Thermodynamics of Aqueous Solutions of Polyelectrolytes: Experimental Results for the Activity of Water in Aqueous Solutions of (a Single Synthetic Polyelectrolyte and Sodium Chloride)

Silke Lammertz,[†] Pedro A. Pessoa Filho,[‡] and Gerd Maurer*[,†]

Lehrstuhl für Technische Thermodynamik, Technische Universität 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, synthetic polyelectrolytes (polysodium acrylate, polysodium methacrylate, polyammonium acrylate, polysodium ethylene sulfonate, and polysodium styrene sulfonate) and sodium chloride at 298.2 K are presented. The experimental work was performed by applying the isopiestic method with sodium chloride as a reference substance. As expected, the activity of water decreases when the concentration of a polyelectrolyte and/or sodium chloride increases. At constant concentration of a polyelectrolyte and sodium chloride, the activity of water depends on the monomer unit and the molecular mass of the polyelectrolyte. The new data are to be used in future work to develop and test models for the Gibbs excess energy of aqueous solutions of polyelectrolytes.

Introduction

The activity of water is one of the most significant thermodynamic properties of aqueous solutions of nonvolatile compounds. Its importance is chiefly related to the fact that it allows a direct assessment of the nonideality of these solutions. In a previous paper,[1] we presented new experimental results for the activity of water in aqueous solutions of 10 single synthetic polyelectrolytes together with a profound characterization of these polyelectrolytes by gel permeation chromatography. The experimental results were obtained with an apparatus that utilizes the isopiestic technique. Although highly dilute solutions were not specifically investigated, it could be observed that the limiting value of the osmotic coefficient at infinite dilution is lower than one. That indicates the occurrence of counterion condensation.[2]

Here, we extend that previous investigation to aqueous solutions of the same synthetic polyelectrolytes that additionally contain sodium chloride. Aqueous solutions of polysodium acrylate (NaPA, two different molar masses), polysodium methacrylate (NaPMA, two different molar masses), polyammonium acrylate (NH_4PA, three different molar masses), polysodium ethylene sulfonate (NaPES, two different molar masses), and polysodium styrene sulfonate (NaPSS) were investigated at concentrations from below 10 mass percent to nearly 40 mass percent. The sodium chloride concentration was between about (0.3 and 14) mass percent. All experiments were carried out at 298.2 K.

Experimental Section

Materials. Table 1 gives a survey of the investigated polyelectrolytes (acronyms, manufacturers, and commercial names). The number following the polyelectrolyte acronym is the relative molecular mass of the polyelectrolyte sample which was provided by the manufacturer. All polyelectrolytes were previously investigated by gel permeation chromatography,[1] and the molecular size distributions were characterized by the following three average molar masses (cf. Table 2):

the number average molar mass M_n

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

the mass average molar mass M_w

$$M_w = \sum_i w_i M_i \tag{2}$$

and the *z*-average molar mass M_z

$$M_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \tag{3}$$

where w_i is the mass fraction of the polyelectrolyte fraction with molar mass M_i. The complete characterization of the polymer size distribution is available elsewhere (Lammertz[3]).

NaPA 15, NaPES 10, and NaPSS 70 were supplied as solids. All other polyelectrolytes were supplied in aqueous solutions. The polymer content of these solutions was provided by the suppliers and checked by freeze-drying analysis. All samples were used as supplied, i.e., without further purification. Prior to the experiments, all solid polyelectrolytes (NaPA 15, NaPES 10, and NaPSS 70) were kept in a desiccator under vacuum [(0.1 to 1) Pa]. Sodium chloride was of analytical grade. Deionized water was used for all experiments.

Methods. The activity of water in aqueous solutions of a single polyelectrolyte and sodium chloride was measured at 298.2 K by applying the isopiestic method. Sodium chloride was employed as a reference substance. Experiments were conducted in an apparatus previously described in the literature.[4]

---

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

[†] Technische Universität Kaiserslautern.

[‡] Escola Politécnica.

10.1021/je8001317 CCC: $40.75

Table 1. Investigated Polyelectrolytes

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 $kg \cdot mol^{-1}$ informed by the manufacturer.

Table 2. Characterization of the Investigated Polyelectrolytes: Number Average Molar Mass (M_n), Mass Average Molar Mass (M_w), *z*-Average Molar Mass (M_z), and Average Number of Monomer Units (Lammertz et al.[1])

polyelectrolyte	$M_n/g \cdot mol^{-1}$	$M_w/g \cdot mol^{-1}$	$M_z/g \cdot mol^{-1}$	n_p
NaPA 5	2600	4300	6100	28
NaPA 15	6900	17300	39700	73
NH_4PA 5	2300	3900	5800	26
NH_4PA 10	7700	13300	19400	87
NH_4PA 20	7300	13600	19200	82
NaPMA 6	6100	10000	15400	56
NaPMA 15	14200	20500	27600	132
NaPES 2	1600	2800	5100	12
NaPES 10	6900	11800	16200	53
NaPSS 70	127000	148000	155000	612

