

Thermodynamic Study of Polyelectrolytes in Aqueous Solutions without Added Salts: A Transition from Neutral to Charged Macromolecules

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A systematic study on aqueous solutions of uni- and polyvalent salts of a strong acid type of polyelectrolyte with very low and medium charge density was carried out after application of a special purification method to minimize the effect of ionic contamination. A very effective gel-deswelling technique was used for the measurement of relative activity of water in a wide range of concentration with reproducibility of $\pm 3 \times 10^{-6} - 2 \times 10^{-5}$ in the range $-5 \times 10^{-6} > \ln a_1 > -2 \times 10^{-3}$ at 298 ± 0.01 K. The analysis of data has shown that the lattice theory of polymer solution could be successfully applied to polyelectrolyte solutions introducing only a slight modification. The osmotic properties of such systems, the degree of dissociation, and related quantities will be discussed in the paper. A new method for separation of ionic effect will also be given.

Introduction

The interdisciplinary character of research on synthetic polyelectrolytes is often emphasized since the majority of biopolymers are carrying groups capable of producing screened and more or less localized electric charge along macromolecules. Also, polyelectrolytes have always played an important role in the colloid and surface science either as stabilizing/flocculating agents or as materials being able to modify dramatically the electric behavior of the interfacial region. There is a quickly growing interest in their widespread technological applications, too.

To understand their properties, studies were carried out predominantly on aqueous solutions focusing on conformation and solution thermodynamics in the presence or absence of different sorts of additives, mainly salts of low molar mass. The latter are likely the most complex solutions which contain one macromolecular component. However, because of some difficulties, relatively little attention was paid to their binary aqueous systems partly as a consequence of the self-dissociation of water itself and because of some experimental problems in the removal of undesirable ionic contaminations.

In thermodynamic studies of polyelectrolyte solutions polyacrylates, highly substituted polystyrene, e.g., polystyrene sulfuric acid and its salts, are the most favorable materials^{1–7} although some cationic polymers^{8–11} as well as sulfated copolymers of poly(vinyl alcohol) (PVA) were also applied.^{12–14} For determination of solvent thermodynamic activity, the isopiestic method was frequently used^{5–7,14} while measurements of the osmotic pressure were less preferred^{1,15–17} though it is, at least in principle, the most accurate method that can give absolute values for the activity of solvent.

However, it has been clearly revealed by a careful study of the literature^{1–17} that there are no systematic thermodynamic data available for polyelectrolytes of low and medium linear charge density and also at low polymer concentration. Therefore, the primary aim of the present work is to provide experimental data for the salt-free aqueous solution of a series of statistical

vinyl alcohol–vinyl sulfate ester copolymers (PVS) based on a well-studied water-soluble neutral polymer PVA. Because of the hydrophilic character of pure PVA it was feasible to study the effect of a transition from a neutral to “polyelectrolyte state” on thermodynamic properties of their solutions. For solubility reasons, this cannot be done with polyelectrolytes derived from polystyrene or from other hydrophobic polymers. These model systems make possible the study of the transition from point to line charge arrangement, too. For determination of the activity of the solvent, a very effective, so-called gel-deswelling (GD) method¹⁸ was applied with a much greater sensitivity than that of the isopiestic measurement, especially in the range of low linear charge density and low polyelectrolyte concentration. Both earlier¹⁹ and newer¹⁸ versions of this technique were successfully applied for the study of thermodynamic properties of neutral hydrogels. Also, details of a new purification procedure will be given that made possible preparation of polyelectrolyte solutions in the form of the lowest ionic contamination. By the application of the “dialysis in bag” method, polyelectrolyte solutions even free of CO₂ could be produced.

Experimental Section

Materials. The inorganic salts (LiCl dried, BDH, England; La(NO₃)₃·6H₂O, Carlo Erba, Italy; MgSO₄ dried, Ferak Berlin, Germany; CuSO₄·5H₂O, NaCl, CsCl, BaCl₂ Reanal, Hungary) used were all analytical grade and were not subjected to further purification. Aqueous solutions of these salts were made with single distilled water of specific conductivity $3.0\text{--}3.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

Synthesis, Purification, and Analysis of Polyelectrolyte Salts. A mild and highly reliable method has been worked out earlier²⁰ for the preparation of PVA and PVS copolymers in a very wide range of linear charge density (vinyl sulfate ester content). It is essentially an equilibrium esterification of a carefully hydrolyzed PVA by sulfuric acid at temperature below 8–10 °C. In the present work, the same parent polymer, namely, a hydrolyzed and partially fractionated PVA sample (POVAL 420, Kuraray Co., Japan), was used, the characteristics of which are given in the previous publication.¹⁸ From this polymer, a series of polyelectrolytes was synthesized with a variation in

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TABLE 1: Characteristic Data of Polyelectrolyte Samples

sample	VSO ₄ ⁻ content (mol %)	$\bar{M}_n \times 10^{-4}$ (g·mol ⁻¹) ^a ±15%	densities of dry polymers ^b (g·cm ⁻³ , 298 K)	molar volume ratio ^c ($\bar{x}_n \times 10^{-3}$)	A in eqs 1 and 2
PVA	0.0	7.0	1.251 ± 0.002	3.1	0.255
PVS/0.64/Na	0.64 ± 0.04	7.1	1.258	3.1	0.259
PVS/1.22/Na	1.22 ± 0.06	7.2	1.264	3.2	0.265
PVS/1.72/Na	1.72 ± 0.08	7.3	1.268	3.2	0.270
PVS/3.62/Na	3.62 ± 0.12	7.6	1.288	3.3	0.289
PVS/3.62/Cu		7.6	1.306	3.3	0.309
PVS/3.62/La		7.7	1.305	3.3	0.308
PVS/5.60/Na	5.60 ± 0.10	7.9	1.306	3.4	0.308
PVS/5.60/Li		7.8	1.289	3.4	0.293
PVS/5.60/Cs		8.9	1.358	3.6	0.361
(PVS/7.8/Na)	7.80 ± 0.20	8.3		(3.5)	
PVS/7.8/Cu		8.4	1.369	3.4	0.372
PVS/7.8/La		8.6	1.369	3.5	0.372
PVS/8.1/Na	8.10 ± 0.20	8.3	1.330	3.5	0.331
PVS/8.1/Mg		8.2	1.330	3.4	0.332
PVS/8.1/Ba		8.9	1.391	3.6	0.392

^a The value for PVA was taken from ref 18; others were calculated from this and from the composition of samples. ^b Calculated from solution density data. ^c (Molar volume of polymer) × (molar volume of water)⁻¹.

the vinyl sulfate content from 0.5 to ~10 mol %. For determination of the ester content, mainly conductometric and, in some selected cases, potentiometric titrations were used. The samples were stored in the form of sodium salts in dried state. The copolymers were found to be chemically stable for years. The decisive step before activity measurement was the preparation of polyelectrolyte solution with the lowest possible ionic contamination. The dialysis is commonly used for this purpose; however, in the laboratory practice there are some difficulties if realization of the highest purity is the main goal. Namely, if the dialysis is performed at atmospheric circumstances, as it is usually done, the absorption of CO₂ (and other components of air) can occur during this long-term process. Also, during dialysis especially against distilled water, the large osmotic effect of the polyelectrolyte solution causes considerable dilution. To overcome these difficulties, the following procedure was used.

