Thermodynamic Characterization of Rare Earth Salts of Strong Polyacid Copolymers

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Stoichiometric La^{3+}, Ce^{3+}, and Nd^{3+} salts of poly[(vinyl alcohol)-*co*-(vinyl sulfate)] (PVAS) copolymer polyacids have been studied in aqueous solution without added salt. All LnPVAS salts were entirely water-soluble in the composition and concentration range investigated. Ratios of the vinyl sulfate and vinyl alcohol units in the copolymers were between 1:5 and 1:107, leading to structural charge densities both above and under the critical value needed for counterion condensation of trivalent counterions. Solvent activity, a_1, has been measured by the gel deswelling method in the concentration range of 5×10^{-4} to 1×10^{-1} mol of counterion/kg of water (0.2−9 w/w% of the polyelectrolyte). Results are unusually high for polyelectrolytes ($-2 \times 10^{-6} > \ln a_1 > -3 \times 10^{-4}$), and they are comparable with values determined in solutions of uncharged polymers. Nevertheless, the different copolymers can be clearly distinguished; the water activity is lowered in the order of the vinyl sulfate content of the polyelectrolytes, except for the one above the critical charge density. No observable difference was caused in the thermodynamic properties by the different lanthanide counterions. Reduced osmotic pressure curves and Flory−Huggins pair interaction parameters have been calculated; both of them were used to estimate degrees of dissociation at zero as well as at finite concentrations. Degrees of dissociation are decreasing with increasing concentration or vinyl sulfate content of the copolymer. They take values between 8−36% at zero polymer concentration and they reach zero value simultaneously at $\sim 1 \times 10^{-3}$ mol of polymer chains/kg of water. The average number of released counterions per polymer chain ($DP_n = 1005$) approaches to a limit of about 4.4 with increasing vinyl sulfate content. This corresponds to average charge distances of $b \geq 19$ nm and charge density parameters of $\xi \leq 0.037$. The latter is, however, a very low value and indicates a 1/9 contraction compared to the rod-like assumption.

Introduction

Binding between polyelectrolytes and metal ions has been a widely studied topic for over 50 years; however, trivalent counterions are not often subjects of these works. Moreover, thermodynamic investigation of polyelectrolytes with trivalent counterions is restricted to one single study.[1] One reason for it may be that common trivalent metal ions (e.g., Fe(III), Cr(III), and Al(III)) are actually not trivalent under usual conditions, for they have a strong tendency to hydrolyze and they are present as their hydroxo complexes unless the solution is definitely acidic, which is, on the other hand, the case of a mixed counterion system. Binding of these cations by several homo- and copolymers containing various chelate-forming ligands was studied at different pH's by the liquid-phase polymer-based retention method during ultrafiltration.[2−5] Investigation of non-hydrolyzing trivalent lanthanide and actinide ions has spread only in the last one or two decades as their significance has risen initiated by environmental considerations[6−7] and by their use as fluorescent probes in coordination chemistry examinations.[8−16] As the main complexing macromolecules in nature (e.g., humic substances) carry carboxylic functional groups, an overwhelming part of the studies was carried out on weak acid type synthetic polyelectrolytes such as poly(acrylic acid) = PAA,[9−14,17−18] poly(methacrylic acid) = PMA,[9−12] poly(acrylic acid-*co*-methyl acrylate),[18] poly(methacrylic acid-*co*-methyl methacrylate),[19] poly(acrylic acid-*co*-acrylamide) = PAAm,[2,12] poly(maleic acid) = PM,[6] and poly(maleic acid-*co*-ethylene) = MAE.[10−12]

Interestingly enough, the first trivalent counterion investigated[17−18] was a complex cation, hexaamminecobalt(III), $[Co(NH_3)_6]^{3+}$. Being an inert complex, it was chosen to avoid intentionally inner-sphere coordination of carboxylate groups, that is, to ensure that only charge-transfer complex (ion pair formation, site binding) can occur. On the contrary, inner sphere coordination occurs between lanthanides and polyelectrolytes, leading to an asymmetry in the coordination environment around the Ln^{3+} counterion that makes possible, in certain cases, a considerable enhancement in fluorescence intensity.[9−11] However, complete binding of Tb(III) to NaPAA is achieved at a similar $-COO^-:M^{3+}$ ratio (~60:1)[9] as in the case of $[Co(NH_3)_6]^{3+}$ (~80:1),[17] despite the fact that it was concluded by comparing PAA and its copolymers at several degrees of neutralization that $[Co(NH_3)_6]^{3+}$ is not attached to three carboxylate groups at the same time[18] while fluorescence lifetime measurements revealed that the Tb(III) ion loses in average 5.1−5.5 out of its 9 coordination water molecules when it is bound to PAA, MAE, PAAm, or PMA.[12] Much lower values (2.5−3.1) were obtained, of course, with the low molar mass mono-, di-, and trimer analogues of PAA.[13] The same hydration numbers were measured for Eu(III) with PAA, PM, and some carbonic acids at pH ≥ 4.[6,14] At lower pH, however, hydration numbers steeply increased to 9, indicating that no more inner sphere coordination occurs with the polyacids. Several works agree that H^+ in the pure acid form can be hardly displaced;[6,9,14] other works affirm that alkali metal cations compete with the trivalent counterion in the order $Rb^+ < K^+ < Na^+ < Li^+$.[9,17] In accordance to the number of lost water molecules, the fluorescence study of anthracene labeled methacrylate copoly-

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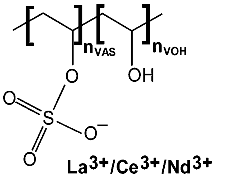
CHART 1: Constitution of Poly[(Vinyl Alcohol)-*co*-(Vinyl Sulfate)] (PVAS) Copolymer Polyelectrolytes[a]



[a] Composition range in the present study: DS = $n_{VAS}/(n_{VAS} + n_{VOH})$ = 0.0093−0.169.

mers revealed that six carboxylate groups are needed to bind a Tb(III) ion.[19] The conformational change, accompanying the binding of Nd(III), Eu(III), and Tb(III), was studied by viscometry[13] and complexation kinetics measurements.[7,14]

