems where molecules interact with each other only at short distance, the energy difference between the free state and the bound state is independent of the volume of the free space. Only the difference of entropy increases with the increase of free space. Therefore, at infinite dilution complete dissociation always takes place.

Let us assume that at a certain value of the volume concentration the number of free counter ions is too large to establish equilibrium between two phases. Then, some of the free counter ions are forced to enter into the bound state. This flow of counter ions from the free state to the bound state can not be stopped by dilution or by the increase of free space. The number of free counter ions must decrease to a critical value where the balance between the contributions of energy and entropy is just satisfied almost independently of the volume concentration by the condition that

$$kT = n^{*}e_0^{2}/\varepsilon_0 l \qquad (13)$$

or

$$\beta Q = 1 \qquad (14)$$

Suppose that at the condition (13) counter ions are in the equilibrium distribution and an additional charge and its counter ion are newly produced in the macroion. If this additional counter ion escapes from the macroion into the free space, the potential energy difference increases and becomes predominant over the entropy difference, namely $kT < (n^{*}+1)e_0^{2}/\varepsilon_0 l$. The counter ion must as a consequence be retained in the macroion. The increase of the entropy difference resulting from the retention of the counter ion is much smaller than the change of the potential energy caused by liberation of the counter ion into the free space, if the volume concentration is low. Thus, the apparent charge can not be increased.

The above analysis is valid for sufficiently small values of the volume concentration ϕ. In the case of the cylindrical model, the apparent volume concentration is not so much different from the net concentration of the chain of the macroion, while in the case of the spherical model the apparent volume is very much larger than the net volume of the chain. In the former case the molar concentration of charged groups $c_p = 0.01$ mole/liter, for instance, corresponds to a fairly small value of ϕ (between 0.01 and 0.001).

In the present case, the mathematical requirement for counter ion condensation is that in Eq. (10) the term $-\ln \phi$ is sufficiently larger than other terms. Since $-\ln \phi$ can be large enough only when ϕ is extremely small, the above analysis seems to be valid only at extremely low concentrations. Fig. 9*a*, however, shows that the activity coefficient is not greatly changed with concentration, and this indicates that counter ion condensation is numerically insensitive to the concentration, especially when ϕ is lower than 0.1.

Another approximation in the two-phase model was that all bound counter ions are fully active in the volume v. Some of them may be localized or at least produce an ionic atmosphere around each charged group. Such an effect decreases the activity of the counter ions in v. Therefore, if the apparent activity coefficient γ^* of counter ions in v is introduced, the left-hand side of Eq. (1) is replaced by $\gamma^*(n-n^*)/v$ and the left-hand side of Eq. (10) must include the term $\ln \gamma^*$. However, at low concentrations of macroions, introduction of the quantity $\ln \gamma^*$ has little effect on the relation of the apparent degree of dissociation or the activity coefficient of counter ions to the concentration, as is shown in Fig. 9*a*. The critical value of the charge density for counter ion condensation is not changed. Estimation of the magnitude of γ^* will be given later (Chapter 6, Section 1).

The discontinuous condensation of counter ions beyond a critical condition is not found in the case of spherical macroions. However, as mentioned in the previous section, Eq. (5), which corresponds to Eq. (13), indicates that for large values of the charge density P, the apparent charge βP increases very slowly (only logarithmically) with increasing P. A situation approximating "condensation of counter ions" occurs, although for spherical macroions there is no specific critical value of the charge density P and the value of the apparent charge depends on the concentration ϕ.

Chapter 3

ELECTRIC POTENTIAL AND FREE ENERGY

I. The Fundamental Equations

We have seen in the preceding section that a simple model can be employed for a rather successful theoretical interpretation of the phenomenon of "counter ion condensation" that is characteristic of polyelectrolytes. In this model the distribution equilibrium of counter ions was considered to occur between two discrete phases, each of which was regarded as a uniform solution of counter ions. Actually the coulomb interaction between ions and charged groups is of long range so that the approximation of uniform phases appears to be too simple and should be reexamined by a more critical consideration. This is performed on the basis of the Poisson–Boltzmann equation (*5*).

Let us consider a random coil macroion or a cylindrical macroion occupying volume v, in which n groups of charge $-e_0$ are distributed. The electric potential ψ and the charge density ρ or the concentration c are related to each other as functions of spatial coordinates x through the equation

$$\Delta\psi = -(4\pi/\varepsilon_0)(\rho_m+\rho_+) = (4\pi/\varepsilon_0)e_0[c_m(x)-c_+(x)] \qquad (15)$$

where Δ is Laplacian; ρ_m and ρ_+ are charge densities and c_m and c_+ are number concentrations of charged groups and counter ions, respectively.

Both potential and density in the above equations are statistically averaged quantities. The average distribution of the charged groups ρ_m can be expressed approximately as a continuous function of the coordinates. (The validity of this approximation will be discussed later.) At a given distribution of the charged groups counter ions are mobile and their distribution is determined by the balance between the electric potential energy and the entropy. The electrochemical potential μ_+ of the counter ions can be written as

$$\mu_+ = kT \ln c_+(x) + e_0\psi(x) + \mu_+{}^0 \tag{16}$$

where $\mu_+{}^0$ is the chemical potential in the standard state. The electrochemical potential must be constant throughout the solution and the Boltzmann equation can be used to express the concentration of counter ions at any point (x) in the solution.

$$c_+(x) = A \exp(-e_0\psi(x)/kT) \tag{17}$$

where the constant A is determined by the condition on the total number of counter ions. If a free volume, V/N, in which electroneutrality is satisfied, is assumed for each macroion, the total number of counter ions in this volume must be n. Then,

$$A = nN/V'$$

with

$$V' = N \int_{V/N} \exp(-e_0\psi(x)/kT)\, dv \tag{18}$$

If the potential $\psi(x)$ is small in the volume V/N, V' is nearly equal to the volume V.

By combination of this equation with Eq. (15) the Poisson–Boltzmann equation is obtained:

$$\Delta\psi = (4\pi e_0/\varepsilon)[c_m(x) - A \exp(-e_0\psi/kT)] \tag{19}$$

The average potential ψ and the average ion distribution ρ are determined by solving this equation under suitable boundary conditions. At the surface of the free volume, the average electric field must be zero.

The electrical internal energy u_e per macroion with n counter ions is given by the following integral in the free volume:

$$\begin{aligned} u_e &= (1/2) \int_{V/N} (\rho_m + \rho_+)\psi\, dv \\ &= \int_{V/N} (\varepsilon_0/8\pi)(\text{grad}\, \psi)^2\, dv \end{aligned} \tag{20}$$

The entropy s of the distribution of counter ions is given by

$$-Ts = kT \int_{V/N} c_+ \ln(c_+/c^0 e)\, dv \tag{21}$$

where c^0 is the number concentration of solvent molecules and c_+/c^0 is the molar fraction of counter ions (*6*). The free energy per macroion with its counter ions is given by

$$f = u_e - Ts \tag{22}$$

The above procedure for the derivation of the free energy is composed of two processes. The first brings the ions to the distribution in the final equilibrium and the second charges the ions and the macroion, their distributions being kept constant.

Another method for the derivation of the free energy gives the expression

$$f = f_0(V/N, n) + f_e \tag{23}$$

where f_0 is the standard free energy of an ideal solution of counter ions without charge, and

$$f_e = 2 \int_0^{e_0} u_e(de_0/e_0) \tag{24}$$

This is proved by the use of the partition function Z given by

$$Z = \int \ldots \int \exp\left(-e_0^2 \sum_{i,j} u_{ij}/kT\right) \prod_k dx_k \tag{25}$$

where the coulomb interaction energy between the ith ion (or charge) and the jth ion (or charge) is proportional to the square of the charge e_0^2 and written as $e_0^2 u_{ij}$. The free energy is given by

$$f = -kT \ln Z \tag{26}$$

Therefore,

$$\begin{aligned} df/de_0 &= -kT\, d(\ln Z)/de_0 \\ &= -kT \frac{\int \ldots \int (-2e_0/kT) \sum u_{ij} \exp\left(-e_0^2 \sum u_{ij}/kT\right) \prod_k dx_k}{\int \ldots \int \exp\left(-e_0^2 \sum u_{ij}/kT\right) \prod_k dx_k} \\ &= 2u_e/e_0 \end{aligned} \tag{27}$$

Thus, by integration of this equation, we have Eq. (23) with Eq. (24).

In the above method the ideal solution of counter ions is first considered and the ions and the macroion are then charged, the ion distribution being changed with charging. The two expressions of the free energy, Eq. (22) and Eq. (23), are equivalent to each other. This is shown by proving the relation

$$d(u_e - Ts)/de_0 = 2(u_e/e_0) \tag{28}$$

with u_e and s given by Eqs. (20) and (21). From Eq. (21) we have

$$\begin{aligned} -d(Ts)/de_0 &= kT(d/de_0)\int c_+ \ln c_+ dv \\ &= kT\int (dc_+/de_0)\ln c_+ dv \\ &= -e_0^2\int (dc_+/de_0)\Phi\, dv \end{aligned} \tag{29}$$

where we put $\psi = e_0\Phi$. On the other hand, from Eq. (20)

$$\begin{aligned} du_e/de_0 &= (1/2)(d/de_0)\int e_0^2(c_m+c_+)\Phi\, dv \\ &= e_0\int (c_m+c_+)\Phi\, dv+(e_0^2/2)(d/de_0)\int (c_m+c_+)\Phi\, dv \\ &= 2u_e/e_0+(e_0^2/2)[\int (dc_+/de_0)\Phi\, dv+\int (c_m+c_+)(d\Phi/de_0)dv] \end{aligned} \tag{30}$$

Therefore,

$$d(u_e-Ts)/de_0 = 2u_e/e_0+(e_0^2/2)\int [(c_m+c_+)(d\Phi/de_0)-\Phi\,(dc_+/de_0)]dv \tag{31}$$

Since

$$\Delta\Phi = -4\pi/\varepsilon_0(c_m+c_+)$$

the second term of the right-hand side of Eq. (31) can be rewritten

$$\begin{aligned} &\int [(c_m+c_+)(d\Phi/de_0)-\Phi(dc_+/de_0)]\, dv \\ &\quad = -(\varepsilon_0/4\pi)\int [\Delta\Phi(d\Phi/de_0)-\Phi(d\Delta\Phi/de_0)]\, dv \\ &\quad = 0 \end{aligned}$$

Thus, the relation (28) was derived and the equivalence of the two expressions of the free energy was proved.

The chemical potential of the solvent molecule μ_0 and that of the counter ion μ_+ can be obtained by differentiation of the free energy. In the present method of approximation, differentiation with respect to the number of solvent molecules means differentiation with respect to the size of the free volume. Performing such differentiation by using the expression (22) with (20) and (21), we can find that the chemical potential of the solvent μ_0 is given by

$$\mu_0 = -kTc_+(R)/c^0+\text{const} \tag{32}$$

where R denotes the coordinate at the surface of the free volume. Namely, the chemical potential is determined by the molar concentration of counter ions at the surface R, where the electric field is zero and solvent molecules have no electrostriction.

The chemical potential of the counter ion is given by

$$\mu_+ = kT\ln c_+(R)+\text{const} \tag{33}$$

This is directly derived from Eq. (16) and also confirmed by differentiation of the free energy, Eq. (22), with respect to the number of counter ions.

The osmotic coefficient g and the activity coefficient γ of counter ions are thus given by

$$\gamma = g = c_+(R)/(nN/V) = c_+(R)/c_p \tag{34}$$

The free energy derived above contains only the contribution of the counter ion distribution in and around the (fixed) macroion. Besides the atmosphere of counter ions around the macroion as a whole, each ion or charged group has an ionic atmosphere about itself. The contribution of such atmospheres must be included in the total free energy.

The free volume of each macroion in which electroneutrality is satisfied is not necessarily equal. Because of the Brownian motion of macroions, the electroneutral volume around each macroion must fluctuate. This fluctuation also makes some contribution to the free energy.

In relation to these corrections, the validity of the Poisson–Boltzmann equation must be reexamined. Such reexamination was partly carried out in Ref. *5*.

Now, despite neglect of several terms, the above expression for the free energy is useful for the analysis of the characteristic properties of polyelectrolytes. The central problem in the following sections is to solve the Poisson–Boltzmann equation and calculate the free energy and also the osmotic coefficient.

The Poisson–Boltzmann equation can be solved exactly only in a special case, i.e., for a rodlike macroion with counter ions in a cylindrical free volume. This case will be treated in Section III of this Chapter. In other cases various methods have been devised to obtain approximate solutions of the Poisson–Boltzmann equation. One of them is the Debye-Hückel approximation, in which the electrical potential energy $|e_0\psi|$ of counter ions is assumed to be much smaller than the kinetic energy kT everywhere in the solution. Herman and Overbeek first applied this approximation to a spherical random coil macroion with smoothed charge distribution in a salt solution and calculated the free energy as a function of the extension of the macroion (*7*).

In their early work, Katchalsky, Kunzle, and Kuhn started from pure coulomb potential due to charged groups of the macroion without counter ions (*8*). The total electric energy was calculated by summing up coulomb interaction energies among all groups. Actually, counter ions are accumulated by the coulomb potential. The energy must be corrected by taking into account these accumulated counter ions. Later, Katchalsky and

Lifson assumed the Debye–Hückel atmosphere of counter ions around each charged group of the macroion and gave the electric free energy as the sum of interactions between charged groups with the counter ion atmospheres (*9*).

Such Debye–Hückel approximation may be valid for macroions of small charges in salt solutions. However, in highly charged macroions which we are interested in, the fact that $|e_0\psi|/kT > 1$ in and around the macroion is essential for the characteristic properties of polyelectrolytes.

The other method of approximation is based on the Donnan equilibrium between two phases, the uniformly charged random coil macroion and the outside. As a first approximation, the charged groups in the macroion are assumed to be completely neutralized by counter ions except at the surface. Kimball calculated the extensive force of the macroion under this first approximation (*10*). Deviation from the Dònnan equilibrium must produce correction terms. Along this line, expansion of the free energy or the extensive force as a power series of the reciprocal of the ionic strength was tried by Flory and others. This method was applied to a spherical macroion in concentrated salt solutions (*11*).

The two phase model in the previous chapter is, in a sense, a variation of the latter method, although it was applied in a wide range of the condition where the charge of the macroion was not necessarily assumed to be mostly cancelled by counter ions in it.

The following section will treat two typical cases; one is a spherical random coil macroion in which deviation from neutrality is small, and the other is a rodlike macroion which can give an exact solution of the Poisson–Boltzmann equation. In both cases the polyelectrolyte solution will be assumed to contain no simple electrolyte ions other than macroions and their counter ions. Polyelectrolytes in the presence of simple electrolytes are discussed in Chapter 6.

II. SMALL DEVIATION FROM NEUTRALITY

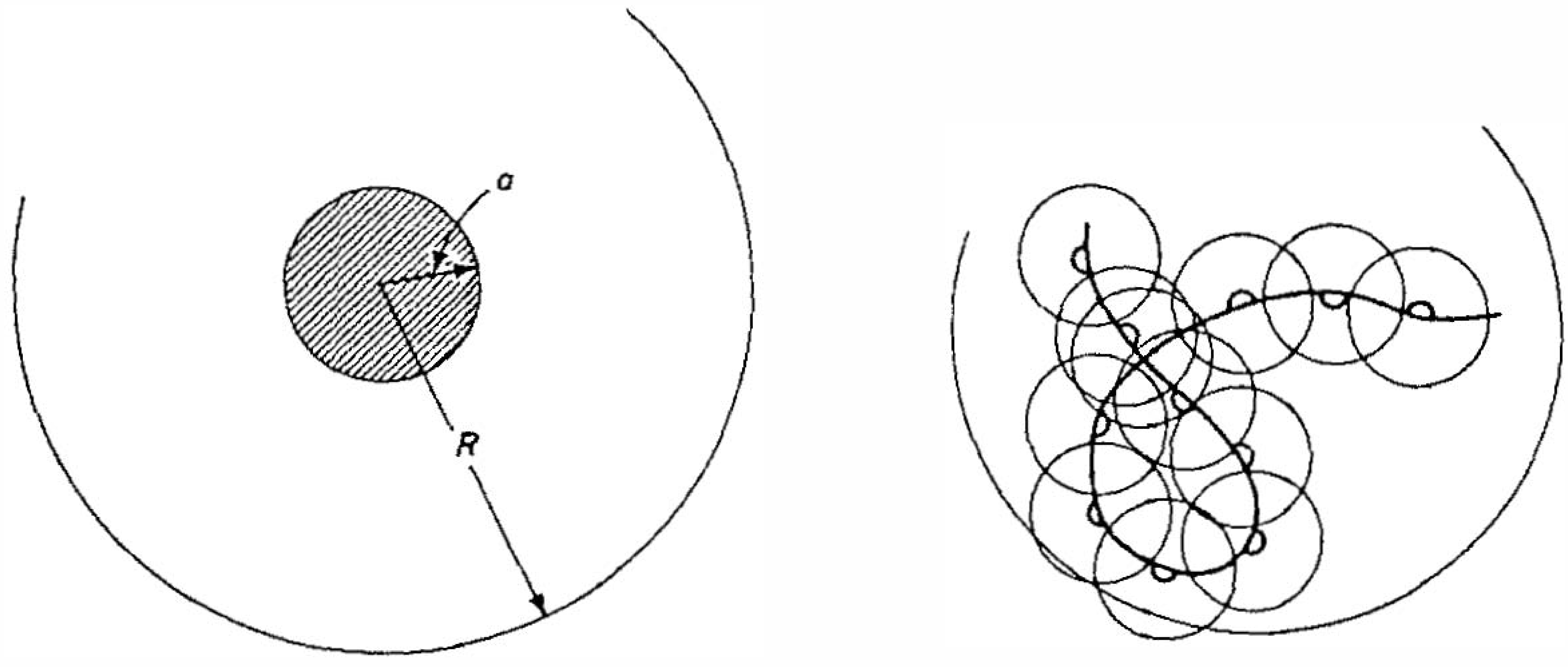
Suppose that a random coil macroion occupies a spherical volume v of radius a, as shown in Fig. 11*a*. The charge density arises from charged groups of the macroions and counter ions. The former is assumed to be expressed as a uniform density in the spherical volume, v, namely,

$$\rho_m = -e_0 n/v \qquad \text{in } v$$

and

$$\rho_m = 0 \qquad \text{outside of } v \tag{35}$$

If the macroion is placed at the center of the spherical free volume of radius R, the potential ψ is a function of the distance r from the center and the Poisson–Boltzmann equation for this system is difficult to solve. A method of approximation has been devised on the basis of the following fact. When there are many charged groups in v, counter ions are strongly attracted by them and most of the counter ions are retained in v. Consequently, most of the charges in v are canceled and the remaining apparent charge becomes much smaller than the original charge of the macroion (*5*).



(a) (b)

FIG. 11. (*a*) A spherical macroion with the uniform distribution of charged groups in a spherical free volume. (*b*) Atmospheres of counter ions around individual charged groups on the chain of the macroion.

According to the notations in the previous chapter, n^* is considered to be much smaller than n or the apparent degree of dissociation β is much smaller than unity. This kind of relation can be assumed everywhere in v. If a new quantity λ is defined as a function of r by

$$(n/v)\lambda = (n/v)-(nN/V')\exp(-e_0\psi/kT) \tag{36}$$

λ is very much smaller than unity in v

$$\lambda \ll 1 \tag{37}$$

By neglecting the quadratic and higher-order terms of λ, we have from Eqs. (35) and (18)

$$\Delta\lambda = \chi^2\lambda \qquad \text{in } v \tag{38}$$

where

$$\chi^2 = (4\pi e_0{}^2/\varepsilon_0 kT)(n/v) \tag{39}$$

This differential equation, which is of the same type as the Debye–Hückel equation for simple electrolytes, can be easily solved. The charge density or λ and the electric potential ψ in v are given as functions of distance r by

$$\lambda = \ln(V'/NvC)\sinh\chi r/(\chi r\cosh\chi a) \tag{40}$$

$$e_0\psi/kT = \ln(V'/NvC)[\sinh\chi r/(\chi r\cosh\chi a)] - \ln(V'/Nv) \tag{41}$$

where the integration constant C is determined by the boundary conditions, that is, by the continuity of the potential and its derivative at the surface of v (at $r = a$). Actually the term $\ln C$ comes from the contribution to the potential of counter ions outside of v. If this contribution is small, $\ln C$ is negligible.

The apparent charge of the macroion n^* is approximately given by

$$n^* = n\langle\lambda\rangle = (\varepsilon_0 kTa/e_0{}^2)\ln(V'/NvC)\{1 - \sinh\chi a/\chi a\cosh\chi a\} \tag{42}$$

where

$$\langle\lambda\rangle = \int_v \lambda\, dv/v$$

and the potential at the surface of v is given by

$$e_0\psi(a)/kT = \ln(V'/NvC)(\sinh\chi a/(\chi a\cosh\chi a)) - \ln(V'/Nv) \tag{43}$$

With the above approximation the distribution of counter ions is not uniform in v. As shown in Eq. (40), the deviation from complete neutrality ($\lambda = 0$) is very small in the central part of v and relatively large in the peripheral part. The maximum value of λ is taken at the surface $r = a$. This maximum is small if $\chi a \gg 1$. Under this condition, the potential $\psi(r)$ is almost uniform in v.

The factor V'/N is determined by the integration of $\exp(-e_0\psi/kT)$ in the total free volume V/N. The previous two-phase approximation corresponds to the condition that

$$V'/N = [(n - n^*)/n^*](V - Nv)/N \tag{44}$$

If this relation is put into Eq. (42) and the term $\ln C$ is neglected, the energy u_e and the free energy f calculated according to Eqs. (20) and (22) are found to be given approximately by

$$u_e = (1/2)n^{*2}e_0{}^2/\varepsilon_0 a \tag{45}$$

$$f = -(1/2)n^{*2}e_0{}^2/\varepsilon_0 a + kTn\ln((n - n^*)/vc^0 e) \tag{46}$$

and the activity coefficient of counter ions is given by

$$\gamma = (n^*/n)(V/(V-Nv)) = \beta/(1-\phi)$$

which is the same result as obtained by the previous two-phase model although the present calculation initially has taken into consideration the nonuniform distribution of counter ions in v. As discussed in the previous chapter, the above result agrees well with experimental data. (See also Ref. *5*).

The quantity χ, defined by Eq. (38), has the same meaning as the κ parameter which appears in the Debye–Hückel theory for simple electrolytes and the quantity $1/\chi$ is the radius of the counter ion atmosphere around each charged group in the macroion whose concentration is given by n/v. If this radius is very much smaller than the radius a of the volume v, most of the charges of the macroion are screened by counter ions inside of v. Only in the peripheral region, the thickness of which is of the order of $1/\chi$, are the charges not expected to be screened effectively, as shown in Fig. 11*b*. This is the origin of relatively large values of λ at the surface. Therefore when

$$\chi a \gg 1$$

the "small deviation from neutrality" approximation is applicable.

As a numerical example, if $n = 1000$ and $a = 230$ Å in water at room temperature, $1/\chi$ becomes about 24 Å, and is much smaller than a. The thickness of the peripheral region where the deviation from neutrality is appreciable is about 1/10 the radius a. Thus, the spherical macroion appears to have a thinly charged layer at its surface.

A more detailed mathematical treatment of the Poisson–Boltzmann equation is necessary for accurate analysis of the ion distribution in and around the macroion. A useful method may be to take into account the higher-order terms of deviation from neutrality as perturbation for the solution of Eq. (38). Such refinement, however, is not expected to bring a large change of the result.

Thus, the approximate treatments in the earlier chapter and in this section are very reasonable. The approximation "small deviation from neutrality" can be applied to any shape and size of macroion having a diffuse but dense distribution of charged groups. When a flexible macroion is extended from spherically coiled conformations to stretched ones with the increase of charge, an ellipsoidal model may cover the whole range.

The other important assumption in the present method consisted of representing the assembly of discrete charges of the macroion by a continuous function $\rho_m(x)$ or $c_m(x)$. This assumption is valid if the atmosphere of counter ions around each charged group overlaps with each other; in other words, it is valid if the average distance d between neighboring charged groups in the macroion is smaller than or of the same order as the diameter of the ionic atmosphere around each group, as shown in Fig. 11*b*. This condition is expressed by

$$\chi d \lesssim 1$$

or

$$(3e_0{}^2/\varepsilon_0 kT)(n/a)^{1/6} \lesssim 1 \tag{47}$$

In the Debye–Hückel theory of simple electrolytes it was shown that the average distance between neighboring ions of the same charge in the solution is always smaller than or of the same order as the radius of the ionic atmosphere, except in an extremely concentrated solution. Similarly, the above condition is satisfied in the wide range of the number of charges and the volume of the macroion. For instance, when $n = 1000$ and $a =$ 230 Å, the average distance d in the sphere is equal to 23 Å which is of the same order as $1/\chi$. As shown in Eq. (47), the quantity χd is insensitive to the change of the number n and the radius a.

If the atmospheres are overlapped, the discreteness of the charges in the macroion has no great effect on the determination of the distribution of counter ions in and around the macroion. As long as the domain occupied by the macroion can be defined separately from the outside domain in the sense that the average concentrations of charges in two domains are considerably different, it is reasonable to represent the charge distribution in the domain by a continuous function of the spatial coordinates.

III. ANALYTICAL SOLUTION FOR A RODLIKE MACROION

In the previous sections the average electric potential in and around a macroion was described by the Poisson–Boltzmann equation. As shown by Fuoss, Lifson, and Katchalsky and by Alfrey and Morawetz in Ref. *12* and *13*, respectively, this equation can be exactly solved for an infinitely long rodlike macroion with counter ions in a cylindrical free volume. This result is briefly described herein, special attention being given to the "counter ion condensation" phenomenon.

In this case, n discrete charged groups on the rodlike macroion of length l and radius a are represented approximately by a uniform charge density $n/l = 1/d$, where d is the average distance between neighboring groups on the rod. This representation is valid when the condition

$$(e_0^2/\varepsilon_0 kT)(d/a^2) \lesssim 1 \tag{48}$$

(instead of Eq. 47) is satisfied by a sufficiently high charge density on the macroion. In water at room temperature, Eq. (48) is rewritten as $7(d/a^2) \lesssim 1$, where d and a are expressed in the angstrom unit. The equation to determine the average potential and the ion distribution outside of the rod is then expressed as

$$\Delta\psi = -(4\pi e_0/\varepsilon_0)c_+(r) = -(4\pi e_0/\varepsilon_0)A \exp(-e_0\psi/kT) \tag{49}$$

where

$$\Delta = (d^2/dr^2) + (1/r)(d/dr)$$

and

$$A = n/\int_a^R \exp(-e_0\psi/kT)\, 2\pi r\, dr$$

The potential ψ must be a function of the distance r from the center of the rod. The radius of the free volume R is chosen to satisfy the condition $Nl\pi R^2 = V$. Counter ions are assumed to be excluded from the rod itself, and its radius a denotes the minimum distance of approach of counter ions to the macroion.

The boundary conditions for the electric field at a and R are then given by

$$(\partial\psi/\partial r)_a = 2e_0/\varepsilon_0 ad; \qquad (\partial\psi/\partial r)_R = 0 \tag{50}$$

respectively. The analytical solutions of the above Poisson-Boltzmann equation were found to be (*12*, *13*)

$$e_0\psi/kT = \ln\{(2Q/B^2)[r^2/(R^2-a^2)] \sinh^2(B \ln br)\} \tag{51}$$

when the integration constant B is real, and

$$e_0\psi/kT = \ln\{(2Q/|B|^2)[r^2/(R^2-a^2)] \sin^2(|B| \ln br)\} \tag{52}$$

when it is imaginary. The integration constants B and b must satisfy the relations:

$$Q = (1-B^2)/[1+B \coth(B \ln(R/a))]$$
$$B \ln b = -B \ln R - \tanh^{-1} B \tag{53}$$

for Eq. (51) and

$$Q = (1+|B|^2)/[1+|B| \cot(|B| \ln(R/a))]$$
$$|B| \ln b = -|B| \ln R - \tan^{-1}|B| \tag{54}$$

for Eq. (52).

The constant B is real and $0 \leq B \leq 1$ for low charge densities in the range $0 \leq Q \leq \ln(R/a)/[1+\ln(R/a)]$. ($Q = e_0{}^2/\varepsilon_0 kTd$). It becomes imaginary for high charge densities where $Q \geq \ln(R/a)/[1+\ln(R/a)]$. When a is sufficiently small, or more exactly when the ratio a/R is sufficiently smaller than unity, the solution has a mathematical abnormality at Q equal to unity.

The electric energy and the electric free energy calculated from the above solutions according to Eqs. (20) and (24) are expressed as (*14*)

$$u_e = (nkT/Q)\{(1+B^2)\ln(R/a)+\ln[((1+Q)^2-B^2)/(1-B^4)]+Q\} \tag{55}$$

and

$$f_e = -u_e+nkT\ln\{[(R^2-a^2)/a^2][(1-Q)^2-B^2]/2Q\} \tag{56}$$

for real B and

$$u_e = (nkT/Q)\{(1-|B|^2)\ln(R/a)+\ln[((1+Q)^2+|B|^2)/(1+|B|^2)]+Q\} \tag{57}$$

and

$$f_e = -u_e+nkT\ln\{[(R^2-a^2)/a^2][(1-Q)^2+|B|^2]/2Q\} \tag{58}$$

for imaginary B. This free energy yields the following expression for the osmotic coefficient or the activity coefficient of counter ions:

$$\gamma = (1-B^2)/2Q-\phi/(1-\phi) \qquad \text{for real } B \tag{59}$$

$$\gamma = (1+B^2)/2Q-\phi/(1-\phi) \qquad \text{for imaginary } B \tag{60}$$

Numerical examples of the value of B as a function of Q are given in Fig. 12*b* (Ref. *14*). It is found that at values of Q larger than unity, the increase of B is very slow and the activity coefficient γ is almost proportional to $1/Q$. With the ratio R/a increasing or with the concentration ϕ decreasing, B tends to $1-Q$ at Q smaller than unity and approaches zero at Q larger than unity. The activity coefficient thus tends to $1-Q/2$ at Q smaller than unity and to $1/2Q$ at Q larger than unity; namely,

$$\begin{aligned} &\gamma \to 1-Q/2 && \text{for } 0 \leq Q \leq 1 \\ &\gamma \to 1/2Q && \text{for } 1 \leq Q \end{aligned} \tag{61}$$

as is shown in Fig. 12*c*.

There results agree qualitatively with those obtained previously with the more simple approach. Thus, the simple two-phase model provides a reasonably meaningful path to the elucidation of a characteristic phenomenon of polyelectrolytes "counter ion condensation." The numerical value of the activity coefficient obtained here, however, is different from the value estimated previously. In the limit of dilution the activity coefficient decreases with increasing Q even at Q smaller than unity and becomes equal to $1/2Q$ instead of $1/Q$ at Q larger than unity. In the present calculation that is based on the analytical solution of the Poisson–Boltzmann equation, the concentration of counter ions outside of the macroion

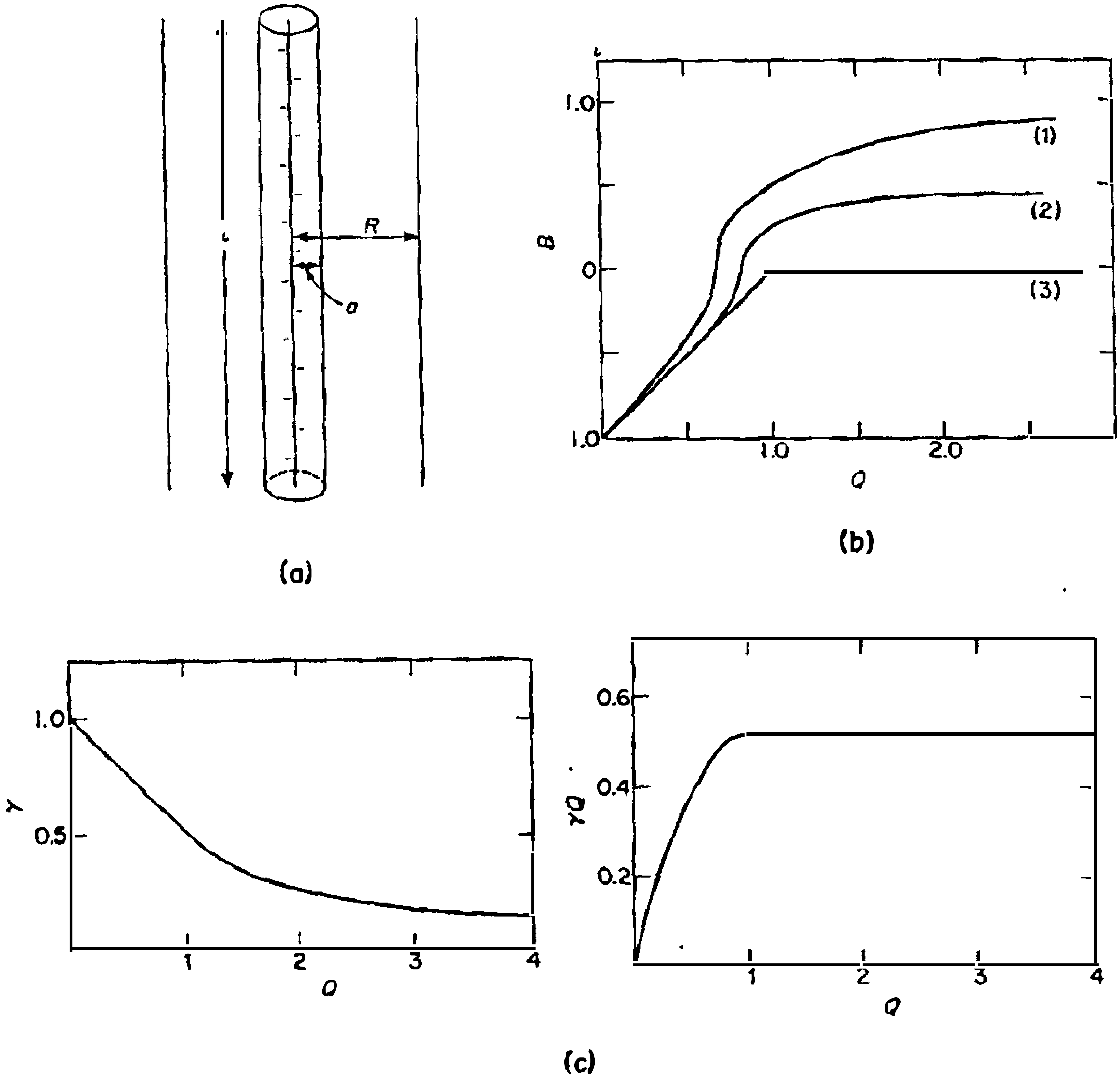


FIG. 12. (a) A cylindrical macroion with the uniform distribution of charged groups in a cylindrical free volume. (b) The value of the constant B as a function of the charge density Q at various values of the volume concentration; (1) $\ln \phi = -2$, (2) $\ln \phi = -5$, and (3) $\ln \phi = -\infty$. (c) The relation between the activity coefficient γ and the charge density Q in the limit of dilution, and the relation between the activity γQ or the number of free counter ions and the charge density Q in the limit of dilution.

continuously decreases with the distance from the macroion. The concentration of counter ions at the surface of the free volume is therefore less than is estimated with the previous approximation of a uniform phase outside of the macroion. A simpler method to derive this result, Eq. (61), is described in Chapter 6, Section III.

Here we add an analysis of the Poisson–Boltzmann equation for a rigid spherical macroion in a spherical free volume, for comparison with the case of the rigid rod. The Poisson–Boltzmann equation is written

$$\Delta\psi = -(4\pi e_0/\varepsilon_0)A \exp(-e_0\psi/kT) \qquad (62)$$

where

$$\Delta = d^2/dr^2 + (2/r)(d/dr)$$

and

$$A = n\Big/\int_a^R \exp(-e_0\psi/kT)4\pi r^2 dr$$

and the boundary conditions are given by

$$(d\psi/dr)_a = ne_0/\varepsilon_0 a^2; \qquad (d\psi/dr)_R = 0 \qquad (63)$$

The differential equation (62) can not be solved analytically, but approximate solutions were derived by Imai (*15*). For a highly charged sphere in a very large spherical free volume, the potential energy $|e_0\psi|$ is expected to be very much larger than the kinetic energy kT in the neighborhood of the sphere. Under such a condition, the approximate solution of Eq. (62) was found to be written in the form

$$e_0\psi/kT \doteqdot -\ln \sinh^2(+B'/r+b')+\text{const} \qquad (64)$$

in the neighborhood of the sphere, and in the form

$$e_0\psi/kT \doteqdot -2B'/r \qquad (65)$$

in the region distant from the sphere. The apparent charge of the sphere n^*e_0 is related to the constant B' by the equation

$$2B'/a = n^*e_0{}^2/\varepsilon_0 kT a = \beta P$$

From the above equations it was shown that the apparent charge n^* increases logarithmically with dilution and is insensitive to the increase of the total number of charges of the sphere. At extremely large values of P, the value of βP tends to the order of $\ln(1/\phi)$. $(n-n^*)$ counter ions are condensed in a thin layer on the surface of the sphere, the thickness of which is very much smaller than the radius a, that is, its ratio to the radius is of the order of $1/\beta P$. These results are very similar to those obtained from the spherical random coil macroion.

Chapter 4

VALENCE AND SIZE OF COUNTER IONS

I. Effect of Valence of Counter Ions

The valence of counter ions strongly influences the counter ion condensation phenomenon. Let us consider a macroion having a total charge $-ne_0$ and counter ions of charge $+ze_0$. The number of counter ions must be n/z. The equation of the distribution equilibrium between counter ions in the simple two phase model is written:

$$\ln(1-\beta)/\beta = \ln \phi/(1-\phi) - ze_0\delta\psi/kT \tag{66}$$

where β, as before, is the apparent degree of dissociation, i.e., the ratio of the apparent charge n^*e_0 to the total charge ne_0. The number of free counter ions is given by n^*/z. The only difference from Eq. (2) comes from introduction of valence z in the potential energy difference. If the cylindrical model is applied,

$$\ln(1-\beta)/\beta = \ln \phi(1-\phi) + \beta z Q \ln(1/\phi) \tag{67}$$

It is found that for values of Q smaller than $1/z$, the degree of dissociation slowly decreases with decreasing concentration ϕ, and then increases, tending to unity at zero concentration. For values of Q larger than $1/z$, however, the degree of dissociation slowly decreases with decreasing concentration, tending to $1/zQ$ at zero concentration. Infinite dilution can not result in complete dissociation. With increase of the total charge of the macroion, the number of free counter ions first increases but then levels off at $Q = 1/z$. In the case of divalent counter ions, for example, the critical value of Q corresponds to an average distance of about 14 Å between (monovalent) charged groups on the macroion in water at room temperature. The number of free counter ions, n^*/z, can not exceed $n/z^2 Q$, which is inversely proportional to the square of the valence. With higher valence of counter ions their condensation takes place at a lower density of charges and a smaller number of free counter ions. The critical value of the charge density is determined by the balance between the entropy and energy difference of bound and free counter ions.

In the two-phase approximation, counter ion condensation is not influenced by the valence of each charged group on the macroion at a given value of the charge density as long as charged groups can be represented by a uniform charge density along the cylinder. It should be noted, however, that the radius of the ionic atomosphere around each multivalent group is small so that reexamination of the applicability of the approximation of uniform charge density is required.

II. MIXTURE OF COUNTER IONS OF DIFFERENT VALENCES

In a mixture of two kinds of counter ions which have different valence, the characteristic phenomenon is deduced from the requirement that equilibrium must be established separately for each of the two kinds of counter ions (*1*).

The number of counter ions of charge ze_0 per macroion is denoted by m and that of charge $z'e_0$ by m'; the total charge of each macroion must be equal to $mze_0 + m'z'e_0 = ne_0$. The degree of dissociation, β and β', of the two kinds of counter ions, respectively, are given by the ratio of the number of these ions inside and outside of v. The ratios q and q' defined by mz/n and $m'z/n$, respectively, are the proportions of the charges carried by the two kinds of counter ions $(q+q' = 1)$. For the cylindrical model the equilibrium conditions are then given by

$$\ln (1-\beta)/\beta = \ln \phi/(1-\phi) + (\beta q + \beta' q') z Q \ln (1/\phi)$$

$$\ln (1-\beta')/\beta' = \ln \phi/(1-\phi) + (\beta q + \beta' q') z' Q \ln (1/\phi) \qquad (68)$$

if the two-phase approximation is employed. For the spherical model, Q is replaced by P and $\ln (1/\phi)$ is replaced by $(1-\phi^{1/3})$.

When the value of Q is smaller than both $1/z$ and $1/z'$, the degree of dissociation of both counter ions tends to unity at zero volume concentration. When, however, Q becomes larger than either $1/z$ or $1/z'$, counter ion condensation takes place even at zero volume concentration, and the condensation of two kinds of counter ions has correlation. Under the assumption that z' is larger than z, it is convenient to classify the value of Q into the following four categories for analysis of the behavior of β and β' at infinite dilution. The degree of dissociation tends to different values determined by the value of Q.

$$\begin{array}{llll}
\beta \to 1 & \text{and} \quad \beta' \to 1 & \text{for} & 0 \le Q \le 1/z' \\
\beta \to 1 & \text{and} \quad \beta' \to (1/q'Qz') - (q/q') & \text{for} & 1/z' \le Q \le 1/qz' \\
\beta \to 1 & \text{and} \quad \beta' \to 0 & \text{for} & 1/qz' \le Q \le 1/qz \\
\beta \to 1/qQz & \text{and} \quad \beta' \to 0 & \text{for} & 1/qz \le Q
\end{array} \tag{69}$$

These results are obtained from the equations listed under (68).

Now, suppose that the charge of the macroion and the number of two kinds of counter ions are increased at a constant ratio q or q'. Such a situation can be realized experimentally by the addition to a solution of polyacid of a mixture of alkali having two cations of different valencies. With increasing Q, the dissociation of counter ions of the larger valence z' begins to be suppressed at $Q = 1/z'$. This critical value of Q is independent of the ratio q of the two kinds of counter ions present. With further increase of Q, the degree of dissociation β' of counter ions of higher valence is decreased and is eventually fully suppressed at $Q = 1/qz'$. All counter ions of higher valence are bound to the macroion. At larger values of Q all free counter ions are of lower valence. The dissociation of counter ions of smaller valence begins to be suppressed at $Q = 1/qz$. With further increase of Q, the degree of dissociation of these counter ions decreases in proportion to $1/Q$. These features of ion condensation are shown in Figs. 13*a* and *b*.

The complete suppression of the dissociation of counter ions of higher valence is a characteristic property of polyelectrolytes. The difference of the valence is remarkably amplified.

Condensation of counter ions of higher valence begins to take place when the charge density Q exceeds the critical value $1/z'$. The degree of binding increases with increasing Q as if all of the counter ions present in the solution were of the same valence z'. The apparent charge number n^* of the macroion is equal to $n[1-(1-\beta')q'] = n(q+\beta'q')$ when the degree of dissociation of counter ions of valence z' is β' and that of counter ions of valence z is equal to unity. As long as the value of $(n^*/n)Q$ or $(q+\beta'q')Q$ is larger than $1/z'$, the binding of counter ions of valence z' must continue. Therefore, β' must attain a value determined by $(q+\beta'q')Q = 1/z'$. The condition of counter ion condensation is determined by the charge density

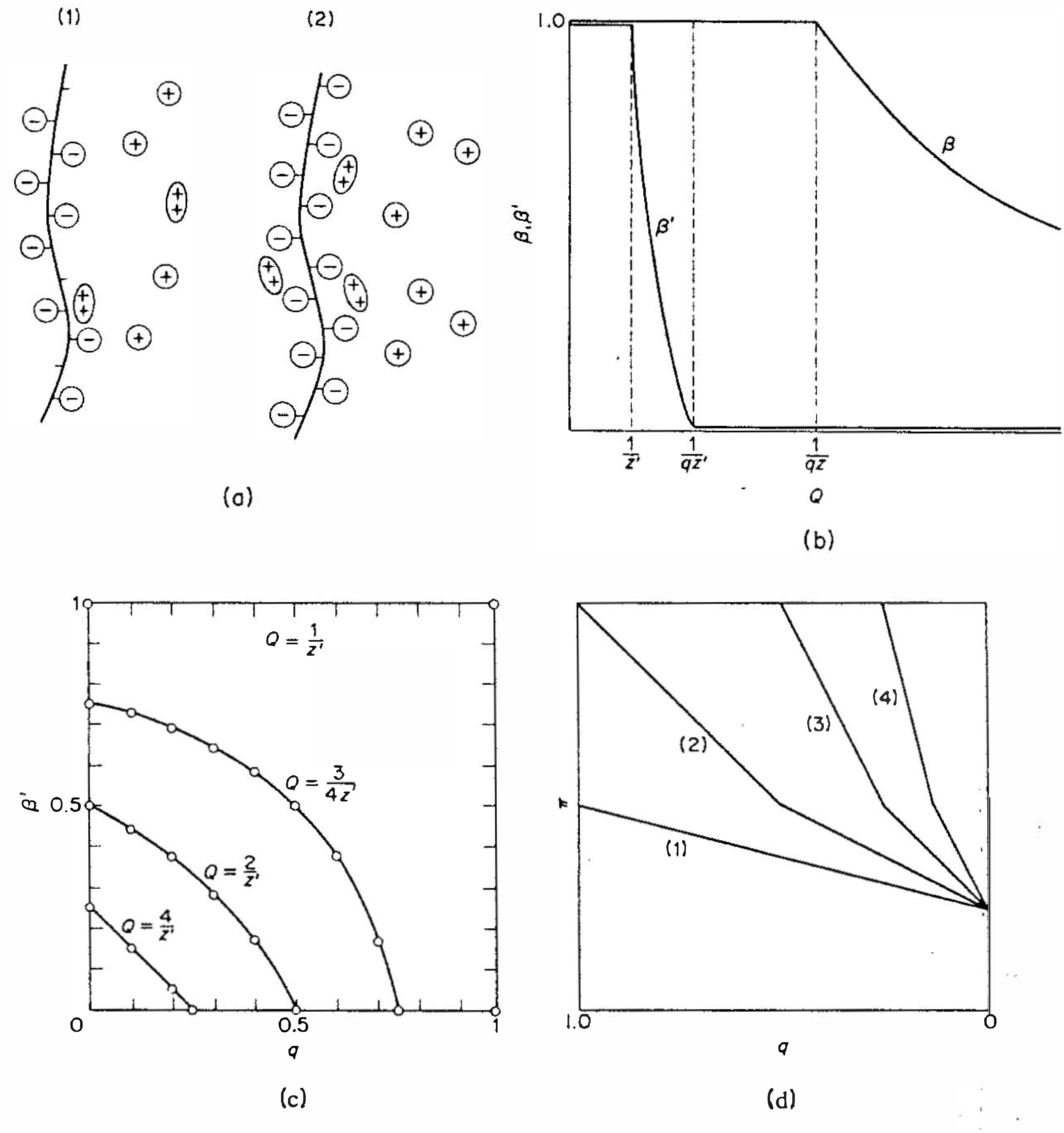


FIG. 13. (*a*) Illustration of binding of counter ions of different valences to a cylindrical macroion. With the increase of the charge density from (1) to (2), bound divalent counter ions increase and only monovalent counter ions remain in the free state. (*b*) Relations between the degrees of dissociation of counter ions β, β' and the charge density Q in a mixture of two kinds of counter ions having different valences z and z' at infinite dilution. (*c*) Relations between the degree of dissociation of counter ions of the larger valence z' and the ratio of two kinds of counter ions at various values of the charge density Q. (*d*) Relations between the osmotic pressure and the ratio of two kinds of counter ions of different valences ($z'/z = 2$) at various values of the charge density Q; (1) $Q = 1/2$, (2) $Q = 1$, (3) $Q = 2$, and (4) $Q = 4$.

of the macroion. It is independent of the number of free ions that are present. When Q is larger than $1/qz'$, the value of $(n^*/n)Q$ can not be less than $1/z'$ even at $\beta' = 0$. Therefore, the binding continues to increase until all counter ions of valence z' are lost from the outside of the macroion. For this reason the degree of dissociation of counter ions of valence z' must be equal to zero at Q larger than $1/qz'$. During decrease of the degree of dissociation of counter ions of higher valence from unity to zero, all of the counter ions of lower valence are in the free state. The binding of these counter ions begins after Q becomes larger than $1/qz$. Therefore, in the range of Q between $1/qz'$ and $1/qz$, all counter ions of higher valence are bound and all counter ions of lower valence are free. Such a range of Q exists independently of the magnitude of the difference between the valence of the two kinds of counter ions.