First, a concentrated (approximately 5 mass %) solution of the sodium salt was prepared in single distilled water, and to this, a large excess of NaCl was added. This ensured that all sulfate ester groups carried Na⁺ counterions and that all other ionic contaminant were displaced from the polymer chains. Then the solution was dialyzed against single distilled water until the specific conductivity of the outer solution had reached the range $4-7 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. At this stage of the experiment, the whole dialysis set up was placed in a double plastic bag which contained also a very effective CO₂ absorbent (Soda Lime, Molecular Product, Essex, England) in an open glass box. The upper part of the bag could be sealed in an airtight manner. Preliminary tests have shown that placing a little amount of good quality double distilled water (Muldestor, Wagner-Munz, Germany) inside plastic bag increased its initial specific conductivity ($0.8-1.0 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) slowly ($0.05-0.2 \mu\text{S/day}$), while in an open-air test, this increment was at least 10 times greater. In the case of the first "closed space" dialysis, approximately 100 cm³ solution was filled into an 90 cm long and 3.1 cm flat size Visking dialysis tubing, which was subsequently immersed into 800 cm³ double distilled water and dialyzed for 24–30 h. During this time, the liquid level in the tubing reached ~75% of the full length of tubing. As the next step, the solution was quickly transferred into a conical flask, then the system was connected to a water jet vacuum pump, and the temperature of the solution was kept around 30 °C. From this carefully sealed system, the excess of water was distilled out (the volume of solution was reduced) under reduced

pressure. At a final volume of 40–50 cm³, the solution was filled in the original dialysis tubing (kept in the closed place until) and dialyzed again against double distilled water. The conductivity control of the outer phase has shown that by the application of this procedure (if necessary it was repeated two or three times) a minimum specific conductivity amounting to about 2.0–3.0 μS could be reached. Taking into account the Donnan effect, the concentration of the possible ionic contamination was assumed to be a little less than $10^{-5} \text{ mol L}^{-1}$. It is important to note here that the freshly degassed stock solutions were used to make a series of solutions for density measurements.

Similar treatment was applied in preparation of polyelectrolyte salts containing counterions other than Na⁺. Here, starting from sodium salts, the first 5 mass % solution was made with single distilled water, then a large excess of the salt ($\times 50$, $\times 100$, depending on its solubility) containing the cation in question was added and dialyzed against single distilled water until a relatively low value of the conductivity of the outer phase. This procedure was repeated at least three times in order to complete the ion-exchange process. (For some selected samples, inductively coupled plasma atomic emission spectroscopic and total reflection X-ray fluorescence measurements were carried out, showing unambiguously that the exchange of cations was exactly stoichiometric.)²¹ As a final step, the "dialysis in a bag" as well as the vacuum concentration method was used to minimize conductivity of the outer phase. The concentrated solutions thus obtained were kept in a refrigerator at 8 °C until use. The pH of solutions was in the vicinity of that of double distilled water (pH \approx 5.8–6.5). All important characteristics of the samples applied during the experiments are summarized in Table 1. The number in the notation means the composition (vinyl sulfate content) of the sample in mole %.

Density and Conductivity Measurements. For determination of densities of polyelectrolyte solutions, DMA 60 Density Meter (Anton Paar, Austria) with a DMA-602 measuring cell was used at $298 \pm 0.001 \text{ K}$. In each case, at least two parallel measurements were performed, and reproducibility within $\pm 5 \times 10^{-6} - 1.0 \times 10^{-5}$ was obtained. In the range studied, the dependence of density on polymer mass fraction was found to be strictly linear (in most of the cases the correlation coefficient was 0.9999) and equations were derived for calculation both the volume fraction, v_2 , and concentration, c , in $\text{g}\cdot\text{cm}^{-3}$

$$v_2 = \frac{w_p}{\rho_p}(0.99705 + Aw_p) \quad (1)$$

and

$$c = w_p(0.99705 + Aw_p) \quad (2)$$

where w_p is the mass fraction of the polymer, ρ_p is the density of the dry polymer calculated from solution densities, and the values of constant A for each polyelectrolyte salt are given in the last column of Table 1.

For measurements of electric conductivity of aqueous solutions and also controlling the purification process, a conductivity meter type OK-102/1 (Radelkis, Hungary) was used. In the cylindrical glass conductivity cell, the temperature (298 ± 0.01 K) was kept constant by a Lauda C12 circulating bath.

Determination of the Activity of Solvent in Binary Solutions of Polyelectrolyte Salts. The essential feature of the GD method¹⁸ is that, if for a swollen gel the dependence of solvent activity is known as a function of polymer concentration in the network and then this “calibrated” gel is placed into a semipermeable tube, the change in the volume (or mass) of gel membrane will be highly sensitive to the activity of solvent of the polymer solution in which this arrangement is immersed. In our case, a water-soluble poly(vinyl alcohol, vinyl acetate) copolymer was cross linked to form a thin gel membrane (denoted in the previous work¹⁸ as 8/10/400), and it was calibrated with solutions of poly(vinyl pyrrolidone) (PVP) in a wide range of polymer concentrations. For this polymer, very reliable osmotic pressure data can be found in the literature,²² so in the water activity range studied, the relative experimental error was thought to be less than 1%. By this method, it was possible to measure the activity of water from ~ 0.999990 to 0.99800 , which is well outside the range available by the isopiestic measurements. The reproducibility of, and the experimental error in, the $\ln a_1$ values around -10^{-4} were $\pm 3-5 \times 10^{-6}$, while at its lower values (at $\sim -10^{-3}$) amounted to a good approximation to $\pm 1 \times 10^{-5}$ when the gels were calibrated with PVP solutions. At activities close to unity, the sensitivity of the gel to a change in $\ln a_1$ was $\cong 1.6 \times 10^{-6}/1.0 \times 10^{-3}$ of change in the mass fraction of polymer in the gel. As a general experience, it can be stated that with increasing charge density the experimental error in $\ln a_1$ went up to 2×10^{-5} for the sample having the highest sulfate content. The temperature of measurements was 298 ± 0.01 K. In the heat-insulated plastic box where the samples, 20–30 at a time, were placed, the fluctuation in the temperature was assumed to be an order of magnitude less. The time necessary to attain equilibrium was 8–10 days. At equilibrium, the mass fractions of the polymers both in the gel membranes and polyelectrolyte solutions were determined by gravimetry with a relative error of $\pm 0.5-1\%$. To minimize the occurrence of accidental contamination during experimental work, special precaution had to be applied when handling both the carefully purified dialysis tubing and gel membranes. They were always touched with hands wearing surgical rubber gloves soaked previously in distilled water and, if necessary, with plastic tweezers.

In this work, the calibration of the gel membranes was extended toward lower solvent activities and the new series of experimental points fit very well to the previously determined¹⁸ $\ln a_1$ vs polymer mass-fraction function (Figure 1S in Supporting Information).

