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Liquid−Liquid Phase Equilibria of (1-Propanol or 2-Propanol + Water) Containing Dipotassium Hydrogen Phosphate

Hirotake Katayama* and Kei Kitagawa

Department of Materials Chemistry, Hosei University, Koganei, Tokyo, Japan 184-8584

Liquid−liquid equilibria (LLE) for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water + K_2HPO_4 were measured at temperatures of (288.15, 298.15, and 308.15) K. The binodal curves of the systems were fitted to a nonlinear equation relating the mass fraction of 1- or 2-propanol to that of K_2HPO_4, and the tie lines were successfully correlated with the Othmer−Tobias and Bancroft equations. LLE results were predicted using a pair of the binodal and Bancroft equations and one of the binodal and Othmer−Tobias equations. Both predictions showed close agreement with experimental values, and the average root-mean-square deviations of the values predicted from the former pair were 0.28 % and 0.27 % for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water + K_2HPO_4, respectively.

Introduction

An aqueous solution of 1-propanol, 2-propanol, or acetone easily separates into two liquid phases upon addition of an ordinary salt such as sodium chloride. But an aqueous solution of ethanol cannot be phase-separated by addition of sodium chloride or even by addition of ammonium chloride, ammonium sulfate, sodium sulfate, or sodium acetate.

In previous work,[1] we found that an aqueous ethanol solution could be separated into two liquid phases upon addition of either dipotassium hydrogen phosphate (K_2HPO_4) or sodium dihydrogen phosphate (NaH_2PO_4) and that an aqueous methanol solution was also separable into two phases upon addition of K_2HPO_4 but not NaH_2PO_4. Addition of KH_2PO_4 or Na_2HPO_4 to an aqueous ethanol or methanol solution did not produce phase separation. Liquid−liquid equilibria (LLE) for the systems ethanol + water + K_2HPO_4, ethanol + water + NaH_2PO_4, and methanol + water + K_2HPO_4 were measured at temperatures of (288.15, 298.15, and 308.15) K, and their phase diagrams were determined.

In the present work, in order to know more general phase diagrams for the systems (aliphatic alcohol + water + K_2HPO_4), LLE for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water + K_2HPO_4 were measured at temperatures of (288.15, 298.15, and 308.15) K. To our knowledge the LLE for these systems has not been investigated.

The knowledge gained from measurement of these phase equilibria will be of application to the separation and purification of biomolecules, such as proteins and amino acids, and of pharmaceutical intermediates by liquid−liquid extraction.

Experimental Section

Materials. 2-Propanol and K_2HPO_4 were purchased from Wako Pure Chemical Industries Ltd. The minimum purities were stated as (99.9 and 99.0) mass %, respectively. 1-Propanol, which was stated to have a minimum purity of 99.5 mass %, was purchased from Tokyo Kasei Industry Co. Ltd. These three reagents were used without further purification. *N*-Methyl formamide (MFA), used as a gas chromatography standard, was supplied from Tokyo Kasei Industry Co. Ltd. (stated to have a minimum purity of 99.0 mass %) and was used after dehydration with 0.3 nm molecular sieves. Distilled water was used throughout.

Apparatus and Procedure. The experimental method and apparatus used were similar to those described by Katayama and co-workers.[1−3] The temperature was measured using an F25 platinum resistance thermometer (supplied by Automatic System Laboratories, Ltd.) with a stated accuracy of ± 0.03 K and a stated resolution of 0.001 K. The temperature fluctuations of the water bath were within ± 0.08 K. Each 50 cm^3 aliquot of the mixtures {(1-propanol or 2-propanol) + water + phosphate} was poured into six flasks sealed with glass stopcocks, and the flasks were immersed in the bath. The mixtures were agitated for 4 h and then allowed to settle for more than 12 h. The apparatus used enable us to speedily perform the LLE measurements as compared with the usual apparatus consisting of a double cylinder equilibrium still connected to a thermostat. Our apparatus gives six LLE data per run.

First, 1 cm^3 samples were withdrawn from each phase using long-needle syringes, and the contents of 1-propanol (or 2-propanol) and water were analyzed by gas chromatography as follows: after the samples (1 cm^3) of both phases, each put into a small bottle, had been weighed on an electronic balance (accuracy of ± 0.0001 g), aqueous solutions (1 cm^3) of 20 wt % MFA were added, and the bottles were weighed again. The addition of MFA solution prevents the samples from separating again into two liquid phases.

