Thermodynamics of Aqueous Solutions of Polyelectrolytes: Experimental Results for the Activity of Water in Aqueous Solutions of Some Single Synthetic Polyelectrolytes

Silke Lammertz, Pedro A. Pessoa Filho, and Gerd Maurer*

Applied Thermodynamics, Department of Mechanical and Process Engineering, University of Kaiserslautern, Erwin Schrödinger Strasse, D - 67653 Kaiserslautern, Germany, and Departamento de Engenharia Química, Escola Politécnica, USP, Caixa Postal 61548, CEP 05424-970 São Paulo, SP, Brazil

Experimental results for the activity of water in aqueous solutions of 10 single polyelectrolytes (two polysodium acrylates, two polysodium methacrylates, three polyammonium acrylates, two polysodium ethylene sulfonates, and one polysodium styrene sulfonate) at (298.2 and 323.2) K are reported. The isopiestic method was employed in these experiments with aqueous solutions of sodium chloride as references. The polyelectrolytes were characterized by three averaged molecular masses determined by gel permeation chromatography. Furthermore, the density and the refractive index increments of the aqueous polyelectrolyte solutions are reported. Although a similar pattern for the activity of water was observed for all systems (i.e., the osmotic coefficient increases with rising polyelectrolyte concentration), the experimental results show that this property depends on the monomer type as well as on the size of the polymer chain. The temperature (varied from (298.2 to 323.2) K) has only a small influence on the activity of water.

Introduction

Aqueous solutions of polyelectrolytes are widely used in many applications, e.g., as stabilizers in ointments, as swelling and gelatinizing agents in foods, as retention aids in the paper industry, and as flocculating agents in the petroleum industry,[1] as well as in drug delivery systems.[2] The thermodynamic properties of these solutions are affected by various factors, e.g., by electrostatic interactions (related to the presence of electric charges arising from the dissociation of the monomer groups) and by excluded volume effects (related to the polymeric nature of the solutes).

Although the thermodynamic properties of aqueous polyelectrolyte solutions have been investigated for many years, and despite the existence of well-established models for highly diluted solutions, such as the cell model by Lifson and Katchalsky[3] and the counterion condensation theory by Manning,[4] there is still a demand for application oriented models that are suited to correlate and predict thermodynamic properties. One of the most important reasons for the lack of application oriented models is the often insufficient characterization of the polyelectrolyte samples that were investigated.

The activity of water is one of the most important thermodynamic properties of polymeric solutions. Here we present the results of experimental investigations by the isopiestic method for the activity of water in aqueous solutions of 10 single synthetic polyelectrolytes: two polysodium acrylates (NaPA), two polysodium methacrylates (NaPMA), three polyammonium acrylates (NH_4PA), two polysodium ethylene sulfonates, (NaPES) and one polysodium styrene sulfonate (NaPSS) at (298.2 and 323.2) K. This work is an extension of previous investigations with the same technique but for aqueous solutions of various neutral polymers (polyethylene glycol,[5] dextran,[6] polyvinyl pyrrolidone,[7] and maltodextrin[8]). The polyelectrolytes were carefully characterized by gel permeation chromatography, and the polymer mass distribution is described by three moments of that distribution.

Experimental section

Materials. Table 1 gives a survey on the investigated polyelectrolytes: commercial names, manufacturers, and lots. The number following the polyelectrolyte abbreviation is the manufacturer's characterization of the average molar mass (in $kg \cdot mol^{-1}$). With the exception of NaPA 15, NaPES 10, and NaPSS 70, all polyelectrolytes were supplied as aqueous solutions. The polymer contents of these solutions were provided by the suppliers and checked by freeze-drying. In most cases, the relative difference between the claimed polymer content and the actual value was less than 6 %. Only for a single polyelectrolyte (NaPES 2), the difference was considerable: the claimed content was 0.25 $g \cdot g^{-1}$, whereas the experimentally determined value was 0.350 $g \cdot g^{-1}$. The aqueous polyelectrolyte solutions were used as supplied or diluted with deionized water. Polyelectrolytes NaPA 15, NaPES 10, and NaPSS 70 were supplied as solids. These solids were kept in desiccators under vacuum [(0.1 to 1.0) Pa] and dissolved in deionized water. All other reagents were of analytical grade.

Experimental Methods

Gel Permeation Chromatography. The investigated polyelectrolytes were characterized by gel permeation chromatography (GPC) to determine the polymer molecular mass distribution. GPC experiments were performed with commercially available equipment. The measurements were conducted using two chromatographic columns with pore sizes of (100 and 1000) Å, respectively (type PSS Suprema from Polymer Standard Service, Mainz, Germany) in series. Only for (the rather low-molecular sample) NaPES 2, a single column with a better

---

* Corresponding author. E-mail: maurer@mv.uni-kl.de.

