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THERMODYNAMIC PROPERTIES OF POLYELECTROLYTE SOLUTIONS CONTAINING MIXTURES OF MONOVALENT AND TRIVALENT COUNTERIONS

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The osmotic coefficients, heats of dilution, and volume changes on dilution of aqueous solutions containing mixtures of polystyrenesulfonic acid and its lanthanum salt have been determined at 25°C. The curve representing the osmotic coefficient as a function of the equivalent fraction of the acid has a maximum; the corresponding curves for the enthalpy and volume changes on dilution have a sigmoidal shape. Experimental results have been compared with predictions of the theory based on the cell model with cylindrical symmetry. A semiquantitative agreement between theory and experiment has been found.

1. Introduction

Various thermodynamic properties of pure polyelectrolyte solutions have mainly been studied with solutions containing as counterions only one ionic species. In a series [1–3] of articles from this laboratory the results of the measurements of the osmotic coefficient, heat of dilution, and volume change on dilution have been published for polyelectrolyte solutions containing monovalent as well as divalent counterions. In this paper our studies of mixed polyelectrolyte solutions have been extended to solutions with mixtures of monovalent and trivalent counterions and a similar set of thermodynamic data has been accumulated. The polystyrenesulfonate ion was chosen as a polyion, as in most of our previous studies, and mixtures of hydrogen and lanthanum ions as counterions.

2. Theoretical

In many previous articles the cell model [4,5] has been successfully applied for the interpretation of various thermodynamic properties of polyelectrolyte solutions. In this paper the same model will be employed for the computation of the osmotic coefficient, heat of dilution, and volume change on dilution for solutions with mixtures of mono- and trivalent counterions.

According to the cell model [4,5] the cylindrical polyion of radius a and length h carries ν negative charges and is enclosed by a larger concentric cylinder of radius R which contains the counterions. Supposing that the charges are uniformly smeared over the cylindrical surface of the polyion, the Poisson–Boltzmann equation and the boundary conditions for the system of mono- and trivalent counterions read

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = -\frac{4\pi e}{\epsilon}\rho, \qquad a \leqslant r \leqslant R, \tag{1}$$

$$\rho = n_1^0 \exp(-e\psi/kT) + 3n_3^0 \exp(-3e\psi/kT),$$

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_{r=a} = \frac{2\nu e}{\epsilon a h}, \qquad \left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_{r=R} = 0, \tag{2}$$

where ψ is the electrostatic potential, r is the distance from the cylinder axis, ϵ is the dielectric constant of the solvent, ρ is the number density of charges, e is the protonic charge, k is the Boltzmann constant, T is the absolute temperature, and n_1^0 and n_3^0 are the numbers of monovalent and trivalent counterions per unit volume at $r = R$, i.e., at $\psi = 0$, respectively.

The osmotic coefficient of this system may be defined by analogy with solutions having only one counterionic species [6] by

$$\varphi = (n_1^0 + n_3^0)/(\bar{n}_1 + \bar{n}_3), \tag{3}$$

where $\bar{n}_1$ and $\bar{n}_3$ are the average number densities of monovalent and trivalent ions, respectively.

The key formulae for heat of dilution, $\Delta H_{\mathrm{D}(c_1\to c_2)}$, and for volume change on dilution, $\Delta V_{\mathrm{D}(c_1\to c_2)}$, are closely analogous. These two properties are defined as the enthalpy and volume changes when a polyelectrolyte solution is diluted from concentration c_1 to c_2 and are calculated per mole of monomer units. Formally they may be split into two terms:

$$\Delta H_{\mathrm{D}(c_1\to c_2)} = \Delta H^0_{(c_1\to c_2)} + \Delta H_{\mathrm{e}(c_1\to c_2)}, \tag{4}$$

and

$$\Delta V_{\mathrm{D}(c_1\to c_2)} = \Delta V^0_{(c_1\to c_2)} + \Delta V_{\mathrm{e}(c_1\to c_2)}, \tag{5}$$

where ΔH^0 and ΔV^0 are the nonelectrostatic and ΔH_e and ΔV_e are the electrostatic contributions. In the present calculation ΔH^0 and ΔV^0 are assumed to be much smaller than ΔH_e and ΔV_e, respectively, and are therefore neglected. This assumption has been successfully applied in the interpretation of the enthalpy and volume changes on dilution of polyelectrolyte solutions containing only one counterionic species [7,8].

