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Phase Behavior of Aqueous Two-Phase PEG + NaOH System at Different Temperatures

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Phase diagrams and liquid−liquid equilibrium (LLE) data of the poly(ethylene glycol) (PEG) (M_n: 6000) + sodium hydroxide system have been determined at (298.15, 308.15, and 318.15) K. As temperature is increased, this aqueous two-phase system exhibits a phase inversion. Specifically, the PEG-rich phase—which at low temperatures is the less dense top phase—becomes the lower phase at elevated temperatures. The effect depends on the concentration of both PEG and sodium hydroxide. At the temperatures 308.15 K and 318.15 K, the system shows inversion; and at these temperatures inversion occurs at lower concentrations of either phase-forming constituent. Also, it was found that as temperature is increased the inversion-phase region expands. The osmotic virial equation with temperature-dependent parameters was used to correlate the phase behavior of this system.

Introduction

Aqueous two-phase systems are useful for separating materials of biological origin. These liquid−liquid systems are formed by adding either two structurally different hydrofilic polymers or one polymer and one inorganic salt to water.[1] Previous studies on aqueous two-phase systems containing a polymer and a salt show that the location of the binodal and of the tie lines depends on the system's temperature. In general, the slope and length of the tie lines increase with increasing system's temperature.[2−4] It has been shown that the effect of temperature on binodals for PEG + salt systems depends on the type of salt.[2] In some PEG + salt systems, such as PEG + $(NH_4)_2SO_4$, an increase in temperature causes the expansion of the two-phase area over the whole concentration range,[4] while for some PEG + salt systems, such as PEG + NaH_2PO_4 and poly(vinylpyrrolidone) + NaH_2PO_4, the crossing of binodals has been observed with varying temperature.[2,5] This means that for the latter systems an increase in temperature causes an expansion of the one-phase area in the PEG-rich region, while for the salt-rich region expansion of the two-phase area has been observed with increasing temperature.[2,5]

Furthermore, for many PEG + salt systems studied so far, the PEG has been observed to enrich the upper, less dense phase, while the salt has been observed to enrich the lower phase. However, for aqueous PEG + ammonium sulfate systems two independent authors[6,7] have observed that the upper phase is rich in salt and the lower phase is rich in PEG. This phenomenon has been called phase inversion by these authors. Cohen[6] noted that at 333.15 K the lower phase of a PEG + ammonium sulfate system of particular concentration becomes PEG-enriched; but, only very limited studies have been performed. Additional studies of the phase behavior of aqueous PEG + ammonium sulfate systems have been conducted by Eiteman[7] to determine the conditions where the observed phase inversion occurs.

In recent years many research groups have focused on the measurement of new equilibrium data for aqueous polymer + salt systems.[2,8−11] However, phase equilibrium data for aqueous PEG + NaOH systems have not been reported. Ananthapadmanabhan et al.[12] reported the only binodal curve for this system. In this work, the detailed study of this system, which exhibits phase inversion behavior, was carried out. For the investigated system, in addition to the effect of temperature on binodals and tie lines, the effect of temperature and component concentration on the phase inversion behavior was studied.

Experimental Section

Materials. The poly(ethylene glycol) (6000) was obtained from Merck. The number average molecular mass of the polymer has been determined previously[2] to be 5886 $g \cdot mol^{-1}$. The sodium hydroxide with a minimum purity of 99% was obtained from Merck. The polymer and salt were used without further purification, and double distilled and deionized water was used.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[2,13,14] A glass vessel, volume 50 cm^3, was used to carry out the phase equilibrium determinations. The glass vessel was provided with an external jacket in which water at constant temperature was circulated using a thermostat. The temperature was controlled to within ±0.05 K. The binodal curves were determined by a titration method. A salt solution of known concentration was titrated with the polymer solution or vice versa, until the solution turned turbid. The composition of the mixture was determined by mass using an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with a precision of $\pm 1 \times 10^{-7}$ kg. The maximum uncertainty was found to be 0.002 in determining the mass fraction of both polymer and salt by the titration method used. For the determination of the tie lines, feed samples (about 20 cm^3) were prepared by mixing appropriate amounts of polymer, salt, and water in the vessel. The thermostat was set at a desired temperature, and the sample was stirred for 1 h. Then the mixture was

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Table 1. Binodal Data for PEG (1) + NaOH (2) + H_2O (3) Systems at (298.15, 308.15, and 318.15) K

