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Phase Equilibrium and Partition of Iodide in an Aqueous Biphasic System Formed by $(NH_4)_2SO_4$ + PEG + H_2O at 25 °C

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The partitioning of iodide was studied in an aqueous biphasic system (ABS) comprised of ammonium sulfate, polyethylene glycol (PEG), and water at 25 °C. The average molecular weights of PEG were (2078, 3819, and 9887) $g\cdot mol^{-1}$. In a prior determination, data for the liquid−liquid equilibrium of this system were obtained and correlated with the nonrandom, two-liquid (NRTL) thermodynamic model. Data on the partition coefficients and percentage extraction of iodide were obtained , which were correlated as a function of the concentration gradient of the PEG between the phases and the average molecular weight of the PEG. The fit equation obtained had a mean deviation of 0.0171 and a mean error of 1.89 %.

Introduction

The extraction and recovery of ions from aqueous solutions has traditionally been done using extraction with organic solvents. In recent years, aqueous biphasic systems (ABS) have come into use for the same purpose, especially those formed of polyethylene glycol (PEG), water, and an inorganic salt. One of the main advantages of these systems is that the partition occurs between two aqueous nonmiscible phases which is beneficial to the environment.[1]

Polyethylene glycol is a nonpolluting, noninflammable, durable solvent, which is available commercially in large quantities at relatively low cost, making it attractive for use in extractive processes.

Aqueous biphasic systems are formed by using water-soluble polymers. The formation of an ABS can be achieved by using two different polymers in water or even an inorganic salt and a polymer in water.[2] The latter alternative is employed in the present study, in which ammonium sulfate is concentrated in the lower aqueous phase and PEG in the upper aqueous phase.

ABSs have typically been used in separations of proteins, blood cells, amino acids, and other biomaterials, particularly with the use of PEG-4000 and inorganic salts or dextran.[3,4] In recent years, ABSs have been used for the separation of metallic ions, generally using PEG-2000.[5,6] This has also been used in the recovery of nanoparticles,[7] in sulfurated mineral extraction processes, and in extraction crystallization of inorganic salts.[8]

The PEG + $(NH_4)_2SO_4$ + H_2O aqueous biphasic system has been applied (a) to the extraction of some metallic ions[9−12] such as Na^+, Cs^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2}, (b) in the extraction of ions by addition of a complexing anion, (c) in the extraction of neutral aromatic and aliphatic ions using PEGs having different molecular weights,[13] and (d) in the partition of proteins.[14]

Data for the liquid−liquid equilibrium of the PEG + $(NH_4)_2SO_4$ + H_2O aqueous biphasic system with PEG molecular weights of (300, 600, 1125, 3400, 6000, 9700, and 20 000) $g\cdot mol^{-1}$ are reported by Zalavsky.[15] In general, the compositions of these liquid−liquid equilibria of this ABS vary widely with the molecular weight of PEG, such that it has become necessary to determine these compositions PEG used. This is true, especially if it is considered that PEG is formed by a group of polymer molecules whose molecular masses are distributed around a mean value which makes necessary their characterization by GPC (gel permeation chromatography) to determine the mean molecular weight and distribution of molecular weights present.

The present article reports on the determination of liquid−liquid equilibrium compositions for this system, using mean molecular weights of PEG of (2078, 3819, and 9887) $g\cdot mol^{-1}$. Densities, refractive indexes, and iodide partition coefficients are reported.

Experimental Section

Materials. Reagents for these measurements included ammonium sulfate (Merck > 99.9 %), predried in an oven at 120 °C for 24 h, and synthesis grade polyethylene glycol (Merck) having nominal molecular weights of (2000, 4000, and 10 000) $g\cdot mol^{-1}$. The PEG was dried in an oven at 50 °C for one week. The GPC analysis showed the actual molecular weights of the PEG to be (2078, 3819, and 9887) $g\cdot mol^{-1}$, respectively. Further data on this analysis are presented in Table 1.

Water as solvent for all the solutions was distilled and deionized and had a mean conductivity of 0.054 $\mu S\cdot cm^{-1}$. Sodium iodide for iodide extraction tests was obtained from Merck (> 99.9 %). The concentration of sodium iodide in the ABS was 0.2 % by mass, which was in the range of industrial interest for extraction of iodide from nitrate deposits.

Experimental Procedures. Data for liquid−liquid equilibrium of the ABS under study were obtained using routine procedures described by Graber et al.[16] The binodal curve was constructed using a turbidimetric method in which small additions (ca. 0.0020−0.0050 g) of $(NH_4)_2SO_4$ or PEG are made to a stirred solution of one phase until detection of a change in turbidity which is the characteristic point indicating the formation of a second liquid phase. The points from the isothermal binodal curve are at 25 ± 0.1 °C.

