Liquid−Liquid Equilibrium of Aqueous Two-Phase Systems Containing Some Synthetic Polyelectrolytes and Polyethylene Glycol†

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Experimental results are presented for the liquid−liquid equilibrium of aqueous two-phase systems containing a synthetic polyelectrolyte (polysodium acrylate, polysodium methacrylate, and polysodium ethylene sulfonate) and polyethylene glycol at (298.2 and 323.2) K. A total of 40 phase diagrams were obtained, comprising data both of the binodal curve (obtained through cloud-point measurements) and of equilibrium compositions. The influences of temperature, the nature of the polyelectrolyte monomer unit, and the chain length of both types of polymers are analyzed and discussed.

Introduction

Polyelectrolytes are polymers that dissociate in aqueous solutions into a charged polymeric backbone and mobile counterions. These polymers have widespread use in areas such as, for example, the chemical (and related) industries[1] and for drug delivery systems.[2] The thermodynamic properties of polyelectrolyte solutions are determined by a variety of phenomena, for example, by electrostatic interactions and by excluded volume effects.

The simultaneous dissolution of two hydrophilic, neutral polymers in water often leads to a phase split resulting in a liquid−liquid equilibrium (aqueous two-phase system) in which two aqueous phases coexist in equilibrium. They are of particular interest in downstream processing in biotechnology. Numerous examples for such biphasic systems are known: to name a few, aqueous two-phase systems can be formed by polyethylene glycol and dextran,[3] polyethylene glycol and polyvinyl alcohol,[4] random copolymers poly(ethylene glycol-propylene glycol) and dextran,[5] and block copolymers poly(ethylene glycol-propylene glycol) and dextran.[6] Aqueous two-phase systems can also be observed when a hydrophilic polymer and a low molecular electrolyte (e.g., a salt) are simultaneously dissolved in water, e.g., polyethylene glycol and either sodium sulfate[7] or potassium phosphate,[8] polyvinyl pyrrolidone and sodium sulfate,[9] and block-copolymers poly(ethylene glycol-propylene glycol) and potassium phosphate.[10,11] Therefore, it is no surprise that aqueous two-phase systems are also found when a neutral hydrophilic polymer and a polyelectrolyte are simultaneously dissolved in water. However, experimental information on the phase behavior of such aqueous two-phase systems is comparatively scarce, mostly restricted to systems containing polysodium acrylate.[12,13]

In the present contribution, experimental results are presented for the liquid−liquid equilibrium in aqueous two-phase systems that are formed when a single, neutral polymer (here, four different polyethylene glycols, abbreviated by PEG or PEO) and a variety of synthetic polyelectrolytes—polysodium acrylate (abbreviated NaPA, two different molar masses), polysodium methacrylate (NaPMA, two different molar masses), and polysodium ethylene sulfonate (NaPES, two different molar masses)—are simultaneously dissolved in water at (298.2 and 323.2) K. The polyelectrolytes were previously characterized, and experimental data on the water activity of their solutions, as well as of solutions containing also sodium chloride as added salt, have already been reported.[14,15] The aim of these investigations was to provide a database for such liquid−liquid equilibrium with well-characterized polyelectrolytes that can serve for testing and development of thermodynamic models for such solutions.

Experimental

Materials. The list of employed polymers (along with manufacturers' and commercial names) is presented in Table 1. The manufacturers' abbreviations PEG (polyethylene glycol) and PEO (polyethylene oxide) are maintained to refer to polymer samples, but there is no actual distinction between these polymers except for the difference in their average molar mass. In the rest of this paper, they will be called solely polyethylene glycols. The number following the polymer acronym is an estimate for the molar mass of the polymer sample (expressed in $\text{kg}\cdot\text{mol}^{-1}$) as given by its manufacturer. All four PEG samples are nearly monodisperse: cf. Table 2. Therefore, it is sufficient to characterize them by a single denomination (the molar mass). The molar mass of the PEG samples varies in a wide range from about 6 $\text{kg}\cdot\text{mol}^{-1}$ to about 103 $\text{kg}\cdot\text{mol}^{-1}$. The polyelectrolyte samples are more polydisperse. They were previously characterized by size exclusion chromatography. Table 2 gives the average number of monomer units in each polymer and the first three moments of the molecular size distribution

$$\text{the number averaged molar mass } M_n = \frac{1}{\sum_i w_i M_i^{-1}}$$

$$\text{the mass averaged molar mass } M_w = \sum_i w_i M_i$$

and

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Table 1. List of Polymers Used in This Work

polymer[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
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
PEG 6	Polyglykol 6000S	Hoechst GmbH, Frankfurt, Germany	E06373616
PEG 34	Polyglykol 35000S	Hoechst GmbH, Frankfurt, Germany	E06373013
PEO 53		Polymer Standard Service, Warwick, USA	PEO30056
PEO 103		Polymer Standard Service, Warwick, USA	PEO13056

[a] The number following the polymer abbreviation is the molar mass (in $\mathrm{kg \cdot mol^{-1}}$) as given by the suppliers.

Table 2. Characterization of the Investigated Polymers: Number Average Molar Mass (M_n), Mass Average Molar Mass (M_w), z-Average Molar Mass (M_z), and Average Number of Monomer Units Per Molecule (n_u)

polymer	M_n/kg·mol^{-1}	M_w/kg·mol^{-1}	M_z/kg·mol^{-1}	n_u	ref[a]
NaPA 5	2.6	4.3	6.1	28	1
NaPA 15	6.9	17.3	39.7	73	1
NaPMA 6	6.1	10.0	15.4	56	1
NaPMA 15	14.2	20.5	27.6	132	1
NaPES 2	1.6	2.8	5.1	12	1
NaPES 10	6.9	11.8	16.2	53	1
PEG 6	6.7	6.95	–	141	2
PEG 34	34.4	35.7	–	781	2
PEO 53	52.9	–	–	1201	3
PEO 103	103.0	–	–	2338	3

[a] Refs: 1, Lammertz et al.;[14] 2, Hasse et al.;[16] 3, Manufacturer.

Table 3. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 5 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.128	0.129	0.120	0.060
	top phase	0.033	0.283	0.035	0.212
	bottom phase	0.191	0.028	0.152	0.007
	feed point	0.150	0.150	0.130	0.100
	top phase	0.036	0.331	0.020	0.298
	bottom phase	0.232	0.023	0.187	0.008
	feed point	0.167	0.196	0.150	0.170
	top phase	0.034	0.406	0.012	0.396
	bottom phase	0.292	0.018	0.261	0.008
	feed point			0.180	0.220
	top phase			0.013	0.485
	bottom phase			0.319	0.008
cloud point curve		0.394	0.014	0.397	0.007
		0.293	0.022	0.298	0.008
		0.195	0.025	0.199	0.007
		0.146	0.037	0.169	0.006
		0.096	0.075	0.129	0.008
		0.092	0.081	0.093	0.068
		0.064	0.126	0.083	0.080
		0.057	0.173	0.042	0.179
		0.032	0.276	0.019	0.285
		0.030	0.373	0.016	0.367
		0.037	0.460	0.012	0.388
		0.017	0.530	0.013	0.485
		0	0.578		

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained by cloud-point and phase equilibrium measurements.

