Liquid-Liquid Equilibrium of Aqueous Mixtures of Poly(propylene glycol) with NaCl

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Experimental liquid-liquid equilibrium tie lines and plait points were obtained for ternary systems consisting of water, sodium chloride, and poly(propylene glycol) 425 at 278, 298, and 333 K or poly(propylene glycol) 725 at 278 and 298 K.

Introduction

Aqueous two-phase systems are useful for separating materials of biological origin (*1*). These liquid-liquid systems are formed by adding either two structurally different hydrophilic polymers, such as dextran and poly(ethylene glycol) (PEG), or a polymer and a salt, such as K_3PO_4 and PEG, to water. Many large biomolecules, such as proteins and enzymes, are partitioned in such systems, with some components being concentrated in one of the phases (*1-4*). The degree of partitioning of all species in the system can be varied by changing the temperature, polymer or salt type, and molecular weight and concentration of solutes. In addition to their use as phase-forming solvents for separating large molecules, biphasic salt systems provide a method of separating phase components from each other.

Poly(propylene glycol) (PPG) is a polymer that is structurally closely related to PEG, a hydrophilic polymer that is often used in aqueous two-phase partitioning studies (*1*). Low molecular weights of PPG are completely soluble in water while high molecular weights are only partially soluble (*5*). Malcolm and Rowlinson (*6*) observed that aqueous solutions of PPG of molecular weight 400 (weight average) form two liquid phases at temperatures above 313 K. Samii et al. (*7*) determined that low molecular block copolymers of PPG and PEG will form two-phase systems when mixed with water and formamide. Kato et al. (*8*) measured the location of the binodal curve of the system PPG 400 + $(NH_4)_2SO_4$ + water at 298 K.

In this study we report liquid-liquid equilibrium data for aqueous mixtures of sodium chloride and PPG 425 at 278, 298, and 333 K or PPG 725 at 278 and 298 K.

Experimental Section

Materials. The PPG was obtained from the Aldrich Co., Milwaukee, WI. The NaCl was obtained from Anachemia, Montreal. The salt was of reagent grade purity and was dried in an oven for 48 h at 393 K before use. The polymers were in liquid form, and the polydispersity index reported by the manufacturers was 1.05. Distilled water of resistivity greater than 0.3 MΩ·cm was used in all experiments.

Apparatus and Procedures. The concentrations of NaCl were determined by sodium analysis using atomic absorption spectroscopy (AAS). The AAS measurements for sodium were performed using a Thermo Jarell Ash Corp. Model Smith-Hieftje II instrument at a wavelength of 330.2 nm. The concentration of PPG was determined using refractive index measurements performed at 298 K using a Carl Zeiss Model 41433 refractometer. Temperatures were maintained within ±1 K of their set points using water baths supplied by Neslab Instruments.

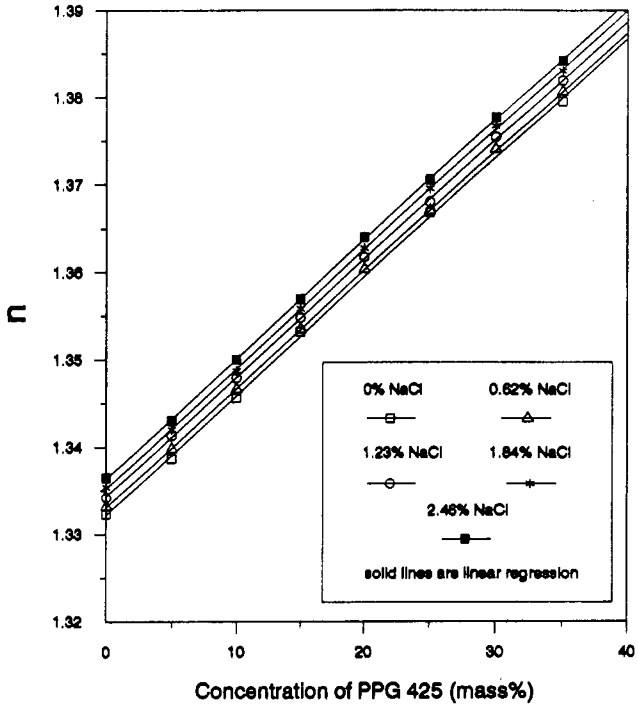

Figure 1. Refractive index calibration curves for PPG 425 + NaCl + water.