Results and Discussion

Chemical Potential of Water and Related Quantities for Polyelectrolyte Salts in Aqueous Solutions. In a work dealing

with thermodynamic properties of solution, one of the most important quantities is the chemical potential of one of the components. If it is known, by making use the Gibbs–Duhem equation, it can be calculated for other components, too. According to the nature of the experimental technique used in this work, it was the chemical potential of water with which we intend to deal.

The dependence of $\Delta\mu_1/RT$ on volume fraction is shown for all sodium salts of the PVS copolymers and also for pure PVA in Figure 1. The solid lines here and in the subsequent figures were obtained by a nonlinear curve-fitting procedure resulting in very good (~ 0.999) correlation coefficients. The curves obtained for the samples PVS/5.6/Li and PVS/5.6/Cs were hardly distinguishable from the corresponding sodium salt (Figure 2S in Supporting Information). Some difference between these has appeared only at higher concentrations. However, a dramatic effect was observed for counterions of higher charge number. Namely, with increasing valency of the counterions, the $\ln a_1$ vs v_2 curves become less steep, and for the La^{3+} salts there was only a slight deviation between curves referring to copolymers with considerable difference in their linear charge density (Figure 2). Although in the present work the osmotic pressure has not been measured directly, it could be calculated easily from the well-known relationship

$$\pi = - \frac{RT \ln a_1}{\bar{V}_1} \quad (3)$$

where π is the osmotic pressure, \bar{V}_1 is the partial molar volume of solvent, and R and T have their usual meaning. The partial molar volume of water was taken to be constant, and a value of $18.069 \text{ cm}^3 \text{ mol}^{-1}$ was accepted. The concentration dependence of osmotic pressure was calculated for all sodium salts, and in case of the sample PVS/8.1/Na, it went up to several atmospheres (several hundred thousands in Pa), showing one of the great advantages of the GD method.

In the polymer science, the reduced osmotic pressure, i.e., πc^{-1} , is widely accepted and applied for the determination of the number average molar mass of a polymer and, for reasons of dimensionality, the concentration should be given in mass/volume of solution unit. The concentration dependence of the osmotic pressure for non ideal solution can be given by the virial expansion

$$\frac{\pi}{c} = A_1 + A_2c + A_3c^2 + \dots \quad (4)$$

where A_1 ($RT\bar{M}_n^{-1}$), A_2 , A_3 , etc. are the osmotic virial coefficients. For neutral polymers, the second and third virial coefficients are usually positive.^{22,23} According to general experiences, for polyelectrolytes, the second virial coefficient has a much higher value and it depends strongly on the linear charge density and ionic strength.^{24,25} However, to the best knowledge of the author, no systematic data are available in the literature for polyelectrolytes without added salts.

The reduced osmotic pressure as a function of polyelectrolyte concentration is given for the PVS sodium salts in Figure 3. Of the unusual form of these functions, much important information can be obtained. First, the curves clearly show two distinct ranges of polyelectrolyte concentration. Below $c \approx 0.02$, both the curvature (determined by the second and third virial coefficients) and the intercepts grow rapidly with the linear charge density. Similar functions were obtained for some Li^+ and Cs^+ salts as well as for counterions of higher charge number (Figures 3S and 4S in Supporting Information). (The experi-

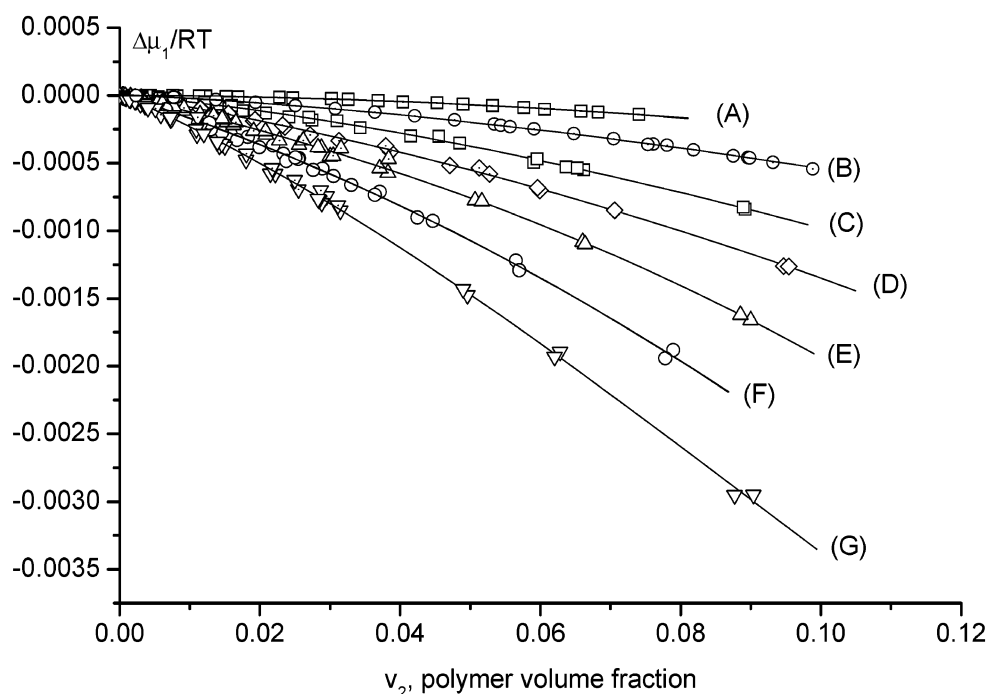


Figure 1. Dependence of $\Delta\mu_1/RT$ on volume fraction of polyelectrolytes at 298 ± 0.01 K. Data refer to all sodium salts. Curves: (A) pure PVA; (B) PVS/0.64/Na; (C) PVS/1.22/Na; (D) PVS/1.72/Na; (E) PVS/3.62/Na; (F) PVS/5.60/Na; (G) PVS/8.1/Na. Solid lines: fitted polynomials.