Special attention was paid when sampling liquid from the lower phase. After the point of the needle of the syringe had reached the bottom of the flask, some pressure was applied to the syringe piston rod to expel tiny air bubbles. Before being added to the small bottle, the withdrawn liquid was adjusted to 1 cm^3 by expelling the excess amount, and the needle was wiped with a piece of tissue paper.[2]

Analysis of the samples was carried out using a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a stainless steel column (2 m long with 3 mm i.d.) packed with Porapack Q. The mass ratio of (1-propanol or 2-propanol) to MFA was obtained from a calibration curve

* Corresponding author. Phone: +81-42-387-6140. E-mail: katayama@k.hosei.ac.jp.

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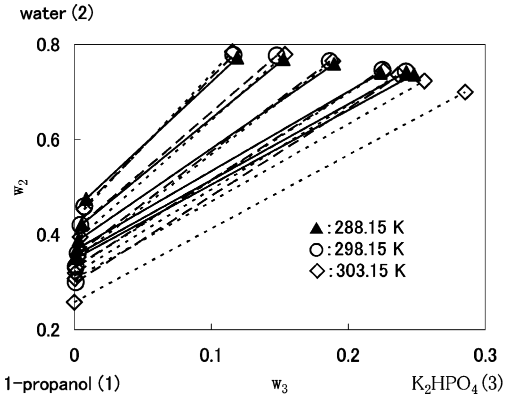

Figure 1. Experimental LLE of the system 1-propanol + water + K_2HPO_4. The solid, broken, and dotted lines stand for the tie lines of (288.15, 298.15, and 308.15) K.

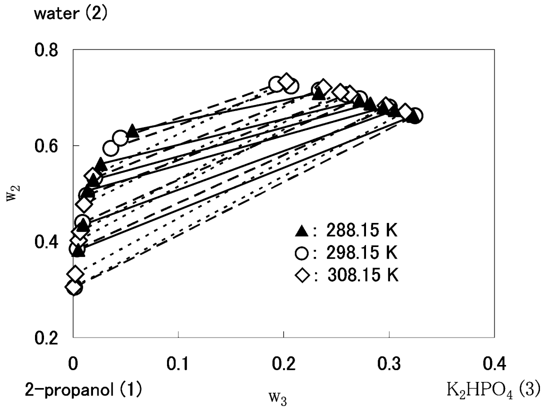

Figure 2. Experimental LLE of the system 2-propanol + water + K_2HPO_4. The solid, broken, and dotted lines are the same as in Figure 1.

Table 1. LLE for the System 1-Propanol (1) + Water (2) + K_2HPO_4 (3)

T	alcohol-rich phase		phosphate-rich phase	
K	w_1^t	w_3^t	w_1^b	w_3^b
288.15	0.648	0.0013	0.0147	0.248
	0.641	0.0015	0.0155	0.243
	0.628	0.0018	0.0358	0.224
	0.609	0.0031	0.0514	0.190
	0.573	0.0054	0.0780	0.153
	0.516	0.0085	0.1085	0.119
298.15	0.699	0.0011	0.0151	0.242
	0.666	0.0011	0.0287	0.225
	0.636	0.0026	0.0488	0.187
	0.575	0.0046	0.0755	0.148
	0.533	0.0073	0.1055	0.116
308.15	0.742	0.0001	0.0144	0.285
	0.692	0.0005	0.0212	0.256
	0.680	0.0008	0.0268	0.236
	0.669	0.0008	0.0291	0.226
	0.644	0.0028	0.0460	0.189
	0.601	0.0043	0.0666	0.154
	0.540	0.0072	0.1000	0.115

Table 2. LLE for the System 2-Propanol (1) + Water (2) + K_2HPO_4 (3)

