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Liquid−Liquid Equilibria for 1-Propanol (or 2-Propanol)−Water Systems Containing Potassium Fluoride

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Liquid−liquid equilibrium (LLE) data for 1-propanol (or 2-propanol)−water−potassium fluoride systems were measured at various temperatures. The salting out efficiency of potassium fluoride was also investigated. It was shown that potassium fluoride has a greater salting out effect on 1-proppanol than on 2-propanol. These data are correlated with the modified Setschnow model, and the results correspond rather well.

Introduction

The salting out effect in the systems aliphatic alcohol (especially propyl and butyl alcohol)−water is of industrial interest. There are lots of LLE data for butanol−water−salt systems, that is, for the 1-butanol−water−NaCl system at 293.2 K, 298.2 K, 303.2 K, and 313.2 K (Santis et al., 1976a,b), 1-butanol−water−KCl and 1-butanol−water−KBr systems at 298.2 K (Li et al., 1995), and tertiary butanol−water−potassium fluoride system at 293.2 K, 298.2 K, 308.2 K, and 318.2 K (Lu et al., 2000). But the LLE data for the propanol−water−salt systems are few. For instance, LLE data for the propanol−water−sodium chloride system at 298.2 K were measured by Santis et al. (1976a). However, the LLE data for the propanol−water−potassium fluoride system have not been reported so far. In this work, LLE data for 1-propanol−water (or 2-propanol)−potassium fluoride at 288.2 K, 298.2 K, 308.2 K, and 318.2 K were measured by means of an equilibrium still proposed, and some related models were used to correlate these data.

Experimental Section

Chemicals and Analysis. Analytical grade 1-propanol (or 2-propanol) was purified by fine distillation. Their purities were checked by gas chromatography, and no impurity peaks were found. Analytical grade (purity > 99.5%) potassium fluoride and sodium chloride were dried at 393.2 K and 413.2 K, respectively, at least for 2−3 h before use. The deionized water was prepared by redistilling water in the presence of $KMnO_4$, and its electrical conductivity was less than 1.2×10^{-6} s·cm^{-1}.

The salt content was measured by carefully evaporating the samples to dryness. The microanalysis of water was carried out by the Karl Fischer titration method. The concentrations of water and 1-propanol (or 2-propanol) were determined by gas chromatography.

The specifications of the gas chromatograph are as follows: detector, thermal conductivity detector; carrier gas, H_2; column length, 3.5 m; column packing, GDX-401; column temperature, 453.2 K; vaporization temperature, 453.2 K; TC current, 143 mA; flow rate of carrier gas, 40 mL/min.

Table 1. LLE Data (wt %) for the 1-Propanol (1)−Water (2)−KF (3) System at Various Temperatures

	aqueous phase			organic phase		
T/K	1-propanol	water	KF	1-propanol	water	KF
288.2	0.64	70.16	29.30	90.13	9.48	0.386
	0.99	73.96	25.05	88.54	11.14	0.317
	3.77	78.65	18.08	83.53	16.05	0.423
	5.64	79.67	14.69	80.20	19.56	0.247
	7.60	80.23	12.17	76.77	22.58	0.642
	13.66	76.33	10.01	69.28	29.06	1.663
298.2	1.10	64.03	34.87	92.98	6.88	0.140
	1.30	68.44	30.26	90.49	9.20	0.313
	2.33	71.85	25.82	87.82	11.57	0.611
	3.07	74.37	22.56	83.98	15.08	0.946
	4.18	76.33	19.49	80.17	18.45	1.384
	5.77	77.24	16.99	75.34	23.15	1.509
308.2	0.30	59.94	39.76	94.70	5.18	0.248
	0.79	66.87	32.34	91.80	7.99	0.215
	1.41	72.81	25.78	88.34	11.23	0.424
	2.28	74.21	23.51	86.82	12.69	0.493
	3.37	75.56	21.07	85.50	14.34	0.161
	3.58	77.75	18.68	83.95	16.04	0.018
	6.19	79.35	14.46	75.97	23.53	0.494
	10.10	77.84	12.06	68.06	30.07	1.872
318.2	0.80	60.02	39.18	92.76	7.13	0.115
	1.09	65.88	33.03	90.38	9.40	0.221
	1.04	69.58	29.38	87.87	11.68	0.446
	1.38	72.86	25.76	85.05	14.27	0.676
	2.37	76.31	21.32	82.13	17.05	0.823
	4.39	78.34	17.27	76.58	24.16	1.261
	9.12	77.33	13.55	68.62	29.17	2.200

Apparatus and Procedure. A glass equilibrium still connected to a thermostat was made to measure the LLE data. A magnetic stirrer provided sufficient agitation within the apparatus. The temperature was controlled and maintained with an accuracy of within ±0.1 K.