Table 1. Refractive Index Calibration Constants

a_0	a_1	a_2
1.3325	NaCl, 1.770×10^{-3}	PPG 425, 1.36×10^{-3} PPG 725, 1.31×10^{-3}

For the AAS measurements, before each analysis of the unknown (diluted) samples, a calibration plot of absorbance versus concentration was prepared. Generally, these were nonlinear for the range 0-120 ppm NaCl by mass, and for each run the concentrations of samples were correlated to the absorbance using a quadratic polynomial equation. Since the refractive index of the phase samples depends on the PPG and salt concentrations, calibration plots of refractive index versus polymer concentration were prepared for different concentrations of NaCl, an example of which is displayed in Figure 1. For both polymer fractions the curves are linear and have similar slopes for the salt concentrations investigated. The following equation describes the relation between the refractive index (n) and the salt (w_s) and PPG (w_p) mass fractions:

$$n = a_0 + a_1 w_s + a_2 w_p \qquad (1)$$

The parameters for the two polymer fractions are listed in

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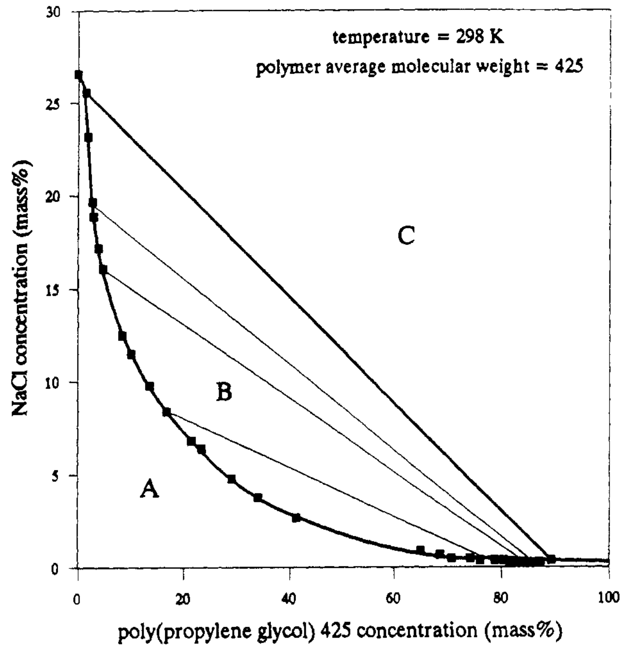

Figure 2. Binodal curve of PPG 425 + NaCl + water at 298 K: (A) one liquid phase, (B) two liquid phases, (C) liquid and solid phases.

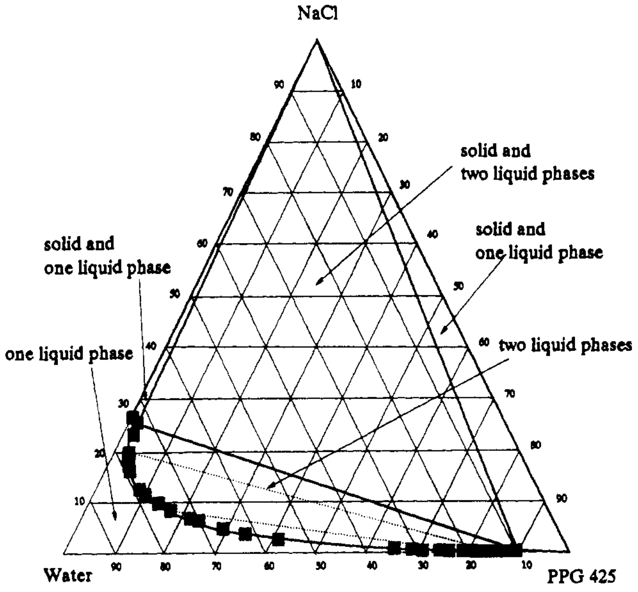

Figure 3. Complete phase diagram of PPG 425 + NaCl + water at 298 K on triangular coordinates.

Table 1. The values of a_0 and a_1 were obtained from refractive index data for binary aqueous NaCl solutions, the intercepts of Figure 1.

The approximate location of the binodal curve was determined by mixing known amounts of the components until two phases were observed. Feed compositions yielding roughly equal volumes of the top and bottom phases were then calculated. Feed samples (60–95 mL) were prepared by mixing appropriate amounts of stock solutions of salt, PPG, and water in 100-mL graduated Pyrex cylinders. These cylinders were capped using either paraffin wax film or, in the case of experiments conducted at 333 K, rubber membranes anchored using rubber bands. The membranes were used because the high temperature softened the wax film and allowed escape of water vapor. The cylinders were placed in a water bath at the desired temperature for 24 h. Since equilibrium compositions depend on the temperature, it was necessary to ensure that phase separation did not occur before the sample attained the temperature of the bath. Hence, the samples were withdrawn and shaken thoroughly at least twice within 1 h of being immersed in the bath.

