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Phase Diagrams of Some Aliphatic Alcohols + Ammonium Dihydrogen Phosphate or Diammonium Hydrogen Phosphate + Water

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Phase diagrams for 1-propanol + ammonium dihydrogen phosphate or diammonium hydrogen phosphate + water and 2-propanol + diammonium hydrogen phosphate + water systems were measured at 25 °C. For these systems binodal and tie line data were determined at 25 °C. Binodal curves were described using a three-parameter equation. Tie lines were satisfactorily described using the Othmer−Tobias and Bancroft equations.

Introduction

Aqueous two-phase systems formed by mixtures of two polymers, or of one polymer and one inorganic salt, are important for separation and purification of enzymes and other biologically active proteins.[1,2] The salts used are usually phosphates, sulfates and citrates. In recent years many research groups have focused on the measurement of new phase equilibrium data for aqueous polymer−salt systems.[3−6] Recently, we have reported LLE data for aqueous poly (ethylene glycol) (PEG) + ammonium dihydrogen phosphate and PEG + diammonium hydrogen phosphate systems.[7]

For large-scale processes, methods for recycling chemicals have been developed.[8,9] Greve and Kula[9] have described the use of some two-phase systems composed of lower aliphatic alcohols + water + inorganic salts for the extraction of salt from the primary bottom phase of protein extraction processes in PEG + salt systems.

In this respect, we have studied phase diagrams of 1-propanol + ammonium hydrogen phosphate or diammonium hydrogen phosphate + water, and 2-propanol + diammonium hydrogen phosphate + water systems. The binodal curve together with a single tie line of the 2-propanol + diammonium hydrogen phosphate + water system at 25 °C has been determined.[10] As far as we know, there is no report on the phase diagrams of 1-propanol + diammonium hydrogen phosphate + water and 1-propanol + ammonium dihydrogen phosphate + water systems.

In the following we describe the phase diagrams of these systems in some detail. These results can be used to develop thermodynamic models of aqueous two-phase systems.[11−13]

Experimental Section

Materials. The alcohols and the salts were obtained from Merck (1-propanol GR, min 99.5%; 2-propanol GR, min 99.7%; ammonium dihydrogen phosphate GR, min 99%; diammonium hydrogen phosphate GR, min 99%). All chemicals were used without further purification. From experimental refractive index measurements at 25 °C, we obtained the values 1.3836 and 1.3753 for 1-propanol and 2-propanol, respectively. These values compare well with the literature values,[14] 1.38370 for 1-propanol and 1.3752 for 2-propanol. The salts were dried in an oven at about 110 °C for 24 h before use. Double distilled and deionized water was used.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[15−17] 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 °C. The binodal curves were determined by a titration method. A salt solution of known concentration was titrated with the alcohol or vice versa, until the solution turned turbid. The composition of the mixture was determined by mass using an analytical balance with a precision of $\pm 1 \times 10^{-7}$ kg. For the determination of the tie lines, feed samples (about 20 cm^3) were prepared by mixing appropriate amounts of alcohol, 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 allowed to settle for 24 h. After separation of the two phases, the concentration of $(NH_4)_2HPO_4$ in the top and bottom phases were determined by titration method using HCl as a titrant. The concentration of $NH_4H_2PO_4$ was determined by the formaldehyde method as described by Gao et al.[18] for the analysis of $(NH_4)_2SO_4$ in PEG + $(NH_4)_2SO_4$ + H_2O system. The analysis of samples with given composition of alcohol and $NH_4H_2PO_4$ did not interfere with the determination. The precision of the mass fraction of $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ achieved using the aforementioned methods was better than 0.2%. The concentration of alcohols in both phases was determined by refractive index measurements performed at 29 °C using a refractometer (QUARTZ RS-232, Ceti, Belgium) with a precision of ± 0.0001. For dilute aqueous solutions containing an alcohol and a salt, the relation between the refractive index, n_D, and the mass fractions of alcohol, w_1, and salt, w_2 is given by