Stability constants are, in general, much lower with strong polyelectrolytes[9,11] than with weak polyelectrolytes, and interactions are considered to be not specific. For example, sodium poly(vinyl sulfonate), NaPVS, was needed in more than an order of magnitude higher (1000:1) amount, compared with PAA (60:1), to completely bind Tb(III).[9] Recently, however, the first direct experimental evidence was provided[15] that the binding of lanthanides by strong acid type polyelectrolytes is also more than a simple electrostatic interaction and the coordination sphere of the counterion is affected due to specific binding to the polyanion. Six coordinated water molecules were lost by Tb(III) also in the case when it was bound to NaPVS instead of NaPAA.[15] For comparison, this value was only one with sodium dodecyl sulfate.[16] The presence of a specific interaction was also supported by a 4 nm blue shift observed in the emission maximum of Ce(III) in the presence of PVS.[15]

The only study devoted to thermodynamic properties[1] reports osmotic coefficients (based on osmotic pressure and freezing point depression measurements), heats of dilution and volume changes on dilution of poly(styrenesulfonate), PSS, solutions containing mixtures of La^{3+} and H^+ counterions of different ratios. Unfortunately, the stoichiometric La^{3+} salt of PSS could not be studied at all, for preparation of soluble salt was hindered by gel formation. The fraction of free and bound mono- and trivalent counterions could also be determined at each ratio, respectively, by measuring transference numbers and electric conductivity in these systems.[20]

In the present work, poly[(vinyl alcohol)-*co*-(vinyl sulfate)] (PVAS) copolymer polyelectrolytes were chosen for the further thermodynamic investigation of trivalent polyelectrolyte salts. Their general constitutional formula is depicted in Chart 1. They were subjects of several of our previous works as well, for they enable the study of charge density effects in the transition region between a polyelectrolyte and its uncharged polymer analogue.[21−22] The transition from the entirely separated randomly distributed point-like charges to a more or less continuous charge distribution was investigated especially in detail in the case of Na^+ counterions by direct osmometry,[23] viscometry,[24] and conductometry.[24] PVAS polyelectrolytes are water-soluble even with very low sulfate content because the neutral parent polymer, poly(vinyl alcohol), PVA, is water-soluble as well. Structural charge density of these copolymers is easily controllable by their composition, i.e., degree of esterification, DS, which gives the fraction of vinyl alcohol monomer units that is esterified by a sulfate group. The synthesis method[25] also guarantees that the number average degree of polymerization, DP_n, of each PVAS copolymer polyelectrolyte is exactly the same as that of the parent polymer, PVA.

TABLE 1: Composition of Poly[(Vinyl Alcohol)-*co*-(Vinyl Sulfate)] (PVAS) Copolymer Polyelectrolytes[a]

DS[b]	n_{VAS}/n_{VOH}[c]	counterions	N_{ci}[d]
0.0093 ± 0.0004	1:107	Ce^{3+}	3.11
0.0340 ± 0.0008	1:28.4	Ce^{3+}	11.4
$0.064_3 \pm 0.001_6$	1:14.5	Ce^{3+}, Nd^{3+}	21.5
0.169 ± 0.001	1:4.92	Ce^{3+}, La^{3+}	56.6

[a] DP_n = 1005 ± 20 [b] Degree of esterification: fraction of vinyl alcohol monomer units esterified by sulfate group (in mol fraction). [c] Ratio of ionizable (VAS) and neutral (VOH) monomer units. $n_{VAS}/n_{VOH} = DS^{-1} - 1$. [d] Stoichiometric number of counterions per polymer chain. $N_{ci} = DS \times DP_n/z$.

Rare earth metal cations are expected to be a good choice as trivalent counterions not only because they hydrolyze just to the extent as, e.g., Ca^{2+} does,[26] but because they also form complexes with sulfate anions thus they may coordinate the half esters of sulfate anions.

According to preliminary water activity measurements made on two La^{3+} salts,[21] the LaPVAS/3.62 and 7.8 salts could not be distinguished from each other. (Numbers, indicated after the abbreviation PVAS, are numeric values of DS in mole percent.) Neither their thermodynamic properties (solvent activity, reduced osmotic pressure, Flory−Huggins pair interaction parameter) nor their degrees of dissociation seemed to be different, only their osmotic coefficient curves ran in a considerable distance from each other. Therefore, in the present work we undertake a detailed systematic study of PVAS polyelectrolytes of four different structural charge densities with three different lanthanide counterions, La^{3+}, Ce^{3+}, and Nd^{3+}, to clear whether charge density effects play a role in the case of trivalent counterions. The gel deswelling measuring technique has been already applied with success in this high water activity region ($-3 \times 10^{-4} < \ln a_1$) for the clear distinction and thermodynamic characterization of uncharged polymers and polymer mixtures.[27−28]

Experimental Methods

Materials. Poly[(vinyl alcohol)-*co*-(vinyl sulfate)], PVAS, copolymer polyelectrolytes were synthesized from the homopolymer poly(vinyl alcohol), PVA, by polymer analogous reaction relying on equilibrium esterification by sulfuric acid at low temperature.[25] As parent polymer, the medium molar mass fraction of a previously fully hydrolyzed and partially fractionated commercial product, Poval 420 (Kuraray Co., Ltd., Japan), was used. Number average degree of polymerization, DP_n, of this PVA fraction was determined osmometrically[23] and found to be DP_n = 1005 ± 20. Copolymer polyacids of four different compositions were prepared; their sulfate contents were determined by both potentiometric and conductometric acid−base titration of the acid functional groups, and by the gravimetric measurement of the total polymer content of the solution. Results are shown in Table 1.

Stoichiometric lanthanide salts of the PVAS polyacids were prepared by ion exchange dialysis, for which a method was worked out earlier to minimize the amount of ionic contamination (including atmospheric CO_2) in the polyelectrolyte solutions.[21] $Ce(NO_3)_3 \cdot 6H_2O$ (p.a., Fluka) and $La(NO_3)_3 \cdot 6H_2O$ (p.a., Carlo Erba, Italy) were used without further treatment. $Nd(NO_3)_3$ solution was obtained by dissolving Nd_2O_3 (puriss., Riedel-de Häen) in a stoichiometric amount of diluted HNO_3 (a.r., Reanal, Hungary). No sign of precipitation was observed upon adding concentrated lanthanide nitrate solutions to 5 w/w% NaPVAS solutions. The dialysis procedure was described previously in detail.[21−22] Dialysis was continued until conductivity of double distilled water remained under 1.5 μS (2.5 μS for PVAS/16.9) over a 24 h period. Double distilled water of a specific conductivity between 0.8−1 μS cm^{-1}, produced in a Muldestor SE quartz still (Wagner+Munz, Munich, Germany), was used for the dialysis and for making dilutions.