That apparatus is equipped with 30 glass cells of about 5.0 cm^3 volume each. Before each experiment, the expected numerical result for the activity of water was used to determine the concentration of sodium chloride in the reference solutions. Two cells were then filled with aqueous solutions that contained more and two with aqueous solutions that contained less sodium chloride. The other cells were filled with solutions (approximately 1.0 g) of a polyelectrolyte and sodium chloride in definite proportions. Each pair of polyelectrolyte/salt masses was investigated in triplicate. At constant ratio of polyelectrolyte to salt, the amounts of water in the cells differed in such a way that during equilibration the water content decreased (at least) in one cell while it increased (at least) in another cell. So at constant ratio of (a certain) polyelectrolyte to salt, the phase equilibrium was approached from both sides (from lower dilution as well as from higher dilution in water). The compositions of up to eight different (polyelectrolyte + NaCl) systems with the same water activity were determined simultaneously. The cell holder was closed, shortly evacuated to minimize the presence of air in the overhead, thermostatted, and left at 298.2 K for an equilibration time of up to four weeks. The temperature was maintained constant by a water bath. Temperature fluctuations were recorded. They were below ± 0.1 K during the equilibration period. The temperature was measured with calibrated platinum thermometers. During equilibration, the cell holder was rotated, and the axis of rotation was slightly declined from the vertical to allow stirring of the aqueous solutions. That stirring was achieved by small spheres of stainless steel in each cell. After equilibration, the composition of each cell was determined by measuring the amount of solution in each cell. As both amounts (of polymer and salt) were known from the initial preparation, the actual equilibrium composition was obtained.

In equilibrium, the partial pressures of water and hence the activities of water attain the same value. That activity was then calculated from the concentration of sodium chloride in the reference cells using Pitzer's correlation.[5] The relative deviation in the mass fractions of sodium chloride in the reference cell was typically less than 0.1 %. This deviation in the compositions of the reference solutions corresponds to an absolute uncertainty for the experimental results for the water activity of less than 0.0001. The sums of solute mass fractions of a certain (polyelectrolyte + NaCl) system in equilibrium also differed by less than 0.001 $g \cdot g^{-1}$. As some of the polymer samples are rather viscous, the estimated absolute uncertainty for the activity of water in aqueous solutions that contain a polymer sample as well as sodium chloride is 0.0002.

Results and Discussion

The new experimental results for the activity of water (a_w) as a function of polyelectrolyte (w_p) and salt (w_{NaCl}) mass fractions are given in Tables 3 to 12. As the activity of water only slightly deviates from one, one often prefers to discuss the liquid-phase nonideality by analyzing the osmotic coefficient

$$\phi = \frac{\ln a_w(T, P, w_p, w_{NaCl})}{\ln a_w^{ideal}(T, P, w_p, w_{NaCl})} \qquad (4)$$

The number for the activity of water in an ideal solution, a_w^{ideal}, depends on the selection of the reference states. For water, the reference state is pure, liquid water at the temperature and pressure of the solution. Here, the reference state for a solute is a hypothetical one molal solution of that solute in pure water where the solute is completely dissociated and experiences the same interactions as in infinite dilution. When the polyelectrolyte consists of n_p monomer units with n_p counterions, the activity of an ideal aqueous solution is

$$\ln a_w^{ideal}(T, P, w_p, w_{NaCl}) = -M_w^*(m_p(1 + n_p) + 2m_{NaCl}) \qquad (5)$$

where m_P and m_{NaCl} are the molalities of the polyelectrolyte and NaCl, respectively, and M_w^* is the molar mass of water divided by 1000 (i.e., 0.018 $kg \cdot mol^{-1}$). The absolute uncertainty in the experimental results for the osmotic coefficient that result from the experimental uncertainty for the activity of water is estimated to be 0.01.

Figures 1 and 2 show the experimental results for the osmotic coefficient for aqueous solutions of two polysodium acrylates (NaPA 5 and NaPA 15). To allow a visual inspection of the experimentally observed behavior, osmotic coefficients are shown as lines for a constant activity of water as a function of an "overall species molality" $\bar{m}$ that is defined by

$$\bar{m} = m_p(1 + n_p) + 2m_{NaCl} \qquad (6)$$

The pattern of these diagrams is common to all other investigated systems. The osmotic coefficient is usually below one, except for highly concentrated solutions. It smoothly decreases at constant activity of water from the polymer-free to the sodium chloride-free solution. For a constant ratio of