Figure 13*c* shows the relation between the degree of dissociation and the ratio of two kinds of counter ions at a constant value of the charge density of the macroion. At the beginning of the addition of counter ions of higher valence they are all bound to the macroion until the apparent charge density is decreased to a critical value for their condensation. At this critical value, further addition begins to produce free counter ions of larger valence.

Consider a macroion of high charge density ($Q > 1$) with monovalent counter ions preserving electroneutrality. Some of the counter ions are condensed in the volume of the macroion. In this condition the charge density is, of course, higher than the critical value for condensation of counter ions of higher valence. If, therefore, divalent counter ions are added, all of them are bound. Bound monovalent counter ions must be freed and the apparent charge is maintained at the critical value for condensation of monovalent ions, thereby facilitating the exchange of bound counter ions.

The activities of two kinds of counter ions are given by $\beta/(1-\phi)$ and $\beta'/(1-\phi)$, respectively. The osmotic pressure of this solution is proportional to the total concentration of free counter ions:

$$(m\beta + m'\beta')/(1-\phi) = n[(q\beta/z) + (q'\beta'/z')]/(1-\phi) \tag{70}$$

Figure 13*d* shows the dependence of the osmotic pressure on the ratio q of two kinds of counter ions at various values of the charge density of the macroion.

The above analysis was made in the limit of extreme dilution by employing the two-phase approximation. It is impossible to obtain an exact solution of the Poisson–Boltzmann equation for the mixture of counter ions of different valence. Results in the preceding chapters suggest that the counter ion distribution derived from the solution of the Poisson–Boltzmann equation is different from that of the two-phase approximation. The difference is in the distribution outside of the volume of the macroion. Comparison between the results of Eqs. (12) and (61) shows that the real distribution outside of the macroion is not uniform; that is, the concentration of counter ions at the periphery of the free volume, which is related to the activity or the osmotic pressure, is considerably smaller than the average concentration outside of the macroion. The ordinate of Fig. 13*b* gives the degree of dissociation of counter ions which is related to the average concentration outside. The activity coefficient of counter ions must be smaller than this ordinate.

Many experimental data support the theoretical results obtained. It has often been observed that polyvalent counter ions are strongly and completely bound by macroions in polyelectrolyte solutions (*16*). The replacement of bound monovalent counter ions by polyvalent ones has been frequently observed as well. Experimental results similar to the theoretical predictions developed in Fig. 13*d* have been obtained in studies of the osmotic pressure or the extensive force of polyelectrolyte gels (*17*). Previously such behaviors were apt to be attributed to a special interaction between polyvalent counter ions and charged groups of the macroion, for instance, the salt bridge. The present theory, however, indicates that these phenomena can occur without such a special interaction. It is simply due to the coulomb potential of the macroion in which the effect of the valence of counter ions is greatly amplified.

III. EFFECT OF SIZE OF COUNTER IONS

Both the chain of the macroion and the counter ion have finite sizes from which other molecules or ions are excluded. When their sizes are large, the minimum distance between the counter ion and the chain must be large, as shown in Fig. 14*a*. As a consequence, the average potential difference between bound and free counter ions is small. Moreover, the space around the chain of the macroion in which bound counter ions are mobile is also small. To analyze such effects of the size of counter ions, Kagawa and Gregor applied the Poisson–Boltzmann equation 1(59) with the boundary condition that counter ions can not enter into the cylindrical volume, the radius of which is given by the sum of the radius of the cylindrical macroion and that of spherical counter ions (*18*). The dependence of the electric potential of bound counter ions on their sizes obtained by this method was found to agree well with experimental results. Here, however, we apply the simpler two-phase approximation and extend the analysis to the mixture of counter ions of different sizes.

Instead of Eq. (1), the equilibrium is given by

$$(n-n^*)/v^* = n^*N/(V-Nv)\exp(-e_0\delta\psi/kT) \tag{71}$$

where v^* is the effective volume of the potential trough or valley in which bound counter ions are mobile. This volume must be distinguished from the total volume v of the potential trough made by each macroion. In other words, the effective volume v^* is given by subtracting from v the volume of the chain skeleton (including charged groups) from which bound ions are excluded. (This excluded volume increases with increasing number of bound counter ions.) The potential difference $\delta\psi$ was previously given by $-e_0\delta\psi/kT = 2\beta Q\ln(R/a)$ for a cylindrical macroion in which the quantity a was defined as the radius of the cylindrical volume apparently occupied by the macroion. However, the quantity a in the above equation must be modified to give the correct value of the average potential of bound counter ions. It can have different values for different chains and counter ions. When the chain skeleton has a large average radius, the distribution of charged groups in the cylinder is diluted and a larger value must be used for a in the above expression of the potential difference. The large radius of counter ions has a similar effect. Thus, by introducing the effective radius a^* in the average potential, the following equation is obtained:

$$\ln(1-\beta)/\beta = \ln\phi/(1-\phi)+\beta Q\ln(1/\phi)+\ln(v^*/v)+\beta Q\ln(a/a^*) \tag{72}$$

The new terms $\ln(v^*/v)$ and $\ln(a/a^*)$ are independent of the apparent volume concentration $\phi(=Nv/V)$ and the charge density Q, and are determined by the radii of the chain skeleton and the counter ion, or by the volumes excluded in their interaction.

In the case of spherical macroions, the same correction $\ln(v^*/v)$ must be introduced, but there seems to be no reason for the above type of correction in the potential difference.

According to Eq. (72), the size has no influence at extreme dilution or in the limit of $\phi\rightarrow 0$. The degree of dissociation tends to unity for Q smaller than unity and tends to $1/Q$ for Q larger than unity. The two correction terms $\ln(v^*/v)$ and $\ln(a/a^*)$ both become more negative for larger radii of counter ions or of the chain skeleton and at finite concentrations the degree of dissociation increases with increasing radii.

Now, let us consider a mixture of two kinds of counter ions of the same valence and different radii. The equations for the distribution equilibrium of these counter ions are given by

$$\ln(1-\beta)/\beta = \ln\phi/(1-\phi)+\ln(v^*/v)+(\beta q+\beta' q')Q[\ln(1/\phi) + \ln(a/a^*)]$$

$$\ln(1-\beta')/\beta' = \ln\phi/(1-\phi)+\ln(v^{*\prime}/v)+(\beta q+\beta' q')Q[\ln(1/\phi) + \ln(a/a^{*\prime})] \tag{73}$$

where $q = 1-q'$ is the fraction of one kind of counter ions. The correction terms due to v^*, a^* and $v^{*\prime}$, $a^{*\prime}$ must be distinguished for the two kinds of ions. In very dilute systems and for large values of Q

$$\beta q+\beta' q' = Q^{-1} \tag{74}$$

and

$$\ln(1-\beta)/\beta-\ln(1-\beta')/\beta' = \ln A \tag{75}$$

where $\ln A$ is the difference in $\ln(v^*/v)+\ln(a/a^*)$ between two kinds of counter ions, being positive when the counter ion of fraction q has a smaller radius than that of fraction q', $(q+q' = 1)$. As a consequence, the degree of dissociation β for the smaller ion-radius is always less than β' for the larger ion-radius. The relation of the degree of dissociation β and β' to the charge density Q and the fraction q has been calculated according to Eqs. (74) and (75) and the results are shown in Fig. 14*b*.

For Q smaller than or equal to unity, both β and β' are equal to unity at $\phi\rightarrow 0$ over the whole range of q. For Q larger than unity, counter ion condensation takes place. Equation (74) shows that the apparent charge density of the macroion is limited at $Q = 1$, independent of the ratio q and the size or the size difference of counter ions, and that the total number of two kinds of free counter ions or the osmotic coefficient g at infinite dilution is kept constant for $Q \geqq 1$, independent of the size difference and the ratio q. However, the number of each kind of free counter ions changes with q and Q. The value of βQ which is proportional to the activity of counter ions of the smaller radius increases slowly with increasing fraction q, tending to Q^{-1} at $q = 1$. The initial gradient of the increase of the activity is given by

$$[\partial(\beta q)/\partial q]_{q\rightarrow 0} = Q^{-1}/[A-Q^{-1}(A-1)] \tag{76}$$

In the example presented, the constant A is larger than unity and the denominator of the right-hand side of the equation is larger than unity. The initial gradient $(\partial(\beta q)/\partial q)_{q\to 0}$ is thus larger than Q^{-1}, which is the value

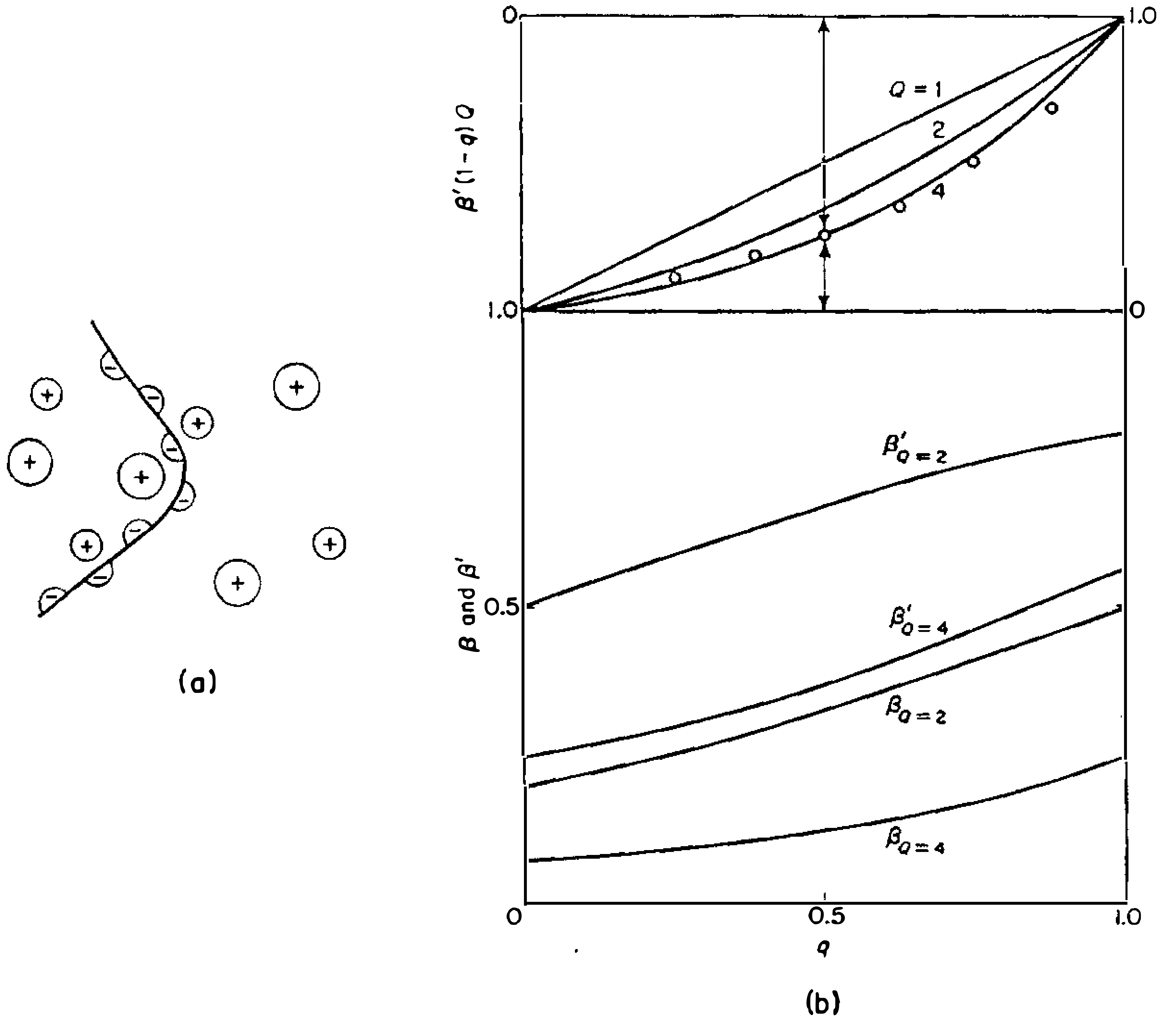


FIG. 14. (*a*) Illustration of binding of counter ions of different sizes to a cylindrical macroion. (*b*) Relations between the degrees of dissociation of counter ions β, β' and the ratio q of two kinds of counter ions in a mixture of counter ions of different sizes, at various values of the charge density Q; and relations between the numbers of free counter ions of different sizes $\beta Q q$ and $\beta' Q(1-q)$ and the ratio of two kinds of counter ions at various values of the charge density Q. The value of the constant $\ln A$ which represents the effect of the size difference was put equal to $\ln 4$.

of βq at $q = 1$. When counter ions of smaller size are added to a solution of macroions containing counter ions of larger size, the activity of the added ions becomes lower than that expected if no correlation between the two kinds of counter ions is assumed. Bound counter ions of larger size are preferentially replaced by counter ions of smaller size. This selective replacement by smaller ions is enhanced by larger values of the charge density Q. The selective binding of counter ions, however, is not as sensitive to counter ion size as it is to counter ion valence.

At finite concentrations the degree of dissociation of two kinds of counter ions must be obtained directly from Eq. (73). Although the calculation is complicated, results are similar to those obtained for the infinite dilution case described above.

Summarizing the above analysis, we have learned that the critical value of the charge density for condensation does not depend on the size, but the composition of bound counter ions depends on the size. In other words, the osmotic pressure is not affected by the size difference, while the activity coefficient of each kind of counter ions depends on the size. Such behavior of counter ions of different sizes (for instance, the selective replacement by counter ions of smaller size), has been observed in thermodynamic and transference measurements (*19*).

In the above treatment the effect of the size on the interaction between counter ions was neglected. A limit to the mutual approach of counter ions must be taken into consideration at high concentrations of counter ions in the volume v. This effect seems to decrease the concentration of bound counter ions, but it is to be noted also that when counter ions can not approach very closely the coulomb repulsion between counter ions becomes smaller.

Chapter 5

POLARIZABILITY OF POLYELECTROLYTES

I. FLUCTUATION OF ION DISTRIBUTION

In the earlier chapters it was emphasized that counter ions bound to the macroion can move in the apparent volume occupied by the macroion where the electric potential forms a trough or a valley. This mobility of bound counter ions can not be proved directly by the analysis of purely thermodynamic quantities which are determined mainly by the contribution of free counter ions. Evidence for this mobility seems to lie in the experimental fact that polyelectrolyte solutions show an extremely large dielectric constant (Fig. 15 (*20*, *21*)).

Let us consider a spherical macroion in and around which counter ions are distributed. At equilibrium, counter ions are distributed with a spherical symmetry and the system has no net electric dipole moment. If this system is placed in an external electric field, the distribution of counter ions is shifted relative to the charged groups of the macroion and an electric dipole is produced. The average dipole moment $\langle\mu\rangle$ of a polyelectrolyte molecule (a macroion with counter ions) in a static electric field E is given by the following averaging procedure.

$$\langle\mu\rangle = \int \mu \exp\left[-f(\mu)/kT + \mu E/kT\right] \mathrm{d}\mu \Big/ \int \exp\left[-f(\mu)/kT + \mu E/kT\right] d\mu \tag{77}$$

where $f(\mu)$ is the free energy of the system in a state with a dipole μ. The free energy has a minimum at $\mu = 0$. Even in the absence of the field E, however, the probability of a state with dipole is proportional to $\exp\left[-f(\mu)/kT\right]$ as a result of thermal fluctuation. From the above equation it is readily found that the polarizability α for a low field is given by

$$\alpha = (d\langle\mu\rangle/dE)_{E=0} = \langle\mu^2\rangle_{E=0}/kT \qquad (78)$$

The quantity $\langle\mu^2\rangle$ is the average of μ^2 resulting from thermal fluctuation in the absence of the field. Therefore, the polarizability is large if the fluctuation of the dipole is large. According to linear-response theory (*22*), this expression of the polarizability (Eq. 78) is generally applicable. In the present system all of the counter ions and the charged groups of the macroion can make contributions to the fluctuating dipole, μ.

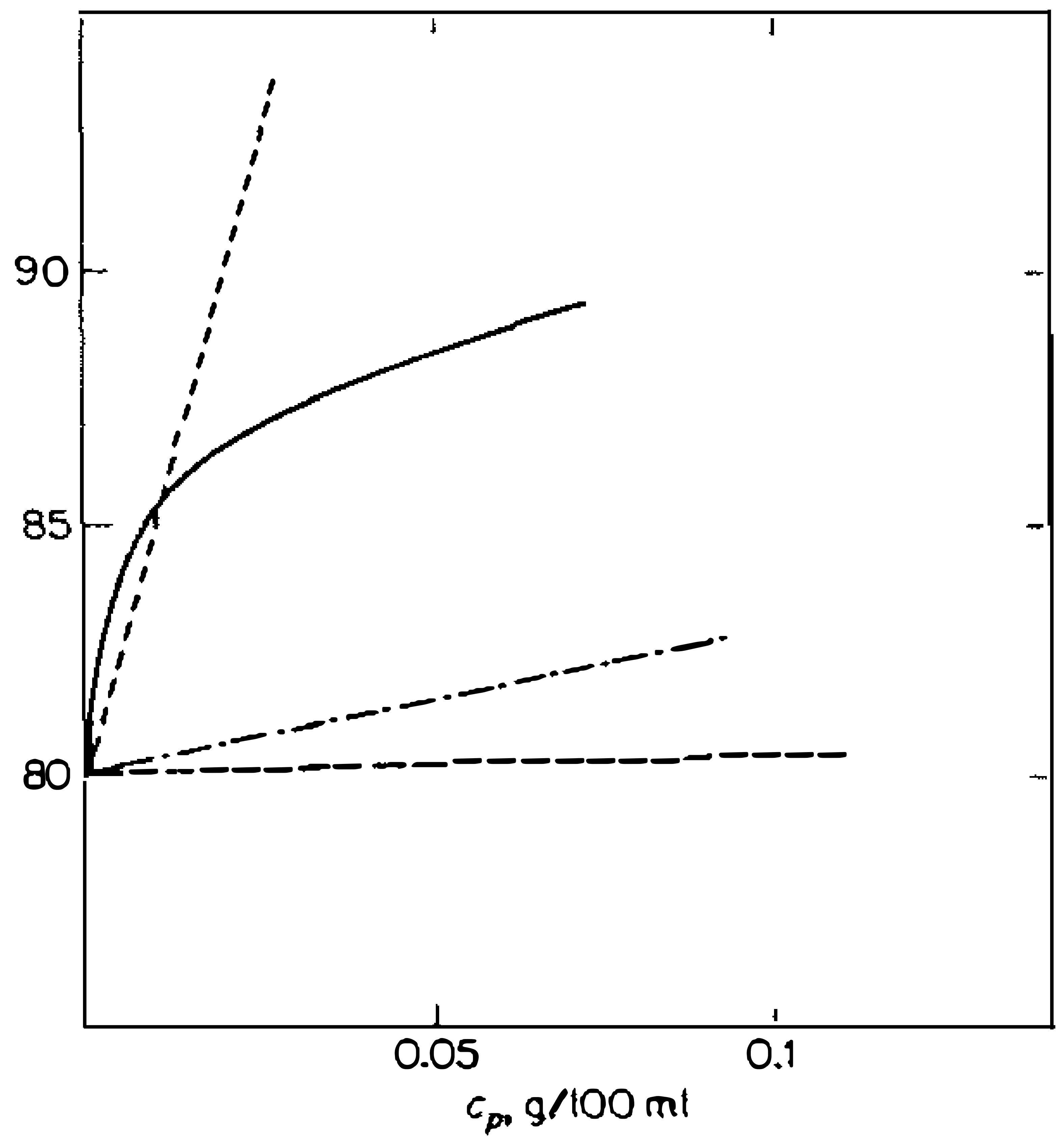


FIG. 15. Dielectric constant of polyelectrolyte solutions. (——): CMC (carboxymethylcellulose); (– –): DNA; and (-/-): serum albumin, in a salt free solvent. (–·): DNA in a $MgCl_2$ solution (*20*).

A dipole moment is produced when the center of the distribution of counter ions is displaced from the center of the distribution of charged groups of the macroion. Therefore, let us define this displacement δ between two centers as one of the coordinates specifying the distribution. Then the dipole moment is written as

$$\mu = ne_0\delta \quad \text{and} \quad \langle\mu^2\rangle = n^2e_0{}^2\langle\delta^2\rangle \qquad (79)$$

The free energy $f(\mu) = f(\delta)$ is obtained by taking into account all possible distributions at a given value of δ.

As a simplest approximation, let us suppose that all counter ions are retained in the volume v with a uniform density n/v, and the fluctuation of the counter ion distribution takes place, keeping the density uniform in the spherical volume v as shown in Fig. 16*a*.

$$f(\mu) = (1/2)(n/v)^2 e_0{}^2/\varepsilon_0 \int\int (1/r_{ij})\, dv_i dv_j \tag{80}$$

This free energy must be proportional to δ^2 for sufficiently small values of δ because it is an even function of δ. It is easily found by dimensional analysis that the integral on the right-hand side is proportional to $v\delta^2$. Actually,

$$f(\delta) = (2\pi/3)(n/v)^2(e_0{}^2/\varepsilon_0)v\delta^2 \tag{81}$$

We know from statistical thermodynamics that the average value of the free energy due to fluctuation is equal to $(1/2)kT$ per degree of freedom. Therefore

$$\langle f(\delta)\rangle = (1/2)kT \tag{82}$$

[The standard free energy at $\delta = 0$ is omitted in the above derivation of $f(\delta)$.] Thus, the average value of $\langle\mu^2\rangle$ is found to be given by

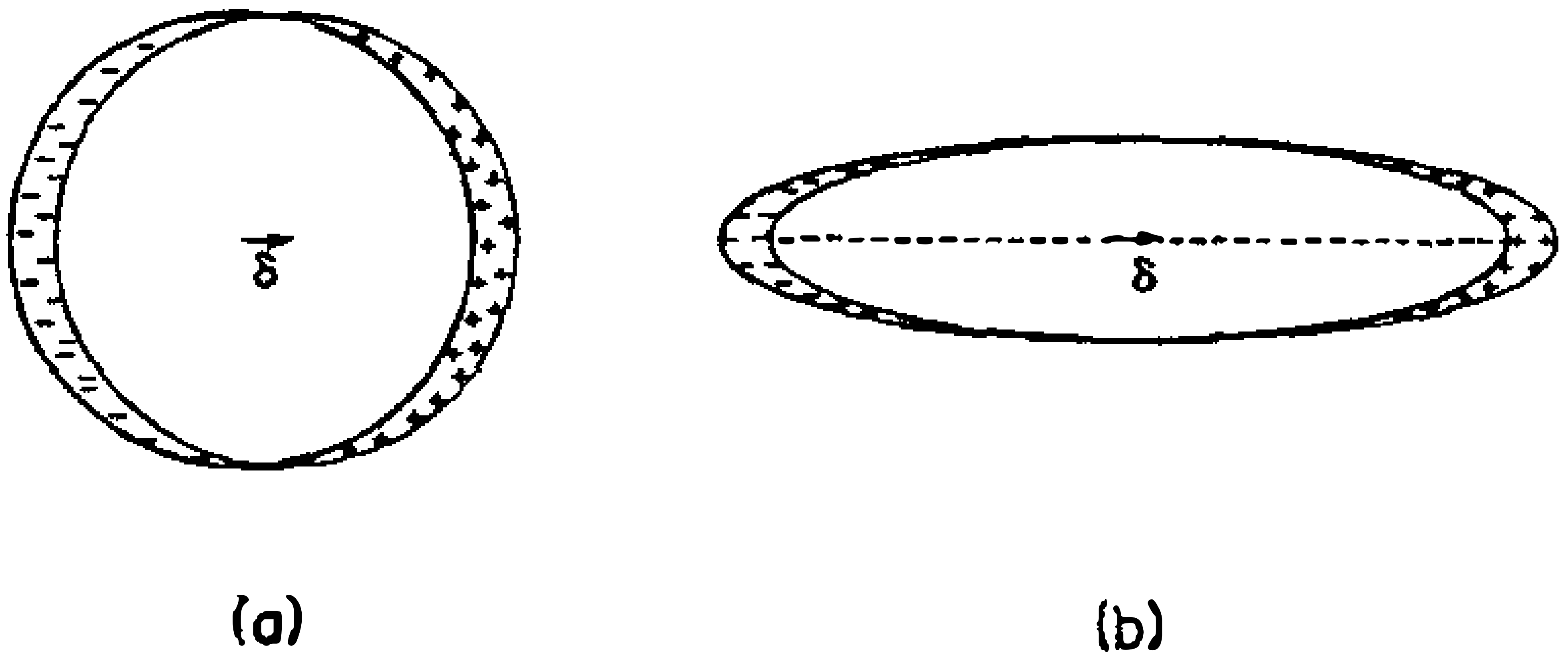


FIG. 16. (*a*) The displacement of the spherical cloud of counter ions bound to a spherical macroion. (*b*) The displacement of the ellipsoidal cloud of counter ions bound to an ellipsoidal macroion.

$$\langle\mu^2\rangle = (3/4\pi)kTv\varepsilon_0 \tag{83}$$

and the polarizability is given by

$$\alpha = (3/4\pi)v\varepsilon_0 \tag{84}$$

This result shows that the polarizability is determined by the volume of the macroion, independent of the charge or the charge density of the macroion. More exactly, it is determined by the volume in which bound counter ions are moving. The dipole moment increases with the charge density at a constant value of the displacement of the counter ion distribution. However, at high charge density the excess free energy due to a constant displacement becomes large, so that the average displacement decreases. As a result, the average dipole moment is not changed by the charge density. The above equation shows that in water at room temperature the root-mean-square of the fluctuating dipole moment is about 1000 Debye units for a sphere of radius 100 Å and about 5000 Debye units for a sphere of radius 300 Å.

The dielectric constant ε of the solution is calculated from

$$\varepsilon E = E + 4\pi P; \qquad P = \sum_i N_i \alpha_i E_i' \tag{85}$$

where the summation is carried out for all macroions and other molecules in the solution, and E' denotes the internal field acting on the macroions and molecules. The increment of the dielectric constant $(\Delta\varepsilon = \varepsilon - \varepsilon_0)$ relative to ε_0 of the solvent (water) is given by

$$(\varepsilon - \varepsilon_0)/\varepsilon_0 = 3(E'/E)(Nv/V) = 3B\phi \tag{86}$$

which results from combination of Eqs. (84) and (85). The constant $B(= E'/E)$ corrects the internal field and is usually a little larger than unity for a polar solvent. The relative increment is proportional to the apparent volume concentration of macroions and the proportionality constant is between 5 and 10. For example, when $\phi = 0.01$, the relative increment is about 0.1.

The above result is similar to the classical result derived by Wagner for a sphere having electrical conductivity (σ_1) in a medium having a different conductivity (σ_0) (*23*). Upon application of the electric field, polarization appears at the surface of the sphere. The theory of electricity for this system showed that the relative increment of the dielectric constant at zero frequency is given by

$$(\varepsilon - \varepsilon_0)/\varepsilon_0 = 3B\phi(\sigma_1 - \sigma_0)^2/(\sigma_1 + 2\sigma_0)^2 \tag{87}$$

The dielectric increment is proportional to the volume of the sphere, and in the limit of the nonconducting medium, Eq. (87) becomes equivalent to Eq. (86), which was obtained under the assumption that all counter ions are bound in the macroion. Some of the counter ions in real solutions are outside the apparent volume of the random coil macroion and produce the finite conductivity σ_0. Equation (87) shows that the dielectric increment is proportional to the square of the difference between conductivities in and outside the macroion.

However, it must also be remarked that the distribution of counter ions outside the macroion is not uniform but forms the diffuse atmosphere around the macroion. The displacement of the diffuse atmosphere from the average makes a contribution to the fluctuating dipole μ. The excess free energy for the displacement may be small. The dielectric increment is then expected to become larger than that given by Eq. (86). A theoretical analysis in which the distribution of all counter ions in and outside the macroion is taken into consideration can be developed by the combination of the Poisson equation and the diffusion equation under the external field (*24*). The contribution of counter ions outside the macroion may be fairly large and then the dielectric increment depends not only on the volume of the macroion but also on the free volume per macroion.

II. POLARIZABILITY AND THE SHAPE OF MACROIONS

In the preceding section it was shown that the polarizability or the dielectric constant of polyelectrolytes is determined by the volume of the macroion in which counter ions are retained, but not by the charge density of the macroion, as long as a domain of bound but mobile counter ions is formed. Experimental results suggested that the dielectric increment depends on the shape of the macroion; rodlike macroions give very much larger increment than spherical macroions, as shown in Fig. 15 (*21*). Moreover, the dielectric increment due to rodlike macroions was found to increase rapidly with increasing length of the macroions (*25*). Therefore, we employ here an ellipsoidal model by which the wide range of conformations from spherical to cylindrical or rodlike can be represented with the change of the axial ratio p from unity to infinity and analyze the effect of the shape of macroions on the dielectric increment.

Charged groups of the macroion are assumed to be uniformly distributed in the ellipsoid and all counter ions are assumed to be retained there. The long axis of the ellipsoid is placed in the x-direction. If the center of the ellipsoid of counter ions is displaced by x, y, and z from the center of charged groups, keeping the ellipsoidal distribution as shown in Fig. 16*b*, the free energy given by an integration similar to Eq. (80) is expressed as the sum of independent contributions of displacements in three directions (*26*);

$$\begin{aligned} f(\mu) &= f(x)+f(y)+f(z) \\ f(x) &= (2\pi/3)(n/v)^2(e_0{}^2/\varepsilon_0)v\wedge(p)x^2 \\ f(y) &= (2\pi/3)(n/v)^2(e_0{}^2/\varepsilon_0)v\cup(p)y^2 \\ f(z) &= z^2f(y)/y^2 \end{aligned} \tag{88}$$

where

$$\wedge(p) = (3/2)p(p^2-1)^{-3/2}\{\ln[p+(p^2-1)^{1/2}]-(p^2-1)^{1/2}/p\}$$

$$\cup(p) = (3/2)p(p^2-1)^{-3/2}\{p(p^2-1)^{1/2}-\ln[p+(p^2-1)^{1/2}]\} \qquad (89)$$

The average of the square of the fluctuating dipole moment of ellipsoidal macroions uniformly distributed in all directions in the solution is given by

$$\langle\mu^2\rangle = 1/3(\langle\mu_x^2\rangle+\langle\mu_y^2\rangle+\langle\mu_z^2\rangle)$$

$$= (1/3)\,n^2e_0^2(\langle x^2\rangle+\langle y^2\rangle+\langle z^2\rangle) \qquad (90)$$

The average displacements are determined by the average free energy of fluctuation

$$\langle f(x)\rangle = \langle f(y)\rangle = \langle f(z)\rangle = (1/2)\,kT \qquad (91)$$

Therefore

$$\langle\mu^2\rangle = \tfrac{1}{3}(3/4\pi)kT\varepsilon_0 v(\wedge(p)^{-1}+2\cup(p)^{-1}) \qquad (92)$$

and

$$\alpha = (1/3)(\alpha_x+2\alpha_y) = (1/3)(3/4\pi)\varepsilon_0 v(\wedge(p)^{-1}+2\cup(p)^{-1}) \qquad (93)$$

The function $\wedge(p)^{-1}$ and $\cup(p)^{-1}$ are both equal to unity for a sphere ($p=1$). With increasing axial ratio p, $\wedge(p)^{-1}$ increases to infinity and $\cup(p)^{-1}$ decreases to 2/3 in the following way

$$\wedge(p)^{-1}\rightarrow(2/3)p^2/(\ln 2p-1)$$

$$\cup(p)^{-1}\rightarrow(2/3)(1-\ln 2p/p^2) \qquad (94)$$

The average dipole is determined by the size and shape of the macroion. The displacement of the counter ion distribution along the long axis of the ellipsoid is much easier than that in the direction perpendicular to the axis. For example, in an ellipsoid of axial ratio 10 with a volume equal to a sphere of radius 300 Å, the root-mean-square of the dipole moment becomes about 10^5 Debye units in the direction of the long axis.

The relative dielectric increment of a solution of ellipsoidal macroions is given by

$$(\varepsilon-\varepsilon_0)/\varepsilon_0 = B\phi(\wedge(p)^{-1}+2\cup(p)^{-1}) \qquad (95)$$

For a very long ellipsoid the relative increment is approximately proportional to $p^2/\ln 2p$ at a constant volume concentration; namely

$$(\varepsilon-\varepsilon_0)/\varepsilon_0 = B\frac{N}{V}(\pi/9)l^3/\ln(l/a) \qquad (96)$$

where l is the length and a is the radius of the ellipsoidal macroion. For example, for $p = 10$ and $\phi = 0.01$, the relative increment becomes about 2.5.

Equation (95) is also equivalent to the classical result obtained for a suspension of ellipsoids having the electrical conductivity in a non-conducting medium (*23*).

Thus, the origin of the extremely large polarizability of polyelectrolytes can be well understood. The polarizability becomes larger for a larger volume and a longer shape of the region in which bound counter ions are mobile. The uniform and continuous distribution of charged groups and the mobility of counter ions bound to them are essential for large polarizability. If these groups were accumulated at a point or a few points in the region, the average of the fluctuating dipole could not be large even when the total charge was very large.

Figures 17*a* and *b* present the experimental dielectric increment obtained at various degrees of neutralization of polyacids (*27*). With the addition of alkali, the number of charged groups of macroions and their counter ions increases and a domain of bound but mobile counter ions begins to form. Then, a large dielectric constant is observed. With further increase of the degree of neutralization the dielectric increment increases and tends to saturation.

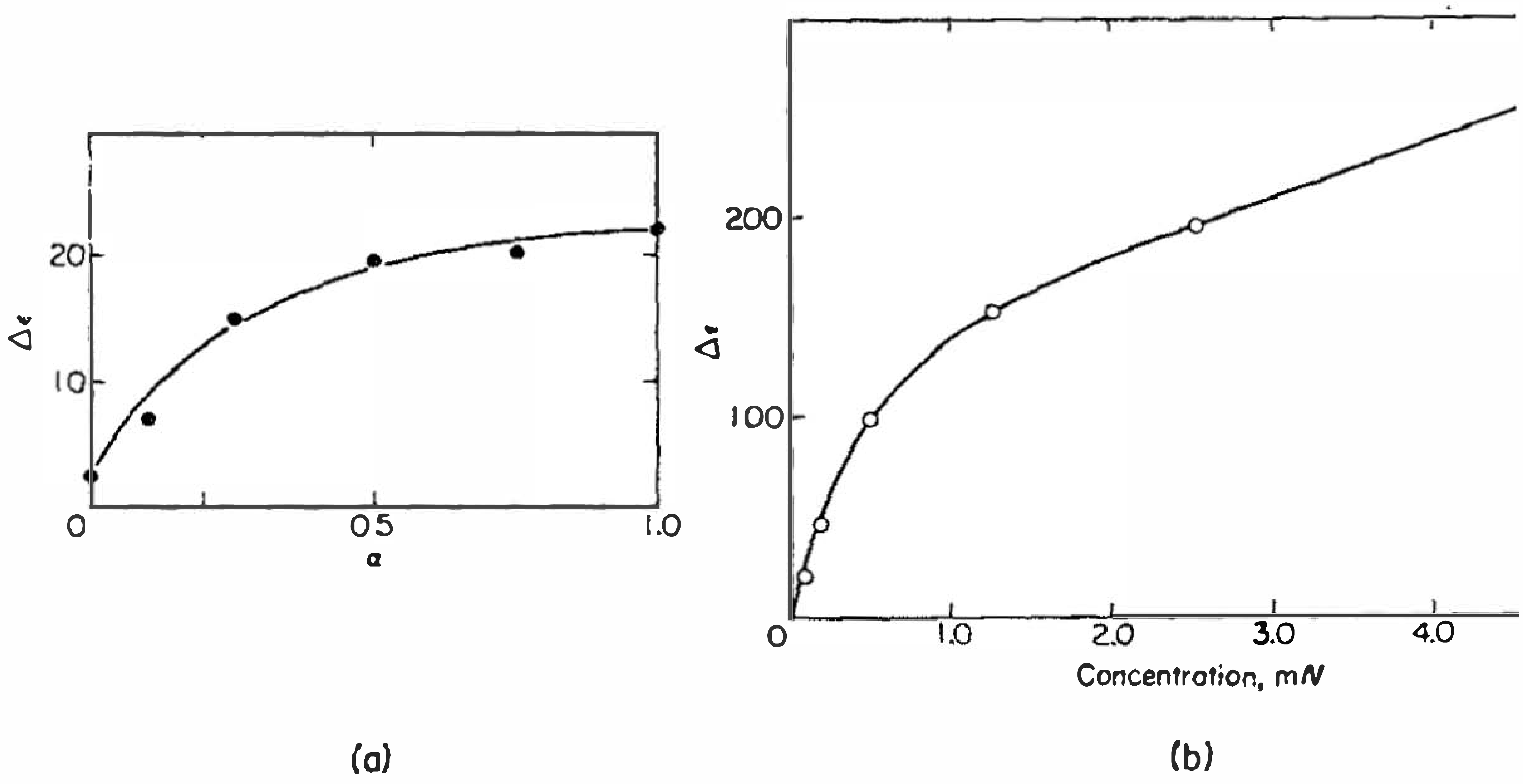
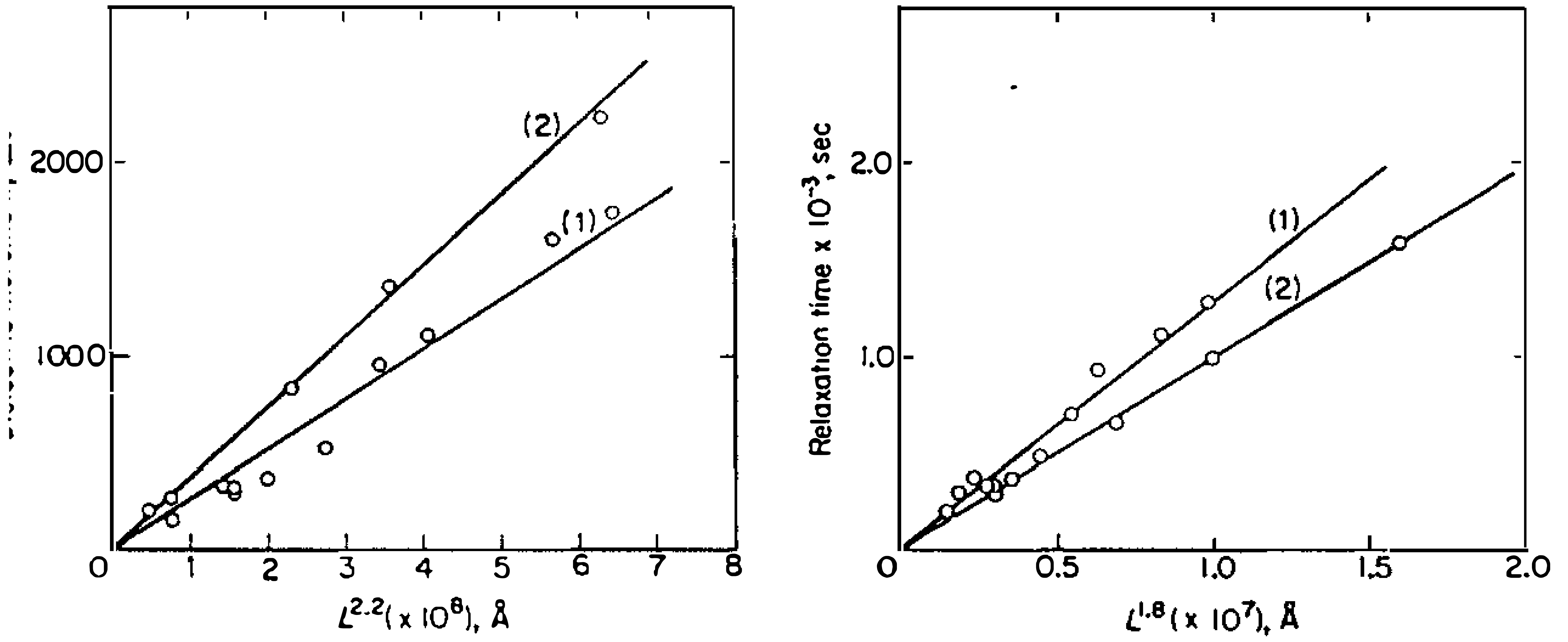


FIG. 17. (*a*) The relation between the dielectric increment and the degree of neutralization in polyacrylic acid solution neutralized by NaOH. (*b*) The relation between the dielectric increment and the concentration of polyacrylic acid fully neutralized by Bu_4NOH (*27*).

The absolute value of the dielectric increment observed, however, is larger than that expected from the spherical model according to Eq. (86). The macroion is elongated and it is better to apply a long ellipsoidal model. Equation (96) predicts that in the case of rodlike or cylindrical macroions of different lengths, the dielectric increment at a constant total (weight) concentration is approximately proportional to the square of the length or the molecular weight of the macroion. Such dependence of the dielectric increment on the molecular weight was actually found in neutralized polyacids and also in DNA, as shown in Figs. 18*a* and *b* (*27*, *25*). This means that the neutralized polyacid molecules are in the stretched conformation.



(a) (b)

FIG. 18. (*a*) The plot of dielectric increment against the length of DNA; (1) salmon sperm DNA; (2) calf thymus DNA; The abscissa is the 2.2 power of the length in angstroms. Concentration is 0.1 mg/ml. (*b*) The plot of dielectric relaxation time against the length of DNA; (1) Salmon sperm DNA; (2) calf thymus DNA; The abscissa is the 1.8 power of the length in angstroms. Concentration is 0.1 mg/ml (*25*).

III. FLUCTUATION OF COUNTER IONS IN VARIOUS MODES

In the above simple theory, we considered only the uniform displacement of the counter ion cloud relative to the macroion. The fluctuation of the counter ion distribution is not limited to the uniform displacement. It takes place at random in various ranges along the macroion and some of them contribute to the electric dipole. In the case of rodlike macroions such situation can be analyzed theoretically by expanding the fluctuation in a Fourier series (*28*).

Let us consider a sufficiently long rod with uniform charge density and counter ions bound to it. On the average these counter ions are assumed to be distributed with the uniform concentration $c_{+0}(=n_{+0}/l)$ along the rod. When the concentration deviates from the average by $\delta c_+(x)$ at the position $x \sim x+dx$, the excess interaction energy $\delta^2 u$ can be given by

$$\delta^2 u = 1/2 \int_0^l \int_0^l \delta c_+(x)\delta c_+(x')\varphi(|x-x'|)dxdx' \tag{97}$$

where $\varphi(|x-x'|)$ is the interaction energy between counter ions at x and x' and can be assumed to be a function of the distance $|x-x'|$. The excess entropy due to the fluctuation $\delta^2 s$ is given approximately by

$$T\delta^2 s = -\tfrac{1}{2}kT(1/c_{+0}) \int_0^l [\delta c_+(x)]^2 dx \tag{98}$$

where the domain along the rod in which counter ions are bound but mobile was regarded as a phase of a solution of counter ions with the average concentration c_{+0}. It is to be noted that in the excess energy and the excess entropy the terms of the first order of fluctuation $\delta c_+(x)$ must vanish since the average distribution is an equilibrium one. The electric dipole produced by the fluctuation $\delta c_+(x)$ is given by

$$\mu = e_0 \int_0^l (x-l/2)\delta c_+(x)dx \tag{99}$$

Here, as shown in Fig. 19, the fluctuation is expanded in a Fourier series as

$$\delta c_+(x) = \sum_k [c_k \cos(2\pi kx/l) + c_k' \sin(2\pi kx/l)] \tag{100}$$

where

$$c_k \text{ (or } c_k') = (2/l) \int_0^l \delta c_+(x) \cos \text{ (or sin)}(2\pi kx/l)dx \tag{101}$$

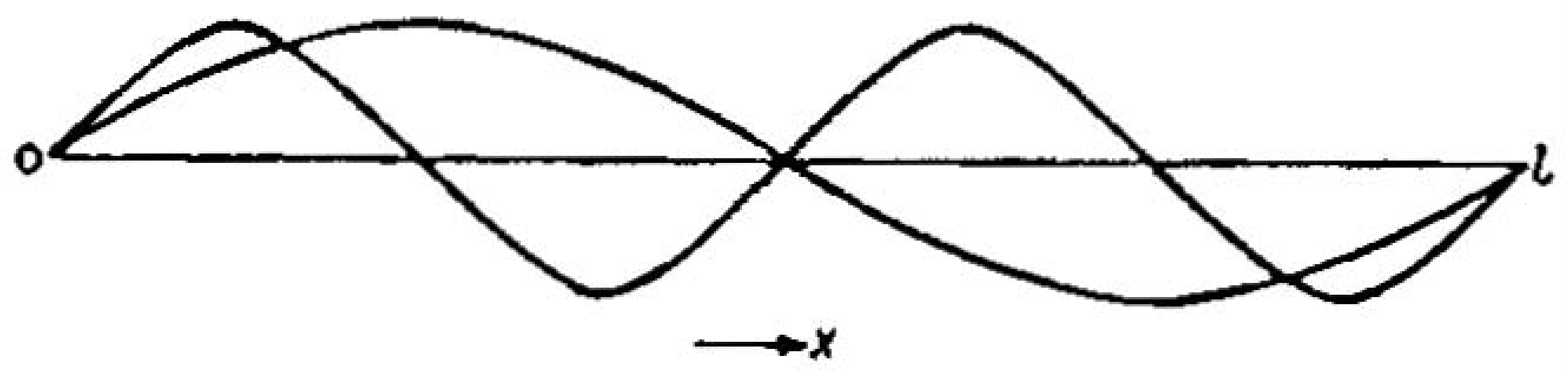


FIG. 19. Various modes of fluctuation of counter ion concentration along a rodlike polyion.