Solutions were concentrated to 8−9 w/w% by evaporation under reduced pressure at 298−308 K. All the stoichiometric LnPVAS salts were entirely water-soluble. Completion of the dialysis could be very sensitively detected by the spectrophotometric measurement of the nitrate ion content ($\epsilon_{201} = 9600$), too. The NO_3^- to Ce(III) ratio was found to be less than 0.5%, which excludes the presence of mixed salts like $[Ln(NO_3)_{1-2}]$-PVAS. Stoichiometry of the LnPVAS salts was also checked by complexometric titration.[29−30] Deviation from the 1:3 Ce(III) ion : sulfate half ester group ratio was between −0.7 − +1.5% even in the case of the highest DS.

Methods. Conductivity measurements were carried out using an OK-102/1 conductivity meter (Radelkis, Hungary) connected with an OK-0902P (Radelkis) conductivity cell having a cell constant of 1 cm^{-1}.

Water activity was measured by the gel deswelling method,[31−33] which enables determination of thermodynamic activity of the solvent in polymer solutions even in a concentration range (0.001−0.1 mol of counterion/kg of water) that is too low for the isopiestic method but at the same time too high for the direct osmometry. The method is based on the phenomenon that the degree of swelling (i.e., the solvent uptake) of a gel highly and explicitly depends on the activity of the solvent if it is placed in a mixture from which the solute cannot enter the network. To achieve the highest sensitivity and precision, the crucial parameters (composition, degree of cross-linking, and size) of the gel laminae were optimized previously,[33] and a chemically cross-linked poly[(vinyl acetate)-*co*-(vinyl alcohol)] copolymer gel of the composition 8/10/400 was found to be the most suitable. The gel consisted of a copolymer carrying 8 mol % vinyl acetate units, the cross-linking reaction was performed by glutardialdehyde (GDA) in an aqueous solution containing 10 w/w% copolymer, and the ratio of the number of monomer units versus that of GDA molecules was 400.

Reaching (de)swelling equilibrium took 10 days while the temperature was kept at 298.00 ± 0.01 K by a Haake F6 B12 circulating bath. The detailed procedure of the gel deswelling measurement was described earlier.[21−22,33] For gravimetry, drying of the polymer samples and the gels was performed in a vacuum oven (Binder VD 23) at 343.0 ± 0.5 K for about 4−7 days (until constant mass). Relative error of the polymer mass fractions is estimated to be 0.5−2%. Before drying, approximately stoichiometric amounts of a dilute NaOH solution were added to the LnPVAS solution samples to avoid acid-catalyzed degradation of the copolymers caused by heating.

The gel laminae were calibrated using very reliable osmotic pressure data determined for poly(vinyl pyrrolidone) (PVP) (Fluka, K 60) solutions.[23,34] To further improve the reliability of the results, water activities were calculated according to two types of calibration curves.[22]

Densities of LnPVAS solutions were determined in 10 cm^3 picnometers (BLAUBRAND) at 298.00 ± 0.01 K in the polyelectrolyte concentration region 1−10 w/w%.

Results and Discussion

Figure 1 shows the water activity curves of the six investigated lanthanide PVAS salts together with a calculated curve for the uncharged parent polymer, PVA. First of all, considering polyelectrolytes, the very low $|\ln a_1|$ values are remarkable, even lower than those of NaPVAS of the lowest DS ever investigated (DS = 0.64%),[21] and are comparable with values measured in solutions of neutral polymers.[27−28] It means an enormous difference to the usual polyelectrolyte behavior, where ΔG of mixing has large negative value resulting mainly from counterion dissociation, and indicates immediately that lanthanide counterions are probably associated with the polyion to an exceptional extent. The polyelectrolytes of the four different DS's are, however, clearly distinguishable. In the case of the three polyelectrolytes of lower DS (DS = 0.0093−0.0643), the higher the sulfate content of the copolymer is the more negative $\ln a_1$ curve it has. This finding is in accordance with expectations because increasing the number of ionizable groups causes an increase of the hydrophilicity of the polymer chain and, at the same time, it also increases the number of dissociable counterions, which both lead to a decrease in ΔG. The two lanthanide salts of the PVAS of the highest DS (DS = 0.169), however, show a strong deviation from this order. This is the first time that a PVAS salt of higher DS precedes that of a lower DS; no example has been found for the reversal of this sequence in the case of either mono- or divalent counterions[21−22] so far. This strange occurrence is affirmed by measurements with three different rare earth counterions; namely, La- and CePVAS/16.9 and Nd- and CePVAS/6.43 gave the same results.

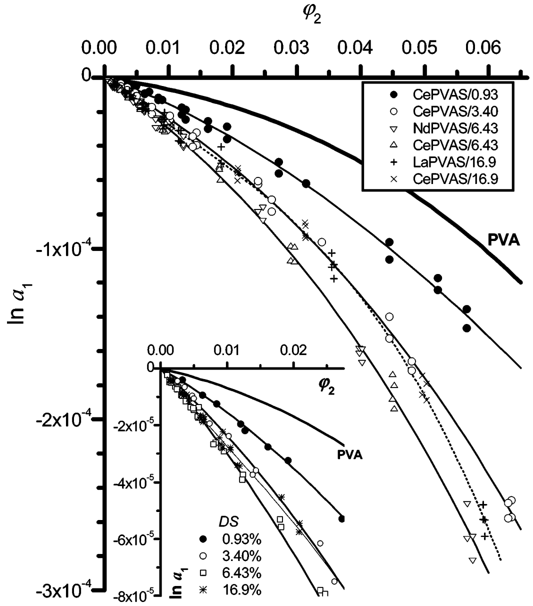


Figure 1. Solvent (water) activity as a function of polymer volume fraction. Data of pure PVA were taken from ref 33. Lines: fitted third-order polynomials. Insert: more diluted region. For clarity, data points obtained by the two calibration methods (see Experimental) are averaged.

