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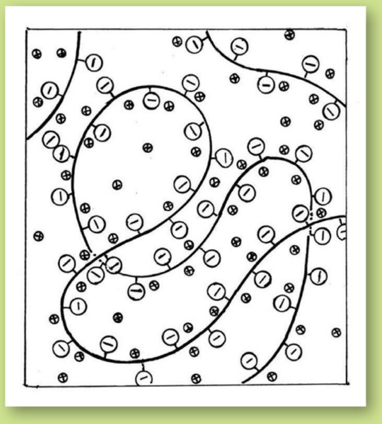
Physical Chemistry of Polyelectrolyte Solutions

Volume 158



Mitsuru Nagasawa

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ADVANCES IN CHEMICAL PHYSICS

VOLUME 158

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PHYSICAL CHEMISTRY OF POLYELECTROLYTE SOLUTIONS

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PREFACE TO THE SERIES

Advances in science often involve initial development of individual specialized fields of study within traditional disciplines followed by broadening and overlap, or even merging, of those specialized fields, leading to a blurring of the lines between traditional disciplines. The pace of that blurring has accelerated in the last few decades, and much of the important and exciting research carried out today seeks to synthesize elements from different fields of knowledge. Examples of such research areas include biophysics and studies of nanostructured materials. As the study of the forces that govern the structure and dynamics of molecular systems, chemical physics encompasses these and many other emerging research directions. Unfortunately, the flood of scientific literature has been accompanied by losses in the shared vocabulary and approaches of the traditional disciplines, and there is much pressure from scientific journals to be ever more concise in the descriptions of studies to the point that much valuable experience, if recorded at all, is hidden in supplements and dissipated with time. These trends in science and publishing make this series, *Advances in Chemical Physics*, a much needed resource.

The *Advances in Chemical Physics* is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

Stuart A. Rice
Aaron R. Dinner

PREFACE

Polyelectrolyte solutions are ubiquitous in nature; their properties define the behavior of important biological and physical processes, and many kinds of synthetic polyelectrolytes are utilized in our daily life and also in industry.

The physical chemistry of polyelectrolyte solutions has been actively investigated since the 1930s as an extension of studies of simple electrolyte solutions, and since the early 1950s as an extension of studies of polymer solutions. The properties of a polyelectrolyte solution are in part hybrids of the properties of simple electrolytes and polymer solutions, but not simple combination of those properties. Fruitful interpretations of the properties have drawn on and extended concepts from electrolyte and polymer solution theory, but the level of theoretical analysis remains less sophisticated than in other aspects of the theory of solutions and much remain to be understood. The physical chemistry of electrolytes and polymer solutions has been well developed and thoroughly described in many books, but very few books that deal with the entire range of properties of polyelectrolyte solutions have been published, possibly because the experimental methods and the theories that are utilized in the study of polyelectrolyte solutions are very diverse, making it difficult for one individual to cover the whole field.

In this book I focus attention on comparing experimental data with theoretical predictions, and I regret that, consequently, some valuable theoretical and purely experimental contributions are ignored. Most of the experimental works quoted in this book were carried out in Nagoya University in cooperation and collaboration with many coworkers. Most of their names are found in this book. I wish to extend my thanks to them for their valuable and independent contributions. I also wish to thank Messrs. Narundo Kato and Haruhisa Choshi for their excellent technical assistance and to the many students I have worked with for their important contributions. Some of the important early works reported in this book were carried out in the laboratories of Professor Stuart A. Rice at The University of Chicago and Professor Alfred Holtzer at Washington University. I thank them for their guidance and hospitality. I also thank the late Professor K. Kanamaru and the late Professor T. Hata at Tokyo Institute Technology, the late Professor I. Kagawa at Nagoya University for their guidance to the present subject and Professor I. Noda for his helpful comments in editing this manuscript.

Mitsuru Nagasawa
Nagoya, Japan
January 2015

INTRODUCTORY REMARKS

A group of linear polymers that have many ionizable or ionized side groups are called **polyelectrolytes**. In 1929, Staudinger prepared the first synthetic polyelectrolyte, poly(acrylic acid) (PAA), by polymerizing an acrylic acid monomer. PAA has many ionizable groups (–COOH) on its backbone and is soluble in water. However, PAA has a limited amount of charges (fixed ions) because the degree of ionization of –COOH group is so low in aqueous solutions and, therefore, does not show any characteristic solution behavior as a polyelectrolyte. If PAA is neutralized with NaOH, the salt, poly(sodium acrylate) (PNaA), is fully dissociated into a poly(acrylate) ion with many fixed charges on its backbone and many sodium ions in aqueous solutions. PNaA shows various characteristic behaviors such as very high solution viscosity. Despite these differences, both PAA and PNaA are categorized as polyelectrolytes. Polyelectrolytes are also prepared by substitution reactions of functional reagents with nonionic polymers. For example, typical polyelectrolytes include carboxymethylcellulose (CMC) prepared by esterifying cellulose with monochloroacetic acid and poly(vinyl alcohol sulfate), which is prepared by esterifying poly(vinyl alcohol) with monochlorosulfonic acid.