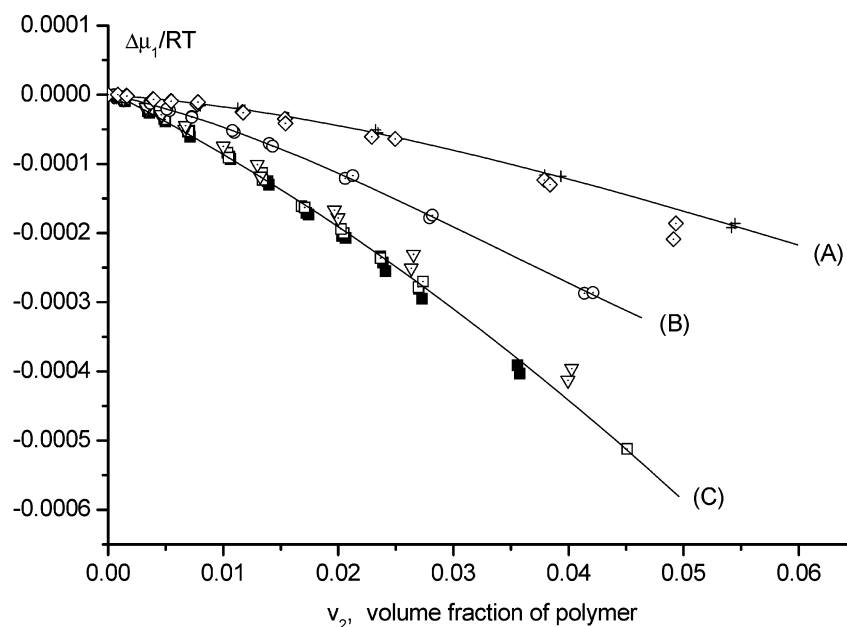


Figure 2. Dependence of $\Delta\mu_1/RT$ on volume fraction of polyelectrolytes at 298 ± 0.01 K. The effect of the quality of bi- and trivalent counterions. (A) Group of data: (+) PVS/3.62/La; (\diamond) PVS/7.8/La. (B) PVS/3.62/Cu. (C) Group of data: (∇) PVS/7.8/Cu; (\blacksquare) PVS/8.1/Mg; (\square) PVS/8.1/Ba. Solid lines: (A) the best fit to the experimental data of sample PVS/3.62/La; (B) the best fit to data of PVS/3.62/Cu; (C) the best fit to data of PVS/8.1/Ba salts.

mental points were fitted with a computer-aided two-step nonlinear curve-fitting procedure.) Because of the experimental error involved in the activity measurement, the scattering in the intercepts was estimated to be at least ± 10 – 20% , while the relative error in the values of the virial coefficients was much higher. The calculated values of these coefficients for the sodium salts are summarized in the Table 2. As regards the data, two essential observations are worth mentioning. First, it is obvious that the intercepts can be related solely to an apparent number average molar masses, $\bar{M}_{n,app}$, of samples, because in dilute solution, a part of the counterions will dissociate and will dramatically increase the number of osmotically active particles

in unit volume of the system. Thus, for such a situation, the osmometry cannot be used for determination of the real molar mass. For samples used in the present work, the intercept should have been around 0.30×10^5 ($\text{Pa} \cdot \text{cm}^3 \cdot \text{g}^{-1}$). Second, as it is listed in Table 2, the third virial coefficients have high negative values which can be an explanation for the “back-folding” character of all the πc^{-1} vs c curves. Functions with similar shape have been published by Oth and Doty²⁶ measuring light scattering of solutions of poly(acrylic acid) with different degrees of neutralization. However, the essential difference between the osmotic and light-scattering method is that for the latter the common intercept of the $(Kc/R_{90})P(90)$ vs c plot is

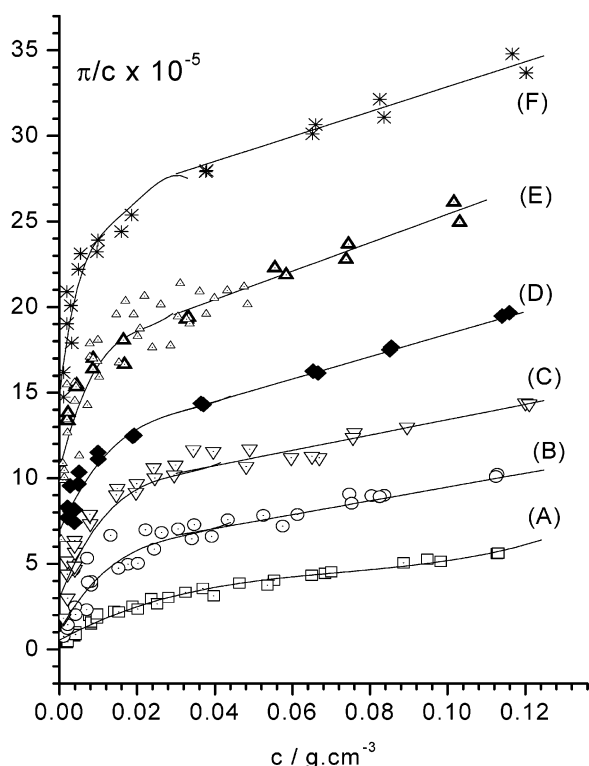


Figure 3. The concentration dependence of the reduced osmotic pressure, π/c , for all sodium salts. Curves: (A) PVS/0.64/Na; (B) PVS/1.22/Na; (C) PVS/1.71/Na; (D) PVS/3.62/Na; (E) PVS/5.6/Na; (F) PVS/8.1/Na. If the “dialysis in bag” method was not used for purification, the scattering of the experimental points was always larger (cf. small Δ symbols in curve E).

TABLE 2: Virial Coefficients for Pure PVA and Sodium Salts of PVS

sample	$A_1 \times 10^{-5}$ (Pa·cm ³ ·g ⁻¹) ±10–20%	$A_2 \times 10^{-5}$ (Pa·cm ³ ·g ⁻¹) ±10–20%	$A_3 \times 10^{-5}$ (Pa·cm ³ ·g ⁻¹) ±10–20%
PVA ^a	0.35 ^a	12	96
PVS/0.64/Na	0.56	120	–1400
PVS/1.22/Na	1.11	406	–11000
PVS/1.72/Na	3.06	570	–16300
PVS/3.62/Na	7.00	500	–12500
PVS/5.60/Na	10.0	930	–37500
PVS/8.1/Na	15.0	1100	–37000

^a For PVA, the intercept gives the real \bar{M}_n .

proportional to the reciprocal mass average molar mass of the polymer. (In the expression given above, K is an optical constant, R_{90} is the excess reduced intensity, and $P(90)$ is the particle-scattering factor.) Therefore, as it can be shown by elementary calculation, the light scattering is not very sensitive to the presence of low molar mass components. More recently, the same type of reciprocal-reduced scattered intensity vs concentration curves have been reported by Hara²⁷ for polystyrene-based ionomers in dimethylformamide.

Although the dissociation itself can be a rather complex equilibrium, especially for counterions of higher valency, the spectacular effect of the linear charge density on position and shape of the reduced osmotic pressure vs concentration curves has initiated us to perform some model calculations assuming close relationship between the effective number of osmotically active particles and the number average apparent molar masses obtained from the intercepts of these curves. The essential feature of the model is that the existence of only two kinds of counterions is assumed: a part of them is fixed to the polyanion