298.15 K		308.15 K		318.15 K	
$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
42.39	1.74	39.20	1.75	44.09	1.33
38.73	1.92	37.38	1.83	42.75	1.38
36.07	2.12	35.99	1.91	41.70	1.42
33.52	2.29	34.77	1.98	40.68	1.47
31.33	2.46	28.08	2.45	39.53	1.54
32.49	2.36	24.85	2.71	38.43	1.58
26.25	2.95	22.04	2.98	36.39	1.73
24.41	3.16	19.42	3.24	35.56	1.76
22.46	3.36	17.06	3.49	33.80	1.90
21.11	3.50	15.17	3.73	30.80	2.09
19.90	3.63	13.52	3.94	27.72	2.29
18.85	3.74	12.13	4.12	24.49	2.54
17.75	3.88	10.96	4.28	22.08	2.72
16.75	4.00	9.89	4.43	19.76	2.94
15.77	4.12	9.00	4.54	17.65	3.13
14.68	4.26	8.21	4.66	15.73	3.33
13.65	4.40	7.49	4.75	14.20	3.51
12.69	4.53	6.90	4.84	12.75	3.66
11.77	4.65	6.39	4.91	11.54	3.81
10.86	4.77	5.95	4.98	10.47	3.93
10.05	4.88	5.64	5.05	9.58	4.03
9.33	5.00	5.33	5.09	8.81	4.12
8.69	5.09	4.80	5.20	7.08	4.31
5.82	5.58	4.25	5.29	6.35	4.40
4.79	5.75	3.82	5.36	4.19	4.67
3.75	5.96	3.25	5.46	2.19	5.00
2.70	6.19	2.38	5.64	1.56	5.14
1.79	6.46	1.73	5.78	1.25	5.35

allowed to settle for 24 h. After separation of the two phases, the concentrations of NaOH in the top and bottom phases were determined by titration with standard HCl solutions. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ±0.001. Following Cheluget et al.,[15] the concentration of PEG in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer (QUARTZ RS-232). The relation between the refractive index, n_D, and the mass fractions of polymer, w_1, and salt, w_2, is given by[15]

$$n_D = a_0 + a_1 w_1 + a_2 w_2 \qquad (1)$$

This equation has been used for phase analysis of the poly(propylene glycol) + NaCl + H_2O system by Cheluget et al.[15] We found that the same method of calibration plots and evaluation of parameters given by Cheluget et al.[15] can also be used for analysis of PEG + NaOH + water systems. The values of the coefficients a_0, a_1, and a_2 for the applied system were obtained as 1.3325, 0.141, and 0.2845, respectively. However, it was found that this equation is only valid for mass fractions of $w_1 \leq 0.1$ and $w_2 \leq 0.05$, for which linear calibration plots of the refractive index of the solution against polymer and salt concentration are obtained. Therefore, before refractive index measurements, it was necessary to dilute the samples to the above mass fraction range. The precision of the mass fraction of PEG achieved using eq 1 was better than 0.002.

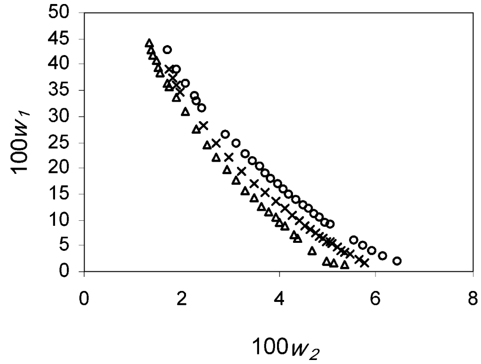

Figure 1. Binodal curves for the PEG_{6000} (1) + NaOH (2) + H_2O (3) system at different temperatures: ○, 298.15 K; ×, 308.15 K; △, 318.15 K.

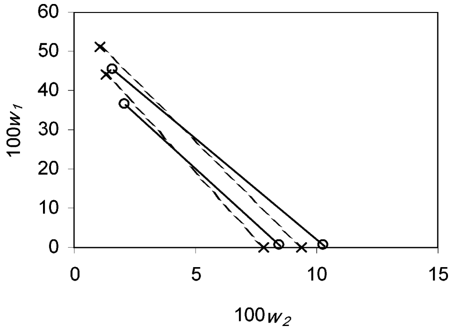

Figure 2. Effect of temperature on the equilibrium phase compositions for the PEG_{6000} (1) + NaOH (2) + H_2O (3) system: ○, 298.15 K; ×, 318.15 K; —, tie lines at 298.15 K; - - -, tie lines at 318.15 K. These tie lines were obtained by connecting the experimental equilibrium phase composition data.