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There are many biological polymers with electrolyte side groups such as alginic acid, sodium pectinate, chondroitin sulfuric acid. DNA also has many charged groups.

A polyelectrolyte molecule is dissociated into a macromolecule with many fixed charged groups and simple ions such as Na^+ or K^+ in solution. In this book, the macromolecular ion is often called "polyion" and simple ions are called "counter-ions". A simple electrolyte such as NaCl, which is chemically inert for polyelectrolytes, is often added to polyelectrolyte solutions. The electrolyte is called "added-salt" and the ion with the same electric charge as the polyion (for example, Cl^- to PNaA) is called a "by-ion." Unless noted otherwise, water is used as the solvent for dissolving polyelectrolytes. Most polyelectrolytes discussed in this book are linear polymers. Proteins are not included in the polyelectrolyte categories but are often discussed from the macroion perspective in this book.

A polyelectrolyte solution is a hybrid of electrolyte and polymer solutions. From the viewpoint of electrochemistry, most polyelectrolytes are a unique type of strong electrolytes. In addition, polyelectrolyte solutions have attracted the interest of many polymer scientists because of their characteristic solution behaviors such as high viscosity.

I. STRONG ELECTROLYTES

Many simple electrolytes are soluble in water with limited solubility and dissociated into cations and anions. In most electrolyte solutions, an ionization equilibrium holds between undissociated molecules and dissociated ions. For example, if acetic acid CH_3COOH is dissolved in water, a part of the acetic acid molecules is dissociated as

$$CH_3COOH = CH_3COO^- + H^+ \tag{1}$$

but most of the molecules remain in the undissociated state. The equilibrium constant of the equilibrium can be related to the bond energy between constituting cation and anion.

In 1906, however, Bjerrum [1] pointed out that some electrolyte molecules are completely dissociated into ions in aqueous solutions, and undissociated molecules are not detected by optical or other physical methods even in concentrated solutions. The group of electrolytes is called "strong electrolytes". The idea of strong electrolytes is now well established. The reason for complete ionization is well explained by

Fowler and Guggenheim [2] and others. In short, water is not merely a solvent for the molecule but participates in ionization by hydration. The ionization free energy of the molecule is substantially decreased because of the solvent's involvement in the ionization process.

Most strong electrolytes are salts of strong acids and strong bases such as NaCl and K_2SO_4. Strong acids, such as HCl and H_2SO_4, and strong bases, such as NaOH, themselves are strong electrolytes. Salts of strong acids with weak bases and salts of strong bases with weak acids, such as NH_4Cl and CH_3COONa, are also strong electrolytes. Sodium acrylate $CH_2{=}CH(COONa)$, which is a monomer for PNaA, is a strong electrolyte. NaCl, a typical strong electrolyte, is frequently used as an inert added-salt in the study of polyelectrolyte solutions.

In spite of complete ionization of strong (simple) electrolytes, the colligative properties or electric conductivity of their aqueous solutions deviate, albeit small, from ideal solution behavior. It has been well confirmed that the source of this deviation is not the formation of undissociated molecules. In 1923, Debye and Hückel [3, 4] clarified the reason for the deviation by applying the Poisson–Boltzmann equation to solve the electrostatic interaction between ions. Their theory agrees with experimental data on colligative properties and electric conductivity of simple strong electrolytes quantitatively but only if the solution is dilute enough. The linearization approximation of the Poisson–Boltzmann equation, which Debye and Hückel used in solving the equation, is now called the Debye–Hückel approximation. The idea of ionic atmosphere around each ion, which they introduced to calculate the electrostatic interaction energy between ions, is now recognized as one of the most important ideas in electrochemistry.

The success of the D–H theory was limited to dilute solutions because of the failure of the D–H approximation in solutions of higher concentrations. Various attempts were presented to extend the D–H theory to more concentrated solutions. Among them, the ion-pair model by Bjerrum [5] may be most practical. Thus, the study of strong electrolyte solutions was one of the most active research fields in physical chemistry for decades.

PNaA is a salt of PAA with NaOH. Its monomer, sodium acrylate, as well as sodium salts of similar organic acids, such as sodium acetate, are surely strong electrolytes. Therefore, it was really amazing when Kern reported that the osmotic pressure of PNaA in aqueous solutions is much lower than the value expected from the complete ionization of PNaA [6]. Moreover, the deviation from complete ionization becomes clearer

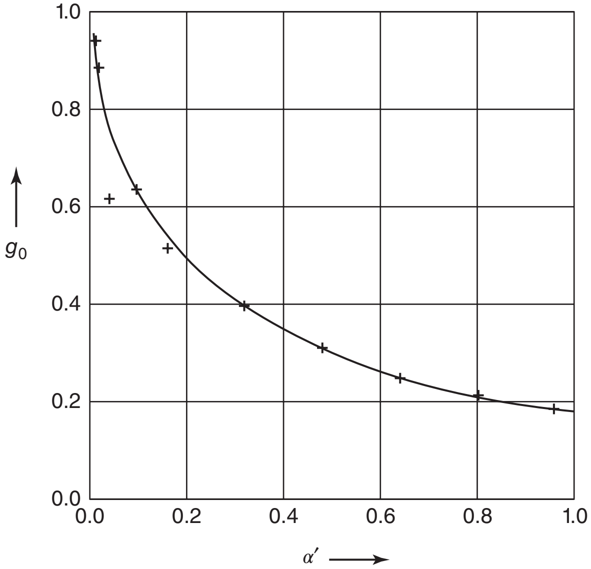

Figure 1. Osmotic coefficient (g_0) versus degree of neutralization of PNaA (α') in pure aqueous solutions. Concn; 0.125 molar concentration of monomer. Degree of polymerization; 340. Temp. 20°C. (Reproduced with permission from Ref. [6]. Copyright Wiley-VCH.)

