Liquid−Liquid Equilibrium of the Poly(ethylene glycol) + Sodium Nitrate + Water System at 298.15 K

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Liquid−liquid equilibrium data for the PEG 4000 + $NaNO_3$ + H_2O system were measured at 298.15 K. The binodal curve was fitted to a three-parameter equation, and the tie line compositions were fitted to both the Othmer−Tobias and Bancroft equations. The refractive indices and densities of several homogeneous ternary solutions used for calibration were also measured in the range 0−40 mass % PEG, 0−18 mass % $NaNO_3$.

Introduction

Aqueous two-phase systems (ATPSs) may be created from a homogeneous aqueous phase by the addition of one or more specific additives. Most of the ATP extraction systems are formed when either two aqueous polymer solutions are mixed or when a polymer and a salt are dissolved together in water (Zaslavsky, 1995; Cabezas, 1996). Aqueous poly(ethylene glycol) (PEG) with several inorganic salts is the most widely studied phase system of the last alternative above (Gao et al., 1991; Voros et al., 1993; Hammer et al., 1994; Mishima et al., 1995; González-Tello et al., 1996; Meller da Silva, 1997). In both cases two liquid phases are formed and several solutes such as biological macromolecules may be unevenly distributed in each phase, thus enhancing the separation (Abbott, 1988; Albertsson, 1990).

In addition to their use in liquid−liquid purification of biomaterials, biphasic systems are also used in other applications such as the extraction of metal ions from aqueous solutions (Rogers et al., 1995; Rogers et al., 1996) and the extractive crystallization of inorganic salts (Brenner et al., 1992; Ting et al., 1992; Lynn et al., 1996; Zijlema et al., 1997).

Chile has abundant rock-deposits—a source of sodium nitrate and iodine. As the largest world producer of iodine, it is interesting to explore the possibility of partitioning iodine in ATP systems formed by aqueous sodium nitrate solutions and a third component as an additive. Preliminary experiments carried out in our laboratory show good iodine partition coefficients by adding (poly ethylene glycol) (PEG) to sodium nitrate/iodine/water systems. As part of a long-term study, we report here liquid−liquid equilibrium composition data for aqueous mixtures of sodium nitrate and PEG 4000 at 298.15 K. No data were found in the literature for this ternary system. In addition to the equilibrium measurements, the refractive indices and densities of solutions in the single-phase region were measured.

Experimental Section

Materials. Synthesis grade samples of poly(ethylene glycol) with an average molecular weight of 4000 (3500−4500) and analytical reagent grade +99.5% sodium nitrate were procured from Merck and used without further purification. Drying for a week at 50 °C showed the polymer to contain 0.46 mass % water. Before use, sodium nitrate was dried at 120 °C. Milli-Q water was used in all experiments.

Experimental Procedure. Before analysis of unknown samples, several calibration solutions in the single-phase region were prepared in triplicate by mass in closed flasks and thermostated at 298.15 K. An analytical balance with a precision of $\pm 10^{-4}$ g was used. After the samples were stirred for more than 24 h, the refractive indices and the densities were measured. The homogeneous solutions used for calibration ranged between 0 and 40 mass % PEG and 0−18 mass % $NaNO_3$. The refractive indices at the sodium D-line were measured with a thermostated Abbe BT refractometer with a precision of ±0.0001. The apparatus was calibrated by using the glass piece of known refractive index supplied with the instrument. The temperature of the sample was kept constant with a cascade bath, which permits stability within ±0.02 K, the temperature being measured with a digital thermometer (Yokogawa 7563). A minimum of three independent readings were taken for each sample. Densities were measured with an Anton Paar DMA 38 vibrating tube densimeter operating under static conditions. Before each series of measurements, the instrument was calibrated with degassed ultrapure water and vacuum. For each sample three runs were developed. The precision in density was ± 0.001 g cm^{-3}.

To obtain the binodal curve, several aqueous solutions of PEG were prepared by mass and equilibrated at 298.15 K in a bath controlled to ±0.05 K. Small amounts of salt were dropwise added and the flasks were shaken and allowed to settle after each addition (0.01 g, approximately). This was continued until a sample just became turbid, indicating the appearance of the second liquid phase.

The tie line values were determined by making mixtures of the three components whose compositions fell within the

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two-phase region. Hence, several solutions (typically 80 g) with appropriate quantities of water, PEG, and salt were prepared by mass and fed into closed flasks to equilibrate. The solutions were thermostated and magnetically stirred for >24 h and then allowed to settle for 24 h at constant temperature. Longer stirring and settling periods did not result in any sensible change in the phase compositions. After equilibrium was achieved, the volume of each phase was measured, the accuracy of the volumetric flasks being ±0.5 cm^3, and triplicate samples of the top and the bottom phases were collected by means of a syringe. The sampling procedure described by Cheluget et al. (1994) was followed. Once the samples were withdrawn, the chemical composition and the density were determined.