Table 4. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 5 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.073	0.080	0.090	0.050
	top phase	0.048	0.125	0.024	0.191
	bottom phase	0.116	0.011	0.115	0.004
	feed point	0.100	0.100	0.110	0.100
	top phase	0.034	0.218	0.012	0.289
	bottom phase	0.164	0.003	0.166	0.004
	feed point	0.113	0.151	0.150	0.150
	top phase	0.029	0.284	0.007	0.401
	bottom phase	0.214	0.003	0.246	0.003
	feed point			0.200	0.200
	top phase			0.004	0.530
	bottom phase			0.332	0.003
cloud point curve		0.364	0.005	0.397	0.002
		0.277	0.004	0.298	0.002
		0.187	0.003	0.198	0.003
		0.130	0.005	0.099	0.003
		0.102	0.025	0.086	0.013
		0.080	0.056	0.075	0.029
		0.058	0.103	0.059	0.066
		0.061	0.108	0.051	0.088
		0.041	0.184	0.026	0.188
		0.027	0.264	0.011	0.291
				0.005	0.395
				0.003	0.496

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained by cloud-point and phase equilibrium measurements.

the third moment (or z-averaged) molar mass

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

where w_i is the mass fraction of a sample with molar mass M_i. All information on the polydispersity of the samples was taken from previous investigations (Lammertz et al.[14] and Hasse et al.[16]). For all polyelectrolyte samples, the complete polymer distribution was given by Lammertz.[17] All four polyethylene glycol samples as well as NaPA 15 and NaPES 10 were received as solids. They were kept in a desiccator under a vacuum of (0.1 to 1) Pa prior to being used. All other polyelectrolyte samples were delivered in aqueous solutions. The polymer content of these samples was checked (and verified) by freeze-drying investigations. All polymer samples were used without further purification. Deionized water was used in all preparations of the aqueous two-phase systems.

Experimental Methods. The phase equilibrium was studied by determining both the binodal curve (i.e., the boundary curve between the one- and two-phase regions of the phase diagram) and the equilibrium compositions of the coexisting phases.

The binodal curve is here approximated by the cloud-point curve. As shown below, the uncertainties that result from this approximation are small when compared to all other experimental uncertainties. The cloud-point curve was determined in a titration process. An aqueous stock solution (of known composition) of one polymer was added stepwise to an aqueous stock solution (of also known composition) of the other polymer until turbidity was visually observed. Both stock solutions were prepared gravimetrically. In a typical experiment, about 5 g of a solution of either polymer was placed in a centrifuge tube (of

Table 5. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 5 and PEO 53) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.100	0.051	0.090	0.051
	top phase	0.046	0.154	0.028	0.192
	bottom phase	0.137	0.002	0.125	0.003
	feed point	0.110	0.080	0.110	0.100
	top phase	0.031	0.219	0.022	0.270
	bottom phase	0.167	0.002	0.173	0.002
	feed point	0.150	0.101	0.151	0.150
	top phase	0.016	0.313	0.004	0.400
	bottom phase	0.224	0.002	0.253	0.002
	feed point	0.170	0.150	0.199	0.202
	top phase	0.004	0.400	0.004	0.522
	bottom phase	0.282	0.002	0.345	0.002
cloud point curve		0.394	0.003	0.394	0.002
		0.296	0.002	0.378	0.011
		0.198	0.003	0.298	0.001
		0.129	0.003	0.286	0.007
		0.113	0.012	0.199	0.001
		0.091	0.031	0.197	0.003
		0.076	0.081	0.099	0.001
		0.041	0.180	0.098	0.003
				0.083	0.019
				0.065	0.031
				0.068	0.042
				0.056	0.086
				0.054	0.088
				0.042	0.133
				0.041	0.135
				0.028	0.189

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained by cloud-point and phase equilibrium measurements.

Table 6. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 5 and PEO 103) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.100	0.050	0.090	0.050
	top phase	0.055	0.120	0.020	0.192
	bottom phase	0.132	0.002	0.119	0.002
	feed point	0.150	0.100	0.110	0.100
	top phase	0.011	0.312	0.015	0.282
	bottom phase	0.219	0.002	0.168	0.003
	feed point	0.170	0.150	0.150	0.151
	top phase	0.005	0.398	0.006	0.419
	bottom phase	0.279	0.002	0.242	0.004
	feed point			0.160	0.101
	top phase			0.008	0.365
	bottom phase			0.218	0.004
cloud point curve		0.395	0.003	0.389	0.003
		0.294	0.003	0.385	0.007
		0.197	0.003	0.293	0.003
		0.149	0.002	0.287	0.007
		0.119	0.003	0.196	0.004
		0.096	0.005	0.100	0.001
		0.086	0.019	0.099	0.002
		0.075	0.057	0.078	0.010
		0.064	0.086	0.064	0.022
				0.062	0.042
				0.052	0.054
				0.052	0.086
				0.046	0.091
				0.034	0.130

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 7. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 15 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.100	0.150	0.110	0.050
	top phase	0.038	0.174	0.021	0.200
	bottom phase	0.146	0.016	0.142	0.004
	feed point	0.098	0.150	0.110	0.120
	top phase	0.032	0.248	0.006	0.281
	bottom phase	0.200	0.011	0.186	0.004
	feed point	0.141	0.150	0.150	0.201
	top phase	0.024	0.312	0.009	0.412
	bottom phase	0.249	0.011	0.295	0.004
	feed point	0.170	0.181	0.200	0.270
	top phase	0.019	0.386	0.006	0.556
	bottom phase	0.299	0.011	0.388	0.003
cloud point curve		0.392	0.017	0.400	0.005
		0.297	0.007	0.296	0.011
		0.247	0.012	0.200	0.005
		0.149	0.011	0.199	0.002
		0.127	0.024	0.118	0.006
		0.091	0.067	0.099	0.017
		0.072	0.094	0.082	0.032
		0.035	0.190	0.058	0.080
		0.023	0.391	0.027	0.182
		0.013	0.496	0.009	0.291
		0	0.579	0.007	0.300
				0.007	0.399
				0.008	0.496

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 8. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 15 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.100	0.050	0.080	0.050
	top phase	0.043	0.152	0.019	0.175
	bottom phase	0.126	0.011	0.108	0.004
	feed point	0.100	0.101	0.150	0.150
	top phase	0.025	0.219	0.008	0.370
	bottom phase	0.161	0.010	0.252	0.004
	feed point	0.100	0.153	0.180	0.231
	top phase	0.017	0.275	0.007	0.487
	bottom phase	0.199	0.010	0.344	0.004
	feed point	0.150	0.150	0.110	0.151
	top phase	0.016	0.336	0.010	0.320
	bottom phase	0.255	0.008	0.209	0.004
	feed point			0.200	0.190
	top phase			0.007	0.485
	bottom phase			0.338	0.004
cloud point curve		0.497	0.005	0.399	0.003
		0.394	0.007	0.398	0.008
		0.297	0.006	0.297	0.010
		0.199	0.007	0.200	0.004
		0.098	0.015	0.101	0.002
		0.078	0.045	0.100	0.010
		0.055	0.095	0.078	0.004
		0.029	0.194	0.056	0.046
		0.018	0.298	0.036	0.096
				0.020	0.196
				0.008	0.293
				0.010	0.297
				0.007	0.399
				0.007	0.489