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Table 1. Results of Gel Permeation Chromatography of Polyethylene glycol

M_N nominal molecular weight (g·mol^{-1})	M_W average molecular weight (g·mol^{-1})	N_M average number of molecular weights	$P = M_W/N_M$ polydispersity (g·mol^{-1})
2000	2078	1997	1.0408
4000	3819	3737	1.0220
10000	9887	9038	1.0939

Table 2. Binodal Curve Data of the $(NH_4)_2SO_4$ + PEG-2000 + H_2O System at 25 °C: Mass Fractions of $(NH_4)_2SO_4$ = (w_1) and of PEG-2000 = (w_2)

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
0.7618	63.6097	3.2217	37.5338	9.5940	14.4388
0.7779	61.9903	3.6569	36.7915	9.9986	13.3978
0.9198	59.5977	3.7872	35.2663	10.4125	12.4047
1.0493	57.7365	4.1029	34.0294	10.8279	11.4594
1.1909	56.1649	4.3311	33.0218	11.3415	10.6881
1.3025	54.7284	4.4856	31.8887	11.9527	9.3854
1.4508	52.9398	4.9587	30.8375	12.9310	7.8272
1.5983	52.2592	5.2826	29.7646	13.4035	6.6448
1.7839	49.9587	5.8886	27.4938	13.9255	5.6357
2.2696	45.9248	6.3581	25.0254	14.4374	4.6728
2.2861	44.6330	6.9411	23.3151	15.3220	3.5314
2.3954	43.3779	7.4349	21.6431	15.7982	2.8596
2.5747	42.0530	7.9859	20.0687	16.7878	1.9482
2.7839	40.8033	8.1611	18.7718	17.7386	1.3198
2.9311	39.7013	8.4862	17.6606		
3.0785	38.5618	9.2378	15.4796		

Table 3. Binodal Curve Data of the $(NH_4)_2SO_4$ + PEG-4000 + H_2O System at 25 °C: Mass Fractions of $(NH_4)_2SO_4$ = (w_1) and PEG-4000 = (w_2)

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
0.6302	63.9130	4.1176	31.9317	8.2921	15.1468
0.7743	61.2937	4.4882	30.5577	8.6101	14.2542
0.9686	58.7580	4.7463	29.1519	8.9494	13.2645
1.1286	56.3504	5.0593	28.2589	9.2843	12.1410
1.3454	55.0624	5.2498	27.0341	9.6795	11.0122
1.4237	52.2120	5.4802	25.6241	10.1350	9.8187
1.5683	50.1468	5.6736	24.6678	10.6003	8.5973
1.8155	49.4139	5.8684	23.6876	11.0271	7.4559
2.0546	46.8304	6.0530	22.8277	11.5155	6.2648
2.3374	44.5778	6.2161	22.0987	12.0767	4.9478
2.5801	42.8099	6.4234	21.3425	12.5983	3.8904
2.8428	40.9824	6.7586	20.0799	13.3452	2.2614
3.1134	38.7811	6.9610	19.3349	14.0894	1.4451
3.3409	37.1902	7.1780	18.5772	14.7460	0.8548
3.5465	35.6841	7.4151	17.7771	16.6219	0.2594
3.7352	34.2873	7.6759	16.8920	17.2849	0.1927
3.9585	33.0279	8.0096	16.0014	17.8739	0.1196

Table 4. Binodal Curve Data of the $(NH_4)_2SO_4$ + PEG-10000 + H_2O System at 25 °C: Mass Fractions of $(NH_4)_2SO_4$ = (w_1) and PEG-10000 = (w_2)

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
2.0162	48.8793	4.3866	27.7847	8.1224	10.2627
2.1426	45.5325	4.5053	26.4039	8.4394	9.2233
2.3568	43.2718	4.6857	25.2535	8.7837	8.2629
2.4896	41.4440	4.9209	24.1151	9.1418	7.2147
2.7916	39.2958	4.9280	24.0058	9.5232	6.0289
2.9770	37.8206	5.1596	23.0342	9.9391	4.7666
3.1464	36.3179	5.3865	21.9114	10.3681	3.6131
3.2776	35.0299	5.6410	20.6637	10.8158	2.5864
3.4379	33.7116	5.9235	19.2532	11.2728	1.7377
3.6245	32.6781	6.2291	17.7255	11.7338	1.1208
3.7809	31.5819	6.6470	15.8828	12.3636	0.6434
3.9560	30.5021	7.0214	14.4699	12.9721	0.5298
4.0903	29.4708	7.4484	12.9280		
4.1901	28.6170	7.8312	11.2103		