It has been shown in previous papers [2,3] that the excess function H_e and V_e, calculated per monomole of polyelectrolyte, are given by

$$H_\mathrm{e} = \frac{RT}{4\lambda}\left(1 + \frac{\mathrm{d}\ln\epsilon}{\mathrm{d}\ln T}\right)\int_0^\gamma \left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)^2 \mathrm{d}t, \tag{6}$$

and

$$V_\mathrm{e} = -\frac{RT}{4\lambda}\,\frac{\mathrm{d}\ln\epsilon}{\mathrm{d}P}\int_0^\gamma \left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)^2 \mathrm{d}t, \tag{7}$$

$$-e\psi/kT = \phi, \quad r = a\exp(t), \quad R = a\exp(\gamma), \tag{8}$$

where R is the gas constant, P is the pressure, and the charging parameter λ has been defined [4] by

$$\lambda = \nu e^2/\epsilon kTh. \tag{9}$$

For the evaluation of the integral in eqs. (6) and (7) we have to solve the Poisson–Boltzmann eq. (1) and (2). Introducing dimensionless quantities of eqs. (8) and (9) and considering the electroneutrality condition, $\nu = (\bar{n}_1 + 3\bar{n}_3)V$, $V = \pi(R^2 - a^2)h$, we obtain on the analogy of a previous paper [9] a more convenient form of eq. (1):

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}t^2} = \frac{4\lambda\exp(2t)}{\xi[\exp(2\gamma)-1]}\left[N_1^0\exp(\phi) + N_3^0\exp(3\phi)\right], \tag{10}$$

where N_1^0 and N_2^0 are the equivalent fractions, d
as

$$N_1^0 = n_1^0/(n_1^0 + 3n_3^0), \qquad N_3^0 = 1 - N_1^0,$$

and

$$\xi = (\bar{n}_1 + 3\bar{n}_3)/(n_1^0 + 3n_3^0).$$

The boundary condition [eq. (2)] and $\psi(R) = 0$
read

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)_{t=0} = -2\lambda, \qquad \left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)_{t=\gamma} = 0, \qquad \phi(\gamma) = 0.$$

The average values of the equivalent fraction
and $\bar{N}_3$ are calculated from

$$N_1^0\int_0^\gamma \exp[2t + \phi(t)]\,\mathrm{d}t = \tfrac{1}{2}\bar{N}_1\,\xi[\exp(2\gamma)-1],$$

$$N_3^0\int_0^\gamma \exp[2t + 3\phi(t)]\,\mathrm{d}t = \tfrac{1}{2}\bar{N}_3\,\xi[\exp(2\gamma)-1]$$

which follows from the electroneutrality condit

Likewise, the osmotic coefficient φ, eq. (3),
expressed with equivalent fractions of monoval
species and ξ:

$$\varphi = (1 + N_1^0)/\xi(1 + \bar{N}_1).$$

For the numerical calculations we have appli
same method as described elsewhere [2]. The c
puted values of the integral in eqs. (6) and (7) a
plotted in fig. 1 against the equivalent fraction
monovalent counterionic species $\bar{N}_1$, for variou
of γ and for the structural value [6] of the char
parameter λ ($\lambda = 2.83$ at 298.15 K with $\epsilon = 78.5$
$h/\nu = 2.52$ Å).

3. Experimental

Sodium polystyrenesulfonate, NaPSS (mol.
100 000; degree of sulfonation, 1.00), purchase
Polysciences Inc. (Rydal, Pa.) was used as starti
material. After careful purification [10] the so
salt was converted to the acid. Solutions with v
ratios of H^+ and La^{+++} ions were prepared by a
appropriate amounts of La_2O_3 to the acid solu
The exact concentrations of the H^+ and La^{+++}
were determined by potentiometric titration an
chelometric EDTA titration with biamperomet
point indication [11], respectively.

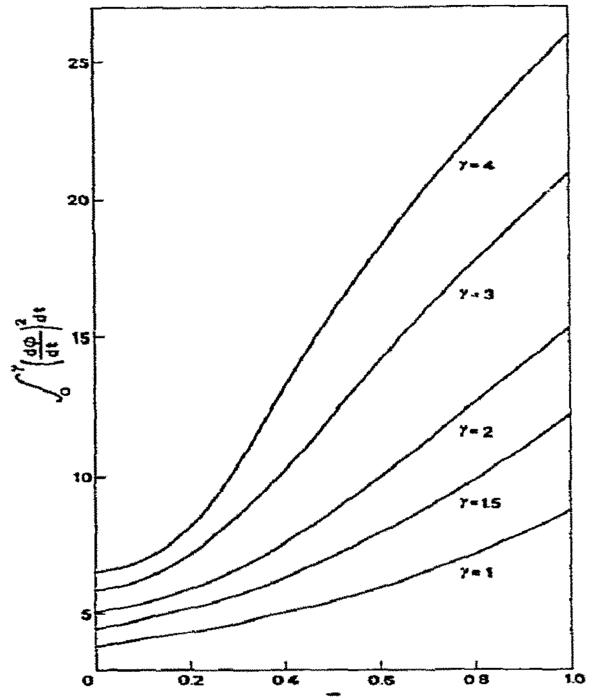

Fig. 1. The integral in eqs. (6) and (7) as a function of the equivalent fraction of the monovalent counterionic species $\bar{N}_1$, for various values of the concentration parameter γ.