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

about 12 cm^3 volume). Small quantities (about 0.04 g each) of a solution of the other polymer were then dropwise added with a syringe. The exact amount of solution in the tube in each titration step was determined using a precision micro balance (model AG 204, Mettler-Toledo, Greifensee, Switzerland, precision $1.0 \cdot 10^{-3}$ g). After each addition, the liquid solution was gently stirred. The temperature of the systems was kept constant by a thermostatted water bath. It varied by less than

Table 9. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 15 and PEO 53) at (298.2 and 323.2) K[a]

		T/K = 298.2		*T*/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.100	0.050	0.080	0.050
	top phase	0.024	0.176	0.031	0.167
	bottom phase	0.131	0.009	0.110	0.002
	feed point	0.120	0.080	0.100	0.100
	top phase	0.015	0.239	0.013	0.264
	bottom phase	0.174	0.008	0.160	0.002
	feed point	0.150	0.120	0.150	0.150
	top phase	0.006	0.323	0.006	0.378
	bottom phase	0.239	0.006	0.256	0.002
	feed point	0.200	0.150	0.180	0.230
	top phase	0.007	0.420	0.003	0.501
	bottom phase	0.314	0.006	0.349	0.002
cloud point curve		0.384	0.008	0.400	0.001
		0.294	0.006	0.297	0.001
		0.192	0.008	0.198	0.001
		0.095	0.016	0.100	0.001
		0.075	0.028	0.084	0.002
		0.066	0.045	0.068	0.018
		0.050	0.083	0.059	0.035
		0.036	0.128	0.043	0.078
		0.023	0.188	0.031	0.127

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 10. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPA 15 and PEO 103) at (298.2 and 323.2) K[a]

		T/K = 298.2		*T*/K = 323.2	
		w_{NaPA}	w_{PEG}	w_{NaPA}	w_{PEG}
coexisting phases	feed point	0.101	0.050	0.080	0.050
	top phase	0.021	0.179	0.019	0.174
	bottom phase	0.137	0.003	0.108	0.003
	feed point	0.120	0.080	0.100	0.100
	top phase	0.010	0.244	0.008	0.263
	bottom phase	0.177	0.003	0.162	0.003
cloud point curve		0.384	0.009	0.403	0.004
		0.287	0.009	0.386	0.002
		0.197	0.003	0.301	0.006
		0.099	0.003	0.296	0.001
		0.074	0.021	0.197	0.002
		0.063	0.041	0.106	0.003
		0.037	0.080	0.099	0.001
		0.037	0.101	0.056	0.019
				0.053	0.035
				0.035	0.084
				0.035	0.092
				0.027	0.139

[a] Polysodium acrylate (w_{NaPA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

0.1 K. The temperature was measured with calibrated platinum resistance thermometers. The uncertainty of experimental results for the temperature does not surmount ± 0.1 K. During the addition, the solution became turbid. It was then kept under stirring in the thermostatted water bath for a period of time of up to 48 h. During that time, the solution was visually checked for turbidity from time to time. When after 48 h the turbidity was still present, it was assumed that the binodal curve was crossed during the last step of the titration process. Once permanent turbidity was observed, the cloud point composition was calculated as the arithmetic mean of the compositions before and after that last titration step. To obtain the complete boundary of the two-phase diagram, that procedure was repeated using solutions of different concentrations. The overall absolute uncertainty of the mass fraction of a solute component under cloud-point conditions is 1 %.

Table 11. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPMA 6 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		*T*/K = 323.2	
		w_{NaPMA}	w_{PEG}	w_{NaPMA}	w_{PEG}
coexisting phases	feed point	0.113	0.070	0.103	0.050
	top phase	0.028	0.188	0.035	0.172
	bottom phase	0.168	0.006	0.132	0.007
	feed point	0.113	0.120	0.113	0.100
	top phase	0.019	0.252	0.025	0.243
	bottom phase	0.204	0.006	0.173	0.006
	feed point	0.123	0.171	0.154	0.150
	top phase	0.017	0.318	0.011	0.373
	bottom phase	0.255	0.008	0.251	0.006
	feed point	0.164	0.220	0.154	0.200
	top phase	0.006	0.436	0.016	0.413
	bottom phase	0.335	0.006	0.287	0.007
cloud point curve		0.298	0.007	0.297	0.009
		0.248	0.006	0.199	0.006
		0.200	0.004	0.148	0.007
		0.149	0.008	0.117	0.008
		0.117	0.025	0.098	0.026
		0.096	0.042	0.084	0.043
		0.073	0.091	0.072	0.076
		0.058	0.122	0.034	0.179
		0.038	0.174	0.022	0.232
		0.027	0.226	0.016	0.284
		0.015	0.285	0.017	0.380
		0.016	0.381		
		0.006	0.540		
		0	0.578		

[a] Polysodium methacrylate (w_{NaPMA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 12. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPMA 6 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		*T*/K = 323.2	
		w_{NaPMA}	w_{PEG}	w_{NaPMA}	w_{PEG}
coexisting phases	feed point	0.100	0.051	0.082	0.050
	top phase	0.046	0.147	0.024	0.167
	bottom phase	0.120	0.009	0.101	0.007
	feed point	0.058	0.140	0.103	0.081
	top phase	0.027	0.192	0.016	0.243
	bottom phase	0.150	0.004	0.147	0.004
	feed point	0.120	0.100	0.123	0.130
	top phase	0.028	0.239	0.010	0.326
	bottom phase	0.186	0.003	0.203	0.005
	feed point	0.150	0.140	0.154	0.200
	top phase	0.018	0.327	0.004	0.435
	bottom phase	0.246	0.002	0.284	0.050
cloud point curve		0.299	0.005	0.298	0.006
		0.200	0.003	0.199	0.004
		0.165	0.013	0.149	0.004
		0.129	0.006	0.100	0.004
		0.098	0.020	0.079	0.011
		0.073	0.045	0.062	0.040
		0.062	0.080	0.049	0.083
		0.060	0.096	0.034	0.133
		0.043	0.176	0.027	0.184
		0.025	0.271	0.016	0.236
		0.005	0.396	0.013	0.288
				0.011	0.383
				0.010	0.474

[a] Polysodium methacrylate (w_{NaPMA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

The composition of equilibrium phases was determined separately. In these experiments, systems containing approximately 10 g of an aqueous feed mixture were prepared by mixing known amounts of stock solutions of the single polymers in centrifuge tubes. These stock solutions were gravimetrically prepared, so the feed point composition was exactly known.