T	alcohol-rich phase		phosphate-rich phase	
K	w_1^t	w_3^t	w_1^b	w_3^b
288.15	0.612	0.0051	0.0156	0.323
	0.555	0.0098	0.0213	0.306
	0.481	0.0137	0.0261	0.295
	0.453	0.0193	0.0301	0.282
	0.412	0.0262	0.0347	0.272
	0.312	0.0563	0.0577	0.233
298.15	0.694	0.0016	0.0137	0.325
	0.612	0.0041	0.0199	0.300
	0.551	0.0093	0.0309	0.272
	0.492	0.0131	0.0349	0.260
	0.447	0.0209	0.0509	0.234
	0.370	0.0362	0.0699	0.207
	0.340	0.0453	0.0798	0.194
308.15	0.695	0.0005	0.0150	0.315
	0.666	0.0023	0.0198	0.297
	0.592	0.0054	0.0300	0.263
	0.573	0.0066	0.0354	0.254
	0.512	0.0104	0.0416	0.238
	0.445	0.0187	0.0645	0.203

relating the area and mass ratios of (1-propanol or 2-propanol) to MFA.

Next, 10 cm^3 and 3 cm^3 amounts were removed from the upper and lower layers, respectively, and dried for more than 2 h at a temperature of 423 K in an oven. The K_2HPO_4 contents were determined gravimetrically. Crystals of K_2HPO_4 are anhydrous at temperatures above 321.5 K.[4]

The compositions of the samples of the system (1-propanol or 2-propanol) + water + K_2HPO_4 were determined as follows. The ratio of sample (mass) to MFA (mass) is expressed as

$$\frac{\text{sample (mass)}}{\text{MFA (mass)}} = \frac{\text{water (mass)}}{\text{MFA (mass)}} + \frac{\text{1-propanol or 2-propanol (mass)}}{\text{MFA (mass)}} + \frac{\text{K}_2\text{HPO}_4\text{(mass)}}{\text{MFA (mass)}}$$

Since the ratio of K_2HPO_4 (mass) to sample (mass) (i.e., the mass fraction of K_2HPO_4 (= α)) has already been obtained by gravimetric analysis, the above relation is converted to

$$\frac{\text{water (mass)}}{\text{MFA (mass)}} + \frac{\text{1-propanol or 2-propanol (mass)}}{\text{MFA (mass)}} = (1 - \alpha)\frac{\text{sample (mass)}}{\text{MFA (mass)}}$$

where K_2HPO_4 (mass)/MFA (mass) = α × sample (mass)/MFA (mass). Since the masses of the sample and MFA were previously measured with the balance, the right-side term of the above equation is known before the sample is injected. The ratio of water (mass) to MFA (mass) is determined by deducting the ratio of 1-propanol or 2-propanol (mass) to MFA (mass) from the right-side term. The compositions were thus determined from the mass ratios of (1-propanol or 2-propanol) to MFA, water to MFA, and K_2HPO_4 to MFA.

The (1-propanol or 2-propanol) and water contents were measured by gas chromatography with an accuracy of ± 0.0002 mass fraction, and the K_2HPO_4 contents were measured by gravimetry with an accuracy of ± 0.0001 mass fraction. However, on the basis of repeated LLE measurements, the mass fractions of the major components were estimated to be reproducible to three decimal places, and those of the minor components were estimated to be reproducible to four decimal places.

Results and Discussion

The experimental results of LLE for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water + K_2HPO_4 are shown in Tables 1 and 2 and in Figures 1 and 2, respectively, in terms of mass fractions of w_1, w_2, and w_3. The subscripts 1, 2, and 3 denote the components of alcohol, water, and phosphate, respectively; the superscripts t and b denote the top phase (alcohol-rich phase) and the bottom phase (phosphate-rich phase), respectively. The results were selected from the

Table 3. Values of Parameters of Equation 1

T/K	a	b	c	d	e	R^2
1-Propanol (1) + Water (2) + K_2HPO_4 (3)						
288.15	−0.4255	0.8166	−37.180	236.22	−624.07	0.9975
298.15	−0.2948	−1.9626	−24.159	164.06	−467.30	0.9986
308.15	−0.2900	−2.7320	−11.866	30.00	−66.63	0.9999
2-Propanol (1) + Water (2) + K_2HPO_4 (3)						
288.15	−0.1182	−5.6986	6.776	−28.47	0.00	0.9998
298.15	−0.1962	−4.5871	2.920	−22.99	0.00	0.9999
308.15	−0.2470	−3.9448	−0.188	−16.86	0.00	0.9998