After thermal equilibrium was reached, agitation was continued for 20−30 min to ensure complete phase equilibrium. Then, the solution was left to settle for 2−3 h for phase separation. The concentration of each component was analyzed by the above-mentioned methods. Each of the measurements was carried out with several repetitions. The standard deviation of the experiments was about 0.05 wt %.

Results and Discussion

LLE data for 1-propanol (1)−water (2)−potassium fluoride (3) and 2-propanol (1)−water (2)−potassium fluoride

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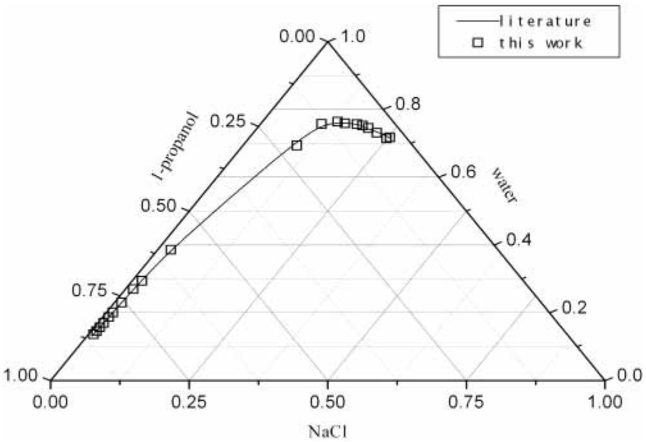

Figure 1. Comparison of LLE data for systems of 1-propanol−water−sodium chloride at 298.2 K.

Table 2. LLE Data (wt %) for the 2-Propanol (1)−Water (2)−KF (3) System at Various Temperatures

	aqueous phase			organic phase		
T/K	2-propanol	water	KF	2-propanol	water	KF
288.2	1.84	61.48	36.68	88.31	11.52	0.166
	2.10	64.13	33.77	86.36	13.38	0.254
	2.82	65.65	31.53	85.31	14.40	0.293
	4.06	68.39	27.55	81.79	17.66	0.548
	5.10	72.36	22.54	77.02	22.39	0.791
	7.09	73.37	19.54	73.09	26.90	1.010
	11.83	74.37	13.79	65.10	33.00	1.900
	18.06	72.05	9.89	58.70	38.14	3.160
298.2	1.45	57.15	41.40	91.00	8.73	0.275
	1.67	60.33	38.00	89.81	9.91	0.276
	2.85	63.9	33.25	86.77	12.71	0.519
	3.00	65.62	31.38	85.31	14.08	0.607
	4.80	69.20	26.00	81.79	17.45	0.760
	7.26	72.74	20.00	73.27	25.24	1.497
	11.32	75.7	12.98	64.03	33.79	2.176
308.2	1.32	63.40	35.28	89.01	10.67	0.321
	2.50	65.92	31.58	86.05	13.06	0.886
	2.77	68.38	28.85	83.94	15.13	0.932
	4.58	71.35	24.07	79.65	19.10	1.249
	6.23	74.37	19.40	74.57	24.08	1.351
	9.11	75.90	14.99	67.81	30.07	2.119
	14.47	73.37	12.16	63.63	34.04	2.332
318.2	1.02	56.33	42.65	91.74	8.18	0.080
	1.30	59.05	39.65	90.73	9.15	0.120
	1.53	63.41	35.06	88.91	10.90	0.191
	2.03	65.87	32.10	86.41	13.13	0.457
	2.07	69.33	28.60	83.36	16.00	0.636
	2.63	72.74	24.63	77.31	21.29	1.412
	6.94	74.82	18.24	71.48	26.82	1.703
	10.12	75.74	14.14	65.48	31.72	2.802

(3) systems at various temperatures were listed in Tables 1 and 2. To verify the accuracy of the LLE equilibrium still, the experimental procedure, and the analysis methods, LLE data for the 1-propanol−water−sodium chloride system at 298.2 K were measured. They were found to be in good agreement with the data of Santis et al. (1976a), as shown in Figure 1.