Namely, c_k is the amplitude of the fluctuation with the wave number k or the wavelength $1/k$. Then from Eq. (97) the excess energy $\delta^2 u$ is found to be expressed as

$$\delta^2 u = (1/2)(l/2)^2 \sum_k (c_k{}^2 + c_k'^2)\varphi_k \tag{102}$$

where φ_k is the Fourier component of the interaction energy $\varphi(r)$ defined by

$$\varphi_k = (2/l) \int_0^l \varphi(r) \cos(2\pi kr/l) dr \tag{103}$$

In the derivation of Eq. (102) under Eq. (103), the length l was assumed to be sufficiently longer than the effective range of the interaction $\varphi(r)$ (*28*). From Eq. (98) the excess entropy is expressed as

$$T\delta^2 s = -(1/2)kT(l/2)(1/c_{+0}) \sum_k (c_k{}^2 + c_k'^2) \tag{104}$$

Since the probability of the fluctuation $\delta c_+(x)$ is proportional to the factor $\exp[-(\delta^2 u - T\delta^2 s)/kT]$, it is found from Eqs. (102) and (104) that the mean square of the fluctuation of each component c_k or c_k' is given by

$$\langle c_k{}^2 \rangle = \langle c_k'^2 \rangle = 1/[(l/2)(1/c_{+0}) + (l/2)^2(\varphi_k/kT)] \tag{105}$$

On the other hand, from Eq. (99) the mean square of the fluctuating dipole is found to be

$$\langle \mu^2 \rangle = e_0{}^2 l^2 \sum_k (1/2\pi k)^2 \langle c_k'^2 \rangle \tag{106}$$

Thus, the polarizability along the rod is obtained from Eqs. (105) and (106) as the sum of contributions of fluctuations of different modes or different wavelengths:

$$\begin{aligned} \alpha &= \sum_k \alpha_k \\ \alpha_k &= (n_{+0} e_0{}^2/kTl) l^3 (2\pi^2)(1/k^2)/(1 + n_{+0}\varphi_k/2kT) \end{aligned} \tag{107}$$

The dielectric increment due to such dipoles can be derived by a procedure similar to the previous case. After simple calculation, the final result is obtained as

$$(\varepsilon - \varepsilon_0)/\varepsilon_0 = B \frac{N}{V} (2/3\pi) l^3 Q_+ \sum_k (1/k^2)/(1 + Q_+ w_k) \tag{108}$$

where

$$\begin{aligned} w_k &= \int_0^l w(r) \cos(2\pi kr/l) dr \\ w(r) &= (\varepsilon_0/e_0{}^2)\varphi(r) \\ Q_+ &= n_{+0} e_0{}^2/\varepsilon_0 kTl \end{aligned} \tag{109}$$

In the case of sufficiently long rods, w_k is independent of k for small values of k. Then, approximately

$$(\varepsilon-\varepsilon_0)/\varepsilon_0 = B\frac{N}{V}(\pi/9)l^3 Q_+/(1+Q_+w) \tag{110}$$

where

$$w = \int_0^l w(r)dr$$

and the relation $\sum_k(1/k^2) = \pi^2/6$ was used. If a long cylindrical free volume model is applied, $w/2$ may be replaced by $\ln(R/a)$.

The expression (110) is very similar to equation (96). The dielectric increment at a constant total concentration is proportional to the square of the length. With the increase of the charge of the rod, the dielectric increment first increases in proportion to the number of bound counter ions and then tends to saturation for large values of Q_+ or n_{+0}. Such behaviors of the increment are actually observed. Equation (110) is nearly equivalent to Eq. (96) at saturation. For example, in the case of neutralized DNA of length 10,000 Å and concentration 0.01 %, the value of Nl^3 is about 35 and the dielectric increment $(\varepsilon-\varepsilon_0)$ calculated becomes several hundreds to a thousand, which is of the same order as the experimental values (*25*).

Thus, the counter ion distribution was analyzed in the form of the Fourier series. The magnitude of the fluctuation in different modes is given by Eq. (105). The magnitude increases slowly with decrease of the wavelength of fluctuation because the component of the repulsive interaction φ_k must decrease with k at large values of k. However, the contribution of the fluctuation to the dielectric increment is proportional to the square of the wavelength as shown in Eqs. (106) and (108). The fluctuation of the short wavelengths makes only a small contribution to the dielectric increment. Therefore, the value of the total dielectric increment Eq. (110) was not very different from that derived under the assumption of the uniform displacement of the counter ion cloud. However, it must be remarked that fluctuations of different modes have different relaxation times. As will be shown in the next section, the above method of the Fourier expansion is most useful for understanding the whole feature of the dispersion of the dielectric constant.

It is easy to extend the above theory to the case of polyvalent counter ions. For counter ions of valence z it is found that the quantity Q_+ in Eqs. (108) or (110) must be replaced by $z^2 n_{+0} e_0{}^2/\varepsilon_0 kTl = z^2 Q_+$, where n_{+0}, as before, is the number of bound counter ions of the valence z.

Real rodlike macroions have discrete charged groups instead of the uniform charge density. The electric potential along the rod is not uniform but consists of many holes, some of which are occupied by counter ions. The number of counter ions in these holes fluctuates. The above method can be modified to be applicable to such a model. The main effect of the presence of the discrete potential holes is that when almost all holes are occupied by counter ions, the fluctuation becomes small. This effect brings, for example, the difference in the dielectric increment between polyacids having hydrogen ions and sodium ions as counter ions, as shown in Fig. 17*a*. (*28*).

As shown in the experiment of Fig. 20, in polyacids neutralized by the mixture of monovalent and divalent counter ions the dielectric increment was found to become highest in the intermediate value of the mixing ratio. For understanding this interesting phenomenon, also, it is necessary to refine the theory by taking into consideration the short range exclusion effect between bound counter ions.

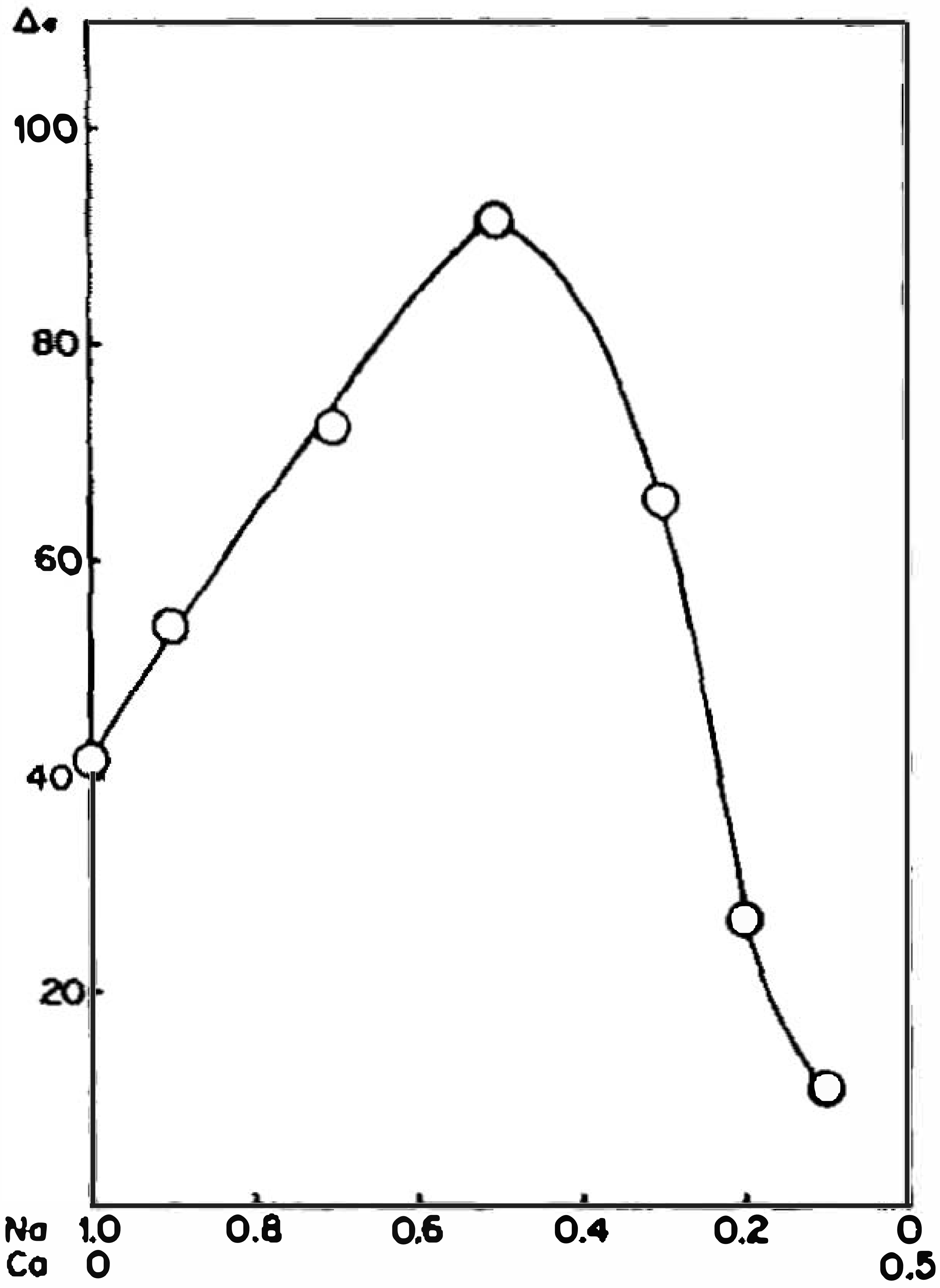


FIG. 20. Low frequency dielectric increment as a function of counter ion ratio in polyacrylic acid solution neutralized by NaOH and/or Ca(OH)$_2$; the polymer concentration $c_p = 1$ m*N*; and the degree of neutralization $\alpha = 1$.

For the polarizability of rodlike macroions, another theoretical approach was made on the basis of the discrete binding site model by Mandel (*30*). In his case interactions among charged groups and counter ions were treated as being of short range. A refined theory along this same line was developed by the use of the matrix method (*29*). This kind of approach is useful in the system where the short range interaction is more important than the long range interaction.

IV. RELAXATION OF THE COUNTER ION DISTRIBUTION

In the previous sections, the large polarizability and dielectric constant of polyelectrolytes in a static field were shown to be attributable to the distribution and the mobility of bound counter ions. In an alternating field, the cloud of counter ions oscillates and at high frequency it can not follow the field. This brings about dielectric dispersion, that is, the decrease of polarizability or dielectric constant at high frequency. Additional electric conductivity appears in the range of frequency where such dispersion occurs. Experiments show that this frequency is significantly lower in polyelectrolyte solutions than in simple electrolytes, as shown in Figs. 21*a* and *c* (*25*, *27*). The relaxation time of counter ion distribution is considerably longer in polyelectrolytes. Here, it is instructive to analyze first the relaxation of the uniform counter ion cloud displaced relative to the macroion.

The equation of motion for each counter ion distributed in the macroion may be written as

$$\zeta \partial x_i/\partial t + \partial u_e/\partial x_i = 0 \tag{111}$$

where x_i is the spatial coordinate of the ith counter ion and ζ is the frictional constant, usually given by $6\pi\eta b$, where b is the effective radius of the counter ion and η is the viscosity of the solvent. The second term of the above equation describes the force exerted by the coulomb potential arising from all other ions and charged groups. If the above equation is summed for all counter ions, the kinetic equation for the motion of the center of distribution of counter ion results. The force due to the interaction between counter ions cancels and only the force due to the interaction of counter ions with charged groups remains:

$$n\zeta \partial\delta/\partial t + \partial f(\delta)/\partial\delta = 0 \tag{112}$$

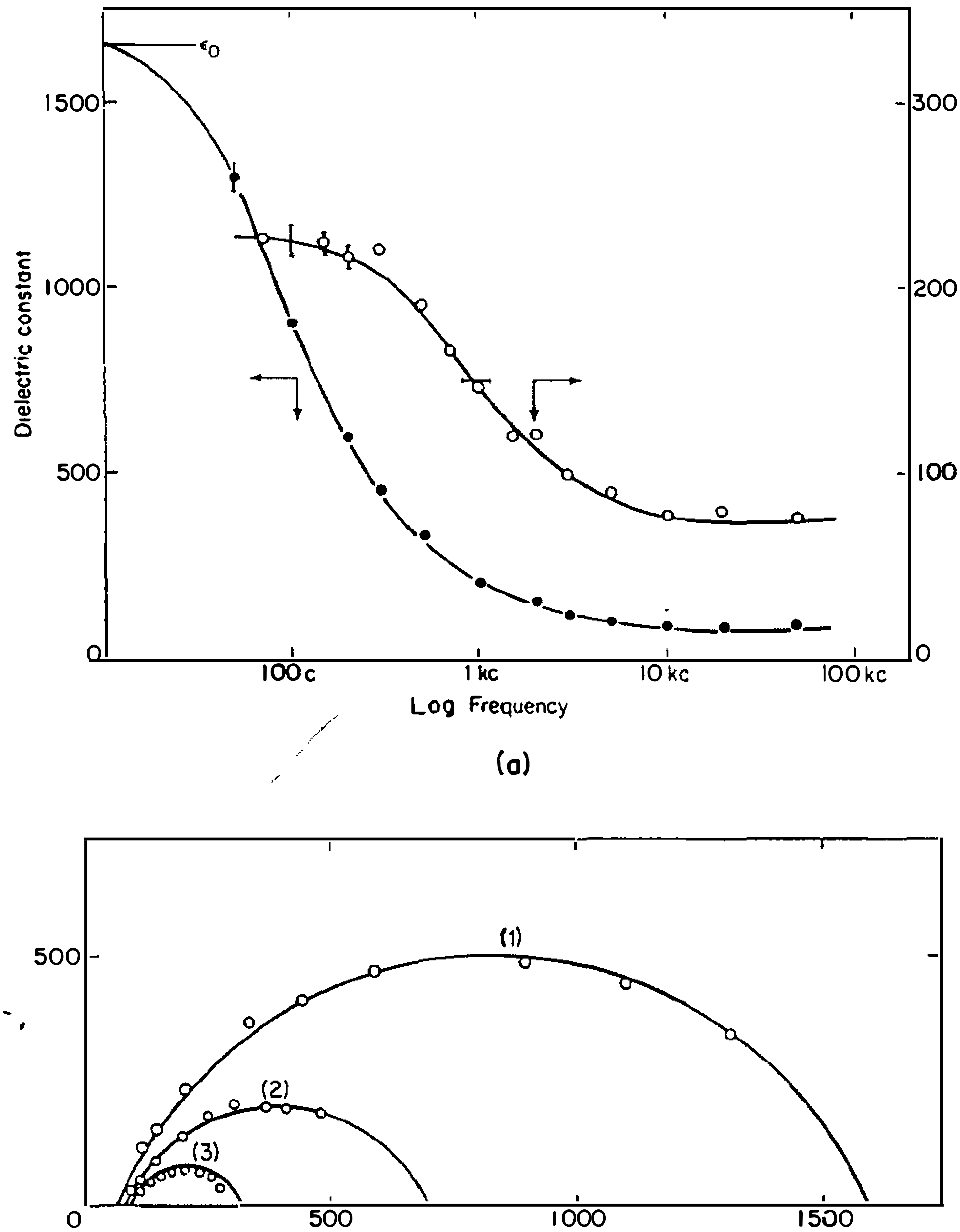
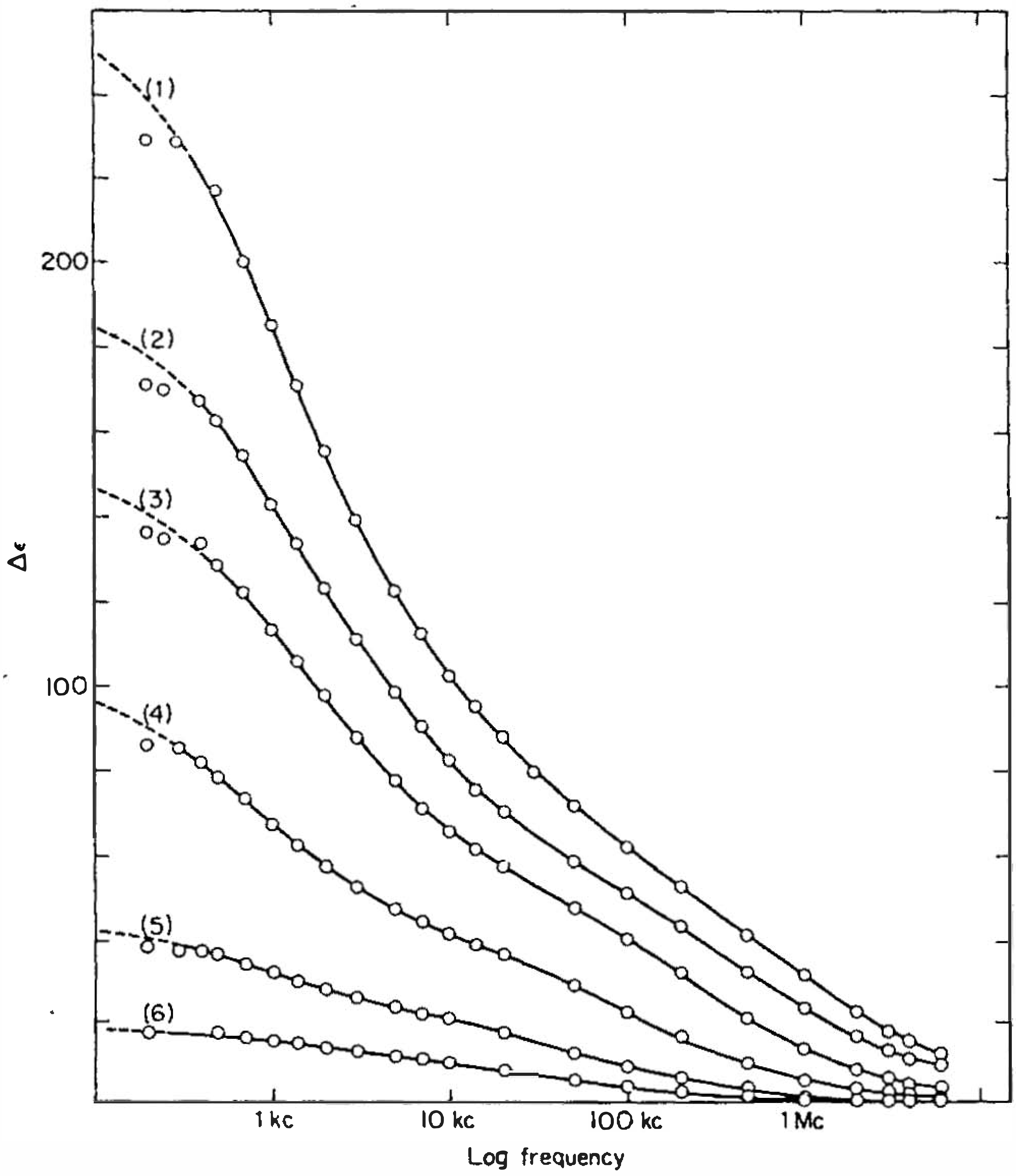
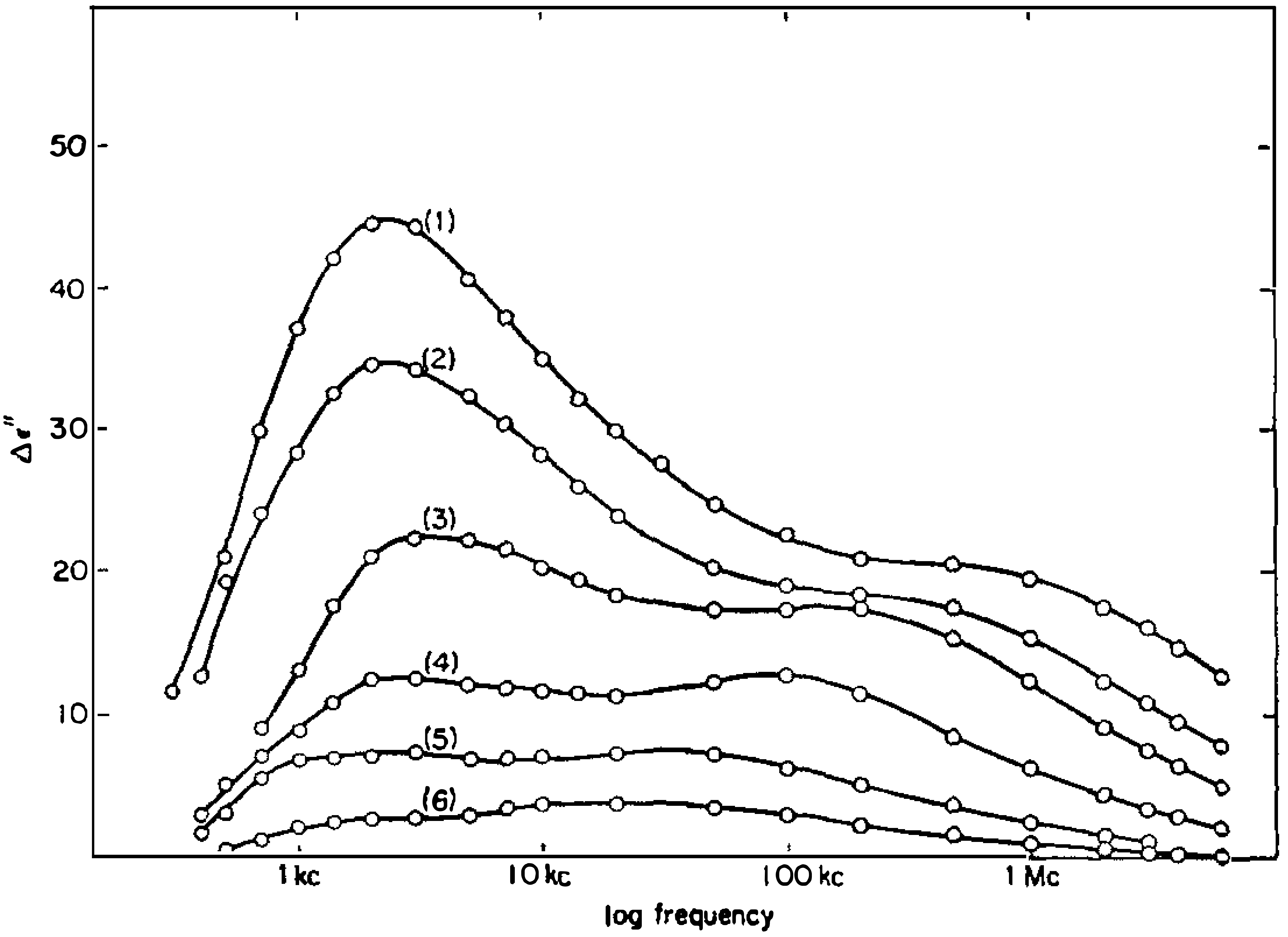


FIG. 21. (*a*) Dielectric dispersion of DNA solutions [with added NaCl; (●) 10^{-5} mole/liter, and (○) 2×10^{-3} mole/liter]. Coordinates for each curve are indicated by arrows. (*b*) The Cole-Cole plot of DNA solutions [with added NaCl; (1) 10^{-5} mole/liter; (2) 10^{-4} mole/liter, and (3) 10^{-3} mole/liter]. The abscissa is the real part of dielectric constant and the ordinate is the dielectric loss (*25*). (*c*) Dielectric dispersion of polyacrylic acid solutions neutralized by Bu_4NOH at various concentrations of polyelectrolytes; (1) concentration $c_p = 5$ m*N*, (2) 2.5 m*N*, (3) 1.25 m*N*, (4) 0.5 m*N*, (5) 0.2 m*N*, and (6) 0.1 m*N*. (*d*) The relation between the dielectric loss and the frequency in polyacrylic acid solutions neutralized by Bu_4NOH under the same condition as in Fig. 21(*c*) (*27*); (1) concentration $c_p = 5$ m*N*, (2) 2.5 m*N*, (3) 1.25 m*N*, (4) 0.5 m*N*, (5) 0.2 m*N*, and (6) 0.1 m*N*.



(c)

FIG. 21 (*cont.*)



(d)

FIG. 21 (*cont.*)

where $\delta = \sum x_i/n$ is the displacement of the center of gravity in a certain direction and the second term is the derivative of the free energy $f(\delta)$ defined in the previous section. Thus the collective motion of the counter ion cloud is described by the equation

$$n\zeta \partial\delta/\partial t + (kT/\langle\delta^2\rangle)\,\delta = 0 \tag{113}$$

Accordingly, the relaxation time of this motion is given by

$$\tau = n\zeta\langle\delta^2\rangle/kT \tag{114}$$

For an ellipsoidal distribution, the displacement is considered in three directions, and the two kinds of relaxation time τ_x and τ_y ($= \tau_z$), corresponding to two directions of motion, are given by

$$\begin{aligned} \tau_x &= (\zeta\varepsilon_0/ne_0{}^2)(3/4\pi)v\cdot \wedge(p)^{-1} \\ \tau_y &= (\zeta\varepsilon_0/ne_0{}^2)(3/4\pi)v\cdot \cup(p)^{-1} \end{aligned} \tag{115}$$

These results indicate that the relaxation time τ is proportional to the volume v of the macroion and to the function $\wedge(p)^{-1}$ and $\cup(p)^{-1}$ in the case of ellipsoids. It is inversely proportional to the number of charged groups n. If p is constant and n is proportional to the length of the ellipsoid, the relaxation time τ_x is proportional to the square of the length.

In the comparison of Eq. (115) with Eq. (95) it is remarkable that the relaxation time, as a function of the size and shape of macroions, is proportional to the dielectric increment. The displacement of counter ions along the long axis of the ellipsoid makes a large contribution to the dielectric increment only in a field of very low frequency.

When $\zeta = 3 \times 10^{-9}$ (reasonable for small ions) and $n = 10^3$, the relaxation time τ estimated from Eq. (115) is 3×10^{-7} sec for a sphere of $p = 1$ and radius 300 Å, and it is about 5×10^{-5} sec for the long axis of an ellipsoid of $p = 10$ having a volume equal to the sphere of radius 300 Å. The dispersion frequencies corresponding to these values of the relaxation time are equal to 5×10^5 and 10^4 cycles, respectively. Thus, the large dielectric dispersion of polyelectrolytes observed at low frequencies can be well understood.

Rodlike polyelectrolytes such as linear polyacids or DNA, however, show broad dispersion curves of dielectric constant at low frequencies which can not be explained by a single relaxation time (Figs. 21*a* and *c*). Such a situation can be clarified by employing the same method as in the previous section. Consider a rodlike macroion along which counter ions are bound but mobile. The fluctuation of the counter ion concentration $\delta c_+(x)$ changes with time t. The diffusion equation of this $\delta c_+(x,t)$ can be written as:

$$\zeta \partial \delta c_+(x,t)/\partial t = (\partial/\partial x)[kT \partial \delta c_+(x,t)/\partial x + c_{+0}(\partial/\partial x)\int_0^l \delta c_+(x',t)\varphi(|x-x'|)dx'] \tag{116}$$

where the first term of the right-hand side comes from the simple diffusion force or the entropy force and the second term comes from the electric force exerted by fluctuating counter ions. This equation is almost equivalent to that proposed by Schwarz for the relaxation of the counter ion atmosphere on a charged spherical particle (*31*). By operating the integral $(2/l)\int_0^l \sin$ or $\cos(2\pi kx/l)dx$ for both sides of the above equation, we obtain the equation for the Fourier components c_k or c'_k of the fluctuating concentration in the form:

$$\partial c_k(t)/\partial t = -(kT/\zeta)(2\pi k/l)^2(1 + n_{+0}\varphi_k/2kT)c_k \tag{117}$$

Therefore, the relaxation time τ_k of the fluctuation of the mode k is given by

$$\tau_k = (\zeta/kT)(l/2\pi k)^2/(1+Q_+w_k) \tag{118}$$

For sufficiently long rods, w_k can be replaced by w of Eq. (109). Then, the relaxation time τ_k is proportional to the square of the wavelength of the fluctuation. It is also proportional to the square of the total length of the rod at a constant density of bound counter ions or Q_+. This agrees with experimental results (*25*).

For small values of the charge density or Q_+ the above equation gives the relaxation time which is equal to the time necessary for the diffusion of small ions with the diffusion constant (kT/ζ) by the distance $l/2\pi k$. The relaxation time decreases with increasing charge density and under the condition that $Q_+w \gg 1$, Eq. (118) becomes almost equivalent to Eq. (115), derived without considering the diffusion force.

Now, the static polarizability α_k of fluctuation of the mode k is given by Eq. (107) and its relaxation time τ_k is given by Eq. (118). Then, the complex polarizability $\alpha_k(\nu)$ of fluctuation of the mode k at frequency ν is expressed as:

$$\alpha_k(\nu) = \alpha_k/(1+i(2\pi\nu)\tau_k) \tag{119}$$

Therefore, the real part of the dielectric constant at frequency ν, $\varepsilon'(\nu)$, is given by

$$[\varepsilon'(\nu)-\varepsilon_0]/\varepsilon_0 = B(N/V)(2/3\pi)l^3\{Q_+/k^2(1+Q_+w_k)[1+(2\pi\nu)^2\tau_k{}^2]\} \tag{120}$$

and its imaginary part, $\varepsilon''(\nu)$, is given by

$$\varepsilon''(\nu)/\varepsilon_0 = B(N/V)(2/3\pi)l^3\{Q_+(2\pi\nu)\tau_k/k^2(1+Q_+w_k)[1+(2\pi\nu)^2\tau_k{}^2]\} \tag{121}$$

In Fig. 22*a*, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ calculated from the above equations are shown as functions of the frequency ν. Figure 22*b* gives the Cole–Cole plot. The plot deviates from the semisphere and the shape of the curve does not depend on the absolute value of the dielectric constant. The Cole–Cole plots experimentally obtained in linear polyacids and DNA are very similar to the calculated one, Fig. 22*b*. (See Fig. 21 and Ref. *25*). The plots observed at different degrees of neutralization had the same shape.

Thus, the broad dispersion of the dielectric constant of polyelectrolytes at low frequencies is attributable to the presence of different modes of fluctuation of the counter ion distribution along the rodlike macroions.

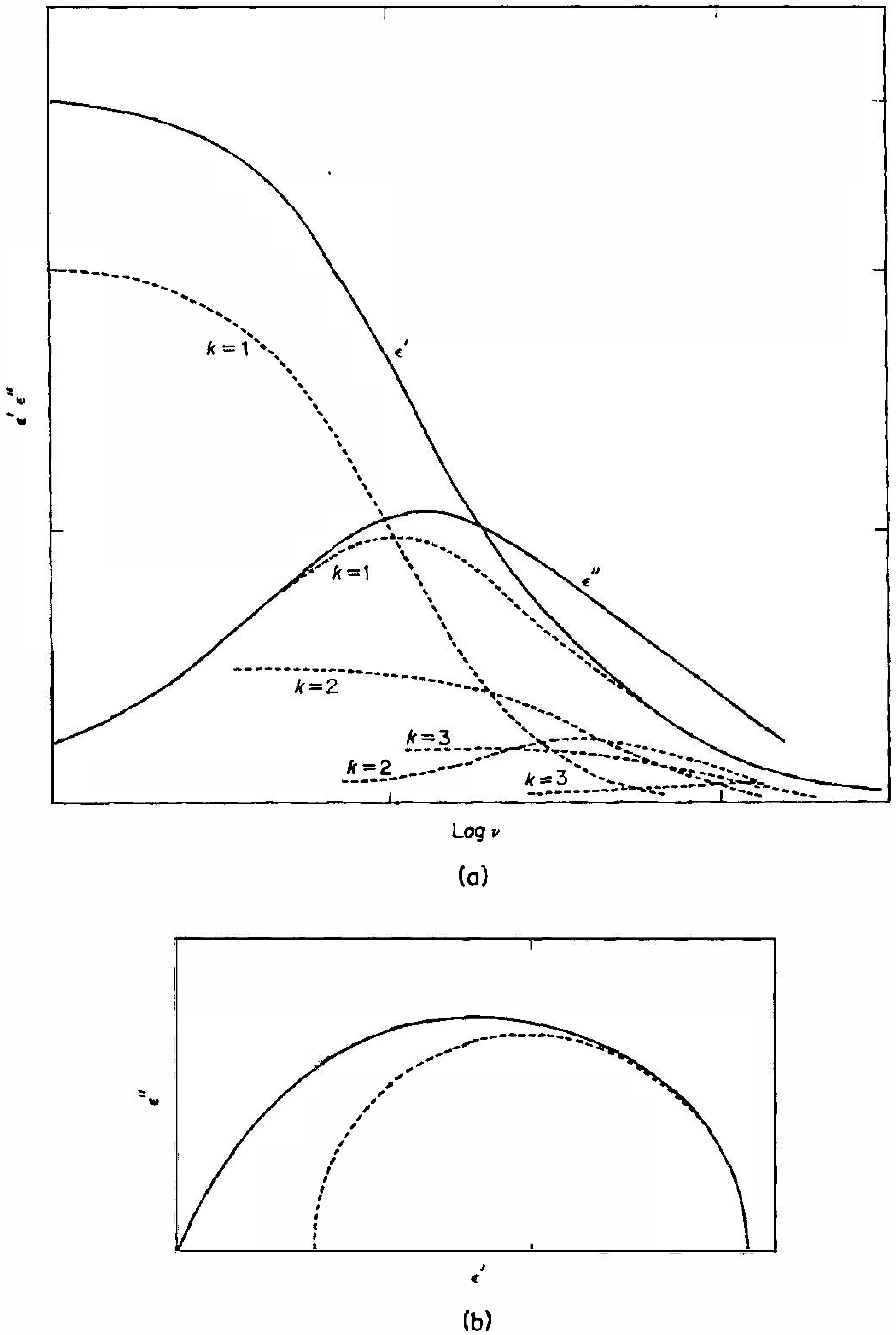


Fig. 22. (*a*) The dielectric dispersion curves. ε' and ε'' are real and imaginary parts of the dielectric constant. The dotted lines show contributions of each mode ($k = 1, 2$, and 3) to ε' and ε''. (*b*) The Cole-Cole plot obtained from Fig. 22(*a*). The dotted line shows a semicircle due to the first mode of fluctuation (*28*).

The numerical value of the lowest relaxation time τ_1 expected from Eq. (118) is of the same order as or a little smaller than that observed experimentally. For example, DNA of 7,800 Å length had a relaxation time of 10^{-3} sec *(25)*, while the above equation gives the time τ_1 of the order of 10^{-4} sec for the same length if the frictional constant ζ of bound counter ions is assumed to be the same as in the normal solution.

Besides the large dispersion at low frequencies discussed above, the dielectric constant of polyelectrolytes usually shows the other smaller dispersion at high frequencies of the order of 10^5–10^6 cycles. The dispersion curve in this frequency range does not depend on the molecular weight of polyelectrolytes but shifts to the high frequency with increasing concentration of polyelectrolytes. The origin of the dielectric dispersion in this range is not clear. However, one possibility may be that it comes from the polarization of the counter ion distribution perpendicular to the chain of the macroion, and the dependence of the dispersion on the concentration suggests the importance of counter ions outside of the macroion.

Chapter 6

STATE OF BINDING OF COUNTER IONS

I. The Ion Pair and Localized Binding

In earlier chapters most of the bound counter ions were assumed to be mobile in the potential trough or valley of the macroion. Many characteristic properties of polyelectrolytes, for instance, counter ion condensation, the complete condensation of polyvalent counter ions, and the large dielectric constant, were explained under this assumption. Actually, however, some of the bound counter ions may be localized at the potential holes formed by individual charged groups. The extent of such binding (localized binding) is examined below.

As already mentioned in Chapter 2, the relation between mobile counter ions and localized ones in the apparent volume of the macroion is analogous to that between free ions and ion pairs in simple electrolyte solutions (*5*). In the case of strong electrolytes the ion pair does not originate as a result of covalent or chemical binding but is a consequence of localization induced by strong short range coulomb interaction. In weak polyelectrolytes the ion pair is partly due to covalent bonding. A similar situation must be considered to exist in polyelectrolytes.

Let us classify the counter ions into three categories; free, bound but mobile, and localized. The number of each kind is denoted by n^*, n' and n'' per macroion, respectively. The total number n is given by the sum $n^*+n'+n''$. The relation between free counter ions and bound but mobile counter ions can be given by an equation similar to (4) or (10) where n in the quantities P and Q must be replaced by $n-n''=n'+n^*$ and the degree of dissociation β must be replaced by the ratio $n^*/(n'+n^*)$ or $n^*/(n-n'')$. The average concentration of bound but mobile counter ions in v is given by n'/v. The degree of localized binding (the ratio of the number of localized counter ions to the total number of counter ions) is given by n''/n. If localized binding can take place on charged groups of the macroion at random, the equilibrium condition between localized and bound but mobile ions is given by the mass action law:

$$(1-\gamma')/\gamma' = K(n'/v) \tag{122}$$

where γ' is equal to $(n-n'')/n$ and K is the equilibrium constant determined by the short range interaction between a counter ion and a charged group. If K is written as $\exp(-\delta f/kT)$, δf denotes the depth of the (free) energy drop at the potential hole of a charged group relative to the potential trough or valley in v.

The apparent degree of dissociation of counter ions n^*/n is equal to $\gamma' n^*/(n-n'')$. The activity coefficient γ^* of counter ions bound in v, which was introduced in Chapter 2, is expressed as $n'/(n-n^*) = n'/(n'+n'')$. The equilibrium values of n^*, n', and n'' are determined as functions of n and v by Eq. (122) and modified equations corresponding to (4) or (10). In the case of strongly dissociative pairs of counter ions and charged groups, the value of K can be estimated according to the Bjerrum theory (*32*). The result obtained in simple electrolytes can be applied. For monovalent ions the degree of localized binding is small if the concentration n'/v is less than 0.1 mole/liter and the distance between the counter ion and the charged group at mutual contact is larger than 1 Å. If the concentration in v becomes larger than the above value, an appreciable number of counter ions is localized. However, in spherical macroions such a high concentration of counter ions can be realized only with an extremely large number of charged groups in the macroion unless simple electrolyte is added.

In cylindrical macroions of high charge density, the concentration of bound counter ions in the potential valley is much larger. It must be noted, however, that the potential drop at each charged group is small relative to the potential valley. Localized binding is expected to be significantly large only in the case of polyvalent counter ions.

In the case of weakly dissociative groups the binding constant K becomes large and γ' and γ^* become appreciably smaller than unity. The effect of γ' on the activity of counter ions in spherical macroions was examined in (*5*). In cylindrical macroions, as shown in Fig. 9, the effect of γ^* on thermodynamic quantities is not important at low concentrations of macroions. The measurement of thermodynamic quantities, which are determined mainly by the concentration of free counter ions, is not sufficiently sensitive to estimate the degree of localized binding.

II. Hydrogen Ion Equilibrium

Localized binding of hydrogen ions is a controlling factor in the relation between the degree of neutralization of weak polyacids and pH during alkali addition. In this case there are two kinds of counter ions, alkali and hydrogen. The situation, however, is rather simple (Fig. 23*a*). In the usual experiment the concentration of free hydrogen ions is very much smaller than that of alkali ions. The number of localized hydrogen ions or the number of acid groups is much larger than the number of mobile hydrogen ions except at very low concentrations of polyacids; while the number of alkali ions in the localized binding state is much smaller than those ions in the mobile binding or free state.

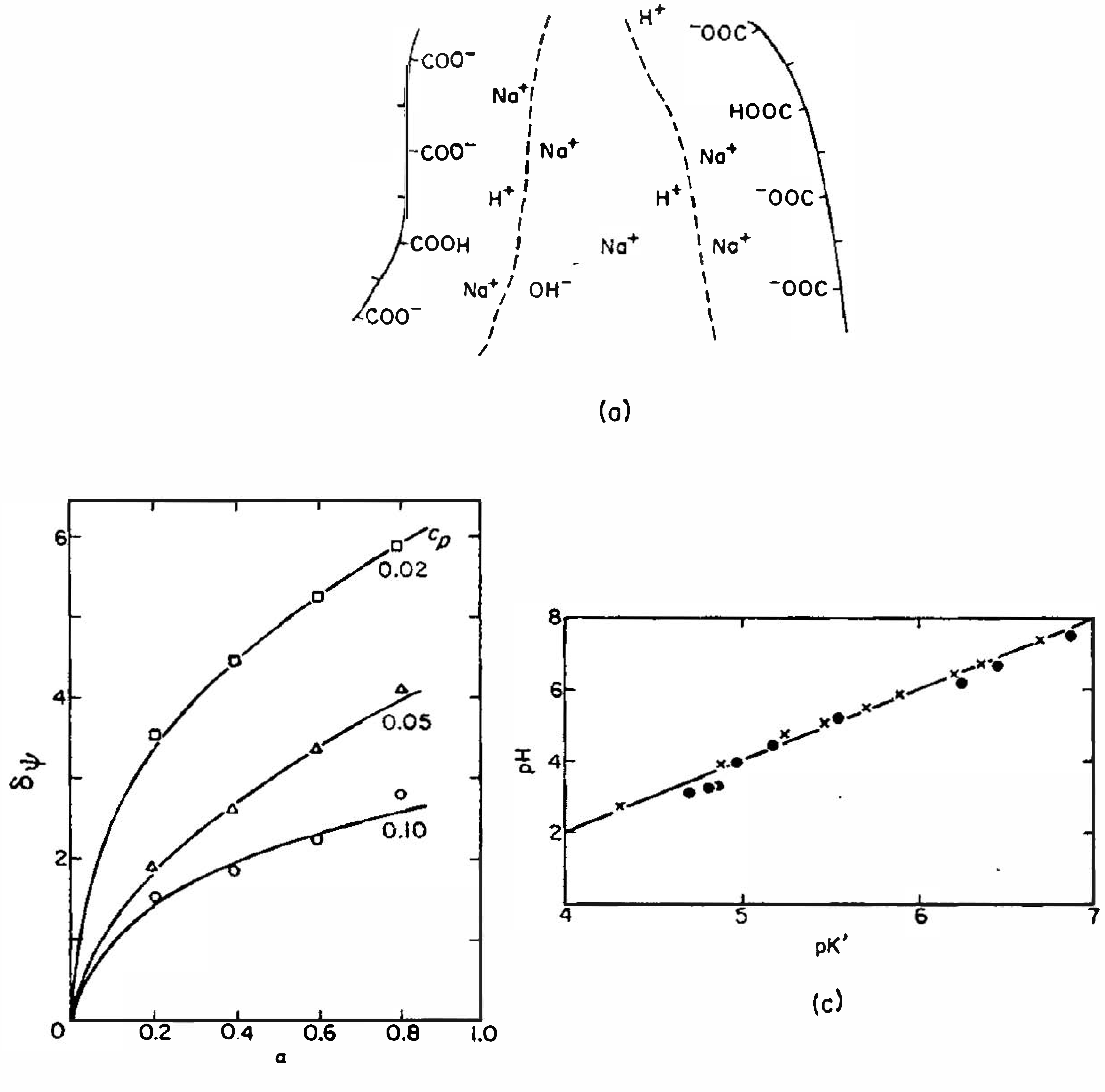
The addition of alkali to a pure polyacid causes approximately an equimolar decrease of the number of locally bound hydrogen ions. For instance, in the case of polyacrylic acid neutralized by sodium hydroxide, the decrease of localized binding of hydrogen ions is given by the reaction

$$-\mathrm{COOH} + \mathrm{NaOH} \rightarrow -\mathrm{COO}^- + \mathrm{Na}^+ + \mathrm{H_2O} \qquad (123)$$

Although the concentration of free H^+ and OH^- ions in the solution is slightly changed during this reaction, the number of these ions needed for this change is so small that the number of COO^- groups produced may be put equal to the number of alkali or OH ions added, except at very low concentrations of polyacids. The number of localized hydrogens that is in equilibrium with bound but mobile hydrogen ions in the volume of the macroion is then given by Eq. (122), the quantity γ' being replaced by the degree of neutralization (the molar ratio of added alkali to acidic groups) α. The concentration of bound but mobile hydrogen ions in this equation is related to the concentration of free hydrogen ions by an equation corresponding to (2). The concentration of free hydrogen ions gives the pH of the solution and the following relation is obtained:

$$\log (1-\alpha)/\alpha = \log K - \mathrm{pH} + 0.43 e_0 \delta\psi / kT \qquad (124)$$

where $\delta\psi$ is the potential difference defined in (2) and $e_0 \delta\psi$ is the change of the electric free energy of a macroion due to the dissociation of an acidic group. Thus, the potential difference $\delta\psi$ is determined from the relation observed between pH and the degree of neutralization, if the dissociation constant K can be assumed to be independent of the charge density.



(a)

(b)

(c)

FIG. 23. (*a*) The hydrogen ion equilibrium in polyacid ions partially neutralized by NaOH. (*b*) The electric potential difference between bound and free hydrogen ions at various degrees of neutralization and various concentrations of polyelectrolytes (polymethacrylic acid neutralized by NaOH) (*33*). (*c*) The relation between pH and the logarithm of dissociation constant pK' defined as pH + log (1 − α)/α in polyacrylic acid solutions neutralized by NaOH. The degree of polymerization (×) 50, and (●) 340. The linear relation between pH and p$K'$is equivalent to the relation (*125*) (*34*).