The osmotic coefficient, Φ, is the most frequently used quantity to characterize the nonideality of polyelectrolyte solutions. Since individual activity coefficients of the counterions cannot be measured, Φ is often considered as a measure of what extent the counterions are bound to the polyion. The main problem with this consideration is that nonideality originating from the polymer chain itself is also assigned to the counterions; thus, this representation can give real information about counterion association at most at infinite dilution. The rational osmotic coefficient is defined by

$$\Phi = \frac{\ln a_1}{\ln x_1} \tag{1}$$

where $\ln a_1$ can be obtained directly from measurement (in most

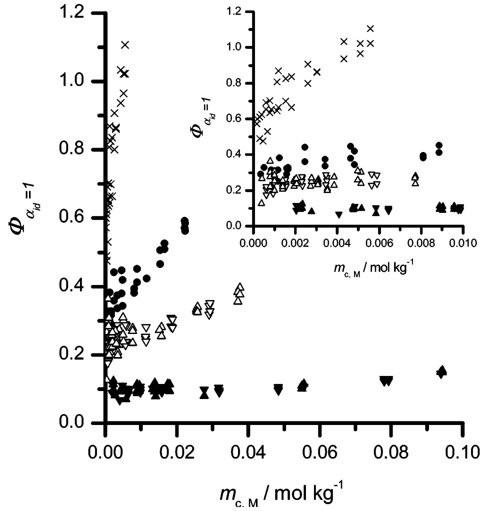


Figure 2. Dependence of the rational osmotic coefficient on counterion molality. (×) CePVAS/0.93, (●) CePVAS/3.40, (△) CePVAS/6.43, (▽) NdPVAS/6.43, (▲) CePVAS/16.9, and (▼) LaPVAS/16.9. Insert: the very low concentration region of the same curves.

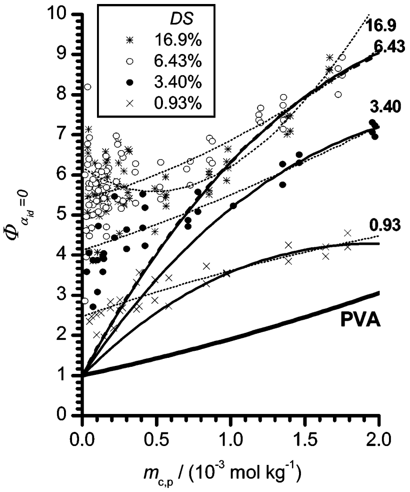


Figure 3. Osmotic coefficients as a function of the molality of the polymer chains. (···) ln a_1/ln x_1($\alpha_{id} = 0$), where ln a_1 is the fitted third-order polynomial in Figure 1. (—) ln a_1(χ_{lin})/ln x_1 ($\alpha_{id} = 0$) (---), same as the solid lines for DS = 16.9%.

cases from isopiestic or osmometric measurements; in the present case from the gel deswelling measurement), while x_1 is the mol fraction of the solvent (water), and it can be calculated as follows:

$$x_1 = \frac{n_1}{n_1 + n_2 \times (\alpha_{id} \times N_{ci} + 1)} \qquad (2)$$

where n_1 and n_2 are the amount of water (solvent) and that of the polymer chains (solute), respectively. N_{ci} denotes the stoichiometric number of counterions per polymer chain:

$$N_{ci} = \frac{\mathrm{DS} \times \mathrm{DP}_n}{z} \qquad (3)$$

where DS is the degree of esterification, DP$_n$ is the number average degree of polymerization, and z is the charge number of the counterions, i.e., 3 in the present case. Numeric values of N_{ci} can be taken from Table 1. It has been shown earlier that the resulting Φ considerably depends on the way of calculation of x_1 (i.e., what degree of dissociation, α_{id}, is considered as ideal).[22] An ideal case can be defined at both extreme values of α, respectively: $\alpha_{id} \equiv 1$ means that counterions would be completely dissociated in the ideal state, or on the contrary, $\alpha_{id} \equiv 0$ represents the case when no dissociation is supposed in the ideal state.

Osmotic coefficients, calculated for the usual case of $\alpha_{id} \equiv 1$, are presented in Figure 2. Four distinct curves are obtained for the PVAS salts of the four different DS's, respectively, while not the slightest difference can be noticed between the different lanthanide counterions. Previously, the same observations were made for Mg^{2+} and Ba^{2+},[21] and also for Co^{2+}, Ni^{2+}, and Cu^{2+} counterions,[22] respectively. In this representation, the order of the curves is entirely in accordance with expectations. Intercepts are decreasing with increasing DS, and they take values approximately half of those obtained for divalent counterions.[22] The Φ values of the LnPVAS salts of the highest DS (16.9%) are in good agreement with that predicted for the stoichiometric LaPSS salt by Škerjanc et al.[1] at the counterion molality 1 × 10^{-3} monomol/kg of water. The osmotic coefficient of LnPVAS/16.9 is almost constant over the whole concentration range investigated, while Φ curves of LnPVAS salts of lower DS have considerably increasing slopes with decreasing DS. This increasing slope of the Φ curves is in connection with the well-known fact that the polymer chain itself has a strong deviation from ideality, too. Neutral polymers also have increasing osmotic coefficients with concentration, so what we see is an overall effect. Due to the way of calculation, the lower the N_{ci}, the higher is the contribution of nonideality of the polymer chain to Φ.

The reasonable contribution of the polymer chain to Φ is better demonstrated in Figure 3 for the case of $\alpha_{id} \equiv 0$. The intercepts give the number of entities that a single polymer chain dissociates at infinite dilution. At finite concentrations, however, Φ of the solution of PVA, the uncharged parent polymer itself, also increases considerably compared to the Φ values determined in solutions of LnPVAS salts, latter being 2−4 times lower than those with divalent counterions.[22] Moreover, it can be supposed that the undissociated hypothetical PVAS copolymers, containing polar and partially ionized sulfate groups, have even higher Φ values than PVA at concentrations other than zero because the enthalpy of mixing is higher in their case.