as the charge density (i.e., the degree of neutralization) of poly(acrylate) increases. Figure 1 shows a decrease in the osmotic coefficient of PNaA with an increasing degree of neutralization. Later studies showed that no optical or other physical observations revealed the formation of a nonelectrostatic bond between Na^+ and $-COO^-$ of PNaA [7].

The characteristic behavior of poly(strong electrolyte), first pointed out by Kern, attracted the interest of researchers. The interaction of counter-ions and polyion has been given various names, including ion-binding, ion-association, ion-fixation (ion-kotei) in Japanese) and ion-condensation. Kern expressed it as “elektrostatische Inaktivierung”. Let us call it “ion-binding” in this book. The physical meanings of these terminologies were also numerous. Ion-binding sometimes refers to the “true” association which can occur in an undissociated simple acid or complex molecules due to the chemical bond though the nature of bond is unknown. The term is also used to describe the ionic association resulting from electrostatic force, such as the ion-pair in simple electrolyte solutions or counter-ions trapped within a polyion domain. All these terminologies seem to imply a similar image of the polyion–counter-ion interaction, which works to decrease the effective charge density of the polyion. All these ion-bindings successfully provided qualitative explanations for some thermodynamic properties of polyelectrolyte solutions [7]. The theories of Manning et al. [8] and Oosawa [9] are well known. However, the usefulness of the ion-binding ideas is limited to thermodynamic properties of polyelectrolyte solutions. There are various fields, such as transport behavior of polyions, in which the ion-binding model is not effective, as is discussed in Chapter "Transport Phenomena of Linear Polyelectrolytes".

II. POLYMER SCIENCE

Although the presence of macromolecular compounds such as cellulose was already known in the 1930s, modern theories on (nonionic) linear polymers began to be actively developed after Flory and Huggins published their work on the thermodynamic properties of concentrated polymer solutions [10–12]. The remarkable progress of polymer science is partly due to the advancement of experimental instruments. In particular, light-scattering techniques have contributed greatly to molecular polymer science. The light-scattering method was theoretically developed by Debye and experimentally established by Zimm, Doty, and their coworkers during 1940s and 1950s. Because of the successful light scattering method, the molecular conformation and radius of gyration of a single molecule have been unambiguously clarified.

In theory, progress was remarkable. Particularly in dilute solutions where polymer molecules are molecularly dispersed, remarkable advances were carried out by many investigators, based on the general theory of McMillan and Mayer [13] as well as others. In 1958 and 1959, Kirkwood and Riseman [14], Debye and Büche [15] and Flory [16] published important papers that sought to understand the variation of radius of gyration or intrinsic viscosity of linear polymers with solvent species or temperature.

Polyelectrolytes are, in general, a group of linear polymers. Typical polyelectrolytes, such as PNaA, have the same flexible backbone as poly(olefin) and other flexible nonionic polymers. Hence, their molecular conformation is fundamentally determined by the same random-flight statistics as that of nonionic polymers. From the view point of polymer science, the difference appears to be simply that the radius of gyration of polyelectrolyte molecules is varied because of the electrostatic interaction between fixed charges, whereas that of nonionic polymers is varied because of the so-called excluded volume effect. Nevertheless, the expansion of radius of gyration of linear polyelectrolytes remains an unsolved problem as is discussed in Chapter “Radius of Gyration and Intrinsic Viscosity of Linear Polyelectrolytes”.

Combination of electrochemistry and polymer science is important for the successful study of polyelectrolyte solutions. In 1948, Kuhn, Künzle, and Katchalsky first published research on the application of polymer science to molecular conformation of polyelectrolytes [17]. They assumed that polyelectrolyte molecules have randomly-kinked conformations consisting of “Kuhn’s segments,” each segment having a fixed charge. It was assumed that counter-ions were removed at the limit of high dilution. This assumption was obviously unrealistic. Using a revised model of Kuhn et al., by taking into account the presence of counter-ions, Katchalsky and Lifson [18] calculated the mean square end-to-end distance of polyelectrolytes, though it was assumed that a certain amount of a simple neutral salt is added to the solution. Although the theory did not fully agree with experiments, the calculation of the electrostatic interaction energy between fixed charges based on the random-flight chain model by Kuhn-, Künzle-, Katchalsky and Lifson was instrumental for future studies.