As compared with the case of simple weak acids, the dissociation of charged groups in the macroion is depressed by the repulsive interaction among charged groups. The (free) energy $e_0\delta\psi$ gives the extent of such depression. With increasing degree of neutralization it increases slowly and is almost saturated at large numbers of charged groups, as shown in Fig. 23*b* (*33*). Such behaviors can be understood according to the theoretical treatment presented in Chapters 2 and 3. The simple two-phase model in Chapter 2 predicted that for cylindrical macroions at infinite dilution the potential difference first increases with increasing charge density and is then completely saturated at the critical value of the charge density $Q = 1$. At finite concentration or for macroions of finite thickness, the potential difference continues to increase very slowly with the charge density even for the density higher than the critical value, as shown in Chapter 3, Section III. A similar situation was also found for spherical macroions in Chapters 2 and 3.

The observed relation between pH and the degree of neutralization was often found to fit the equation

$$\mathrm{pH} = pK + m \log \alpha/(1-\alpha) \tag{125}$$

(unless α is near unity or zero), where m is a constant larger than unity. As shown in Fig. 23*c* (*34*, *35*), the change of pH is nearly proportional to $\log \alpha/(1-\alpha)$. The case of $m = 1$ corresponds to the titration of simple weak acids. The value of $m - 1$ gives the magnitude of the effect of repulsive interaction among charged groups. The empirical relation (125) means that the potential difference is approximately proportional to the factor $\log \alpha/(1-\alpha)$; namely, it shows logarithmic increase with the charge density. Such logarithmic increase is expected from calculation in Chapters 2 and 3.

It is to be noted that since hydrogen ions are much smaller than other counter ions, the potential difference of (124) is not necessarily equal to, but a little larger than, the potential difference expected for alkali ions. This dependence can be explained on the basis of calculations developed in Chapter 4.

III. HYDRATION OF THE MACROION

Counter ions bound to macroions have been classified into two types; nonlocalized (bound but mobile) and localized. The number of the latter was estimated to be small in strongly dissociative polyelectrolytes. It is not simple, however, to analyze experimentally the microscopic state of bound counter ions. If the localized binding introduces some change in the electronic or vibrational state of the ion, measurement of the optical absorption spectrum, for example, is one useful method that may be employed to provide direct information on the state of binding. Magnetic resonance study may be also useful, for example, in the case of hydrogen ions. This kind of study actually gave valuable information (*36*). The applicability of such methods, however, is limited to special cases, and the use of a more general probing method is of advantage. For this purpose it may be convenient to investigate the effect of charged groups and counter ions on the structure of the solvent (water).

Charged groups of macroions are expected to form layers with a special structure of water around them. This structure may be changed by the binding of counter ions. If counter ions are tightly bound to individual groups, the water molecules around them must be wholly rearranged. If counter ions are not localized but mobile around the macroion, the influence on the water structure around charged groups may be small. Thus, the state of binding should be closely related to the change of the water structure associated with the binding. The change of the water structure can be estimated by the measurement of the density or the refractive index. The refractive index is determined by the numbers of various kinds of atoms (molecules) and ions in a unit volume (density) and their polarizabilities. Since the polarizability of atoms or ions is not much affected by the state of interaction between them, the density in the solution can be related simply to the refractive index. In the present case, the water structure made by the charged groups is expected to have a density larger than the structure in normal water. Therefore, the average density or the average refractive index of the solution should increase on account of this special structure. The destruction of this structure to the normal one should decrease the density or the refractive index.

The measurement of ultrasonic velocity, which is determined by the density and the compressibility of a solution, is also useful for the examination of the water structure. The compressibility of the special water structure around charged groups is expected to be smaller than that of normal water, and small compressibility is related to high ultrasonic velocity. Here, the results of refractive index measurement carried out by Ikegami (*37*) are described and their utility for investigating the state of counter ion binding is discussed. The ultrasonic measurement also gave similar results (*38*).

Let us consider first the case of simple ions. When a simple monovalent acid is neutralized by a simple monovalent base, the refractive index of the solution is smalller than the mean of the refractive indices of the two separate solutions of acid and base before neutralization. The difference of the refractive index between the solution and the weighed mean of components is proportional to the degree of neutralization, i.e., to the amount of the base added at a constant concentration of the acid, as shown in Fig. 24*a*. In the case of the neutralization of strong acid this decrement of the index is associated with the reaction

$$H^+ + OH^- \rightarrow H_2O \tag{126}$$

and in the case of weak acid (for example, acetic acid) it is associated with

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \tag{127}$$

By combining these two reactions the change of the refractive index or the density associated with dissociation of the carboxyl group is obtained. The decrease of the volume due to the dissociation,

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \tag{128}$$

was estimated to be 15.5 ml/mole at 25°C (*37*).

If in the process of neutralization of a polyacid by alkali, the counter ions are bound to the macroion and change the water structure around it, it is difficult to isolate the effect due to the formation of the water structure by ionization of the macroion alone. It is desirable, therefore, to use alkali with cations that will have no influence on the water structure around the macroion, even if they are bound. Alkali with cations of a very large volume were chosen on account of their inert property. If the special water structure is limited to the close neighborhood of the chain of the macroion, such cations are not expected to have large effects on this water structure. When this kind of alkali is added to a weak polyacid, at low degree of neutralization the decrement of the refractive index due to mixing is found to increase in proportion to the amount of alkali added, as in the case of simple acids. The result is shown in Fig. 24*b* for polyacrylic acid neutralized with tetrabutylammonium hydroxide. At high degrees of neutralization, however, this decrement is not increased further but rather is decreased by the addition of alkali.

By subtracting the effect of reaction (126) from the observed result corresponding to (127), the change of the refractive index due to the dissociation of carboxyl groups is obtained over the whole range of neutralization. The change of refractive index can be translated to the change in the volume. Figure 24*c* gives the relation between the volume change due to the dissociation of a carboxyl group and the degree of neutralization or the number of charged groups. At low degrees of neutralization, each

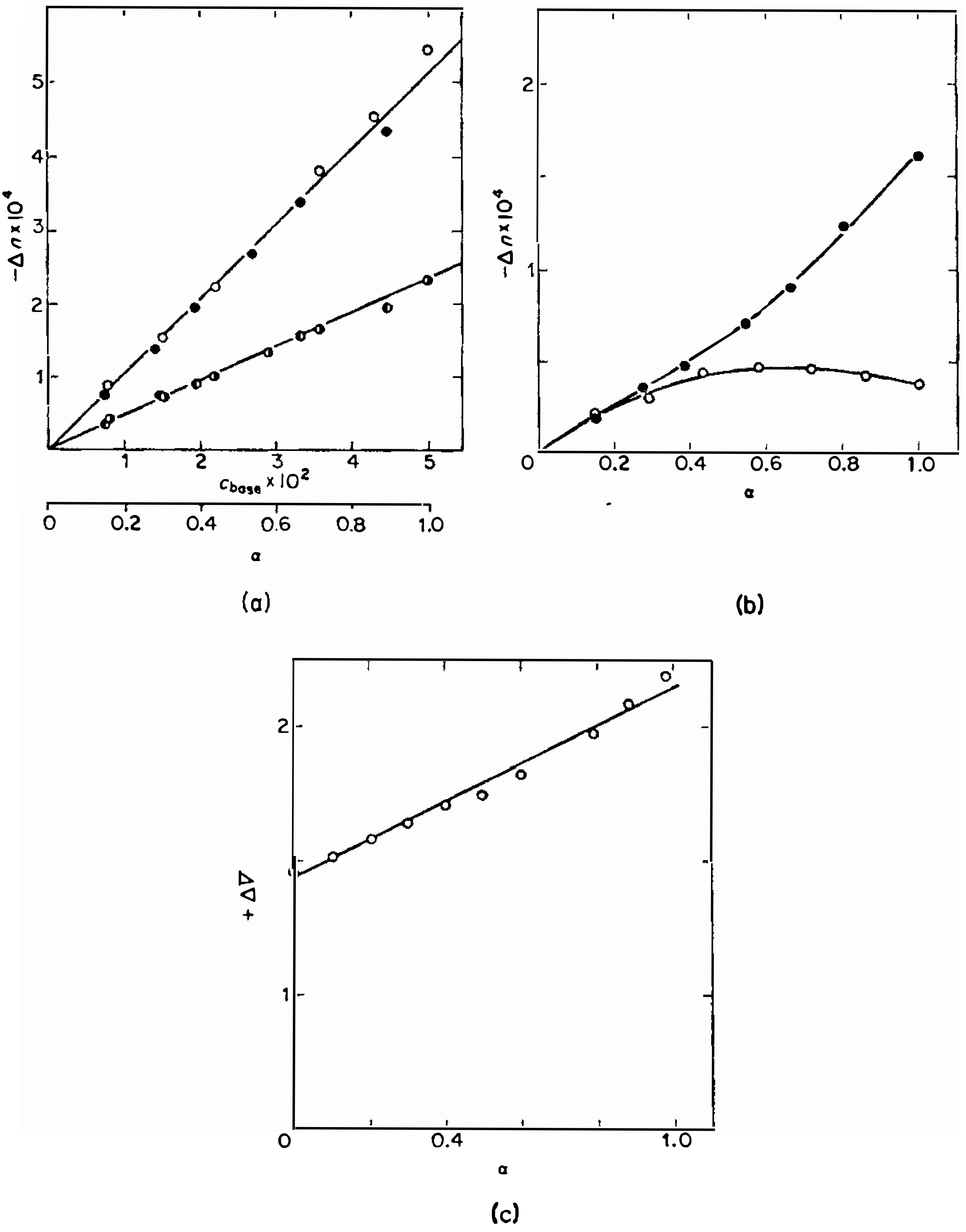


FIG. 24. (*a*) The relation between the decrement of the refractive index Δn of acid solutions and the degree of neutralization α. Solutions of 0.05 *N* HCl were neutralized by (○) Bu_4NOH and (●) NaOH; solutions of 0.05 *N* CH_3COOH were neutralized by (◑) Bu_4NOH and (◐) NaOH. (*b*) The relation between the decrement of the refractive index Δn of polyacid solutions and the degree of neutralization α. Solutions of 0.05 *N* polyacrylic acid were neutralized by (○) Bu_4NOH and (●) NaOH. (*c*) The volume decrease accompanying the dissociation of carboxyl groups of polyacrylic acid at various degrees of neutralization by Bu_4NOH (*37*).

charged group forms an independent small region of special water structure around it. The probability of overlap or interaction between two regions belonging to different groups is small. If each region is assumed to be a sphere of average density 1.1, its radius is estimated to be about 3.1 Å from the experimental data in Fig. 24c.

At high degrees of neutralization, in excess of the individual spherical regions around charged groups, special water structure is formed in proportion to the square of the degree of neutralization. This aspect is fully illustrated in Fig. 25. At low degrees of neutralization individual spherical regions of the special water structure are formed at charged groups. The spherical regions begin to overlap when the density of charged groups on the macroion exceeds a certain limit. In the case of polyacrylic acid, if the charged groups are uniformly distributed and the radius of a sphere is about 3.1 Å, this limit corresponds to a degree of neutralization of about 0.3. Above this degree of neutralization the individual regions must fuse into cylindrical regions along the chain of the macroion. At full neutralization, if this cylindrical region is assumed to have the same radius as the sphere initially formed, the whole volume of the cylinder is too small to explain the magnitude of the total volume change observed. The radius of this cylinder of the special water structure is estimated to be about 5.6 Å for polyacrylic acid.

If a cylindrical model having uniform charge density is employed for the macroion, the electric field around the cylinder is given by

$$2\alpha n e_0/\varepsilon_0 r \tag{129}$$

at the degree of neutralization α and the distance r. The electric field must be larger than a certain limit to reorient water molecules. Therefore, the above expression of the field suggests that the radius of the cylindrical region of the special water structure increases in proportion to the degree of neutralization; its volume increases in proportion to the square of the degree of neutralization. Thus, the model of Fig. 25 is reasonable in comparison with experimental data.

If the macroion is in a stretched conformation, the above region of the special water structure is essentially a straight cylinder. If it is coiled, the cylinder is curved and overlapping of cylinders may occur in the macroion. In the region of overlap the electric field must be weak and the special water structure disappears. Therefore, from the standpoint of the water structure, we must also distinguish the three regions in and around the macroion; potential holes at individual charged groups, cylindrical regions along the chain where the electric field is strong, and a residual region where the electric field is weak as a result of the summed effect of surrounding charged chains. In the former two regions two kinds of special water structure are formed. In the third region water has the normal structure.

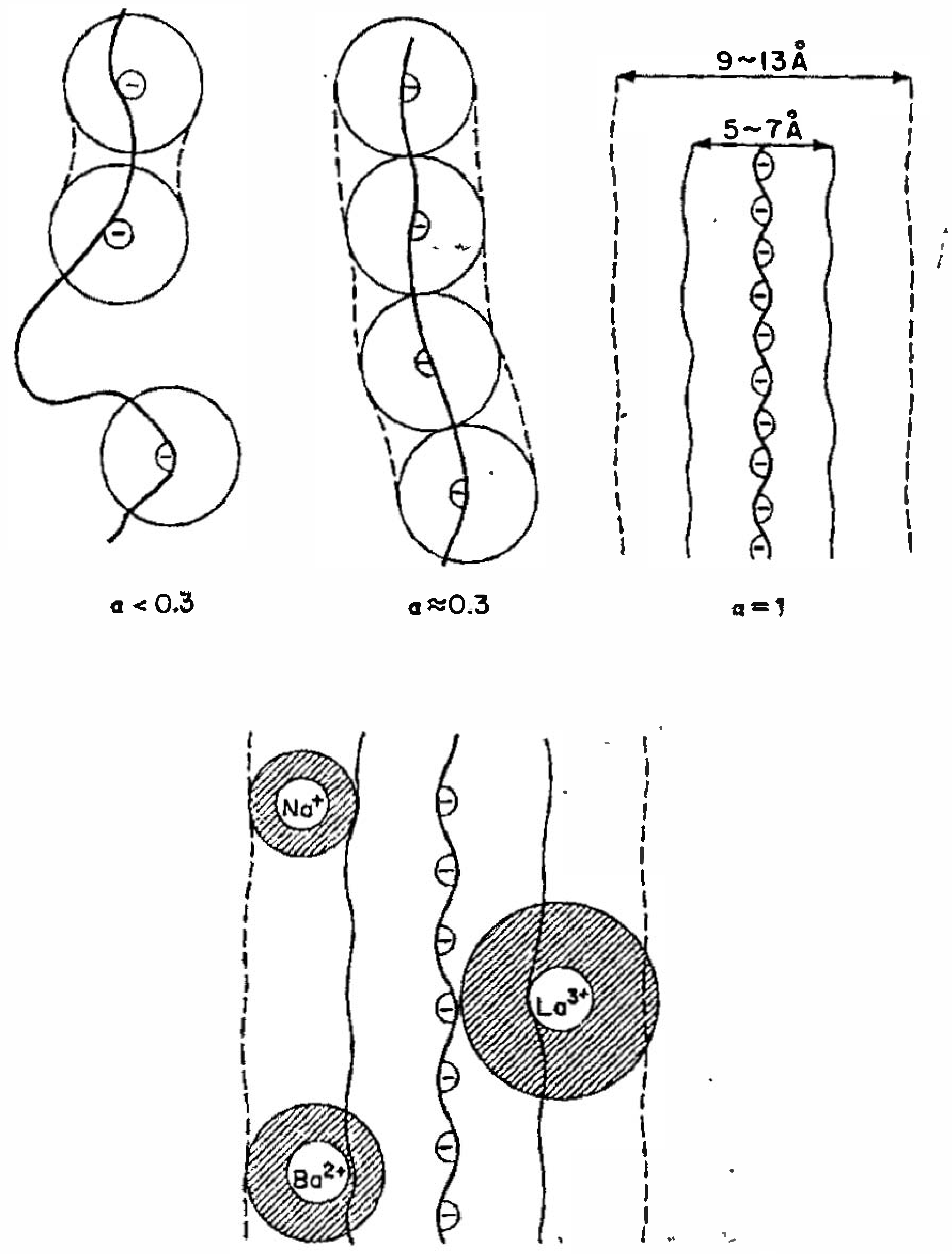


FIG. 25. Illustration of spherical and cylindrical hydration regions around a cylindrical macroion at various charge densities, and the state of binding of various counter ions.

IV. HYDRATION AND BINDING OF COUNTER IONS

What kind of effects on the water structure is found when counter ions are bound to the macroion? In the previous section, inert cations of large volume were employed to prevent their entry into the hydration region around the macroion. If counter ions of smaller size are used, the change of water structure due to their binding can be estimated. In Fig. 24*b*, the change of the refractive index in the process of neutralization is compared for two kinds of counter ions. In the case of sodium ions, the decrease of the refractive index or the increase of the volume due to mixing with polyacids is larger than in the case of tetrabutylammonium ions. Tetrabutylammonium ions are supposed to be bound but have little effect on the hydration region along the macroion, while sodium ions are bound in the hydration region and break the special water structure to bring the increase of the volume of water. The difference in the value of the ordinate between two curves in Fig. 24*b* gives the total change of the refractive index due to binding of sodium ions. The relation between the total change and the degree of neutralization α is given in Fig. 26*a*.

In the next experiment, sodium ions are added to solutions of polyacid neutralized by tetrabutylammonium hydroxide to various degrees. Upon the addition of sodium salt, the refractive index decreases or the volume increases in comparison with the sum of indices or volumes of individual solutions of polyacids and salt. This increase of the volume continues up to a critical concentration of sodium salt which depends on the degree of neutralization, as shown in Fig. 26*b*. Above this critical concentration the further addition of sodium ion produces only a small increase of volume which is independent of the degree of neutralization. The first steep increase of volume is due to the binding of sodium ions in the hydration region around the macroion, and saturation of binding occurs at the critical concentration. Beyond this concentration the slow increase of volume is due to a simple salt effect. This interpretation is supported by the fact that the value of the change of the refractive index at critical points dependent on the degree of neutralization is in good agreement with the value estimated by the previous method in Fig. 26*a*.

On account of the great difference in the size the binding of sodium ions is very predominant over that of tetrabutylammonium ions. By assuming that all sodium ions added are bound up to the critical concentration, the number of bound ions at saturation can be compared with the total number of charged groups in the macroion. Figure 26*c* gives the relation between the amount of bound sodium ions at saturation and the degree of neutralization or the charge number on the macroion. The relation obtained is the same as was previously predicted in the counter ion condensation theory for the cylindrical macroion model in Chapters 2 and 3. With polyacrylic acid the value of α at which condensation just begins corresponds to the condition that $Q = 1$. Above this critical value of α, the gradient of the straight line in Fig. 26*c* is almost equal to unity. That is, the excess amount of counter ions is bound to the macroion until the apparent charge of the macroion is reduced to the limit corresponding to the critical α or $\beta Q = 1$.

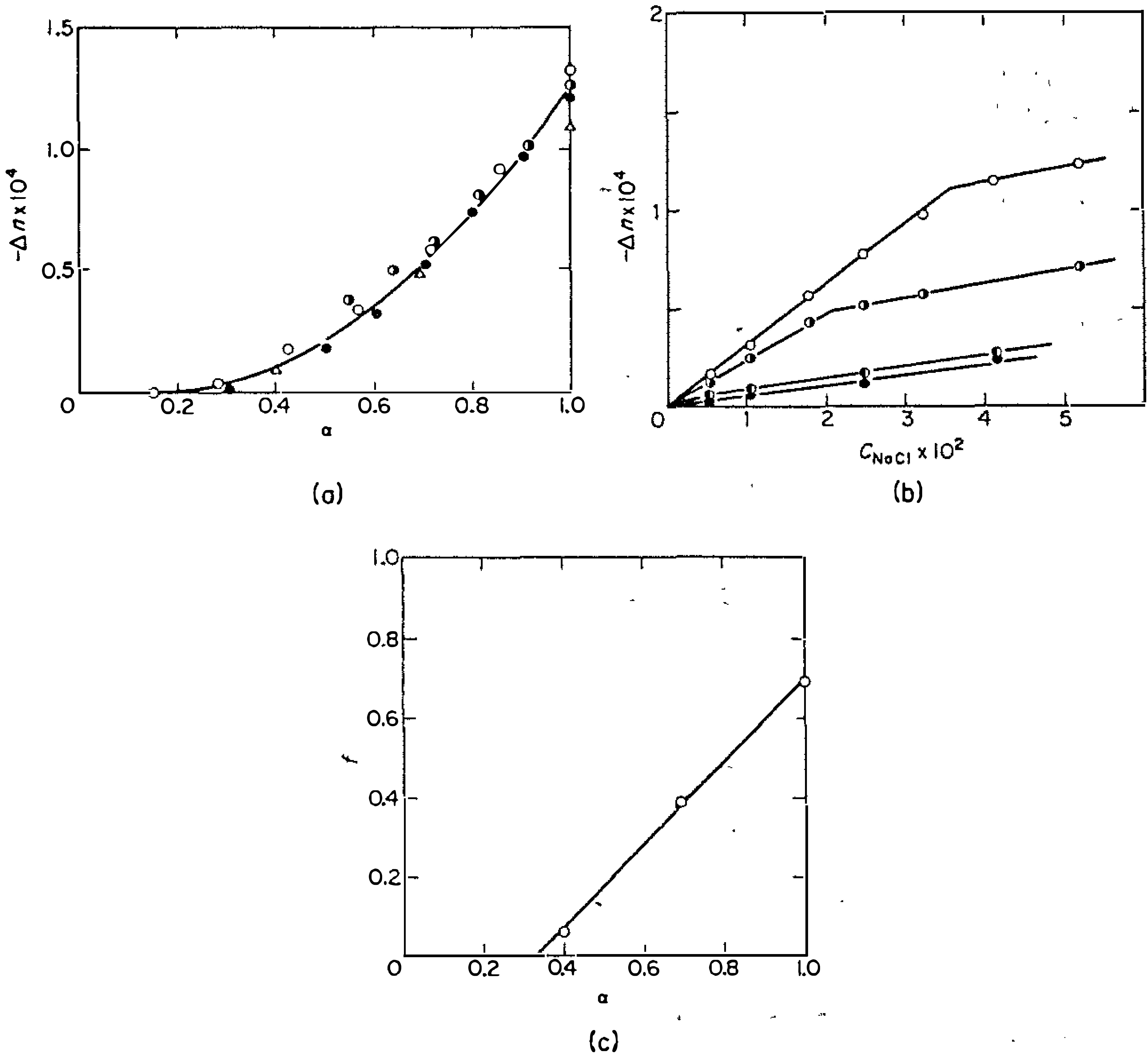


FIG. 26. (*a*) The decrement of the refractive index accompanying the binding of sodium ions to polyacrylic acid ions neutralized at various degrees, obtained by the comparison between two curves in Fig. 24(*b*). (*b*) The decrement of the refractive index accompanying the binding of sodium ions when NaCl was added to solutions of polyacrylic acid partially neutralized by Bu_4NOH; (○) the degree of neutralization $\alpha = 1.0$, (◑) 0.69, (◐) 0.40, and (●) 1.0 neutralized by NaOH. (*c*) The relation between the fraction of bound sodium ions at saturation and the degree of neutralization estimated from the data in Fig. 26(*b*).

Thus, the counter ion condensation phenomenon has also been confirmed by the measurement of refractive index. The agreement of the present analysis with the previous thermodynamic analysis on the amount of bound counter ions suggests that all bound counter ions (of small size such as sodium ions) are in the hydration region.

In Fig. 27 the magnitude of the volume change associated with the binding of sodium ions is compared with that associated with the dissociation of carboxyl groups or the binding of hydrogen ions. The former

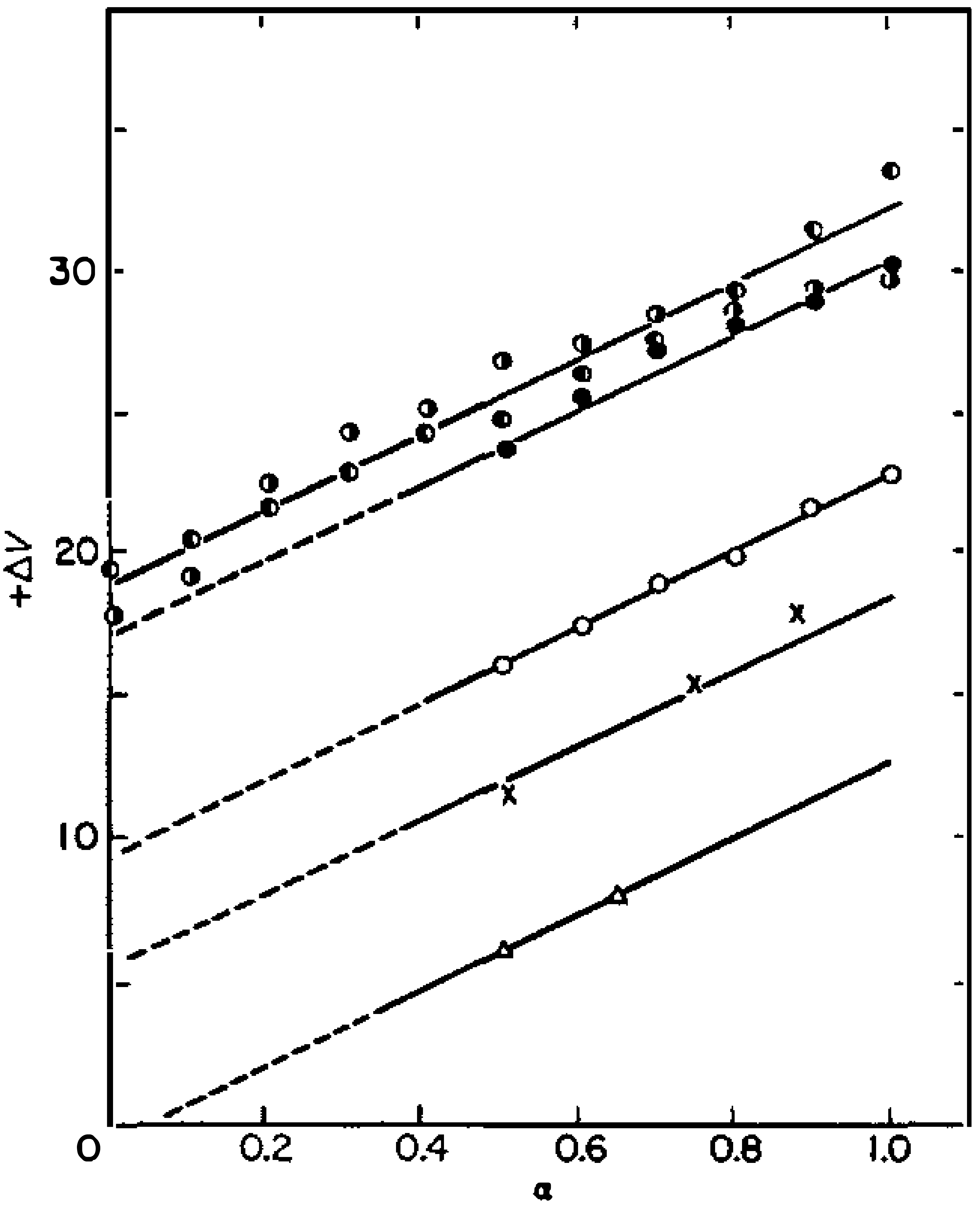


FIG. 27. The volume decrease accompanying the binding of various counter ions to macroions at various degrees of neutralization α. Polyacrylic acid neutralized by Bu_4NOH was used as the standard. (◐, ◑) H^+, (Δ) Na^+, (×) Mg^{2+}, (○) Ba^{2+}, and (●) La^{3+}.

is considerably smaller than the latter. The bound hydrogen ions are evidently localized to individual charged groups and the water structure around them is therefore completely rearranged. The change of the water structure by bound sodium ions is much smaller. It is very likely that sodium ions are not localized at individual charged groups but are mobile in the second cylindrical region of the water structure as illustrated in Fig. 25.

This idea is supported by the fact that the magnitude of the volume change by sodium ions is of the same order as the difference that is observed between the volume changes by hydrogen ions at high and low degrees of neutralization (Fig. 27). Bound sodium ions have an effect only on the excess volume of the special water structure made by the cooperation of charged groups in the macroion. Therefore, as shown in Fig. 27, the effect on the water structure slightly decreases with decreasing degree of neutralization.

Similar analyses have been carried out to examine the effect of polyvalent counter ions on the water structure. As shown in Fig. 27, in the case of divalent counter ions, the magnitude of the volume change associated with the binding is between that observed for hydrogen ions and sodium ions. The bound divalent cations are partially localized and partially mobile. The former destroy the water structure around individual charged groups and the latter are retained in the second cylindrical hydration region. Trivalent cation produces a volume change of the same order as hydrogen ion. The water structure around the macroion is largely destroyed by the binding of trivalent counter ions.

Thus, the binding state of counter ions depends on their size and valence. The property of the resultant polyelectrolytes therefore depends on the size and valence of counter ions. For example, polyacrylic acid neutralized by sodium hydroxide is easily precipitated by the addition of polyvalent counter ions. At full neutralization the amount of counter ions needed for precipitation of polyanions is almost the same for all kinds of polyvalent counter ions, as shown in Fig. 28*a*. This may be related to the loss of the hydration region due to the binding of these counter ions (*17*).

It must be noted here that at low degrees of neutralization there is a great difference in the critical amount of different polyvalent counter ions for precipitation of polyanions. This phenomenon is an interesting example of the relationship between properties common to all polyelectrolytes and properties specific to the species of macroions and counter ions. Among various divalent counter ions, barium ions in a very small amount can precipitate half neutralized polyacrylic acid, while magnesium ion can not at all, as shown in Fig. 28*b*.

It was confirmed that such a difference in the ability for precipitation is not due to the difference in the amount of bound counter ions (*39*). As predicted by the counter ion condensation theory in Chapter 4, all kinds of divalent counter ions are bound to polyanions to the same extent. That is, when divalent cations are added to polyacrylic acid neutralized by sodium hydroxide to the degree of neutralization of 0.3, all divalent

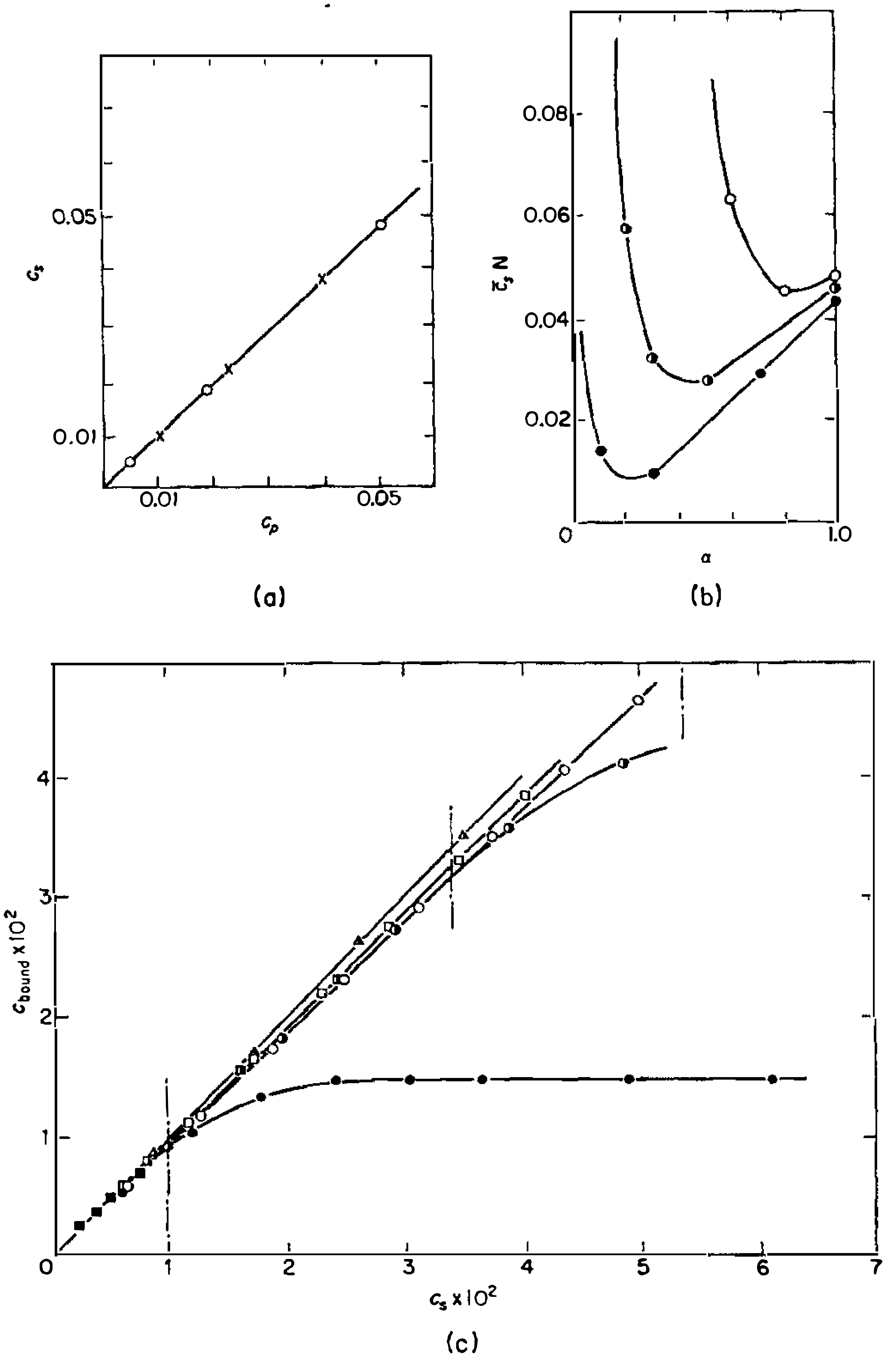


FIG. 28. (*a*) The relation between the critical salt concentration for precipitation and the polymer concentration in polyacrylic acid solutions fully neutralized by NaOH in different kinds of divalent cations; (×) $MgCl_2$, and (○) $CaCl_2$, (*39*). (*b*) The relation between the critical salt concentration for precipitation and the degree of neutralization in polyacrylic acid solutions neutralized by NaOH; (○) $MgCl_2$, (◐) $CaCl_2$, and (●) $BaCl_2$. (*c*) The relation between the amount of bound divalent cations c_{bound} and the concentration of added salts c_s at various degrees of neutralization α in polyacrylic acid solutions of concentration 60 m*N*/l; (○) $MgCl_2$, $\alpha = 1.0$, (□) $BaCl_2$, $\alpha = 1.0$, (◐) $MgCl_2$, $\alpha = 0.7$, (□) $BaCl_2$, $\alpha = 0.7$, (●) $MgCl_2$, $\alpha = 0.25$, (■) $BaCl_2$, $\alpha = 0.25$, and (△) HCl, $\alpha = 0.7$ (*39*).

cations added are bound to polyanions up to a certain limit. Figure 28*c* gives the amount of bound divalent cations estimated from the measurement of electrical conductivity of polyacrylic acid solutions (*39*). Both barium and magnesium ions are fully bound to polyanions until the apparent charge of the polyanion is depressed to a common critical value for condensation of divalent counter ions. Therefore, it must be concluded that polyanions having the same number of bound divalent counter ions show different solubilities depending on the species of the counter ion. That is, at low degrees of neutralization barium polyacrylate has a very low solubility, while magnesium polyacrylate is highly soluble.

This difference is consistent with the result of the refractive index measurements. Among various divalent cations, the volume change associated with the binding of barium ions is larger than that associated with the binding of magnesium ions, as shown in Fig. 27. Barium polyacrylate has the hydration region of a smaller volume than magnesium polyacrylate. It is likely that the structure $COO—Mg^+$ is more stable and soluble than the structure $COO—Ba^+$. The latter has a higher tendency to make a linkage of the form COO—Me—OOC than the former. Such a difference is expected to be amplified when the density of charged groups COO^- in the polyanion is not too large. Thus, the species specificity of counter ions manifests itself in the intermediate range of the degree of neutralization. This interpretation is also supported by the result of titration experiments in the presence of divalent cations (*40*).

THE EFFECT OF LOW MOLECULAR SALTS

I. THE ADDITIVITY LAW

In the earlier chapters only salt-free polyelectrolytes were considered for an analysis of characteristic properties. In this chapter the effect of the addition of simple salts to polyelectrolytes is examined. The number of small ions becomes larger than the number of charged groups in macroions on the addition of salts. All small ions of charge opposite to that of the macroions (counter ions) come from polyelectrolytes and the simple salts added, and all ions of the same charge (co-ions) come from the salts.

If a large charge is fixed in a solution of simple salt, the effect of the coulomb potential from this charge is screened by the ionic atmosphere due to the small ions. This screening becomes more effective with an increase in the salt concentration. It may therefore be expected that the apparent charge of a macroion in polyelectrolytes decreases with the addition of simple salt. For instance, let us consider that sodium chloride is added to a solution of polyacrylic acid neutralized by sodium hydroxide. In the absence of sodium chloride, some sodium ions are already retained in the macroion. The activity of sodium ion is given by the concentration of free ions outside the macroion. The charge of the macroion is not completely canceled by bound counter ions and a sizable potential drop between the inside and the outside of the macroion continues to exist according to Eq. (2). When sodium chloride is added to this solution, sodium ions added are attracted by this potential drop and chloride ions are repelled. As a consequence, the apparent charge of the macroion is decreased. The activity of sodium ions may then be expected to be smaller than the sum of the contribution from the sodium ions of the polyelectrolyte (in the absence of sodium chloride) and sodium chloride (in the absence of the polyelectrolyte).

However, experiments give the following characteristic results. The activity of counter ions is best expressed as a sum of the independent contributions of counter ions from the polyelectrolyte and the added salt; i.e., the activity is

$$\gamma_p c_p + \gamma_s{}^+ c_s = a^+ \tag{130}$$

where c_p and c_s are concentrations of counter ions from the polyelectrolyte and the added salt, respectively, γ_p is the activity coefficient of counter ions of pure polyelectrolyte in the absence of added salt, and $\gamma_s{}^+$ is the activity coefficient of counter ions of added salt in the absence of polyelectrolyte.

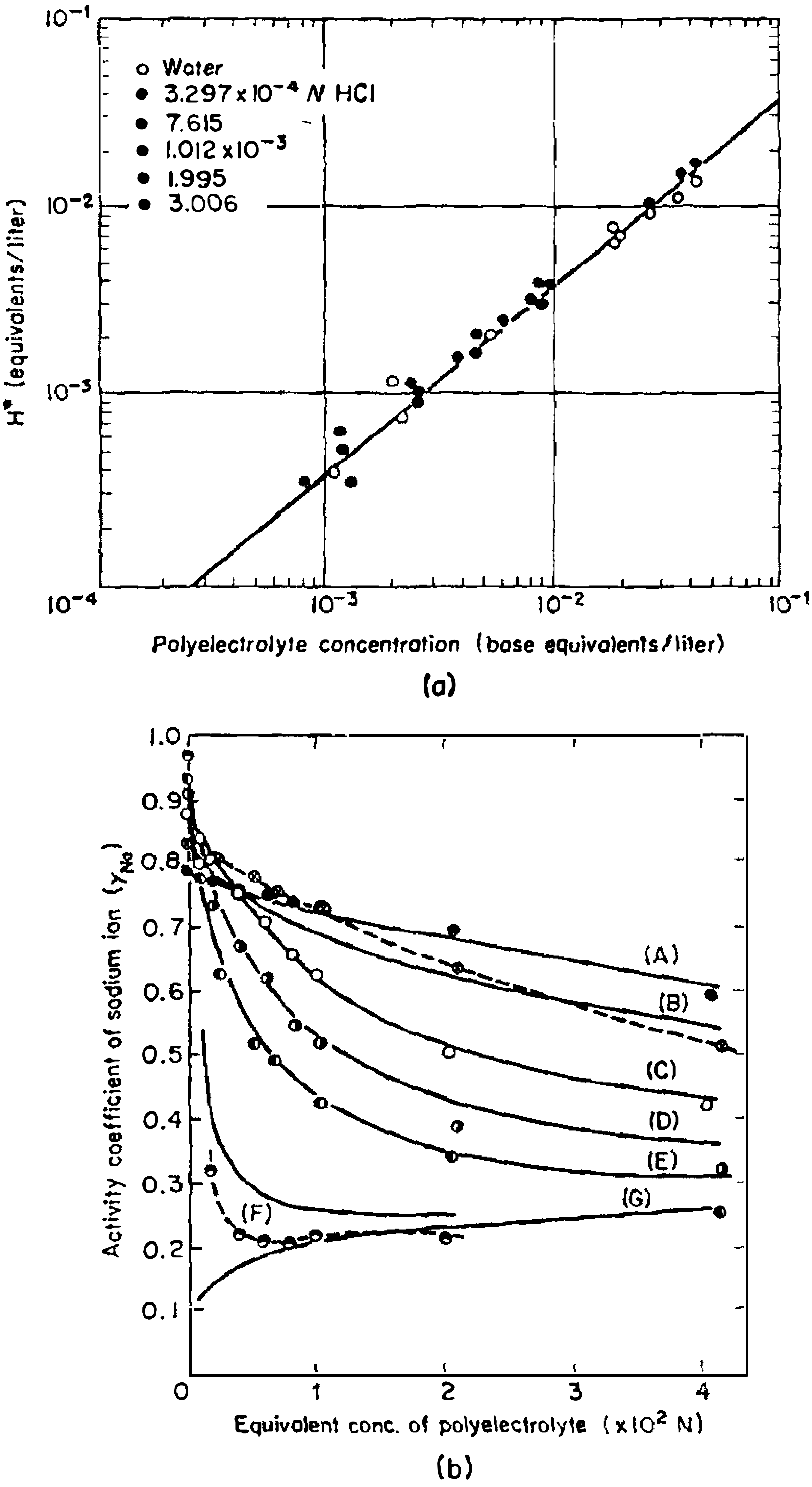
The osmotic pressure (against the pure solvent) of polyelectrolyte solutions containing simple salt is also given by the sum of the osmotic pressure of the polyelectrolyte solution without salt and of the salt. The electric conductivity is found to be the sum of the conductivities of the pure polyelectrolyte and the pure salt as well.

The experimental results of Mock and Marshall (*41*), and Nagasawa et al. (*42*) and Alexandrowicz (*43*) for neutralized polyacids, and those to Iida and Imai (*44*) for proteins are presented in Fig. 29*a*, *b* and *c* to demonstrate this unique behavior of polyelectrolyte–salt mixtures.

The thermodynamic and transference properties of salt-containing polyelectrolytes are thus described as a superposition of the individual properties of the pure components by an additivity law. The counter ions from added salt seem not to be bound to macroions. This apparent capability of a macroion to distinguish counter ions originating from itself and from added salt is at first glance a most surprising result. The secret to this riddle appears to reside in the long range coulomb potential of the highly charged macroion. The examination of this feature which follows shows the additivity law to be an essential rather than accidental property of polyelectrolytes.

II. THEORETICAL DERIVATION OF THE ADDITIVITY LAW

We have seen that the most characteristic property of polyelectrolytes, counter ion condensation, was well explained by applying a two-phase approximation to a cylindrical model of the macroion. The logarithmic form of the potential that resulted from the use of this model provided good insight with respect to this property. Here, the additivity law is



o Water
● 3.297 x 10⁻⁴ N HCl
● 7.615
● 1.012 x 10⁻³
● 1.995
● 3.006
H* (equivalents/liter)
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻³
10⁻²
10⁻¹
Polyelectrolyte concentration (base equivalents/liter)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
Activity coefficient of sodium ion (γNa)
Equivalent conc. of polyelectrolyte (x 10² N)
(A)
(B)
(C)
(D)
(E)
(F)
(G)

(a)

(b)

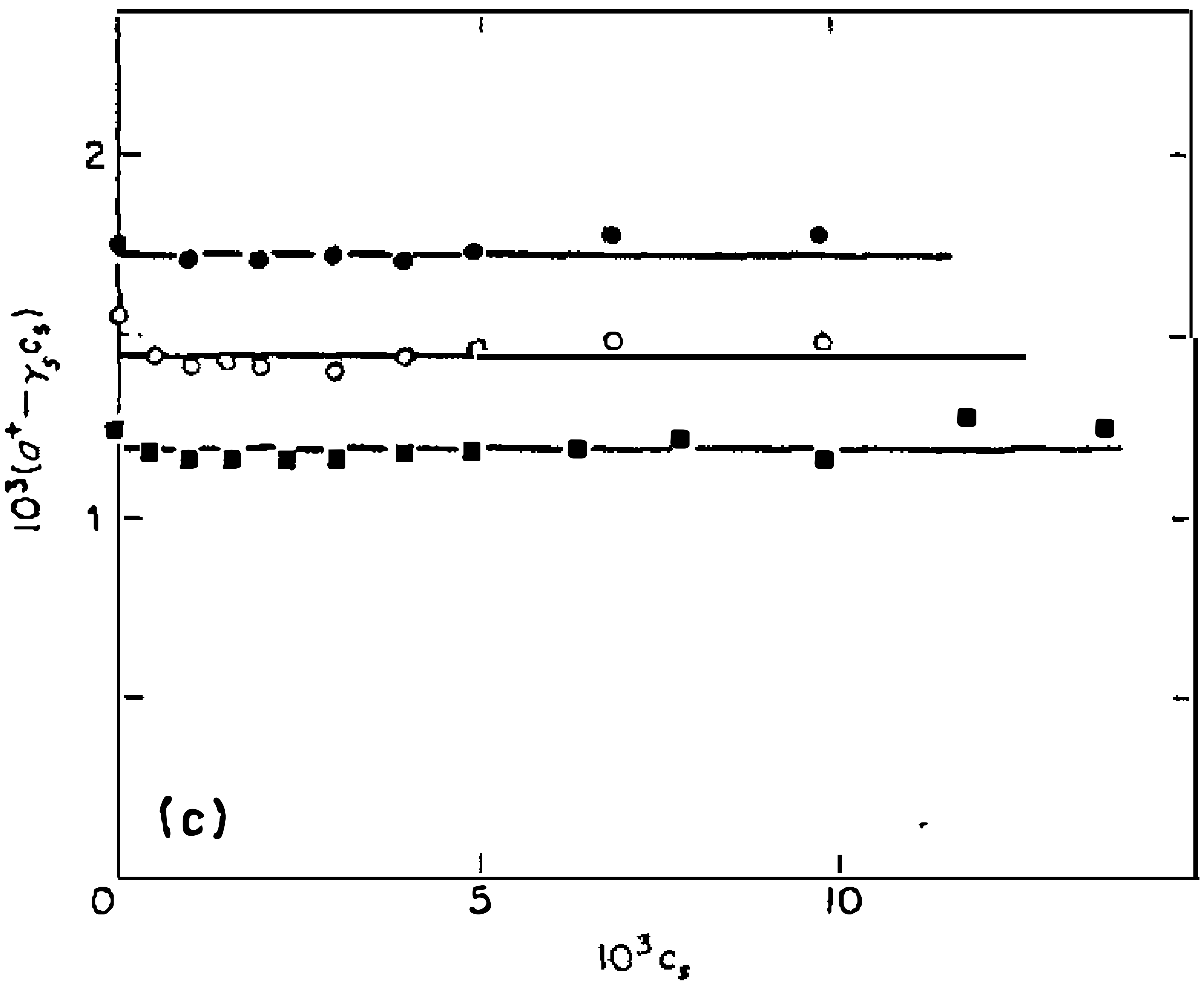


FIG. 29. (*a*) The relation between the activity of counter ions and the concentration of macroions. The activity of hydrogen ions was measured in solutions of vinyltoluene-styrene copolymer sulfonic acid in the presence of various concentrations of HCl. The ordinate represents the value of H^* when the activity of hydrogen ions or pH of the solutions is expressed as $\mathrm{pH} = -\log(H^* + H^0)$, where H^0 is the activity of hydrogen ions in solutions of HCl at the same concentrations in the absence of macroions. The fact that all data at various concentrations of HCl are on a line supports the additivity law (*42*). (*b*) The relations between the activity coefficient of counter ions (sodium ions) and the concentration of macroions (polyvinylsulfonate) in the presence of various concentrations of salts (NaCl). The NaCl concentrations are: (A) 0.1 *N*; (B) 0.05 *N*; (C) 0.02 *N*; (D) 0.01 *N*; (E) 0.005 *N*; (F) 0.001 *N*; (G) 0. Solid lines are calculated from the additivity law at these concentrations of salts (*43*). (*c*) Sodium ion activity against added NaCl concentration at three pH's in tropomyosin solutions. The ordinate represents the difference between sodium ion activity in tropomyosin solutions and in simple salt solutions at the same salt concentration. (●) pH 9.98, (○) pH 8.14, and (■) pH 7.06 (*44*).

derived by use of the cylindrical model once again and the logarithmic potential is found to play an important role as before. The following treatment is based on (*45*).

