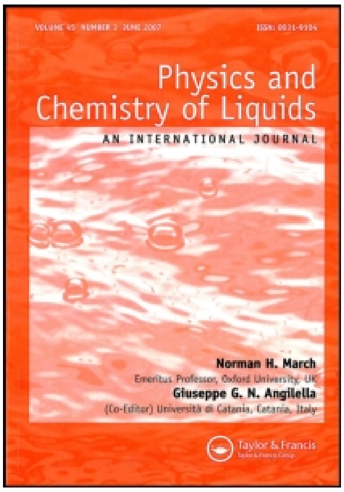

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Liquid-liquid equilibria for aliphatic alcohols + water + potassium carbonate systems; experiment and correlation

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Liquid–liquid equilibria for aliphatic alcohols + water + potassium carbonate systems; experiment and correlation

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Liquid–liquid equilibrium (LLE) data were measured at 298.15 K for some aliphatic alcohols + water + potassium carbonate systems. The alcohols used were ethanol, 1-propanol, 2-propanol and 2-methyl-2-propanol. The LLE data were correlated with the Othmer–Tobias and Bancroft equations. A calculated method was also proposed to correlate the experimental tie-line data. This method is based on the Wilson model for alcohol + water mixture, the Pitzer equation for electrolyte solution and an empirical equation for the binodal curves.

Keywords: Thermodynamic model; Two-phase system; Phase diagram; Aliphatic alcohols; Potassium carbonate

1. Introduction

The salting effect on the liquid–liquid equilibrium (LLE) of organic aqueous solutions could be applied to many fields in the chemical industry, such as recycling of an organic solvent in a mixed-solvent system, design of extractors, biological process, etc. In recent years, research groups have focused on the measurements of phase equilibrium data for these systems [1–7]. In our previous work, LLE of some aqueous alcohols containing inorganic salts was investigated [5,8]. As far as we know there is no report on the LLE data for aliphatic alcohol and water aqueous solutions of potassium carbonate salt. Due to the salting out effect, adding K_2CO_3 into the alcohols–water systems leads to an organic-rich phase with negligible salt and a water-rich phase with negligible alcohol, so large amount of water can be separated from alcohols by simple and efficient phase separation.

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In this research work, we report LLE data for the ternary systems ethanol + H_2O + K_2CO_3, 1-propanol + H_2O + K_2CO_3, 2-propanol + H_2O + K_2CO_3 and 2-methyl-2-propanol + H_2O + K_2CO_3 at 298.15 K. The experimental LLE data were correlated with the Othmer–Tobias [9] and Bancroft [10] equations. A calculated method was also proposed to correlate the experimental tie-lines data. This method is based on the Wilson model for alcohol + water mixture, the Pitzer equation for electrolyte solution and an empirical equation for the binodal curves. The Wilson parameters, which were used to describe the interactions of alcohol–water, were obtained from Gmehling *et al.* [11], the Pitzer model parameters for water–K_2CO_3 were obtained from Pitzer *et al.* [12] and the two empirical coefficients for binodal curves were obtained from our experimental data. The proposed method has been applied to correlate the experimental data measured by this work and has demonstrated that the method could predict well the salting effect on LLE of organic aqueous solutions.

2. Experimental

2.1. *Materials*

The alcohols and potassium carbonate were obtained from Merck (alcohols GR, min 99.8% and potassium carbonate GR, min 99.5%). All chemicals were used without further purification. The stock solution of potassium carbonate was prepared with triply distilled water.

2.2. *Apparatus and experimental procedure*

Experimental apparatus and aqueous two-phase equilibrium experiment were described previously [5]. A glass vessel, volume 50 cm^3, was used to carry out the phase equilibrium determinations. It had an external jacket in which water at constant temperature was circulated from a thermostat. The temperature was controlled to be within ±0.1 K. The binodal curves were determined by the cloud point method. An aqueous potassium carbonate solution of known concentration was titrated with alcohol, until the solution turned turbid. The composition of the mixture was followed by mass using an analytical balance with a precision of $\pm 1 \times 10^{-7}$ kg. For the determination of the tie-lines alcohols, salt and water were mixed to give a defined point in the two-phase region of the phase diagram. The mixture was stirred for 2 h and then allowed to settle overnight. After equilibrium was achieved, phases were separated with care and analyzed for water, alcohol and salt concentration.