10.1021/je800108u CCC: $40.75

Table 1. List of Polyelectrolytes Investigated in This Work

polyelectrolye[a]	commercial name	manufacturer	lot
NaPA 5	Rohagit SL 137	Roehm GmbH, Darmstadt, Germany	LJ 13124/30
NaPA 15	Sokalan SA 40	BASF AG, Ludwigshafen, Germany	68-E5512
NH_4PA 5	Rohagit SL 135	Roehm GmbH, Darmstadt, Germany	12-601-2022
NH_4PA 10	Rohagit SL 159	Roehm GmbH, Darmstadt, Germany	LJ 13175/39
NH_4PA 20	Rohagit SL 252	Roehm GmbH, Darmstadt, Germany	10-508-T21-603
NaPMA 6		Sigma-Aldrich Chemie GmbH, Steinheim, Germany	07604 PG
NaPMA 15		Polysciences Europe GmbH, Eppelheim, Germany	414267
NaPES 2		Polysciences Europe GmbH, Eppelheim, Germany	420677, 462618
NaPES 10	Natriumpolat PIPU 005	Hoechst GmbH, Frankfurt, Germany	W900
NaPSS 70		Sigma-Aldrich Chemie GmbH, Steinheim, Germany	79022

[a] The number following the polyelectrolyte abbreviation is the molar mass expressed in $kg \cdot mol^{-1}$ given by the manufacturer.

Table 2. Density and Refractive Index Increment of Aqueous Polyelectrolyte Solutions at 298.2 K

	density (cf. eq 5)		(dn/dc)
polyelectrolye	a	b	$cm^3 \cdot g^{-1}$
NaPA 5	0.5353	0.4686	0.1878
NaPA 15	0.5881	0.2220	0.1820
NH_4PA 5	0.3818	−0.0312	0.2173
NH_4PA 10	0.4074	0.1686	0.2116
NH_4PA 20	0.4162	−0.0249	0.2210
NaPMA 6	0.5774	0.2443	0.2163
NaPMA 15	0.5959	0.5132	0.2261
NaPES 2	0.8231	0.3652	0.1381
NaPES 10	0.5875	0.2159	0.1373
NaPSS 70	0.4405	0.1988	0.1789

separation efficiency for lower polymer masses (type MCX 500 also from Polymer Standard Service, Mainz, Germany) was used. Polyelectrolyte samples had a concentration between 6 $g \cdot dm^{-3}$ and 15 $g \cdot dm^{-3}$. The eluent was an aqueous solution of either sodium sulfate (0.05 M) or disodium hydrogen phosphate (0.07 M). Both eluents also contained a small amount ($5 \cdot 10^{-4}$ $g \cdot g^{-1}$) of the bactericide sodium azide. A multiangle laser light scattering photometer (type DAWN DSP from Wyatt Technology Corp., Santa Barbara, Ca. USA) and a refractive index detector (type Optilab 903, also from Wyatt Technology Corp., Santa Barbara, Ca. USA) were used in series. All chromatographic experiments were conducted at 298.2 K. Each chromatogram was determined in triplicate for each polyelectrolyte with both eluents. Only for the rather low-molecular samples NaPMA 6 and NaPES 2, a single eluent (aqueous solution of disodium hydrogen phosphate) was used. More details on the experimental procedures and the evaluation of the direct experimental results (i.e., the signals from both detectors) were described by Lammertz.[9]

The evaluation requires the densities and the refractive indices of the aqueous polymer solution, and hence both properties were determined (see below). The evaluation resulted in a chromatogram to which the parameters of a polymer distribution function were fitted using the software Origin 6.1

$$\frac{dw_i}{d\log M_i} = y_0 + A\left(\frac{2}{\pi}\frac{m_u a}{(M_i - M_c) + a^2} + \frac{(1 - m_u)}{a}\sqrt{\frac{4\ln 2}{\pi}}\exp\left(\frac{4\ln 2}{a^2}(M_i - M_c)^2\right)\right) \tag{1}$$

The symbols in eq 1 are as follows: w_i is the mass fraction with molecular mass M_i; y_0 is the baseline displacement; A is a parameter; m_u is a shape factor; a is a parameter that characterizes the width of the molecular mass distribution amplitude; and M_c is the molecular mass of the fraction that yields the peak maximum. The parameters y_0, A, m_u, a, and M_c were optimized by the software to give a good representation of the experimental results for the gradient $(dw_i)/(d \log M_i)$.

The resulting distribution function $w_i(M_i)$ was used to determine three moments which represent the number average molar mass (M_n), the mass average molar mass (M_w), and the z-average molar mass (M_z)

$$M_n = \frac{1}{\sum_i w_i M_i^{-1}} \tag{2}$$

$$M_w = \sum_i w_i M_i \tag{3}$$

$$M_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \tag{4}$$

Density and Refractive Index Increment. The evaluation of the direct experimental data from the GPC measurements requires the density ρ of the aqueous polyelectrolyte solution and the change of its refractive index n with the volume concentration c of the polymer (the refractive index increment) at 298.2 K.

The density was determined with a vibrating tube density meter (model DMA 602, Heraeus, Graz, Austria). The density meter was calibrated using water and tetrachloromethane. The specific densities of these pure liquids at 298.2 K were taken from the literature[10] (H_2O, 0.99705 $g \cdot cm^{-3}$; CCl_4, 1.5850 $g \cdot cm^{-3}$). The estimated uncertainty of the density measurement is below 0.0002 $g \cdot cm^{-3}$.

The refractive index increment dn/dc was determined with a refractive index detector (model Optilab 903, Wyatt Technology Corp., Santa Barbara, Ca. USA). That equipment was calibrated with aqueous solutions of sodium chloride and potassium chloride at 293.2 K. The refractive index increments of these aqueous solutions were taken from Huglin[11] (NaCl, dn/dc = 0.177 $cm^3 \cdot g^{-1}$; KCl, dn/dc = 0.137 $cm^3 \cdot g^{-1}$). Details of the calibration procedure were described by Lammertz.[9] The estimated relative uncertainty of the experimental results for the refractive index increment is 1.2 %.

