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Influence of Molecular Weight of the Polymer on the Liquid−Liquid Equilibrium of the Poly(ethylene glycol) + $NaNO_3$ + H_2O System at 298.15 K

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Liquid−liquid equilibria for the poly(ethylene glycol) (PEG) + $NaNO_3$ + H_2O system, with PEG of molecular weights 2000, 6000, and 10 000, have been measured at 298.15 K. The binodal curve was fitted using a three-parameter equation, and the compositions of the tie lines at equilibrium were fitted using the Othmer−Tobias equation. These equations were used to develop a mathematical model for interpretation of the equilibrium data of these aqueous two-phase systems (ATPS's). Data on the densities and refractive indexes are also given for the solutions at equilibrium. It was found that an increase in the molecular weight of the PEG produced a displacement of the binodal curve toward the origin and increased the liquid−liquid biphasic zone. The ATPS's studied may be used in separation of iodine and other compounds.

Introduction

Aqueous two-phase systems (ATPS's) have been used for over 30 years for the extraction of biological materials such as cells and proteins.[1−3] In the past decade they have also been employed in the extraction of metal ions[4,5] and recently in the extractive crystallization of inorganic salts[6] and in the extraction process of sulfide minerals.[7]

To form an ATPS, two aqueous polymer solutions are required, generally poly(ethylene glycol) (PEG) and dextran. One of the polymers may be replaced by an inorganic salt such as $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, K_3PO_4, Na_2CO_3, or Na_2SO_4.

One of the ATPS's of major practical interest is formed by aqueous solutions of PEG and inorganic salts, given that this polymer is low in cost, nontoxic, noninflammable, and easy to handle. The ATPS's with PEG and salt have proved to be efficient in partitioning processes both with biomaterials and with metal ions. Several studies have been made on their liquid−liquid equilibrium behavior using different PEG molecular weights and various inorganic salts.[8−12]

Zaslavsky[13] presents a useful summary of experimental data and phase equilibrium diagrams for ATPS's formed by polymers and water. The main inorganic salts described include $(NH_4)_3PO_4$, Na_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, NaOH, KOH, Na_2CO_3, and K_2CO_3.

Snyder and co-workers[8] provided partial information for the phase diagrams for aqueous solutions of PEG with $MgSO_4$, Na_2SO_4, $CaCO_3$, $(NH_4)_2SO_4$, and K_2HPO_4. Ho-Gutierrez et al.[14] present data on the liquid−liquid equilibria for aqueous mixtures of PEG with Na_2SO_4 and NaCl at 301 and 308 K. They worked with PEG with molecular weights of 1000, 3350, and 8000. Hammer et al.[9] measured the liquid−liquid equilibrium in aqueous solutions of PEG and sodium sulfate. They worked with PEG with molecular weights between 1550 and 6000, pH between 5.2 and 8.1, and temperatures between 293.15 and 313.15 K. Gonzalez-Tello et al.[10] studied the liquid−liquid equilibrium of the PEG + $MgSO_4$ + H_2O system at 298 K. They worked with PEG with molecular weights of 1000, 3350, and 8000.

Recently Graber et al.[12] presented data on the liquid−liquid equilibrium of the PEG + $NaNO_3$ + H_2O system at 298.15 K using PEG with a molecular weight of 4000. The present study complements this previous work, by evaluating this system using PEG with molecular weights of 2000, 6000, and 10 000. This ATPS is of potential interest for the extraction of iodine and other anions originating from sodium nitrate and iodine in mineral deposits in northern Chile. These nitrate deposits are among the major commercial sources of iodine in the world.

Experimental Section

Materials. Reagents utilized included sodium nitrate p.a. (Merck) and synthesis grade poly(ethylene glycol) (Merck) with molecular weights of “2000” (MW = 1900−2000), “6000” (MW = 5000−7000), and “10000” (MW = 9000−12500). The sodium nitrate was dried at 120 °C for 48 h to eliminate moisture. The humidity of the PEG was determined in triplicate by measuring the mass after drying 20 g in a desiccator at 50 °C until the mass remained constant (about 1 week). The percentage humidity was 0.04 to 0.07% depending on the molecular weight of the PEG. Milli-Q quality distilled water was used throughout.