2.3. *Analytical methods*

The concentrations of various alcohols and water were determined by a gas chromatography with thermal conductivity detector manufactured by Shimadzu (Shimadzu 6A). The column and injector temperatures were 453 and 473 K for all systems. The maximum experimental errors for the top and bottom phase analyses were less than 0.1 mass%. The water content of some samples was also measured with Kyoto mks-210 Karl Fischer instrument.

The titration method used for the determination of potassium carbonate using titro processor Metrohm 686. Determinations made for solutions of known salt concentrations indicated that this method is very accurate and reproducible. For the analysis of the bottom phase, 0.1 g and for the top phase 1 g of the samples were used.

3. Results

The experimentally measured LLE and the binodal curve data of the four ternary systems at 298.15 K are given in tables 1 and 2 as mass fraction. The phase diagrams are shown in figures 1–4. In each system, the upper layer was the alcohol-rich, salt-poor phase, and the lower layer was the water-rich, salt-rich phase. For this reason, the water-rich phase can be calculated by the Pitzer theory and the alcohol-rich phase by the Wilson equation, as described in theory section. The binodal curve data for the investigated systems are plotted in figure 5. This figure shows that reducing the number of the carbon atoms in the chain improves the miscibility, as expected. The effect of the molecular shape of 2-propanol as compared with that of 1-propanol

Table 1. LLE data for aliphatic alcohols (1) + water (2) + K_2CO_3 (3) ternary system at 298.15 K.

Organic phase			Aqueous phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
Ethanol					
44.82	53.04	2.14	9.28	70.61	20.11
58.60	40.4	1.00	3.97	67.52	28.51
68.74	30.68	0.58	1.90	63.50	34.60
76.82	22.76	0.35	1.38	59.82	38.80
82.01	17.73	0.26	0.80	55.14	44.06
87.17	12.73	0.20	0.34	50.16	49.50
1-Propanol					
68.57	68.99	0.42	6.94	77.92	15.14
70.81	28.83	0.36	4.26	77.32	18.42
76.70	23.01	0.29	1.90	72.98	25.12
83.35	16.42	0.23	0.56	69.43	30.01
88.12	11.70	0.18	0.18	65.57	34.25
89.91	10.06	0.13	0.00	55.71	44.29
2-Propanol					
48.54	49.65	1.81	8.99	75.89	15.12
59.89	39.09	1.02	4.73	74.86	20.41
68.06	31.08	0.86	2.21	73.30	24.49
75.16	24.26	0.58	0.79	69.79	29.42
83.23	16.38	0.39	0.21	64.87	34.92
92.85	7.07	0.18	0.05	50.45	49.50
2-Methyl-2-propanol					
66.48	33.52	0.00	6.29	79.91	13.80
76.11	23.89	0.00	1.10	76.07	22.83
82.03	17.97	0.00	0.96	68.07	30.97
87.47	12.53	0.00	0.89	62.08	37.03
92.12	7.88	0.00	0.57	53.59	45.84
93.88	6.12	0.00	0.15	49.87	49.98

Table 2. Binodal curve data as mass fraction for aliphatic alcohols (1) + water (2) + K_2CO_3 (3) at 298.15 K.

$100w_1$	$100w_3$	$100w_1$	$100w_3$
Ethanol + water + K_2CO_3			
41.5	2.9	23.7	8.9
37.2	3.8	20.5	10.4
32.5	5.2	17.5	12.6
26.5	7.5	14.6	15.1
1-Propanol + water + K_2CO_3			
51.4	1.4	24.9	6.1
42.4	2.4	21.1	7.4
36.7	3.3	14.5	10.3
31.2	4.4	10.7	12.5
2-Propanol + water + K_2CO_3			
44.5	2.3	24.4	7.2
38.6	3.3	19.1	9.1
34.5	4.3	14.2	11.8
28.7	5.7	12.5	12.9
2-Methyl-2-propanol + water + K_2CO_3			
55.0	0.4	20.2	5.9
45.0	1.1	15.5	7.5
37.5	2.2	11.5	9.8
25.8	4.3	8.3	11.9