Isopiestic Measurements. The activity of water in aqueous polyelectrolyte solutions was measured at (298.2 and 323.2) K with the isopiestic method, using sodium chloride as the reference substance. The experiments were conducted as described previously[12] with two different cell holders. One cell holder is able to handle up to 9 cells, the other up to 30 cells. The volume of each cell is about 5 cm^3. In an experiment, four cells were filled with solutions of the reference substance. The expected result for the water activity was roughly estimated, and the corresponding molality of sodium chloride was determined. Afterward, two cells were filled with an aqueous solution that contained more and two cells with an aqueous solution that contained less sodium chloride.

Table 3. Characterization of the Investigated Polyelectrolytes: Number Average Molar Mass (M_n) and Standard Deviation ($\sigma(M_n)$), Mass Average Molar Mass (M_w) and Standard Deviation ($\sigma(M_w)$), z-Average Molar Mass (M_z) and Standard Deviation ($\sigma(M_z)$), Polydispersity Index (M_w/M_n), and Average Number of Monomer Units

polyelectrolyte	M_n / $g \cdot mol^{-1}$	$\sigma(M_n)$ / $g \cdot mol^{-1}$	M_w / $g \cdot mol^{-1}$	$\sigma(M_w)$ / $g \cdot mol^{-1}$	M_z / $g \cdot mol^{-1}$	$\sigma(M_z)$ / $g \cdot mol^{-1}$	M_w/M_n	n_p
NaPA 5	2600	110	4300	190	6100	400	1.65	28
NaPA 15	6900	370	17300	540	39700	890	2.51	73
NH_4PA 5	2300	90	3900	190	5800	320	1.70	26
NH_4PA 10	7700	320	13300	460	19400	770	1.73	87
NH_4PA 20	7300	250	13600	390	19200	970	1.82	82
NaPMA 6	6100	470	10000	370	15400	690	1.64	56
NaPMA 15	14200	260	20500	520	27600	320	1.44	132
NaPES 2	1600	40	2800	120	5100	370	1.75	12
NaPES 10	6900	330	11800	910	16200	950	1.71	53
NaPSS 70	127000	6200	148000	12600	155000	9700	1.17	612

Table 4. Experimental Results for the Activity of Water (a_w) in Aqueous Solutions of NaPA 5 Solutions as a Function of Polyelectrolyte Mass Fraction (w_p) at 298.2 K

$w_p/g \cdot g^{-1}$	a_w
0.1322	0.9887
0.1469	0.9880
0.1476	0.9881
0.1680	0.9842
0.1929	0.9798
0.2000	0.9788
0.2097	0.9777
0.2402	0.9701
0.2426	0.9690
0.2593	0.9646
0.2756	0.9617
0.2773	0.9588
0.2932	0.9526
0.2936	0.9523
0.2962	0.9531
0.3401	0.9307

Each of the remaining 5 (or 26) cells was filled with an aqueous polyelectrolyte solution (approximately 1.0 g) of known polyelectrolyte content. When the large cell holder was used, up to five different polyelectrolytes were simultaneously investigated. The cell holder was closed, shortly evacuated to minimize the presence of air in the vapor space above the cells, and left at the desired temperature for a period of up to four weeks to attain equilibrium. The temperature of the water bath that was used to keep the temperature of the cell holder constant varied over this period of time by less than 0.1 K. That temperature was measured with calibrated platinum resistance thermometers. The uncertainty of the experimental result for the temperature is also less than 0.1 K. During equilibration, the cell holder was rotated. The axis of rotation was declined to allow a stirring of the aqueous solutions in the cell. That stirring was favored by small spheres of stainless steel that were placed in each glass cell. During equilibration, water is transported through the vapor phase between the cells until the activity of water in each of the cells (and consequently the partial pressure of water above each cell) attains the same value. At the end of an experiment, the cells were removed from the cell holder, and the amount of solution in each cell was determined using a high precision balance. From that data and the amount of solid substance in each cell, known from the preparation, the solute concentration in each of the coexisting solutions was calculated. The activity of water in all four reference cells was calculated from Pitzer's correlation for the activity of water in aqueous solutions of sodium chloride.[13] Typically, the relative deviations in the mass fraction of a solute in an aqueous solution of a single solute (either sodium chloride or a polyelectrolyte) differed by less than 0.1 %. These differences in the molality of sodium chloride in all four reference solutions correspond to an absolute difference of less than 0.0001 in the activity of water, resulting in an estimated uncertainty for the activity of water in a polymer solution of 0.0002.

Results and Discussion

Density and Refractive Index Increment. The experimental results for the density ρ of polyelectrolyte solutions at 298.2 K were correlated with the mass fraction w_p of the polymer in the solution using a quadratic relation:

$$\rho/\rho_w = 1 + aw_p + bw_p^2 \tag{5}$$

where ρ_w is the specific density of water (at 298.2 K, $\rho_w = 0.99705\ g \cdot cm^{-3}$) and a and b are polyelectrolyte specific coefficients. These coefficients are given in Table 2. The correlations reproduce the experimental results within the estimated uncertainty (i.e., 0.0002 $g \cdot cm^{-3}$).