Table 13. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPMA 15 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPMA}	w_{PEG}	w_{NaPMA}	w_{PEG}
coexisting phases	feed point	0.100	0.080	0.104	0.050
	top phase	0.041	0.179	0.021	0.197
	bottom phase	0.152	0.019	0.137	0.005
	feed point	0.115	0.130	0.125	0.101
	top phase	0.015	0.269	0.012	0.289
	bottom phase	0.200	0.017	0.189	0.005
	feed point	0.135	0.151	0.156	0.150
	top phase	0.015	0.318	0.010	0.381
	bottom phase	0.240	0.018	0.257	0.005
	feed point	0.156	0.200	0.177	0.220
	top phase	0.004	0.409	0.009	0.479
	bottom phase	0.300	0.016	0.324	0.005
cloud point curve		0.294	0.020	0.198	0.002
		0.196	0.017	0.198	0.010
		0.096	0.038	0.119	0.005
		0.058	0.124	0.099	0.016
		0.036	0.181	0.065	0.079
		0.009	0.338	0.033	0.178
		0.010	0.388	0.013	0.286
		0.011	0.478	0.017	0.378
		0.004	0.543		
		0	0.578		

[a] Polysodium methacrylate (w_{NaPMA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 14. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPMA 15 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPMA}	w_{PEG}	w_{NaPMA}	w_{PEG}
coexisting phases	feed point	0.082	0.200	0.150	0.101
	top phase	0.027	0.281	0.008	0.357
	bottom phase	0.228	0.008	0.200	0.008
	feed point	0.140	0.110	0.150	0.170
	top phase	0.025	0.277	0.014	0.416
	bottom phase	0.213	0.007	0.246	0.008
	feed point	0.140	0.060	0.075	0.075
	top phase	0.051	0.204	0.018	0.193
	bottom phase	0.178	0.008	0.120	0.008
	feed point	0.170	0.140		
	top phase	0.007	0.366		
	bottom phase	0.265	0.007		
cloud point curve		0.298	0.008	0.301	0.008
		0.197	0.008	0.200	0.009
		0.149	0.007	0.198	0.002
		0.110	0.033	0.100	0.006
		0.099	0.068	0.079	0.004
		0.093	0.063	0.066	0.026
		0.054	0.167	0.046	0.085
		0.029	0.277	0.028	0.182
		0.005	0.390	0.012	0.288
				0.012	0.383

[a] Polysodium methacrylate (w_{NaPMA}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

The absolute mass fraction uncertainty is 0.1 % for either solute in that feed solution. Feed points were chosen in such a way that in equilibrium both phases had about the same volume. The systems thus prepared were left under stirring for 48 h in a thermostatic bath. After this period, the tubes were centrifuged for 8 h at 2300*g* in a thermostatted centrifuge (model Rotina 48R, Hettich, Tuttlingen, Germany). The uncertainty in the temperature during centrifugation is about ± 1 K. Therefore, after centrifugation, the systems were kept in the thermostatic bath for at least 30 min before samples of both phases were carefully taken, using a conventional syringe for the top phase and a syringe with an extended needle for the bottom phase.

Table 15. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 2 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point			0.154	0.060
	top phase			0.050	0.185
	bottom phase			0.203	0.002
	feed point			0.182	0.100
	top phase			0.011	0.306
	bottom phase			0.261	0.001
	feed point			0.182	0.150
	top phase			0.034	0.334
	bottom phase			0.301	0.001
	feed point			0.224	0.201
	top phase			0.010	0.456
	bottom phase			0.385	0.001
cloud point curve		0.162	0.349	0.248	0.002
		0.156	0.364	0.198	0.002
		0.117	0.414	0.147	0.006
		0.115	0.414	0.110	0.023
		0.084	0.445	0.079	0.068
		0.055	0.488	0.079	0.062
		0.026	0.533	0.076	0.073
		0.010	0.559	0.030	0.176
		0	0.579	0.013	0.284
				0.009	0.385
				0.011	0.480

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 16. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 2 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.140	0.050	0.112	0.050
	top phase	0.072	0.130	0.040	0.151
	bottom phase	0.178	0.008	0.144	0.004
	feed point	0.154	0.091	0.140	0.090
	top phase	0.052	0.206	0.032	0.241
	bottom phase	0.230	0.006	0.208	0.004
	feed point	0.168	0.150	0.154	0.130
	top phase	0.015	0.315	0.007	0.322
	bottom phase	0.304	0.006	0.246	0.004
	feed point	0.210	0.200	0.182	0.180
	top phase	0.008	0.419	0.007	0.389
	bottom phase	0.394	0.004	0.329	0.003
	feed point			0.150	0.140
	top phase			0.007	0.330
	bottom phase			0.243	0.003
	feed point			0.110	0.101
	top phase			0.012	0.236
	bottom phase			0.177	0.004
cloud point curve		0.249	0.005	0.248	0.003
		0.198	0.009	0.199	0.002
		0.149	0.006	0.099	0.002
		0.124	0.006	0.075	0.019
		0.097	0.027	0.060	0.045
		0.088	0.033	0.047	0.081
		0.068	0.073	0.021	0.184
		0.047	0.162	0.008	0.290
		0.015	0.283	0.005	0.392
		0.005	0.392	0.007	0.486

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

The amount of water in each sample was determined by freeze-drying (model Lyovac GT 2, Amsco/Finn-Aqua, Hürth, Germany). In a typical freeze-drying analysis, a known amount (between (1.5 and 3) g) of a sample was diluted by ap-

Table 17. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 2 and PEO 53) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.140	0.050	0.112	0.050
	top phase	0.054	0.149	0.038	0.163
	bottom phase	0.185	0.006	0.143	0.003
	feed point	0.154	0.090	0.140	0.090
	top phase	0.045	0.211	0.038	0.239
	bottom phase	0.238	0.005	0.203	0.003
	feed point			0.154	0.130
	top phase			0.008	0.321
	bottom phase			0.250	0.004
	feed point			0.182	0.181
	top phase			0.001	0.411
	bottom phase			0.316	0.005
cloud point curve		0.244	0.005	0.249	0.001
		0.194	0.006	0.199	0.001
		0.146	0.006	0.099	0.001
		0.097	0.018	0.072	0.019
		0.074	0.053	0.063	0.038
		0.063	0.076	0.048	0.079
		0.053	0.112	0.032	0.130
		0.027	0.179		

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 18. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 2 and PEO 103) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.140	0.050	0.112	0.050
	top phase	0.042	0.165	0.059	0.130
	bottom phase	0.187	0.004	0.149	0.001
	feed point	0.153	0.090	0.140	0.060
	top phase	0.001	0.258	0.005	0.242
	bottom phase	0.234	0.004	0.181	0.001
cloud point curve		0.242	0.006	0.247	0.001
		0.195	0.005	0.197	0.001
		0.146	0.005	0.099	0.001
		0.118	0.005	0.074	0.009
		0.090	0.020	0.055	0.043
		0.060	0.040	0.043	0.081
		0.031	0.091	0.024	0.131