Table 3. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPA 5 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.2097	
0.0089	0.1667	
0.0168	0.1271	0.9777
0.0241	0.0872	
0.0380	0.0000	
0.0000	0.2756	
0.0148	0.2255	
0.0282	0.1740	0.9617
0.0413	0.1177	
0.0630	0.0000	
0.0000	0.3521	
0.0224	0.2895	
0.0426	0.2289	0.9343
0.0652	0.1580	
0.1011	0.0000	
0.0000	0.3939	
0.0289	0.3230	
0.0526	0.2614	0.9140
0.0797	0.1858	
0.1260	0.0000	

Table 4. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPA 15 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.2228	
0.0040	0.2009	
0.0077	0.1793	
0.0112	0.1586	
0.0146	0.1382	0.9778
0.0179	0.1194	
0.0210	0.0999	
0.0243	0.0805	
0.0379	0.0000	
0.0000	0.2783	
0.0066	0.2491	
0.0125	0.2219	
0.0183	0.1938	
0.0238	0.1663	0.9657
0.0297	0.1395	
0.0352	0.1095	
0.0417	0.0789	
0.0570	0.0000	
0.0000	0.3273	
0.0087	0.2949	
0.0162	0.2587	
0.0239	0.2330	
0.0315	0.2000	0.9522
0.0388	0.1685	
0.0467	0.1333	
0.0556	0.0933	
0.0769	0.0000	
0.0000	0.3696	
0.0094	0.3426	
0.0192	0.3118	
0.0295	0.2783	
0.0399	0.2431	0.9291
0.0505	0.2063	
0.0612	0.1680	
0.0723	0.1288	
0.1077	0.0000	

Table 5. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NH_4PA 5 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.1871	
0.0085	0.1475	
0.0163	0.1099	0.9787
0.0234	0.0740	
0.0365	0.0000	
0.0000	0.2407	
0.0125	0.1925	
0.0242	0.1447	0.9672
0.0356	0.0944	
0.0547	0.0000	
0.0000	0.2854	
0.0162	0.2309	
0.0314	0.1750	0.9545
0.0470	0.1145	
0.0736	0.0000	
0.0000	0.3186	
0.0194	0.2600	
0.0377	0.2010	0.9415
0.0572	0.1341	
0.0917	0.0000	

Table 6. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NH_4PA 10 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.2051	
0.0086	0.1650	
0.0160	0.1242	0.9787
0.0229	0.0851	
0.0365	0.0000	
0.0000	0.2592	
0.0123	0.2086	
0.0238	0.1584	0.9672
0.0346	0.1062	
0.0547	0.0000	
0.0000	0.3015	
0.0159	0.2464	
0.0308	0.1891	0.9545
0.0458	0.1277	
0.0736	0.0000	
0.0000	0.3321	
0.0189	0.2742	
0.0367	0.2150	0.9415
0.0557	0.1456	
0.0917	0.0000	

Table 7. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NH_4PA 20 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.2054	
0.0086	0.1665	
0.0168	0.1289	0.9766
0.0243	0.0904	
0.0398	0.0000	
0.0000	0.2984	
0.0148	0.2280	
0.0282	0.1728	0.9618
0.0410	0.1134	
0.0629	0.0000	
0.0000	0.3951	
0.0231	0.3196	
0.0425	0.2542	0.9281
0.0609	0.1880	
0.1090	0.0000	

sodium chloride to polyelectrolyte the osmotic coefficient increases with increasing “overall species molality”. Figure 3 shows the experimental results that were already shown in Figure 2 (for NaPA 15) in a different representation. There the “overall molality” of the polyelectrolyte $\bar{m}_P$ ($= m_p(1 + n_p)$) is plotted versus the “overall molality” of sodium chloride $\bar{m}_{NaCl}$ ($= 2m_{NaCl}$). The experimental results are presented as lines of constant activity of water. In this presentation, the lines of constant water activity are nearly straight lines, but—as expected—the slope S ($= d\bar{m}_P/ d\bar{m}_{NaCl}$) of these lines varies (in the investigated range of concentrations by a factor of about two).

Although the results for NaPA 5 and for NaPA 15 are very similar, there are some differences. Following the lines of

Table 8. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPMA 6 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

w_{NaCl}/g·g^{-1}	w_p/g·g^{-1}	a_w
0.0000	0.2072	
0.0029	0.1913	
0.0056	0.1760	
0.0079	0.1618	0.9799
0.0108	0.1470	
0.0132	0.1308	
0.0161	0.1198	
0.0345	0.0000	
0.0000	0.2602	
0.0062	0.2350	
0.0120	0.2097	
0.0176	0.1839	
0.0233	0.1564	0.9674
0.0288	0.1298	
0.0346	0.1009	
0.0408	0.0695	
0.0544	0.0000	
0.0000	0.3015	
0.0085	0.2741	
0.0157	0.2490	
0.0231	0.2216	
0.0306	0.1931	0.9528
0.0380	0.1627	
0.0466	0.1266	
0.0562	0.0862	
0.0760	0.0000	
0.0000	0.3262	
0.0103	0.2974	
0.0197	0.2682	
0.0285	0.2392	
0.0355	0.2153	0.9408
0.0449	0.1816	
0.0552	0.1435	
0.0674	0.0971	
0.0926	0.0000	
0.0473	0.2439	
0.0597	0.2064	
0.0736	0.1640	0.9142
0.0899	0.1145	
0.1257	0.0000	
0.0646	0.2211	
0.0797	0.1757	0.9031
0.0979	0.1221	
0.1384	0.0000	