Results and Discussion

Experimental Results. The equilibrium compositions of the aqueous two-phase systems PEG + NaOH determined at (298.15, 308.15, and 318.15) K are shown in Table 1, and the tie-line data are given in Table 2. In Table 2, the superscripts "top" and "bot" represent the top and bottom phases, respectively. The effect of temperature on the binodal curves is illustrated in Figure 1, which shows that increasing the temperature causes expansion of the two-phase region. As shown in Figure 2, the slope and length of the tie lines for aqueous PEG + NaOH systems increase with an increase in the temperature. Similar behavior was observed for aqueous PEG + Na_2HPO_4 and NaH_2PO_4 systems.[2]

Table 2. Experimental Phase Equilibrium Compositions for the PEG (1) + NaOH (2) + H_2O (3) Systems at (298.15, 308.15, and 318.15) K

298.15 K				308.15 K				318.15 K			
$100w^{top}$		$100w^{bot}$		$100w^{top}$		$100w^{bot}$		$100w^{top}$		$100w^{bot}$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
50.88	1.28	0.00	11.76	51.40	1.08	0.00	10.82	51.06	1.08	0.00	9.39
45.23	1.61	0.25	10.33	48.20	1.24	0.00	10.15	49.98	1.11	0.10	8.96
41.49	1.81	0.47	9.50	44.54	1.51	0.54	9.19	48.39	1.14	0.00	8.55
37.95	2.08	0.00	8.76	41.80	1.67	0.51	8.32	0.00	7.80	43.98	1.34
36.22	2.15	0.25	8.48	36.51	1.89	0.50	7.60	0.00	7.00	40.59	1.46
29.63	2.70	0.92	7.57	0.87	7.02	32.06	2.24	0.00	6.48	36.06	1.69
23.59	3.30	2.18	6.68	1.09	6.63	28.92	2.42	0.96	5.53	26.55	2.35
				2.20	6.04	24.51	2.82				

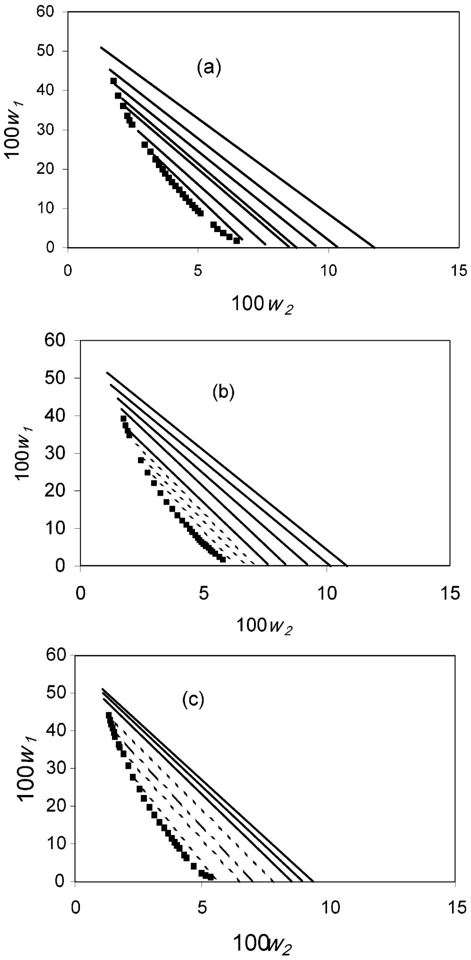

Figure 3. Phase behavior of the PEG$_{6000}$ (1) + NaOH (2) + H_2O (3) system: (a) 298.15 K; (b) 308.15 K; (c) 318.15 K; —, ordinary region tie lines; - - -, inversion region tie lines; ■, binodal.

Phase Inversion. For aqueous PEG + salt systems, the PEG has been observed to enrich the upper phase, while the salt has been observed to enrich the lower phase. For the aqueous PEG + NaOH system, we observe similar phase behavior at 289.15 K. However, close examination of the tie-line data given in Table 2 indicate that the aqueous PEG + NaOH system at (308.15 and 318.15) K exhibits phase inversion. This means that the PEG-enriched phase, which is the less dense upper phase at 298.15 K, becomes the lower phase at elevated temperatures. According to the data given in Table 2, the inversion takes place at different temperatures in phase systems of different PEG and/or salt concentration. As shown in Figure 3, inversion occurs at lower concentrations of either phase-forming constituents, and as temperature is increased, the inversion-phase region is expanded.