Experimental Procedure. Details of the experimental procedure were previously described by Graber et al.[12] The binodal curve of each ATPS was determined using a turbidimetric method, adding small masses of $NaNO_3$ or PEG (typically 0.01 g) to (shaken) 10 g solutions of each phase until the characteristic change in turbidity appeared, indicative of the formation of a second liquid phase. All points of the binodal curve were determined isothermically at 298.15 K ± 0.1 K.

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Table 1. Binodal Curve Data of the Sodium Nitrate (1) + Water (2) + PEG-2000 (3) System at 298.15 K as Mass Fraction w

w_3	w_1	w_3	w_1	w_3	w_1
0.3788	0.2523	0.1532	0.3300	0.0707	0.3759
0.3407	0.2585	0.1492	0.3316	0.0670	0.3784
0.3330	0.2599	0.1449	0.3341	0.0562	0.3856
0.3199	0.2634	0.1407	0.3364	0.0466	0.3919
0.3004	0.2684	0.1295	0.3418	0.0298	0.4069
0.2835	0.2735	0.1228	0.3457	0.0251	0.4118
0.2653	0.2804	0.1164	0.3487	0.0170	0.4280
0.2409	0.2889	0.1087	0.3534	0.0137	0.4343
0.2233	0.2957	0.1016	0.3574	0.0098	0.4458
0.2096	0.3016	0.0963	0.3597	0.0054	0.4642
0.1964	0.3081	0.0794	0.3704	0.0043	0.4771
0.1708	0.3204	0.0743	0.3732		

Table 2. Binodal Curve Data of the Sodium Nitrate (1) + Water (2) + PEG-6000 (3) System at 298.15 K as Mass Fraction w

w_3	w_1	w_3	w_1	w_3	w_1
0.4161	0.2305	0.1613	0.2756	0.0249	0.3462
0.3998	0.2302	0.1585	0.2767	0.0205	0.3507
0.3876	0.2312	0.1194	0.2925	0.0100	0.3685
0.3383	0.2338	0.1179	0.2928	0.0093	0.3687
0.2811	0.2425	0.0718	0.3144	0.0028	0.4060
0.2295	0.2506	0.0597	0.3217	0.0027	0.4520
0.1916	0.2639	0.0416	0.3305	0.0014	0.4780

The tie lines were determined in triplicate from mixtures of known overall composition above the binodal curve (typically 40 g in capped, graduated flasks), which were agitated for 48 h in a rotatory bath with temperature controlled at 298.15 K ± 0.1 K. The biphasic solutions obtained were separated by isothermic sedimentation over 48 h. Longer stirring and settling periods did not result in any observable changes in the phase compositions.

Once the solutions in equilibrium were separated, samples were taken in triplicate to determine the composition of each phase (reproducibility was ±1.8%). The density and refractive index were also measured for each solution in equilibrium.

Refractive index was measured using a Mettler Toledo model RE50 refractometer having a precision of ±0.0001 nD, and density was measured in a Mettler Toledo model DE50 densimeter with a precision of ±0.000 05 g/mL. Both physical properties were measured under isothermic operating conditions at 298.15 K ± 0.1 K.

The concentration of PEG in the samples was determined by measurement of refractive index and density.[12] Calibration curves were obtained by preparation of standard solutions of $NaNO_3$ between 0 and 24% and of PEG between 0 and 40% for each different PEG utilized. No variation in the physical properties was observed in relation to the molecular weight of the PEG.

Nitrate was determined by molecular absorption at 220 nm using a 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 nitrate. At these dilutions, no influence of the initial concentration of PEG was observed on the spectrophotometric readings. The concentration of nitrate was checked by analysis of sodium, determined by atomic absorption (AA) at 589 nm using a Phillips PU9400 flame spectrophotometer.

Results and Discussion

Binodal Curve. Tables 1−3 present the experimental data obtained for the binodal curves for PEG at the molecular weights 2000, 6000, and 10 000, respectively.

Table 3. Binodal Curve Data of the Sodium Nitrate (1) + Water (2) + PEG-10000 (3) System at 298.15 K as Mass Fraction w

w_3	w_1	w_3	w_1	w_3	w_1
0.4258	0.2246	0.1793	0.2547	0.0188	0.3303
0.4171	0.2248	0.1492	0.2636	0.0089	0.3434
0.3764	0.2274	0.1139	0.2785	0.0040	0.3526
0.3041	0.2320	0.0928	0.2883	0.0020	0.3626
0.2742	0.2349	0.0651	0.2995	0.0004	0.4783
0.2477	0.2397	0.0525	0.3076		
0.2148	0.2478	0.0356	0.3165		

Table 4. Values of the Parameters of Eq 1

PEG	a	b	c	mean dev[a] (%)
PEG-2000	2.0769	1.4039	2.8295	0.84
PEG-4000	2.2591	2.9980	0.5010	2.12
PEG-6000	2.1524	4.3744	−1.4357	2.77
PEG-10000	2.3866	4.4045	−1.8276	2.61

[a] Mean deviation.