A. Light Scattering

The light-scattering method may be the most powerful tool for studying the molecular conformation, radius of gyration and molecular weight of linear polymers. Light is an electromagnetic wave. If a molecule is placed in an oscillating electric field of light, an oscillating dipole is induced in the molecule due to the constituent electrons in the molecule. The oscillating dipole becomes a new source of light radiating from the particle. The scattering lights from different particles generally have a difference in phase so that they may interact with one another. Linear polymers are composed of many segments, each of which may be an oscillating dipole. If the size of the polymer is smaller than about $\tilde{\lambda}/20$ where $\tilde{\lambda}$ is the wave length of incident light, phase difference of scattering lights from different segments in a molecule is so small that the whole molecule is regarded as a single scattering source. However, most linear polymers, which we are concerned with, are usually larger than $\tilde{\lambda}/20$ but smaller than a wave length. Therefore, scattering lights from different segments inside the molecule interfere with one another to give angular dependence of scattering light. By extrapolating the scattering light intensity to infinite dilution, we can obtain the angular dependence of scattering light from a molecule, P(θ), which allows us to discuss the conformation of the polymer.

The basic theory of light scattering from polymer solutions was first presented by Debye [19–21] and further developed by many scholars including Zimm, Doty, and their coworkers [22–25] in 1940–1950. Textbooks on the topic [26, 27] explain the details of those theories. This book presents only a summary of light scattering methods used to study molecular conformations and thermodynamic properties of linear polymers.

Light-scattering data from nonionic polymer solutions in a single solvent (i.e., two-component systems) are expressed by the following equations, when unpolarized light is used. Since ordinary linear polymers are not monodisperse with respect to molecular weight but are mixtures of molecules with different molecular weights (polydisperse polymer), the molecular characteristics (e.g., molecular weight, radius of gyration), determined by the light-scattering method are an average of values.

$$\frac{KC}{\Delta R_\theta} = \frac{1}{M_\mathrm{w} P(\theta)} + 2A_{2,LS}\frac{P_2(\theta)}{P(\theta)^2}C + \ldots \tag{2}$$

where

$$K = \frac{2\pi^2 \tilde{n}_0^2}{N_\mathrm{A} \tilde{\lambda}_0^4}(\partial\tilde{n}/\partial C)^2 \tag{3}$$

and ΔR_θ is the difference between the Rayleigh ratio of the sample solution and solvent,

$$\Delta R_\theta = R_\theta(\text{solution}) - R_\theta(\text{solvent}) \tag{4}$$

$$R_\theta = \frac{i_\theta}{I_0} r^2 \frac{1}{1+\cos^2\theta} \tag{5}$$

M_w is the weight-average molecular weight defined by

$$M_\mathrm{w} = \frac{\sum_i N_i M_i^2}{\sum_i M_i} \tag{6}$$

where N_i is the number of polymer molecules with a molecular weight M_i in a unit volume. A_2 is the second virial coefficient, C is the concentration of polymer (gram/ml), $\tilde{n}_0$ is the refractive index of solvent, $(\partial\tilde{n}/\partial C)$ is the refractive index increment, $\tilde{\lambda}_0$ is the wave length *in vacuo*, and N_A

is Avogadro's number. I_0 and i_θ are respectively the intensities of the incident light and the light scattered at an angle θ, r is the distance between the solution and the detector, and $P(\theta)$ and $P_2(\theta)$ are the particle scattering factors from one and two polymer molecules, respectively. $P(\theta)$ allows us to discuss the conformation of polymer molecules.

In practice, the data of $KC/\Delta R_\theta$ are obtained as a function of scattering angle θ and sample concentration C. From the experimental data, we can obtain (1) the polymer concentration (C) dependence of $KC/\Delta R_\theta$ at the limit of $\theta = 0$ and (2) the scattering angle (θ) dependence at the limit of $C = 0$. A Zimm's plot [23], that is, the plot of $KC/\Delta R_\theta$ versus $\sin^2(\theta/2) +$ constant C conveniently presents an overall view of these dependencies and is widely used.

1. Molecular Weights and the Second Virial Coefficient

At the limit of $\theta = 0$, the lights scattered from all segments inside a molecule do not interfere with one another, so $P^{-1}(\theta) = 1$ at $\theta = 0$ since the molecules are randomly oriented. Therefore, at the limit of $\theta = 0$, eq (2) becomes

$$\lim_{\theta \to 0} \frac{KC}{\Delta R_\theta} \equiv \frac{KC}{\Delta R_0} \tag{7}$$

$$= \frac{1}{M_\mathrm{w}} + 2A_{2,LS}C + 3/2A_{3,LS}C^2 + \ldots \tag{8}$$

That is, the scattering light intensity at $\theta = 0$ is the same as that for small particles. This equation was derived from the fluctuation theory. Let us observe a small volume in solution, which is small compared with the wave length of incident beam but contains some solutes. The light-scattering intensity from the small volume may be due to the fluctuation of the dielectric constant (D), that is, the local refractive index ($\tilde{n}$) ($D = \tilde{n}^2$). The fluctuations of dielectric constant may be consisted of density and solute concentration fluctuations. As the effect of density fluctuation may be canceled between the solution and solvent if the solution is dilute, the excess scattering intensity may be caused by solute concentration fluctuation. This can be related to the osmotic pressure of the solution, which is explained by Einstein's theory [28]. Thus, we have