(it may be called “condensed”), while others are distributed homogeneously throughout the system. The independency of the dissociated counterions means that they contribute additively to the total osmotic pressure of solution in question. If the number average degree of polymerization of a copolymer carrying both neutral and charged groups is \bar{P}_n , then the molar mass of the neutral part of the chain is $\bar{P}_n(1 - X)M_{VA}$, where X is the mole fraction of the vinyl sulfate units and M_{VA} (44) is the molar mass of the vinyl alcohol repeat units. The molar mass contribution of the dissociated VSO_4^- can be expressed as $\alpha\nu_-M_{VSO_4^-}$. Here ν_- is the total number of anionic groups in the copolymer, $M_{VSO_4^-}$ is their molar mass, and α is the degree of dissociation. Then, for the nondissociated part of the chain the following expression holds

$$(1 - \alpha)\nu_-(M_{VSO_4^-} + M^+/z)$$

where z is the charge number of counterions and M^+ is their molar mass. Finally the number average apparent molar mass can be given

$$\bar{M}_{n,app} = \frac{\bar{P}_n(1 - X)M_{VA} + \nu_-(M_{VSO_4^-} + M^+/z)}{1 + \frac{\nu_-}{z}\alpha} \quad (5)$$

where for polyanions usually $\nu_- \gg 1$ and ν_-/z must give integers. From eq 5, the degree of dissociation can be easily expressed

$$\alpha = \left(\frac{M_n}{M_{n,app}} - 1 \right) \frac{z}{\nu_-} \quad (6)$$

It is important to emphasize that eq 6 is of universal validity because it is based on the law of mass conservation. It can predict for a given polyelectrolyte the lower and upper limit of $\bar{M}_{n,app}$. For real systems, the values are between the two extremes. It is interesting to note that a similar equation has been derived for colloid systems in the presence of 1:1 electrolytes by means of Donnan approximation by Hiemenz and Rajagopalan²⁸

$$\bar{M}_n = \bar{M}_{n,app}(1 + \nu_-) \quad (7)$$

which is identical to eq 6 when the dissociation is complete. Since these calculations are referred to infinite dilution therefore the interactions among polyions were considered to be negligible. However, within the statistical coils due to the “connectedness” of chains, they can be still effective. The estimated values of the degree of dissociation for all polyelectrolyte salts are summarized in Table 3. For the series of sodium salts, an interesting tendency was observed. Namely, with increasing the linear charge density from very low values to a moderate one, the degree of dissociation first steeply increases then it remains nearly constant. This is supported also by data obtained for the Li^+ and Cs^+ salts. This trend, however, is in just contrast with what is called an ionic “condensation”.²⁹ Perhaps the charge density of these copolymers is not high enough to reach a certain critical value that would be necessary for fixation of more counterions.

A general experience shows that with increasing charge number of the counterions α values decrease rapidly due to the stronger electrostatic interaction with the polyanion. For Cu^{2+} ions, there is some spectroscopic indication that, in addition to the Coulombic forces, they can form other bonds with the

TABLE 3: Data Calculated from the Osmotic Pressure and Degree of Dissociation for All Polyelectrolyte Samples When $c \rightarrow 0$

sample	$A_1 \times 10^{-5}^a$	ν_-	$\bar{M}_{n,app} \times 10^{-4}$	z	α
PVA ^b		0	7.00 ^b		
PVS/0.64/Na		10.2	4.43	1	0.059
PVS/1.22/Na		19.4	2.23	1	0.11
PVS/1.72/Na		27.4	0.81	1	0.29
PVS/3.62/Na		57.0	0.354	1	0.36
PVS/5.60/Na		89.0	0.248	1	0.35
PVS/8.10/Na		129	0.165	1	0.38
PVS/5.60/Li	10.5	89.0	0.236	1	0.36
PVS/5.60/Cs	7.5	89.0	0.330	1	0.29
PVS/8.10/Ba	5.2	129	0.476	2	0.27
PVS/8.10/Mg	6.0	129	0.413	2	0.29
PVS/3.62/Cu	2.7	57.0	0.917	2	0.26
PVS/7.80/Cu	3.7	124	0.670	2	0.19
PVS/3.62/La	1.3	57.0	1.905	3	0.16
PVS/7.80/La	1.3	124	1.905	3	0.09

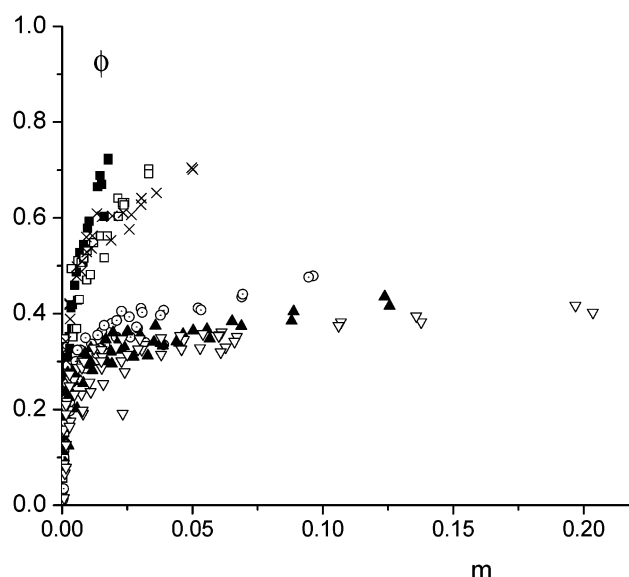
^a A_1 : Intercepts of πc^{-1} vs c curves. Data for the sodium salts are collected in Table 2. ^b For PVA, it is the real number average molar mass.

polymer, too. Where comparison could have been made, it turned out that all values of α obtained for these polyelectrolytes were much smaller than those of their low molar mass analogues. One of the possible explanations of this observation is that the anionic groups of these copolymers are covalently bonded to a chain skeleton with a much lower dielectric permittivity than that of water. No doubt, this will strengthen the interionic interactions and may induce association between the counterions and the pendant groups along the chains. Likely, this can be the reason for the low α values obtained for the copolymers of the lowest linear charge density. Namely, at such circumstances, the ionic groups are surrounded mainly by the less polar vinyl alcohol units within the statistical coil, and with an increase in the sulfate content, the chains become more and more polar, thus ensuring a more favorable condition for dissociation of the counterions. It is conceivable that this conclusion would be applicable for other polyelectrolytes, too.

It is quite common in many works dealing with thermodynamics of polyelectrolyte solutions that the deviation from the ideal mixture behavior is characterized by the osmotic coefficient. However, it must be born in mind that for real systems both $\ln a_1$ (or the activity coefficient of the solvent) and α can be rather complicated functions of composition, therefore it is not easy to draw any conclusion as to the main cause of the observed deviation from unity. In case of polyelectrolytes, the polymeric character of the solute would be sufficient alone to introduce great deviation from the behavior of ideal mixtures. Despite this complexity, just for the sake of comparison, the molal osmotic coefficient³⁰ for our polyelectrolytes was calculated with the application of eq 8

$$\ln a_1 = -\frac{\nu m M_1}{1000} \Phi \quad (8)$$

In these calculations the molality, m , was expressed as moles of the anionic groups/1000 g water, M_1 is the molar mass of water, and ν was taken to be 2. The dependence of Φ on molality for all sodium salts is given in Figure 4. For copolymers of low charge density, the curves form a separate group and their Φ values are relatively high. For the samples of higher sulfate content, the osmotic coefficients are in the same range as has been found earlier in the literature (cf. refs 31–35). For counterions of higher charge number, also in agreement with the published data,^{31–35} the values of Φ decrease considerably

**Figure 4.** Dependence of osmotic coefficient on molality for all sodium salts. (■) PVS/0.64/Na; (□) PVS/1.22/Na; (×) PVS/1.71/Na; (○) PVS/3.62/Na; (▲) PVS/5.6/Na; (▽) PVS/8.1/Na.

with increasing valency (Figure 5S in Supporting Information). However, the most striking feature of all these functions is that they decrease rather steeply with increasing dilution, making almost impossible the extrapolation to zero concentration. This has not been observed so far, likely because the concentrations, in the majority of cases, were much higher due mainly to the smaller sensitivity of the widely used isopiestic method.