In recent years, models of phase equilibrium in mixed-solvent electrolytes have become of considerable interest. These models included the electrolyte NRTL model (Chen et al., 1982) and its modified form (Mock et al., 1986; Austgen et al., 1989, 1991; Liu et al., 1996), the extended Setschnow equation (Tang et al., 1995), and the electrolyte UNIQUAC model (Sander et al., 1986) and so forth.

The extended Setschnow equation was given by Tang et al. (1995) to express the salt effect for partially miscible systems or completely miscible systems. But the results were not very satisfactory for this work. Therefore, the modified Setschnow equation was put forward by the author.

The expressions of the modified Setschnow equation are as follows:

$$\ln(\gamma_1/\gamma_{10}) = k_{13}x_3 - x_{a1}$$

$$\ln(\gamma_2/\gamma_{20}) = k_{23}x_3 - x_{a2}$$

where x_{a1} is an additional parameter for an organic compound and x_{a2} is an additional parameter for water. Other characters have the same meaning as with the extended Setschnow equation (Tang et al., 1995).

The salt effect constant (k_{13}, k_{23}) depends on the solvent-electrolyte pair and on the temperature. *k* which is positive accounts for the salting-out effect, and the larger the value of *k*, the greater the salting-out efficiency; *k* which is negative characterizes the salting-in effect. But the two additional parameters (x_{a1}, x_{a2}) are independent of the temperature. The temperature dependency relations of the salt effect constant can be expressed by the following equations for a small range of temperature (Santis et al., 1976b).

$$k_{13} = a_{13} + b_{13}/T; \quad k_{23} = a_{23} + b_{23}/T$$

The data correlation was carried out in this paper using a data regression system based on the maximum likelihood principle. The minimization objective function of the modified Setschnow model was

$$F = \sum_{j=1}^{n}\sum_{i=1}^{2}(\alpha_{\mathrm{O}(j,i)} - \alpha_{\mathrm{W}(j,i)})^2$$

where α is the activity of a component; *i* is the number of components; *j* is the serial number of the experimental points; *n* is the total number of points; and O and W denote the organic phases and aqueous phases, respectively.

Results of data correlation for the LLE data of these systems by the modified Setschnow model are given in Table 3.

From Table 3, it is observed that the salt effect constant for the electrolyte 1-propanol is larger than the value for the electrolyte 2-propanol at the same temperature.

The accuracy of the calculated results was represented by the average deviation in liquid mole fractions Δ*x*

$$\Delta x = \sqrt{\frac{\sum_{j=1}^{n}\sum_{i=1}^{2}(x_{j,i}^{(\mathrm{exp})} - x_{j,i}^{(\mathrm{cal})})^2}{2n}}$$

Table 3. Parameters in Modified Setschnow Model

system	a_{13}	a_{23}	b_{13}	b_{23}	x_{a1}	x_{a2}
1-propanol (1)−water (2)−KF (3)	19.726	−3.082	−35.932	42.098	0.340	−0.102
2-propanol (1)−water (2)−KF (3)	15.653	−3.204	−40.094	40.842	0.492	−0.201

Table 4. Correlation Results of the LLE Data Using the Modified Setschnow Model

system	T/K	Δx/%
1-$C_3H_7OH-H_2O-KF$	288.2	0.91
1-$C_3H_7OH-H_2O-KF$	298.2	1.07
1-$C_3H_7OH-H_2O-KF$	308.2	1.79
1-$C_3H_7OH-H_2O-KF$	318.2	1.26
2-$C_3H_7OH-H_2O-KF$	288.2	1.21
2-$C_3H_7OH-H_2O-KF$	298.2	0.97
2-$C_3H_7OH-H_2O-KF$	308.2	0.87
2-$C_3H_7OH-H_2O-KF$	318.2	1.89

The results of Δx were listed in Table 4.

Conclusions

LLE data were measured for the ternary systems 1-propanol (2-propanol)−water−potassium fluoride at 288.2 K, 298.2 K, 308.2 K, and 318.2 K using the LLE equilibrium still. It was shown that potassium fluoride had a greater salting out effect on 1-propanol than on 2-propanol. In this paper, the modified Setschnow equation was put forward to correlate the LLE data for the ternary systems containing salt, and the results corresponded rather well.

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