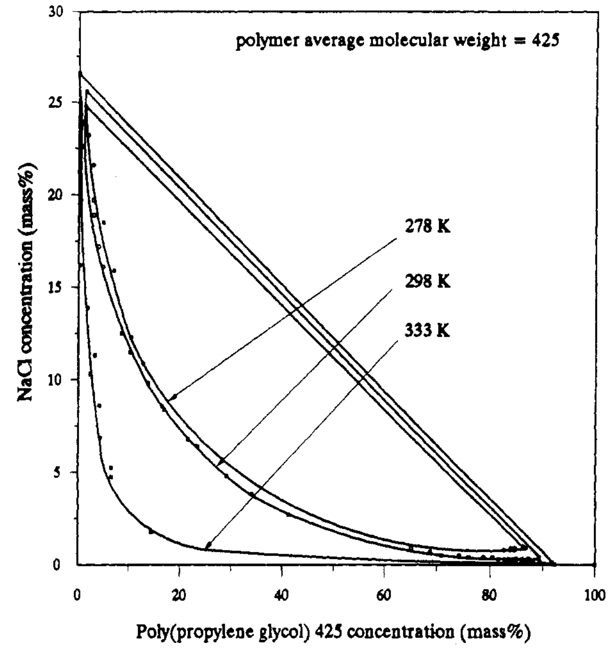

Figure 4. Effect of temperature on the binodal curve of PPG 425 + NaCl + water.

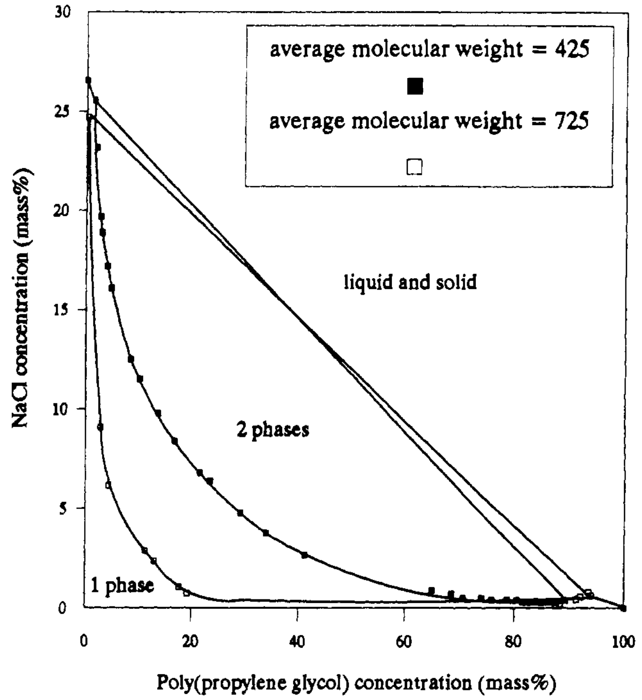

Figure 5. Effect of molecular weight on the binodal curve of PPG + NaCl + water at 298 K.

After equilibrium was achieved, the cylinders were withdrawn and phase volumes recorded. Aliquots of 15 mL were withdrawn using syringes. The top phase was sampled first, with care being taken to leave a layer of material at least 0.5 cm thick above the interface. The bottom phase was withdrawn using a syringe with a long needle. A tiny bubble of air was retained in the needle tip and expelled once in the bottom phase to prevent contamination from upper phase material. In cases where precipitated solid salt was present, care was taken to ensure that the sample was withdrawn gently, with the needle tip well away from salt crystals. For samples at 333 K, the above operations were performed

Table 2. Tie Line Data for PPG 425 at 278 K

bottom phase		top phase	
mass % NaCl	mass % PPG 425	mass % NaCl	mass % PPG 425
8.6	16.4	1.5	75.3
10.9	12.7	1.5	79.5
12.3	10.4	0.8	82.6
15.9	7.0	0.8	83.8
18.5	4.9	0.9	83.9
21.6	2.9	0.8	84.6
24.0	1.2	0.9	84.7
24.7	1.4	0.9	86.2
24.7[a]	1.4	0.9	86.3
24.7[a]	1.4	1.0	86.3
24.8[a]	1.3	0.9	86.7

[a] Solid NaCl present.

Table 3. Tie Line Data for PPG 425 at 298 K

bottom phase		top phase	
mass % PPG 425	mass % NaCl	mass % PPG 425	mass % NaCl
41.2	2.7	65.1	0.9
34.0	3.8	68.7	0.7
29.1	4.8	70.9	0.5
23.4	6.4	74.3	0.5
21.5	6.8	76.1	0.4
16.8	8.4	78.8	0.4
13.7	9.8	80.5	0.4
10.2	11.5	81.6	0.3
8.5	12.5	82.8	0.3
4.8	16.1	83.6	0.3
4.0	17.2	84.5	0.3
3.0	18.9	85.0	0.3
2.8	19.7	86.1	0.3
1.9	23.2	87.3	0.3
1.5	25.6[a]	89.3	0.4

[a] Solid NaCl present.