The refractive index increment was determined at 298.2 K for aqueous solutions of all single polyelectrolytes at polymer concentrations from $4 \cdot 10^{-4}\ g \cdot g^{-1}$ to $2.4 \cdot 10^{-3}\ g \cdot g^{-1}$. Within that concentration range, the scattering of the results was smaller than 0.5 %, i.e., about 50 % of the estimated experimental uncertainty. The results are also given in Table 2.

Polyelectrolyte Characterization. The detailed experimental results for the polymer mass distribution functions were given by Lammertz.[9] The results for M_n, M_w, and M_z are given in Table 3 together with the standard deviations from the multiple measurements. The comparison between the mass-averaged molecular mass from the GPC measurements and the suppliers' crude estimates for that property reveals large differences for NaPSS 70 (70 000 versus 148 000), for NH_4PA 20 (20 000 versus 13 600), for NaPA 6 (6000 versus 10 000), and for NaPMA 15 (15 000 versus 20 500). This indicates that the suppliers' declaration is not always sufficient to characterize a polymer sample. This statement strongly holds for the samples of NH_4PA 10 and NH_4PA 20. The supplier's declarations for these two samples indicate a difference of about two in the average molecular mass, but the GPC experiments show that the difference is within the standard deviations of the GPC results (13 500 ± 400). Table 3 also gives for each polymer sample the ratio M_w/M_n (i.e., the so-called polydispersity factor). When the polymer molecular mass distribution becomes broader, the polydispersity factor increases; i.e., it deviates more and more from one. All investigated polyelectrolyte samples are not very disperse, as the polydispersity is at minimum about 1.2 (for NaPSS 70) and at maximum about 2.5 (for NaPA 15).

Isopiestic Measurements. The new experimental results for the activity of water are given in Tables 5 to 13. On one side, the activity of water only slightly deviates from one, and on the other side, the relative uncertainty of the experimental results for the activity of water increases drastically in the high-dilution area. Therefore, no experiments were carried out at polymer mass fractions below about 10 %.

Table 5. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPA 15 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1406	0.9887	0.1398	0.9888
0.1795	0.9842	0.1807	0.9847
0.2090	0.9798	0.2081	0.9801
0.2228	0.9778	0.2587	0.9706
0.2620	0.9690	0.2946	0.9614
0.2776	0.9646	0.3149	0.9550
0.2783	0.9657	0.3457	0.9420
0.2974	0.9588		
0.3123	0.9523		
0.3149	0.9529		
0.3155	0.9526		
0.3412	0.9402		
0.3557	0.9307		
0.3607	0.9299		
0.3696	0.9291		
0.4144	0.8958		

Table 6. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NH_4PA 5 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1202	0.9887	0.1250	0.9888
0.1536	0.9842	0.1550	0.9847
0.1794	0.9798	0.1864	0.9801
0.1871	0.9787	0.2308	0.9706
0.2367	0.9690	0.2793	0.9614
0.2407	0.9672	0.3050	0.9550
0.2556	0.9646	0.3428	0.9420
0.2781	0.9588		
0.2854	0.9545		
0.2865	0.9571		
0.2989	0.9523		
0.3506	0.9307		

Table 7. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NH_4PA 10 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1361	0.9887	0.1423	0.9888
0.1715	0.9842	0.1749	0.9847
0.1974	0.9798	0.2058	0.9801
0.2051	0.9787	0.2479	0.9706
0.2571	0.9690	0.3016	0.9614
0.2592	0.9672	0.3272	0.9550
0.2756	0.9646	0.3623	0.9420
0.2975	0.9588		
0.3015	0.9545		
0.3061	0.9571		
0.3158	0.9526		
0.3190	0.9523		
0.3207	0.9529		
0.3442	0.9402		
0.3678	0.9299		
0.3681	0.9307		

Table 8. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NH_4PA 20 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1282	0.9887	0.1344	0.9888
0.1615	0.9842	0.1655	0.9847
0.1875	0.9798	0.1957	0.9801
0.2054	0.9766	0.2396	0.9706

Table 9. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPMA 6 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1077	0.9926	0.1587	0.9866
0.1517	0.9876	0.1958	0.9809
0.2054	0.9802	0.2002	0.9800
0.2072	0.9799	0.2248	0.9750
0.2153	0.9784	0.2652	0.9651
0.2381	0.9728	0.2660	0.9644
0.2588	0.9675	0.2803	0.9595
0.2602	0.9674	0.3052	0.9495
0.3006	0.9533		
0.3015	0.9528		
0.3262	0.9408		
0.3280	0.9396		

Table 10. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPMA 15 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1435	0.9893	0.1734	0.9866
0.1663	0.9867	0.2084	0.9800
0.1977	0.9823	0.2324	0.9750
0.2598	0.9697	0.2689	0.9651
0.3017	0.9519	0.2712	0.9644
0.3257	0.9388	0.2850	0.9595
		0.3102	0.9495

Table 11. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPES 2 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.2551	0.9677	0.1290	0.9866
0.3560	0.9431	0.1704	0.9809
0.4497	0.9054		

From the activity of water, the osmotic coefficient is calculated[14]

$$\phi = \frac{\ln a_w(T, P, w_p)}{\ln a_w^{\text{ideal}}(T, P, w_p)} \tag{6}$$

where a_w^{ideal} is the activity of water in an *ideal* aqueous solution. The reference state for the chemical potential of the solvent is the pure solvent at temperature and pressure of the solution. The reference state for the chemical potential of a solute is a one molal solution in the pure solvent where the solute experiences the same interactions as at infinite dilution. Assuming that at infinite dilution in the solvent the polyelectrolyte is completely dissociated into a charged polymer backbone and mobile counterions and only a single counterion dissociates from one monomer unit, we get for the activity of water in an ideal mixture

$$\ln a_w^{\text{ideal}}(T, P, w_p) = -M_w^* m_p(1 + n_p) \tag{7}$$

where m_p is the molality of the polymer; n_p is the number of monomer units that constitute the polyelectrolyte; and M_w^* is the molar mass of water expressed in kg·mol^{-1}.