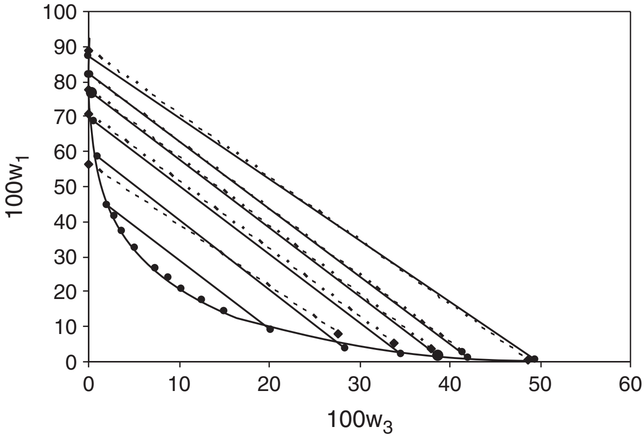

Figure 1. Binodal curve and tie-lines for ethanol (1) + water (2) + K_2CO_3 (3) at 298.15 K (solid line: experiment, dotted line: calculated).

is visible from the shift in the binodal curves. These trends are in agreement with the experimental of our previous work [5].

4. Theory

In this work, first, the reliability of the measured tie-line compositions was ascertained by the correlation equations given by Othmer–Tobias (equation (1)) and

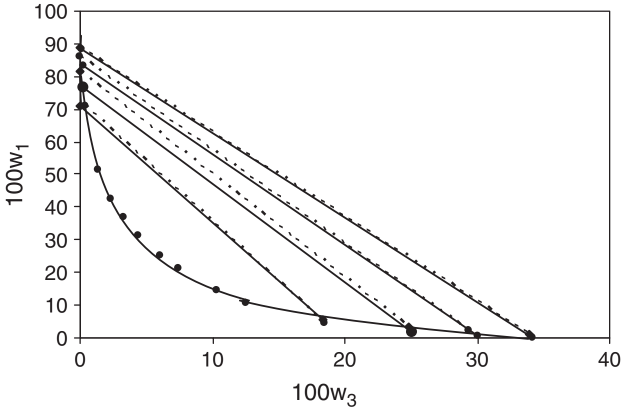

Figure 2. Binodal curve and tie-lines for 1-propanol (1) + water (2) + K_2CO_3 (3) at 298.15 K (solid line: experiment, dotted line: calculated).

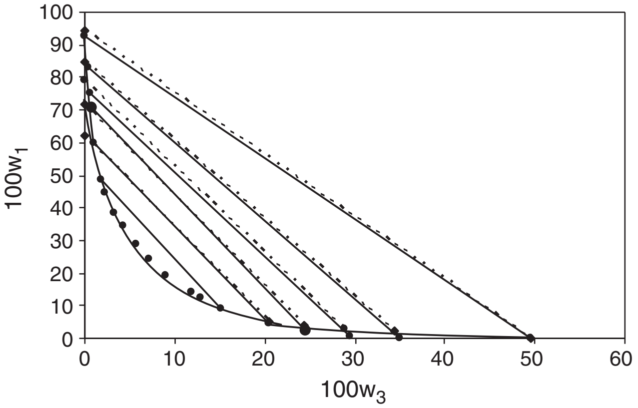

Figure 3. Binodal curve and tie-lines for 2-propanol (1) + water (2) + K_2CO_3 (3) at 298.15 K (solid line: experiment, dotted line: calculated).

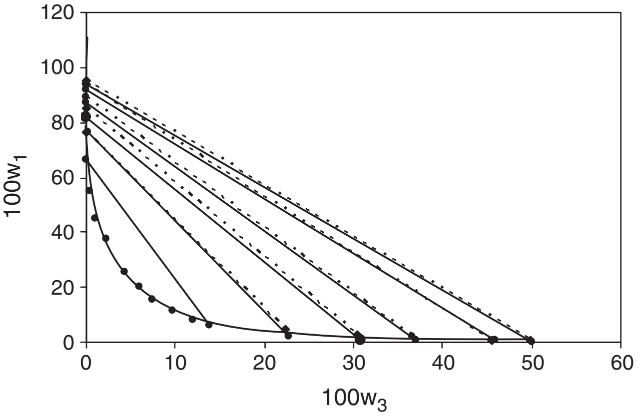

Figure 4. Binodal curve and tie-lines for 2-methyl-2-propanol (1) + water (2) + K_2CO_3 (3) at 298.15 K (solid line: experiment, dotted line: calculated).