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 19. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 10 and PEG 6) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.145	0.111	0.120	0.100
	top phase	0.034	0.211	0.050	0.182
	bottom phase	0.270	0.005	0.212	0.004
	feed point	0.152	0.145	0.139	0.145
	top phase	0.020	0.260	0.026	0.274
	bottom phase	0.315	0.005	0.278	0.004
	feed point	0.198	0.200	0.151	0.180
	top phase	0.010	0.370	0.023	0.316
	bottom phase	0.420	0.005	0.322	0.004
	feed point			0.190	0.201
	top phase			0.014	0.388
	bottom phase			0.389	0.004
cloud point curve		0.393	0.009	0.398	0.007
		0.296	0.013	0.297	0.011
		0.196	0.017	0.199	0.005
		0.140	0.057	0.177	0.014
		0.097	0.095	0.144	0.042
		0.090	0.111	0.112	0.090
		0.045	0.189	0.088	0.116
		0.015	0.293	0.062	0.148
		0.008	0.395	0.048	0.190
		0.007	0.481	0.032	0.286
		0	0.579	0.017	0.394
				0.006	0.399

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

proximately 25 g of deionized water and shock-frozen. Freeze-drying was then performed for between 2 and 3 days at about 243 K (about 50 Pa). Afterward, the dried samples were kept in a desiccator (with silica gel) under a vacuum of (0.1 to 1) Pa at room temperature for about 3 days before the mass of a dried sample was determined, and the total polymer content was calculated by a mass balance. The accuracy of the freeze-drying analysis was checked with samples of aqueous solutions of the single polymers of known composition. Each phase equilibrium experiment was performed at least in triplicate.

The concentration of the polyelectrolyte in a sample of a liquid phase was determined by atomic emission spectroscopy using a spectrometer model SpektrAA 100 (Varian Inc., Palo Alto, Ca., USA). The concentration of sodium ions was determined by measuring the emission at 589 nm. The relationship between the intensity of emission and the sodium concentration was determined through a calibration curve using sodium chloride solutions as standards. The calibration curve was checked after eight measurements, and each spectrophotometric analysis was performed in triplicate. It was verified that the presence of polyethylene glycol does not influence the results of the spectrophotometric analysis beyond the scattering of the results from multiple measurements. From these results, the concentration of the polyelectrolyte was determined and that of the PEG sample was calculated using the results from the freeze-drying experiments. The experimental results for the amount of water in both samples (of the coexisting liquids) can be used to calculate the amounts of mass of both coexisting phases. The solute concentrations can then be used in a mass balance to determine the difference between the amounts of each of the polymers in the feed solution and these amounts found in the analysis. These results were used to estimate the total uncertainty of the experimental results for the compositions of the coexisting phases. That total uncertainty includes not only the uncertainties of the analysis but also those from the approximation that the cloud-point curve agrees with the binodal curve. The total (absolute) uncertainty for the mass fraction of any solute (PEG or polyelectrolyte) in any one of the coexisting phases does not surmount 1.1 %.

Results and Discussion

The new experimental results for the equilibrium compositions are presented in Tables 3 to 22. To analyze the various factors affecting the phase behavior, some typical results for two-phase systems are additionally presented in figures. As expected, both coexisting phases are water-rich, and their water mass fraction is typically around (70 to 80) %. The upper phase is the PEG-rich phase. It contains only small mass fractions [(1 to 5) %] of the other polymer. The lower, polyelectrolyte-rich phase vice versa contains very little PEG (less than one mass percent). The experiments with high molar mass fractions of PEG were wearisome and difficult as the PEG-rich phase of such a two-phase system is very viscous, and both phase equilibration and phase separation are difficult to achieve. For

Table 20. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 10 and PEG 34) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.101	0.070	0.150	0.050
	top phase	0.025	0.184	0.070	0.130
	bottom phase	0.167	0.003	0.200	0.005
	feed point	0.140	0.110	0.150	0.100
	top phase	0.019	0.256	0.030	0.210
	bottom phase	0.241	0.003	0.255	0.005
	feed point	0.140	0.180	0.150	0.150
	top phase	0.014	0.321	0.010	0.285
	bottom phase	0.311	0.003	0.315	0.005
	feed point	0.180	0.200	0.100	0.200
	top phase	0.015	0.374	0.010	0.285
	bottom phase	0.375	0.003	0.312	0.005
	feed point	0.140	0.151	0.141	0.135
	top phase	0.013	0.293	0.022	0.243
	bottom phase	0.282	0.003	0.285	0.003
	feed point			0.199	0.201
	top phase			0.420	0.003
	bottom phase			0.005	0.380
cloud point curve		0.398	0.002	0.498	0.006
		0.397	0.008	0.399	0.006
		0.297	0.007	0.296	0.005
		0.200	0.006	0.199	0.005
		0.150	0.002	0.148	0.025
		0.149	0.005	0.093	0.090
		0.118	0.016	0.090	0.094
		0.095	0.060	0.065	0.145
		0.086	0.068	0.037	0.193
		0.066	0.093	0.011	0.295
		0.062	0.101	0.003	0.399
		0.049	0.133		
		0.022	0.196		
		0.016	0.294		

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

Table 21. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 10 and PEO 53) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.150	0.050	0.110	0.070
	top phase	0.045	0.161	0.051	0.124
	bottom phase	0.205	0.002	0.153	0.002
	feed point	0.150	0.100	0.187	0.147
	top phase	0.032	0.214	0.017	0.308
	bottom phase	0.259	0.002	0.325	0.001
	feed point	0.170	0.150		
	top phase	0.011	0.298		
	bottom phase	0.339	0.002		
	feed point	0.200	0.200		
	top phase	0.003	0.384		
	bottom phase	0.430	0.001		
cloud point curve		0.403	0.002	0.398	0.001
		0.299	0.001	0.299	0.001
		0.198	0.003	0.199	0.001
		0.186	0.011	0.129	0.002
		0.149	0.026	0.114	0.009
		0.141	0.034	0.092	0.038
		0.104	0.065	0.069	0.083
		0.096	0.081	0.053	0.130
		0.082	0.111		
		0.057	0.132		
		0.044	0.155		

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

a single pair of polymers (PEG 6 and NaPES 2) at 298.2 K, phase separation (in cloud-point measurements) was observed only at excessively high polymer concentrations, and no two-phase system could be investigated.

Table 22. Experimental Results for the Liquid−Liquid Equilibrium in Aqueous Two-Phase Systems of (NaPES 10 and PEO 103) at (298.2 and 323.2) K[a]

		T/K = 298.2		T/K = 323.2	
		w_{NaPES}	w_{PEG}	w_{NaPES}	w_{PEG}
coexisting phases	feed point	0.150	0.050	0.110	0.071
	top phase	0.044	0.162	0.036	0.170
	bottom phase	0.200	0.008	0.168	0.002
	feed point	0.150	0.080	0.140	0.180
	top phase	0.034	0.191	0.005	0.343
	bottom phase	0.230	0.008	0.302	0.002
	feed point	0.120	0.051		
	top phase	0.046	0.128		
	bottom phase	0.166	0.008		
cloud point curve		0.400	0.001	0.387	0.003
		0.297	0.001	0.286	0.005
		0.204	0.003	0.200	0.002
		0.145	0.007	0.129	0.001
		0.119	0.021	0.094	0.019
		0.100	0.034	0.080	0.045
		0.086	0.044	0.065	0.083
		0.068	0.065	0.044	0.134
		0.059	0.089		

[a] Polysodium ethylene sulfonate (w_{NaPES}) and polyethylene glycol (w_{PEG}) mass fractions obtained in cloud-point and equilibrium measurements.