Table 9. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPMA 15 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

w_{NaCl}/g·g^{-1}	w_p/g·g^{-1}	a_w
0.0000	0.3017	
0.0078	0.2785	
0.0155	0.2567	
0.0228	0.2293	
0.0301	0.1983	0.9519
0.0383	0.1672	
0.0467	0.1317	
0.0564	0.0890	
0.0772	0.0000	
0.0000	0.3257	
0.0101	0.3052	
0.0197	0.2771	
0.0286	0.2491	
0.0362	0.2247	0.9388
0.0455	0.1904	
0.0556	0.1500	
0.0685	0.1032	
0.0952	0.0000	

Table 10. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPES 2 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

w_{NaCl}/g·g^{-1}	w_p/g·g^{-1}	a_w
0.0000	0.2551	
0.0080	0.2182	
0.0159	0.1810	0.9677
0.0233	0.1457	
0.0539	0.0000	
0.0000	0.3560	
0.0138	0.3033	
0.0267	0.2533	0.9431
0.0425	0.1899	
0.0895	0.0000	
0.0000	0.4497	
0.0192	0.3890	
0.0385	0.3262	0.9054
0.0632	0.2449	
0.1359	0.0000	

Table 11. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPES 10 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

w_{NaCl}/g·g^{-1}	w_p/g·g^{-1}	a_w
0.0000	0.3179	
0.0047	0.2686	
0.0083	0.2340	
0.0118	0.1998	
0.0147	0.1717	0.9803
0.0172	0.1465	
0.0194	0.1238	
0.0215	0.1028	
0.0337	0.0000	
0.0000	0.3911	
0.0073	0.3379	
0.0137	0.2862	
0.0194	0.2408	
0.0243	0.2028	0.9687
0.0288	0.1670	
0.0329	0.1335	
0.0368	0.1027	
0.0523	0.0000	
0.0000	0.4057	
0.0070	0.3590	
0.0134	0.3162	
0.0194	0.2706	
0.0253	0.2243	0.9667
0.0310	0.1817	
0.0370	0.1369	
0.0430	0.0892	
0.0554	0.0000	
0.0000	0.4462	
0.0082	0.4015	
0.0160	0.3553	
0.0234	0.3101	
0.0307	0.2632	0.9559
0.0383	0.2142	
0.0463	0.1628	
0.0551	0.1053	
0.0715	0.0000	
0.0000	0.4979	
0.0101	0.4560	
0.0197	0.4122	
0.0291	0.3675	
0.0387	0.3200	0.9345
0.0489	0.2686	
0.0607	0.2095	
0.0744	0.1371	
0.1008	0.0000	

constant water activity in Figures 1 and 2, one notices that the major differences occur when the molality of sodium chloride becomes very low. This could be expected since the typical polymer effects such as excluded volume effects and counterion condensation become more important. However, considering that many phenomena are involved in the nonideality of these solutions (such as the counterion condensation phenomenon, the influence of sodium chloride on that phenomenon, the stretching/shrinking of polymer chains, excluded volume effects), any discussion on the relative importance of these factors

Table 12. Experimental Results for the Activity of Water a_w in Aqueous Solutions of (NaPSS 70 + NaCl) at 298.2 K as a Function of Polyelectrolyte (w_p) and Salt (w_{NaCl}) Mass Fractions

$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w	$w_{NaCl}/g \cdot g^{-1}$	$w_p/g \cdot g^{-1}$	a_w
0.0000	0.2475		0.0000	0.4460	
0.0038	0.2187		0.0104	0.3956	
0.0075	0.1932		0.0196	0.3513	
0.0111	0.1683		0.0280	0.3075	
0.0146	0.1439	0.9794	0.0365	0.2644	0.9417
0.0182	0.1198		0.0459	0.2194	
0.0219	0.0947		0.0568	0.1673	
0.0257	0.0683		0.0704	0.1012	
0.0352	0.0000		0.0913	0.0000	
0.0000	0.3288		0.0000	0.4867	
0.0063	0.2910		0.0127	0.4280	
0.0123	0.2545		0.0231	0.3800	
0.0181	0.2196		0.0326	0.3368	
0.0238	0.1841	0.9674	0.0421	0.2935	0.9292
0.0300	0.1477		0.0524	0.2465	
0.0366	0.1079		0.0647	0.1908	
0.0441	0.0632		0.0810	0.1181	
0.0548	0.0000		0.1076	0.0000	
0.0000	0.3909		0.0895	0.2157	
0.0083	0.3467		0.1009	0.1667	
0.0158	0.3056		0.1173	0.1036	0.8987
0.0230	0.2662		0.1401	0.0126	
0.0303	0.2267	0.9551	0.1432	0.0000	
0.0382	0.1848		0.1066	0.2205	
0.0469	0.1375		0.1200	0.1738	0.8748
0.0574	0.0816		0.1380	0.1072	
0.0727	0.0000		0.1677	0.0000	

that is only based on the experimental data alone (i.e., without a molecular thermodynamics model for the excess Gibbs energy of such solutions) would be conjectural.