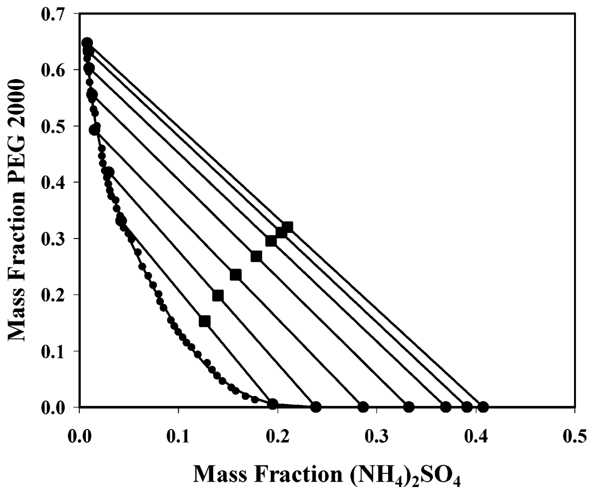

Figure 1. Experimental equilibrium for the system $(NH_4)_2SO_4$ + PEG 2000 + H_2O at 25 °C: ●, experimental binodal curve; □, experimental tie lines.

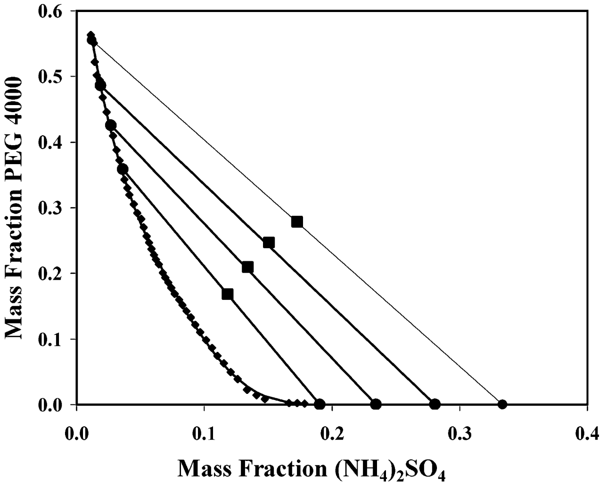

Figure 2. Experimental equilibrium for the system $(NH_4)_2SO_4$ + PEG 4000 + H_2O at 25 °C: ●, experimental binodal curve; □, experimental tie lines.

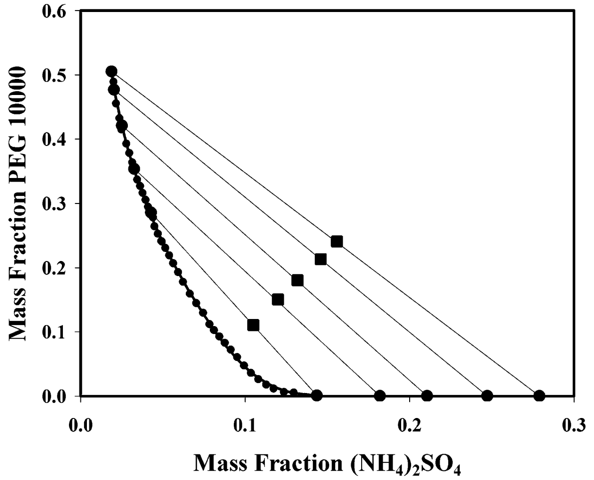

Figure 3. Experimental equilibrium for the system $(NH_4)_2SO_4$ + PEG 10000 + H_2O at 25 °C: ●, experimental binodal curve; □, experimental tie lines.

The union lines are determined from the overall composition of the solutions in the biphasic region, which were stirred for 24 h in a rotator isothermic bath at 25 ± 0.1 °C. The separation of the phases was achieved using isothermic sedimentation at 25 °C, for 24 h; longer times had no effect on the degree of separation of the phases. Triplicate samples were obtained from each phase and analyzed for the sulfate ion using a standard