Table 4. Values of Parameters of Equations 2 and 3

T/K	k_1	n	R^2	k_2	r	R^2
1-Propanol (1) + Water (2) + K_2HPO_4 (3)						
288.15	0.284	0.582	0.987	7.642	1.527	0.975
298.15	0.184	0.779	0.988	7.713	1.138	0.986
308.15	0.193	0.732	0.974	8.280	1.235	0.986
2-Propanol (1) + Water (2) + K_2HPO_4 (3)						
288.15	0.0881	2.761	0.970	2.346	0.326	0.992
298.15	0.1058	2.073	0.986	2.828	0.437	0.987
308.15	0.1066	1.817	0.991	3.246	0.504	0.967

experimental values of more than four times through eliminating the irregularly scattered values. Figures 1 and 2 both show that for the respective systems the binodal curves of the three temperatures are almost identical, but the positive slopes of their tie lines do slightly decrease with decreasing temperature. This decrease is considered to be due to a decrease in the solubility of phosphate (K_2HPO_4) in water with decreasing temperature. That is, the affinity of phosphate to water is weakened as the temperature is lowered. The decrease in temperature, however, also enhances the intermolecular hydrogen bond-force between alcohol and water, so that some water in the lower phase moves into the upper phase when the temperature is decreased. The temperature dependence of the 1-propanol system (Figure 1) is less than that of the 2-propanol system (Figure 2). This may be because the affinity of 1-propanol to water is smaller than that of 2-propanol to water.

The binodal curves were correlated with the following nonlinear equation:[5]

$$\ln w_1 = a + b w_3^{0.5} + c w_3 + d w_3^{2} + e w_3^{3} \tag{1}$$

where w_1 and w_3 are the mass fractions of alcohol and phosphate, respectively. The coefficients of eq 1 for the two systems investigated along with the squared correlation coefficients R^2 for w_1 are given in Table 3. The R^2 values indicate that the experimental data are well-correlated with eq 1.

The compositions of the tie lines were correlated with the equations of Othmer−Tobias (eq 2)[6] and Bancroft (eq 3):[7]

$$\left(\frac{1 - w_1^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right) = k_1\left(\frac{1 - w_3^{\mathrm{b}}}{w_3^{\mathrm{b}}}\right)^n \tag{2}$$

$$\left(\frac{w_2^{\mathrm{b}}}{w_3^{\mathrm{b}}}\right) = k_2\left(\frac{w_2^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right)^r \tag{3}$$

where the values k_1 and n are the fit parameters of eq 2, and k_2 and r are the parameters of eq 3. These parameters, along with R^2, obtained from the least-squares method, are listed in Table 4. The tie lines of the systems were found to be satisfactorily correlated by both eqs 2 and 3.

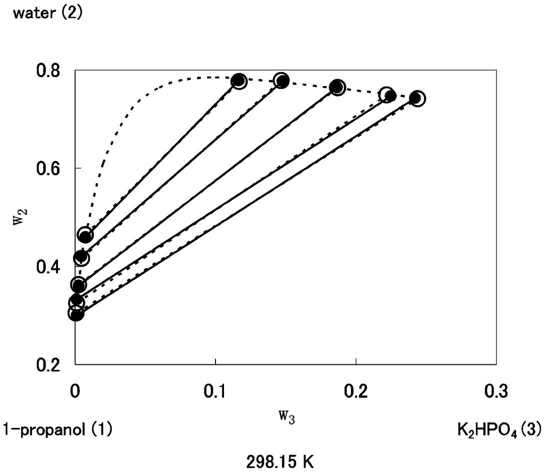

Figure 3. Comparison of predicted (○) and experimental LLE (●) values for the system 1-propanol + water + K_2HPO_4 at 298.15 K. Dotted binodal curves: values predicted using eq 1. Dotted tie lines: predicted values using eqs 1 and 3. Solid tie lines: experimental values.

