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Generalized Correlations of Mean Activity Coefficients of Polyelectrolytes with Monovalent Gegenions in Aqueous Solutions

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In recent years, correlations have been presented whereby the mean ionic activity coefficients of many types of electrolytes can be estimated in both pure and mixed aqueous solutions at temperatures of 0 to 100°C, and at concentrations up to saturation (Meissner and Tester, 1972; Meissner and Kusik, 1972; Meissner et al., 1972; Kusik and Meissner, 1973; Meissner and Peppas, 1973; Kusik and Meissner, 1975; Kusik and Meissner, 1978). These correlations have been applied to monobasic acids, their neutral mono- and polyvalent salts, polybasic acids and their salts. It is desirable to extend these simple correlations to more complex ionic solutions, and especially to polyelectrolytic solutions.

Natural and synthetic polyelectrolytes are macromolecules with ionizable groups on their backbone chains. When dissolved in water they show characteristics of linear polymers and of electrolytes. Because of the combination of both features, their thermodynamic and hydrodynamic behavior in solution may be complicated. Typical synthetic polyelectrolytes include poly(styrene sulfonates), poly(acrylates) and poly(ethylene sulfonates). Their thermodynamic properties are of great importance in applications for ion-exchange resins, surfactants, etc. In addition, the study of polyelectrolytes can provide valuable information towards the understanding of the physicochemical behavior of biological molecules in solution, since polyelectrolytes are simplified models for these biomacromolecules.

The significance of the mean activity coefficient of polyelectrolytes in aqueous solutions was not fully recognized until the first contribution on the direct determination of this thermodynamic parameter was published (Ise and Okubo, 1965). Previously, attention had been paid only to the single-ion activity of gegenions or of ions of coexisting simple electrolytes. However, the single-ion activity can neither be a substitute for the solute activity nor represent physical phenomena correctly.

Determination of thermodynamic properties such as osmotic pressure of a mixed solution of a polyelectrolyte and a neutral salt, and ionic mobility, and analysis of polyelectrolytic transport phenomena such as viscosity, sedimentation, diffusion, electrophoresis and swelling call for preliminary knowledge of the mean activity coefficient, $\gamma_{\pm}$, at various temperatures and concentrations (Nagasawa, 1975). Indeed, the present work was undertaken because of the need to quantify thermodynamic phenomena related to the diffusion of polar solutes through novel resins of poly(styrene sulfonates) (Peppas et al., 1981).

Most of the experimental data available for $\gamma_{\pm}$ of polyelectrolytes in aqueous solutions at various temperatures and concentrations are well summarized in a standard reference (Ise, 1971). These data are frequently presented in graphical form by curves of $\gamma_{\pm}$ at 25°C for several electrolytes plotted against concentration, expressed as molality (moles of macromolecule per 100 g water). Inspection of these graphs (Ise, 1971) indicates that the variation of $\gamma_{\pm}$ with molality differs widely from one electrolyte to the next, and that considerable crossing of the curves occurs, so that no generalized graphical representation of all the data can be achieved.

Here the objective is to present a simplified graphical method for representation of activity coefficients of polyelectrolytes in aqueous solutions, applicable from low concentration to saturated solutions; and to show how this method can be used to determine the mean activity coefficient, $\gamma_{\pm}$, at any concentration if a single value of this parameter at a single concentration is known.

THEORY

In the proposed correlation, use is made of the reduced activity coefficient Γ, defined as

$$\Gamma \equiv \gamma_{\pm}{}^{1/z_{+}z_{-}} \tag{1}$$

Here z_{+} and z_{-} are the charges of the cation and anion of the polyelectrolyte in question. For example, in the case of poly(styrene sulfonate), z_{-} denotes the charge of the macroion poly(styrene sulfonate), and z_{+} denotes the charge of the gegenion.

Concentrations in the aqueous solution are expressed by the ionic strength, μ, defined as:

$$\mu = \frac{1}{2} m(\nu_{+} z_{+}^{2} + \nu_{-} z_{-}^{2}) \tag{2}$$

where ν_{+} and ν_{-} are the g-equivalents of gegenions and macroions respectively, which are formed upon dissociation of one mole of polyelectrolyte, and m is the molality of the polyelectrolyte expressed as mol/100 g H_2O.