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

This equation has been used for phase analysis of the poly

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Table 1. Coefficients of Equation 1

system	a_0	a_1	a_2
1-propanol + $(NH_4)_2HPO_4$ + H_2O	1.3321	0.0897	0.0019
2-propanol + $(NH_4)_2HPO_4$ + H_2O	1.3321	0.0841	0.0019
1-propanol + $NH_4H_2PO_4$ + H_2O	1.3321	0.0885	0.0013

Table 2. Binodal Data as Mass Fraction for the Alcohols (1) + Salts (2) + H_2O (3) at 25 °C

$100w_1$	$100w_2$	$100w_1$	$100w_2$
1-Propanol + $(NH_4)_2HPO_4$ + H_2O			
4.80	24.03	38.82	8.19
5.89	21.33	41.32	7.28
8.38	19.51	43.20	6.68
11.48	17.85	45.89	5.91
15.77	16.20	47.50	5.31
19.38	14.85	48.54	4.96
22.82	13.61	48.89	4.81
26.16	12.50	50.52	4.34
29.67	11.30	53.19	3.53
33.04	10.20	55.00	3.00
36.29	9.13	60.80	1.30
2-Propanol + $(NH_4)_2HPO_4$ + H_2O			
2.28	34.99	17.46	12.85
3.25	32.16	21.11	9.85
4.34	29.44	24.94	7.54
4.85	27.85	27.95	5.95
6.97	24.27	29.98	5.13
9.78	20.49	32.14	4.41
12.31	17.73	35.03	3.99
14.90	15.17	39.67	2.71
1-Propanol + $NH_4H_2PO_4$ + H_2O			
11.68	15.20	35.16	5.56
12.61	13.74	36.59	5.25
14.37	12.35	38.04	4.93
16.31	11.02	39.41	4.62
19.27	9.76	40.77	4.33
22.08	8.77	42.04	4.05
24.74	8.03	44.13	3.68
26.75	7.54	46.51	3.21
28.54	7.09	49.24	2.75
31.80	6.35	52.23	2.32
33.60	5.95		

(propylene glycol) + NaCl + H_2O system by Cheluget et al.[19] We found that the same method of calibration plots and evaluation of parameters given by Cheluget et al.[19] can also be used for analysis of alcohol + salt + water systems. The values of coefficients a_0, a_1 and a_2 for the systems studied are listed in Table 1. However, it should be noted that this equation is only valid for dilute solutions of alcohol and salt for which linear calibration plot of refractive index of solution against alcohol and salt are obtained. The precision of the mass fraction of alcohol achieved using eq 1 was better than 0.25%.

Results and Discussion

For aqueous systems containing 1-propanol + diammonium hydrogen phosphate, 1-propanol + ammonium dihydrogen phosphate and 2-propanol + diammonium hydrogen phosphate the binodal and tie line data at 25 °C are shown in Tables 2 and 3, respectively. The binodal curve for 2-propanol + diammonium hydrogen phosphate + water system is given in Figure 1 and compared with the literature. There is fair agreement between the literature and our experimental data.

The binodal curves were fitted using the following nonlinear expression of Mistry et al.[20]

$$\ln w_1 = a + b w_2^{0.5} + c w_2^{3} \qquad (2)$$

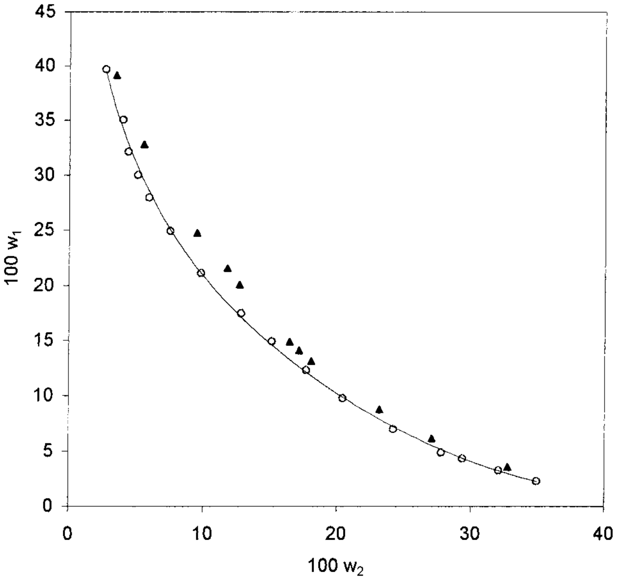

Figure 1. Comparison of binodal curves for the 2-propanol (1) + $(NH_4)_2HPO_4$ (2) + H_2O (3) system at 25 °C: (○) present work; (—) calculated from eq 2; (▲) Ginnings et al.[10]