The number of monomer units n_p was calculated for all polyelectrolytes investigated in the present work from the number averaged molecular mass M_n and the molecular mass of a monomer unit. These numbers (which are also given in Table 3) were used to convert the water activity data to osmotic coefficients. The uncertainties of the experimental results for

Table 12. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPES 10 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.0793	0.9974	0.2438	0.9866
0.2113	0.9883	0.3061	0.9809
0.3179	0.9803	0.3139	0.9800
0.3911	0.9687	0.3543	0.9750
0.4057	0.9667	0.4031	0.9651
0.4171	0.9647	0.4135	0.9644
0.4462	0.9559	0.4253	0.9595
0.4777	0.9485	0.4570	0.9495
0.4979	0.9345		
0.5295	0.9270		

Table 13. Experimental Results for Water Activity (a_w) as a Function of Polyelectrolyte Mass Fraction (w_p) in NaPSS 70 Solutions at (298.2 and 323.2) K

T/K = 298.2		T/K = 323.2	
w_p/g·g^{-1}	a_w	w_p/g·g^{-1}	a_w
0.1082	0.9933	0.1847	0.9866
0.1696	0.9884	0.2389	0.9800
0.2475	0.9794	0.2738	0.9750
0.2759	0.9749	0.3240	0.9651
0.3013	0.9707	0.3303	0.9644
0.3288	0.9674		
0.3851	0.9558		
0.3909	0.9551		
0.4460	0.9417		
0.4867	0.9292		

the activity of water Δa_w and for the polyelectrolyte mass fraction Δw_p were used to evaluate the uncertainty of the reported osmotic coefficients. This value is estimated to be 0.01. The influence of the length of the polymer chain is shown in Figures 1 and 2 for sodium acrylates and ammonium acrylates at 298.2 K. The molecular masses of both sodium acrylates differ by a factor of about three. At higher polymer concentration, the absolute difference between the osmotic coefficients of both polymers is nearly constant ($\approx$ 0.1). With increasing dilution, that difference becomes smaller, and although a reliable extrapolation to pure water is very difficult, the experimental results for the osmotic coefficients at infinite dilution of both polyelectrolytes do not reveal a large difference. However, that limiting value is well below one, which obviously indicates that the polymer is not completely dissociated at infinite dilution. This behavior (commonly called "counter ion condensation") was found for all investigated polyelectrolytes. As shown in Figure 2, the osmotic coefficients of aqueous solutions of NH_4PA differ at constant polymer mass fraction by less than 0.1. At low polymer concentrations, the counterion condensation phenomenon dominates the osmotic coefficient, and the molecular mass of the polyelectrolyte exerts only a small influence on that effect.

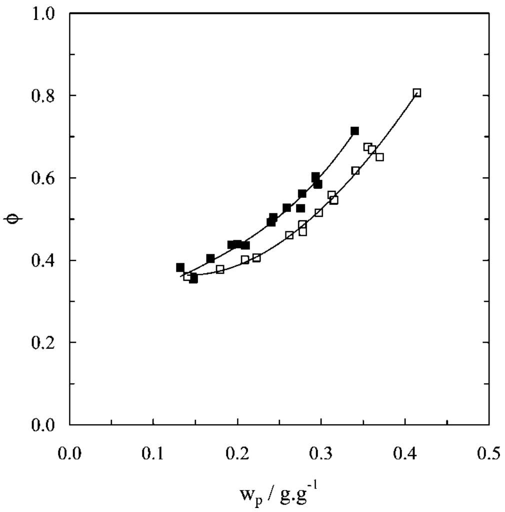

Figure 1. Osmotic coefficient (ϕ) of aqueous solutions of polysodium acrylate at 298.2 K as a function of polyelectrolyte mass fraction (w_p). ■, NaPA 5; □, NaPA 15. Lines are shown to guide the eyes.

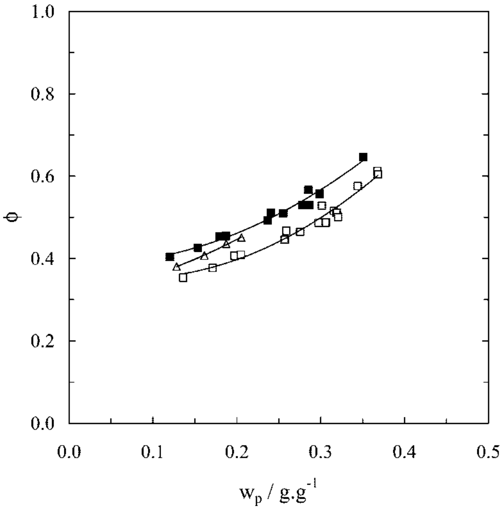

Figure 2. Osmotic coefficient (ϕ) of aqueous solutions of polyammonium acrylate at 298.2 K as a function of polyelectrolyte mass fraction (w_p). ■, NH_4PA 5; □, NH_4PA 10; Δ, NH_4PA 20. Lines are shown to guide the eyes.