Correlation

To represent the LLE data for the investigated system showing phase inversion, an attempt was made to correlate the LLE data with several known models. The extended NRTL and Flory−Huggins models presented in our previous work[5] and the UNIQUAC model developed by Gao et al.[16] were unsuccessful. However, a fairly satisfactory result was obtained with the osmotic virial equation adopted by Edmond et al.[17]

Table 3. Interaction Parameters β_{ij} of the Osmotic Virial Equation and Correlation Performance for the PEG (1) + NaOH (2) + H_2O (3) Systems at (298.15, 308.15, and 318.15) K

T/K	β_{11}^0	β_{11}^1	β_{12}^0	β_{12}^1	β_{22}^0	β_{22}^1	dev[a]
298.15	−73.45	−54500	−22.78	2670	−7.32	1696	0.66
308.15							0.49
318.15							3.77

[a] Dev $= 1/(6N)\sum_{i=1}^{3}\sum_{l=1}^{N}[(w_{i,l,\mathrm{exp}}^{\mathrm{top}} - w_{i,l,\mathrm{cal}}^{\mathrm{top}})^2 + (w_{i,l,\mathrm{exp}}^{\mathrm{bot}} - w_{i,l,\mathrm{cal}}^{\mathrm{bot}})^2]$, where N is the number of tie lines.

In the osmotic virial equation adopted by Edmond et al.,[17] the chemical potentials of polymer (1) and salt (2) as a function of molality of polymer and salt, m_i, can be written as

$$\mu_1 = \mu_1^0 + RT(\ln m_1 + \beta_{11}m_1 + \beta_{12}m_2) \tag{2}$$

$$\mu_2 = \mu_2^0 + RT(\ln m_2 + \beta_{22}m_2 + \beta_{12}m_1) \tag{3}$$

where β_{ij} is a constant characterizing the interaction between a molecule of component i and a molecule of component j, and μ_i^0 is the standard-state chemical potential of component i. The standard state of components 1 and 2 is a hypothetical state of ideal solution at unit molality. Using the Gibbs−Duhem relation, the chemical potential for water (3) is then obtained as

$$\mu_3 = \mu_3^0 - RTV_3\rho\left(m_1 + m_2 + \frac{\beta_{11}}{2}m_1^2 + \frac{\beta_{22}}{2}m_2^2 + \beta_{12}m_1m_2\right) \tag{4}$$

In eq 4, the standard state of component 3 is pure water. In these relations, V_3 and ρ are the molar volume and density of water, respectively.

For the interaction parameters β_{ij}, a temperature-dependent function was assumed as follows:

$$\beta_{ij} = \beta_{ij}^0 + \frac{\beta_{ij}^1}{T} \tag{5}$$

The model parameters of the osmotic virial equation were estimated by minimizing the following objective function:

$$\mathrm{OF} = \sum_T\sum_p\sum_l\sum_i(w_{T,p,l,i}^{\mathrm{calc}} - w_{T,p,l,i}^{\mathrm{exp}})^2 \tag{6}$$

where $w_{T,p,l,i}$ is the weight percent of component i in phase p at temperature T for lth tie line. LLE data of Table 2 were correlated using eq 6 and the following relation

$$(\mu_i)^{\mathrm{top}} = (\mu_i)^{\mathrm{bot}} \tag{7}$$

The fitting parameters of the osmotic virial equation along with the corresponding deviations are given in Table 3. On the basis of obtained deviations, we conclude that the correlated results are in fairly good agreement with experiment.

Conclusions

Liquid−liquid equilibrium data for the system PEG$_{6000}$ + NaOH + H_2O at (298.15, 308.15, and 318.15) K were measured. As temperature is increased, this aqueous two-phase system exhibits a phase inversion. Also, the inversion-phase region is expanded by increasing temperature from 308.15 K to 318.15 K. It was also found that the slope and length of tie lines for this system increase with an increase in the temperature. Further, a thermodynamic model, based on the osmotic virial equation, was applied to correlate the phase behavior of the investigated system; the correlated results are in fairly good agreement with experiment.

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