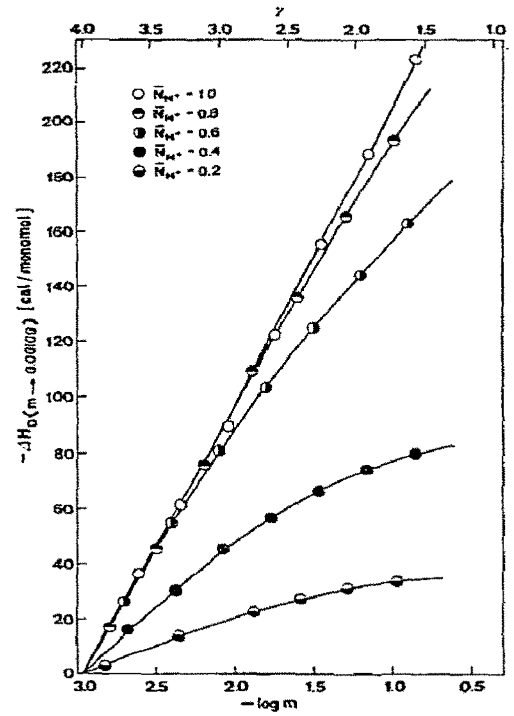

Fig. 2. Enthalpies of dilution of aqueous solutions containing mixtures of polystyrenesulfonic acid and its lanthanum salt at 25°C as a function of polyelectrolyte monomolality and for various equivalent fractions of the acid $\bar{N}_{H^+}$.

For a few equivalent fractions of the acid the osmotic coefficients were obtained from the freezing point depression measurements. Since relatively large amounts of polymer material are required in these experiments [10], in later measurements the osmotic pressure method was applied. The results of the two methods were in good agreement. The osmometer was a commercial Melabs recording osmometer Model CSM-2. Experimental details have been described elsewhere [12].

Calorimetric measurements were carried out at 25°C using the same calorimeter as in our previous heat of dilution measurements [13].

Linderstrom–Lang dilatometers were used for volume change measurements. Typical experiments were performed at 25°C by mixing 4.00 ml of a polyelectrolyte solutions with 4.00 ml of water, and observing the resulting volume decrease. All details concerning experimental technique have been described previously [8].

4. Results and discussion

Experimental osmotic coefficients, enthalpies of dilution, and volume changes on dilution were plotted against the logarithm of monomolality m for various constant equivalent fractions of the acid. An example of such variation is shown for the enthalpy of dilution in fig. 2. The values of φ, ΔH_D, and ΔV_D for pure acid ($\bar{N}_1 = 1$) were taken from our recent articles [12,2,8] in which the same polymer sample as in the present studies was used. Because a gel formation was observed at the equivalent fractions of the acid lower than 0.1, the lowest fraction studied was $\bar{N}_1 = 0.14$. The upper scale in fig. 2 gives the value of the concentration parameter γ, which has been defined by eq. (8) and which is related to the monomolar concentration c by [14]

$$\gamma = \ln (R/a) = \tfrac{1}{2} \ln (10^3/\pi a^2 b N_A) - \tfrac{1}{2} \ln c. \qquad (16)$$

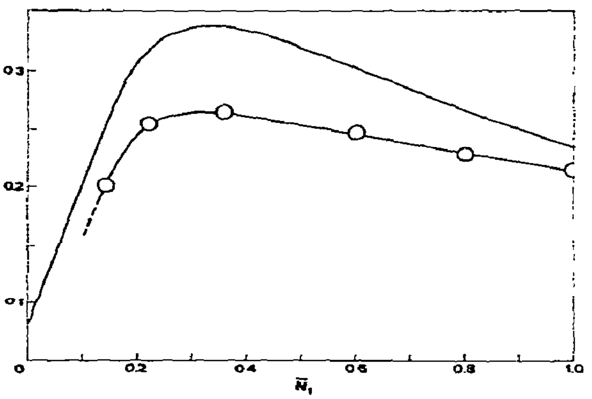

Fig. 3. Comparison of the experimental osmotic coefficients of mixtures of HPSS and LaPSS in water at 25°C (points) with those predicted by theory (upper curve). Polymer concentration: 0.001 monomol/kg H_2O.