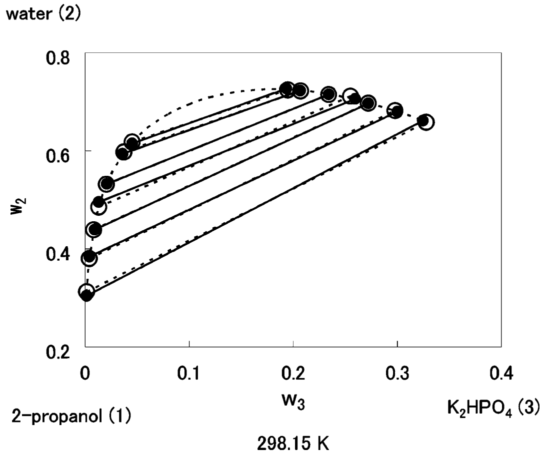

Figure 4. Comparison of predicted (○) and experimental (●) LLE values for the system 2-propanol + water + K_2HPO_4 at 298.15 K. The dotted and solid lines are the same as in Figure 3.

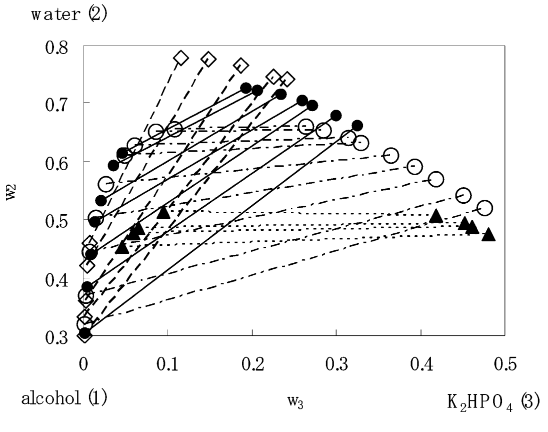

Figure 5. Comparison of LLE for the systems aliphatic alcohol + water + K_2HPO_4 at 298.15 K. Experimental values of the systems ▲, methanol + water + K_2HPO_4; ○, ethanol + water + K_2HPO_4; ●, 2-propanol + water + K_2HPO_4; and ◇, 1-propanol + water + K_2HPO_4. Dotted lines, broken and dotted lines, solid lines, and broken lines show the tie lines for the respective systems.

Predictions of LLE can be conducted using any two of eqs 1, 2, and 3 with the accuracy indicated by the root-mean-square deviations (rmsd) between experimental and predicted values.

The rmsd was given by

$$\text{rmsd} = \sqrt{\frac{\sum_{n=1}^{N}\sum_{k=1}^{2}\sum_{j=1}^{3}(w_{n,k,j,\text{cal}} - w_{n,k,j,\text{exp}})^2}{6N}} \times 100.0 \qquad (4)$$

where j is the number of components (1, 2, and 3), *k* is the number of phases (1, 2), and *n* is the number of LLE data (1 to $N = 5-7$). The results predicted using eqs 1 and 2 for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water K_2HPO_4 had the rmsd values of 0.30 % and 0.35 %, respectively. The results predicted using eqs 1 and 3 for the two systems had the rmsd values of 0.28 % and 0.27 %, respectively. Thus, eqs 1 and 3 gave slightly better predictions than eqs 1 and 2. LLE predictions for the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water K_2HPO_4 at 298.15 K using eqs 1 and 3 are shown in Figures 3 and 4, respectively. The figures show good agreement between the predicted and experimental values.

Figure 5 shows LLE for the systems methanol + water + K_2HPO_4,[1] ethanol + water + K_2HPO_4,[1] 2-propanol + water + K_2HPO_4, and 1-propanol + water + K_2HPO_4 at 298.15 K. The tie lines of the system methanol + water + K_2HPO_4 are almost horizontal, but as the number of carbons in the alcohol increases, the slope of the tie lines becomes increasingly positive. Among the systems, the LLE area for the 1-propanol system is the largest, and the area for the methanol system is the smallest.

Conclusions

LLE of the systems 1-propanol + water + K_2HPO_4 and 2-propanol + water + K_2HPO_4 were studied at temperatures of (288.15, 298.15, and 308.15) K. The binodal curves of these systems were correlated using a nonlinear equation with five parameters, and the tie lines were satisfactorily described with the Othmer−Tobias and Bancroft equations. LLE predictions were successfully carried out using both the binodal and Othmer−Tobias equations and the binodal and Bancroft equations.

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