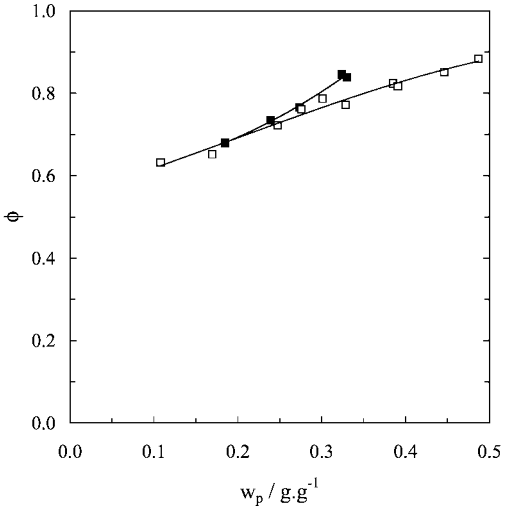

Figure 3. Osmotic coefficient (ϕ) of aqueous solutions of polysodium styrene sulfonate as a function of polyelectrolyte mass fraction (w_p). □, NaPSS 70 at 298.2 K; ■, NaPSS 70 at 323.2 K. Lines are shown to guide the eyes.

The osmotic coefficient changes only slightly when the temperature increases from (298 to 323) K. A typical example is shown in Figure 3 (for NaPSS 70).

The type of the monomer unit has an important influence on the osmotic coefficient. This is shown in Figure 4, where the experimental results for the osmotic coefficient of aqueous solutions of NaPA 15 and NaPMA 6 are shown. The difference between the molecular masses (and the number of monomer units) of these polyelectrolytes falls within experimental uncertainty, and hence the main difference is the presence of an additional methyl group in the methacrylate monomer unit. The osmotic coefficients differ

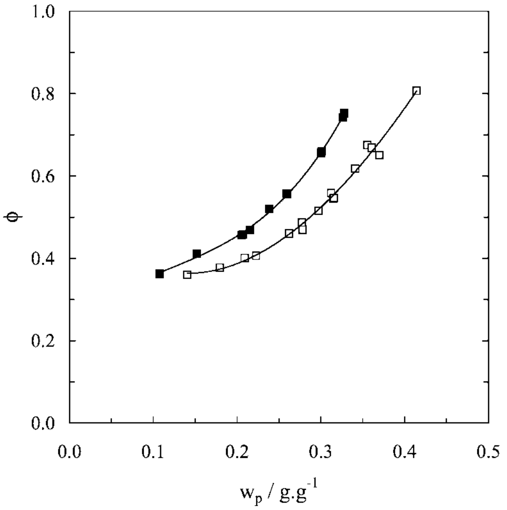

Figure 4. Osmotic coefficient (ϕ) of aqueous solutions of polyelectrolytes at 298.2 K as a function of polyelectrolyte mass fraction (w_p). □, NaPA 15; ■, NaPMA 6. Lines are shown to guide the eyes.

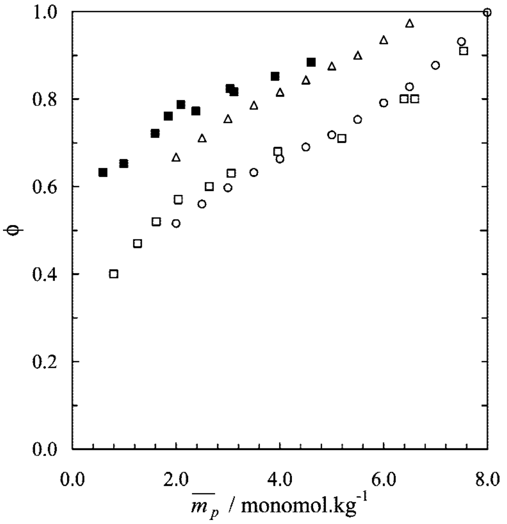

Figure 5. Osmotic coefficient (ϕ) of aqueous solutions of polysodium styrene sulfonate at 298.2 K as a function of polyelectrolyte monomolality ($\bar{m}_p$): comparison with literature data. ■, NaPSS 70, this work; □, NaPSS 500, Reddy and Marinsky;[17] △, NaPSS 400; and ○, NaPSS 70, Bonner and Overton.[18]

by about 0.1 to 0.2 at high polyelectrolyte mass fractions, but this difference decreases as the polyelectrolyte concentration decreases. The behavior at high dilutions (not investigated in this work) is expected to be similar: the counterion condensation is the main factor influencing the osmotic coefficient in this region, and large differences are not expected, considering the similarity between both polyelectrolytes. At higher concentrations, such as those investigated in this work, the nature of the polyelectrolyte backbone becomes significant, as excluded volume effects and short-range interactions play an important role, and therefore high differences are observed.