Although the form of the osmotic coefficient diagram is common for all investigated polyelectrolytes, the nature of the polyelectrolyte has an influence on the results for the osmotic coefficient. Figure 4 depicts the behavior of systems containing NaPMA 6 and NaCl. While the polyelectrolyte chain size of NaPMA 6 is close to that of NaPA 15 (cf. Table 2), there are some quantitative differences between the results for both aqueous solutions. Solutions containing NaPMA 6 without added NaCl reach higher values of osmotic coefficient at comparatively lower values of overall molalities, resulting in a diagram where the lines for the sodium chloride-free and the polymer (NaPMA 6)-free solutions lie closer together. Furthermore, the lowest investigated activities of water (0.9142 and 0.9031) were not accessible with aqueous solutions of NaPMA 6 that contain no sodium chloride. Such low water activities require very high polyelectrolyte concentrations. However, such solutions are either too viscous for an investigation by the isopiestic method or they lie even beyond the (unknown) solubility limit of that polymer in water.

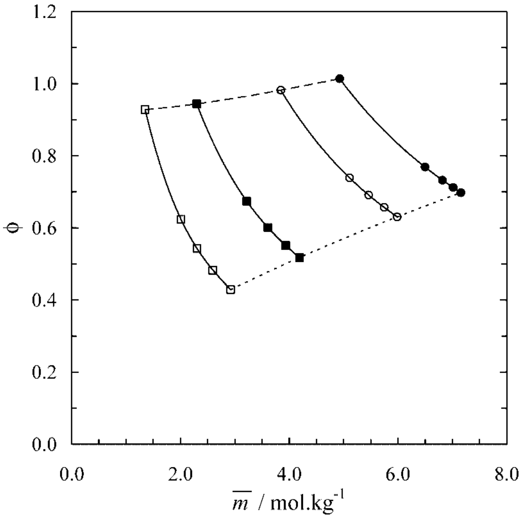

Figure 1. Experimental results for the osmotic coefficient (ϕ) of aqueous solutions of NaPA 5 and NaCl at 298.2 K and constant activity a_w of water as a function of "overall species molality" $\bar{m}$: □, $a_w = 0.9777$; ■, $a_w = 0.9617$; ○, $a_w = 0.9343$; ●, $a_w = 0.9140$, together with results for polymer-free (•••••••) as well as sodium chloride-free (------) aqueous solutions.

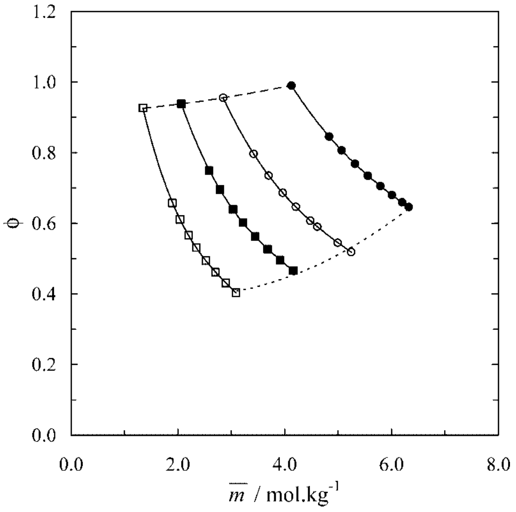

Figure 2. Experimental results for the osmotic coefficient (ϕ) of aqueous solutions of NaPA 15 and NaCl at 298.2 K and constant activity a_w of water as a function of "overall species molality" $\bar{m}$: □, $a_w = 0.9778$; ■, $a_w = 0.9657$; ○, $a_w = 0.9522$; ●, $a_w = 0.9291$, together with results for polymer-free (•••••••) as well as sodium chloride-free (------) aqueous solutions.