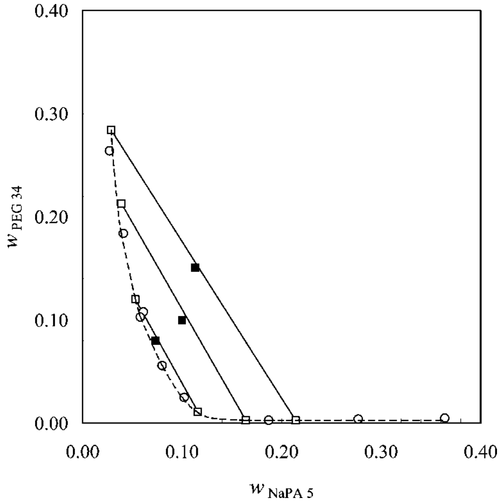

Figure 1. Liquid−liquid phase diagram of aqueous solutions of (NaPA 5 and PEG 34) at 298.2 K: PEG 34 mass fractions $w_{\mathrm{PEG\ 34}}$ as functions of NaPA 5 mass fractions $w_{\mathrm{NaPA\ 5}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

As is well-known and expected, the molar mass of the constituting polymers is an important factor for the behavior of the investigated aqueous two-phase systems, in particular when that molar mass is still rather small. Increasing the molar mass of either one of both polymers results in an extension of the two-phase region (i.e., in a larger miscibility gap) and in a stronger segregation of the constituent polymers. However, when the molar mass of the phase-forming polymers is rather large, the influence of the molar mass on the phase behavior is nearly negligible. This effect is widely documented in the literature for aqueous two-phase systems with neutral polymers (cf., for instance, results for systems containing polyethylene glycol and dextran by Forciniti et al.[18] and Groβmann et al.[3]). The effect of the polyelectrolyte chain size can be seen by comparing Figures 1 and 2, which show the experimental results for the binodal line and the tie-lines at 298.15 K of the aqueous systems with (NaPA 5 + PEG 34) and with (NaPA 15 + PEG 34),

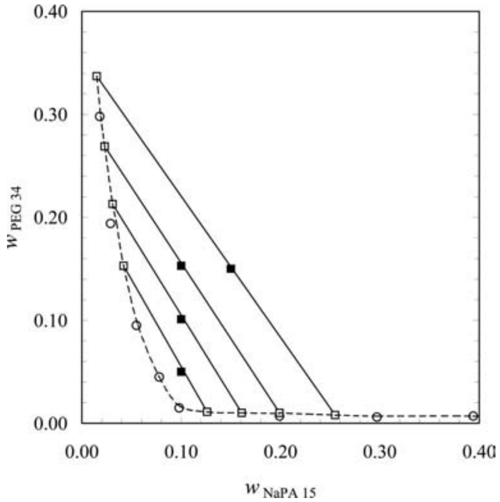

Figure 2. Liquid−liquid phase diagram of aqueous solutions of (NaPA 15 and PEG 34) at 298.2 K: PEG 34 mass fractions $w_{\text{PEG 34}}$ as functions of NaPA 15 mass fractions $w_{\text{NaPA 15}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

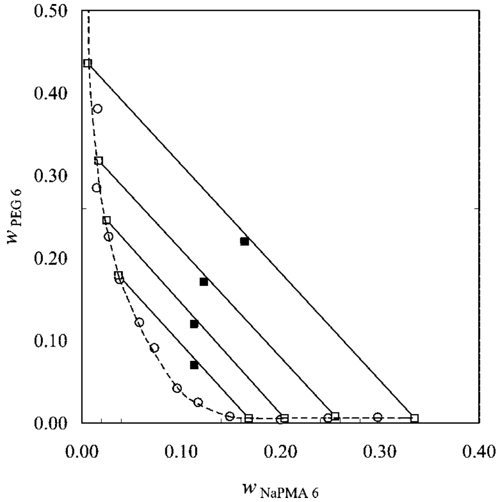

Figure 3. Liquid−liquid phase diagram of aqueous solutions of (NaPMA 6 and PEG 6) at 298.2 K: PEG 6 mass fractions $w_{\text{PEG 6}}$ as functions of NaPMA 6 mass fractions $w_{\text{NaPMA 6}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

respectively. In a 10 % mass fraction aqueous solution of PEG 34, the content of NaPA that is required to induce a phase split decreases from mass fractions of about 6 % (for NaPA 5) to about 5 % (for NaPA 15). Vice versa, in an aqueous solution that contains a mass fraction of 10 % of NaPA, the mass fraction of PEG 34 that is required to induce a liquid−liquid phase split decreases from above to below 2 % when NaPA 5 is replaced by NaPA 15. As shown in Figures 1 and 2, the corresponding differences are smaller (and hardly significant) for more concentrated solutions where the mass fraction of NaPA (PEG) in the PEG-rich (NaPA-rich) phase changes only slightly with the mass fraction of PEG (NaPA) along the binodal line. Among the polymer systems investigated in the present work, there is only a single exception from the behavior shown in Figures 1 and 2. This exception was observed when NaPES 2 and NaPES 10 were the phase-forming polyelectrolytes. In systems with those polyelectrolytes, the increase of the molar mass of NaPES results in a decrease of the two-phase region. There is no straightforward explanation for this behavior. However, in a recent study on the activity of water in aqueous solutions of the same single polyelectrolytes (Lammertz et al.[14]), also a more or less unexpected difference between aqueous solutions of NaPES 2 and NaPES 10 was found. At the same mass fraction and the same temperature, the osmotic coefficient of an aqueous solution of NaPES 2 was nearly twice the osmotic coefficient of an aqueous solution of NaPES 10. As the osmotic coefficient is a measure for the nonideality of a solution and nonidealities constitute the cause of liquid−liquid phase splits, the results of the previous (on the activity of water) and the present work (on the liquid−liquid equilibrium) seem to point toward a common explanation.

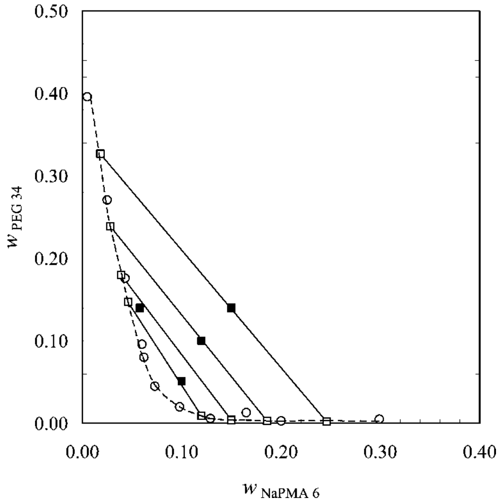

Figure 4. Liquid−liquid phase diagram of aqueous solutions of (NaPMA 6 and PEG 34) at 298.2 K: PEG 34 mass fractions $w_{\text{PEG 34}}$ as functions of NaPMA 6 mass fractions $w_{\text{NaPMA 6}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

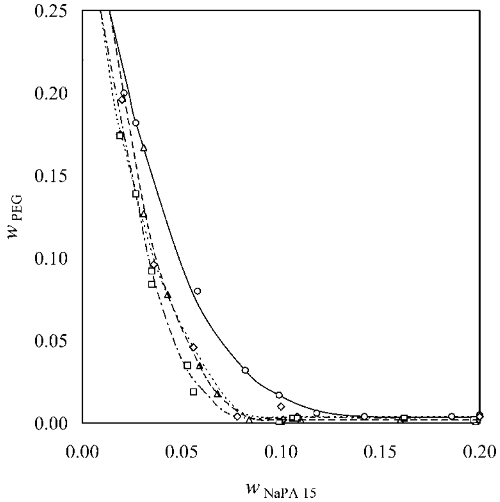

Figure 5. Binodal lines of aqueous solutions of (NAPA 15 and PEG) at 298.2 K: PEG mass fractions w_{PEG} as functions of NaPA 15 mass fractions $w_{\text{NaPA 15}}$. ○, PEG 6; ◇, PEG 34; Δ, PEO 53; □, PEO 103. Curves are traced to guide the eyes.