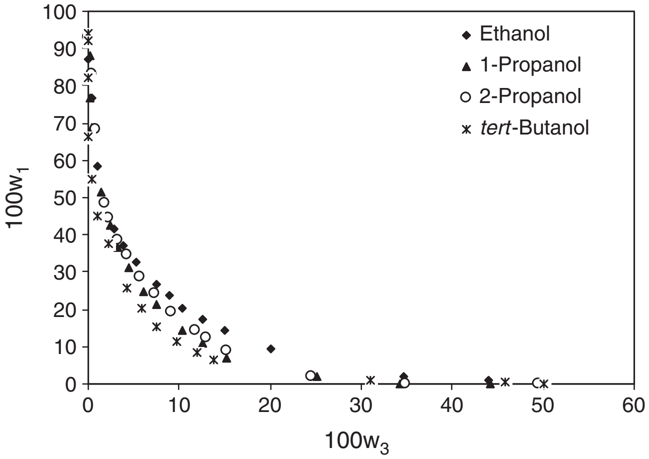

Figure 5. Binodal curves of aliphatic alcohols (1) + water (2) + K_2CO_3 (3) at 298.15 K.

Table 3. Values of parameters of equations (1) and (2) for various alcohol + water + K_2CO_3 systems.

System	k_1	n	k_2	r	R_1	R_2
Ethanol	0.151	1.586	3.050	0.580	0.995	0.997
1-Propanol	0.083	1.040	9.340	0.864	0.977	0.977
2-Propanol	0.078	1.558	4.821	0.601	0.998	0.998
2-Methyl-2-propanol	0.074	1.124	8.890	0.832	0.986	0.988

Bancroft equation (2)):

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

$$\frac{w_2^{\mathrm{b}}}{w_3^{\mathrm{b}}} = k_2 \left(\frac{w_2^{\mathrm{t}}}{w_1^{\mathrm{t}}} \right)^r \tag{2}$$

where w_1^{t} is the mass fraction of aliphatic alcohol in the top phase, w_3^{b} the mass fraction of K_2CO_3 in the bottom phase, w_2^{b} and w_2^{t} are the mass fraction of water in the bottom and top phase, respectively. k_1, k_2, n and r represent fit parameters. The values of the parameters are given in table 3. A linear dependency of the plots $\ln((1 - w_1^{\mathrm{t}})/w_1^{\mathrm{t}})$ against $\ln((1 - w_3^{\mathrm{b}})/w_3^{\mathrm{b}})$ and $\ln(w_2^{\mathrm{b}}/w_3^{\mathrm{b}})$ against $\ln(w_2^{\mathrm{t}}/w_1^{\mathrm{t}})$ indicates an acceptable consistency of the results. The corresponding correlation coefficient values, R_1 and R_2 for equations (1) and (2) are also given in table 3. The average absolute deviations for mass percent of alcohol and salt for equation (1) are $\delta_1 = 1.2$ and $\delta_3 = 1.3$ respectively and equation (2) are $\delta_1 = 4.2$ and $\delta_3 = 1.6$. The average absolute deviations were obtained using the following equation:

$$\delta\% = \frac{1}{N} \sum_i \left| w_i(\mathrm{ca}) - w_i(\mathrm{ex}) \right| \times 100 \tag{3}$$

where N is the number of experimental points and the 'ex' and 'ca' denote the experimental and calculated values respectively.

A calculated method was also proposed to correlate the experimental tie-lines data. This method is based on the Wilson model for alcohol + water mixture, the Pitzer equation for electrolyte solution and an empirical equation for the binodal curves. The water activity for the water-rich phase with negligible alcohol can be calculated by the following equation

$$\ln a_\mathrm{w} = -0.001\nu_\mathrm{s} m_\mathrm{s} M_\mathrm{w} \phi_\mathrm{s} \tag{4}$$

which, ν_s is the salt stoichiometric coefficient, m_s is the salt molality, M_w is solvent molecular weight, and ϕ_s is the practical osmotic coefficient and can be obtained from Pitzer theory as follows:

$$\phi - 1 = f^\phi + \left(\frac{2\nu_1\nu_2}{\nu}\right) m_\mathrm{s} B^\phi + m_\mathrm{s}^2 \left(\frac{2(\nu_1\nu_2)^{1.5}}{\nu}\right) C^\phi \tag{5}$$

where

$$f^\phi = -\frac{A_\phi |Z_1 Z_2| \sqrt{I}}{1 + b\sqrt{I}} \tag{6}$$

and

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp\left[-\alpha(1)\sqrt{I}\right] \tag{7}$$

In these equations $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ are Pitzer ionic interaction parameters. These parameters for aqueous potassium carbonate solution are as $\beta^{(0)} = 0.1288$, $\beta^{(1)} = 1.433$ and $C^\phi = -0.0005$ [12].