Several three-component solutions were prepared in order to delimit a three-phase region (25 mass % PEG, 37 mass % $NaNO_3$, and 38 mass % H_2O was a typical composition of these samples). Two liquid phases and a solid phase coexist at equilibrium in this zone. After equilibration, samples of both liquids were collected and analyzed. Samples of the solid phase were also taken off, characterized by X-ray diffraction, and chemically analyzed, always resulting in pure $NaNO_3$.

The concentration of nitrate was determined by molecular absorption at 220 nm, using an Unicam flame spectrophotometer UV 2. The calibration line was obtained from aqueous solutions of $NaNO_3$ prepared by mass at concentrations ranging from 0 to 30 ppm of nitrate. At these dilutions no significant influence of the initial polymer concentration on the spectrophotometric readings was observed. Approximately 10 g of each unknown liquid-phase sample was taken, diluted, and analyzed. Three replicates were measured, and the reproducibility was ±0.5%. On the basis of standard solution measurements, an accuracy of $\pm 3 \times 10^{-2}$ kg of $NaNO_3$/100 kg of solution was established. The nitrate concentration was checked by sodium atomic absorption at 589 nm using a Philips PU9400 flame spectrophotometer.

The concentration of PEG in samples was determined from refractive index measurements and tested using density measurements. Once the salt concentration was determined, the samples were diluted, if necessary, to adjust to the calibration ranges. The accuracy was ±0.3 kg of PEG/100 kg of solution.

Having determined the sodium nitrate and PEG concentrations, the water content is given by the difference.

Results and Discussion

The calibration refractive index $n(D)$ and density ρ measurements were related to the concentrations of both salt and polymer through the following equations:

$$n(D) = 1.3325 + 0.117w_1 + 0.151w_3 \tag{1}$$

$$\rho/(\mathrm{g{\cdot}cm^{-3}}) = 0.997 + 0.702w_1 + 0.179w_3 \tag{2}$$

w_1 and w_3 being the mass fraction of $NaNO_3$ and PEG, respectively, and 1.3325 and 0.997 being the refractive index and density of pure water at 298.15 K, respectively. The mean relative standard deviation in this concentration range was 0.036% for refractive indices and 0.1% for densities. The maximum relative deviation is 0.09% for refractive indices and 0.2% for densities.

Binodal Curve. The binodal experimental data are reported in Table 1 and plotted in Figure 1. A single liquid phase exists in zone A in Figure 1. The liquid phase splits in region B into two equilibrium immiscible liquid phases: a PEG-poor, $NaNO_3$-rich bottom layer and a PEG-rich upper phase which also contains an appreciable concentration of nitrate. Once the liquid phase splits, any addition of salt will alter the compositions of both immiscible phases (tie lines). The two-liquid envelope occupies a small portion of the total phase diagram. Finally, in the three-phase region C, the system is saturated with salt, and the composition of each liquid phase will remain constant even though the relative amount of the two liquids will change, as predicted by the phase rule.

Table 1. Binodal Curve Data of the Sodium Nitrate (1) + Water (2) + PEG (3) System at 298.15 K as Mass Fraction *w*

$100w_1$	$100w_3$	$100w_1$	$100w_3$	$100w_1$	$100w_3$
23.60	39.5	27.03	19.4	36.41	2.3
23.55	36.3	28.53	16.2	37.03	2.1
23.71	33.3	29.25	14.1	37.10	2.0
24.12	30.0	30.72	10.8	37.59	1.3
24.65	27.9	32.75	7.8	39.11	0.8
25.28	25.8	33.68	5.5	39.87	0.6
25.70	23.6	35.30	3.9	40.92	0.4
26.41	21.3	35.33	3.7		

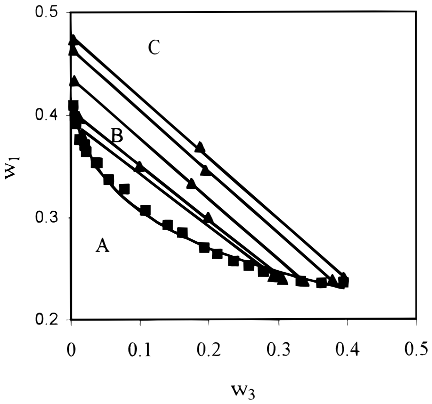

Figure 1. Binodal curve of PEG 4000 + $NaNO_3$ + water at 298.15 K: (A) one liquid phase; (B) two liquid phases; (C) liquid and solid phases.