To estimate the hypothetical osmotic coefficient of the PVAS chains without counterion dissociation, their solvent−segment interaction parameter, $\chi_{1,2}$, should be determined that enables the calculation of their contribution to ln a_1. The $\chi_{1,2}$ parameter was introduced in the Flory−Huggins theory, describing the Gibbs free energy change for mixing a polymer with a solvent, to estimate the enthalpy change of mixing.[35] It is based on the exchange energy when a segment of the polymer and solvent molecules are brought in contact, and its value ranges up to 0.5 for "good" solvents of the given polymer above which the solvent is considered to be "poor". The following relationship holds between ln a_1 and $\chi_{1,2}$:

$$\ln a_1 = \ln(1 - \varphi_2) + \left(1 - \frac{v_1}{v_{2,\alpha=0}}\right) \times \varphi_2 + \chi_{1,2} \times \varphi_2^{\,2} \qquad (4)$$

where φ_2 is the volume fraction of the polymer in the solution and v_1 and $v_{2,\alpha=0}$ are molar volumes of the solvent and the polymer, respectively. The polymer/solvent molar volume ratios, $v_{2,\alpha=0}/v_1$, summarized in Table 2, were determined by means of density data of LnPVAS solutions as described previously.[22] The $\chi_{1,2}$ parameters, determined from the experimentally obtained ln a_1 values, are depicted in Figure 4. The curves have the same shape as it was found in the case of mono- and divalent

TABLE 2: Data Characterizing the Dissociation of Stoichiometric LnPVAS Salts

sample	$v_{2,a=0}$ ($v_1 \pm 2\%$)	$\alpha_0(\chi)^a$	M_n (g mol^{-1} ± 2%)^b	$(\Pi/c)_0$ (10^5 Pa cm^3 g^{-1})	$M_{n,\mathrm{app}}$ (g mol^{-1})	α_0 ($(\Pi/c)_0$)^c
LnPVAS/0.93	1.86×10^3	0.36 ± 0.03	4.54×10^4	1.15 ± 0.09	2.16×10^4	0.36 ± 0.06
LnPVAS/3.40	1.91×10^3	0.23 ± 0.01	4.86×10^4	1.80 ± 0.13	1.38×10^4	0.22 ± 0.02
LnPVAS/6.43	1.93×10^3	0.200 ± 0.006	5.24×10^4	2.56 ± 0.09	0.97×10^4	0.20 ± 0.01
LnPVAS/16.9	2.10×10^3	0.078 ± 0.002	6.56×10^4	2.15 ± 0.07	1.15×10^4	0.083 ± 0.004

[a] By the χ method. [b] Number average molar mass of the polymer chains with counterions. In the case of different Ln^{3+} counterions, difference between numeric values is less than 1% at same DS. [c] By the Π/c method.

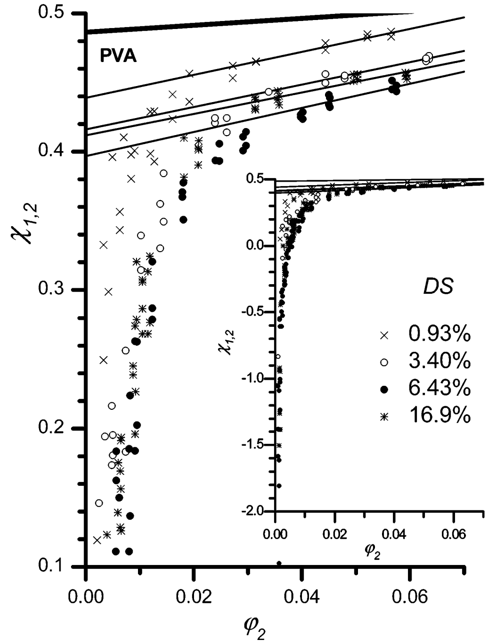


Figure 4. Flory−Huggins pair interaction parameters as a function of polymer volume fraction. Insert: the same figure with larger magnification of the ordinate. Data of pure PVA were taken from ref 33.

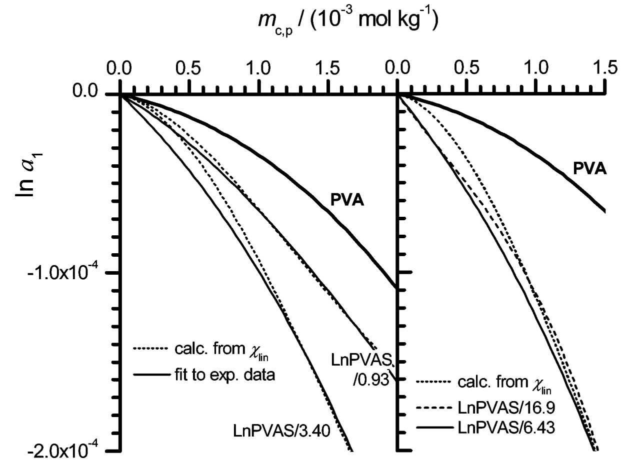


Figure 5. Comparison of solvent activities obtained experimentally and calculated on the basis of χ_{lin} as a function of the molality of the polymer chains.

counterions,[21,22] which has never been observed for neutral polymers. Normally, $\chi_{1,2}$ values of neutral polymers show a slight linear increase with concentration, as can be seen in the same figure for PVA. PVAS polyelectrolytes, however, behave like ordinary uncharged polymers exclusively at high polymer volume fractions, while a steep downward curvature appears under $\varphi_2 \approx 0.03$ leading to extremely low negative values approaching zero polymer concentration. The straight lines, χ_{lin}, were considered to be the "real" Flory−Huggins pair interaction parameters for the PVAS chains, and the "back-folding" was explained by counterion dissociation.[21−22] As χ_{lin} reflects the strength of the solvent−segment interaction, charged polymers have lower pair interaction parameter values than neutral ones; accordingly, lower χ_{lin} values belong to polyelectrolytes with higher charge density. In contrast to mono- and divalent metal salts of PVAS, χ_{lin} curves of LnPVAS salts have considerably higher values and lower slopes. Moreover, they run quasiparallel to each other and all the intercepts remain in the height of 0.4, suggesting a pronounced reduction in the hydrophilic character compared to the other metal salts. LnPVAS/16.9 breaks the order in this representation, as well, since its χ_{lin} region falls significantly above that of PVAS/6.43. All these observations imply that not, or not only, counterion chemical quality and the amount of sulfate groups in the copolymer determines χ_{lin}. Maybe the effective charge number of the polymer chain also plays a role, although χ_{lin} explicitly does not depend on the degree of dissociation of the counterions.

The contribution of the polymer chain alone to ln a_1 can be calculated by replacing $\chi_{1,2}$ by χ_{lin} in eq 4. The resulting ln $a_1(\chi_{\mathrm{lin}})$ values are compared with the experimentally obtained ln a_1 values in Figure 5. Curves representing the former quantity are less negative than the latter ones, since they do not contain the effect of the dissociated counterions. Interestingly enough, the calculated ln $a_1(\chi_{\mathrm{lin}})$ curves of the two polyelectrolytes LnPVAS/6.43 and 16.9 are indistinguishable in this representation, which is completely unexpected since they have different chemical compositions.