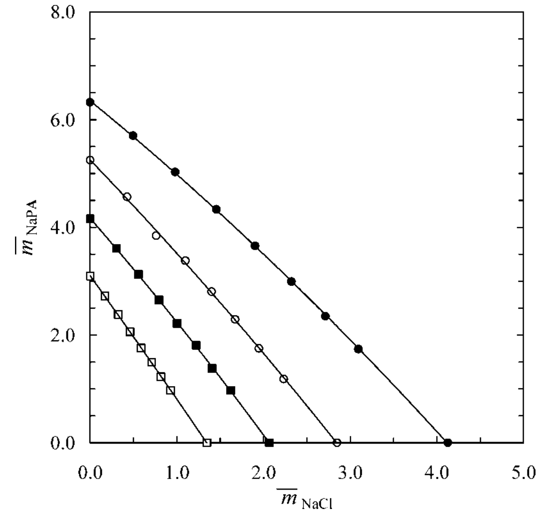

Figure 3. Overall molality of NaPA 15, $\bar{m}_{NaPA}$, as a function of overall molality of NaCl, $\bar{m}_{NaCl}$, at constant activity a_w of water at 298.2 K: □, $a_w = 0.9778$; ■, $a_w = 0.9657$; ○, $a_w = 0.9522$; ●, $a_w = 0.9291$.

Due to the experimental procedure, it is impossible to fix a certain value of water activity and determine a set of system compositions that yield exactly this value, which makes direct comparison among systems with different polyelectrolytes a difficult task. By accident, there are two sets of experimental data for two pairs of aqueous polyelectrolyte solution systems which nearly even values for the activity of water. There is one set with aqueous solutions of NaPA 5 and NaPA 15 where the activity of water is about 0.9777 and two sets with aqueous solutions of NH_4PA 5 and NH_4PA 10 where the activity of water

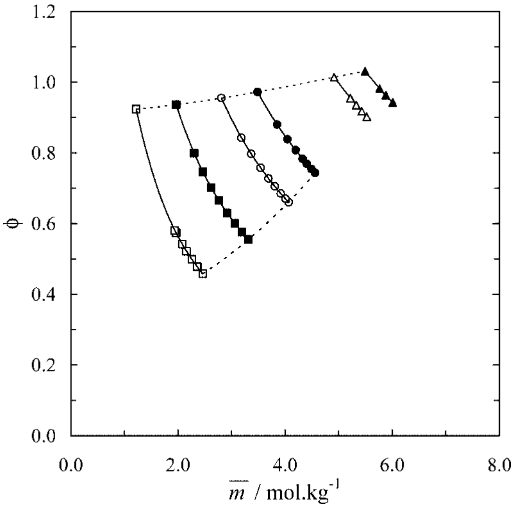

Figure 4. Experimental results for the osmotic coefficient (ϕ) of aqueous solutions of NaPMA 6 and NaCl at 298.2 K and constant activity a_w of water as a function of “overall species molality” ($\bar{m}$). □, systems with a_w = 0.9799; ■, systems with a_w = 0.9674; ○, systems with a_w = 0.9528; ●, systems with a_w = 0.9408; Δ, systems with a_w = 0.9142; ▲, systems with a_w = 0.9031, together with results for polymer-free (•••••••) as well as sodium chloride-free (------) aqueous solutions.

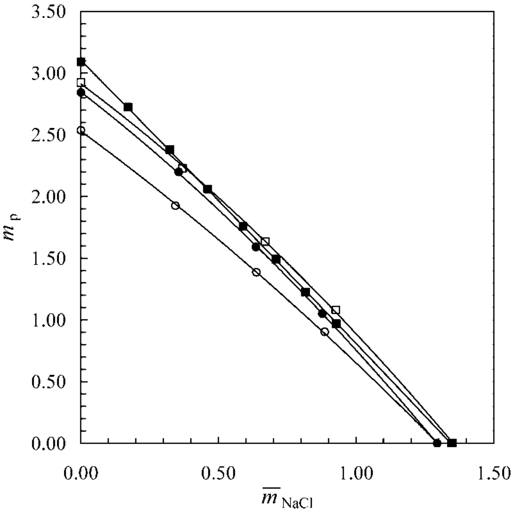

Figure 5. Overall molality of polyelectrolytes, $\bar{m}_p$, as a function of overall molality of NaCl, $\bar{m}_{NaCl}$, at constant activity a_w of water at 298.2 K: □, a_w = 0.9777, NaPA 5 + NaCl; ■, a_w = 0.9778, NaPA 15 + NaCl; ○, a_w = 0.9787, NH_4PA 5 + NaCl; ●, a_w = 0.9787, NH_4PA 10 + NaCl.

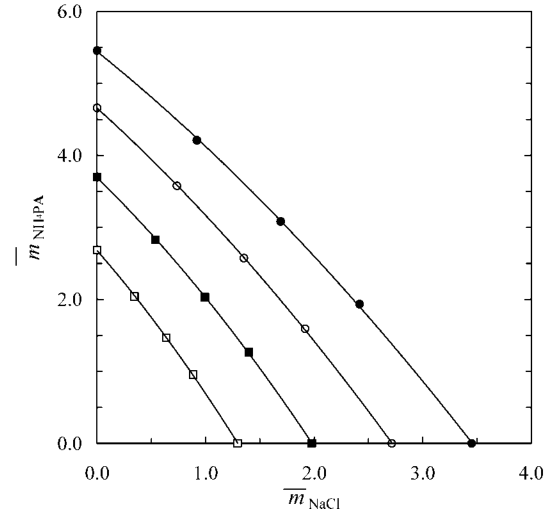

Figure 6. Overall molality of NH_4PA 5, $\bar{m}_{NaPA}$, as a function of overall molality of NaCl, $\bar{m}_{NaCl}$, at constant activity a_w of water at 298.2 K: □, a_w = 0.9787; ■, a_w = 0.9672; ○, a_w = 0.9545; ●, a_w = 0.9415.