$$\lim_{\theta \to 0} \frac{KC}{\Delta R_\theta} = \frac{1}{RT}\frac{\mathrm{d}\pi}{\mathrm{d}C} \tag{9}$$

where the osmotic pressure π is thermodynamically given by

$$\pi/C = 1/M_n + A_{2,OS}C + A_{3,OS}C^2 + \ldots \tag{10}$$

Both eqs (8) and (10) are commonly used in the study of dilute solution properties of linear polymers to determine M_N, M_w, and second virial coefficient A_2. If the polymer sample is monodisperse with respect to molecular weight, we have $M_n = M_\mathrm{w}$ and $A_{2,OS} = A_{2,LS}$, and so forth.

The graphical extrapolation of $KC/\Delta R_0$ versus C or π/C versus C plots to $C = 0$ gives the weight-average and number-average molecular weights, respectively, while the second virial coefficients are determined from their slopes. To determine the second virial coefficients, however, this may require some consideration particularly if the sample has a narrow molecular weight distribution (NMWD). The assumption on the third virial coefficient $A_{3,LS}$ may considerably affect the determined value of $A_{2,LS}$. The following procedure may be recommended to determine A_2 with high accuracy. First, molecular weight M_w is determined by using the following "square-root plot" proposed by Berry [29], though the accuracy of A_2 is somewhat sacrificed.

$$\lim_{\theta\to 0}(KC/R_\theta)^{1/2} = (1/M_\mathrm{w})^{1/2}(1 + A_2M_\mathrm{w}C) \tag{11}$$

where the third virial coefficient A_3 is assumed to be

$$A_3 = (1/3)A_2^2M \tag{12}$$

Next, A_2 is determined with high accuracy by using Stockmayer and Casassa's method [30], such as

$$\frac{\lim\limits_{\theta\to 0}(KC/R_\theta) - 1/M_\mathrm{w}}{2C} = A_{2,ls} + (3/2)A_{3.ls}C + \ldots \tag{13}$$

and is almost free from the assumption on A_3. Noda and Kitano provide a detailed explanation of the aforementioned procedure [31].

2. *Particle Scattering Factor ($P(\theta)$)*

By extrapolating experimental data $KC/\Delta R_\theta$ to infinite dilution at each value of θ, we can determine $P(\theta)$ as a function of θ such as

$$P(\theta)^{-1} \equiv (i(\theta)/i(\theta = 0))^{-1} \tag{14}$$

$$= \lim_{C\to 0}(KC/R_\theta)\cdot M_\mathrm{w} \tag{15}$$

As θ increases, $P^{-1}(\theta)$ increases, by a factor designated as $P(\theta)$, because of the interference effect of scattering lights from different segments.

Debye produced the following general equation of $P(\theta)$, such as

$$P(\theta) = \frac{1}{\sigma^2} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} \frac{\sin \mu r_{ij}}{\mu r_{ij}} \tag{16}$$

where μ is the absolute value of the scattering vector

$$\mu \equiv \frac{4\pi}{\tilde{\lambda}} \sin(\theta/2) \tag{17}$$

and $\tilde{\lambda}$ is the wave length in the solution.

$P(\theta)$ has been derived for various types of polymer molecules. The following equation of $P(\theta)$ derived by Debye for linear polymers with the Gaussian distribution function, $W(\vec{r}_{ji})$, is well known.

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] \tag{18}$$

where

$$u = \mu^2 \langle S^2 \rangle \tag{19}$$

$$= (16\pi^2/\tilde{\lambda}^2)\langle S^2 \rangle \sin^2(\theta/2) \tag{20}$$

In the range of low θ, $P(\theta)$ for polydisperse polymers may be expanded into the following form:

$$P(\theta)^{-1} = 1 + \frac{1}{3}\mu^2 \langle S^2 \rangle_z + o(\mu^2 \langle S^2 \rangle_z) \tag{21}$$

where $\langle S_i^2 \rangle_\mathrm{z}$ is the z-averaged radius of gyration defined as

$$\langle S_i^2 \rangle_\mathrm{z} = \frac{\sum_i N_i M_i^2 \langle S^2 \rangle_i}{\sum_i N_i M_i^2} \tag{22}$$

N_i, M_i, and $\langle S^2 \rangle_i$ are the number of molecule, molecular weight, and mean square radius of gyration of component i, respectively. This expansion form is independent of conformation of polymer, and $\langle S^2 \rangle_z$ may be determined from the initial slope of $P(\theta)^{-1}$ versus $\sin^2(\theta/2)$ plot of whatever conformation the sample has. However, the applicability of the linear relationship in eq (21) is so limited that $\langle S^2 \rangle_z$ cannot always be determined from the limiting slope with high accuracy. In such cases, the radius of gyration $\langle S^2 \rangle$ may be determined to have good agreement between eq (18) and experimental $P(\theta)$ if the molecule is a Gaussian chain. It is to be noted that the general equation of $P(\theta)$, eq (16), and hence eq (18) for ideal chains is given only for monodisperse polymers with respect to molecular weight.