Knowledge of ln $a_1(\chi_{\mathrm{lin}})$ enables the calculation of the real Φ's ($\alpha_{\mathrm{id}} \equiv 0$) of the undissociated polymer chains that are also depicted in Figure 3. Intercepts of all these four curves equal 1, which is in accordance with expectations for neutral polymers and confirms that their physical meaning is correct. At finite concentrations, PVAS copolymers have obviously larger deviation from the ideal value 1 than PVA. This difference, however, increases until only DS = 0.0643, and the curves of PVAS/6.43 and 16.9 exactly coincide with each other.

The difference, ln a_1 − ln $a_1(\chi_{\mathrm{lin}})$, corresponds to the effect of the dissociated counterions. Thus a new, corrected osmotic coefficient, Φ_{corr}, can be defined on the basis of this difference that can express exclusively the counterion contribution to nonideality:

$$\Phi_{\mathrm{corr}} = \frac{\ln a_1 - \ln a_1(\chi_{\mathrm{lin}})}{\ln x_1} \tag{5}$$

where

$$x_1 = \frac{n_1}{n_1 + N_{ci} \times n_2} \tag{6}$$

This is in fact the case of $\alpha_{\mathrm{id}} \equiv 1$, the only difference to eq 2 is the omission of 1 from the denominator since the polymer

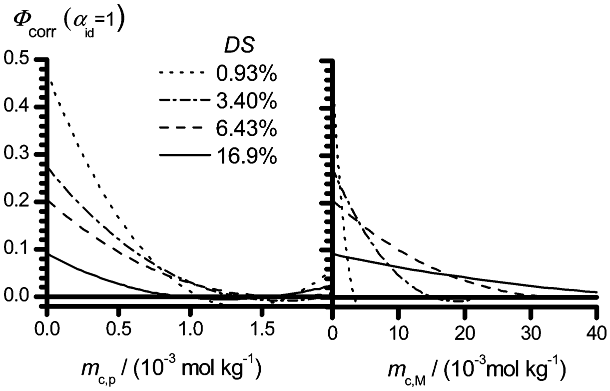


Figure 6. Corrected osmotic coefficients calculated by eq 5 as a function of polymer chain molality (left) and counterion molality (right). $m_{c,M} = N_{ci} \times m_{c,p}$.

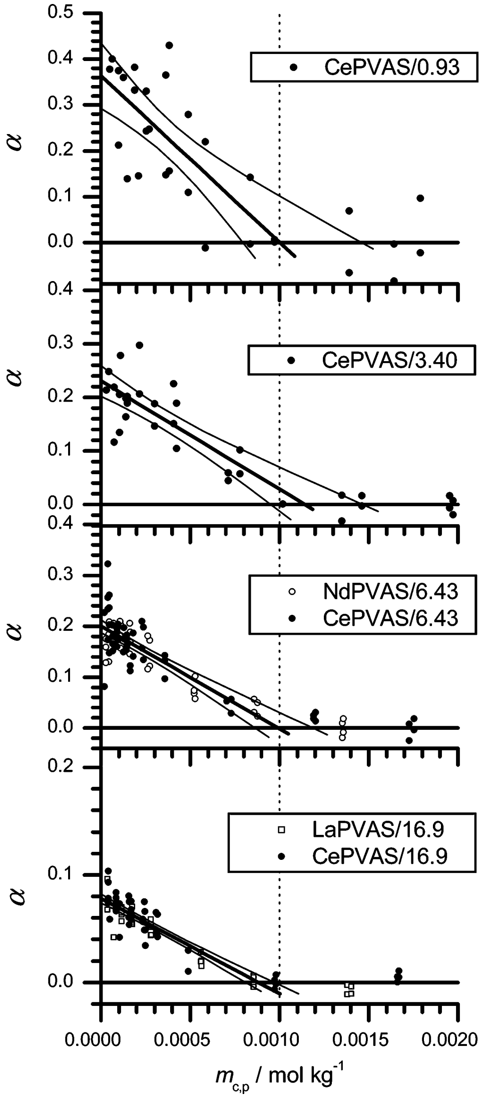


Figure 7. Dependence of the degree of dissociation calculated by the χ method (eq 7) on the molality of the polymer chains.

chain has been already taken into account when its effect was eliminated from ln a_1. The obtained Φ_{corr} curves in Figure 6 reflect a similar behavior what one would expect for the activity coefficient of the counterions.

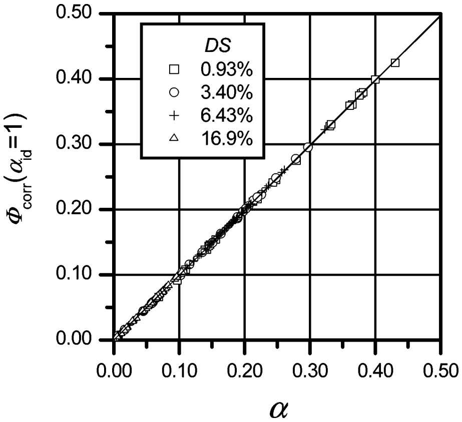


Figure 8. Equivalence of osmotic coefficient (eq 5) and degree of dissociation (eq 7) of LnPVAS polyelectrolytes. Straight lines: linear fits through zero; slopes are between 0.992 and 0.996.

As it can be seen in Figures 7 and 8, practically the same values result for the kind of degree of dissociation, α, of the counterions that was introduced by a calculation method, called the χ method, previously:[21−22]

$$\alpha = \varphi_2 \times (\chi_{lin} - \chi_{1,2}) \times \frac{v_{2,\alpha=0}}{v_1} \times \frac{1}{N_{ci}} \qquad (7)$$

This calculation also relies on the linear section of the $\chi_{1,2}$ curve, and the resulting α is based on the number of osmotically active entities in the polyelectrolyte solution. It gives the fraction of free counterions for such a model solution in which the solvent activity is the same as in the investigated one but in which the counterions can either freely mix with the solvent (and have an additive contribution to the colligative properties) or can be fixed (associated) to the polyion (and become osmotically inactive). The resulting α is, of course, an apparent value that cannot give information about the distribution of the counterions but can serve as a measure of the overall attachment. Both Figure 6 and Figure 7 (and also previous results for divalent counterions) agree that quantitative binding occurs with good approximation above 1×10^{-3} mol polymer chains/kg water molality for all DS. This decreasing tendency of α contradicts the calculations of Manning who predicted that the limiting charge fraction of the polyelectrolyte chain remains constant up to concentrations ≈ 0.1 M.[36] Interestingly enough, this finding would hold in our case only if the χ parameter of PVA was taken into account in all cases for the calculation of α by the χ method. As it can be seen in Figure 3, Φ curve of the PVA solution and those of the PVAS solutions run parallel with each other, i.e., their difference is constant which would mean a constant number of entities that the polyelectrolyte dissociates to. However, it is obvious that the same χ parameter cannot be valid for PVA and PVAS at the same time as any changes in chemical structure very sensitively appear in χ.