To understand the thermodynamic behavior of polyelectrolytic solutions, it is important to understand the conformation of a macroion in solution. The macroion chain (polymer) attains a more or less randomly coiled conformation and it is surrounded by a cylindrical ionic atmosphere. It may be reasonable to assume that the macroion is represented by a rod which has smeared charges

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TABLE 1. POLYELECTROLYTE CHARGES AT 25° C IN AQUEOUS SOLUTIONS

Polyelectrolyte	Abbreviation	Degree of Polymerization	ξ	Effective Macroion Charge z_-	Reference for $\gamma_\pm$
Sodium Poly(Acrylate)	NaPAA	1640	2.85	1640	Ise and Okubo, 1965, 1967a
Sodium Poly(Ethylene Sulfonate)	NaPES	770	2.85	770	Ise and Asai, 1968
Sodium Poly(Styrene Sulfonate)	NaPSS	1090	2.85	1090	Ise and Okubo, 1968a
Sodium Poly(Vinyl Sulfate)	NaPVAS	1700	0.67	380	Ise and Okubo, 1967b
Sodium Poly(Vinyl Alcohol Glyoxalate) with 6 mol % Acetalization	NaPVAG-1	1700	0.29	172	Ise and Okubo, 1966a
Sodium Poly(Vinyl Alcohol Glyoxalate) with 10 mol % Acetalization	NaPVAG-2	1700	0.13	82	Ise and Okubo, 1966a

on its surface. It is also evident that not all charged species will be effectively "available" to contribute to a thermodynamic phenomenon and that the average molecular weight, which controls the end-to-end vector of the macroion, will also control the "effective charge" of the macroion in solution.

Therefore, the main problem for application to polyelectrolytes of theories similar to the ones developed for simple electrolytes (e.g., Meissner and Tester, 1972) is the determination of the effective charge z_- of the macroion in an aqueous solution. This problem can be overcome by using the Manning and Zimm (1965a,b) analysis of a polyelectrolyte. According to this theory, the effective macroion charge can be determined via a nonadjustable parameter, ξ, by replacing a real polyelectrolyte chain by an infinite linear charge. This parameter ξ characterizes an effective charge of the ions and it is expressed as:

$$\xi = \frac{e^2}{kTDb} \tag{3}$$

where e and D are the electronic change and dielectric constant of the polyelectrolyte, b is the distance between *neighboring charges on the macroion*, k is the Boltzman constant, and T is the absolute temperature.

Using this analysis it is possible to calculate the effective macroion charge for any polyelectrolyte of known molecular weight, as outlined by Ise and Okubo (1978). Calculated values of z_- for a series of polyelectrolytes are presented in Table 1. Values of the effective charge, z_-, are in certain cases smaller than the actual degree of polymerization, and they depend on the molecular conformation of the polyelectrolyte. Intense interactions between gegenions and macroions are known to deprive some of the gegenions of the freedom of motion, due to generations of extremely high electrostatic fields.

GENERALIZED CURVES

Based on the values of effective macroion charge, z_-, and using Eqs. 1 and 2, experimental data for a series of polyelectrolytes with monovalent gegenions were recalculated and plotted in Figure 1 (Ise and Okubo, 1965, 1966a, 1966b, 1967a, 1967b, 1968a, 1968b; Ise and Akai, 1968). These experimental data were obtained through electromotive force or osmotic pressure measurements. For simplicity, curves for only nine of these electrolytic salts are shown. It is noted that by plotting the mean activity coefficient data in terms of the reduced activity coefficient Γ, a family of nonintersecting curves was obtained. The activity coefficients in this paper are the values relative to those at a reference concentration of 10^{-3}M.

A generalized family of curves was obtained by use of polynomial computer fitting with horizontal and vertical shifting. The generalized graphs are shown in Figure 2.

The generalizations presented here apply to all polyelectrolytes for which experimental data of $\gamma_\pm$ versus m were available in the literature, with the exception of poly(ethyleneimine-hydrochlorides) (PEI-HCl) (Ise and Okubo, 1966b). The inability to apply this technique to PEI-HCl is attributed to the low degree of polymerization of the electrolytes studied (D.P. $\simeq$ 100), where the Manning analysis may not be applicable.

In general, attempts to extend this work to polyelectrolytes whose macroion is the cation have been limited by the lack of experimental data of $\gamma_\pm$ for this type of electrolytes.

APPLICATIONS

The main feature of the new generalized family of graphs is the absence of crossing curves for different polyelectrolytes. Therefore, knowledge of the value of the mean ionic activity coefficient, $\gamma_\pm$, of a polyelectrolyte at a single ionic strength, μ, makes it possible to determine $\gamma_\pm$ at a wide range of ionic strengths by simply tracing the entire curve within the family of curves of Figure 2. Although this characteristic feature of the Meissner method of electrolytic behavior has been retained in our analysis of polyelectrolytic behavior (Meissner and Tester, 1972; Meissner and Peppas, 1973) it is important to note that the shape of the family of generalized curves for polyelectrolytes (Figure 2 of this contribution) is different than the shape of the family of generalized