Table 5. Tie Lines for the $(NH_4)_2SO_4$ + PEG-2000 + H_2O System at 25 °C: w_1 and w_2 Mass Fractions of $(NH_4)_2SO_4$ and PEG-2000, Density (ρ), and Refractive Index (n_D)

initial composition		top phase				bottom phase			
$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D
12.6473	15.3002	4.1960	33.1041	1081.12	1.3873	19.4965	0.5591	1109.85	1.3641
14.0000	19.8050	2.9259	40.9089	1088.32	1.3983	23.8827	0.0331	1134.56	1.3700
15.7751	23.5248	1.5843	50.3254	1095.60	1.4077	28.6420	0.0007	1160.74	1.3766
17.8749	26.8251	1.2719	55.5786	1102.50	1.4170	33.2677	0.0004	1188.21	1.3837
19.3742	29.5237	0.9989	60.2943	1107.32	1.4230	36.9904	0.0000	1209.23	1.3891
20.4246	30.9995	0.9321	63.1555	1109.97	1.4268	39.1082	0.0000	1222.11	1.3923
20.9999	31.9998	0.8031	64.9420	1111.46	1.4294	40.7487	0.0000	1229.94	1.3942

Table 6. Tie Lines for the $(NH_4)_2SO_4$ + PEG-4000 + H_2O System at 25 °C: w_1 and w_2 Mass Fractions of $(NH_4)_2SO_4$ and PEG-4000, Density (ρ), and Refractive Index (n_D)

initial composition		top phase				bottom phase			
$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D
11.8464	16.8315	3.6383	35.8730	1080.98	1.3908	19.0691	0.0219	1107.88	1.3627
13.4338	20.8880	2.6828	42.5035	1089.09	1.4007	23.4697	0.0000	1134.56	1.3691
15.0969	24.6491	1.8749	48.6024	1096.56	1.4096	28.0700	0.0000	1132.48	1.3759
17.2691	27.7883	1.1989	55.4938	1103.61	1.4183	33.3571	0.0000	1186.29	1.3831

Table 7. Tie Lines for the $(NH_4)_2SO_4$ + PEG-10000 + H_2O System at 25 °C: w_1 and w_2 Mass Fractions of $(NH_4)_2SO_4$ and PEG-10000, Density (ρ), and Refractive Index (n_D)

initial composition		top phase				bottom phase			
$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D	$100\,w_1$	$100\,w_2$	ρ (kg·m^{-3})	n_D
10.4998	10.9998	4.2817	28.5352	1071.13	1.3795	14.3661	0.0565	1081.33	1.3558
11.9999	14.9999	3.2658	35.3756	1080.31	1.3906	18.2119	0.0000	1102.36	1.3611
13.1998	17.9998	2.5103	42.0667	1086.71	1.3982	21.0725	0.0000	1120.07	1.3658
14.5999	21.2998	2.0347	47.6623	1093.32	1.4055	24.7356	0.0000	1141.20	1.3715
15.5997	23.9995	1.8885	50.5436	1097.89	1.4109	27.8964	0.0000	1158.39	1.3760

gravimetric method, with errors less than 1 %. The density and refractive index were measured for each solution in equilibrium.

Density was measured using a model DE50 Mettler Toledo oscillation densimeter, having a precision of $\pm\, 5 \cdot 10^{-5}$ g·mL^{-1}. The refractive index was measured using a model RE40 Mettler Toledo refractometer having a precision of $\pm\, 1 \cdot 10^{-4}$ n_D units. Both properties were measured at 25 ± 0.1 °C.

The concentration of PEG in the solutions was measured using mass balance and experimental values of the density and volume of the phases.

The partition of iodide was carried out in duplicate, each experiment using 30 g of the ABS solution with known overall composition, with all of the liquid−liquid equilibrium points having been previously determined. Each ABS solution received 0.0625 g of NaI, vigorously mixed using a vortex mixer at 25 °C for 3 min. Previous tests carried out over periods greater than 3 min had no effect on the results. Once phase equilibrium was reached, the phases were separated at 25 °C in a model 32R Universal temperature-controlled centrifuge at 3500 rpm, after which the volume and density of each phase were measured, taking 2 mL samples of each phase for iodide determination. Analysis of iodide content was done using an oxide-reduction method having an error of no greater than 3 %.

Results and Discussion

Tables 2 to 4 show points on the binodal curve obtained for the PEG + $(NH_4)_2SO_4$ + H_2O aqueous binary solution at 25 °C, PEG-2000 (M_w = 2078 g·mol^{-1}), PEG-4000 (M_w = 3819 g·mol^{-1}), and PEG-10000 (M_w = 9887 g·mol^{-1}). These represent immersion points; i.e., they define the boundary between one region of the two liquid phases and that of a single-phase region. It can be seen from these tables that by increasing the molecular weight of the PEG the concentrations of PEG and ammonium sulfate decrease; that is, the water content of the system increases. This is due to the fact that the larger-sized PEG molecules have a greater quantity of folds and cavities which trap water molecules, thus increasing the hydration layer on these molecules.