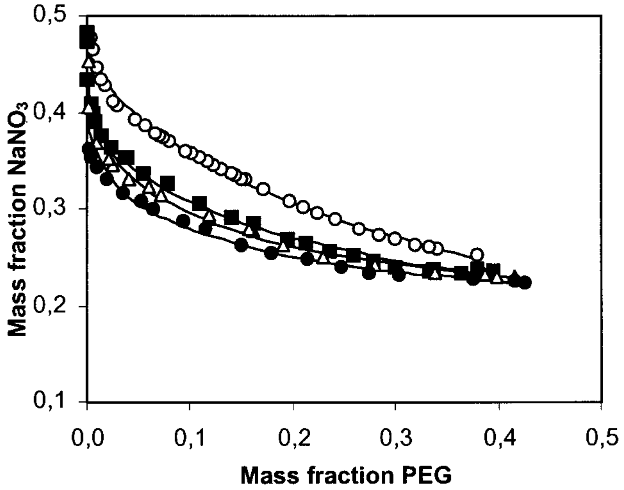

Figure 1. Binodal curves of $NaNO_3$ + PEG + H_2O at 298.15 K: ○, PEG-2000; ■, PEG-4000; △, PEG-6000; ●, PEG-10000. Lines were obtained using eq 1.

These data were fitted using the following expression:

$$\frac{1}{w_1} = a + b\sqrt{w_3} + cw_3 \qquad (1)$$

where w_1 and w_3 are the mass fractions of $NaNO_3$ and PEG, respectively. The parameters a, b, and c for each type of PEG utilized are listed in Table 4.

Figure 1 presents the binodal curves obtained with experimental data points and lines obtained using eq 1. This figure also includes the binodal curve previously obtained using PEG-4000.[12] It is observed that at higher molecular weights of PEG there is a displacement of the binodal curve toward the origin and that eq 1 adequately represents the experimental points with a mean deviation of <2.8%.

Figure 1 shows that, at a higher molecular weight of PEG, a lower concentration of nitrate is required to obtain phase separation in the system. This may be explained by the lower solubility in water of the higher molecular weight polymer.

It is also observed that, at higher molecular weights of PEG, the difference between binodal curves is less. For mass fractions of PEG > 0.38 the binodal curves tend to join the binodal curves obtained with PEG 6000 and 10 000. A similar effect occurs for concentrations of $NaNO_3$ > 0.39 for the binodal curves obtained with PEG 4000, 6000, and 10 000.

Table 5. 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			
molec. wt PEG	mass fraction		mass fraction		density	refractive index	mass fraction		density	refractive index
	w_1	w_3	w_1	w_3	kg·m^{-3}		w_1	w_3	kg·m^3	
2000	0.3590	0.1194	0.2735	0.2835	1241.3	1.4090	0.4032	0.0314	1332.0	1.3845
2000	0.3566	0.1504	0.2670	0.3104	1241.9	1.4145	0.4351	0.0145	1347.7	1.3869
2000	0.3541	0.1813	0.2567	0.3506	1242.4	1.4170	0.4523	0.0073	1363.3	1.3872
2000	0.3566	0.1905	0.2563	0.3603	1245.4	1.4221	0.4675	0.0066	1385.1	1.3896
2000	0.3591	0.1997	0.2551	0.3727	1246.1	1.4226	0.4781	0.0000	1385.5	1.3905
6000	0.3153	0.1359	0.2418	0.2815	1218.0	1.4053	0.3893	0.0038	1297.5	1.3776
6000	0.3284	0.1663	0.2326	0.3306	1223.9	1.4138	0.4168	0.0007	1328.0	1.3815
6000	0.3403	0.1959	0.2301	0.3859	1232.0	1.4209	0.4528	0.0004	1360.1	1.3863
6000	0.3543	0.2221	0.2305	0.4288	1237.4	1.4262	0.4811	0.0000	1385.9	1.3902
10000	0.3001	0.1200	0.2371	0.2507	1214.4	1.3968	0.3579	0.0042	1274.7	1.3751
10000	0.3106	0.1599	0.2266	0.3173	1220.3	1.4073	0.3951	0.0011	1307.8	1.3791
10000	0.3229	0.1794	0.2235	0.3563	1225.4	1.4137	0.4272	0.0000	1322.2	1.3821
10000	0.3356	0.2094	0.2242	0.4108	1233.9	1.4208	0.4599	0.0000	1360.8	1.3872
10000	0.3495	0.2218	0.2259	0.4251	1238.1	1.4258	0.4801	0.0000	1388.6	1.3899