Let us employ the Poisson-Boltzmann equation for a cylindrical or rodlike macroion in a cylindrical free volume (Fig. 12*a*);

$$\Delta\psi = -(4\pi/\varepsilon_0)\sum_i \rho_i \tag{131}$$

where, in the presence of simple salt, the charge density on the right-hand side is composed of charged groups, counter ions, and co-ions; i denotes the ionic species. If the spatial coordinate, the distance from the center of the rod, is represented by the relative distance, $r/a = x$, the ratio of the distance to the radius of the rod, the above equation is transformed into:

$$d^2\phi/dx^2 + (1/x)(d\phi/dx) = \sum_i A_i \exp(-z_i\phi) \tag{132}$$

where

$$\phi = e_0\psi/kT$$

and

$$A_i = (4\pi e_0^2/\varepsilon_0 kT)(n_i z_i/l)/\int_1^{R/a} \exp(-z_i\phi)\, 2\pi x\, dx \tag{133}$$

The boundary conditions are written as

$$[x(d\phi/dx)]_{R/a} = 0, \qquad [x(d\phi/dx)]_1 = -(2e_0^2/\varepsilon_0 kTd) \tag{134}$$

where $d = l/n$ is the average distance between neighboring charges on the macroion and n_i is the total number of small ions of the ith species per macroion. The electroneutrality condition is satisfied in the cylindrical volume of radius R.

The above set of equations shows that the potential energy-kinetic energy ratio $\phi(= e_0\psi/kT)$ can be expressed as a function of the ratio r/a and the ratio R/a. Consequently, it is easily found from Eq. (32) that the electric energy u_e and the electric free energy f_e can both be expressed as functions of the ratio R/a. They do not contain R or a separately. (This situation is found also in the previous result in Chapter 3, Section III.) The total free energy per macroion is thus always of the form

$$f = f_e(R/a) + f_0(V/N) \tag{135}$$

where the standard free energy f_0 is a function of V/N or $(R^2 - a^2)$.

The additivity law expressed in osmotic pressure terms can be derived from the fact that the electric free energy is a function of the ratio R/a. The osmotic pressure Π of the solution (against pure solvent) is given by

$$\Pi = -N(\partial f/\partial V)_{d,n_i,a} = -(1/2\pi R^2 l)[R(\partial f/\partial R)] \tag{136}$$

because the addition of a solvent molecule simply leads to an increase of the free volume, i.e., the radius R. Since the free energy f_e is a function of R/a,

$$R(\partial f_e/\partial R) + a(\partial f_e/\partial a) = 0 \tag{137}$$

The derivative of the electric free energy with respect to the radius of the free volume is related to its derivative with respect to the radius of the macroion. Therefore,

$$R(\partial f/\partial R) = -a(\partial f/\partial a)+a(\partial f_0/\partial a)+R(\partial f_0/\partial R)$$

$$= -a(\partial f/\partial a)+2V(\partial f_0/\partial V) \tag{138}$$

or

$$2\pi R^2 l\Pi = 2(V/N)\Pi_0+a(\partial f/\partial a)$$

where $\pi(R^2-a^2)l=(V/N)$ and Π_0 is the osmotic pressure of a hypothetical solution of counter ions and co-ions in the absence of macroions.

If the osmotic pressure of two solutions is compared, the following equation is obtained:

$$\Pi_2-\Pi_1 = (\Pi_{20}-\Pi_{10})+(N/2V)[a(\partial f/\partial a)_1-a(\partial f/\partial a)_2] \tag{139}$$

where (V/N) is nearly equal to $\pi R^2 l$. Subscripts in the equation denote the kind of solution. If solution 1 denotes polyelectrolyte without simple salt and solution 2 denotes polyelectrolyte with simple salt, the difference in the osmotic pressure of two hypothetical solutions $(\Pi_{20}-\Pi_{10})$ can be approximated by the osmotic pressure Π_s of a solution of salt without polyelectrolytes

$$\Pi_{20}-\Pi_{10} = \Pi_s \tag{140}$$

The term $(\partial f/\partial a)$ denotes the free energy variation due to the change of the radius of the macroion. In the absence of simple salt, it consists of the variation of the electric energy of the macroion and bound counter ions and of the entropy of bound counter ions. In other words, $(\partial f/\partial a)_1$ is related to the pressure ΔP_1 acting on the surface of the rod by the equation

$$(\partial f/\partial a)_1 = 2\pi a\Delta P_1 \tag{141}$$

and this pressure is expressed as:

$$\Delta P = -(\varepsilon_0/8\pi)E^2(a)-kTc_+(a) \tag{142}$$

where the first term comes from the energy of the electric field $E(=-\partial\psi/\partial r)$ at the surface and the second term comes from the osmotic pressure of the solution of counter ions at the surface (*46*). Equation (142) can be derived by differentiation of energy u_e and entropy s given in Chapter 3, Section I with respect to the radius a.

If the charge density on the macroion is low, the concentration of counter ~~ions~~ $c_+(a)$ at the surface is finite when radius a becomes infinitely small. On the other hand, the electric field E increases infinitely in proportion to $1/a$. Therefore, when a is sufficiently small and the charge density is lower than a certain critical value, the term $(\partial f/\partial a)_1$ consists only of the energy of the electric field, i.e.,

$$(\varepsilon_0/8\pi)E^2(a) = (n^2 e_0^{\,2}/2\pi\varepsilon_0 a^2 l^2)$$

and

$$a(\partial f/\partial a)_1 = -n^2 e_0^{\,2}/\varepsilon_0 l = -nQkT \tag{143}$$

This situation is not changed by the addition of simple salt because the concentration of ions at the surface still remains finite. Therefore, the same expression as the above can be applied to $(\partial f/\partial a)_2$ of a solution of the same macroion in the presence of simple salt. That is,

$$(\partial f/\partial a)_1 = (\partial f/\partial a)_2$$

Then,

$$\Pi_2 = \Pi_1 + \Pi_s \tag{144}$$

The osmotic pressure of a polyelectrolyte in the presence of simple salt is given by the sum of the osmotic pressure of the polyelectrolyte solution without salt and that of the salt solution without the polyelectrolyte.

When the charge density of the macroion exceeds the critical value given by $Q = 1$, the condensation of counter ions begins at the surface of the macroion. Even if the radius a of the macroion becomes infinitely small, the number of condensed counter ions $n - n^*$ is not decreased but remains constant. Therefore, the two terms of Eq. (142) are given by

$$(\varepsilon_0/8\pi)E^2(a) = (n^{*2} e_0^{\,2}/2\pi\varepsilon_0 a^2 l^2) \tag{145}$$

and

$$kTc_+(a) = kT(n-n^*)/\pi a^2 l$$

Since both terms are of the same order as functions of a,

$$\begin{aligned} a(\partial f/\partial a)_1 &= -n^{*2} e_0^{\,2}/\varepsilon_0 l - 2kT(n-n^*) \\ &= +n^*kT - 2nkT \\ &= [(n/Q) - 2n]kT \end{aligned} \tag{146}$$

This expression of $a(\partial f/\partial a)$ can be shown to be insensitive to the addition of simple salt. By resorting to the two-phase equilibrium concept developed in the previous chapter, equations corresponding to (10) can be assumed to describe the distributions of counter ions and co-ions. Then, at high values of Q the equation for counter ions requires the existence of a limit to the apparent charge density of the macroion at infinite dilution. This limit is given by the condition that $\beta Q - 1 = 0$, where β is the ratio of the apparent charge $n^* e_0$ to the total charge ne_0 of the macroion. Therefore, the value of n^* at the limit is independent of the presence of simple salt. Since co-ions are repelled from the small region v, the same value of n^* means that approximately the same number of counter ions are condensed in v. The change in the number of counter ions bound in v by the addition of salt is sufficiently smaller than the total number of counter ions bound in v. (The change is not exactly zero.) Consequently, the term $a(\partial f/\partial a)$ in the presence of salt has approximately the same value as that given by Eq. (146) in the absence of salt. The additivity of the osmotic pressure is thus satisfied even when the charge density of the macroion becomes large.

By use of the expressions

$$\Pi_1/kT = g_p c_p \tag{147}$$

and

$$\Pi_s/kT = g_s c_s$$

where g_p and g_s are the osmotic coefficients, the additivity law (143) is rewritten as

$$\Pi_2/kT = g_p c_p + g_s c_s \tag{148}$$

In this treatment the osmotic pressure is nearly proportional to the sum of the concentration of counter ions and co-ions at the periphery of the free volume R. The additivity of the osmotic pressure is directly related to the additivity of the total ion concentration at the periphery and the additivity of electrical conductivity is satisfactorily explained.

The additivity of the osmotic pressure does not always mean the additivity of the concentration of each kind of ion, for instance, counter ions alone at the periphery. By assuming, however, that the concentration of co-ions at the periphery in the presence of the macroion is approximately equal to that in the absence of the macroion, the concentration of counter ions is expected to be given by the sum of the concentration in the absence of salt and in the absence of the macroion. The additivity of the activity of counter ions is then approximately established. Actually the activity coefficient of co-ions is not very much smaller than unity. Even if it changes with the concentration of salt, the change is small.

The expressions of $a(\partial f/\partial a)$ in Eqs. (143) and (146) were approximate. If at a constant concentration of simple salt, the radius a of the macroion or the concentration of the macroion is made infinitely small, they are exact. In actual cases, however, the radius of the macroion and the concentration are finite and the ratio a/R is not always sufficiently small. Moreover, real macroions may assume shapes varying from cylindrical to spherical, depending on the charge density and the concentration. For spherical macroions, the Poisson–Boltzmann equation must contain a spatial coordinate besides the relative distance r/a; then the additivity law can not be readily derived for this conformation.

Experimentally, however, the additivity law is found to be satisfied over a wide range of concentrations of macroion and added salt. One reason for this may be that the macroion retains its cylindrical character even when the macroion as a whole is coiled. It has also been theoretically shown that in the cylindrical model of finite thickness, or even in the spherical model, the additivity law is approximately satisfied if the charge density of the macroion is sufficiently large. Katchalsky proved the additivity law of the activity coefficient of counter ions under the assumption that the activity coefficient of co-ions is always equal to unity, independent of the shape of the macroion (*47*). Alexandrowicz (*48*) derived the additivity law from the approximate solution of the Poisson–Boltzmann equation for the mixture of simple salt and macroions of high charge density. By applying the cluster integral method to a rodlike macroion having discrete charged groups in simple salt, Manning and Zimm found that the additivity law is approximately satisfied (*49, 50*).

Thus, it is concluded that the additivity law which describes one of the most characteristic properties of polyelectrolytes is a result of the special feature of the integrated coulomb potential due to the macroion.

III. MIXTURE OF SALTS

The additivity law was derived with counter ions of the same species. It can be applied to counter ions of any valence and size, as long as they are of the same species. It is of interest to examine its applicability in a mixture of different salts. It has already been shown that in a mixture counterion condensation depends on the valence and the size of counter ions. The valence changes the critical value of the charge density for condensation. The size changes the amount of condensation at finite concentrations of macroions.

Let us consider a macroion with monovalent counter ions. When salts having polyvalent counter ions are added to the solution, these polyvalent ions are selectively bound to the macroion and the effective charge of the macroion is changed. The derivative $(\partial f/\partial a)$ can not be kept constant as is required for the additivity law to be satisfied. In such a case it is convenient to consider first the equilibrium between the macroion and polyvalent counter ions. Polyvalent counter ions are condensed to the macroion until the effective charge is reduced to the critical value given by $n^*e_0{}^2/\varepsilon_0 kTl = 1/z$ or $z\beta Q = 1$, where z is the valence.

If the total number of polyvalent counter ions in the solution is smaller than that necessary for this reduction of the effective charge, all of them are condensed and no free polyvalent ions remain, as mentioned in Chapter 4. Such a phenomenon is expected to occur independent of the amount of monovalent counter ions coexisting. Then the equilibrium between the macroion and monovalent counter ions is established at the charge density to which the macroion was reduced by the binding of polyvalent counter ions. It is not necessary to take into consideration the direct correlation between two kinds of counter ions.

In general, when the total number of polyvalent counter ions is smaller than that corresponding to the total charge of the macroion, it is convenient to define solution 1 to contain macroions, all of the polyvalent counter ions, and sufficient monovalent counter ions to equal to the total charge of the macroion. Solution 2 is obtained by the addition of the remaining monovalent salt. This addition of monovalent salt to solution 1 does not change the effective charge or the number of condensed counter ions on the macroion. The additivity law can be satisfied by the osmotic pressure of solution 1 and 2 defined above. If solution 1 is defined as containing macroions and monovalent counter ions and solution 2 as containing polyvalent salt in addition, the additivity law can not be satisfied.

When the total number of polyvalent counter ions is larger than that corresponding to the total charge of the macroion, these ions are bound until the effective charge of the macroion is reduced to the critical value and no monovalent counter ions are bound. Therefore, the addition of monovalent salts does not change the effective charge or number of condensed ions.

Let us next consider a mixture of two kinds of monovalent counter ions of different size. At sufficiently low concentrations of macroions, the effective charge of the macroion can not exceed a critical value common to monovalent counter ions. If the charge density of the macroion is larger than the critical value, i.e., if Q is larger than unity, some of the monovalent counter ions must be bound. The ratio of the numbers of two kinds of bound counter ions is determined by their size and the charge density of the macroion. (See the analysis in Chapter 4.) However, the total number of bound ions is determined by the charge density alone, since the remaining charge of the macroion must always be equal to the critical value. Therefore, the value of $(\partial f/\partial a)$ is approximately independent of the ratio of two kinds of bound counter ions. Solution 1 is then supposed to contain macroions with two kinds of monovalent counter ions and solution 2 also contains a mixture of monovalent salts in addition to the macroions and the counter ions. The values of $(\partial f/\partial a)$ for the two solutions are equal and the additivity law is expected to be satisfied when applied to the osmotic pressure of the mixture.

As mentioned in the previous section, however, counter ions of smaller size are bound more than those of larger size. Therefore, the additivity law can not be expected to describe the activity of each kind of counter ion in the mixture. If salt of counter ions of smaller size is added to a solution of macroions with counter ions of larger size, bound counter ions must be exchanged.

IV. OSMOTIC PRESSURE AGAINST SALT SOLUTIONS

Equation (138) is rewritten as

$$\Pi = \Pi_0 + (N/2V)a(\partial f/\partial a) \tag{149}$$

For a salt-free polyelectrolyte

$$\Pi_0 = nNkT/V \tag{150}$$

If the expressions of $a(\partial f/\partial a)$ in Eqs. (142) and (145) are put into Eq. (149), the same result as Eq. (61) is obtained for the osmotic pressure at extreme dilution. In the presence of simple salt the osmotic pressure is obtained by adding the osmotic pressure of the salt solution. Then we have

$$\begin{aligned} \Pi &= (nNkT/V)(1-Q/2)+\Pi_s \qquad 0 \le Q \le 1 \\ \Pi &= (nNkT/V)(1/2Q)+\Pi_s \qquad 1 \le Q \end{aligned} \tag{151}$$

This procedure of calculation to derive Eq. (151) indicates that the expression (61) or (151) of the osmotic pressure as a function of the charge density Q results from the fundamental property of the Poisson–Boltzmann equation for a cylindrical system which led us to the additivity law.

It must be remarked, however, that the above osmotic pressure Π refers to the pure solvent. In the presence of salt the osmotic pressure that is measured experimentally refers to the salt solution since the semipermeable membrane for measurement is impermeable only to macroions.

The activity of counter ions and that of co-ions in a solution of macroions is written as

$$\gamma_p c_p + \gamma_s{}^+ c_s$$

and

$$\gamma_s{}^- c_s \tag{152}$$

respectively, according to the additivity law. If this solution is in osmotic equilibrium with a salt solution of concentration c_{s0}, the relation

$$(\gamma_p c_p + \gamma_s^+ c_s)(\gamma_s^- c_s) = \gamma_{s0}^+ \gamma_{s0}^- c_{s0}^2 \tag{153}$$

must be established. This is the equilibrium condition for transfer of simple salt across the membrane. Thus, the concentration of salt c_s in the solution of macroions is given as a function of the concentration of macroions and of the salt outside.

The osmotic pressure Π' of the solution of macroions against the salt solution is given from Eq. (148) by

$$\Pi'/kT = g_p c_p + g_s c_s - g_{s0} c_{s0} \tag{154}$$

This is the equilibrium condition for transfer of a solvent (water) molecule across the membrane. From Eqs. (153) and (154) the osmotic pressure can be solved as a function of concentrations c_p and c_{s0}. In the present method of approximation it is meaningless to distinguish osmotic coefficients and activity coefficients, as described in Chapter 3. Therefore, here we put $\gamma_p = g_p$, $2\gamma_s = g_s$ and $2\gamma_{s0} = g_{s0}$. Then we have

$$\Pi'/kT = \gamma_p c_p[(1+x^2)^{1/2} - x] \tag{155}$$

where

$$x = 2\gamma_{s0} c_{s0}/\gamma_p c_p$$

The quantity $\gamma_p c_p$ gives the osmotic pressure Π in the absence of salt and the additivity law indicates that this γ_p is independent of the salt concentration. Therefore, the ratio of the osmotic pressure in the presence of salt to that in the absence of salt is a function only of the ratio x. The relation of this osmotic pressure Π' to the macroion concentration at a constant value of the salt concentration is shown in Fig. 30*a*.

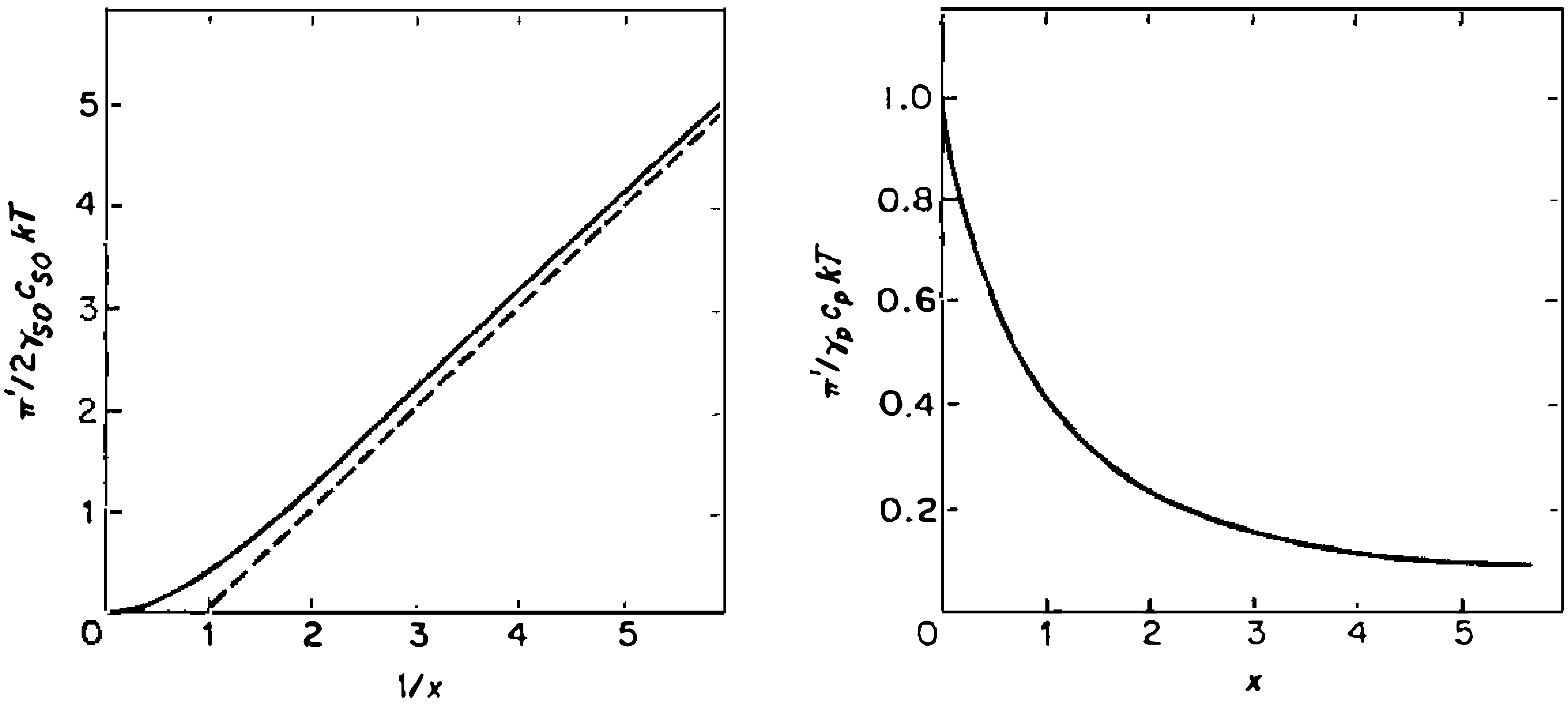
Figure 30*b* shows the relation of the osmotic pressure to the concentration of salt at a constant concentration of macroion. The pressure decreases with the addition of salt. At low concentrations of salt, i.e., for small values of the ratio of the salt concentration to the counter ion concentration originating in the macroion x, the pressure is approximately given by

$$\Pi'/kT = \gamma_p c_p - 2\gamma_{s0} c_{s0} + 2\gamma_{s0}^2 c_{s0}^2/\gamma_p c_p \tag{156}$$

The osmotic pressure of a polyelectrolyte against a salt solution of low concentration is approximately given by the difference between the osmotic pressure of the polyelectrolyte against the pure solvent and that of the salt solution against the pure solvent. The correction term in Eq. (156) is the product of the ratio x and the osmotic pressure of the salt solution divided by 2.

According to Eq. (155), at high concentrations of salts or low concentrations of macroions the osmotic pressure Π' is given by

$$\Pi'/kT = \gamma_p^2 c_p^2/4\gamma_{s0}c_{s0} \tag{157}$$



(a) (b)

FIG. 30. (*a*) The relation between the osmotic pressure and the concentration of macroions at a constant concentration of the salt solution outside. $x = 2\gamma_{s0}c_{s0}/\gamma_p c_p$. (*b*) The relation between the osmotic pressure and the concentration of salts outside at a constant concentration of the macroions.

Thermodynamically, however, in the limit of low concentrations of macroions the osmotic pressure against a salt solution must be given by the number concentration of macroions. The contribution of the mixing entropy of macroions was not taken into account in the expression of the osmotic pressure (154). Therefore, Eq. (157) must be rewritten

$$\Pi'/kT = c_p/n + \gamma_p^2 c_p^2/4\gamma_{s0}c_{s0} \tag{158}$$

which is regarded as a series expansion of the osmotic pressure with respect to the concentration of macroions. The second term gives the second virial coefficient of the osmotic pressure A_2 against the salt solution;

$$A_2 = \gamma_p^2 kT/4\gamma_{s0}c_{s0} \tag{159}$$

The positive value of the second virial coefficient is a consequence of the repulsive force between macroions. The repulsive force is decreased by the addition of salts. The fact that the virial coefficient is inversely proportional to the salt concentration has been experimentally confirmed and this result is shown in Fig. 31*a* and *b* (*51*).

The light scattering of a polyelectrolyte solution in the presence of simple salt is mainly due to the fluctuation of the concentration of macroions in the salt solution. It is inversely proportional to the derivative of the osmotic pressure Π' with respect to the concentration of macroions at a constant external salt concentration c_{s0}. From the above expression of Π' the scattering intensity is found to be increased by the addition of salts. Some experimental data are in qualitative agreement with the result derived from Eq. (158) (*52*).

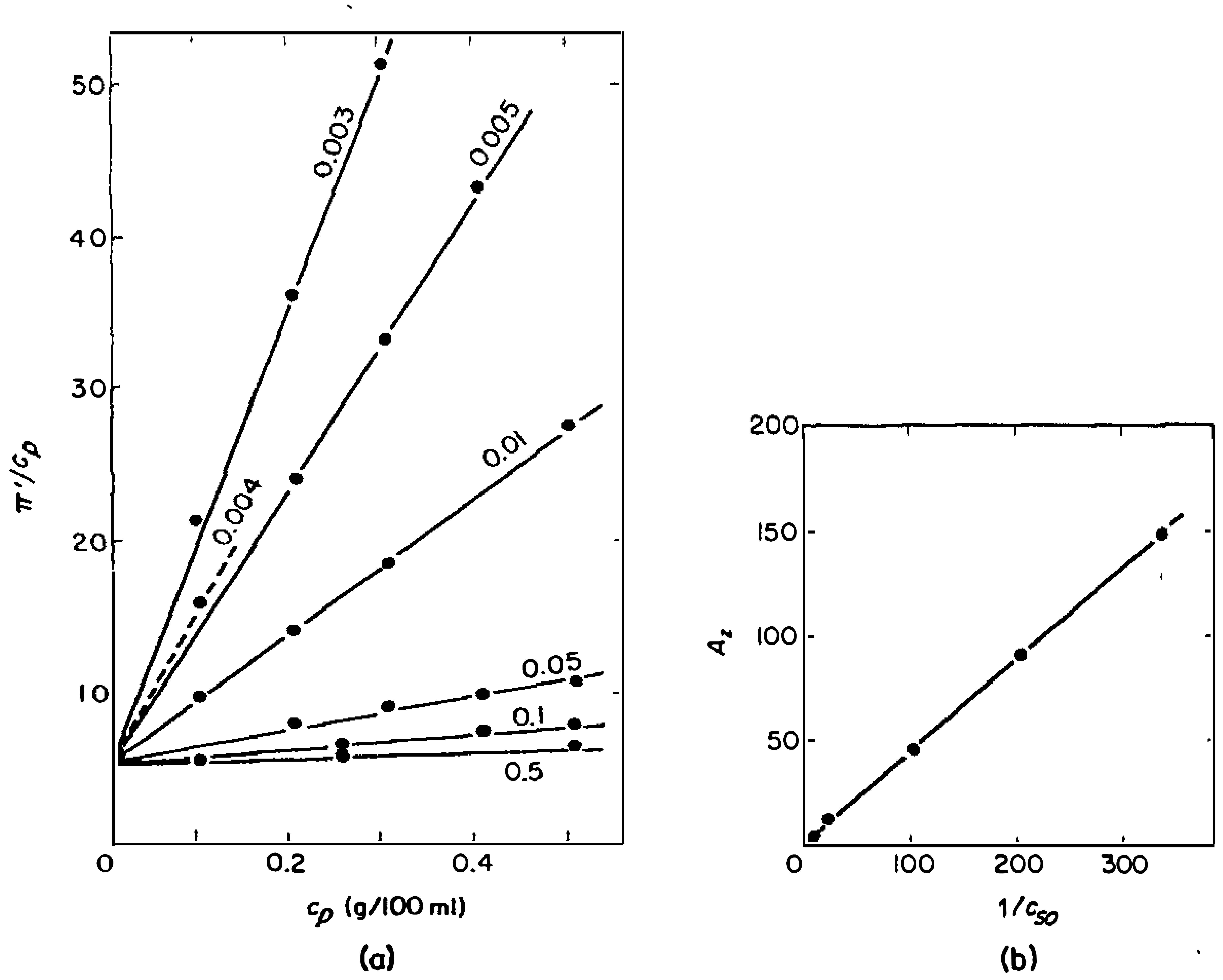


Fig. 31. (*a*) The relation between the osmotic pressure and the concentration of sodium pectinate solutions in equilibrium with various concentrations of NaCl. The numbers on the lines denote the NaCl concentrations (*N*). (*b*) The relation between the second virial coefficient A_2 and the concentration of low molecular salts obtained from the data in Fig. 31*a*. (*51*).

All of the above theoretical results were obtained from the additivity law and the equivalence between the osmotic coefficient and the activity coefficient.

It must be noted that the second virial coefficient is obtained experimentally from the gradient of the change of the osmotic pressure or the light scattering with concentration by extrapolation to infinite dilution. Another theoretical method of determination of A_2 must be calculation of the interaction between two macroions placed in a salt solution. This problem is discussed in later chapters.

Finally it is emphasized again that in the absence of salts the osmotic pressure is determined by the concentration of free counter ions, while in the limit of high concentrations of salts it is determined by the (number) concentration of macroions. Between these two limits, the salt concentration greatly changes the osmotic pressure and various other properties of polyelectrolytes.

Chapter 8

CHEMICAL POTENTIALS AND THE SALT CONCENTRATION

I. THE CHEMICAL POTENTIAL OF MACROIONS

The effect of simple salt on the chemical potential, μ_p, of macroions with counter ions is analyzed below by employing the additivity law derived in the previous chapter. In the absence of salt the free energy f of polyelectrolyte solution per macroion with its counter ions is given by expression (22). The total free energy of the solution containing N macroions is then Nf. (The mixing entropy of macroions in the solution must be added to this free energy, but this entropy term has no influence on the discussion in this chapter.) The chemical potential of the macroion with counter ions can be obtained by differentiation of this total free energy $F = Nf$ with respect to the number, N, of macroions. In the differentiation it must be remembered that the free energy f is a function of N through the size of the free volume of the macroion. The chemical potential, μ_0, of the solvent molecule is obtained by the differentiation of $F = Nf$ with respect to the number of solvent molecules n_0N $(= N_0)$. In this differentiation the free volume also changes. The total volume of the solution V is written as

$$V = N_0 v_0 + (nv^+ + v_m)N \tag{160}$$

where v_0 is the volume of the solvent molecule, v^+ is the volume of the counter ion, and v_m is the volume of the macroion. Therefore, we have

$$\begin{aligned}\mu_p = (\partial F/\partial N) &= f + N[\partial f/\partial(V/N)][\partial(V/N)/\partial N] \\ &= f + [\partial f/\partial(V/N)][-(n_0 v_0)] \qquad (161)\end{aligned}$$

$$\begin{aligned}\mu_0 = (\partial F/\partial N_0) &= N[\partial f/\partial(V/N)][\partial(V/N)/\partial N_0] \\ &= [\partial f/\partial(V/N)]v_0 \qquad (162)\end{aligned}$$

From these relations it is found that

$$F = Nf = N(\mu_p + n_0\mu_0) \qquad (163)$$

This is a thermodynamic relation which must be generally satisfied between the free energy and chemical potentials.

In the presence of simple salt

$$F = Nf = N(\mu_p + n_0\mu_0 + n_s\mu_s) \qquad (164)$$

where n_s is the total number of salt molecules per macroion and μ_s is the chemical potential of the salt (including both counter ions and co-ions).

The chemical potential of the salt μ_s, if we consider the additivity law to be valid, may be expressed as

$$\mu_s = kT \ln(\gamma_p c_p + \gamma_s{}^+ c_s)(\gamma_s{}^- c_s) \qquad (165)$$

where c_p is, as in the previous section, the concentration of counter ions from the macroion and c_s is the concentration of counter ions and co-ions from the salt. The additivity law, theoretically derived for the case of rodlike or cylindrical macroions in the previous chapter, has been experimentally established over a very wide range of macroion and salt concentrations, and the assumption that it provides a general relationship between the chemical potential of salt and its concentration is felt to be appropriate.

When the free energy is written in the form of Eq. (164), the thermodynamic relation

$$\partial\mu_i/\partial n_j = \partial\mu_j/\partial n_i \qquad (166)$$

must be satisfied in the arbitrary combination of two components i and j. As a special case, we have

$$\partial\mu_p/\partial c_s = n(\partial\mu_s/\partial c_p) \qquad (167)$$

The right-hand side can be calculated from Eq. (165) to be

$$n(\partial\mu_s/\partial c_p) = nkT\gamma_p(1 + \partial \ln \gamma_p/\partial \ln c_p)/(\gamma_p c_p + \gamma_s{}^+ c_s) \qquad (168)$$

The difference between the chemical potential of macroions (with counter ions) in the absence and in the presence of salts can be calculated as follows, by the use of Eqs. (167) and (168)

$$\mu_p(c_s) - \mu_p(0) = \int_0^{c_s} (\partial \mu_p/\partial c_s)\, dc_s$$

$$= nkT(\gamma_p/\gamma_s{}^+) \ln (1 + \gamma_s{}^+ c_s/\gamma_p c_p) \qquad (169)$$

In the integration it was assumed that the derivative $\partial \ln \gamma_p/\partial \ln c_p$ is very much smaller than unity and the activity coefficient of salt ions is replaced by its average over the entire range of the salt concentration. This simplification is reasonable because the activity coefficient of counter ions in the absence of salt is insensitive to the concentration of the macroion, as shown in Chapter 3. The chemical potential of macroions with counter ions is thus obtained as a function of the salt concentration. Since the above derivation is based on the assumption that the additivity law is obeyed over the whole range of salt concentration, the relation is only as applicable as the additivity law.

Expression (169) can be interpreted as follows. Let us suppose that small molecules are added to a solution of macromolecules. Small molecules are assumed to have different affinities for macromolecules in different states. The chemical potential of macromolecules in a state having a strong affinity for small molecules is decreased to a large extent by addition of such small molecules (*54*). If a repulsive force acts between small molecules and macromolecules, their addition increases the chemical potential of macromolecules. In expression (169) the addition of simple salt to macroions (with their counter ions) increases the chemical potential of macroions. This result corresponds to the case of repulsive interaction, the repulsion between macroions and salt being stronger the larger the value of γ_p. Thus, in the conformation having a larger apparent charge or a larger concentration of free counter ions, salt ions as a whole are repelled more strongly by macroions. Since the concentration of free counter ions is larger in the extended conformation than in the coiled one, the repulsion is weaker in the latter, and consequently, the addition of salt increases the concentration of macroions in the coiled conformation.

This situation can be understood from the osmotic equilibrium of a solution of macroions with a salt solution, where the concentration of salt ions in the solution of macroions is lower than that in the salt solution outside. (See the concentration of co-ions.) The difference is larger for macroions having the larger apparent charge.

If small molecules are bound to a macromolecule in state j with the binding constant K_j at m_j binding sites, the chemical potential of macromolecules in state j is decreased by the addition of these small molecules by

$$-m_j kT \ln(1+K_j c) \tag{170}$$

where c is the concentration of *free* small molecules. This expression is analogous to Eq. (169) except for the negative sign. That is, according to Eq. (169) the influence of salt ions on the chemical potential of macroions is as if they have a stronger affinity for macroions in the state having a smaller activity coefficient of counter ions, although actually the interaction between macroions and salts is repulsive.

II. HYDROGEN ION EQUILIBRIUM IN THE PRESENCE OF SALTS

Another example of the application of the additivity law is given below to describe the effect of salt on the titration behavior of polyacids or polybases (*55*). In the case of partially neutralized weak polyacids or polybases the solution can be regarded as being composed of four components; solvent molecules (e.g., H_2O), polyacid or polybase molecules (e.g., polyacrylic acid), alkali or acid (e.g., NaOH), and neutral salt molecules (e.g., NaCl). The total number of these molecules in the solution are denoted by n_0N, N, n_aN, and n_sN, respectively. The chemical potentials are denoted by μ_0, μ_p, μ_a, and μ_s, respectively. All small ions and charged groups on the macroions are assumed to be of the same valence and, moreover, counter ions from alkali or acid and those from neutral salts are assumed to be of the same species. Each macroion has approximately n_a charged groups on the average. The degree of neutralization of macroions α is given by the ratio n_a/n.

The total free energy of the system must be written as

$$F = Nf = (n_0\mu_0 + \mu_p + n_a\mu_a + n_s\mu_s)N \tag{171}$$

It should be noted that instead of taking the partially neutralized macroion as an independent component, we define the polyacid (polybase) and the alkali (acid) as two independent components. Then, derivatives of the chemical potentials with respect to the number of component molecules yield thermodynamic relations of the type introduced in Eq. (166). One of them may be written as

$$\partial\mu_s/\partial c_a = \partial\mu_a/\partial c_s \tag{172}$$

where c_a is the number concentration of alkali (acid) added. In the present case application of the additivity law for expression of the activity of counter ions gives the relation

$$\mu_s = kT \ln (\gamma_p c_a + \gamma_s{}^+ c_s)(\gamma_s{}^- c_s) \tag{173}$$

the concentration of counter ions from macroions being equal to c_a. Here, γ_p designates the activity coefficient of these counter ions in the absence of salt.

By the use of Eqs. (172) and (173), the difference between the chemical potential of alkali (acid) in the absence and in the presence of salt can be calculated as was done previously for the macroion with counter ions. The result is

$$\begin{aligned} \mu_a(c_s) - \mu_a(0) &= \int_0^{c_s} (\partial \mu_s / \partial c_a)\, dc_s \\ &= kT(\partial(\gamma_p c_a)/\partial c_a)/\gamma_s{}^+) \ln (1 + \gamma_s{}^+ c_s / \gamma_p c_a) \end{aligned} \tag{174}$$

On the other hand, the chemical potential of counter ion is given by the additivity law and the difference between the potential in the absence and in the presence of salt is given by

$$kT \ln (\gamma_p c_a + \gamma_s{}^+ c_s) - kT \ln \gamma_p c_a = kT \ln (1 + \gamma_s{}^+ c_s / \gamma_p c_a) \tag{175}$$

Since alkali is composed of counter ions and hydroxyl ions, the chemical potential of hydroxyl ions is obtained by subtracting Eq. (175) from Eq. (174). The chemical potential of hydrogen ion is then given by

$$\mu_{\mathrm{H}}(c_s) - \mu_{\mathrm{H}}(0) = -kT\{[\partial(\gamma_p c_a)/\partial c_a]/\gamma_s{}^+ - 1\} \ln (1 + \gamma_s{}^+ c_s / \gamma_p c_a) \tag{176}$$

We learn from this result that at a constant value of the degree of neutralization, α, the pH of the solution is changed by the addition of neutral salts in accordance with

$$\mathrm{pH}(c_s) - \mathrm{pH}(0) = \{[\partial(\gamma_p c_a)/\partial c_a]/\gamma_s{}^+ - 1\} \log_{10} (1 + \gamma_s{}^+ c_s / \gamma_p c_a) \tag{177}$$

The derivative $[\partial(\gamma_p c_a)/\partial c_a]$, which corresponds to the increase of free counter ions with increase of the degree of neutralization in the absence of salt, is usually positive but smaller than unity. Therefore, the coefficient on the right-hand side of Eq. (177) is negative. That is, the pH decreases with increasing concentration of simple salt in proportion to the term $\log_{10} (1 + \gamma_s{}^+ c_s / \gamma_p c_a)$. The ratio $\gamma_s{}^+ c_s / \gamma_p c_a$ defines the number of free counter ions from added salt relative to that from alkali. When this ratio is small, the pH change is proportional to the salt concentration c_s; when it is large, the pH change is proportional to the logarithm of the salt concentration.

In Fig. 32*a* the pH of partially neutralized polyacrylic acid solutions is plotted against the salt concentration at various degrees of neutralization (*56*). A logarithmic decrease of pH is found at high salt concentrations. The gradient of the straight line in this figure is plotted against the degree of neutralization in Fig. 32*b*. The value of the derivative $[\partial(\gamma_p c_a)/\partial c_a]$ or $[\partial(\gamma_p \alpha)/\partial \alpha]$ estimated from the gradient by the use of Eq. (177) is also given in the same figure. At high degrees of neutralization the derivative becomes very small, so that $\gamma_p \alpha$ becomes almost constant.

This result is consistent with the earlier experimental and theoretical analyses on activity of counter ions described in preceding chapters.

In Fig. 32*a* the value of the salt concentration at which the extrapolated straight line (the pH vs. log c_s line) reaches the horizontal line corresponding to the pH observed at zero salt concentration must satisfy the condition $\gamma_p c_a = \gamma_s^{+} c_s$. The relation between $\gamma_p c_a$ and the degree of neutralization obtained by this method is shown in Fig. 32*c*. The value of $\gamma_p c_a$ increases with increasing degree of neutralization and is almost saturated at high degrees of neutralization. Such behaviors of $\gamma_p c_a$ agree well with previous experimental and theoretical results.

The other experimental example is concerned with a rodlike protein, tropomyosin. The relation obtained between the pH and the salt concentration at constant concentrations of tropomyosin and alkali in the neutral pH region is shown in Fig. 33*a* (*57*). At high salt concentrations the pH decreases in proportion to the logarithm of the salt concentration. In the whole range of salt concentration the relation observed is in very good agreement with Eq. (177), as shown in Fig. 33*b*. In this case independent measurements of the activity of counter ions were carried out in the same solution. The value of the activity directly measured coincides with the activity estimated from the intercept of the extrapolated straight line (the pH vs. log c_s line) with the horizontal line corresponding to the pH at zero salt concentration in Fig. 33*a*. In Fig. 33*b* the value of $\gamma_p c_a$ obtained by this method was used to determine the value of the abscissa.

Tropomyosin molecules exist as long fibrous polymer strands in the absence of salt and they are depolymerized into monomer with the addition of salt. In spite of this sizable change in the state of polymerization the relation between the pH and the salt concentration is well explained by the present theory. This success of theory is due to the fact that the activity of counter ions is determined mainly by the charge density along the rodlike molecule, which is not significantly changed by polymerization.

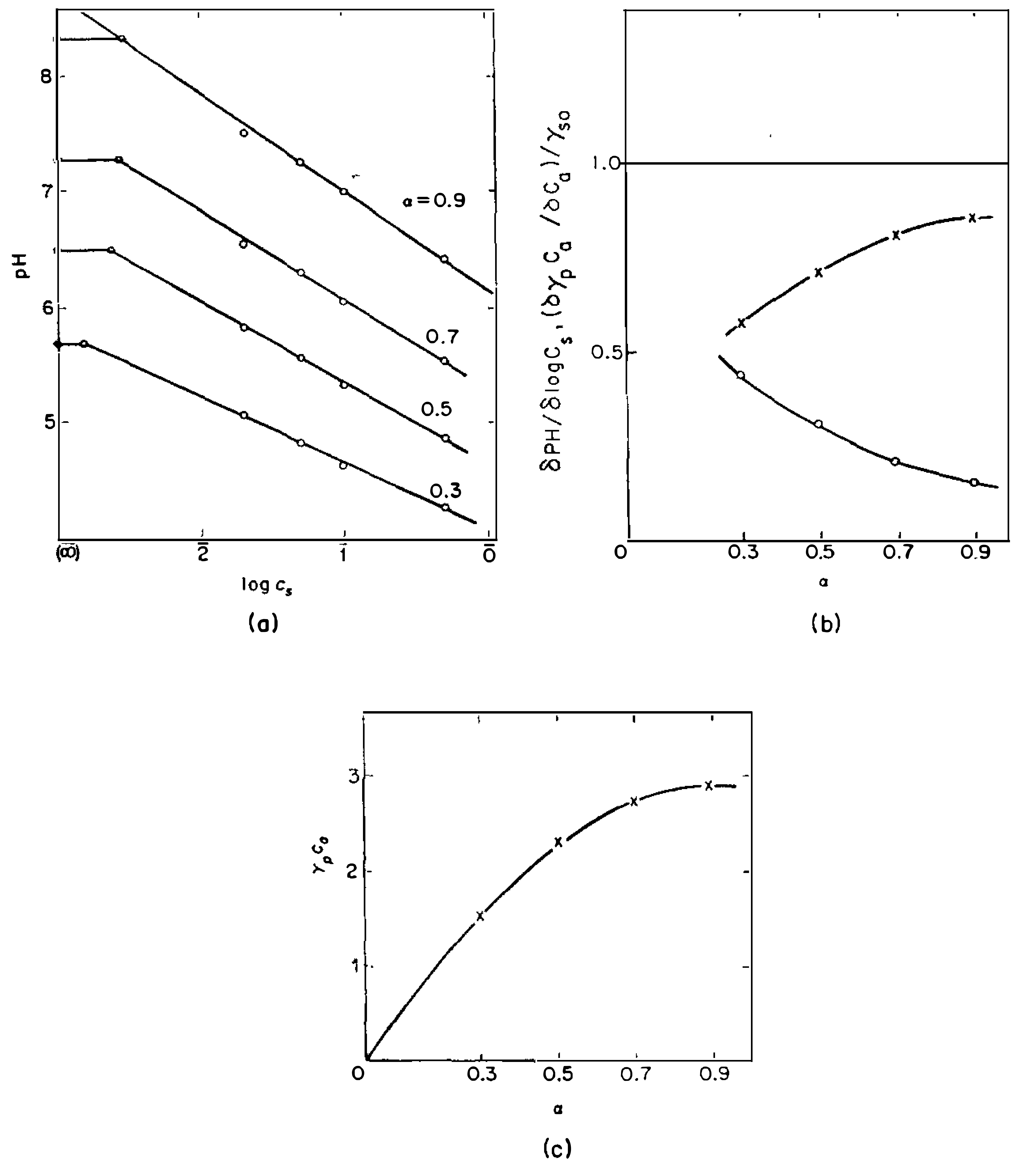


FIG. 32. (*a*) The relation between pH and the logarithm of the salt (NaCl) concentration log c_s at constant degrees of neutralization α in 7.1 mN polyacrylic acid solutions neutralized by NaOH. (●) Observed in the absence of salts, and (◑) intercepts obtained by extrapolation of straight lines at high salt concentrations (see text) (*56*). (*b*) The relations between (×) the gradient of the pH vs log c_s (straight lines in Fig. 32(*a*)) and the degree of neutralization α, and (○) the derivative $(\partial(\gamma_p c_a)/\partial c_a)$ and α (*55*). (*c*) Values of $\gamma_p c_a$ obtained from the intercept of the pH vs log c_s straight lines with the horizontal lines of pH at $c_s = 0$ in Fig. 32*a* at different degrees of neutralization α (*55*).