Tables 5 to 7 present data on the liquid−liquid equilibrium for the PEG + $(NH_4)_2SO_4$ + H_2O aqueous binary system at 25 °C, PEG-2000, PEG-4000, and PEG-10000, together with densities and refractive indexes of the equilibrium phases. It is observed that the density of the upper phase varies between 1071.13 and 1111.46 kg·m^{-3} and that the lower phase varies between 1081.33 and 1229.94 kg·m^{-3}. The refractive index for the upper phase was between 1.3795 and 1.4292 and for the lower phase was between 1.3558 and 1.3942. Both physical properties increase with an increase in the concentration of ammonium sulfate and PEG in each equilibrium phase.

Figures 1 to 3 show the experimental points of the binodal curve, by the compositions of the aqueous solutions in equilibrium. Continuous lines represent the equilibrium curve, which were determined by union of the overall concentration points with those experimentally determined for the upper and lower phases. It can be seen, by comparison of these figures, that the biphasic region increases with the molecular weight of the PEG and in general requires a lower concentration of ammonium sulfate to obtain separation of the phases in the ABS under study. This situation becomes infeasible for PEG percentages above 40 % in mass because the binodal curves tend to join here for the three molecular weights of PEG in this study.

Thermodynamic Model. The nonrandom, two-liquid (NRTL) thermodynamic model is based on the concept of local composition and is applicable to partially soluble systems. Chen et al.[17] extended the original NRTL model to electrolyte systems which contained small molecules. A modified NTRL was proposed by Wu et al.[18] for aqueous biphasic systems containing polymers and a salt. Sé and Aznar[19] successfully applied the original NRTL model to describe the liquid−liquid equilibrium of the

ABS PEG 4000 + water + potassium phosphate at four temperatures.

The NRTL is a theoretical model in which each coefficient has a physical meaning. Nevertheless, using this original version with dissociated molecules, a semiempirical model is being used, as the interaction coefficients do not account for actual physical interactions among dissolved species. In spite of this new treatment, the performance of the model in achieving a correlation of equilibrium points was significantly better than alternative formulations such as the Othmer−Tobias equation. The NRTL model typically uses mole fractions, but when using polymer systems, conversion to mass fractions is more convenient because polymers have high molecular weights producing extremely small mole fractions. The NRTL model using mass fractions, as employed by various authors (Sé and Aznar,[19] Batista et al.,[20] Litomen et al.,[21] Graber et al.[22]), was used in the present study. For a multicomponent mixture, the NRTL equation, expressed in terms of mass fraction is[19]

$$\ln(\gamma_i) = \frac{\sum_j \frac{\tau_{ji}G_{ji}w_j}{M_j}}{\sum_j \frac{G_{ji}w_j}{M_j}} + \sum_j \left[\frac{w_j G_{ij}}{M_j \sum_k \frac{G_{kj}w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_k \frac{\tau_{kj}G_{kj}w_k}{M_k}}{\sum_k \frac{G_{kj}w_k}{M_k}} \right) \right] \tag{1}$$

where

$$\tau_{ij} = \frac{A_{ij}}{T} \tag{2}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{3}$$

where M = molecular weight of the components; w = mass fraction of the components; T = absolute temperature of the system; A_{ij} and A_{ji} are the characteristic interaction energies $i-j$; and α_{ij} are the parameters related to the nonrandom behavior of the mixture.

The experimental data obtained on the liquid−liquid equilibrium were used to estimate the molecular interaction and the nonrandom parameters of the mixture. These parameters were determined by minimizing the objective function, f_{obj}, defined by

$$f_{\text{obj}} = \sum_{i=1}^{3}\sum_{k=1}^{n}(w_{ik}^{\text{T,exptl}} - w_{ik}^{\text{T,mod}})^2 + \sum_{i=1}^{3}\sum_{k=1}^{n}(w_{ik}^{\text{B,exptl}} - w_{ik}^{\text{B,mod}})^2 \tag{4}$$

Here $w_{ik}^{\text{T,exptl}}$ and $w_{ik}^{\text{T,mod}}$ represent the experimental and NRTL calculated mass fractions of component i in the top phase; $w_{ik}^{\text{B,exptl}}$ and $w_{ik}^{\text{B,mod}}$ represent the experimental and NRTL calculated mass fractions of component i in the bottom phase; and n represents the total number of data or interconnecting lines modeled. Optimization was achieved using the Generalized Reduced Gradient algorithm in which the original problem is reduced to another problem not having restrictions and which is solved using a system of equations which are basic for some variables and nonbasic for the remaining variables. A quasi-Newton method was used as a criterion for determining the direction of the search, which instead of using a Hessian matrix uses an approximation of this matrix.