Comparison with Literature Data. Some of the new experimental results can be compared with literature data. For example, experimental results for the osmotic coefficient of aqueous solutions of NaPSS at 298.2 K were reported by Oman,[15] Takahashi et al.,[16] Reddy and Marinsky,[17] and Bonner and Overton.[18] Figure 5 shows a comparison between literature data and the new experimental data in a presentation where the osmotic coefficient is plotted versus the polyelectrolyte's "monomolality", i.e., the molality of monomer units, defined by

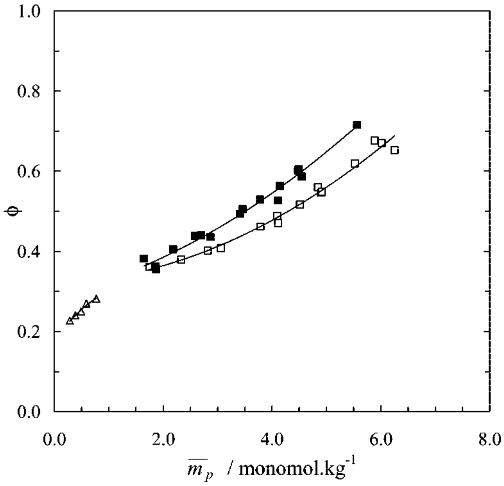

Figure 6. Osmotic coefficient (ϕ) of aqueous solutions of polysodium acrylate at 298.2 K as a function of polyelectrolyte monomolality ($\bar{m}_p$): comparison with literature data. ■, NaPA 5, this work; □, NaPA 15, this work; Δ, NaPA 260, Kakehashi et al.[19] Lines are shown to guide the eyes.

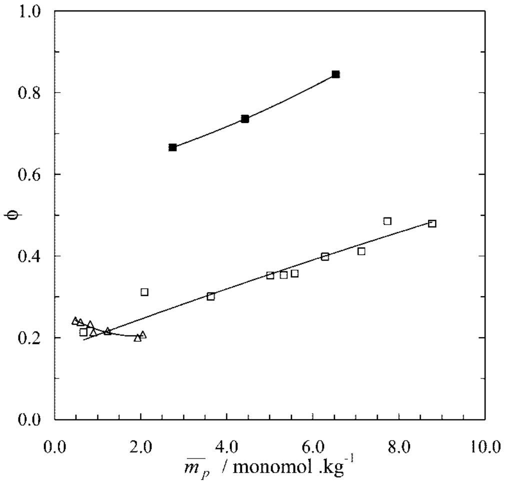

Figure 7. Osmotic coefficient (ϕ) of aqueous solutions of polysodium ethylene sulfonate at 298.2 K as a function of polyelectrolyte monomolality ($\bar{m}_p$): comparison with literature data. ■, NaPES 2, this work; □, NaPES 10, this work; Δ, NaPES 100, Ise and Asai.[20] Lines are shown to guide the eyes.

$$\bar{m}_p = m_p n_p \tag{8}$$

The monomolality is independent both of the size of the polymer chain and of the polydispersity. It is a common phenomenon that literature data for the osmotic coefficient of aqueous polyelectrolyte solutions reveal a large scattering. The new experimental data lie systematically above the results of Bonner and Overton[18] that were also reported for a NAPSS 70 sample. The same authors also gave osmotic coefficients of aqueous solutions of NaPSS with a higher molecular mass (NaPSS 400). These data agree with our new results nearly within the combined experimental uncertainties. However, the experimental data by Reddy and Marinsky[17] for NaPSS 500 agree well with the data that were reported by Bonner and Overton[18] for NaPSS 70. One of the reasons for these differences might be an insufficient characterization of the molecular mass distributions of the polymer samples investigated before.

Figure 6 shows a comparison between the experimental results for aqueous solutions of both NaPA samples and the data reported by Kakehashi.[19] Kakehashi determined the osmotic coefficient of aqueous solutions of NaPA 260 by membrane osmometry at very low polyelectrolyte concentrations. As the polymer concentration range of his experiments does not overlap with the range of the isopiestic investigations of the present work, only a qualitative comparison is possible: both sets of data seem to be in good agreement.

Figure 7 shows experimental results for the osmotic coefficient of aqueous solutions of NaPES. The results of Ise and Asai[20] for aqueous solutions of NaPES 100 reveal an unexpected influence of the polymer concentration on the osmotic coefficient. However, we assume that this small decrease of the osmotic coefficient with increasing polymer concentration lies within the experimental uncertainty of that data. The differences between the results of Ise and Asai[20] for NaPES 100 and the new results for NaPES 10 lie within the scattering of the new data.

Nomenclature

a = distribution amplitude, parameter in eq 1
a = parameter in eq 5
A = amplitude, parameter in eq 1
a_w = water activity
a_w^{ideal} = water activity of a hypothetical ideal solution of same composition
b = parameter in eq 5
c = polyelectrolyte mass concentration [$\mathrm{g \cdot cm^{-3}}$]
M_c = peak abscissa, parameter in eq 1 [$\mathrm{g \cdot mol^{-1}}$]
M_w^* = water molar mass [$0.018\ \mathrm{kg \cdot mol^{-1}}$]
M_i = molar mass of polyelectrolyte fraction i [$\mathrm{g \cdot mol^{-1}}$]
M_n = number average molar mass [$\mathrm{g \cdot mol^{-1}}$]
m_p = polyelectrolyte molality [$\mathrm{mol \cdot kg^{-1}}$]
m_p = polyelectrolyte monomolality [$\mathrm{monomol \cdot kg^{-1}}$]
m_u = shape factor, parameter in eq 1
M_w = mass average molar mass [$\mathrm{g \cdot mol^{-1}}$]
M_z = z-average molar mass [$\mathrm{g \cdot mol^{-1}}$]
n = refractive index
n_p = number of polyelectrolyte monomers in polyelectrolyte molecule
P = pressure
T = temperature
w_p = mass fraction of polyelectrolyte [$\mathrm{g \cdot g^{-1}}$]
w_i = mass fraction of polyelectrolyte fraction i [$\mathrm{g \cdot g^{-1}}$]
y_0 = the baseline displacement, parameter in eq 1