At 298.15 K sodium nitrate is rather soluble in water (Mullin, 1993). Examination of Figure 1 reveals that the addition of PEG decreases the solubility and that a concentration of PEG as low as 0.2% yields two liquid phases, providing the mixture is rich in $NaNO_3$. However, the drowning out effect is small in this system because the salt concentration was never below 23.73% even at high PEG concentrations.

The binodal curve was fitted by the following expression:

$$\frac{1}{w_1} = a + b{w_3}^{0.5} + cw_3 \tag{3}$$

w_1 and w_3 being the mass fractions of $NaNO_3$ and PEG, respectively. The parameters $a = 2.259$, $b = 2.998$, and $c = 0.501$ were obtained by least squares. The mean relative deviation between experimental and calculated values was 1.2%

Tie Lines. The tie line compositions are given in Table 2. The phase concentrations are also plotted in a phase diagram in Figure 1. The tie lines are determined by connecting each corresponding set of total, top, and bottom phase compositions. The coexisting phases are close in composition. A mass balance check was made between the initial mass of each component and the amounts in the bottom and top phases on the basis of equilibrium compositions. The mass of each phase was calculated from volume

Table 2. Tie Lines for the Sodium Nitrate (1) + Water (2) + PEG (3) System at 298.15 K at Various Initial Mass Fractions

initial comp		top phase			bottom phase		
$100w_1$	$100w_3$	$100w_1$	$100w_3$	ρ/ $kg{\cdot}m^{-3}$	$100w_1$	$100w_3$	ρ/ $kg{\cdot}m^{-3}$
34.98	9.95	24.20	29.2	1228.8	38.10	1.6	1313.1
30.02	19.90	23.92	30.6	1229.1	39.69	1.2	1318.6
33.32	17.50	23.73	33.7	1232.0	43.33	0.5	1341.4
34.61	19.52	23.88	37.9	1238.1	46.32	0.4	1372.8
36.90	18.74	24.07	39.5	1241.0	47.31	0.4	1385.0
37.00[a]	25.00	24.04	39.6	1241.3	47.61	0.2	1389.5

[a] Saturation conditions.

Table 3. Values of the Parameters of Eqs 4 and 5

k	n	R^2 [a]	k_1	r	R^2 [a]
1.366	1.213	0.991	1.151	0.645	0.990

[a] Linear regression index.

and density measurements. The relative error in the mass balance was <3%. The densities of the top phases were close to 1.2 g/cm^3 while those of the bottom phases ranged from 1.3 to 1.4 g/cm^3. The density difference between the phases increased with the tie line length. A plait point of 29.30 mass % $NaNO_3$, 57.40 mass % water, and 13.30 mass % PEG was estimated from the midpoint of the tie lines.

Contrary to what happens in many water/PEG/inorganic salt ATP systems, the nitrate concentration in the top liquid phase is rather high and almost constant. Hence, the system shows a small salting effect. The partition coefficient, defined for $NaNO_3$ as w_{1b}/w_{1t}, ranges from 1.57 to 1.98, giving us an indication of the separation obtained by adding an amount of PEG to a given brine solution. It may be concluded that the system seems not to be attractive to crystallize the salt. However, it might be useful as an ATPS for partitioning iodine or other compounds.

The reliability of measured tie line compositions was ascertained by the Othmer-Tobias (eq 4) and the Bancroft (eq 5) correlation equations.

$$\left(\frac{1 - w_{3t}}{w_{3t}}\right) = k\left(\frac{1 - w_{1b}}{w_{1b}}\right)^n \tag{4}$$

$$\left(\frac{w_{2b}}{w_{1b}}\right) = k_1\left(\frac{w_{2t}}{w_{3t}}\right)^r \tag{5}$$

where w_{3t} is the mass fraction of PEG in the top phase, w_{1b} is the mass fraction of $NaNO_3$ in the bottom phase, w_{2b} and w_{2t} are respectively the mass fractions of water in the bottom and top phases, and k, n, k_1, and r are parameters. A linear dependency of the plots $\log\{(1 - w_{3t})/w_{3t}\}$ against $\log\{(1 - w_{1b})/w_{1b}\}$ and $\log \{w_{2b}/w_{1b}\}$ against $\log \{w_{2t}/w_{3t}\}$ indicated an acceptable consistency of the results. The values of the parameters are given in Table 3.

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