3. Light Scattering from Multicomponent Systems

It is important to note that the aforementioned theories are given for two-component systems of a homogeneous polymer in a single solvent. In most studies on thermodynamic properties or intrinsic viscosity of linear polyelectrolytes, a neutral simple salt such as sodium chloride is added. Only with a certain concentration of added-salt, the size or radius of gyration of a polyion is nearly independent of the polymer concentration and within the range of $\lambda/20 - \lambda/2$, as is required for rigorous analysis by light scattering. Since the concentration of added-salt in the medium surrounding the polyion is different from the average value in the solution and changes with polymer concentration because of the electrostatic interaction between polyion and simple ions, the light scattering from polyelectrolytes in added-salt solutions may be a typical example of a multicomponent system.

Light scattering from (nonionic) linear polymers in mixed solvents was first studied by Ewart et al. [20]. They found that the apparent molecular weight of a polymer obtained by a conventional light-scattering method in a mixed solvent varies with the composition of the mixed solvent. They concluded that the observed variation of molecular weight is due to the selective adsorption of a solvent by the polymer and presented a theoretical equation for coefficient K in eq (3);

$$K = \frac{2\pi^2 \tilde{n}_0^2}{N_{\mathrm{A}} \tilde{\lambda}_0^4} [(\partial \tilde{n}/\partial C)^2 - (\partial \phi/\partial C)(\partial \tilde{n}/\partial \phi_0)] \tag{23}$$

where ϕ_0 is the volume fraction of a solvent in the mixed solvent and ϕ is its value in the medium surrounding the polymer domain. If the specific adsorption of a solvent by the polymer is not changed with polymer concentration, that is, if $\partial\phi/\partial C = 0$, eq (23) reduces to that for a binary mixture. The theory of Ewart et al. is applicable only at infinite dilution and they showed only that the molecular weight obtained in a mixed solvent may not always be the true one. In relation to the fluctuation theory of light scattering, Kirkwood and Goldberg [32], Stockmayer [33], and other researchers later carried out detailed discussions about the effect of the fluctuation of the third component on excess scattering intensity. They showed that not only the molecular weight depends on the composition of the mixed solvent, but also the second virial coefficient depends on this composition.

Detailed discussions on light scattering from linear polyelectrolytes in aqueous solutions with added-salt can be found in works by Casassa and Eisenberg [34–36] and Vrij and Overbeek [37]. Casassa and Eisenberg pointed out that if the chemical potentials of added-salt in the medium surrounding the polyelectrolyte is kept constant, the polyelectrolyte solution with added-salt may be regarded as a two-component system. Consequently, Eisenberg and Casassa suggested that eqs (2)–(5), which were presented as applicable to nonionic polymers in two-component systems, are also applicable to polyelectrolyte solutions if the sample solutions are dialyzed against an infinite volume of a solvent containing a certain concentration of a neutral salt. Moreover, it was suggested that if a mother solution is dialyzed against a solvent (e.g., a NaCl solution), the remaining dilute solutions may be prepared by diluting the mother solution with the solvent. The solution composition and refractive index increment ($\partial\tilde{n}/\partial C$) of the diluted solution are close enough to the values of the solutions dialyzed [38]. This suggestion was a great contribution to the study of dilute polyelectrolyte solutions. This conclusion agrees with the classical theory of the Donnan membrane equilibrium on osmotic pressure of colloidal electrolytes (see Chapter "Thermodynamic Properties of Polyelectrolyte Solutions", Section "Donnan Membrane Equilibrium (Concentrated Solution)").

III. POLYELECTROLYTE SOLUTIONS

Polyelectrolyte solutions are a hybrid composed of electrolyte and polymer solutions. In order to understand the solution behavior of polyelectrolyte solutions, merging the theories of both fields is required. Polyions are high valent, nonsolid ions. It would be very difficult to apply the Debye and Hückel theory for dilute simple electrolyte solutions to the polyelectrolyte system. Considering the difference in views in electrochemistry and polymer science, the content of this book is classified into the following six chapters.

Chapter "Thermodynamic Properties of Polyelectrolyte Solutions." While understanding thermodynamic properties may be one of the final goals of this study, an initial focus on

Kuhn–Künzle–Katchalsky–Lifson's theory may help elucidate the problems associated with merging of polymer and electrolyte solutions. Moreover, to understand the thermodynamic properties of polyelectrolyte solutions, it is important to know how the study on thermodynamic properties of nonionic polymers has progressed. Taking into consideration the progress of the study on nonionic polymers, the thermodynamic properties of polyelectrolyte solutions are discussed separately in terms of concentrated and dilute solutions.

Chapter "Ionization Equilibrium and Potentiometric Titration." Titration of a weak polyacid such as PAA with NaOH is an experimental procedure that charges up polymer molecules. A comparison between potentiometric titration data of weak polyacids and theoretical calculations of electrostatic free energy of polyion helps clarify the ionic atmosphere around a polyion. This chapter also focuses on the application of potentiometric titration to the study of helix–coil transition of ionic poly(peptide)s and the association–dissociation phenomena of spherical proteins.