The comparison between the experimental data and those obtained from the model was made using the mean deviation, given by

$$\Delta w = 100 \sqrt{\frac{\sum_{i=1}^{3}\sum_{k=1}^{n}[(w_{ik}^{\text{T,exptl}} - w_{ik}^{\text{T,mod}})^2 + (w_{ik}^{\text{B,exptl}} - w_{ik}^{\text{B,mod}})^2]}{n}} \tag{5}$$

Table 8 shows the values of the parameters A_{ij}, A_{ji}, and α_{ij}. The values of the parameter interaction energy (A_{ij}) do not show variation with the molecular weight of the PEG. In contrast, the specific parameters of the mixture (α_{ij}) for PEG + H_2O and PEG + $(NH_4)_2SO_4$ increase with an increase in the molecular weight of the PEG which is attributable to the randomness or disorder which originates in the PEG molecules by folding back upon themselves with an increase in the disorder of hydration or of interaction with their structure. Figures 4 to 6 show the experimental tie lines with continuous lines, and dotted lines represent the obtained data from the model for each phase. The mean error between the experimental data and the equilibrium compositions obtained with the model was 3.6 %, whereby it is concluded that the NTRL model is a tool useful for satisfactory correlation of data on the liquid−liquid equilibrium of the ABS formed by PEG, $(NH_4)_2SO_4$, and H_2O.

Iodide Partition. The partition of iodide was studied on the basis of percentage extraction of iodide and the partition coefficient (ratio between the iodide concentrations in the upper and lower phases), as a function of the difference in PEG concentrations between the phases, which acts as a driving force in the extraction process.

Table 9 shows the values of the partition coefficients and the percentages of extraction of iodide for the different equilibrium compositions of the ABS previously shown in Tables 5 to 7. Mass fractions of PEG and ammonium sulfate are also given, as are volumes of each equilibrium phase, the length of equilibrium lines L, and mass of iodide in each phase. It can be seen from this table that the extraction percentage for iodide is from 84 to 95 % and that both the partition coefficient and the percent extraction of iodide do not follow a linear tendency with different concentrations of PEG or ammonium sulfate between the phases nor with the lengths of the ABS equilibrium lines. A slight increase in the extraction of iodide was, however, noted with an increase in the molecular weight of PEG.

Starting with the Flory−Huggins theory and measuring the difference in electrostatic potential between phases, King et al.[23] found that in some ABSs formed by PEG and potassium sulfate and phosphate the partition coefficient of some proteins varied in a semilogarithmic form with the length of the tie line. Following the same concept, with the objective of obtaining an equation for correlating the data in the partition of iodide, we considered that the difference in electrostatic potential between the phases was dependent on the differences in concentration of ammonium sulfate between the phases.

Given that the system under study shows a direct relation between the concentration of ammonium sulfate and PEG (Table 9) and the length of the tie lines, we employed the difference in the concentration of PEG as the forcing function for the extraction of iodide using the following semilogarithmic equation

$$\ln\left(\frac{E}{\Delta w_{\text{PEG}}}\right) = a - b\cdot\Delta w_{\text{PEG}} \tag{6}$$

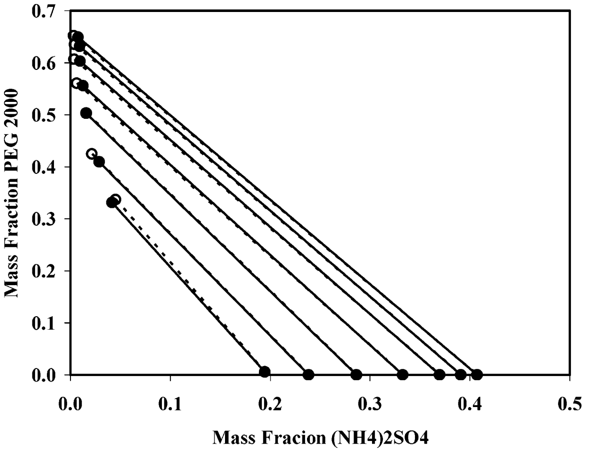

Figure 4. Experimental and calculated liquid−liquid equilibrium for the system $(NH_4)_2SO_4$ + PEG 2000 + H_2O at 25 °C: ●, experimental compositions; —, experimental tie lines; ○, NRTL compositions; ----, NRTL tie lines.