Increasing the molar mass of PEG shifts the two-phase region in the same direction as increasing the molar mass of the polyelectrolyte. This behavior is demonstrated in Figures 3 and 4 for aqueous systems that contain NaPMA 6 and PEG (either PEG 6 or PEG 34) at 298.2 K. In a 10 % mass fraction aqueous solution of NaPMA 6, the mass fraction of PEG that is required

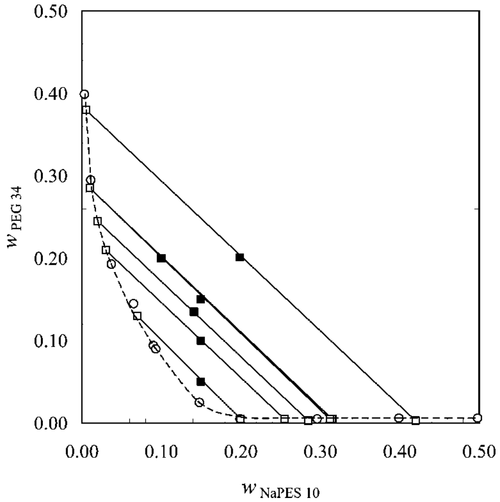

Figure 6. Liquid−liquid phase diagram of aqueous solutions of (NaPES 10 and PEG 34) at 298.2 K: PEG 34 mass fractions $w_{\text{PEG 34}}$ as functions of NaPES 10 mass fractions $w_{\text{NaPES 10}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

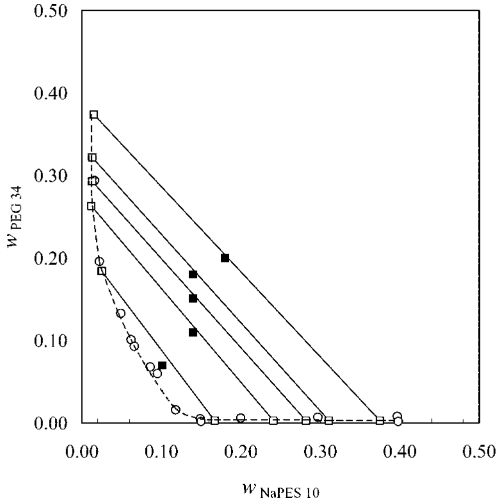

Figure 7. Liquid−liquid phase diagram of aqueous solutions of (NaPES 10 and PEG 34) at 323.2 K: PEG 34 mass fractions $w_{\text{PEG 34}}$ as functions of NaPES 10 mass fractions $w_{\text{NaPES 10}}$. ○, compositions obtained through the cloud-point technique; ■, feed point compositions; □, equilibrium compositions along with tie lines (full lines) and the binodal curve (broken line) traced to guide the eyes.

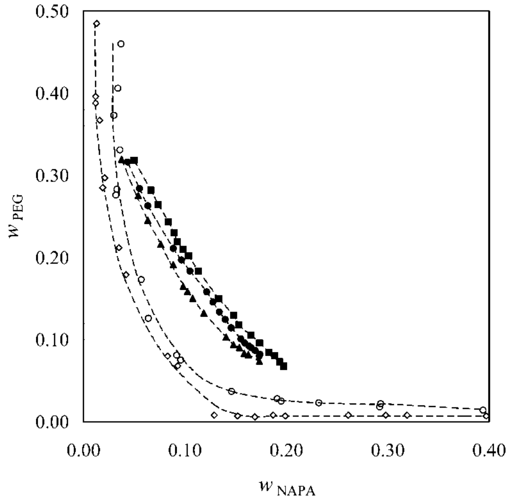

Figure 8. Cloud-point curves of aqueous solutions of (NaPA and PEG): PEG mass fractions w_{PEG} as functions of NaPA mass fractions w_{NaPA}. From this work for (NaPA 5 and PEG 6): ○, 298.2 K; ◇, 323.2 K. From Saravanan et al.[13] for (NaPA with average molar mass 2.1 kg·mol^{-1} and PEG 6): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K. Binodal curves (broken lines) traced to guide the eyes.

to induce a phase split decreases from about 4 % (for PEG 6) to about 2 % (for PEG 34). Vice versa, in an aqueous solution that contains a mass fraction of 10 % of PEG, the mass fraction of NaPMA 6 that is required to induce a liquid−liquid phase split decreases from above to below 6 % when PEG 6 is replaced by PEG 34. As shown in Figures 3 and 4, the corresponding differences are smaller (and hardly significant) for more concentrated solutions only along the polyelectrolyte-rich branch of the binodal curve, whereas in contrast to the behavior shown in Figures 1 and 2, the influence of the molar mass of PEG reverses along the PEG-rich branch of the binodal curve. For example, in a 10 % mass fraction aqueous solution of PEG, the content of NaPMA 6 that is required to induce a phase split increases slightly from a mass fraction of about 3 % to about 4 % when the molar mass of PEG increases from about 6 kg·mol^{-1} (i.e., PEG 6) to about 34 kg·mol^{-1} (i.e., PEG 34). However, if the molar mass of PEG is further increased, this effect is no longer so pronounced. This is shown in Figure 5, where the results for the binodal curve in the region close to the critical point of four systems containing the polyelectrolyte NaPA 15 and different PEG samples are plotted. While systems with PEG 6 clearly differ from all other systems, the differences between systems containing larger PEG molecules are small and lie mostly within experimental uncertainty.

As is shown in Figures 1 to 4, a variation in the molar mass of either the polyelectrolyte or polyethylene glycol has only a small effect on the slope of a tie-line. For all systems shown in Figures 1 to 4, differences in the slopes of the tie-lines are barely noticeable. Within experimental uncertainty, no influence of the molar mass of PEG on the slope of a tie-line can be detected. Obviously the differences between the natures of the polymer monomeric units are much more important for the extent of the two-phase region than the lengths of the polymer chains.

An example for the influence of the polyelectrolyte's monomer unit upon the phase equilibrium can be found by comparing Figures 2 and 4. Both figures are for PEG 34 as the neutral polymer, but Figure 2 is for NAPA 15 and Figure 4 is for NaPMA 6 as the polyelectrolyte. Both polyelectrolytes have nearly the same molar masses and numbers of monomer units but differ by a methyl group per monomer in the polymethacrylate chain. The phase behavior of both systems reveals only small differences.