Chapter "Molecular Conformation of Polyelectrolyte Molecules." Both nonionic flexible polymers and polyelectrolyte molecules have more or less random-flight conformations if enough amount of a neutral simple salt is added. However, expansion of the radius of gyration of nonionic polymers is due to the excluded volume effect, whereas in the case of polyelectrolyte molecules, it is due to an electrostatic repulsive force. The molecular conformations of nonionic polymers and polyelectrolytes are compared and contrasted.

Chapter "Radius of Gyration and Intrinsic Viscosities of Linear Polyelectrolytes." Theories on the expansion factor of the radius of gyration of nonionic polymers in good solvents are tested from the molecular weight dependence of the expansion factor, by using molecular weight as the sole parameter. On the other hand, the expansion factor of polyelectrolytes can be tested by using two independent parameters, (i.e., molecular weight and concentration of an added-salt such as NaCl).

Chapter "Transport Phenomena of Linear Polyelectrolytes." If the radius of gyration in the presence of added-salt is determined experimentally, some transport phenomena such as sedimentation and diffusion can be fundamentally explained with the same nondraining sphere model as assumed for nonionic polymers, though there is an effect of ionic atmosphere around polyion coil. In electrophoresis, however, polyion coils behave like free-draining spheres at the limit of high ionic strength. The experimental results are very important to consider about the nature of ion-binding.

Chapter "Ion-binding." In this chapter, discussion is focused mainly on the behavior of counter-ions. In most other chapters, counter-ions are assumed to behave ideally. The electrostatic interaction between ions is effective mutually. If polyion is affected by counter-ions, counter-ions should also be affected by the effect from fixed charges on polyion. This chapter focuses on the behavior of counter-ions and the discussion on the nature of ion-binding, based on the experimental data accumulated about the behavior of counter-ions.

A. Models of Polyelectrolyte Molecules

Most polyelectrolyte molecules are essentially flexible polymers and all fixed charges are surrounded by their ionic atmospheres not only when a neutral salt is added to the solution but also in pure aqueous solutions so long as the ionic strength (i.e., polyelectrolyte concentration) is finite. The most realistic model of linear flexible polyelectrolytes such as PNaA in aqueous solutions with added-salt may be a random-flight chain on which charged groups are fixed discretely and each fixed charge is surrounded by its ionic atmosphere, as was employed by Kuhn–Künzle–Katchalsky–Lifson (pearl necklace model). The model is schematically shown in Figure 2A.

Although originally presented for simple salt solutions, the Debye-Hückel theoretical equation was assumed for the electrostatic potential distribution around a fixed charge on the flexible chain in almost all theories (including that of Katchalsky and Lifson). Because of the mismatch between the basic idea behind the D-H theory and the molecular structure of polyelectrolytes, which is discussed in the following chapters, there has been no reported agreement between the experimental data and theories.

In most theoretical approaches, therefore, different models are assumed based on what is appropriate for the research purpose. Consider the Kratky plot in the study of polymer conformation with small-angle scattering of X-ray (see Chapter "Molecular Conformation of Linear Polyelectrolytes", Section "Study on Local Conformation of Polyion Chains"). It highlights that if we observe a polymer molecule from a very low scattering angle, we can see the whole molecule to determine its radius of gyration. If we observe the molecule from a higher scattering angle, we can see a part

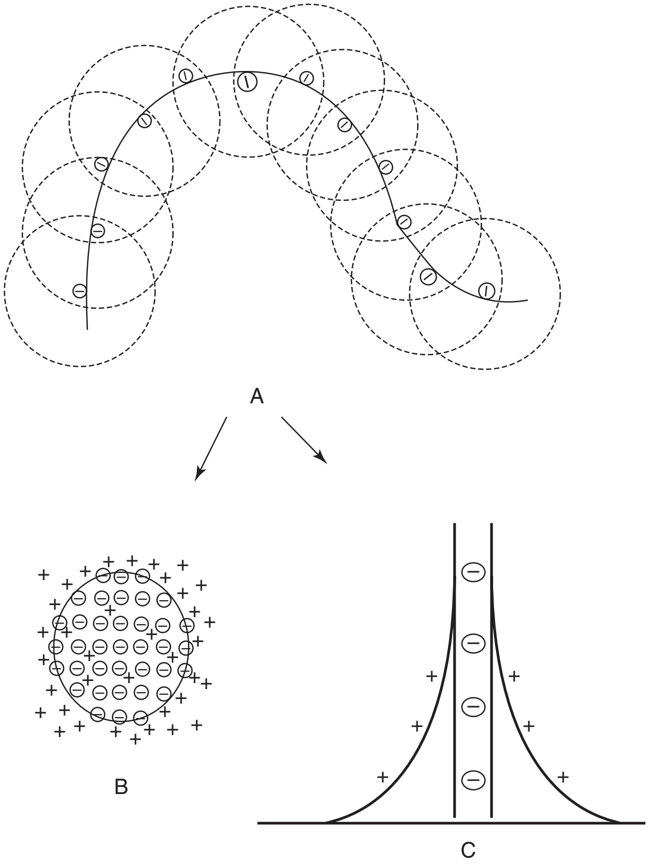

Figure 2. Models of polyelectrolyte molecule.

of the polymer molecule with a Gaussian distribution of segments. If we observe it from a point very close to the polymer chain, we only see part of the polymer chain, so that the polymer chain may be assumed to be a rod.