III. The Electric Potential at the Macroion

In Eq. (124), which gives the relation between the pH and the degree of neutralization, the effect of simple salt must come from the change of the electric potential difference $\delta\psi$ with the salt concentration. By comparing Eqs. (177) and (124) we have

$$-(e_0/kT)[\delta\psi(c_s)-\delta\psi(0)] = \{[\partial(\gamma_p c_a)/\partial c_a]/\gamma_s^+ - 1\} \ln (1+\gamma_s^+ c_s/\gamma_p c_a) \tag{178}$$

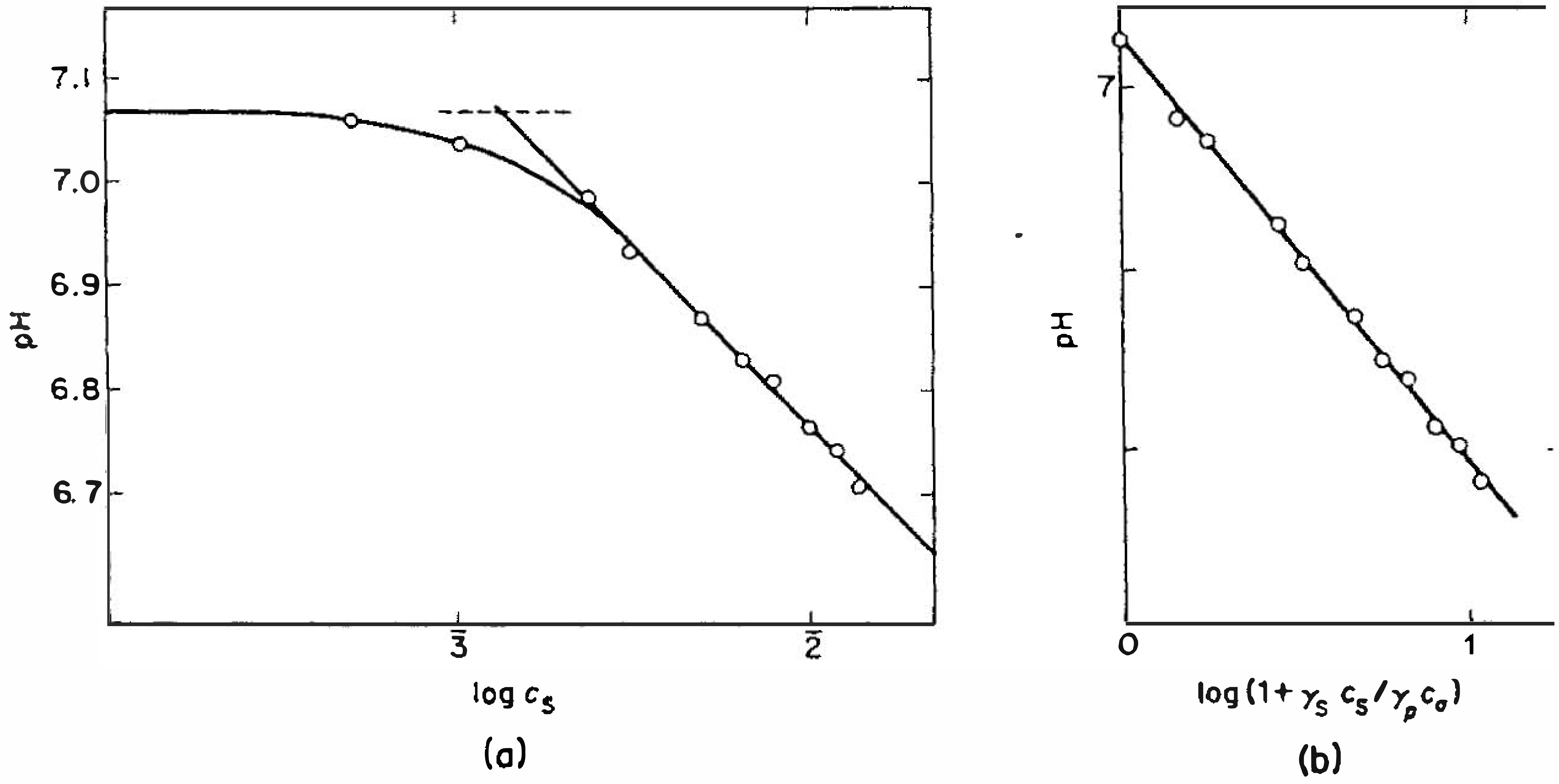


Fig. 33. (*a*) The relation between pH and the logarithm of the salt (NaCl) concentration log c_s at a constant degree of neutralization in a tropomyosin solution neutralized by NaOH. (*b*) The relation between pH and log $(1+\gamma_s c_s/\gamma_p c_a)$ where $\gamma_p c_a$ in the absence of salts was independently measured to be 1.27×10^{-3} mole (*44*).

The potential difference $\delta\psi$ decreases in proportion to the logarithm of the salt concentration at high salt concentrations. At low salt concentrations the potential decrease is proportional to the salt concentration.

It has often been stated that the coulomb potential of highly charged macroions is screened by the addition of a small amount of simple salt. The above result indicates, however, that this screening effect is not very large. Appreciable screening takes place only after the amount of salt ions added is comparable to the amount of free counter ions from macroions in the absence of salt.

The depression of the potential takes place in a logarithmic way and the effect of the integrated coulomb potential from the highly charged macroion is still sizable in the presence of a large amount of salt. In other words, even at high salt concentrations the further addition of salt can continue to depress the potential. The extensive force of the flexible macroion due to the electric free energy, for example, is not completely eliminated even at high salt concentrations. This is discussed in some detail in a later chapter.

The concentration of counter ions c' in the vicinity of the macroion, i.e., in the potential valley, is given by the product of the concentration of free counter ions outside the macroion and the factor $\exp(-e_0\delta\psi/kT)$. The concentration of free counter ions is equal to the activity and it is easily shown with Eq. (178) that the change of concentration of counter ions in the potential valley due to the addition of salt can be given by

$$\ln c'(c_s) - \ln c'(0) = \{[\partial(\gamma_p c_a)/\partial c_a]/\gamma_s^+\} \ln (1 + \gamma_s^+ c_s/\gamma_p c_a) \tag{179}$$

As previously mentioned, the derivative $[\partial(\gamma_p c_a)/\partial c_a]$ is very much smaller than unity, so that the change of the counter ion concentration in the potential valley is small. In the ideal case of counter ion condensation the apparent charge density of the macroion can not exceed a certain limit and the derivative $[\partial(\gamma_p c_a)/\partial c_a]$ should become zero above this limit. Then, the counter ion concentration in the potential valley should not be changed by the addition of salt. Such constancy of the counter ion concentration was anticipated by the theoretical derivation of the additivity law in the previous chapter. Experimentally, the derivative $[\partial(\gamma_p c_a)/\partial c_a]$ is not zero but takes a small positive value. The number of counter ions condensed on the macroion is increased slightly by salt.

The decrease of the absolute value of the potential at the macroion due to the addition of salt denotes the change of the charge density around the macroion. The charge density near the macroion must increase with increasing concentration of salt. The increase of the number of counter ions must exceed the increase of the number of co-ions. The additivity law does not imply that the ion distribution is additive everywhere in the solution.

Finally, the relation between pH and the salt concentration at various degrees of neutralization must satisfy Eq. (177) in the polyelectrolyte solution in which the activity of counter ions satisfies the additivity law. It is not always true, however, that when the pH is expressed by a relation of the type of Eq. (177) as a function of the salt concentration, the additivity law is found for the activity. It must be noted here that a relation apparently similar to Eqs. (177) or (178) has been derived from a quite different theoretical foundation (*58*).

Chapter 9

INTERACTION BETWEEN MACROIONS

I. Interaction between Parallel Rodlike Macroions

Repulsion is expected between macroions of the same charge. It is depressed by counter ions accumulated in the neighborhood of these macroions. Such depression of the force by the ionic atmosphere was first analyzed on the basis of the Debye–Hückel approximation by Verwey and Overbeek (*59*). However, their analysis is not readily applicable to the case of highly charged macroions, because of large electric potential around macroions. In this chapter a more appropriate method is presented and the force between parallel rodlike macroions is obtained as a function of the charge density of macroions and the distance between them (*60*).

As shown in Fig. 34, two rodlike macroions of charge $-ne_0$, length l, and radius a are placed in parallel at distance X in a large cylindrical free volume of radius R, where electroneutrality is satisfied. The middle point of X is assumed to coincide with the center of the free volume. In the absence of simple salt, $2n$ counter ions of charge e_0 are distributed in the free volume. The Poisson–Boltzmann equation for this system was solved analytically without approximation by Imai (*61*) and the force between the rods was calculated by the use of this solution (*62*). Here, however, this system is treated by a simple theoretical method which is the same as that used in the derivation of the additivity law. Without knowledge of details of the solution of the Poisson–Boltzmann equation, the exact expression can be derived for the force between thin rods which approach closely (*60*).

In the cylindrical coordinates (r θ) with the origin at the center of the free volume, the Poisson–Boltzmann equation can be written as

$$(\partial^2\phi/\partial x^2)+(1/x)(\partial\phi/\partial x)+(1/x^2)(\partial^2\phi/\partial\theta^2) = A\exp(-\phi) \qquad (180)$$

$$A = (4\pi 2ne_0{}^2/\varepsilon_0 lkT)/\int\int \exp(-\phi)x\,dx\,d\theta$$

where the relative spatial coordinate $x = r/a$ was used instead of r and the ratio of the potential energy to the kinetic energy ϕ was used instead of ψ. The boundary conditions are given by

$$\int x(\partial\phi/\partial x)d\theta = 0 \qquad \text{at } x = R/a$$

$$\int y(\partial\phi/\partial y)d\varphi = -2ne_0{}^2/\varepsilon_0 lkT \qquad (181)$$

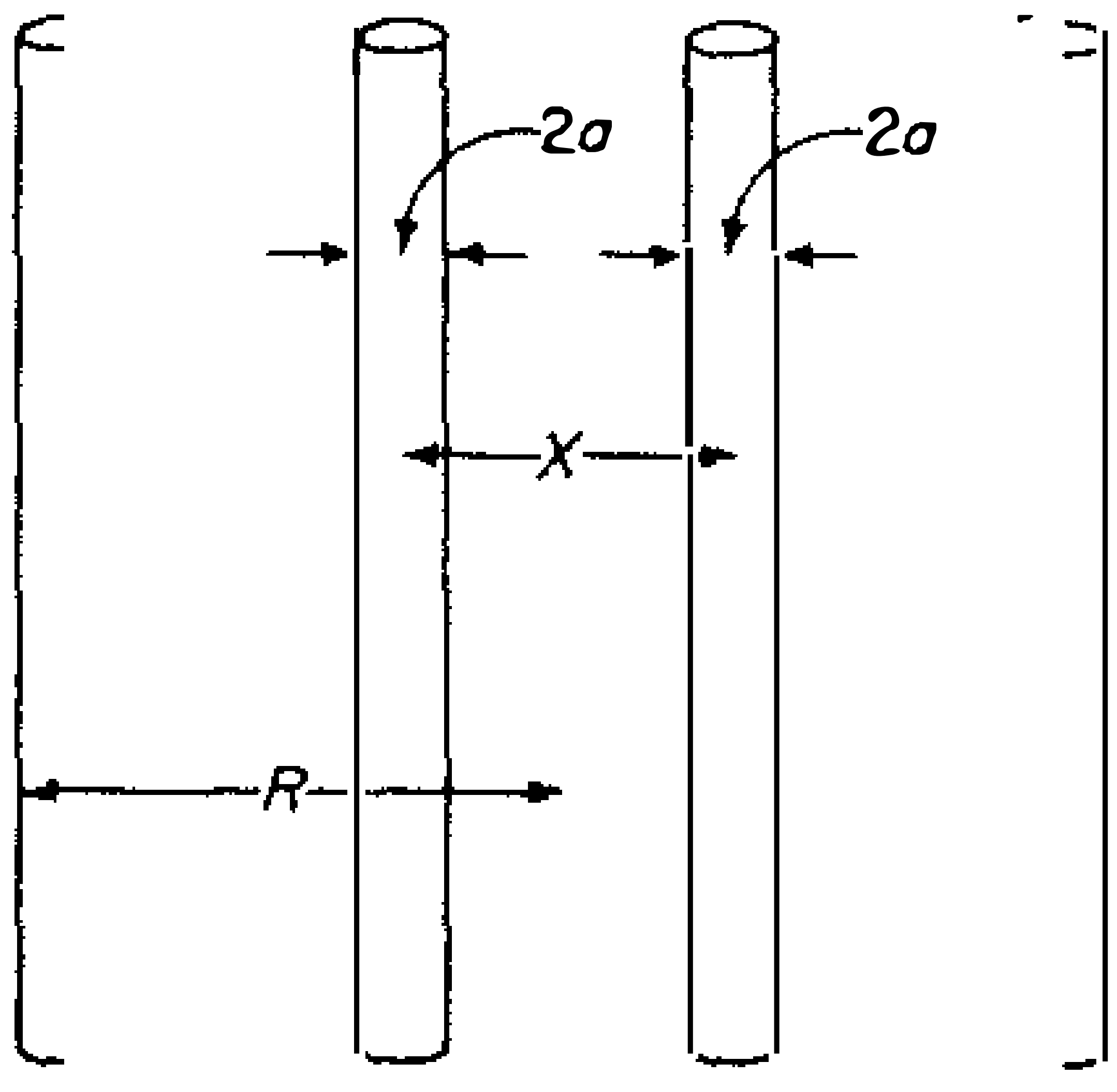


FIG. 34. Two parallel rodlike macroions in a free volume where the electroneutrality is satisfied.

at the surface of each rod ($y = 1$), where (y, φ) are the cylindrical coordinates with the center at the center of the rod, and $y^2 = x^2+b^2-2xb\cos\theta$, where $b = X/2a$. Therefore, the solution of the above Poisson–Boltzmann equation ϕ must be expressed as a function of the relative coordinates x, θ and the constants R/a and $X/2a$. Then, the electric energy and the electric free energy contain only the ratios among R, a, and X as quantities specifying the geometry of the system. They do not contain R, a, or X separately. Thus, the total free energy f per macroion must be expressed as:

$$f = f_0(\pi(R^2-2a^2))+f_e(R/a,\ X/2a) \qquad (182)$$

where f_0 is the standard free energy of the non charged system, which is a function of the volume $\pi(R^2-2a^2)$, and f_e is the electric free energy.

Now, the force between two rods is given by the derivative $(\partial f/\partial X)$. From Eq. (182) the derivative is transformed into:

$$\begin{aligned} X(\partial f/\partial X)_{a,R} &= X(\partial f_e/\partial X)_{a,R} = -a(\partial f_c/\partial a)_{R,X} - R(\partial f_c/\partial R)_{a,X} \\ &= -a(\partial f/\partial a)_{R,X} - R(\partial f/\partial R)_{a,X} + a(\partial f_0/\partial a)_{R,X} \\ &= -a(\partial f/\partial a)_{R,X} + 2(V/N)[c(R) - c_p] \qquad (183) \end{aligned}$$

where $c(R)$ is the concentration of counter ions at the periphery of the free volume R, and c_p is the average concentration of counter ions in the whole volume, that is, $c_p = 2nN/V$. The first term $a(\partial f/\partial a)_{R,X}$ is the self-extensive force of the rods.

For sufficiently thin rods, this extensive force has been calculated as a function of the charge density in Chapter 7. Since the present system is composed of two rods, it is found from Eqs. (143) and (146) that

$$\begin{aligned} a(\partial f/\partial a) &= -2nQkT & &\text{for } 0 \leq Q \leq 1 \\ &= -2(2n - n/Q)kT & &\text{for } 1 \leq Q \qquad (184) \end{aligned}$$

where $Q = ne_0{}^2/\varepsilon_0 kTl$.

The concentration of counter ions at the periphery R can be easily calculated if the radius of the free volume R is very much larger than the distance X. Under this condition $c(R)$ can be approximated by the concentration of counter ions at the periphery for the single rod system having the charge density $2Q$ placed at the center of the free volume. Then,

$$a(\partial f/\partial a)_R = 2(V/N)kT[c(R) - c_p] \qquad (185)$$

which is equivalent to Eq. (138), is available and $c(R)$ is obtained from the value of $a(\partial f/\partial a)$ for the single rod having $2Q$. The result is

$$\begin{aligned} c(R) &= c_p(1-Q) & &\text{for } 0 \leq Q \leq 1/2 \\ &= c_p/4Q & &\text{for } 1/2 \leq Q \qquad (186) \end{aligned}$$

From Eqs. (183), (184), and (186) we have

$$\begin{aligned} -X(\partial f/\partial X)_{a,R} &= (2nkT)Q & &\text{for } 0 \leq Q \leq 1/2 \\ &= (2nkT)(2 - Q - 1/2Q) & &\text{for } 1/2 \leq Q \leq 1 \\ &= (2nkT)(1/2Q) & &\text{for } 1 \leq Q \qquad (187) \end{aligned}$$

Figure 35*a* shows the relation between the force and the charge n or the charge density Q. Since Q is proportional to n, the force $(\partial f/\partial X)$ is proportional to n^2 for small values of n and it becomes constant for large values of n or for Q larger than unity. The ratio of the force to the charge is nearly constant for Q between 1/2 and 1, having a maximum at an intermediate value of $Q (= 1/\sqrt{2})$. Such behavior of the force as a function of the charge n is a characteristic property of macroions resulting from the counter ion condensation. The force is proportional to $1/X$ for small values of distance X.

It is necessary to compare this result with the result expected from the pure coulomb repulsion between two infinitely thin rods with no counter ions. The coulomb repulsion is proportional to the square of the charge, being given by $2n^2e_0^2/lX = 2nQkT/X$. As shown in Fig. 35*a*, for Q smaller than 1/2, the force between two rods that approach closely in a solution of counter ions coincides with the force due to pure coulomb repulsion; in the limit of $X \to 0$ or $R \to \infty$, no counter ions are condensed on or between two rods. For Q larger than 1/2, however, even in the limit of $X \to 0$ or $R \to \infty$, the force between two rods becomes considerably smaller than the pure coulomb repulsion; the two rods come into contact, keeping some of the counter ions in their close vicinity. This is reasonable because when two rods come into contact, the total charge of two rods, $2Q$, exceeds the critical value, unity, for the counter ion condensation. At $Q = 1$, the force between two rods is just half the pure coulomb repulsion. The repulsion is equal to the extensive force of a single thin rod having the charge density $Q = 1$. This reduction of the force is due to counter ions condensed on the two approaching macroions. For Q larger than unity, the repulsion is kept constant at the value for $Q = 1$. Such saturation is understood from the fact that the apparent charge of each macroion can not exceed the critical value corresponding to $Q = 1$ because of the counter ion condensation. In the case of monovalent charged groups and counter ions, the condition $Q = 1$ corresponds to an average distance of about 7 Å between neighboring charges on the rods at room temperature in water, and the condition $Q = 1/2$ to an average distance of about 14 Å.

When the valence of counter ions is z, a similar calculation shows that the force between two parallel thin rods of the uniform charge density in a large free volume is given, instead of by Eq. (187), by

$$\begin{aligned} -X(\partial f/\partial X)_{a,R} &= (2nkT)\,Q && \text{for } 0 \le Q \le 1/2z \\ &= (2nkT)(2/z - Q - 1/2z^2 Q) && \text{for } 1/2z \le Q \le 1/z \\ &= (2nkT)(1/2z^2 Q) && \text{for } 1/z \le Q \qquad (188) \end{aligned}$$

The repulsive force becomes weaker for counter ions of the larger valence. The force, however, is always repulsive. For $Q = 1/z$, the force is $1/2z^2$ of the direct coulomb repulsion between two rods of the charge density $Q = 1/z$. The force for the case of $z = 2$ is compared with that for $z = 1$ in Fig. 35*a*.

Since the concentration of counter ions at the periphery $c(R)$ must increase with increasing distance X, for large distance the force between two rods decreases more rapidly than in proportion to $1/X$. The force is expected to become zero when the distance X is of the same order as R. That is, the equidistant arrangement of parallel rods must be most stable in the solution. Figure 35*b* shows the relation between the force and the distance obtained from the analytical solution of the Poisson–Boltzmann equation for this system (*62*).

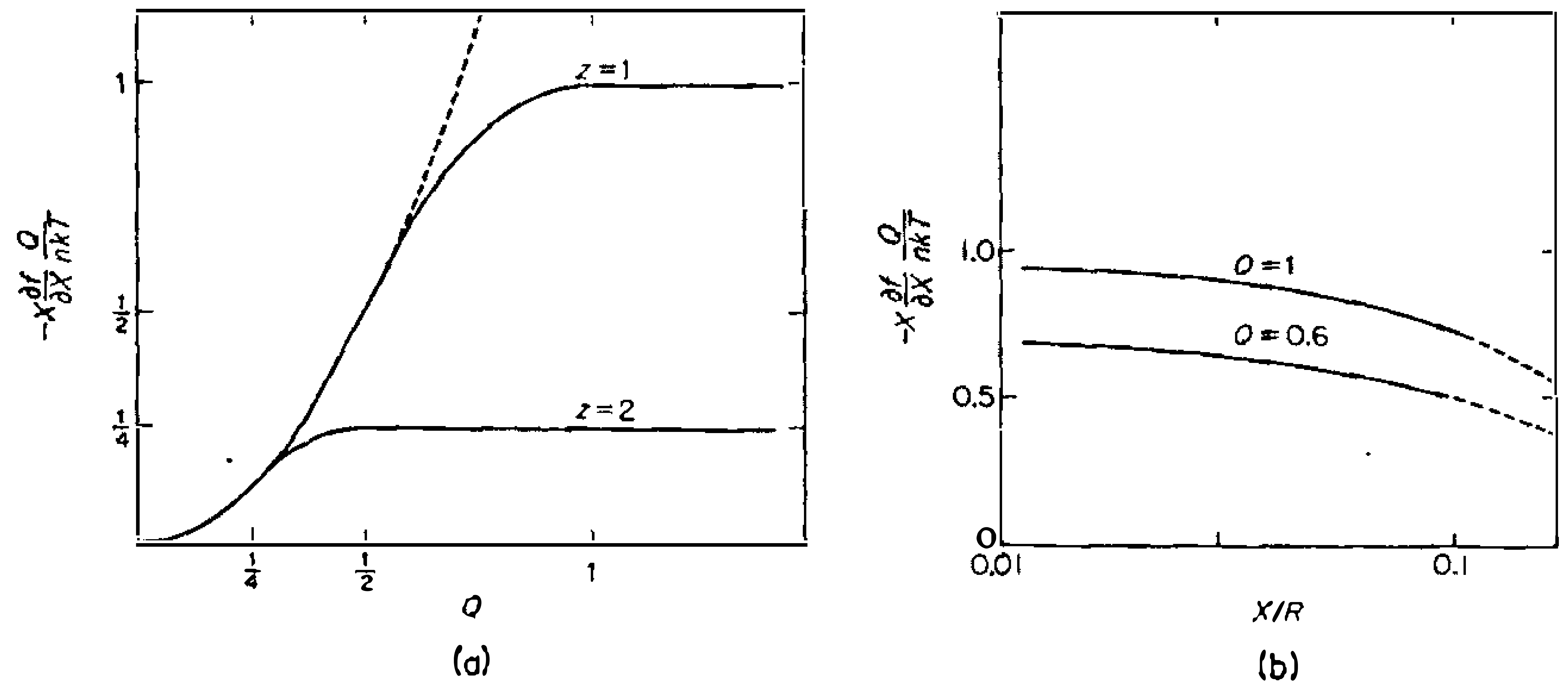


FIG. 35. (*a*) The relation of the repulsive force between two parallel rods and their charge density. The broken line gives the direct coulomb force. (*b*) The relation of the repulsive force between two parallel rods and the distance between them at two different charge densities (*62*).

II. EXTENSIVE FORCE OF AN ASSEMBLY OF RODLIKE MACROIONS

The above method of calculation can be extended to an assembly of parallel charged rods. Let us suppose there are m rods in the central region of the free volume; the position of each rod is given by the cylindrical coordinates (r_i, θ_i), $i = 1, 2, \ldots, m$. Consider only the proportional extension of the assembly to $(\alpha r_i, \theta_i)$ with a common value of α for each rod. Then, the coordinates of the assembly can be represented by only one variable, the extension of the assembly which is denoted by X as in the previous case. The free energy of this system is found, as before, to be a function of the relative coordinates R/a and X/a. Therefore, Eq. (183) is applicable to the present case. The sum of the self-extensive force of m rods, each of which has the charge density Q, is given by

$$\begin{aligned} a(\partial f/\partial a)_{X,R} &= -mnQkT && \text{for } 0 \leq Q \leq 1 \\ &= -m(2n-n/Q)kT && \text{for } 1 \leq Q \end{aligned} \tag{189}$$

which is obtained by multiplying $m/2$ by $a(\partial f/\partial a)$ for the two rod system.

If the extension X is very much smaller than R, the concentration $c(R)$ can be approximated by the concentration at R when a single rod of charge density mQ is placed at the center of the free volume. The second term of Eq. (183) can be obtained with this approximation. The final result for the extensive force of the assembly is found to be

$$\begin{aligned} -X(\partial f/\partial X)_{a,R} &= nm(m-1)QkT && \text{for } 0 \leq Q \leq 1/m \\ &= nm(2-Q-1/mQ)kT && \text{for } 1/m \leq Q \leq 1 \\ &= nm((m-1)/mQ)kT && \text{for } 1 \leq Q \end{aligned} \tag{190}$$

For Q smaller than $1/m$, the extensive force is equal to the direct coulomb repulsion due to m rods. For Q larger than $1/m$, the force is suppressed by the accumulation of counter ions among the rods, as shown in Fig. 36. In the limit of fusion of m rods into a single rod of the charge mQ, the apparent total charge density can not exceed the critical value $mQ = 1$. At Q equal to unity, the extensive force of the assembly is $1/m$ of the direct coulomb repulsion. For Q larger than unity, the increase of the charge density does not increase the extensive force.

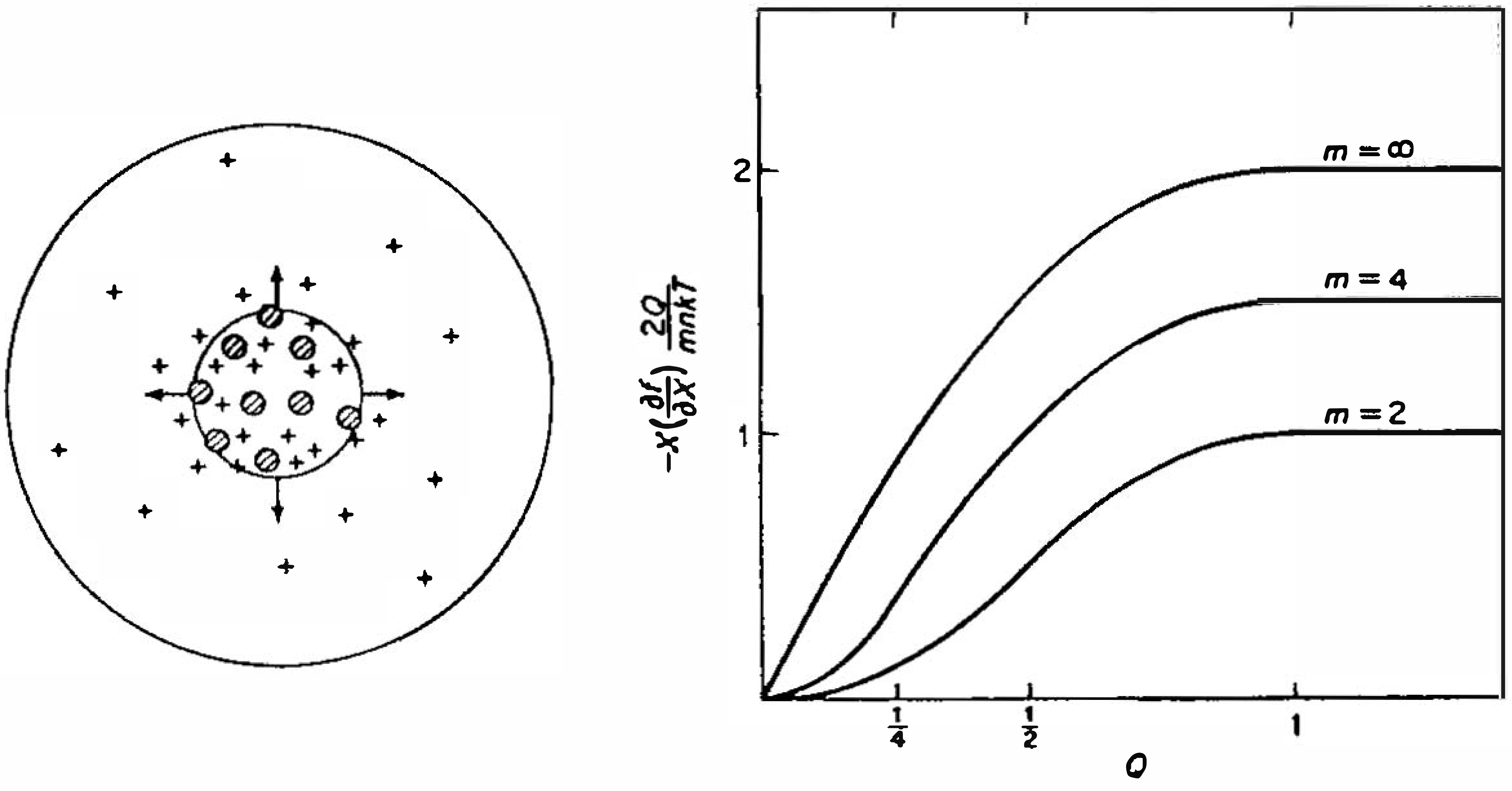
When the number of rods is very large, namely, when m is sufficiently larger than unity, Eq. (190) is rewritten as

$$\begin{aligned} -X(\partial f/\partial X)_{a,R} &= nm(2-Q)kT && \text{for } 0 \leq Q \leq 1 \\ &= (nm/Q)kT && \text{for } 1 \leq Q \end{aligned} \tag{191}$$

Since the apparent volume of the assembly of m rods is proportional to X^2, the extensive force of the volume v is given by

$$\begin{aligned} -(\partial f/\partial v) &= (nm/v)(1-Q/2)kT && \text{for } 0 \leq Q \leq 1 \\ &= (nm/v)(1/2Q)kT && \text{for } 1 \leq Q \end{aligned} \tag{192}$$

In the derivation of this result it was assumed that the extension of the assembly, X, is very much smaller than the free volume and that the number of rods is very large. In such a case, the system can be regarded to be composed of two phases; the assembly phase and the outside phase. Most of the counter ions are condensed among the rods and the charge of the rods is almost completely neutralized in the assembly phase. Then,



(a) (b)

FIG. 36. (*a*) Illustration of the extensive force of an assembly of m rods. (*b*) The extensive force of the assembly as functions of the charge density. When m tends to infinity, the force becomes equivalent to the osmotic pressure of the phase of many parallel rods.

the extensive force $(\partial f/\partial v)$ means the osmotic pressure of this phase. The quantity nm/v, in the right-hand side of Eq. (192), means the average concentration of counter ions in this phase. Therefore, the remaining factor $(1-Q/2)$ or $1/2Q$ corresponds to the osmotic coefficient (or activity coefficient of counter ions). It is quite remarkable that these expressions of the coefficient are just the same as those obtained for a simple solution of charged rods in previous chapters. (See Eqs. (61) and (151.)

As long as the proportional extension of the assembly as a whole is concerned, Eq. (192) is always applicable for any arrangement of m rods. This corresponds to the situation that the osmotic coefficient is almost independent of the concentration of charged rods in the solution, as discussed previously.

III. INTERACTION IN THE PRESENCE OF SALTS

The interaction between macroions having many charges is expected to be screened by the addition of simple salt. At high concentration of salt the repulsion between macroions of the same charge may be greatly suppressed. Such an effect of salts on the interaction was now analyzed by a method similar to that used in the above sections. The result showed that the current understanding on the screening effect of salts must be corrected *(60)*.

Let us consider once again parallel rods in a large free volume. Even in the presence of simple salt the electric free energy of this system must be a function of the relative coordinates R/a and $X/2a$, because in this case also the Poisson–Boltzmann equation can be expressed in the form of Eq. (180) where $A \exp(-\phi)$ must be replaced by the summation $\Sigma_i A_i \exp(-z_i\phi)$ including counter ions and co-ions. Therefore, Eq. (183) is applicable. The concentration $c(R)$ denotes the total concentration of small ions at the periphery R of the free volume. If the distance X is very much smaller than R, it can be replaced by the concentration at R in a single rod system of the same total charge. For the single rod system, the additivity law was proved in Chapter 7. That is, the concentration of small ions at R in the presence of simple salt is nearly equal to the sum of the counter ion concentration in the absence of simple salt and the average concentration of added salt ions. In other words, the concentration difference $c(R) - (c_p + c_s)$ is almost independent of the concentration of added salt. If the rods are sufficiently thin and long, the extensive force of each rod is also independent of the salt concentration as proved in Chapter 7. Consequently, the repulsive force between rods given by Eq. (183) is not changed by the addition of salt. Thus, it is concluded that under the restrictive condition that if (a) the rods are sufficiently thin, (b) the ratios a/R and X/R are sufficiently smaller than unity, and (c) the salt concentration is not too high, the repulsive force between charged rods is not depressed by the addition of salt.

This strange result, which is contrary to the current concept of the screening effect of salt ions, is due to the special character of the integrated coulomb potential around rodlike macroions that was essential for the additivity law.

It is instructive to consider again the assembly of many charged rods to understand the above result. The extensive force of the assembly in a large free volume is just the osmotic pressure of the assembly phase. When simple salts are added, the osmotic pressure against the salt solution can be calculated by employing the additivity law, as shown in Chapter 7, Section IV. If the salt concentration is low, the decrease of the osmotic pressure by the addition of salts is proportional to the salt concentration and

$$(\partial f/\partial v) = -(nm/v)\gamma kT + 2c_{so}kT \tag{193}$$

where γ is the osmotic coefficient in the absence of salts given by the same formula as Eq. (192). The quantity $(nm/v)\gamma$ is the concentration of counter ions retained but mobile in the assembly phase and c_{so} is the salt concentration in the outside phase. For a dense assembly of many rods, $(nm/v)\gamma$ is large. From Eq. (193) we see that if the condition

$$nm\gamma/n_s \gg (X/R)^2 \tag{194}$$

is satisfied, the effect of salt on the extensive force of the assembly is negligible.

In the case of two rods, an analogous criterion can be stated as follows: As long as the concentration of counter ions at the middle point of the distance X between two rods is sufficiently larger than the average concentration of salt in the whole free volume, the depression of the repulsive force by salt is negligible.

When the salt concentration is high or when the distance X is large, the extensive force is depressed by salt to an appreciable extent. In this case; however, it is difficult to obtain an exact expression of the force. For a large distance X the concentration of small ions at the periphery can not be approximated by that for the single rod system. The deviation becomes appreciable when the ratio X/R becomes larger than 0.01 (*62*). Then, the additivity of the concentration of small ions at the periphery or the constancy of $c(R)-(c_p+c_s)$ is not guaranteed in the presence of added salts.

Another way to estimate the effect of salt on the interaction between macroions may be achieved in the following manner. When macroions in a solution are uniformly distributed at an equal distance from neighboring macroions, no repulsive or attractive forces act between them. If two macroions approach, repulsion begins to appear. If this repulsion is small, the fluctuation of the macroion concentration in the solution becomes large. The concentration fluctuation thus provides a measure of the magnitude of the repulsive force between macroions.

Now, the concentration fluctuation is in general determined by the derivative of the osmotic pressure with respect to the concentration (*63*).

For the fluctuation of the free volume per macroion, it is found that

$$\langle (v_f-\langle v_f\rangle)^2\rangle/\langle v_f\rangle^2 = (1/n)(1/\partial(\Pi'/kT)/\partial c_p) \qquad (195)$$

In this formula the free volume per macroion is denoted by v_f and the average of v_f, $\langle v_f\rangle$, is equal to V/N. In the presence of salt the osmotic pressure Π' must be the pressure against the salt solution. By the use of the result in Chapter 7, Section IV, the right-hand side of Eq. (195) can be calculated. In the absence of salt

$$\langle (v_f-\langle v_f\rangle)^2\rangle/\langle v_f\rangle^2 = 1/n\gamma \qquad (196)$$

The fluctuation of the macroion concentration is much smaller by the factor $1/n\gamma$ than that expected in the case of nonelectrolytic macromolecules, but it is larger than that expected in macroions interacting through pure coulomb force without counterions. The repulsion between macroions is much stronger than that between noncharged macromolecules but is weaker than direct coulomb force.

At low salt concentrations, from Eq. (156)

$$\partial(\Pi'/kT)/\partial c_p = \gamma_p(1-2\gamma_{s0}^2 c_{s0}^2/\gamma_p^2 c_p^2) \qquad (197)$$

The derivative decreases with the addition of salt and the fluctuation consequently increases. The ratio $\gamma_{s0}c_{s0}/\gamma_p c_p$ determines the effect of salt on the fluctuation and the increase of the fluctuation occurs according to the square of this ratio. Therefore in the range of $\gamma_p c_p/\gamma_{s0}c_{s0} \gg 1$, the fluctuation is not greatly affected by the addition of salt. In other words, the repulsion between macroions is not much depressed.

At sufficiently high salt concentrations the electric potential must be small everywhere in the solution, so that the Debye–Hückel approximation is available to solve the Poisson–Boltzmann equation. In this case the interaction was analyzed in details by Verwey and Overbeek (*59*). By the use of the potential derived by them, the radial distribution function for two macroions was also calculated (*64*). At the infinitely high salt concentration, the interaction vanishes and the right-hand side of Eq. (195) tends to unity; a result corresponding to the case of non-electrolytic macromolecules.

Finally it must be noticed that all of the above analyses were made under the condition that the number of charged groups on the macroions is kept constant, independently of the distance between them. However, this is not always true in actual systems. For example, in the case of weak polyacids at the intermediate degree of neutralization, the number of charged groups may be decreased when two macroions approach at a fixed value of pH.

IV. ATTRACTIVE FORCE DUE TO THE COUNTER ION FLUCTUATION

In the above theory the force between two macroions was calculated for the average equilibrium distribution of counter ions. The counter ions, however, are not fixed at the average distribution. On account of thermal fluctuation, the distribution deviates from the average one. This fluctuation gives rise to the transient dipole moment of the macroion as described in Chapter 5. The cloud of counter ions around a rodlike macroion is momentarily concentrated in some places and diluted in others, although on the average it is uniform along the rod. When two macroions approach each other, the fluctuation of the counter ion distribution around them is interrelated. The fluctuation giving the lower interaction energy takes place more frequently. This correlative behavior results in an attractive force between the macroions, just as in the case of van der Waals interaction between atoms and molecules. The large polarizability of macroions that was proved in the previous chapter suggests the existence of the large attractive force as a consequence of the counter ion fluctuation.

For example, let us consider two rodlike macroions placed in parallel at a distance X from each other which is very much smaller than the length l of the macroion, as shown in Fig. 37*a*. The average (equilibrium) density of counter ions condensed on each macroion is denoted by n'/l. At a certain time t and position x along the rod, the density deviates from the average by $\delta c_+(x)$. For the sake of simplicity, the charged groups on the macroion are represented by a fixed uniform density n/l.

The additional interaction energy between two macroions due to the counter ion fluctuation can be expressed approximately as

$$\delta^2 u = (e_0{}^2/\varepsilon_0) \int\int \delta c_+(x_1)\, \delta c_+(x_2)/x_{12}\, dx_1\, dx_2 \tag{198}$$

where $x_{12} = [X^2 + (x_1 - x_2)^2]^{1/2}$ is the distance between two points x_1 and x_2 on the two macroions, respectively. The average of the product $\delta c_+(x_1) \cdot \delta c_+(x_2)$ is not zero if the fluctuations on two macroions correlated with each other. When $\delta c_+(x_1)$ is positive, $\delta c_+(x_2)$ becomes negative with higher probability because of the lower energy. Calculation of the above energy u_e and its average may be performed by the same method as that employed for calculation of polarizability in Chapter 5, Section III where the fluctuation δc_+ was expanded in a Fourier series. Such calculation, however, is complicated and moreover, contrary to the case of spontaneous polarization of the macroion, in the case of interaction between two macroions approaching closely, the fluctuation of counter ions with the short wavelength is expected to make a large contribution.

Therefore, we try to estimate the average of $\delta^2 u$ by assuming that the higher-order correlation of fluctuations at three or more different points on two macroions can be neglected (*60*).

Under this assumption, the average of the interaction energy between two points x_1 and x_2 is given by

$$[\langle \delta c_+(x_1)^2 \rangle \cdot \langle \delta c_+(x_2)^2 \rangle] z^2 e_0^2 / \overset{2}{\varepsilon_0} x_{12}^2 kT \qquad (199)$$

and the average of the total interaction energy is given by the integration of this energy with respect to the two points x_1 and x_2 along the two macroions. The average of $\delta c_+(x)^2$ in (199) must be taken under the condition that there is no correlation between two macroions. When the fluctuation $\delta c_+(x)$ takes place at $x \sim x + dx$, the excess interaction energy among these counter ions is approximately given by

$$[(\delta c_+(x)\, dx)^2 z^2 e_0^2 / \varepsilon_0\, dx]$$

where z is the valence of counter ions, if the fluctuation of counter ions in different places has no correlation. The excess entropy is approximately given by

$$-\quad k[\delta c_+(x)\, dx]^2 / (n'\, dx/l)$$

Therefore, by the same procedure as in Chapter 5, the mean square of the fluctuation is

$$\langle [\delta c_+(x)\, dx]^2 \rangle = n'(dx/l)/(1 + n' z^2 e_0^2 / \varepsilon_0 kTl) \qquad (200)$$

Putting this into (199) and performing the integration, it is found that

$$\langle \delta^2 u \rangle = -[(n'/n) z^2 Q]^2 / [1 + (n'/n) z^2 Q]^2 (l/X) kT \qquad (201)$$

The attractive force between two macroions due to this additional energy, $(\partial \langle \delta^2 u \rangle / \partial X)$, is given by

$$X(\partial \langle \delta^2 u \rangle / \partial X) = [(n'/n) z^2 Q]^2 / [1 + (n'/n) z^2 Q]^2 (l/X) kT \qquad (202)$$

This expression gives only a rough estimation of the attractive force due to the counter ion fluctuation, since the higher order correlation of fluctuations which was neglected in the above derivation may have appreciable influences. However, some interesting facts can be deduced from Eq. (202).

It was shown in the previous section that for sufficiently large values of the charge density Q, the repulsive force between the macroions with the average distribution of counter ions is given by

$$\begin{aligned} -X(\partial f/\partial X) &= 2nkT/2z^2 Q \\ &= (l/z^2 d^*) kT \qquad (203) \end{aligned}$$

where $d^* = e_0^2/\varepsilon_0 kT$ corresponds to an average distance between charged groups at the critical condition for monovalent counter ion condensation (about 7 Å at room temperature in water). On the other hand, the attractive force from Eq. (202) tends to $(l/X^2)kT$ for sufficiently large values of Q. Therefore, if X is smaller than z^2d^*, the attractive force becomes predominant over the repulsive force, as shown in Fig. 37b.

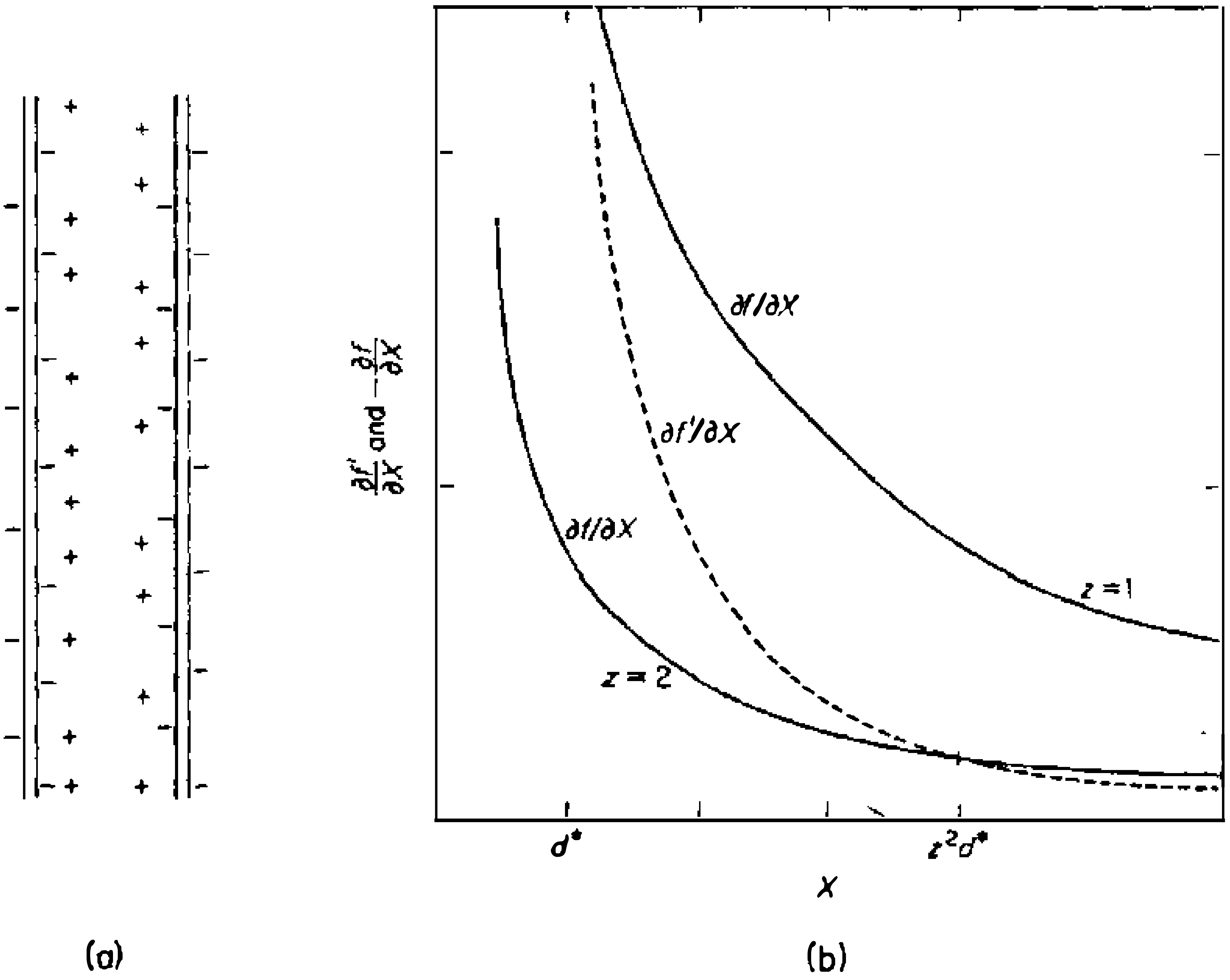


FIG. 37. (a) Two parallel rodlike macroions along which bound counter ions fluctuate with some correlation. (b) Comparison between the attractive force due to the counter ion fluctuation $\partial f'/\partial X (= \partial \delta^2 u/\partial X)$ and the repulsive force between charges $\partial f/\partial X$.