Since the salt in the organic phase is negligible, the original Wilson equation was used to obtain the water activity coefficient in the organic phase. This equation for activity coefficient of water is as follows:

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{8}$$

where Λ_{12} and Λ_{21} are the solvent–solvent interaction parameters, were obtained from Gmehling *et al.* [11] for the binary water + alcohols systems.

On the other hand, the experimental binodal curves for the ternary alcohols (1) + water (2) + salt (3) systems were correlated by the following empirical equation:

$$x_1 = \alpha x_3^\beta \tag{9}$$

where x_1 and x_3 are the mole fraction of alcohol and salt respectively. The empirical coefficients α and β, for the investigated systems are given in table 4.

5. Phase diagram calculation

To correlate experimental two-phase data at equilibrium condition, the experimental tie-lines and binodal curves was solved simultaneously. The LLE condition for water at a fixed temperature and pressure is:

$$a_2^\mathrm{w} = a_2^\mathrm{o} \quad \text{or} \quad (x_2\gamma_2)^\mathrm{w} = (x_2\gamma_2)^\mathrm{o} \tag{10}$$

Table 4. Empirical coefficients of equation (9) for various alcohol + water + salt systems.

System	α	β
Ethanol + water + K_2CO_3	0.0015	−0.8903
1-Propanol + water + K_2CO_3	0.0001	−1.1902
2-Propanol + water + K_2CO_3	0.0003	−1.1374
2-Methyl-2-propanol + water + K_2CO_3	0.0005	−0.8568

where a_2^{w} is activity of water in aqueous phase, which comes from equation (4), and a_2^{o} is activity of water in organic phase, which comes from equation (8). On the other hand, the equation (9) can be used for aqueous phase as well as organic phase and with

$$\sum x_i^{\mathrm{w}} = \sum x_i^{\mathrm{o}} = 1 \tag{11}$$

The resulting five simultaneous equations (equation (9), once for the aqueous phase and once for the organic phase, equation (10) for water and equation (11)) contain six unknowns (x_1^{w}, x_2^{w}, x_3^{w}, x_1^{o}, x_2^{o}, x_3^{o}), where x_1^{w}, x_2^{w}, x_3^{w} are mole fraction of alcohol, water and salt in aqueous phase and x_1^{o}, x_2^{o}, x_3^{o} are mole fraction of alcohol, water and salt in organic phase respectively.

The phase diagram tie-lines can be calculated by assuming a value for the composition of one of the solutes, and then calculating the other compositions. In this work, the phase diagrams for the four different water + alcohol + salt systems have been calculated using the proposed model. The calculated phase diagrams were compared with experimental phase diagrams and illustrated in figures 1–4. The average absolute deviations (δ) are $\delta_1 = 1.2$, $\delta_2 = 1.1$ and $\delta_3 = 0.5$ for alcohol, water and salt, respectively. Although a slight deviation will be introduced by the simplicity, it gives the proposed method the ability to correlate the salting effect on the LLE only using two empirical coefficients, α and β for binodal curves.

6. Conclusions

In the present work, we have measured the LLE data for four ternary systems of ethanol + H_2O + K_2CO_3, 1-propanol + H_2O + K_2CO_3, 2-propanol + H_2O + K_2CO_3 and 2-methyl-2-propanol + H_2O + K_2CO_3 at 298.15 K. The reliability of the measured tie-line compositions was ascertained by the correlation equations given by Othmer–Tobias and Bancroft. The results show that the correlation of tie-lines data with Othmer–Tobias equation is better than Bancroft equation. In this work, a simple method based on the Wilson model for organic–water mixture, Pitzer model for the electrolyte solution and an empirical two parametric equation for binodal curve, was proposed for correlation of the LLE data for these systems. The interaction parameters required by the proposed method come from binary alcohol–water and water–salt systems. The correlated LLE data by the proposed method agree well with the experimental data for the four ternary systems of alcohol–water–salt.

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