To summarize the osmotic properties of polyelectrolytes studied in the present work, it can be stated that in determining the shape and position of the reduced osmotic pressure vs concentration curves the degree of dissociation and, to all probability, its dependence on the polyelectrolyte concentration plays a dominant role. The new form of the Φ vs m curves can be also related to the variation in the value of ν which may also depend on the overall polymer concentration. However, the separation of the possible effects, especially at finite polyelectrolyte concentration, is not possible solely on the ground of osmotic pressure measurement.

Test of the Lattice Theory of Polymer Solutions for Polyelectrolytes. According to the Flory–Huggins theory of polymer solutions, the Gibbs energy of mixing can be given³⁶

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi_{1,2} n_1 v_2) \quad (9)$$

where n_1 and n_2 are the quantities of solvent and polymer and v_1 and v_2 are the volume fractions of the solvent and polymer, respectively. The $\chi_{1,2}$ pair-interaction parameter, in addition to the quality of the polymer–solvent pair, is dependent on concentration and temperature. Equation 9 has been derived for neutral polymers, and its validity has never been tested for polyelectrolyte solutions. Since eq 9 cannot be checked directly by experiments, it is the solvent chemical potential that can be used for such a purpose

$$\Delta \mu_1 = RT \left[\ln(1 - v_2) + \left(1 - \frac{1}{\bar{x}_n}\right) v_2 + \chi_{1,2} v_2^2 \right] \quad (10)$$

Here \bar{x}_n is the ratio of number average molar volume of a polydisperse polymer to molar volume of solvent, which can be obtained from molar mass and density data. If it is known, then from the volume fraction dependence of the solvent activity, the interaction parameter can be calculated.

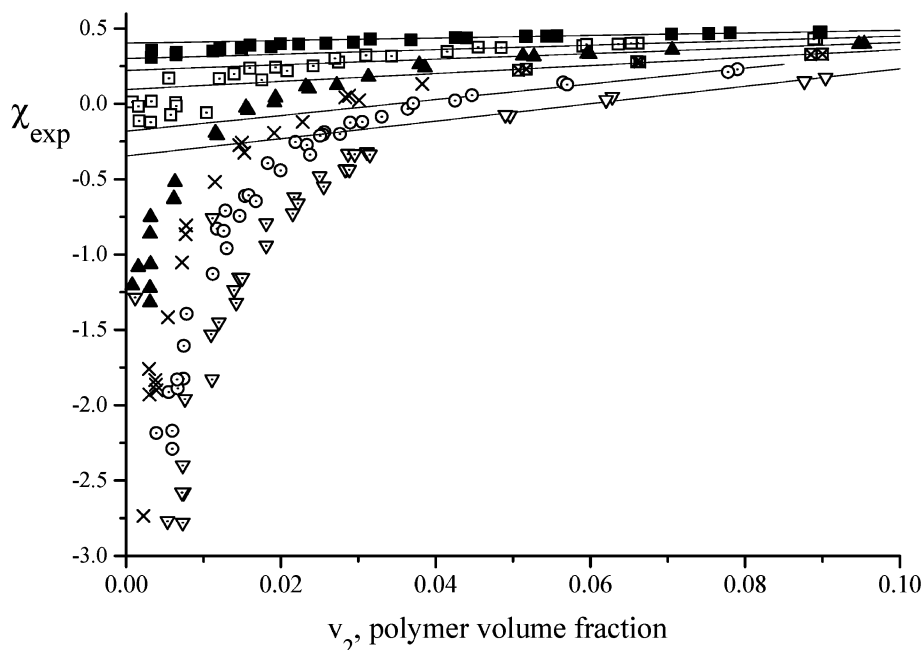


Figure 5. Dependence of the experimentally determined pair interaction parameter, χ_{exp} , on volume fraction of polyelectrolytes. (■) PVS/0.64/Na; (□) PVS/1.22/Na; (▲) PVS/1.71/Na; (×) PVS/3.62/Na; (○) PVS/5.6/Na; (▽) PVS/8.1/Na.

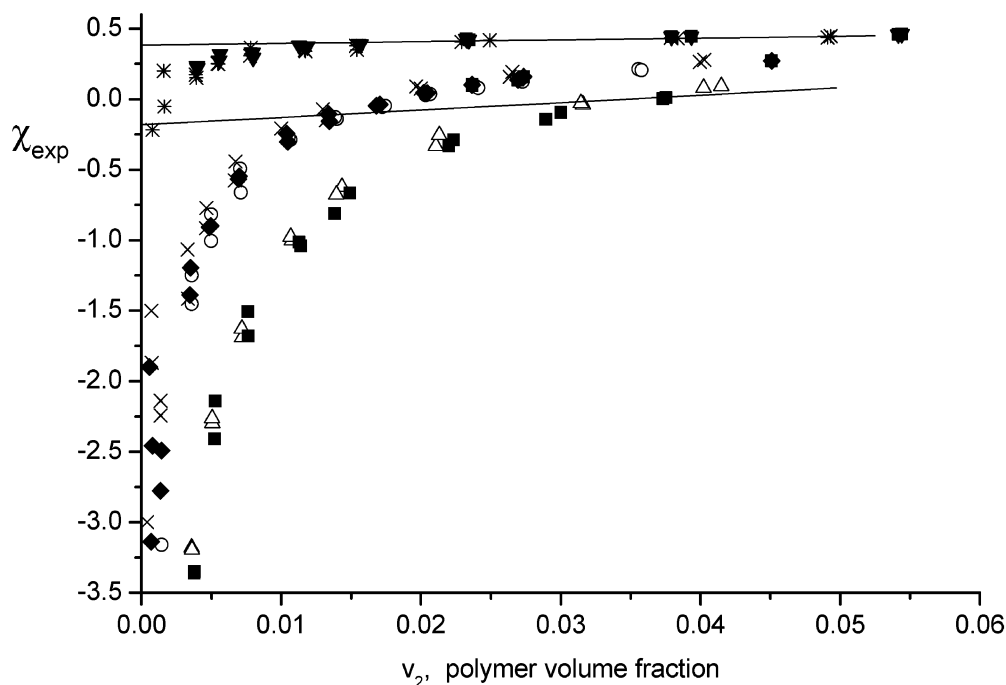


Figure 6. Dependence of the pair interaction parameter, χ_{exp} , on volume fraction of polyelectrolytes. (■) PVS/5.6/Li; (△) PVS/5.6/Cs; (×) PVS/7.8/Cu; (◆) PVS/8.1/Ba; (○) PVS/8.1/Mg; (▼) PVS/3.62/La; (*) PVS/7.8/La. The lower fitted straight line is the same as that for sample PVS/5.6/Na.