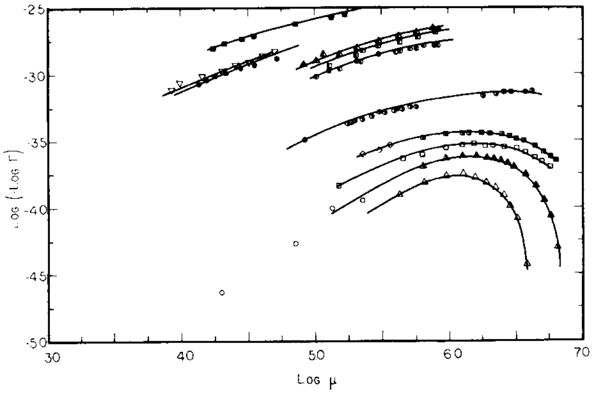

Figure 1. Variation of reduced mean activity coefficient of polyelectrolytes Γ with ionic strength μ in aqueous solutions at 25°C. Polyelectrolytes: ◑ NaPAA; ○ KPAA; △ LiPSS; ◨ NH_4PSS; □ KPSS; ▲ NaPSS; ● LiPVAS; ▽ NaPVAS; ■ KPVAS; ◐ LiPES; ◇ NH_4PES; ◨ NaPES; ▲ KPES.

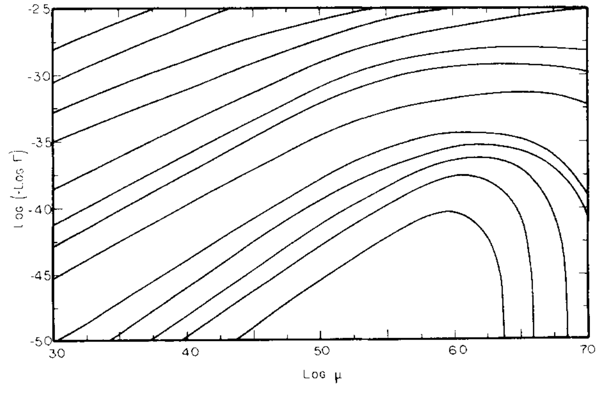

Figure 2. Generalized graphs of reduced mean activity coefficient of polyelectrolytes Γ versus ionic strength μ.

curves for electrolytes of low molecular weight (Figure 1 of Meissner and Peppas, 1973). In addition, these graphs do not converge to a value of $\gamma_\pm = 1$ at infinite dilution of the polyelectrolytic solution (as observed for simple electrolytic solutions), since intramacroion interactions still exist at infinite dilution. The mean activity coefficient of polyelectrolytes assumes values other than unity at infinite dilution. These values depend on the distance between ionized groups, which is determined by the conformation of macroions at this concentration.

The precision of estimation of $\gamma_\pm$ for polyelectrolytes using this method is satisfactory for industrial calculations. Maximum error of 4.2% was estimated for the polyelectrolytes used here. An example of the methodology of application of the new graphs follows.

Consider an aqueous solution of sodium poly(acrylate) for which a single value of $\gamma_\pm$ has been experimentally determined for a single molality. For convenience we shall use the value of $\gamma_\pm = 0.180$, which was determined for NaPAA of degree of polymerization D.P. = 1,640 at molality $m = 0.143$ and at 25°C (Ise and Okubo, 1967a). According to the analysis of Manning and Zimm (1965a) and the discussion of Ise and Okubo (1978), $z_- = 1{,}640$ and $z_+ = 1$. Using Eq. 1 the reduced activity coefficient is calculated as $\Gamma = 0.999$, whereas the ionic strength is calculated from Eq. 2 as $\mu = 1.92 \times 10^5$. These two values define a point (5.28, −3.35) in the generalized graphs of Figure 2. By tracing the single generalized graph which passes through this point, one can determine values of the mean activity coefficient of the same polyelectrolyte at other values of the ionic strength (molality) without performing additional experiments. For example, the point (6.35, −3.14) of Figure 2 gives $\gamma_{\pm}$, calc = 0.064 for $m = 1.65$. The corresponding experimental value (Ise and Okubo, 1967a) at the same molality is $\gamma_{\pm,\mathrm{exp}} = 0.066$.

The method of calculation of $\gamma_\pm$ can be applied to temperatures other than 25°C, since the general shape of the generalized curves is not dependent on temperature. Therefore, knowing one value of $\gamma_\pm$ at a single ionic strength μ and at temperature of 50°C, one can determine the mean activity coefficients of this polyelectrolyte at 50°C for the whole range of ionic strengths covered in Figure 2. Application of the generalized graphs at higher temperatures assumes that no molecular degradation of the macroion occurs at higher temperatures.

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NOTATION

b = distance between neighboring charges on a polymer macroion, Å
D = dielectric constant
e = electronic charge
k = Boltzman constant
m = molality of electrolyte, moles/100 g H_2O
T = absolute temperature
z_- = charge of macroion
z_+ = charge of gegenion

Greek Letters

$\gamma_\pm$ = mean activity coefficient of electrolyte
Γ = reduced activity coefficient
μ = ionic strength of electrolytic solution
ν_- = g-equivalents of macroion
ν_+ = g-equivalents of gegenion
ξ = Manning parameter

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