For monovalent counter ions z^2d^* is about 7 Å and for divalent counter ions it is about 28 Å, and two rods approaching closer than this distance attract each other. Practically, it may be concluded that attraction appears between two rodlike macroions before their direct contact only in the case of polyvalent counter ions. It is to be noted also that with increasing charge density the repulsive force ceases to increase, while the attractive force continues to increase. That is, the effect of the attractive force becomes important at high charge densities.

The insolubilization of polyelectrolytes caused by the addition of a small amount of polyvalent counter ions at high charge densities which was described in Chapter 6, Section IV may be understood on the basis of the above theoretical result. Under ordinary conditions strong repulsion acts between macroions in solution. The solution is characterized by a large osmotic pressure and a small light-scattering intensity. The second virial coefficient of the osmotic pressure is positive, owing to this repulsion. As a consequence of this repulsion, macroions are highly soluble. However, they can be precipitated by polyvalent salts. Binding of polyvalent counter ions decreases the repulsion and introduces the attraction between macroions. This attraction can be regarded as a result of the fluctuation of the counter ion distribution, although microscopically this may be equivalent to the formation of a kind of bridge formed by polyvalent counter ions locating between charged groups of two macroions.

Anisotropic phases of tactoid or paracrystal formed by rodlike macroions can be treated from the viewpoint presented above (*65*). One of the principal causes for the formation of such anisotropic phases is the entropic effect of long rodlike macromolecules arranged in parallel (*66*). However, the electric repulsion and attraction analyzed here both play important roles, as suggested by the fact that the stability of the tactoid phase of tobacco mosaic virus, for example, is changed by the pH and the salt concentration (*67*). The ordinary van der Waals interaction may also be important. It may be that parallel arrangement of actin and myosin filaments in muscle is maintained as a result of a combination of all these interactions (*68*). Actually, it was found that long actin filaments make paracrystals in the presence of divalent cations (*69*). The present theory is also applicable to the effect of the ionic circumstances on the separation of two strands of DNA (*70*).

Chapter 10

EXTENSIVE FORCE OF MACROIONS

I. EXTENSIVE FORCE OF SPHERICAL MACROIONS

If the macroion is a flexible chain in the random coil conformation, the force to extend the macroion appears as a result of the electrical interaction among charged groups and counter ions. As an example, let us consider a macroion occupying a spherical volume v of radius a on the average. Charged groups are assumed to be distributed uniformly in this volume. Counter ions are distributed in and around this volume. The equilibrium distribution is well described by the two-phase approximation. Among n counter ions from each macroion, $n' = n - n^*$ counter ions are bound in the potential trough made by the macroion, and the apparent charge of the macroion is equal to $-n^*e_0$. Most of the bound counter ions are assumed to be mobile in the volume v. Other counter ions, the number of which is n^* per macroion, move outside the volume v.

The force to extend the macroion can be calculated by differentiating the free energy of the system with respect to the volume v at constant values of the charge or the number of counter ions n and the concentration of macroions N/V in the solution. Although the number of bound counter ions changes with the change of v, this need not be taken into consideration in the differentiation because the number of bound ions is determined by the minimum condition of the free energy. Then, with the two-phase approximation, it is found that the extensive force is composed of two parts: One is equal to the extensive force of a sphere having charge $-n^*e_0$ and the other comes from the osmotic pressure of counter ions bound in v (*71*).

The macroion tends to extend due to coulomb repulsion between charged groups. This extensive force, expected to increase with increasing number of charged groups, is decreased, however, by the binding of counter ions. The origin of coulomb repulsion is the effective charge remaining on the macroion. Since the energy of a sphere having an effective charge $-n^*e_0$ is given by $(1/2)n^{*2}e_0{}^2/\varepsilon_0 a$, the extensive force F_1 due to the decrease of this electric energy is given by

$$\begin{aligned} F_1/kT &= (1/2)(n^{*2}e_0{}^2/\varepsilon_0 kTa^2)(\partial a/\partial v) \\ &= (1/6)(n^{*2}e_0{}^2/\varepsilon_0 kTa)(1/v) \qquad (204) \end{aligned}$$

Now, most of the bound counter ions are assumed to move freely in v. These counter ions are the origin of an extensive force to increase the space in which they can move (see Fig. 38*a*). This force F_2 resembles the osmotic pressure of a solution. In other words, it is due to the pressure caused by the solvent molecules forced to enter into the solution of counter ions in the potential trough of v, where the concentration of counter ions is larger than the outside of v. In the absence of simple salt, the pressure is given by the differentiation of the entropy $k(n-n^*)$ ln $v+kn^*$ ln $(V-Nv)$ and is proportional to the difference between the concentration of counter ions inside and outside.

$$\begin{aligned} F_2/kT &= (n-n^*)/v-n^*N/(V-Nv) \\ &= [(1-\beta)-\beta\phi/(1-\phi)](n/v) \\ &= (1-\gamma)(n/v) \qquad (205) \end{aligned}$$

The total extensive force is given by the sum of the two kinds of force:

$$F = F_1+F_2 = kT\{(1/6)\beta^2P+(1-\gamma)\}(n/v) \qquad (206)$$

The relation of these two kinds of force to the concentration and the charge of macroions is shown in Fig. 38*b*.

It was shown previously that in the spherical macroion the apparent charge n^* decreases with increasing concentration ϕ. Therefore, the electrical force, F_1, decreases with increasing ϕ. On the other hand, the osmotic force, F_2, is very small in extremely dilute solutions because the counter ion concentrations both inside and outside of v are very small. With increasing concentration, force F_2 increases because counter ions begin to be bound in v. For very high concentrations, however, the counter ion concentration outside increases and the concentration difference decreases. Force F_2 consequently reaches a maximum value at an inter-

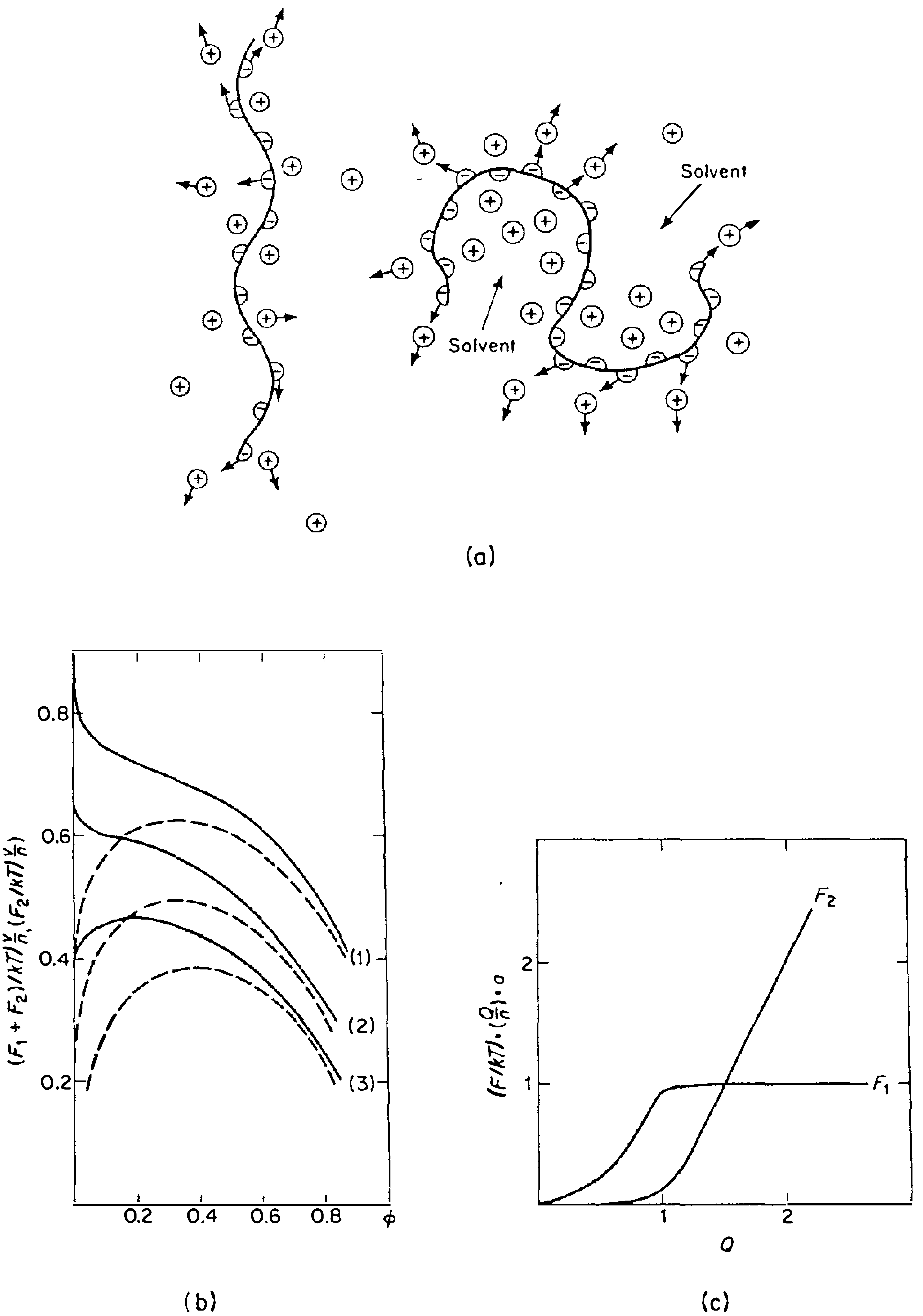


FIG. 38. (*a*) The extensive force of a coiled macroion and a cylindrical macroion. (*b*) The extensive force of spherical macroions with uniform charge densities. F_2(– – –) is the osmotic force and F_1+F_2(—) is the total extensive force. (1): the charge density $P=7$; (2): $P=4$; (3): $P=2.5$. (*c*) The extensive force of cylindrical macroions at various charge densities Q. F_1 is the coulomb force of the effective charge and F_2 is the osmotic force. The forces parallel and perpendicular to the cylinder change with the charge density in a similar way.

mediate concentration of the macroion. This maximum is found at an apparent volume concentration of about 0.4 (Fig. 38*b*). It corresponds to the minimum in the osmotic coefficient described previously and graphically illustrated in Fig. 5*a*.

The ratio of the two kinds of force is given by

$$F_1/F_2 = (1/6)\beta^2 P/(1-\gamma) \tag{207}$$

At extreme dilution this ratio is very large. With increasing concentration the ratio decreases. At a constant concentration ϕ, the value of β decreases with increasing numbers of charged groups or increasing value of P and the value of the above ratio is found to decrease. Summarizing these analysis, the contribution of the osmotic pressure of counter ions bound in v exceeds the contribution due to coulomb repulsion of the apparent charge when the concentration or the charge of the macroion increases. Such situation has been pointed out in several theories (*71–73*).

When the number of charged groups increases with v in such a way that n is proportional to v or a^3, the value of P increases. Then the contribution due to the osmotic pressure of counter ions becomes more predominant for larger volumes of the macroion. In the limit, when a very large macroion is in a solution of counter ions, its extensive force is wholly due to the osmotic pressure.

The distinction between the coulomb force and the osmotic force has no absolute meaning. The osmotic force may be interpreted as being due to the attractive force exerted on charge groups by counter ions which are going to escape to the outside of the macroion because of the entropy effect.

In the above derivation all bound counter ions are assumed to be mobile. If some of them are localized at charged groups, the osmotic force is decreased by the apparent activity coefficient γ^* of the bound counter ions. The quantity $(1-\gamma)$ in F_2 must be replaced by $\gamma^*(1-\gamma)-\gamma(1-\gamma^*)\phi$.

Expression (206) is applicable only when extension of the macroion occurs, keeping a spherical shape in which bound counter ions are uniformly mobile. However, even when the macroion is in a more or less coiled conformation, most of the counter ions are bound and mobile in the cylindrical potential valley along the chain and the cylindrical or rodlike model is more suitable than the spherical model, as has been repeatedly emphasized. Then, the effective volume in which bound counter ions are mobile does not increase very much with the extension of the coiled macroion. Even in the coiled conformation the osmotic force estimated from Eq. (205) is too large. This problem is discussed again in the next chapter. The above treatment, however, is useful for understanding the origin of the extensive force of flexible macroions.

II. EXTENSIVE FORCE OF CYLINDRICAL MACROIONS

In the cylindrical case, the extensive forces are different along the long axis, $F_{\parallel}$ and perpendicular to this axis, $F_{\perp}$. Each force is composed of two parts as before. One is due to the electrical repulsion of the effective charge on the cylinder and the other is due to the osmotic pressure of counter ions bound in the cylindrical volume of the macroions. The former is given by the differentiation of the energy $n\beta^2 Q \ln (R/a)$ by a or l, and the latter by the differentiation of the entropy. The differentiation is performed, keeping the free volume $\pi l R^2$ constant.

In the absence of simple salt, the two parts of each force in the two directions are given by, respectively,

$$\begin{aligned} F_{1\perp} &= (n^{*2}e_0{}^2/\varepsilon_0 kT)(1/a)kT = n\beta^2 Q(1/a)kT \\ F_{2\perp} &= (n-n^*)(2/a)kT = n(1-\beta)(2/a)kT \end{aligned} \tag{208}$$

and

$$\begin{aligned} F_{1\parallel} &= n\beta^2 Q(1/l)(\ln (R/a)+2)kT \\ F_{2\parallel} &= n(1-\beta)(1/l)kT \end{aligned}$$

The force in the perpendicular direction, $F_{\perp}$, is equivalent to that derived in the previous chapter, Eqs. (143) and (146). For $Q \geqq 1$, βQ can be put equal to unity at low concentrations of macroion. The sum and the ratio of the two forces are given by

$$\begin{aligned} F_{\perp} &= F_{1\perp}+F_{2\perp} \\ F_{\parallel} &= F_{1\parallel}+F_{2\parallel} \\ F_{1\perp}/F_{2\perp} &= \beta^2 Q/2(1-\beta) \\ F_{1\parallel}/F_{2\parallel} &= \beta^2 Q(-(1/2)\ln \phi+2)/(1-\beta) \end{aligned}$$

One of the important differences between the spherical macroion and the cylindrical one is in the force at extreme dilution. The cylindrical macroion of high charges has counter ions condensed in its volume even at extreme dilution. The contribution to the osmotic pressure of these ions must be taken into account over the whole range of concentration. With increasing number of charged groups on the macroion, the contribution of the osmotic pressure becomes more important and the ratio of F_1 to F_2 decreases. The contribution of coulomb repulsion is predominant only when both the charge density and the concentration are low, as shown in Fig. 38*c*.

If the extension of the cylindrical macroion is performed at a constant (apparent) volume $\pi l a^2$, the osmotic pressure does not contribute. In this case, the force F^* due to the repulsion of the effective charge is given by

$$F^* = (1/2)n\beta^2 Q(1/l)(-\ln \phi)kT = -u_e/l \tag{210}$$

For large values of Q at low concentrations of macroions

$$F^* = (1/2)n\beta(1/l)\ln(1/\phi)kT \tag{211}$$

If the concentration of macroions is very low and the length l is smaller than the radius R of the free volume, the extensive force is given by

$$F^* = (1/2)n\beta^2 Q(1/l)\ln(l/a)kT \tag{212}$$

A more exact expression of the extensive force of rodlike macroions can be obtained from analytical solution of the Poisson–Boltzmann equation for this system. It should be noted that the final relation between the stretching force at a constant volume F^* and the electric internal energy u_e (Eq. 210) can be derived directly from the Poisson–Boltzmann equation without resort to any approximations. From this equation and the boundary conditions for the rodlike macroion, it is found that the ratio $e_0\psi/kT$ is a function of r/a and R/a as spatial coordinates and of $n_i e_0^2/\varepsilon_0 kTl$ as charge densities, where n_i denotes the number of charged groups and small ions per macroion. The electric free energy f_e has the form

$$f_e = l(kT/e_0)^2 G(R/a, n_i e_0^2/\varepsilon_0 kTl) \tag{213}$$

As a function of the length l and the charge e_0

$$f_e = g(e_0^2/l) \tag{214}$$

By use of this expression for f_e and relation (22) to relate f_e and u_e, it is readily shown that the stretching force at constant volume is given by

$$F^* = (\partial f/\partial l) = (\partial f_e/\partial l) = -u_e/l \tag{215}$$

This relation is valid even when simple salt is added. Since for sufficiently thin rods the effective charge n^* is not changed by the addition of salt, the stretching force at a constant volume is not appreciably changed by salt.

According to Eqs. (208) and (210), the extensive force of cylindrical macroions is proportional to n/l or the energy per unit length. The force is thus independent of the absolute length if the charge density is given. The extensive force of local linear parts is equal to that of the total chain for the same total extension. In a long chain the uniform extension of the whole chain and the local extension of a part, the length of the other parts remaining constant, give rise to approximately the same resistance if the two extension modes result in an equivalent change of the total length.

III. Force in the Presence of Salts

Analysis of the effect of simple salt on the extensive force of macroions is most easily achieved by applying the formula of the chemical potential of macroions at different salt concentrations derived in Chapter 8 on the basis of the additivity law. The extensive force is obtained by differentiation of the chemical potential with respect to the conformation. By introducing a parameter l to designate the conformation, the difference of the chemical potential of the macroion at l is approximately given by

$$\mu_p(l, c_s) - \mu_p(l, 0) = nkT(\gamma_p(l)/\gamma_s) \ln (1 + \gamma_s c_s/\gamma_p c_p) \qquad (216)$$

where the activity coefficient of counter ions $\gamma_p(l)$ in the absence of salt is a function of the conformation parameter l. The additivity law was assumed to be applicable for a solution of macroions in which the conformation fixed at l is presumed to be independent of the salt concentration. Thus, the difference between the extensive forces in the absence and the presence of salt is given by

$$\begin{aligned} F_s &= F(c_s) - F(0) \\ &= nkT(\partial \gamma_p(l)/\partial l)/\gamma_s \ln (1 + \gamma_s c_s/\gamma_p c_p) \qquad (217) \end{aligned}$$

(Here, the activity coefficient γ_p contained in the logarithmic term must be interpreted to be the average in the whole solution.) This result (Eq. 217) can also be derived by direct differentiation of the total free energy given by Eq. (164).

The concentration of free counter ions usually increases with increasing size or length of the macroion at a constant total number of charges. Accordingly, the derivative $(\partial \gamma_p/\partial l)$ is positive if the parameter l is taken as a quantity that increases with size or length. The force given by Eq. (217) is thus a contractile force. That is, the extensive force in the presence of salt is smaller than it is in the absence of salt.

The magnitude of the effect of salt on the extensive force is determined by the sensitivity of the activity coefficient of counter ions to the conformation $(\partial \gamma_p/\partial l)$, and the ratio of the concentration of added salt to the concentration of free counter ions from the macroion, $\gamma_s c_s/\gamma_p c_p$.

If the concentration of free counter ions is not sensitively changed by the change of the conformation, the magnitude of the depression of the extensive force by salt is also small. When the ratio $\gamma_s c_s/\gamma_p c_p$ is small, the extensive force of the macroion decreases in proportion to the concentration of added salt. When it is large, the extensive force decays logarithmically with the addition of salt. Even at fairly high concentrations of salt, further addition of salt continues to have sizable effect on the extensive force.

For example, let us consider a very thin rod of high charge density. In this case $\beta Q = 1$ and $(\partial\gamma_p/\partial l) = \beta/l$. Therefore, combining the result in the previous section, we have the total extensive force

$$\begin{aligned} F &= F_1 + F_2 + F_s \\ &= -nkT(\beta/l)[\ln(R/a) + (1-\beta)/\beta - (1/\gamma_s)\ln(1+\gamma_s c_s/\gamma_p c_p)] \end{aligned} \tag{218}$$

The total force is determined by the charge density n/l and is independent of the total length or the total charge. The first term comes from the resultant coulomb repulsion and the second term comes from the osmotic pressure of bound counter ions. When $\gamma_p = 0.25$ and $\gamma_s = 1$, the last term is half of the second term at $\gamma_s c_s/\gamma_p c_p = 12$. When $\phi = 10^{-3}$ and $\gamma_s = 1$, the last term is half of the first term at $\gamma_s c_s/\gamma_p c_p = 10$. The extensive force is reduced by half at a salt concentration about ten times higher than the original concentration of free counter ions. In this range of salt concentration the last term can be approximated by $\ln \gamma_s c_s/\gamma_p c_p$.

Detailed analyses on the relation between the conformation and the salt concentration will be made in the next chapter with the comparison with experimental data on the viscosity.

IV. CONTRACTILE FORCE AND FLEXIBILITY

Linear flexible macroions can take numerous different shapes or conformations on account of the freedom of internal rotation of bonds in the chain. Each of these conformations has a different free energy, energy, and entropy. Each microscopic conformation can be specified by a sequence of the values of internal rotation angles of successive bonds in the main chain and by the geometry of side chains. If the sequence has any regular repetition, the conformation is helical, and if not, it is random coil. The free energy of each microscopic conformation is the sum of the free energies from various sources.

The probability of each microscopic conformation i is proportional to the factor exp $(-f(i)/kT)$ where $f(i)$ is the free energy of conformation i. Let us define a conformation parameter l such as the end-to-end distance, the radius of gyration, the apparent volume, and the axial ratio. A large number of microscopic conformations i's correspond to the same value of this parameter l. The probability of the conformation specified by assigning a definite value to parameter l is proportional to

$$\sum_{i(l)} \exp(-f(i)/kT) = \exp(-f(l)/kT) \tag{219}$$

where all i states in the summation have the same value of l and $f(l)$ denotes the free energy of conformation l. The free energy due to the variety of microscopic conformations belonging to l is called the conformational free energy $f_c(l)$. The standard free enegy f_0 and the electric free energy $f_e(l)$ defined in the previous chapters are also contained in $f(l)$ of Eq. (219).

It must be cautioned that separation of the total free energy into the above parts is not always reasonable. For example, let us make the end-to-end distance conformation parameter l. There are many extended and contracted conformations along the chain that belong in this conformational category l. An extended conformation has a lower electric free energy than a contracted one. At high charge densities the macroion takes the former conformation more frequently than the latter with the fixed end-to-end distance. As a consequence, each microscopic conformation must have different statistical weights dependent on the electric free energy. Therefore, the conformational free energy can not be calculated separately from the electric free energy. Usually, however, such correlation between the two free energies is not taken into consideration and the total free energy is expressed as the sum of free energies separately obtained.

The most probable value of the conformation parameter l is determined by the maximum of the factor (219) or the minimum of the free energy $f(l)$. When the free energy $f(l)$ is expressed as the sum $f_c+f_0+f_e$, the minimum is given by the condition

$$(\partial f_c/\partial l)+(\partial f_e/\partial l) = 0 \tag{220}$$

which denotes the equality between the conformational contractile force and the electric extensive force.

Now, the contractile force can be estimated in the following way. When bonds between monomers in the macroion can rotate freely, the contractile force $F_c = \partial f_c/\partial l$ is easily calculated. If the end-to-end distance h is taken as the parameter, we have

$$h/mb = L(bF_c/kT) \tag{221}$$

where $L(x)$ is the Langevin function ($\coth x - 1/x$), m is the number of monomers, and b is the length of the monomer; mb is consequently the length of the fully stretched macroion. If the rotation of monomers in the macroion is restricted to a certain extent, it is convenient to choose the quantities m and b to represent the real chain as an equivalent chain composed of freely rotatable monomers. At a fixed value of the product mb, a small value of m and a large value of b mean the low local flexibility of the chain. The inverse relation of Eq. (221) is written

$$bF_c/kT = L^{-1}(h/mb) \tag{222}$$

When the end-to-end vector can take all directions three-dimensionally, the term $-2b/h$ must be added to the right-hand side of the above equation. For small values of h

$$F_c/kT = 3h/mb^2 - 2/h \tag{223}$$

The most probable value of the square of the end-to-end distance of a free chain, h_0, at $F_c = 0$ is given by

$$h_0^2 = (2/3)mb^2 \tag{224}$$

The flexibility or the extensibility of the chain can be defined by the derivative $(\partial h/\partial F_c)$ which is calculable with the above equation. Statistical thermodynamics shows that the mean end-to-end distance under the external force F is given by

$$\langle h\rangle = \frac{\int h \exp\{-f_c(h)/kT + F\cdot h/kT\}dh}{\int \exp\{-f_c(h)/kT + F\cdot h/kT\}\,dh} \tag{225}$$

Therefore, the magnitude of spontaneous thermal fluctuation of the end-to-end distance h is connected with the flexibility or extensibility by the formula

$$\langle \delta h^2\rangle = \langle (h - \langle h\rangle)^2\rangle = kT(\partial h/\partial F_c) \tag{226}$$

When the end-to-end distance h is not very much larger than the distance h_0 in the free state, application of Eq. (223) shows that the mean square of the relative fluctuation of h is given by

$$\langle \delta h^2\rangle/\langle h\rangle^2 = (1/2)/[(\langle h\rangle/h_0)^2 + 1] \tag{227}$$

For example, in the free state ($h = h_0$) the fluctuation is of the same order of magnitude as the end-to-end distance itself. (See Fig. 39.) Such large

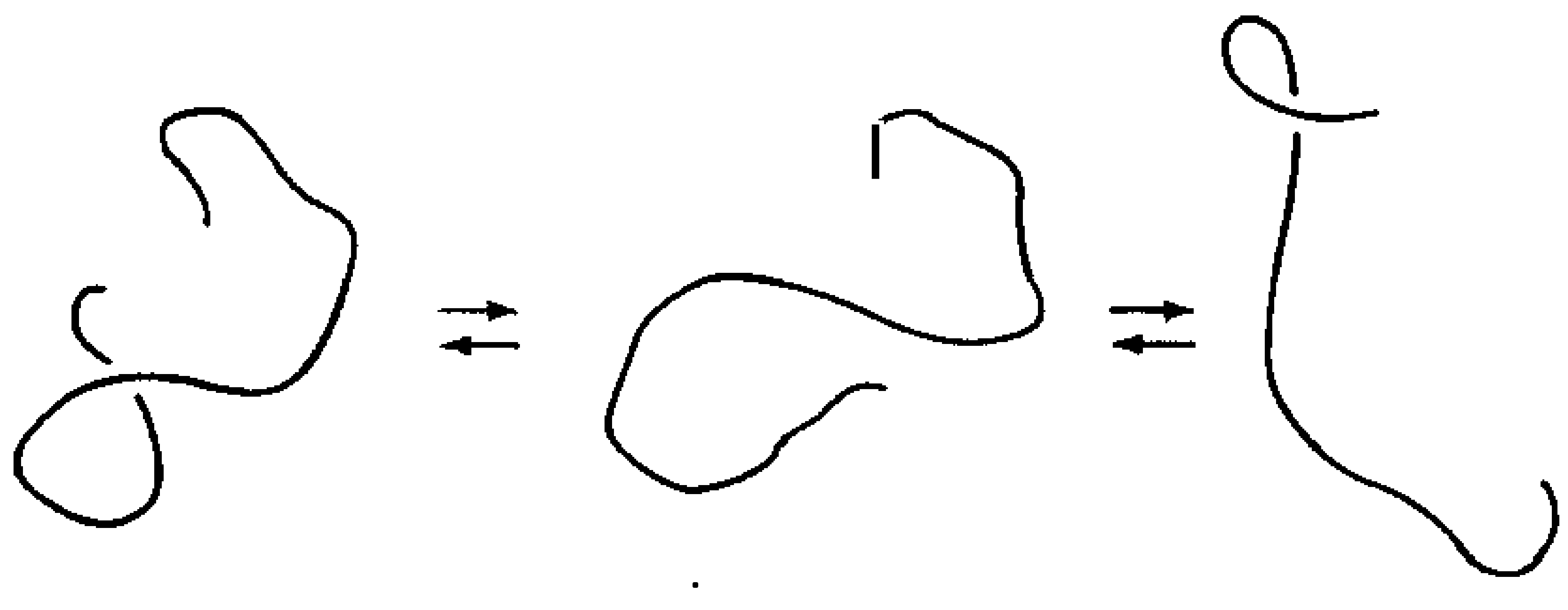


FIG. 39. Fluctuation of the end-to-end distance of a linear chain-like macromolecule.

fluctuation is a characteristic property of linear macromolecules in the random coil conformation.

The above equation shows that the fluctuation of the end-to-end distance under a constant external force is determined by the ratio $\langle h\rangle/h_0$ which compares the extension with the extension in the free state. The relative fluctuation is independent of the total length and of the local flexibility of the chain (specified by quantities m and b in Eq. (223)) which determines the absolute value of the extension h_0. It decreases with increasing relative extension h/h_0. For large values of h, fluctuation $\langle \delta h^2\rangle$ is proportional to ${h_0}^2$ as long as the chain is not stretched much. Notice that Eq. (227) can be applied to estimate the relative fluctuation of the end-to-end distance of a part of a long chain.

In the case of linear macroions the conformation fluctuation must also be large. The end-to-end distance of macroions is increased by the extensive force arising from the electric interaction among ionized groups and small ions. The wide applicability of the cylindrical model for ionic balance described in the previous chapters suggests that this electric interaction does not control the overall conformation of the macroion directly but through the change in the flexibility or the local curvature of chain segments composed of a number of monomers. The extended conformation of linear chainlike macroions with many ionized groups may be approximately equivalent to the conformation of macromolecules having small local curvature or flexibility. They are extended but still in the random coil conformation in the sense that the mean square of the end-to-end distance is approximately proportional to the total number of monomers (at sufficiently large values of this number). If this model is an appropriate one, the conformation fluctuation of the extended macroions is expected to be of the same order as its average conformation, according to Eq. (227).

Let us compare the magnitude of the contractive force derived above with the extensive force $(\partial f_e/\partial l)$. According to Eqs. (204) or (209), the ratio Fl/kT or Fa/kT is of the order of $n\beta \ln (R/a)$ or $n(1-\gamma)$. On the other hand, the ratio $F_c \cdot h/kT$ is of the order of h^2/mb^2. In the case of a contracted random coil, the value of h^2/mb^2 is of the order of unity. Therefore, if l or a is taken as the same order as h, the ratio of the extensive force to the contractive force becomes of the order of $n\beta$. That is, the extensive force becomes very much larger than the contractile force. Only in the almost fully stretched conformation can the contractile force become comparable to the extensive force. This comparison, however, is based on the cylindrical model or the uniform spherical model being applied to the whole macroion directly. For actual coiled macroions the cylindrical model must be applied to their local parts and the extensive force of the whole macroion becomes much smaller than estimated. This situation is discussed further in the next chapter.

Chapter 11

CONFORMATIONAL CHANGE OF MACROIONS

I. EFFECT OF CONCENTRATIONS OF MACROIONS AND SALTS ON CONFORMATION

Linear flexible macroions extend with increase of the number of charged groups and contract with increase of the concentration of macroions and simple salts. The most probable conformation of macroions is determined by the minimum condition of the free energy as a function of the conformation, or by a balance between the contractile force due to the conformational free energy and the extensive force due to the electric free energy. Since the electric free energy is a function of the concentration of macroions and salts, the extensive force changes with the change of these concentrations. On the other hand, the differentiation of free energy with respect to the concentration gives the chemical potential of the component. Therefore, the change of the extensive force with concentration must be related to the change of the chemical potential with conformation. It is intended in this section to discover relationships between the thermodynamic and conformational properties of macroions and to draw a consistent picture of macroion behaviors in solution (*74*).

As in the previous chapters, let us consider a solution composed of N macroions, n_pN counter ions from macroions, n_sN counter and co-ions from salt, and n_0N solvent molecules. The free energy of the solution is a function of the number concentration of these components. When one concentration changes, the most probable conformation l_m changes in accordance with the minimum condition for the free energy, i.e. $(\partial f(l)/\partial l) = 0$.

Therefore, the relation between the change of concentration and conformation is given by:

$$\partial l_m/\partial x = -(\partial/\partial x)(\partial f/\partial l)/(\partial^2 f/\partial l^2)$$

$$= -(\partial/\partial l)(\partial f/\partial x)/(\partial^2 f/\partial l^2) \qquad (228)$$

where x designates the concentration or number of one of the four components and the derivative $(\partial f/\partial x)$ is the chemical potential of that component. As discussed in the previous chapter, the second derivative $(\partial^2 f/\partial l^2)$ is related to the flexibility of the macroion or the mean square of the thermal fluctuation of the conformation by

$$\partial^2 f/\partial l^2 = kT/(\langle(l-l_m)^2\rangle) = kT/\langle\delta l^2\rangle \qquad (229)$$

By applying Eq. (228) to the solvent and salt components,

$$\partial l_m/\partial n_0 = -\langle\delta l^2\rangle(\partial(\mu_0/kT)/\partial l) \qquad (230)$$

$$\partial l_m/\partial n_s = -\langle\delta l^2\rangle(\partial(\mu_s/kT)/\partial l) \qquad (231)$$

The effect of macroion and salt concentration on conformation can be analyzed by these equations.

We assume the additivity law to be applicable for the solution of macroions and salt; the chemical potentials μ_0 and μ_s are expressed as

$$\mu_0 = -kT(g_p c_p + g_s c_s) \qquad (232)$$

$$\mu_s = kT \ln\,(\gamma_p c_p + \gamma_s^{+} c_s)(\gamma_s^{-} c_s) \qquad (233)$$

where $c_p = n_p/n_0$ and $c_s = n_s/n_0$. The first equation represents the additivity of the osmotic pressure and the second represents that of the activity of counter ions. The coefficients g_p and γ_p are for the pure components, being independent of the salt concentration. These coefficients are thus considered to be functions only of the conformation of the macroion. Consequently, when these expressions are combined with Eqs. (230) and (231)

$$\partial l_m/\partial c_p{}^{*} = -\langle\delta l^2\rangle(n_p/c_p)(\partial g_p/\partial l) \qquad (234)$$

$$\partial l_m/\partial c_s = -\langle\delta l^2\rangle(n_p/(\gamma_p c_p + \gamma_s c_s))(\partial \gamma_p/\partial l) \qquad (235)$$

The first equation gives the change of conformation associated with increase of the concentration of macroions and counter ions from macroions. Designation of the derivative $(\partial l_m/\partial n_p)$ with an asterisk denotes that the concentration of macroions is changed by the removal or the addition of solvent; therefore, the concentration of simple salt, if present, is also changed by this procedure. The second equation gives the change of the conformation associated with increase of the concentration of simple salt at a constant concentration of macroions. Equation (235) can also be derived directly from Eq. (209), which gives the extensive force in the presence of salt.

The above equations show that the conformational change of macroions is determined by three factors. One is the magnitude of the fluctuation of the conformation or the flexibility of the macroion ($\langle \partial l^2 \rangle$). A large fluctuation means that the conformation is easily changed by a change of the medium condition. The second is the concentration of macroions (or counter ions from macroions) and salt ions. At low concentrations the conformational change is large. At the same total concentration of counter ions a macroion having a large number of charged groups shows a large conformational change. The third factor is the derivative of the activity coefficient of counter ions or the osmotic coefficient with respect to the conformation. If the activity coefficient change is sensitive to the conformation, the conformational change due to the concentration change of macroions and salt ions becomes large. It must be remembered that $(\partial g_p/\partial l)$ and $(\partial \gamma_p/\partial l)$ are derivatives obtained in the absence of salt.

If parameter l represents extension of the macroion, the values of these derivatives are positive because the number of free counter ions is usually increased by extension of the macroion. Accordingly, Eqs. (234) and (235) indicate that the macroion extends with decrease of the concentration of macroion or salt.

The approximate integration of Eq. (234) and (235) can be carried out in the following way. Experimentally, it was found that in the absence of simple salt, the osmotic coefficient and the activity coefficient of counter ions are both almost constant over a wide range of macroion concentration. The derivatives $(\partial g_p/\partial l)$ and $(\partial \gamma_p/\partial l)$ are thus almost independent of c_p. The relative magnitude of the conformational fluctuation $(\langle \partial l^2 \rangle / l_m{}^2)$is also insensitive to c_p and c_s. Then, the variables l and c_p or c_s in Eqs. (234) and (235) can be separated and the integration gives the relation between the conformation l_m and the concentration c_p or c_s. Moreover, if the derivatives $(\partial \ln g_p/\partial \ln l)$ and $(\partial \ln \gamma_p/\partial \ln l)$ and the relative fluctuation $(\langle \delta l^2 \rangle / l_m{}^2)$ are all independent of the conformation l, the final result can be written as

$$\ln l_m(c_p)^* - \ln l_m(c_p')^* = -A_1(\ln c_p - \ln c_p')^* \tag{236}$$

$$A_1 = n_p g_p(\langle \delta l^2 \rangle / l^2)(\partial \ln g_p/\partial \ln l) \tag{237}$$

and

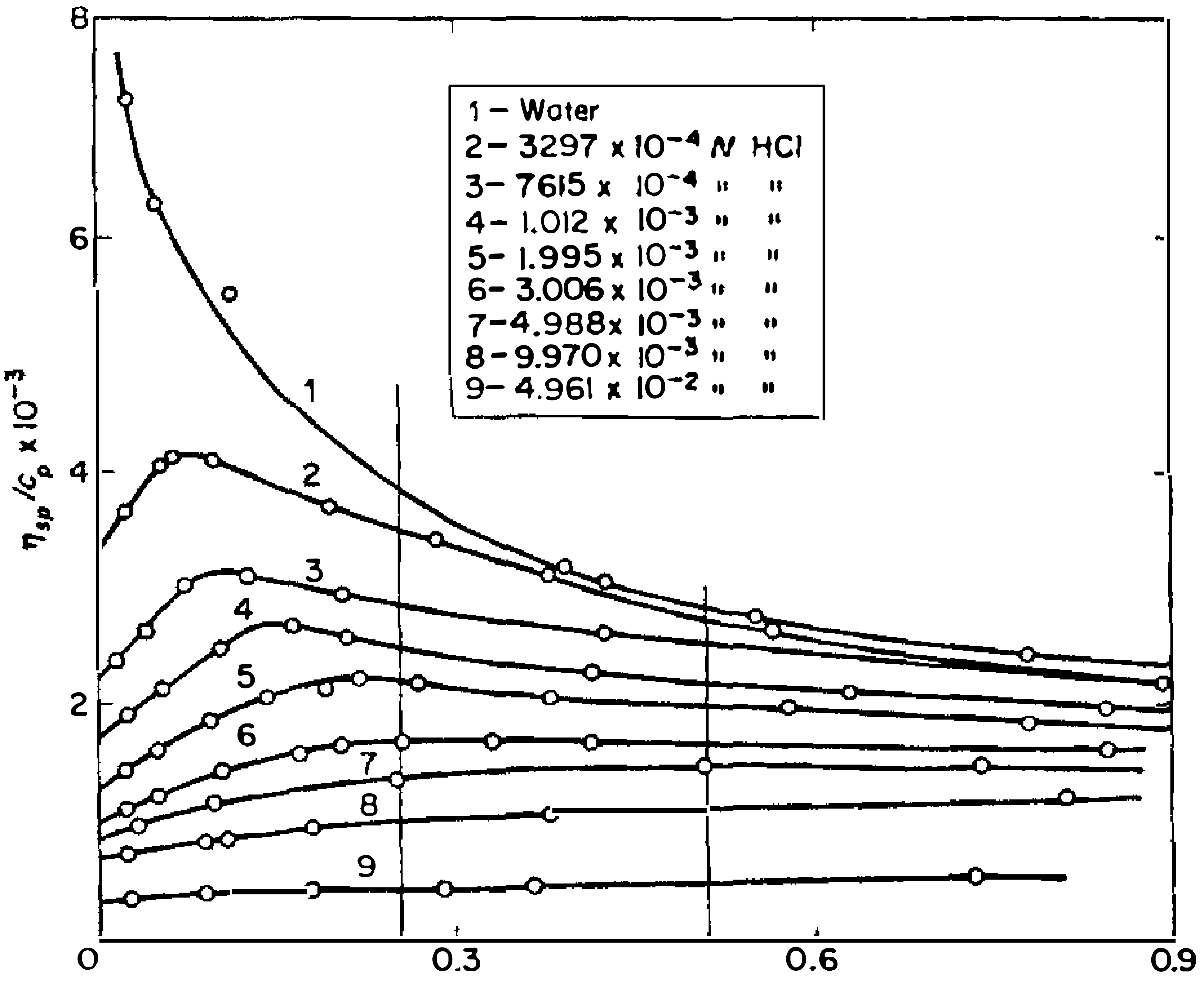
$$\ln l_m(c_s) - \ln l_m(0) = -A_2 \ln (1 + \gamma_s c_s/\gamma_p c_p) \tag{238}$$

$$A_2 = n_p(\gamma_p/\gamma_s)(\langle \delta l^2 \rangle / l^2)(\partial \ln \gamma_p / \partial \ln l) \tag{239}$$

The change of ln l_m due to dilution by the addition of solvent is expected to be proportional to the change of ln c_p. The change of ln l_m due to the addition of salt is expected to be proportional to the change of ln c_s at high salt concentration.

If l is a parameter representing the overall extension of the macroion, for example, the end-to-end distance and the radius of gyration, the change of ln l_m should be approximately proportional to the change of the logarithm of the viscosity per macroion. Experimental data on viscosity obtained at different concentrations of macroion and salt are shown in Figs. 40*a* and *b*. The particular data that are presented were chosen because the discovery of the additivity law on the counter ion activity was made with the same solution (*42*). In the absence of simple salt, the logarithm of the reduced viscosity is found to decrease in proportion to the logarithm of the macroion concentration (Fig. 40*c*). Even in the presence of salt if the salt concentration is decreased in parallel with the macroion concentration, the same proportionality is found between ln (reduced viscosity) and ln (macroion concentration). The proportionality constants are equal in the absence and in the presence of salt (Fig. 40*c*), as is expected from the theoretical result Eqs. (236) and (237).

The relation between the reduced viscosity and the salt concentration is also found to be represented very well by Eq. (238) for a wide range of macroion and salt concentration. In each curve of Fig. 40*d* the macroion concentration was kept constant. At high salt concentrations, ln (reduced viscosity) decreases in proportion to ln c_s. Such a proportionality between viscosity and salt concentration was pointed out several years ago (*75*, *76*), and the above analysis shows that this proportionality is observed at finite concentrations of macroions. Its origin is the additivity behavior of thermodynamic properties. The meaning of the gradient of the straight line in Fig. 40*d* is made clear by Eq. (239). In this figure, when the straight line is extrapolated to low concentrations of salt, it crosses with the horizontal line for the viscosity at zero salt concentration at the condition that $\gamma_s c_s = \gamma_p c_p$. That is, the value of $\gamma_p c_p$ can be determined from the value of the abscissa at this intercept. The value obtained in Fig. 40*d* is in very good agreement with the result of independent measurements of the activity of counter ions γ_p in the same solutions, given in Fig. 29*a* (*42*).