With the application of the $\ln a_1$ vs v_2 experimental data as well as molar volume ratio data (see Table 1) the pair-interaction parameters were directly calculated from eq 10. This is denoted by χ_{exp} . The volume fraction dependence of χ_{exp} for all sodium salts is shown in Figure 5 and for other samples in Figure 6. Such volume fraction dependence of the interaction parameter has never been observed, and as can be discernible from both figures, these curves are composed of two distinct ranges. Namely, at volume fractions above ~ 0.03 , i.e., at moderate and higher polymer concentration they are all, to a good approximation, linear, while for the more dilute systems, a very definite downward curvature appears. This tendency becomes more pronounced with increasing linear charge density, and for the

sample PVS/8.10/Na, the χ_{exp} values were unusually low (~ -20) at very low polyelectrolyte concentrations. As to the effect of charge number of counterions, it is also obvious that at comparable circumstances the downward curvature becomes less and less pronounced and for the La^{3+} salts it almost disappears (cf. Figure 6). A comparison shows that the lower parts of the linear range of χ_{exp} vs v_2 functions are close to that range of polymer concentration where the “back-folding” character of the reduced osmotic pressure vs concentration curves sets in. To check the reliability of χ_{exp} values, they were plotted as a function of VSO_4 content at two fixed volume fractions (at 0.04 and 0.08). As it can be seen in Figure 7, the linear extrapolation of these functions to zero charge density (to pure PVA) has

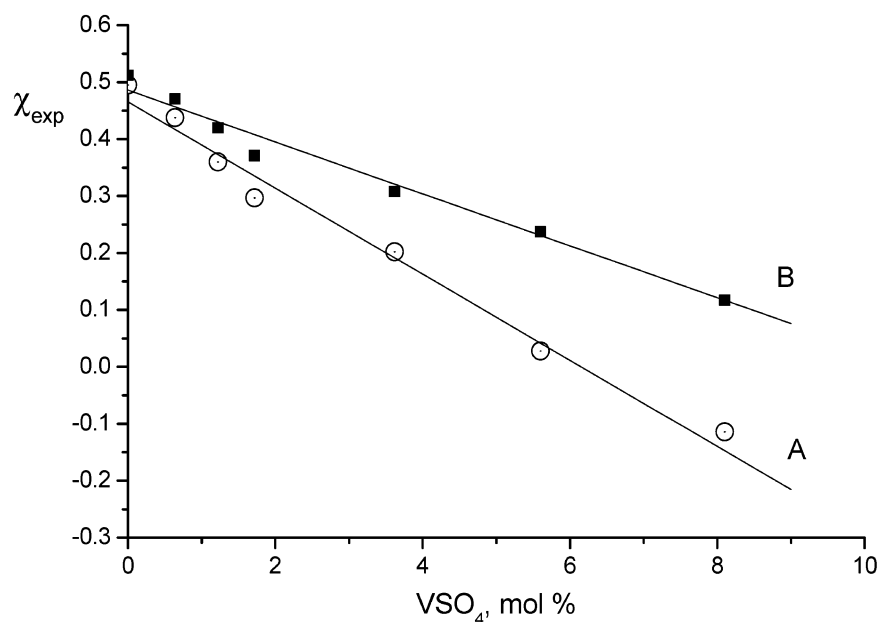


Figure 7. Dependence of χ_{exp} on the linear charge density (VSO_4 content) for sodium salts. (A) $v_2 = 0.04$; (B) $v_2 = 0.08$.

resulted in χ_{exp} values that are very close to the best literature data.¹⁸ Also, the observed tendency indicates unambiguously that with increasing polarity of the chains the polymer–solvent interaction becomes stronger, thus the original meaning of the pair interaction parameter is justified. All in all, it can be stated that at least at moderate and high polyelectrolyte concentration the Flory–Huggins theory of polymer solution can be successfully applied.

However, the question remains open: What could the explanation be for the downward curvature of the χ_{exp} vs v_2 functions? It is evident that no rational physical reason can be given for such dramatic change in the concentration dependence of χ solely on the basis of any possible change in the type and strength of intermolecular interactions. But, if all experimental findings discussed previously are taken into account and also the fact that eq 10 should be sensitive to any change in the number of solute particles (to the number average molar mass of the solute), then it becomes obvious that if in a system the polymer molecules can release smaller particles, i.e., they can dissociate to a large polyanion and much smaller counterions, the \bar{x}_n value will no longer be constant but it becomes a varying quantity. Of course, this is quite unusual in the thermodynamics of solutions of neutral polymers.

To test this idea, eq 10 can be rearranged

$$\bar{x}_n^* = \{1 - [\ln a_1 - \ln(1 - v_2) - \chi_{\text{exp}} v_2^2] v_2^{-1}\}^{-1} \quad (11)$$

where \bar{x}_n^* is the number average of the apparent polymer/solvent molar volume ratio. Now the only assumption to be made is that the linear dependence of χ_{exp} on the polymer volume fraction extends to the full range of polyelectrolyte concentration. Hence, in this model the deviation from the linearity in the more dilute systems is completely attributed to the variation in \bar{x}_n^* . Some preliminary calculations carried out for selected systems (Figure 6S in Supporting Information) have clearly shown that the numerical values of the apparent molar volume ratios (number average apparent molar masses) and their variation as a function of linear charge density were fully consistent with data obtained from the reduced osmotic pressure vs c curves without any assumption. To check full consistency of this concept, for some selected cases, the apparent molar

masses were deduced and put into eq 6 to calculate the concentration dependence of degree of dissociation. The results are shown in Figure 8 for some univalent salts and also for counterions of higher charge number (Figure 7S in Supporting Information). Although the scattering is relatively large, the α^* values are close to those calculated from the osmotic pressure data. For example, in the case of the sample PVS/5.60/Na and PVS/8.10/Na, the points in the dilute range are between 0.30 and 0.50. For the bivalent counterions (Mg^{2+} , Ba^{2+}) and for La^{3+} , the agreement is much better. What is important to emphasize here is, however, that to the best knowledge of the author, this is the first case in the literature when a thermodynamic method is given and tested experimentally for determination of the dependence of degree of dissociation on concentration of polyelectrolytes. It is also worth mentioning that in agreement to the dependence of α^* on the linear charge density no ion “condensation” was observed but here a new kind of rather sharp transition from a partially dissociated to a nondissociated state is discovered with increasing polyelectrolyte concentration.