Table 3. Tie Line Data as Mass Fraction for the Alcohols (1) + Salts (2) + H_2O (3) at 25 °C

alcohol-rich phase		water-rich phase	
$100w_1$	$100w_2$	$100w_1$	$100w_2$
1-Propanol + $(NH_4)_2HPO_4$ + H_2O			
67.99	0.50	4.70	23.81
66.45	0.57	4.93	23.14
64.78	0.74	5.28	22.34
63.66	0.84	5.87	21.54
2-Propanol + $(NH_4)_2HPO_4$ + H_2O			
40.25	3.22	2.68	33.77
34.82	3.90	4.17	29.71
33.75	4.09	4.70	28.39
33.17	4.27	5.14	27.48
27.59	6.21	7.86	23.09
26.86	6.56	8.62	22.09
24.73	7.74	9.70	20.55
1-Propanol + $NH_4H_2PO_4$ + H_2O			
59.97	2.05	13.49	13.03
58.80	2.06	13.91	12.72
58.02	2.07	14.75	12.14
57.71	2.08	15.33	11.66
57.13	2.10	15.94	11.19
55.54	2.11	17.50	10.46
54.16	2.12	19.51	9.63

Table 4. Values of Parameters of Eq 2

system	a	b	c	sd[a]
1-propanol + $(NH_4)_2HPO_4$ + H_2O	−0.236	−2.120	−176.271	0.65
2-propanol + $(NH_4)_2HPO_4$ + H_2O	−0.270	−4.020	−26.892	0.39
1-propanol + $NH_4H_2PO_4$ + H_2O	0.137	−4.987	−156.799	0.98

[a] sd = $((100w_1^{cal} - 100w_1^{exp})^2/N)^{0.5}$ where N is the number of binodal data.

Recently, this empirical equation has been used for the correlation of binodal curve of PEG + Na_2CO_3 + H_2O system by Taboada et al.[21] The coefficients of eq 2 along with the corresponding standard deviations for the investigated systems are given in Table 4. On the basis of obtained standard deviations, we conclude that the eq 2 can be satisfactorily used to correlate the binodal curves of the investigated systems. As an example, the calculated binodal curve for 2-propanol + diammonium hydrogen phosphate + water system is given in Figure 1.

The correlation equations[22] given by Othmer−Tobias (eq 3) and Bancroft (eq 4) have been used to correlate the tie

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

system	*k*	*n*	*R*	*k*₁	*r*	*R*	sd₁	sd₂
1-propanol + $(NH_4)_2HPO_4$ + H_2O	0.086	1.473	0.992	4.813	0.619	0.994	0.18	0.08
2-propanol + $(NH_4)_2HPO_4$ + H_2O	0.753	1.029	0.997	1.359	0.991	0.998	0.25	0.19
1-propanol + $NH_4H_2PO_4$ + H_2O	0.197	0.651	0.990	9.441	1.158	0.988	0.31	0.13

[a] $\mathrm{sd}_j = \left\{\frac{1}{2L}\sum_{i=1}^{L}[(100w^{\mathrm{t}}_{i,j,\mathrm{cal}} - 100w^{\mathrm{t}}_{i,j,\mathrm{exp}})^2 + (100w^{\mathrm{b}}_{i,j,\mathrm{cal}} - 100w^{\mathrm{b}}_{i,j,\mathrm{exp}})^2]\right\}^{0.5}$, where *L* is the number of tie lines, and *j* = 1 and 2. sd₁ and sd₂ represent the mass percent standard deviations for alcohol and salt, respectively.