It was demonstrated previously that degrees of dissociation at zero concentration, α_0, could be obtained by another way, called the Π/c method, as well.[21−22] In the case of neutral polymers, intercepts of reduced osmotic pressure curves, $(\Pi/c)_0$, serve for the determination of the number average molar mass, M_n, of the polymer chains. However, all the PVAS polyelectrolytes investigated so far had much higher intercepts, and therefore much lower apparent M_n, than it could be calculated from the known DP_n and DS of the copolymers. This finding was explained by the increased number of osmotically active entities in the solution caused by counterion dissociation,

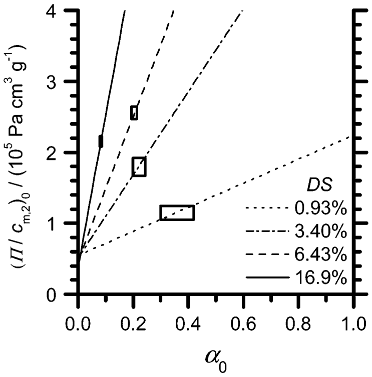


Figure 9. Reduced osmotic pressure of CePVAS salts as a function of degree of dissociation at zero polymer concentration based on eq 8. Framed areas: uncertainty of the actual results of the measurements in the present study.

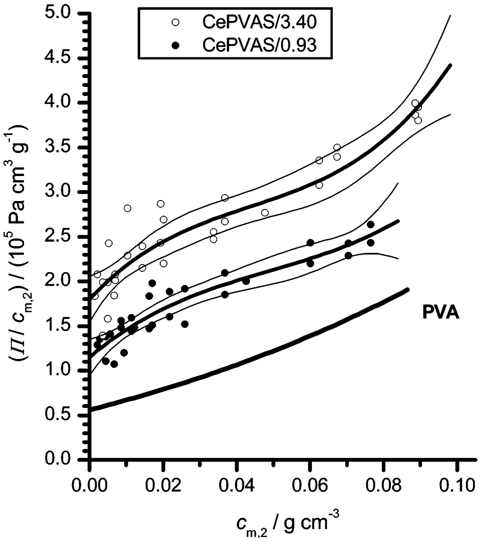


Figure 10. Reduced osmotic pressure of the two CePVAS salts of lower sulfate content as a function of polymer mass concentration. Data of pure PVA were taken from ref 33. Lines: fitted third-order polynomials with their 95% confidence bands.

and a linear relationship was established between $(\Pi/c)_0$ and α_0:

$$\left(\frac{\Pi}{c_{m,2}}\right)_{c_{m,2}\to 0} = \frac{RT}{\overline{M}_n} \times (\alpha_0 N_{ci} + 1) \tag{8}$$

Its graphical representation for the investigated LnPVAS polyelectrolytes can be seen in Figure 9. Values of real M_n can be taken from Table 2 and were calculated as follows:

$$\overline{M}_n = \overline{DP}_n \times \left[\overline{M}_{VOH} + DS \times \left(\overline{M}_{VAS} + \frac{\overline{M}_{ci}}{z} - \overline{M}_{VOH}\right)\right] \tag{9}$$

where M_{VOH} is the molar mass of the vinyl alcohol monomer units ($M_{VOH} = 44.05$ g mol^{-1}), M_{VAS} is that of the vinyl sulfate units (without counterion) ($M_{VAS} = 123.10$ g mol^{-1}), and M_{ci} is that of the counterion of charge z.

Figure 9 reveals that intercepts of reduced osmotic pressure curves of LnPVAS polyelectrolytes should be around 4−5 × 10^4 Pa cm^3 g^{-1} if no dissociation took place. As it can be seen in Figure 10 and Figure 11 (and numerically in Table 2), intercepts of the measured curves lie in fact 3−6 times higher than the theoretical values, although, at the same time, they are 4−8 times lower than those with mono- or even with divalent counterions.[21−22] Intercepts of PVAS polyelectrolytes were found to be increasing with increasing DS for all counterions investigated so far, in spite of the fact that polymers with higher M_n should have lower $(\Pi/c)_0$. The reversal is caused by the increasing number of released counterions as DS increases. This tendency is also followed by the LnPVAS salts of DS = 0.93−6.43%, however, LnPVAS salts of the highest DS (DS = 16.9%) do not fit in these series: their reduced osmotic pressure curves run definitely under those of DS = 6.43%. This return to the regular order is caused by the very low degree of dissociation: the increment of the number of osmotically active entities is not large enough compared to the intercept lowering effect of the higher M_n. A $(\Pi/c)_0$ value higher than 3 × 10^5 Pa cm^3 g^{-1} would be obtained only in the case if α_0 was >0.12, which lies far outside of the error limit (see, e.g., Figure 7). As to the shape of the curves, reduced osmotic pressure curves of LnPVAS salts at higher concentration ($c_{m,2} > 0.03$ g cm^{-3}) look like those of neutral polymers; i.e., they have the usual concave shape. At low concentrations, however, the same curves of the two CePVAS salts of lower DS (and therefore of higher degree of dissociation) have a similar convex shape observed for NaPVAS salts.[21] It is a further evidence for the supposition of a general behavior that reduced osmotic pressure curves of all polyelectrolytes may be convex at low concentrations and concave at high concentrations. No experimental method could have spanned completely these regions so far.

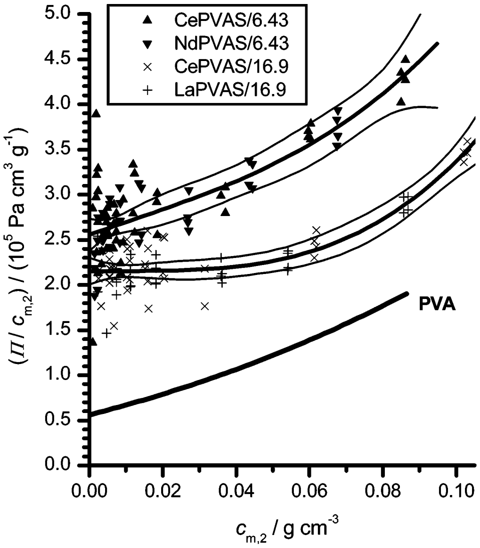


Figure 11. Reduced osmotic pressure of the polyelectrolytes of higher DS as a function of polymer mass concentration. Data of pure PVA were taken from ref 33. Lines: fitted third-order polynomials with their 95% confidence bands.