The temperature also affects the phase diagram. Figures 6 and 7 show the liquid−liquid equilibrium of aqueous solutions of (NaPES 10 and PEG 34) at (298.2 and 323.2) K, respectively. That temperature difference has only a small influence on the phase diagram: the two-phase region is larger at 323.2 K than at 298.2 K. The temperature also affects the slope of the tie-lines: at 298.2 K, the tie-line slopes are (absolutely) somewhat smaller than at 323.2 K.

Comparison with Literature Data. Among the systems investigated in the work presented here, only some information on aqueous two-phase systems of (polysodium acrylate and polyethylene glycol) was found in the literature. Johansson et al.[19,20] described some promising applications in biotechnology of these systems. The binodal curves of the aqueous systems of (poly(acrylic acid) and polyethylene glycol) were described by Gupta et al.[21] However, only Saravanan et al.[13] reported experimental results for the phase behavior of aqueous systems of (NaPA with molar mass 2.1 kg·mol^{-1} and PEG 6) at (293.15, 303.15, and 313.15) K. Figure 8 shows a comparison between the data of Saravanan et al.[13] and the new experimental results reported here for systems containing NaPA 5 and PEG 6 (the closest in similarity of components). Both sets of data reveal the same trends. For example, an increase in temperature results in a larger extent of the two-phase region. However, both sets reveal rather large quantitative differences. The reason for these discrepancies remains an open question. We assume that some of the deviations are caused by differences in the molar masses of the polymer samples. The NaPA 5 sample used in the present work has a number-averaged molar mass of only 2.6 kg·mol^{-1}, but there is no detailed information (beyond the supplier's characterization) of the polymer sample used by Saravanan et al.[13] Considering the differences observed between claimed and experimentally determined molar masses of the polyelectrolyte samples used here,[14] there might be a significant contribution from such differences. Johansson et al.[19,20] did not present data on the phase equilibrium, but they studied aqueous two-phase systems containing mass fractions of about 6 % of NaPA 8 and 6 % of diverse PEG samples, with the addition of small amounts of salt. These relatively low concentrations require a large two-phase region, which is compatible with the new experimental data. Gupta et al.[21] also suggest a larger two-phase region for the system poly(acrylic acid) (molar mass about 250 kg·mol^{-1}) and PEG 6.

To the best of our knowledge, no experimental data on the phase equilibrium of aqueous two-phase systems containing polyethylene glycol and either polysodium methacrylate or polysodium-ethylene sulfonate are available in the open literature.

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) 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.

(4) Walter, H.; Johansson, G.; Brooks, D. E. Partitioning in aqueous two-phase systems: recent results. *Anal. Biochem.* **1991**, *197*, 1–18.

(5) Johansson, H.-O.; Lundh, G.; Karlström, G.; Tjerneld, F. Effects of ions on partitioning of serum albumin and lysozyme in aqueous two-phase systems containing ethylene oxide/propylene oxide co-polymers. *Biochim. Biophys. Acta* **1996**, *1290*, 289–298.

(6) Tada, E. S.; Loh, W.; Pessôa Filho, P. A. Phase equilibrium in aqueous two-phase systems containing ethylene oxide-propylene oxide block copolymers and dextran. *Fluid Phase Equilib.* **2004**, *218*, 221–228.

(7) Taboada, M. E.; Rocha, O. A.; Graber, T. A.; Andrews, B. A. Liquid−liquid and solid-liquid equilibria of the poly(ethylene glycol) plus sodium sulfate plus water system at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 308–311.

(8) Groβmann, C.; Tintinger, R.; Zhu, J.; Maurer, G. Aqueous two-phase systems of poly(ethylene glycol) and di-potassium hydrogen phosphate with and without partitioning biomolecules - experimental results and modeling of thermodynamic properties. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 700–712.

(9) Fedicheva, N.; Ninni, L.; Maurer, G. Aqueous two-phase systems of poly(vinyl pyrrolidone) and sodium sulfate: experimental results and correlation/prediction. *J. Chem. Eng. Data* **2007**, *52*, 1858–1865.

(10) Silva, L. H. M.; Silva, M. C. H.; Mesquita, A. F.; Nascimento, K. S.; Coimbra, J. S. R.; Minim, L. A. Equilibrium phase behavior of triblock copolymer + salt + water two-phase systems at different temperatures and pH. *J. Chem. Eng. Data* **2005**, *50*, 1457–1461.

(11) Haraguchi, L H.; Mohamed, R. S.; Loh, W.; Pessôa Filho, P. A. Phase equilibrium and insulin partitioning in aqueous two-phase systems containing block copolymers and potassium phosphate. *Fluid Phase Equilib.* **2004**, *215*, 1–15.

(12) Perrau, M. B.; Iliopoulos, I.; Audebert, R. Phase separation of polyelectrolyte nonionic polymer systems in aqueous solution - effects of salt and charge density. *Polymer* **1989**, *30*, 2112–2117.

(13) Saravanan, S.; Reena, J. A.; Rao, J. R.; Murugesan, T.; Nair, B. U. Phase equilibrium compositions, densities and viscosities of aqueous two-phase poly(ethylene glycol) + poly(acrylic acid) system at various temperatures. *J. Chem. Eng. Data* **2006**, *51*, 1246–1249.

(14) 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.

(15) 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 (a single synthetic polyelectrolyte and sodium chloride). *J. Chem. Eng. Data* **2008**, in press, doi: 10.1021/je8001317.

(16) Hasse, H.; Kany, H.-P.; Tintinger, R.; Maurer, G. Osmotic virial coefficients of aqueous poly(ethylene glycol) from laser-light scattering and isopiestic measurements. *Macromolecules* **1995**, *28*, 3540–3552.

(17) Lammertz, S. Thermodynamische Eigenschaften wässriger Polyelektrolytlösungen, Ph D. Thesis, Technische Universität Kaiserslautern, Shaker Verlag, Aachen, 2005.

(18) Forciniti, D.; Hall, C. K.; Kula, M. R. Influence of polymer molecular-weight and temperature on phase composition in aqueous 2-phase systems. *Fluid Phase Equilib.* **1991**, *61*, 243–262.

(19) Johansson, H.-O.; Magaldi, F. M.; Feitosa, E., Jr. Protein partitioning in poly(ethylene glycol)/sodium polyacrylate aqueous two-phase systems. *J. Chromatogr. A* **2008**, *1178*, 145–153.

(20) Johansson, H.-O.; Ishii, M; Minaguti, M.; Feitosa, E.; Penna, T. C. V.; Pessoa, A., Jr. Separation and partitioning of Green Fluorescent Protein from Escherichia coli homogenate in poly(ethylene glycol)/sodium-poly(acrylate) aqueous two-phase systems *Sep. Purif. Technol.* **2008**, *62*, 166–174.

(21) Gupta, V.; Nath, S.; Chand, S. Role of water structure on phase separation in polyelectrolyte-polyethylene glycol based aqueous two-phase systems. *Polymer* **2002**, *43*, 3387–3390.

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