Table 4. Tie Line Data for PPG 425 at 333 K

top phase		bottom phase	
mass % PPG 425	mass % NaCl	mass % PPG 425	mass % NaCl
81.07	0.06	6.53	5.26
81.90	0.05	6.61	4.75
82.70	0.07	4.16	8.62
83.55	0.08	3.30	11.32
84.30	0.07	4.30	6.87
84.55	0.08	2.36	10.30
86.01	0.09	1.81	13.89
86.48	0.11	0.28	16.20
86.55	0.11	0.44	19.70
88.18	0.12	0.79	22.60
89.41	0.13	0.63	23.91
91.79	0.14	0.01	26.08
88.25	0.18	0.21	26.99[a]
89.45	0.17	0.07	26.89[a]

[a] Solid NaCl present.

rapidly, as the temperature of the cylinders fell quickly after removal from the bath. This was particularly important for the measurement of density which was carried out immediately after sample withdrawal.

The densities of both phases were determined using a 10-mL pycnometer and a balance reading ±0.1 mg, following which a 5-mL sample of each phase was pipetted and diluted by a volumetric factor of 2000 for sodium analysis. Another 5-mL pipet sample was withdrawn for refractive index analysis. The refractive index samples were equilibrated in a second water bath, maintained at 298 K. For refractive index measurement, the samples were diluted by a factor of 2–8.

Table 5. Tie Line Data for PPG 725 at 278 K

top phase		bottom phase	
mass % PPG 725	mass % NaCl	mass % PPG 725	mass % NaCl
87.29	0.91	21.55	1.98
89.10	1.31	11.32	5.29
90.33	1.04	3.41	9.26
91.66	0.84	1.59	12.83
93.14	0.82	1.22	15.82
93.93	0.72	1.16	22.30
93.99	0.64	1.36	25.18

Table 6. Tie Line Data for PPG 425 at 298 K

top phase		bottom phase	
mass % PPG 725	mass % NaCl	mass % PPG 725	mass % NaCl
87.53	0.13	19.31	0.75
87.57	0.18	17.75	1.08
88.28	0.23	11.31	2.92
88.37	0.13	13.04	2.39
91.27	0.44	4.43	6.19
92.04	0.58	2.84	9.11
93.44	0.81	0.24	24.73

Table 7. Plait Points

		plait point	
system	temp (K)	mass % PPG	mass % NaCl
PPG 425 + NaCl + H_2O	278	43.0	4.0
PPG 425 + NaCl + H_2O	298	56.0	2.0
PPG 425 + NaCl + H_2O	333	50.0	0.5
PPG 725 + NaCl + H_2O	278	52.0	1.0
PPG 725 + NaCl + H_2O	298	56.0	0.4

Results and Discussion

Phase separation was achieved within 1 h of shaking, resulting in clear phases. The top phases were rich in PPG and low in salt, while the bottom phases contained most of the salt and little polymer. The top phases were viscous and had densities, at 298 K, in the range 1.030–1.036 g/mL for PPG 425 and 1.022–1.031 g/mL for PPG 725. The bottom phases were less viscous and had corresponding densities in the ranges of 1.069–1.100 and 1.062–1.0131 g/mL.

The binodal curve of the PPG 425 + NaCl + water system at 298 K is shown in Figure 2. Tie line compositions were verified by performing mass balances to determine if the amounts of NaCl and PPG used to create the feed phase corresponded to the amounts in the top and bottom phases, on the basis of equilibrium compositions. The mass balances for tie lines closed to within 6%. Replicates of tie lines had a standard deviation of 0.38 mass % corresponding to a 95% confidence interval of ±0.43. Figure 3 shows the complete phase diagram for this system plotted on triangular coordinates. Most of the phase diagram consists of either a solid–liquid–liquid or solid–solid–liquid region. The two-liquid region occupies a small portion of the total phase diagram, although the coexisting phases are generally quite different in composition. There are two single liquid–solid regions, one with a liquid rich in water and another with a liquid rich in PPG. The effect of temperature on the binodal curve of the PPG 425 + NaCl + water system is illustrated in Figure 4. For both polymer fractions the effect of increasing the temperature is to increase the area of two-phase coexistence. Similarly, the effect of increasing the molecular weight of the polymer, shown in Figure 5, is to increase the size of the two-phase region. The higher molecular weight fraction is not completely miscible with water at 298 K. The equilibrium data are listed in Tables 1–6. The locations of plait points were estimated by extrapolation from the midpoints of tie lines (*1*), and the values are listed in Table 7.

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