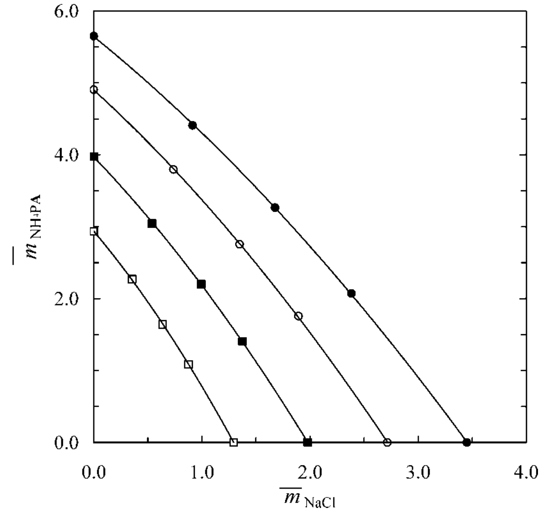

Figure 7. Overall molality of NH_4PA 10, $\bar{m}_{NaPA}$, as a function of overall molality of NaCl, $\bar{m}_{NaCl}$, at constant activity a_w of water at 298.2 K: □, a_w = 0.9787; ■, a_w = 0.9672; ○, a_w = 0.9545; ●, a_w = 0.9415.

is about 0.9787. These are relatively diluted systems. According to previously presented experimental data,[1] aqueous solutions of these polysodium acrylates (without added sodium chloride) tend to reach the same limiting value for the osmotic coefficient when the polymer concentration reaches zero. Therefore, one expects that the relationship between $\bar{m}_P$ and $\bar{m}_{NaCl}$ along a line of constant water activity is approximately the same. Figure 5 shows that this expectation is fulfilled by the experimental results: differences are most of the time within experimental uncertainty. On the other hand, the behavior of an aqueous solution of NH_4PA 5 differs rather from that of an aqueous solution of NH_4PA 10, as the limiting numbers for the osmotic coefficients of aqueous solutions of these polymers are different. Therefore, one expects a different relationship between $\bar{m}_P$ and $\bar{m}_{NaCl}$ along a line of constant water activity. As shown in Figure 5, the experimental results support this expectation: the line for NH_4PA 10 lies systematically above the line for NH_4PA 5. The complete diagrams for NH_4PA 5 and NH_4PA 10 (cf. Figures 6 and 7) show that this difference is observed also for more concentrated solutions (i.e., lower water activities).

Although there are well-established thermodynamic models for dilute aqueous solutions of polyelectrolytes (e.g., the cell model of Lifson and Katchalsky[6] and the counterion condensation theory of Manning[2]), there is a lack of extensively tested models for concentrated polyelectrolyte solutions with (or even without) added salts. Although some experimental studies on the thermodynamic properties of aqueous solutions of polyelectrolytes are available in the literature, the open literature does not provide sufficient experimental data to develop and test such models. One of the main reasons for that lack seems to be the often insufficient characterization of the investigated polyelectrolytes, a disadvantage that the data presented here aim to avoid.

Comparison with Literature Data. Experimental data for the activity of water in aqueous solutions of a single polyelectrolyte (either NaPSS or NaPA) and sodium chloride at 298.2 K can be found in the literature. For example, osmotic equilibrium data for solutions containing NaPSS and NaCl were reported by Takahashi et al.[7] and Koene et al.[8] (along with related data, such as from light scattering experiments[9]), and data for

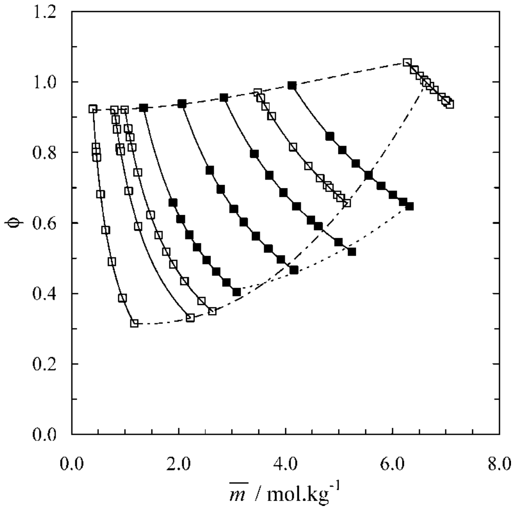

Figure 8. Experimental results for the osmotic coefficients (ϕ) of aqueous solutions of NaPA and NaCl at 298.2 K and constant activity a_w of water as a function of "overall species molality" ($\bar{m}$). ■, systems containing NaPA 15, this work; □, systems containing NaPA 60, Okubo et al.,[10] together with results for polymer-free (•••••••) as well as sodium chloride-free aqueous solutions, from this work (------) and from Okubo et al.[10] (-•-•-•-•-).