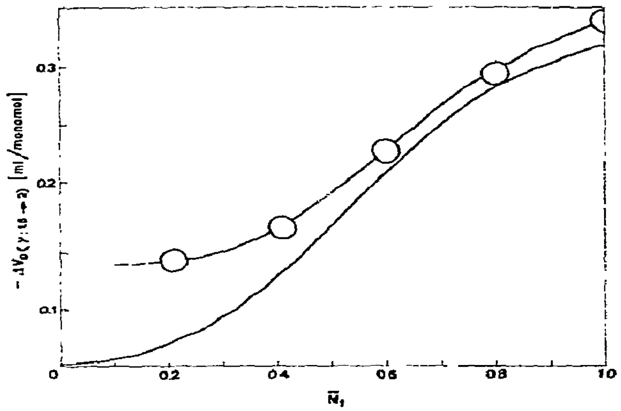

Fig. 5. Comparison of the experimental volume change on dilution of mixtures of HPSS and LaPSS in water at 25°C (points) with that predicted by theory (lower curve). Concentration range from 0.163 to 0.0600 monomolar.

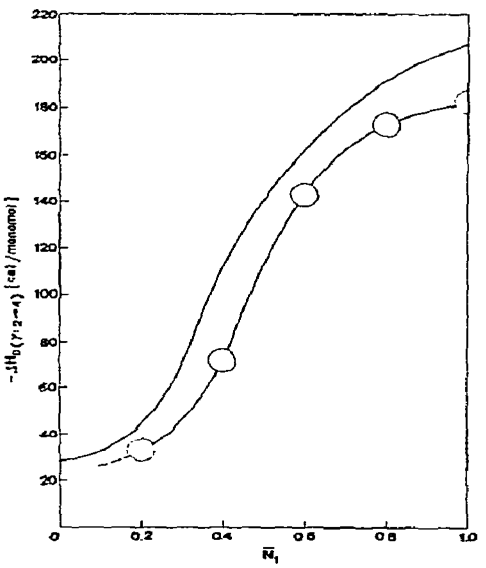

Fig. 4. Comparison of the experimental enthalpy of dilution of mixtures of HPSS and LaPSS in water at 25°C (points) with that predicted by theory (upper curve). Concentration range from 0.0600 to 0.00110 monomolar.

In this equation b is the length of a monomeric unit and N_A is Avogadro's number. In calculating γ from eq. (16) the difference between molality and molarity was neglected.

The experimental and theoretical curves, presented in figs. 3, 4, and 5, show the variation of φ, ΔH_D, and ΔV_D with the equivalent fraction of the acid, respectively. The points were taken from experimental curves, such as the one for ΔH_D shown in fig. 2, while the corresponding theoretical curves were calculated from eqs. (15), (4), (5), (14), (6), and (7), using for the charging parameter λ its structural value 2.83. For the parameters characteristic for solvent, the values for water at $T = 298.15$ K and $P = 1$ bar were used [15]: $\epsilon = 78.36$, $\mathrm{d}\ln\epsilon/\mathrm{d}\ln T = -1.368$, $\mathrm{d}\ln\epsilon/\mathrm{d}P = 4.71 \times 10^{-5}$ bar^{-1}, and the value 8.0 Å was taken for the macromolecular radius a.

It is seen that the agreement between experimental and calculated values is not quantitative, however, the characteristic shapes of the curves are properly predicted. This finding generally accords with the results of previous studies on thermodynamic properties of pure polyelectrolyte solutions. They disclosed [6] that observed values are equal to the calculated ones for the truly rodlike polyelectrolyte such as DNA, but for flexible-chain polyelectrolytes, for which the rodlike model is a relatively crude approximation, experimental and theoretical values differ to a certain extent. The point should be stressed that similar behavior of φ, ΔH_D, and ΔV_D as observed in the present studies, has also been found with polystyrenesulfonate solutions containing mixtures of monovalent and divalent counterions [1–3], experimental values of φ and ΔH_D being lower and those of ΔV_D higher than the theoretical ones. One of the reasons for too low calculated values of ΔV_D, discussed previously [3], originates from the fact that a minor simplification has been made in the calculation leading to eq. (7). The error introduced in this way has been estimated [3] to about 10% in the concentration range of this study. This can explain too low calculated values of ΔV_D only at equivalent fractions $\bar{N}_1$ higher than 0.5 but cannot explain a large difference between calculated and experimental values at low $\bar{N}_1$. The reason for this discrepancy can be sought in the fact that the theory is a purely electrostatic one and does not take into account the increasing noncoulombic interactions between ions at higher concentrations at which the volume change measurements were carried out.

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