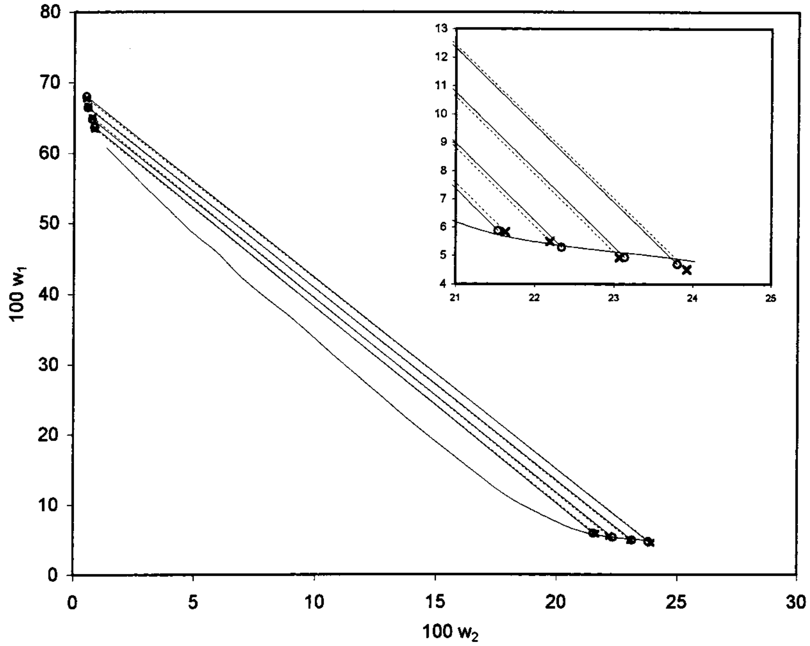

Figure 2. Tie lines for the 1-propanol (1) + $(NH_4)_2HPO_4$ (2) + H_2O (3) system at 25 °C: (—○—) experimental; (--×--) calculated from eqs 3 and 4; (—) binodal.

line compositions.

$$\left(\frac{1 - w_1^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right) = k\left(\frac{1 - w_2^{\mathrm{b}}}{w_2^{\mathrm{b}}}\right)^n \qquad (3)$$

$$\left(\frac{w_3^{\mathrm{b}}}{w_2^{\mathrm{b}}}\right) = k_1\left(\frac{w_3^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right)^r \qquad (4)$$

where *k*, *n*, k_1, and *r* represent fit parameters. Superscript "t" and "b" stand for alcohol-rich phase and water-rich phase, respectively. The values of the parameters are given in Table 5. Recently, eqs 3 and 4 have been used for the assessment and correlation of tie line compositions of PEG + $NaNO_3$ + H_2O and PEG + Na_2CO_3 + H_2O systems.[3,20]

A linear dependency of the plots $\log((1 - w_1^{\mathrm{t}})/w_1^{\mathrm{t}})$ against $\log((1 - w_2^{\mathrm{b}})/w_2^{\mathrm{b}})$ and $\log(w_3^{\mathrm{b}}/w_2^{\mathrm{b}})$ against $\log(w_3^{\mathrm{t}})/w_1^{\mathrm{t}})$ indicated an acceptable consistency of the results. The corresponding correlation coefficient values, *R*, are also given in Table 5. Furthermore, on the basis of standard deviations, sd₁ and sd₂, given in Table 5, we conclude that the eqs 3 and 4 can be satisfactorily used to correlate the tie line data of the investigated systems. To show the reliability of the model, comparison between the experimental and correlated tie lines are shown in Figure 2, as an example, for 1-propanol + diammonium hydrogen phosphate + water system.

The locations of plait point for these systems were estimated by extrapolation from the midpoints of the different tie lines, and the values are listed in Table 6.

Table 6. Plait Points at 25 °C

system	100w_1	100w_2
1-propanol + $(NH_4)_2HPO_4$ + H_2O	10.25	33.12
2-propanol + $(NH_4)_2HPO_4$ + H_2O	13.53	16.78
1-propanol + $NH_4H_2PO_4$ + H_2O	5.21	36.83

Conclusions

For 1-propanol + diammonium hydrogen phosphate or ammonium dihydrogen phosphate + water, and 2-propanol + diammonium hydrogen phosphate + water systems binodal and tie line data have been determined at 25 °C. It was found that tie line data for these systems can be satisfactorily described by Othmer−Tobias and Bancroft equations.

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