Greek Letters

ϕ = osmotic coefficient
ρ = specific density of polyelectrolyte solution [$\mathrm{g.cm^{-3}}$]
ρ_w = specific density of water [$\mathrm{g \cdot cm^{-3}}$]
σ = standard deviation

Abbreviations

NaPA = polysodium acrylate
NaPMA = polysodium methacrylate
NH_4PA = polyammonium acrylate
NaPES = polysodium ethylene sulfonate
NaPSS = polysodium styrene sulfonate

Literature Cited

(1) Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, C.; Stscherbina, D. *Polyelectrolytes*; Hanser Publishers: Munich, 1994.
(2) Hartig, S. M.; Greene, R. R.; Dikov, M. M.; Prokop, A.; Davidson, J. M. Multifunctional Nanoparticulate Polyelectrolyte Complexes. *Pharm. Res.* **2007**, *24*, 2353–2369.
(3) Lifson, S.; Katchalsky, A. The Electrostatic Free Energy of Polyelectrolyte Solutions. II. Fully Stretched Macromolecules. *J. Polym. Sci.* **1954**, *13*, 43–55.
(4) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions. I. Colligative Properties. *J. Chem. Phys.* **1969**, *51*, 924–933.
(5) Hasse, H.; Kany, H.-P.; Tintinger, R.; Maurer, G. Osmotic virial coefficients of aqueous polyethylene glycol) from laser-light scattering and isopiestic measurements. *Macromolecules* **1995**, *28*, 3540–3552.
(6) Kany, H.-P.; Hasse, H.; Maurer, G. Thermodynamic properties of aqueous dextran solutions from laser-light-scattering, membrane osmometry, and isopiestic measurements. *J. Chem. Eng. Data* **1999**, *44*, 230–242.
(7) Kany, H.-P.; Hasse, H.; Maurer, G. Thermodynamic properties of aqueous poly(vinylpyrrolidone) solutions from laser-light-scattering, membrane osmometry, and isopiestic measurements. *J. Chem. Eng. Data* **2003**, *48*, 689–698.
(8) Ninni, L.; Meirelles, A. J. A.; Maurer, G. Thermodynamic properties of aqueous solutions of maltodextrins from laser-light scattering, calorimetry and isopiestic investigations. *Carbohyd. Polym.* **2005**, *59*, 289–303.
(9) Lammertz, S. *Thermodynamische Eigenschaften wässriger Polyelektrolytlösungen - PhD. Thesis, Technische Universität Kaiserslautern*; Shaker Verlag: Aachen, 2005.
(10) *VDI-Wärmeatlas*, 10th ed.; Springer-Verlag: Berlin, 2006.
(11) Huglin, M. B. *Light scattering from polymer solutions*; Academic Press: London, 1972.
(12) Groβmann, C.; Tintinger, R.; Zhu, J.; Maurer, G. Aqueous two-phase systems of poly(ethylene glycol) and dextran - experimental results and modeling of thermodynamic properties. *Fluid Phase Equilib.* **1995**, *106*, 111–138.
(13) Pitzer, K. S. *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press: Boca Raton, 1991.
(14) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria*, 3rd. ed.; Prentice Hall PTR: NJ, 1999.
(15) Oman, S. Osmotic coefficients of aqueous polyelectrolyte solutions at low concentrations, 1. Polystyrenesulfonates with mono- and bivalent counterions. *Die Makromolekulare Chemie* **1974**, *175*, 2133–2140.
(16) Takahashi, A.; Kato, N.; Nagasawa, M. The osmotic pressure of polyelectrolyte in neutral salt solutions. *J. Phys. Chem.* **1970**, *74*, 944–946.
(17) Reddy, M.; Marinsky, J. A. A further investigation of the osmotic properties of hydrogen and sodium polystyrenesulfonates. *J. Phys. Chem.* **1970**, *74*, 3884–3891.
(18) Bonner, O. D.; Overton, J. R. The investigation of the behavior of some polysulfonates in concentrated aqueous solutions. *J. Phys. Chem.* **1963**, *67*, 1035–1039.
(19) Kakehashi, R.; Yamazoe, H.; Maeda, H. Osmotic coefficients of vinylic polyelectrolyte solutions without added salt. *Colloid Polym. Sci.* **1998**, *276*, 28–33.
(20) Ise, N.; Asai, K. Mean activity coefficient of polyelectrolytes IX. measurements of poly(ethylenesulfonates) of various gegenions. *J. Phys. Chem.* **1968**, *72*, 1366–1369.

Received for review February 12, 2008. Accepted April 23, 2008. P.A.P.F. gratefully acknowledges a scholarship from CAPES (Brasilia, Brazil, process BEX 2941/07−4).

JE800108U