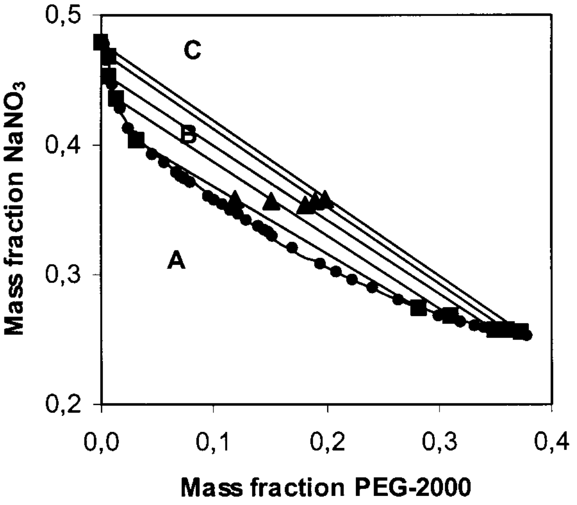

Figure 2. Phase diagram of $NaNO_3$ + PEG-2000 + H_2O at 298.15 K: (A) one liquid phase; (B) two liquid phases; (C) two liquid and one solid phases; ●, binodal; ■, PEG and $NaNO_3$ compositions of the system; ▲, overall system composition.

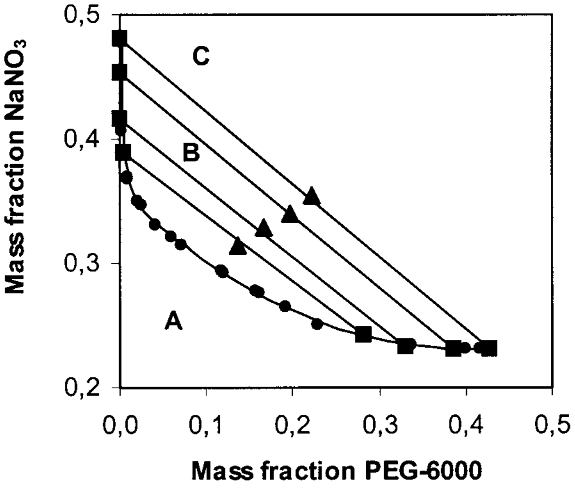

Figure 3. Phase diagram of $NaNO_3$ + PEG-6000 + H_2O at 298.15 K: (A) one liquid phase; (B) two liquid phases; (C) two liquid and one solid phases; ●, binodal; ■, PEG and $NaNO_3$ compositions of the system; ▲, overall system composition.

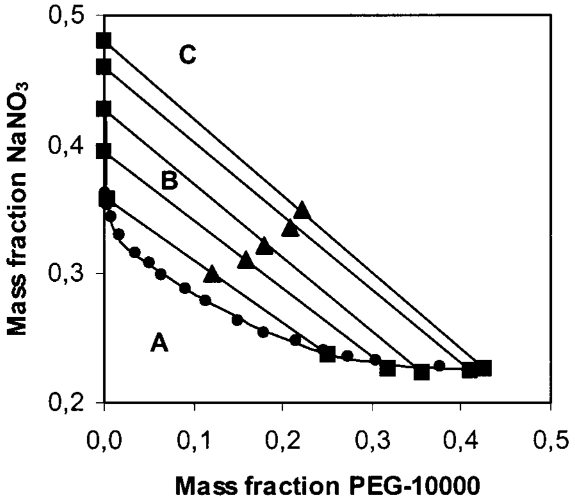

Figure 4. Phase diagram of $NaNO_3$ + PEG-10000 + H_2O at 298.15 K: (A) one liquid phase; (B) two liquid phases; (C) two liquid and one solid phases; ●, binodal; ■, PEG and $NaNO_3$ compositions of the system; ▲, overall system composition.