However, there are other possibilities to separate the “ionic” effect from that of the simple polymer–solvent interaction. Namely, accepting the linear χ_{exp} vs v_2 function, it is possible to calculate the dependence of $\ln a_1$ on volume fraction of the polymer without dissociation. Also, from the $\ln a_1$ vs c , curves it is feasible to calculate the concentration dependence of the reduced osmotic pressure with or without dissociation. As an example, this is shown in Figure 9 for three sodium salts. The deviations between the curves clearly show the high sensitivity of osmotic pressure to a change in number of osmotically active particles. The very low common intercept of the curves calculated without dissociation indicates the complete self-consistency of our separation method. Although the “back-folding” character of these curves partly remains, it is not uncommon in the case of neutral polymers either.³⁷ In addition to the literature data, it can be pointed out by a relatively simple model calculation that if the dependence of the Flory–Huggins parameter on volume fraction takes the form

$$\chi = \chi_0 + k v_2 \quad (12)$$

then there exists a critical value of k above which the “back-

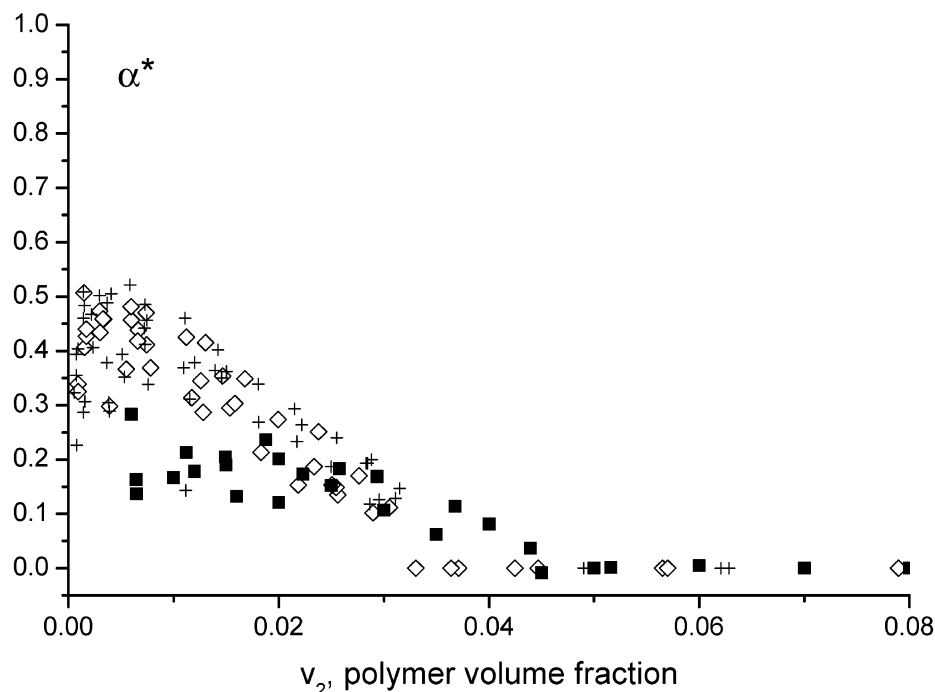


Figure 8. The volume fraction dependence of degree of dissociation, α^* , calculated from the apparent molar volume ratio. (■) PVS/0.64/Na; (◇) PVS/5.6/Na; (+) PVS/8.1/Na.

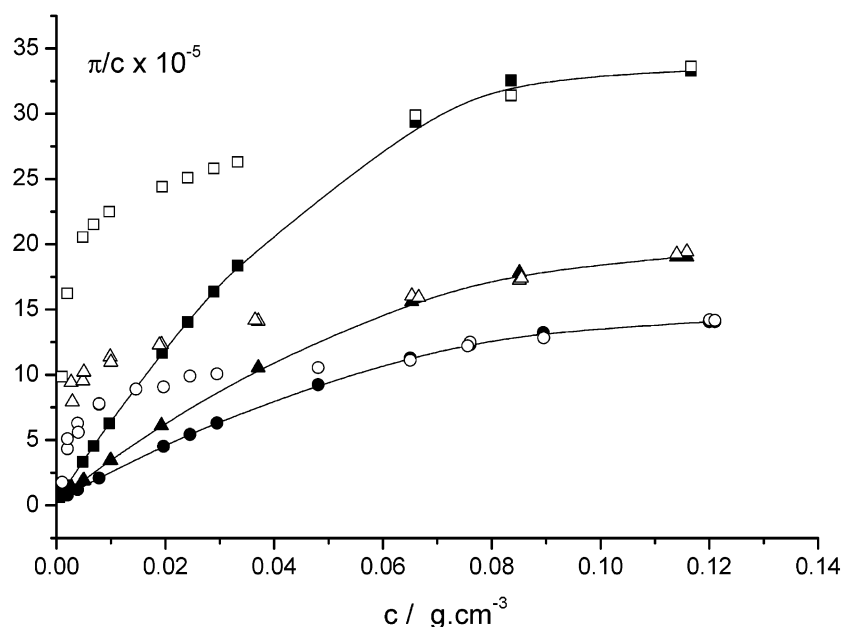


Figure 9. Concentration dependence of the reduced osmotic pressure, π/c , for selected polyelectrolyte samples. Open symbols, experimental data; solid symbols, calculated without dissociation. Circles, PVS/1.71/Na; triangles, PVS/3.62/Na; squares, PVS/8.1/Na.

folding" shape of the curve sets in. If, for instance, $\chi_o = 0.450$ and $\bar{x}_n = 3000$, by the application of eq 10, $\ln a_1$ can be calculated as a function of polymer concentration. From this, the reduced osmotic pressure vs c curves can be easily obtained. It turned out from these calculations that the critical value of k is around 0.40 since at this value the third virial coefficient was found to be zero. Below 0.40 it was positive (normal curvature), and an increase in its value caused more and more pronounced "reversed" curvature.

If the volume fraction dependence of χ is known from experiments, eq 9 can be used to calculate the Gibbs energy of mixing for a given system. Such data were obtained for some selected systems (Figure 8S in Supporting Information) because this kind of information can be useful to characterize energetic

relations of idealized biochemical processes, for instance, in case of contractile systems, where the expansion or contraction is governed partly by the ionic environment of biopolymers.

Conclusions

1. On the basis of experimentally determined $\ln a_1$ vs volume fraction functions obtained for polyelectrolytes in the low and medium range of linear charge density, it can be stated that the transition from a neutral to a charged state is smooth and continuous. At comparable circumstances, it turned out that the effect of the charge number of counterions is very spectacular.

2. A new type of functions for the concentration dependence of the reduced osmotic pressure was discovered and discussed

in detail. These functions enable us to calculate the degree of dissociation at the limit of infinite dilutions by making use of a new equation. It was pointed out that the intercepts and curvature of these functions are determined mainly by the state of partial dissociation of these polyelectrolytes and by the high negative values of the third virial coefficients. This statement is unambiguously supported by data obtained for counterions of higher charge number. A discontinuous change in the molal osmotic coefficients as a function of the linear charge density as well as the low values of the degree of dissociation can be explained by the proximity of the nonpolar part of the polymeric chain ("organic ligand") to the charge carrier groups. This may effect the local dielectric permittivity and so the interionic interactions.

3. The classical (lattice) theory of polymer solutions was successfully applied to polyelectrolytes in the medium and high volume fraction range. The considerable deviations observed for the more dilute solutions has made possible to work out a new method for calculation of the concentration dependence of degree of dissociation and to separate its effect from the polymer-solvent interaction. It is clearly shown by some selected examples that only this kind of thinking can give a self-consistent explanation for all phenomena observed for these systems. As a new phenomenon, a relatively sharp transition from the partially dissociated state to a nondissociated one was observed with increasing polyelectrolyte concentration. This can be considered as a kind of ionic condensation above a critical value of polymer concentration.

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Supporting Information Available: Figures depicting the dependence of $\Delta\mu_1/RT$ on mass fraction, volume fraction, reduced osmotic pressure, and molal osmotic coefficient and figures depicting the variation of apparent molar volume ratio and volume fraction dependence on degree of dissociation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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