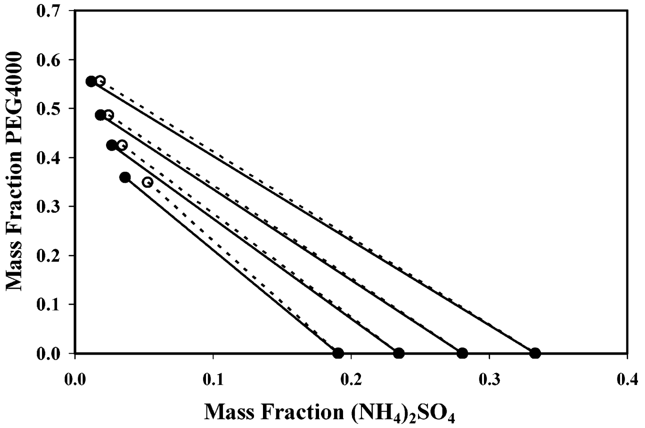

Figure 5. Experimental and calculated liquid−liquid equilibrium for the system $(NH_4)_2SO_4$ + PEG 4000 + H_2O at 25 °C: ●, experimental compositions; —, experimental tie lines; ○, NRTL compositions; ----, NRTL tie lines.

Table 8. NRTL Parameters of the Model for the ABS: $(NH_4)_2SO_4$ + PEG-10000 + H_2O

nominal weight of PEG	interaction	A_{ij} (K)	A_{ji} (K)	α_{ij}
	PEG 2000 + H_2O	−1647.84	623.40	0.2068
2000	PEG 2000 + $(NH_4)_2SO_4$	−573.95	−1236.78	0.4533
	$(NH_4)_2SO_4$ + H_2O	−866.03	−8.14	0.2000
	PEG 4000 + H_2O	−1647.84	623.40	0.3153
4000	PEG 4000 + $(NH_4)_2SO_4$	−573.95	−1236.78	0.5388
	$(NH_4)_2SO_4$ + H_2O	−866.03	−8.14	0.2000
	PEG 10000 + H_2O	−1647.84	623.40	0.4307
10000	PEG 10000 + $(NH_4)_2SO_4$	−573.95	−1236.78	0.5694
	$(NH_4)_2SO_4$ + H_2O	−866.03	−8.14	0.2000

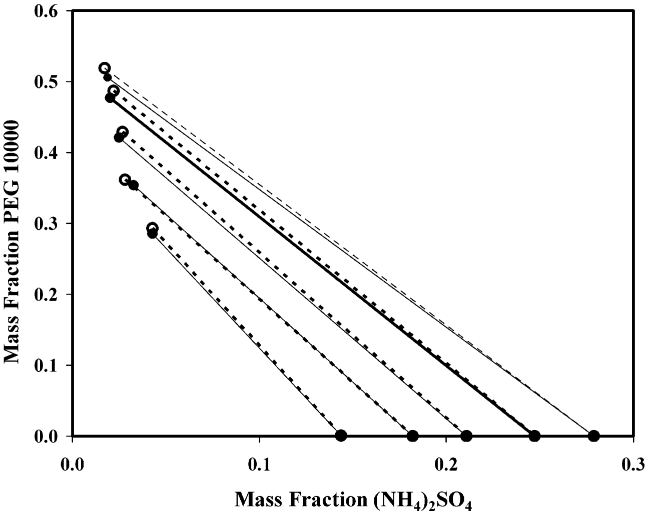

Figure 6. Experimental and calculated liquid−liquid equilibrium for the system $(NH_4)_2SO_4$ + PEG 10000 + H_2O at 25 °C: ●, experimental compositions; —, experimental tie lines; ○, NRTL compositions; ----, NRTL tie lines.

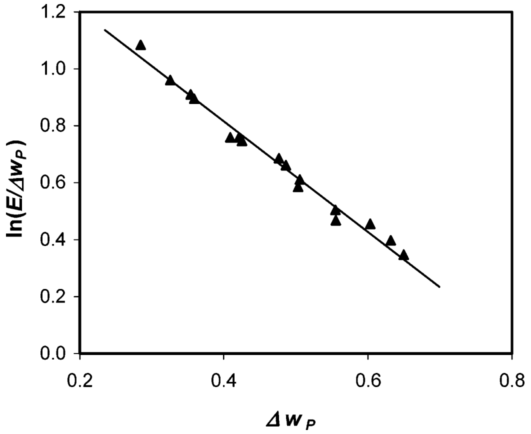

Figure 7. Equation 6 for the extractions of iodide in the three ABS with PEG-2000, PEG-4000, and PEG-10000.