Tie Lines. Table 5 shows the compositions of the liquid–liquid equilibrium obtained at 298.15 K with PEG 2000, 6000, and 10 000. This table also includes values for density and refractive index for the solutions in equilibrium.

The tie lines were determined by connecting each corresponding set of total, top phase, and bottom phase compositions. A mass balance was obtained for each component by comparing its' initial mass with the amounts in the bottom and top phases according to the composition of the phase equilibrium. The mass of each phase was determined by the measurement of volume and density. The relative error in the mass balance was <3%.

In the systems studied, the density of the top phase varied between (1214 and 1246) kg·m^{-3} and that of the bottom phase between (1274 and 1388) kg·m.$^{-3}$ The difference in density between the phases increased with the length of the tie lines. The refractive index for the top phase varied between 1.3968 and 1.4262 nD and that for the bottom phase between 1.3751 and 1.3902 nD.

Figures 2–4 show the equilibrium diagrams of the phases for the three systems studied. In these figures, zone A contains a single, unsaturated liquid phase. Zone B includes two immiscible liquid phases. The bottom phase is rich in $NaNO_3$ and poor in PEG. The top phase is rich in PEG and also contains an appreciable quantity of nitrate. Zone B occupies a small portion of the complete phase diagram and increases with an increase in the molecular weight of the PEG, by means of a displacement of the binodal curve toward the origin. In the three-phase region C, the system is saturated with salt, and the composition of each liquid phase is constant.

Table 6. Values of the Parameters of Eq 2

PEG	n	k	R^2
2000	1.39	1.4784	0.9675
4000	1.51	1.3071	0.9970
6000	1.72	1.1566	0.9968
10000	1.58	1.1445	0.9866

At the working temperature of 298.15 K, sodium nitrate is highly soluble in water (47.8% $NaNO_3$). Figures 2−4 show that an addition of PEG decreased this solubility and that a concentration of PEG as low as 0.02% produced immiscible liquid phases. However, the drowning-out effect was small in this system because the concentration of the salt never decreased below 22.5% even at high PEG concentrations.

Tie lines for each system were fitted using the Othmer−Tobias equation (eq 2). In this, w_{1b} represents the mass fraction of $NaNO_3$ in the bottom phase, w_{3t} represents the mass fraction of PEG in the top phase, and k and n are equation parameters.

$$\frac{1 - w_{3t}}{w_{3t}} = k\left[\frac{1 - w_{1b}}{w_{1b}}\right]^n \tag{2}$$

A linear dependence between $\ln((1 - w_{3t})/w_{3t})$ and $\ln((1 - w_{1b})/w_{1b})$ indicates adequate consistency of the results. Table 6 lists the parameters for eq 2 and the coefficient of linear regression R^2. Equations 1 and 2 provide a mathematical model useful for analysis of the equilibrium data of the ATPS studied. These analyses can be made using values of w_{3b} and calculating w_{1b}, w_{3t}, and w_{1t} from eqs 1, 2, and 1, respectively.

In contrast to what occurs in some ATPS's formed by PEG and other inorganic salts such as $MgSO_4$, Na_2CO_3, and so forth, nitrate becomes distributed in important concentrations in both aqueous phases. Thus, the system demonstrates a small salting-out effect. The partition coefficient of $NaNO_3$, defined as the ratio of concentrations of nitrate between top and bottom phases (w_{1t}/w_{1b}), varies between 0.5 and 0.7 depending on the molecular weight of the PEG, indicating that this ATPS may not be useful for crystallization. It may, however, be of use in partitioning iodine and other compounds. Regarding the latter, preliminary tests carried out with molecular iodine have shown that I_2 concentrates in the top phase of the ATPS formed by $NaNO_3 + PEG + H_2O$. Minor partitioning was observed with the I^- ion, whose partition coefficient in the ATPS formed by 16.8% PEG and 34.1% $NaNO_3$ at 298.15 K varied between 1.14 (PEG-2000) and 2.38 (PEG-10000). This coefficient could be increased 600% in an acid environment, indicating the potential for use of the ATPS's studied. In these experiments iodine was analyzed using γ spectroscopy using the isotope I^{131}.

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