solutions containing NaPA and NaCl were reported by Okubo et al.[10] (light scattering results are also available for solutions of these compounds[11]). Nevertheless, the majority of these studies is concerned with the dilute region of the phase diagram, which does not allow a direct comparison with the new experimental data reported here. A sole exception is the set of isopiestic measurement data reported by Okubo et al.[10] for the system NaPA and NaCl at 298.2 K. Figure 8 shows lines of constant activity of water from Okubo et al.[10] together with those for aqueous solutions of NaPA 15 and NaCl given in Table 4. Okubo et al. characterized their polymer sample by the number of monomers in the polymer. That number was adopted here (i.e., $n_p = 640$). It corresponds to a polymer sample with a relative molecular mass of about 60 000. The general pattern of the "isoactivity lines" from both investigations is very similar at water activities down to about 0.95, despite the difference between the molecular masses of both polymers. Small differences occur in the limit $m_{NaCl} = 0$, which could be expected. For more concentrated systems, the difference between the osmotic coefficient of an aqueous solution of NaCl and that of an aqueous solution of the polyelectrolyte is smaller when NaPA 60 instead of NaPA 15 is dissolved in water. However, there are some doubts if that difference is really caused by the difference in the molecular mass of the polyelectrolytes. These doubts are based on the very short equilibration time (only three days versus up to four weeks in the present investigation) in the experiments by Okubo and Ise. From our experience, it is questionable if such a short equilibration time is sufficient to achieve phase equilibrium between concentrated (and therefore viscous) aqueous solutions in an isopiestic experiment. Okubo et al. report differences of 2 % in the composition of the coexisting concentrated solutions that should—in equilibrium—contain the same amount of polyelectrolyte and sodium chloride. These differences are considerable larger than the differences observed in the experimental investigations of the present work (0.1 %). These differences may account, at least, for some of the differences between both experimental investigations.

Literature Cited

(1) Lammertz, S.; Pessôa Filho, P. A.; Maurer, G. Thermodynamics of aqueous solutions of polyelectrolytes: experimental results for the activity of water in aqueous solutions of some single synthetic polyelectrolytes. *J. Chem. Eng. Data* **2008**, *53*, 1564−1570.
(2) Manning, G. S. Limiting laws and counterion condensation in polyelectrolyte solutions. I. Colligative properties. *J. Chem. Phys.* **1969**, *51*, 924–933.
(3) Lammertz, S. Thermodynamische Eigenschaften wässriger Polyelektrolytlösungen, Ph. D. Thesis, Technische Universität Kaiserslautern, Shaker Verlag, Aachen, 2005.
(4) Gro*β*mann, 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.
(5) Pitzer, K. S. *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press: Boca Raton, 1991.
(6) Lifson, S.; Katchalsky, A. The Electrostatic Free Energy of Polyelectrolyte Solutions. II. Fully Stretched Macromolecules. *J. Polym. Sci.* **1954**, *13*, 43–55.
(7) Takahashi, A.; Kato, N.; Nagasawa, M. The osmotic pressure of polyelectrolytes in neutral salt solutions. *J. Phys. Chem.* **1970**, *74*, 944–946.
(8) Koene, R. S.; Nicolai, T.; Mandel, M. Scaling relations for aqueous poly-electrolyte salt-solutions. 3. Osmotic pressure as a function of molar mass and ionic strength in the semidilute regime. *Macromolecules* **1983**, *16*, 231–236.
(9) Koene, R. S.; Nicolai, T.; Mandel, M. Scaling relations for aqueous poly-electrolyte salt-solutions. 2. Quasi-elastic light-scattering as a function of poly-electrolyte concentration and salt concentration. *Macromolecules* **1983**, *16*, 227–231.
(10) Okubo, T.; Ise, N.; Matsui, F. Mean activity coefficient of polyelectrolytes in the ternary system water-sodium polyacrylate-sodium chloride. *J. Am. Chem. Soc.* **1967**, *89*, 3697–3703.
(11) Orofino, T. A.; Flory, P. J. The second virial coefficient for polyelectrolytes. Theory and experiment. *J. Phys. Chem.* **1959**, *63*, 283–290.

Received for review February 21, 2008. Accepted June 13, 2008. P.A.P.F. gratefully acknowledges a scholarship from CAPES (Brasilia, Brazil, process BEX 2941/07-4).

JE8001317