1 – Water
2 – 3297 x 10⁻⁴ N HCl
3 – 7615 x 10⁻⁴ " "
4 – 1.012 x 10⁻³ " "
5 – 1.995 x 10⁻³ " "
6 – 3.006 x 10⁻³ " "
7 – 4.988 x 10⁻³ " "
8 – 9.970 x 10⁻³ " "
9 – 4.961 x 10⁻² " "
ηsp/cp x 10⁻³
8
6
4
2
0
0.3
0.6
0.9
cp (g/ml) x 10²
1
2
3
4
5
6
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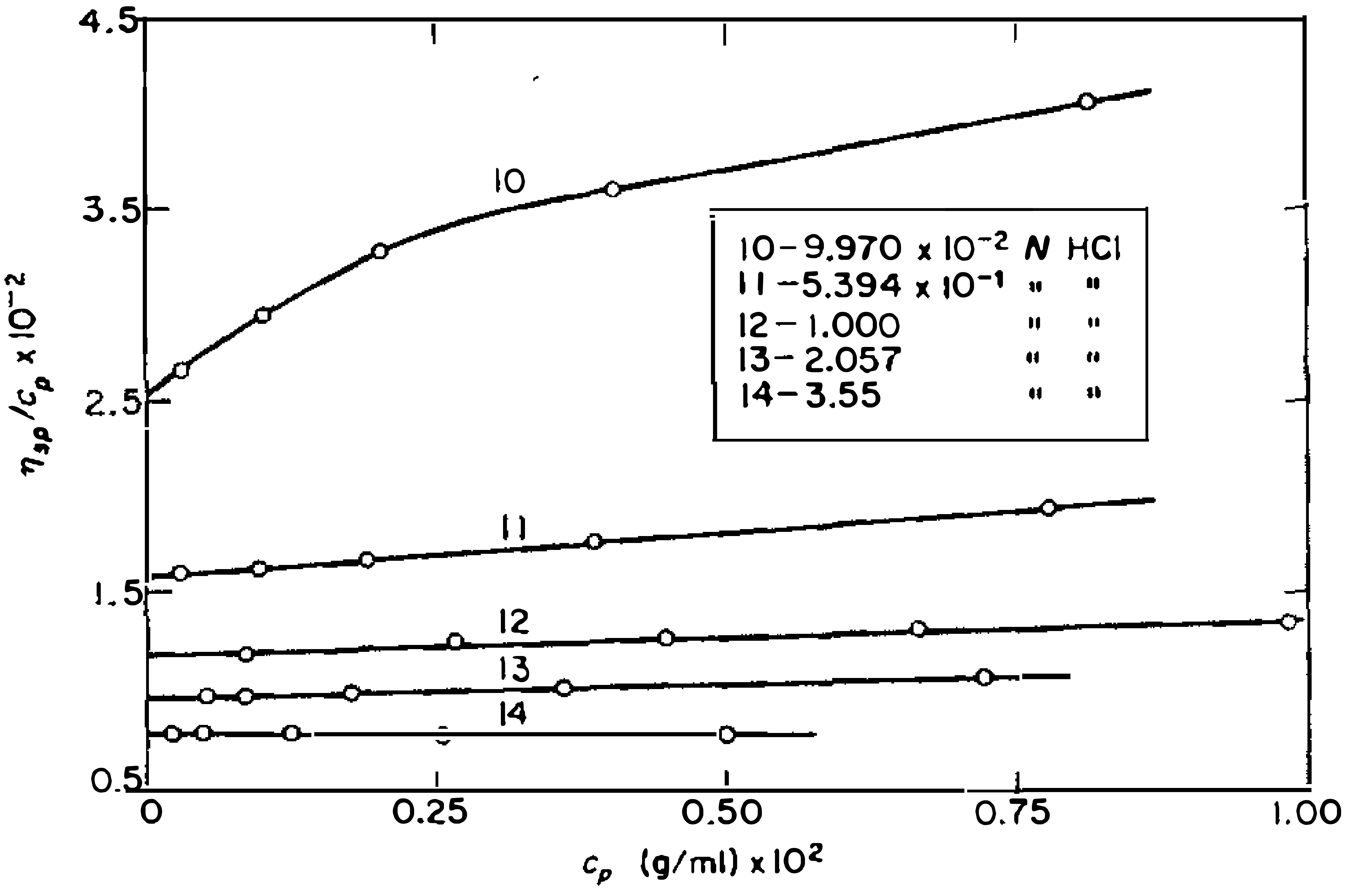
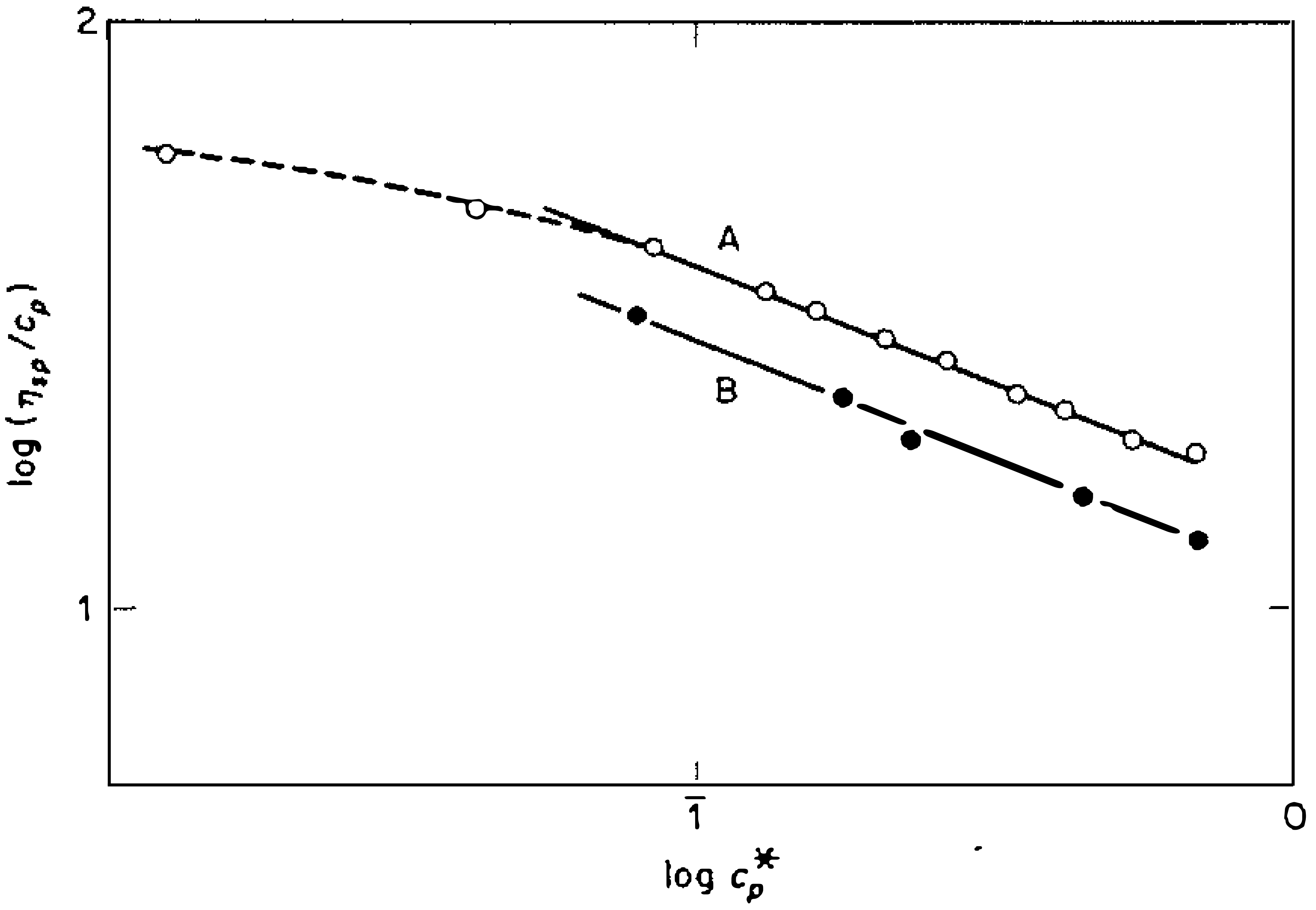
8
9

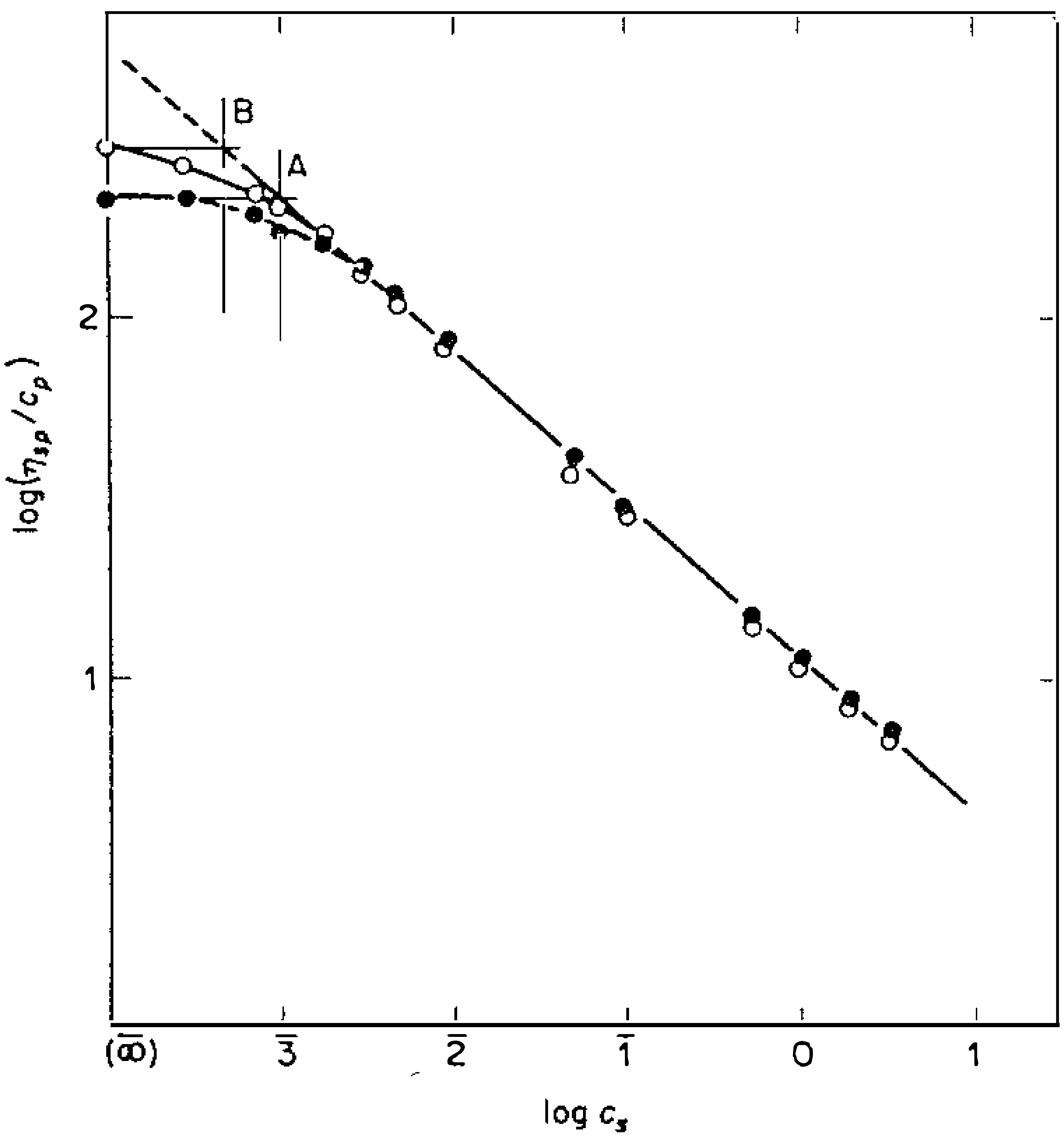
(a)


10 – 9.970 x 10⁻² N HCl
11 – 5.394 x 10⁻¹ " "
12 – 1.000 " "
13 – 2.057 " "
14 – 3.55 " "
ηsp/cp x 10⁻²
4.5
3.5
2.5
1.5
0.5
0
0.25
0.50
0.75
1.00
cp (g/ml) x 10²
10
11
12
13
14

(b)



(c)



(d)

FIG. 40. (*a*) and (*b*) The relation between the reduced viscosity (η_{sp}/c_p) and the polyelectrolyte (polysulfonic acid) concentration c_p in the presence of various concentrations of small ions (HCl) (*42*). (*c*) The relation between the logarithm of the reduced viscosity [log (η_{sp}/c_p)] and the logarithm of the polyelectrolyte concentration (log c_p); (A) in the absence of salts; (B) the polymer concentration was decreased by the addition of solvent to the salt solution of the polymer in which the polymer concentration was 6.0×10^{-3} g/ml and the salt concentration was 2.0×10^{-3} mole/liter. The experimental data were translated from Figs. 40*a* and *b* (*74*). (*d*) The relation between the logarithm of the reduced viscosity [log (η_{sp}/c_p)] and the logarithm of the salt concentration (logc_s) at constant concentrations of polyelectrolytes. Experimental data expressed by ○ and ● were translated from Figs. 40*a* and *b*. Polymer concentration; (○) 2.5×10^{-3} g/ml, and (●) 5×10^{-3} g/ml. The values of $\gamma_p c_p$ determined from intercepts A and B are about 1×10^{-3} mole and 5×10^{-4} mole, in good agreement with the activity of hydrogen ions in Fig. 29*a* measured separately at the above concentrations of polyelectrolytes (*74*).

The gradients of the straight lines in Figs. 40*c* and *d* that illustrate the relation between ln (reduced viscosity) and ln c_p or ln c_s are found to be comparable. That is, when we write

$$\ln\,(\eta_{sp}(c_p)/c_p{}^*) = -A_1{}'\ln c_p{}^* + \text{const} \tag{240}$$

$$\ln\,(\eta_{sp}(c_s)/c_p) = -A_2{}'\ln c_s + \text{const} \tag{241}$$

the constants $A_1{}'$ and $A_2{}'$, which are determined from data of Fig. 40*c* and *d*, have almost the same value, $A_1{}'$ being a little smaller than $A_2{}'(A_1{}' = 0.41$ and $A_2{}' = 0.44)$. The expressions of A_1 and A_2 given in Eqs. (237) and (239) indicate that $A_1{}'$ and $A_2{}'$ must be of the same order.

Such agreement between theory and experiment strongly suggests that the approximations employed in the derivation of Eqs. (236)–(239) are all reasonable.

Equation (238) can not be readily applied to the limit of zero concentration of polyelectrolytes. However, since the additivity law has been experimentally found to be satisfied even at very low concentrations of polyelectrolytes, it may be expected from Eq. (238) that the intrinsic viscosity $[\eta]$ also is approximately proportional to the $-A_2{}'$ power of the concentration of simple salts:

$$[\eta] \propto c_s^{-A_2} \tag{242}$$

Such expectation was realized in experimental data of Fig. 41 (*75*) where $A_2{}' = 0.4 \sim 0.5$.

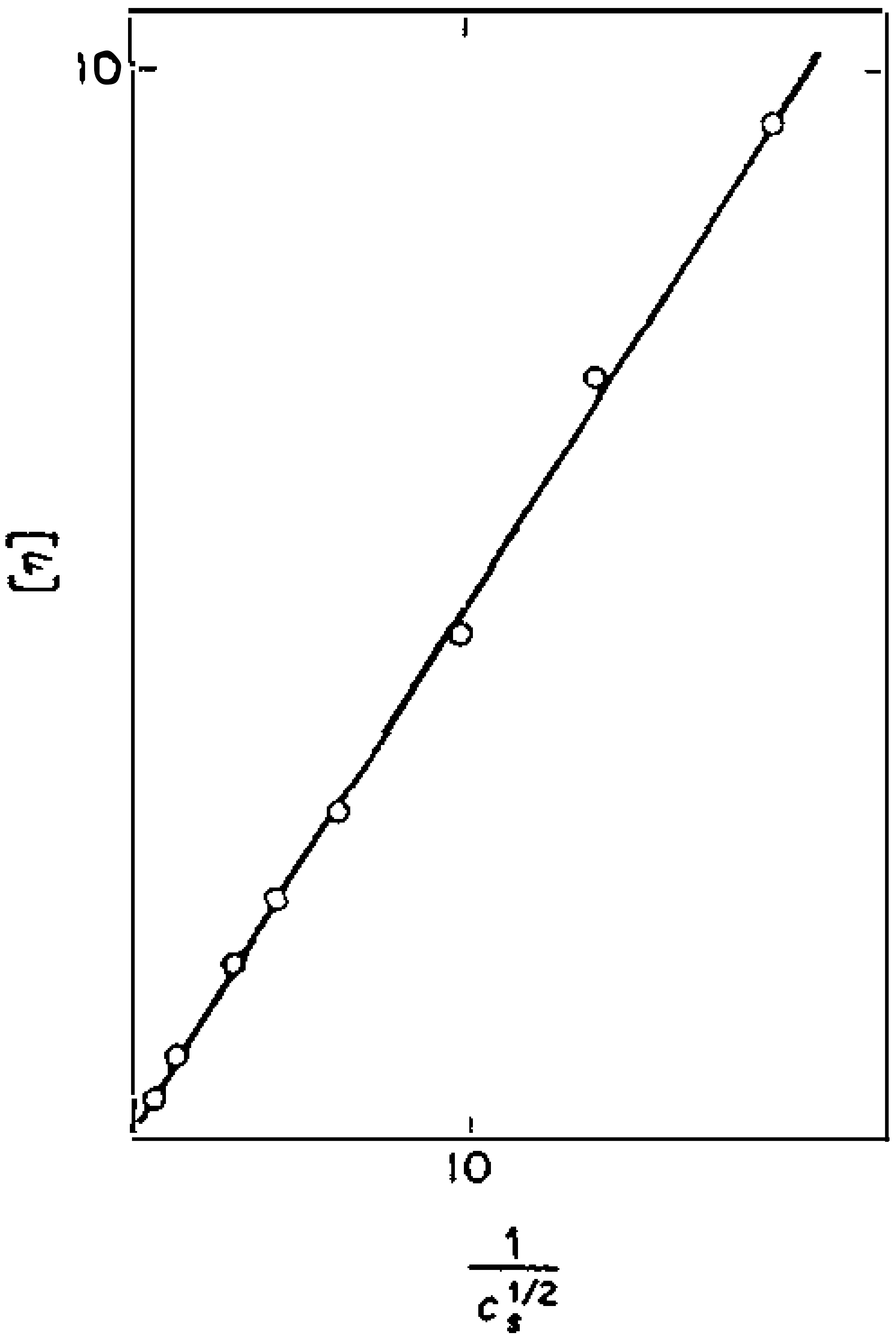


FIG. 41. The relation between the intrinsic viscosity and the salt concentration in a solution of sodium polyacrylate in the presence of various concentrations of NaBr; translated from the original data in (*75*).

II. EFFECT OF THE CHARGE DENSITY ON THE CONFORMATION

The above method can be applied to analysis of the effect of the charge density on the conformation of macroions. The number of charged groups is changed by the addition of alkali or acid in the case of weak polyacids or polybases, and the number of alkali or acid molecules added is taken as the variable x in Eq. (219). Then

$$\partial l_m/\partial n_a = -\langle \delta l^2 \rangle (\partial(\mu_a/kT)/\partial l) \tag{243}$$

In the case of a polyacid, the chemical potential μ_a is composed of the chemical potential of alkali ion and that of hydroxyl ion. Hence the above equation is rewritten as

$$\partial \ln l_m/\partial \alpha = -(\langle \delta l^2 \rangle / l^2) n \{\partial[(\mu_+ - \mu_{\mathrm{H}})/kT]/\partial \ln l\} \tag{244}$$

The derivative in the right-hand side is approximately equal to the derivative $(\partial \ln (n'/v)/\partial \ln l)$, where n'/v denotes the concentration of counter ions bound in the vicinity of the macroion (or in the potential valley along the macroion). The concentration of these bound counter ions usually decreases with extension of the macroion. Consequently, the derivative is negative and the macroion extends with the addition of alkali or with increase of the charge density, as shown in Fig. 42. The magnitude of the conformational change is determined by the change of the concentration of bound counter ions along the macroion with extension. If the volume v for bound counter ions does not change with the change of the overall conformation, the right-hand side of Eq. (244) can be rewritten as $-(\langle\delta l^2\rangle/l^2)n(\partial \ln n'/\partial \ln l)$. From the two-phase approximation we have the approximate relation:

$$\partial \ln l_m/\partial\alpha = (\langle\delta l^2\rangle/l^2)n(\gamma_p/(l-\gamma_p))(\partial \ln \gamma_p/\partial \ln l) \tag{245}$$

This result can also be obtained from calculation of $(\partial/\partial\alpha)(\partial f_e/\partial l)$ by using the expression for $(\partial f_e/\partial l)$ derived in Chapter 10.

By comparing Eq. (245) with Eq. (238) it is found that at low degrees of neutralization the effect of alkali on the conformational change is greater than that of neutral salts but that at high degrees of neutralization the alkali effect is smaller than the salt effect.

The previous analysis showed that the activity coefficient is a function of the charge density Q along the chain of the macroion. The "length" l

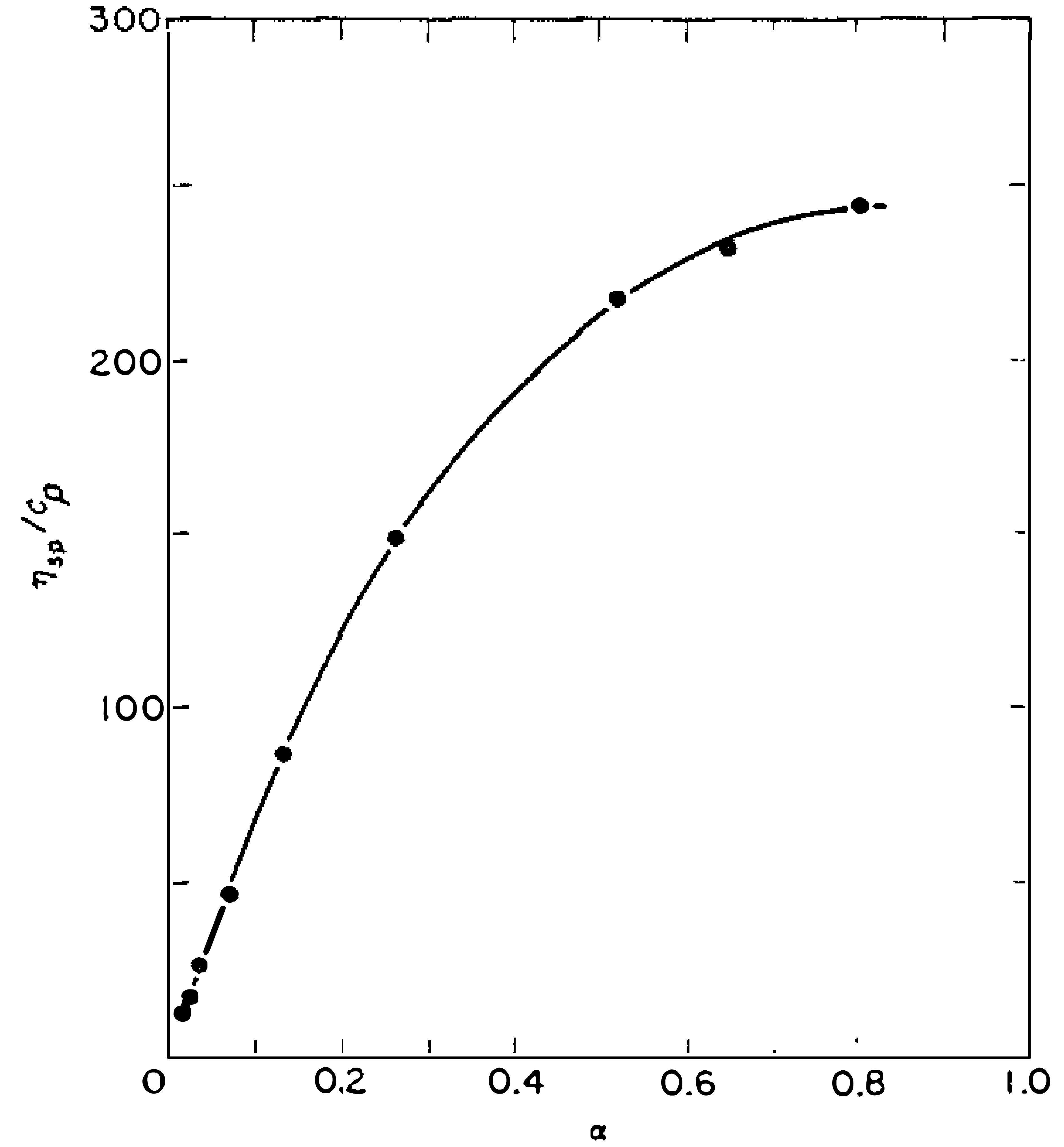


FIG. 42. The relation between the reduced viscosity and the degree of neutralization in a solution of polyacrylic acid neutralized by NaOH.

which appeared in Q is not always identical with the conformational parameter l that is used to designate the overall conformation in the case of linear flexible macroions. However, the two l's are closely related to each other.

III. CONFORMATION AND INTERACTION WITH COUNTER IONS

It was shown in the previous sections of this chapter that the change of counter ion activity or osmotic pressure with the conformational change of macroions is the most important factor for determining the sensitivity of conformation to the concentration of simple salt or macroion. If small molecules having different affinities for macromolecules in different conformations are added to the solution, the conformation exhibiting the strongest affinity is made favourable. If the interaction is repulsive, the conformation is shifted to accommodate weaker repulsion. As pointed out before, the interaction between macroions (with counter ions) and simple salts as a whole is repulsive. The repulsion is stronger for macroions having a higher concentration of free counter ions. Therefore, the increase of the number of free counter ions with extension of the macroions determines the magnitude of the conformational change by simple salts.

The experimental data in Fig. 37 show that the value of (∂ ln (reduced viscosity)/$\partial \ln c_p)^*$ or (∂ ln (reduced viscosity)/$\partial \ln c_s$) is about 0.4; therefore, $(\partial \ln l_m/\partial \ln c_p)^*$ or $(\partial \ln l_m/\partial \ln c_s)$ must be of the same order of magnitude if l_m is defined as the apparent overall volume of the macroion. As mentioned in the preceding chapter, the fluctuation of the conformation $\langle \delta l^2 \rangle / l^2$ is not very much smaller than unity for macroions in a random coil conformation. Thus it is deduced that the derivatives $(\partial \ln g_p/\partial \ln l)$ and $(\partial \ln \gamma_p/\partial \ln l)$ are approximately equal to or not very much larger than $1/n_p g_p$ and $1/n_p \gamma_p$, respectively. In the case of linear macroions having many charges, n_p is very much larger than unity and g_p and γ_p are of the order of 0.1. Therefore, the above derivatives are very much smaller than unity. The osmotic coefficient and the activity coefficient must be insensitive to the overall conformation.

If the simple rod model or the uniform sphere model is directly applied to the macroion, the above derivatives are approximately equal to unity. Therefore, these models produce too large a conformational change with the change of concentrations of macroions or salts, as discussed at the end of Chapter 10. This is the reason why most theories on the conformational change of polyelectrolytes have failed to obtain quantitative agreement with experimental data.

Actually, the osmotic coefficient and the activity coefficient are found to be almost constant over a wide range of the concentration of macroions in spite of the large conformational change indicated by the viscosity change in this concentration range. This fact suggests again that thermodynamic quantities such as the osmotic coefficient and the activity coefficient are determined by the interaction between small ions and parts of the linear chain, while the viscosity is determined by the overall conformation of the chain. This idea is also supported by the earlier result that the value of these coefficients are well explained by applying the cylindrical model to parts of the linear chain, even when the chain is in the coiled conformation.

Apparently the conformation of these local parts of the chain does not change markedly with the change of the overall conformation. For example, the charge density along the chain remains almost constant. Consequently, the equilibrium between bound and free counter ions is not strongly influenced.

The above discussion does not mean that the osmotic coefficient and the activity coefficient are completely independent of the overall conformation. If these coefficients were not changed at all with the overall conformation, the conformational change with the change of the concentrations of macroions and salts could not take place. Actually the derivatives $(\partial \ln g_p/\partial \ln l)$ and $(\partial \ln \gamma_p/\partial \ln l)$ can not be zero but must have small positive values. The number of free counter ions must increase slowly with extension of the conformation. A purely theoretical derivation of the value of these derivatives is too difficult because of the complexity of this problem. It is likely, however, that the electrical interaction determines the local curvature of parts of macroions composed of many monomers, the number of which is very much larger than unity but much smaller than the total number of monomers in the macroion. Stretching of parts of the macroion results in the extension of the overall conformation. Even when each part is greatly stretched, the macroion as a whole is in the random coil conformation and conformational fluctuation is still large.

Now, the fact that overall conformation of macroions is changed by the change of the charge density indicates coupling between fluctuations of conformation and charge. This coupling may influence the property of macroions. Such a situation can be understood in the following example.

Let us first consider a copolymer formed by the alternative arrangement of two kinds of monomers, one of which has an acidic group and the other no ionizable group. When fully neutralized by alkali, this copolymer has a definite alternative arrangement of ionized and nonionized groups; that is, all of the solute macroions have the same structure. On the other hand, consider a homopolymer which is composed of monomers with acidic groups. When alkali is added to neutralize just half of these groups, the macroion formed can be regarded as a kind of copolymer with a varied arrangement of ionized and nonionized groups. On the average, the number of ionized groups is equal to the number of nonionized groups. At a fixed uniform conformation, the electrical energy may be a minimum for the alternative arrangement of these groups. However, the distribution of ionized groups on each macroion is not fixed and the solution is a mixture of copolymers having a fluctuating arrangement of ionized groups.

In the case of the first macroion, the distribution of ionized groups does not change with the conformation. The extended macroion and the contracted one have the same number of ionized groups, although the interaction of the groups with counter ions may depend on the conformation so that the apparent charge changes with the conformation.

In the case of the second macroion, the distribution of ionized groups depends on the conformation. The extended macroion has a larger number of ionized groups than the contracted one, as shown in Fig. 43. When an extended macroion contracts to a certain extent, the electrical free energy usually becomes higher. If the number of ionized groups is allowed to decrease with the contraction, this free energy increase is smaller than that expected from the fixed number of ionized groups. Therefore, the conformational fluctuation is made larger by coupling with the charge fluctuation.

Thus, the two kinds of macroion in the above example exhibit conformational fluctuation of different magnitude, even when the most probable value of the conformation parameter is equal. Under the condition that these macroions have the same total length and the same intrinsic local flexibility, the half-neutralized homopolymer has a wider variety of conformations than the fully neutralized copolymer. Therefore, it is expected that the solution of the homopolymer shows a higher viscosity than the solution of the copolymer.

IV. TRANSITION BETWEEN DISCRETE CONFORMATIONS

The transition between discrete conformations of macroions can be treated by a method similar to the one described in the previous section. Let us suppose a macroion can take two kinds of conformation, for example, the helical and the random coil conformation. In these conformations the macroion has different free energies which depend on the charge density, the concentrations of salt and macroion, the temperature, the nature of the solvent, as well as on a number of other experimental conditions. The macroion takes the conformation of the lower free energy. Consider the case where the macroion undergoes the transition between the two conformations with a change of the solvent condition. At the transition point the chemical potential of the macroion (with its counter ions) in the two conformations a and b must be equal.

$$\mu_{pa} = \mu_{pb} \tag{246}$$

Since the chemical potential is a function of the solvent condition, this equation gives the solvent condition at the transition point. For example,

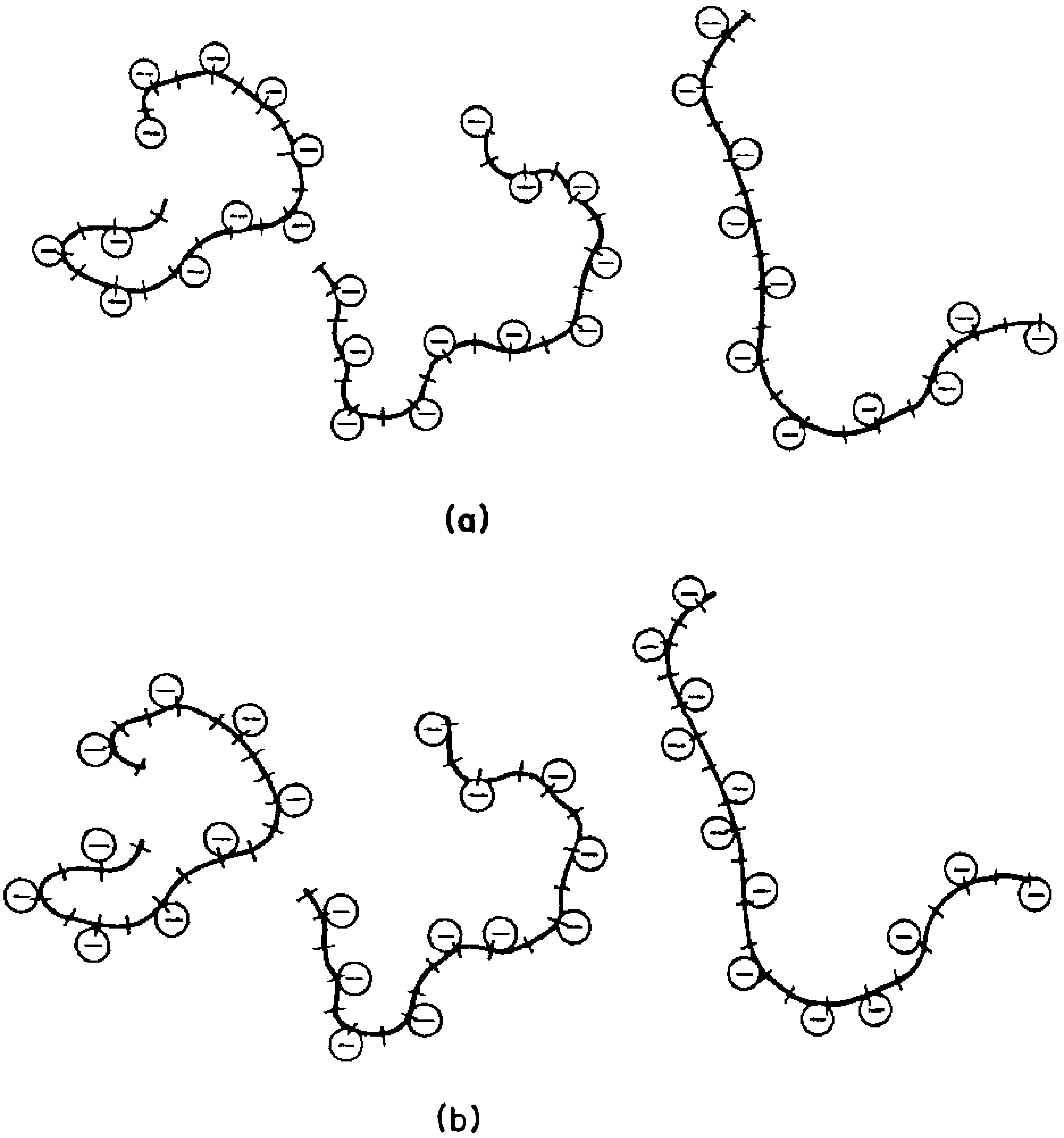


FIG. 43. (*a*) The conformational fluctuation of a copolymer with a fixed alternating arrangement of ionized groups. (*b*) The conformational fluctuation of a half-neutralized homopolymer with variable arrangements of ionized groups.

the relation between the transition temperature and the salt concentration can be explored.

Let us denote the transition temperature in the absence of salt as T_{m0} and in the presence of salt of concentration c_s as T_m. Then

$$\mu_{pa}(T_{m0}, 0) = \mu_{pb}(T_{m0}, 0)$$

$$\mu_{pa}(T_m, c_s) = \mu_{pb}(T_m, c_s) \tag{247}$$

If we put

$$\Delta\mu_{pj}(c_s) = \mu_{pj}(T_m, c_s) - \mu_{pj}(T_m, 0) \qquad (j\text{: } a \text{ or } b) \tag{248}$$

and

$$L_{ab} = -T_m[(\partial\mu_{pa}/\partial T) - (\partial\mu_{pb}/\partial T)] \tag{249}$$

we have

$$\Delta\mu_{pa}(c_s) - \Delta\mu_{pb}(c_s) = L_{ab}\Delta T_m/T_m \tag{250}$$

where the shift of the transition temperature by the addition of salt $\Delta T_m = T_m - T_{m0}$ is assumed to be small, and L_{ab} denotes the heat absorbed in the transition from conformation *b* to *a*. If the change of the chemical potential of the macroion with the addition of salt can be calculated, the above equation gives the relation between T_m and the salt concentration c_s.

A similar equation can be derived for the relation between T_m and the macroion concentration c_p; namely,

$$\Delta\mu_{pa}(c_p) - \Delta\mu_{pb}(c_p) = L_{ab}\Delta T_m/T_m \tag{251}$$

where

$$\Delta\mu_{pj}(c_p) = \mu_{pj}(T_m, c_p) - \mu_{pj}(T_m, c_p') \qquad (j\text{: } a \text{ or } b) \tag{252}$$

Now, the additivity law is assumed to describe the activity and the osmotic pressure in a solution of macroions in conformation *a* and *b*. The transition point is defined as the region in which equal amounts of macroion coexist in the two conformations. Then, the modified additivity law can be employed in the following way:

$$\mu_s = kT \ln(\gamma_{pa}c_{pa} + \gamma_{pb}c_{pb} + \gamma_s c_s)(\gamma_s c_s) \tag{253}$$

and

$$\mu_0 = -kT(g_{pa}c_{pa} + g_{pb}c_{pb} + g_s c_s) \tag{254}$$

where γ_{pj} and g_{pj}(j: *a* or *b*) are, respectively, the activity coefficient of counter ions and the osmotic coefficient in the solution of macroions in conformation *j* in the absence of salt and c_{pj}(j: *a* or *b*) is the concentration of counter ions from macroions in conformation *j*. Such an extension of the additivity law to a mixture of macroions in different conformations is considered to be reasonable, although it has not been directly confirmed by experiment. The chemical potential changes $\Delta\mu_{pj}(c_s)$ and $\Delta\mu_{pj}(c_p)$, obtained according to the procedure used in the previous sections where thermodynamic relations expressed between derivatives of the chemical potentials were employed, are given by

$$\Delta\mu_{pj}(c_s) = n_p kT(\gamma_{pj}/\gamma_s) \ln(1+\gamma_s c_s/\gamma_p c_p) \tag{255}$$

and

$$\Delta\mu_{pj}(c_p)^* = kTn_p g_{pj} \ln(c_p/c_p')^* \tag{256}$$

where γ_p is the mean of two activity coefficients γ_{pj} (at the transition point $\gamma_{pj}=(\gamma_{pa}+\gamma_{pb})/2$) and the asterisk denotes that if salt coexists, the concentration of macroion and salt is changed in the same way by the removal or addition of solvent; in the derivation of Eq. (255) the derivative $(\partial \ln \gamma_{pj}/\partial \ln c_p)$ was assumed to be very much smaller than unity.

Thus, we have the following relations to describe the shift of the transition temperature with change of the salt or the macroion concentration:

$$\Delta T_m = kT_m^2(n_p/L_{ab})[(\gamma_{pa}-\gamma_{pb})/\gamma_s] \ln(1+\gamma_s c_s/\gamma_p c_p) \tag{257}$$

and

$$\Delta T_m = kT_m^2(n_p/L_{ab})(g_{pa}-g_{pb}) \ln(c_p/c_p')^* \tag{258}$$

If L_{ab} is positive, in other words, if heat is absorbed in the transition from b to a, the transition temperature T_m increases with increasing concentration of salt c_s when γ_{pa} is larger than γ_{pb} or when the number of free counter ions is larger for the macroion in conformation a than in b. At sufficiently high concentrations of salt the transition temperature is expected to change in proportion to the logarithm of the salt concentration.

When L_{ab} is positive and g_{pa} is larger than g_{pb}, the transition temperature is decreased by the addition of solvent in proportion to the logarithm of the macroion concentration.

A typical example of the transition of macroions between two discrete conformations is the melting of deoxyribonucleic acid molecules (DNA). With rising temperature they are transformed from the two-stranded helix to the random coil. The transition temperature increases with the addition of neutral salt. Even though dissociation of molecules is associated with the transition in this case, the above theoretical treatment can be applied.

Experiments show that the transition temperature of DNA increases approximately in proportion to the logarithm of the salt concentration and that the gradient of the temperature increase defined by $(d\Delta T_m/d \log_{10} c_s)$ is about 20°C as shown in Fig. 44 (77, 78). The charge density along the chain is larger in the helical conformation than in the random

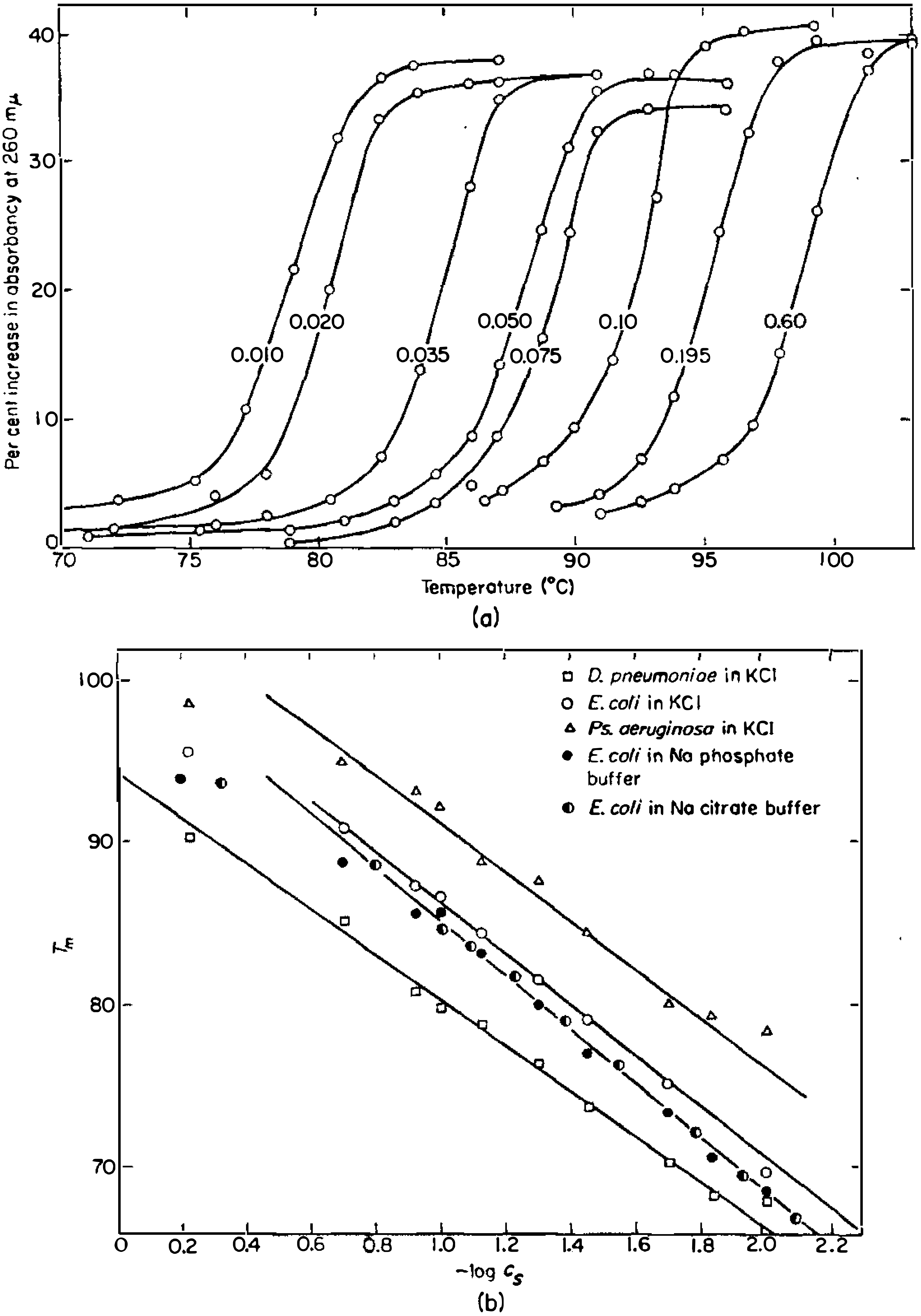


FIG. 44. (*a*) Temperature dependence of the absorbancy of DNA at a salt concentration between 0.01 and 0.6 *N*. The increase of absorbancy means transition to the random coil. (*b*) The relation between the melting temperature of DNA of various origins and the logarithm of the salt concentration (*78*).

coil, so that the activity coefficient of counter ions is lower in the helix than in the random coil. Actually it is found experimentally that the activity coefficient difference between the two conformations, $\gamma_{pa}-\gamma_{pb}$, where a denotes the random coil and b the helix, is between 0.25 and 0.30 (*80*). Theoretical estimates based on the two-phase approximation also give approximately the same value for $\gamma_{pa}-\gamma_{pb}$. The heat L_{ab} is positive because the high temperature favors the random coil conformation. The heat per monomer (L_{ab}/n_p) is found experimentally to be of the order of several kilocalories per mole. If we put $\gamma_{pa}-\gamma_{pb}=0.25$ and $L_{ab}/n_p=$ 5 kcal/mole, the gradient $(d\Delta T_m/d\log_{10} c_s)$ that is calculated with Eq. (257) is equal to about 20°C, a value which agrees well with the experimental results. This agreement between experiment and theory is gratifying and provides support for the assumption that the additivity law is applicable for the expression of the activity of DNA molecules in the helical and random coil conformation.

LIST OF SYMBOLS

a	The (apparent) radius of a macroion.
b	The length of freely rotatable monomers.
c_p	$= nN/V$, the total number concentration of charged groups or counter ions.
c_a	The number concentration of alkali.
c_s	The number concentration of the simple salt added.
c^0	The number concentration of solvent molecules.
c_m	The number concentration of charged groups of a macroion.
c_+	The number concentration of counter ions.
d	$= l/n$, the average distance between neighboring ionized groups.
e_0	The electronic charge.
f	The free energy of the solution per macroion.
f_e	Electric free energy of the solution per macroion.
g	The osmotic coefficient.
g_s	The osmotic coefficient of simple salt solutions.
g_p	The osmotic coefficient of solutions of macroions with counter ions.
h	The end-to-end distance of a macroion.
k	The Boltzmann constant.
l	The length of a cylindrical macroion (or the conformation parameter).
m	The number of freely rotatable monomers.
n	The number of ionized groups on a macroion.
n'	$= n-n^*$, the number of bound counter ions in a macroion.
n^*	$= n-n'$, the apparent number of charges of a macroion.
p	The axial ratio of an ellipsoidal macroion.
q	The proportion of counter ions of different valences or sizes.
r	The distance from the center of a macroion.
s	The entropy of the solution per macroion.
t	The time.

The internal energy of the solution per macroion.
The electric energy of the solution per macroion.
The (apparent) volume of a macroion.
Spatial coordinates.
The valence of counter ions.
= nN/V', the normalization factor for the counter ion distribution.
The external electric field.
The total free energy of the solution or the extensive force of the macroion.
The association constant for localized binding of counter ions.
The latent heat at the conformation transition.
The total number of macroions.
= $ne_0^2/\varepsilon_0 kTa$, a nondimensional quantity giving a measure of the electric potential energy in a spherical macroion.
= $e_0^2/\varepsilon_0 kTd$, a nondimensional quantity giving a measure of the electrical potential energy at a cylindrical macroion.
The radius of the free volume for a macroion.
The absolute temperature.
The total volume of the solution.
= $N\int_{V/N} \exp(-e_0\psi/kT)dv$, the normalized volume.
The degree of neutralization (or the polarizability in Chapter 5).
n^*/n, the (apparent) degree of dissociation of counter ions.
The activity coefficient of counter ions.
The activity coefficient of simple salt ions added.
The activity coefficient of counter ions from macroions.
The displacement of the counter ion atmosphere of a macroion.
The dielectric constant of the solution.
The dielectric constant of the solvent (water).
Specific viscosity.
Intrinsic viscosity.
The frictional constant for a counter ion.
The frequency of alternating electric field.
The relaxation time of the polarization of counter ions.
The electrical conductivity.
Dipole moment of a macroion with counter ions.
The chemical potential of counter ions.
The standard chemical potential of counter ions.
The chemical potential of the simple salt added.
The chemical potential of macroions with counter ions.
The charge density of counter ions.
The charge density of charged groups of a macroion.
= Nv/V, the (apparent) volume concentration of macroions, (or = $e_0\psi/kT$).
The electric potential.
The electric potential difference between bound counter ions and free counter ions.
= $\{(4\pi e_0^2/\varepsilon_0 kT)(n/v)\}^{1/2}$, the radius of ionic atmospheres around ionized groups in a macroion.
The degree of deviation from neutralization.
Laplacian.

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