Figure 2B and C shows two examples of a model for linear, flexible polyelectrolyte molecules. Figure 2B is the porous sphere model of Hermans and Overbeek (see Chapter "Transport Phenomena of Linear Polyelectrolytes"), in which fixed charges are uniformly distributed inside a sphere [39]. This model may be useful when discussing the general behavior of a polyelectrolyte molecule such as viscosity, sedimentation, or diffusion (see Chapter “Transport Phenomena of Linear Polyelectrolytes”). Figure 2C is the rod-like model of Nagasawa and others (see Chapter “Ionization Equilibrium and Potentiometric Titration of Weak Polyelectrolytes”). This means that if we see the shape of a polyion from the position of counter-ions, which is close to the polyion, the flexible polymer chains may be regarded as a cylindrical rod. Nagasawa et al. assumed that fixed charges are distributed and smeared uniformly on the surface of the rod.

Each model has a limit of applicability. It is difficult to take into account the ionic atmosphere around fixed charges in the porous sphere model. Consequently, the expansion factor calculated is much higher than observed values (see Chapter “Radius of Gyration and Intrinsic Viscosity of Linear Polyelectrolytes”). Using a rod-like model makes it difficult to take into account the change in conformation of the polyion chain with the change in charge density of the polyion (see Chapter “Ionization Equilibrium and Potentiometric Titration of Weak Polyelectrolytes”).

Many works on polyelectrolytes were published about the system with added neutral salts. In the absence of added-salt, the electrostatic interaction between polymer molecules is so strong that it is not possible to extrapolate experimental data to include infinite dilution to obtain data per molecule. A different technique such as small-angle neutron scattering is required for the study of polyelectrolytes in pure aqueous solutions (see Chapter “Radius of Gyration and Intrinsic Viscosity of Linear Polyelectrolytes”).

IV. (SUPPLEMENT) PREPARATION OF LINEAR POLYMERS WITH NARROW MOLECULAR WEIGHT DISTRIBUTION (NMWD)

Monodisperse polymers, in which all molecules have an identical molecular weight, are not only required for the study of $P(\theta)$ but are also required for various rigorous studies in polymer science. It is well known that poly(styrene), poly(α-methyl styrene), and other nonionic polymers prepared by Szwarc’s et al. anionic polymerization method have NMWDs [40]. By modifying the methods of Szwarc, Fujimoto, Kitano, Choshi, and their coworkers prepared characteristic samples with NMWDs, including

1. **Poly(*tert*-butyl crotonate) (PTBC)** (nonionic stiff polymer) [41]: If *tert*-butyl crotonate monomer is highly purified, the monomer can

be polymerized with an anionic initiator. The polymerization occurs through a living mechanism. The PTBC has a stiff backbone due to steric hindrance between *β*-methyl and *t*-butyl groups and also NMWDs.

2. **Poly(sodium acrylate) (PNaA)** (polyelectrolyte) [42]: In anionic polymerization of acrylate monomers, anionic initiators usually attack both the α-proton and carbonyl group of the acrylate monomers. The latter can be protected by a bulky *t*-butyl group, as is well known. Kitano and Fujimoto found that the attack on the α-proton occurs only when anionic initiator and monomer are mixed, but a growing poly(acrylate) anion is not strong enough to attack the α-proton. The molecular weight distributions of poly(*t*-butyl acrylate) and poly(acrylic acid), obtained by its hydrolysis, were found to be narrow enough. Moreover, we can have the samples with very high molecular weights in addition to NMWD.
3. **Poly(styrene) with very high molecular weights and very NMWD** [43]: If a drop of *n*-hexylbenzene solution of *n*-butyllithium is added to the THF solution of styrene monomer purified as usual with strong stirring, the initiator is distributed uniformly to react with impurity while the drop is dissolving into the THF. The first drop does not start polymerization, but the second drop usually starts polymerization that proceeds without termination. The molecular weight distribution of poly(styrene) prepared in this way is much sharper than the molecular weight distribution of commercial poly(styrene) with NMWD, and the molecular weight goes over ten millions. Poly(α-methyl styrene) with very NMWDs can be prepared with a polymerization method based on the same idea as poly(styrene) [44]. The polydispersity index M_w/M_N of poly(α-methyl styrene)s is found to be as low as 1.01 or lower.
4. **Block copolymers of deuterated-styrene** for SANS experiments [45]: Commercial deuterated-styrene monomers contain impurities that are different from ordinary h-styrene monomers because of the difference in their preparation methods. Matsushita and Fujimoto et al. first carried out satisfactory anionic polymerization of d-styrene by removing these impurities.

These samples with NMWDs were essential for some of the researches discussed subsequently. Discussion on anionic polymerization, however, is out of the scope of this book.

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