A comparison of the α_0 values obtained by the two methods for trivalent (and previously for divalent) counterions is presented in Figure 12 and Table 2. There is an excellent agreement between the results of the two independent ways, although, the Π/c method has a greater uncertainty than the χ method in both cases. The widening of the confidence intervals with decreasing DS is not caused by an increase in experimental error but it is a consequence of error propagation, as it is clearly demonstrated in Figure 9. A decreasing α_0 with DS corresponds to expectations, however, just the opposite tendency was found for monovalent counterions previously.[21] This can mean that either the sulfate half ester functional group has a kind of selectivity concerning the valence of the counterions or the highly diluted region cannot be reached because the experi-

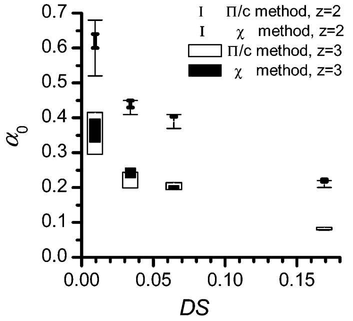


Figure 12. Degree of dissociation of di- and trivalent counterions at zero polymer concentration obtained by different calculation methods as a function of the vinyl sulfate content (DS in mole fraction) of the copolymers. Data for divalent counterions (Co^{2+}, Ni^{2+}, and Cu^{2+}) are taken from ref 22.

TABLE 3: Free Counterions of Stoichiometric LnPVAS Copolymer Polyelectrolytes[a]

sample	N_{ci}	$\alpha_0 \times N_{ci}$[a]	L_0/L[b]
LnPVAS/0.93	3.11	1.1	35:1
LnPVAS/3.40	11.4	2.7	15:1
LnPVAS/6.43	21.5	4.3	9:1
LnPVAS/16.9	56.6	4.4	9:1

[a] Number of counterions dissociated from a single polymer chain at zero polymer concentration = one-third of the resultant charge on a chain. [b] Estimated contraction ratios compared to the rod-like model.

mental method is limited already at higher concentrations by the much smaller effects in the case of di- and trivalent counterions.

As to the values of α_0, a degree of dissociation of ~0.16 was predicted by Kogej and Škerjanc,[20] based on conductance measurements, for the stoichiometric LaPSS salt by model calculations, whereas 0.4 was measured for HPSS at 0.01 M polymer monomol concentration. This latter quantity is in amazingly good agreement with the value 0.38 that was measured for NaPVAS/8.1 previously by our method and to which α_0 of NaPVAS salts approached with increasing sulfate content.[21] Investigation of (H, La) mixed counterion salts of PSS has revealed[20] that the fraction of free La^{3+} ions practically equals zero over the whole composition range where the number of H^+ ions exceeds that of the La^{3+} ions. It means that if the Ln^{3+} content is low compared to the other, monovalent, counterion, which is the case in all lanthanide fluorescence experiments,[6−16] all the trivalent counterions are "bound", and practically only the monovalent counterions dissociate. So it is no wonder that quantitative binding and relatively high formation constants[9,19] were obtained by those methods whereas finite α_0-s have been determined in the present work.

A much more interesting phenomenon can be observed if, instead of α_0, the average number of counterions released per polymer chain, $\alpha_0 \times N_{ci}$, is examined (cf. Table 3). This quantity was monotonously increasing with increasing DS in the case of both mono- and divalent counterions in the DS range investigated; however, it seems to approach to a constant value of about 4.4 for trivalent counterions. This can indicate some type of counterion condensation that restricts the charge density parameter along the chain to $\xi \leq 0.0375$ and maintains an average charge distance of $b \geq 19$ nm. On he contrary, the Manning-theory predicts counterion condensation for trivalent counterions above DS ≈ 11.7% (that alone is not a large difference from DS = 6.43% or 16.9%) but with $\xi = 0.333$ and $b = 2.2$ nm. One reason for the discrepancy between the results is that the rod-like model surely does not hold for the investigated LnPVAS polyelectrolytes (and probably in general for all polyelectrolytes with low structural charge density). It must be kept in mind that the solvent−segment interaction, characterized by the χ parameter, strongly affects chain dimensions in solution: a higher χ_{lin}, just as in the case of LnPVAS, means a more compact conformation of the polymer chain at the same time. An almost 3:1 reduction of the mean end-to-end distance of the polymer chains was detected by viscometry (in the presence of a great excess supporting electrolyte) upon adding Tb(III) to NaPAA until the $-COO^-$/Tb(III) ratio of 5:1.[13] An even much more pronounced effect must be expected in salt-free solutions where monovalent counterions do not compete with the trivalent ones, and no contraction of the polymer coil is caused by salting-out. Contraction ratios compared to the rod-like model, leading to charge density parameters that would fulfill the condition for counterion condensation according to theory, are indicated in Table 3. The biggest value (~35) for the lowest DS is not too large if we consider the end-to-end distance ratio of the fully stretched chain and the random coil which equals $(DP_n)^{0.5} = (1005)^{0.5} = 32$.

Conclusions

1. Preparation of completely water-soluble rare earth salts of copolymers carrying vinyl sulfate anionic groups in different proportions made possible a detailed thermodynamic study of polyelectrolytes with counterions of three charge number. According to literature data, this kind of study usually cannot be made simply for solubility reasons.

2. Formulas were derived for characterization of degree of dissociation and rational osmotic coefficients as a function of polyelectrolyte concentration as well as DS of the copolymers. These equations take into account all essential measurable quantities that can affect α and Φ. It turned out that the effect of each rare earth counterions on both α and Φ is indistinguishable but the effect of DS is considerable.

3. Comparison of shape of the reduced osmotic pressure vs concentration curves reveals that, in addition to the previously observed strongly back-folding ones, an inflection appears which is then followed by an opposite curvature.

4. The formation of soluble salts means that these counterions are relatively easily exchangeable (can be relatively easily displaced by adding excess of other ions); therefore, systems containing this kind of copolymers can be potentially applied in ion chromatography or, for example, reversible recovery of rare earth in the form of their salts.

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