Table 9. Partition of Iodide in the ABS: $(NH_4)_2SO_4$ + PEG-10000 + H_2O^a

exp.	M_{peg}	L	ΔW_{peg}	D	% E
1	2078	0.7611	0.3255	11.37	91.91
2	2078	0.7380	0.4088	15.57	93.96
3	2078	0.7022	0.5033	19.66	95.16
4	2078	0.6413	0.5558	7.93	88.80
5	2078	0.5714	0.6029	9.37	90.36
6	2078	0.4593	0.6316	6.89	87.32
7	2078	0.3596	0.6494	5.71	85.10
8	3819	0.6414	0.3585	11.41	91.94
9	3819	0.5521	0.4250	16.31	94.22
10	3819	0.4731	0.4860	8.69	89.68
11	3819	0.3903	0.5549	7.12	87.68
12	9887	0.5684	0.2848	13.68	93.19
13	9887	0.5279	0.3538	17.49	94.59
14	9887	0.4598	0.4207	8.94	89.94
15	9887	0.3840	0.4766	7.23	87.86
16	9887	0.3021	0.5054	5.34	84.23

[a] M_{peg}= average molecular weight of PEG; L = tie line length; D = partition coefficient; % E = extraction percent.

in which E is the fraction of iodide extracted (% extraction/100); Δw_{PEG} represents the difference in mass fraction of the PEG between the liquid phases in equilibrium; and a and b are parameters to be determined.

Figure 7 shows eq 6, and a linear relation can be seen for the extraction of iodide in the three ABSs with PEG-2000, PEG-4000, and PEG-10000. The correlation coefficient is 0.9959. By calculating the value of the parameters in eq 6 for each ABS, the dependence on the molecular weight of the PEG is obtained. Table 10 lists the values of the parameters in eq 6. Here it can be seen that the two parameters (a and b) increase with an increase in the average molecular weight of the PEG (M_{PEG}) in the ABS. Assuming that these parameters vary in a linear manner with the average molecular weight of the three PEGs,

Table 10. Parameter Values Obtained from Equation 6

M_{peg}	a	b
2078	1.5174	1.8076
3819	1.5824	1.9303
9887	1.6612	2.0844

a final equation is obtained for the extraction of iodide in the ABS formed by PEG + $(NH_4)_2SO_4$ + H_2O at 25 °C.

$$\ln\left(\frac{E}{\Delta w_{\mathrm{PEG}}}\right) = 1.4976 + 1.7001\cdot 10^{-5} M_{\mathrm{PEG}} - (1.768 + 3.2829\cdot 10^{-5} M_{\mathrm{PEG}})\Delta w_{\mathrm{PEG}} \quad (7)$$

Equation 7 correlates the experimental data on the extraction of iodide with a mean deviation of the extraction fraction E of ± 0.0171 and a maximum deviation of 0.0398, with a mean percentage error of 1.89 %.

Conclusions

Precise data are presented on the liquid−liquid equilibrium of the aqueous biphasic system formed by ammonium sulfate, polyethylene glycol (PEG), and water at 25 °C for molecular weights of PEG of (2078, 3819, and 9887) $g\cdot mol^{-1}$.

It was found that an increase in molecular weight of PEG produces an increase in the biphasic region by a displacement of the binodal curve toward the origin, which is attributable to the increase in the hydration layer of the PEG molecules.

The density and refractive index of the equilibrium solutions in the ABS increase with an increase in the concentration of PEG and ammonium sulfate. The density varied between 1.07 and 1.12 $g\cdot cm^{-3}$, and the refractive index varied from 1.36 to 1.42.

The NRTL thermodynamic model showed satisfactory correlation of the mass fractions of the components of the ABS. In general, the square root overall difference between the calculated and experimental values associated with the fit of the mass fractions did not exceed 0.05 %. The specific parameters of the mixture (α_{ij}) of the NRTL model were the most sensitive to changes in the molecular weight of the polymer and to the interaction between PEG and the other components of the system.

The partition of iodide in the ABS formed by ammonium sulfate, polyethylene glycol (PEG), and water at 25 °C showed high yields of extraction (between 84 and 95 %) within the conditions studied. The influence of the molecular weight of the PEG on this extraction was very low.

An equation was obtained which correlated well the experimental data on iodide extraction and mean deviation of the extraction fraction E of ± 0.0171, with a mean error of 1.89%.

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