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Liquid-liquid phase diagrams of $H_2O + 2$ -butanol + potassium phosphate and $H_2O + 2$ -butanol + Na_2CO_3 systems at 298.15 K

Alireza Salabat^a; Mahmod Hashemi^a; M. T. Zafarani-Moattar^b

^a Chemistry Department, Arak University, Arak, Iran ^b Faculty of Chemistry, Department of Physical Chemistry, University of Tabriz, Tabriz, Iran

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Liquid–liquid phase diagrams of $\text{H}_2\text{O} + 2\text{-butanol} + \text{potassium phosphate}$ and $\text{H}_2\text{O} + 2\text{-butanol} + \text{Na}_2\text{CO}_3$ systems at 298.15 K

ALIREZA SALABAT*[†], MAHMUD HASHEMI[†]
and M. T. ZAFARANI-MOATTAR[‡]

[†]Chemistry Department, Arak University, P.O. Box 38156-879, Arak, Iran

[‡]Faculty of Chemistry, Department of Physical Chemistry,
University of Tabriz, Tabriz, Iran

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The phase diagrams for the ternary systems $\text{H}_2\text{O} + 2\text{-butanol} + \text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH = 7) and $\text{H}_2\text{O} + 2\text{-butanol} + \text{Na}_2\text{CO}_3$ at 298.15 K were determined. Experimental binodals and tie lines for these systems are presented. The experimental results were correlated using an improved regular solution theory. The agreement between the correlation and experimental data is good.

Keywords: Liquid–liquid equilibrium; Ternary systems

1. Introduction

Liquid–liquid extraction utilizing aqueous two-phase systems resulting from the salting out of polymer by inorganic salts has been used to separate and purify biological products from the complex mixtures in which they are produced [1,2]. This extraction technology offers the advantages of high capacity, high activity yields and being easy to scale up.

For large-scale processes, methods for recycling chemicals have been developed. Greve and Kula [3] and Hustedt [4] exploited aqueous two-phase systems composed of aliphatic alcohols and salts for the extraction of salts from the primary bottom phase of a protein extraction process in polymer–salt systems. Aqueous solutions of some aliphatic alcohols and salts are not miscible at all concentrations and will often yield two immiscible liquids. The alcohol-rich top phases can be utilized to extract salts from complex mixtures.

*Corresponding author. Fax: +98-861-2767306. Email: a-salabat@araku.ac.ir

In our previous work, the liquid–liquid equilibrium (LLE) of some aqueous alcohols containing inorganic salts was investigated [5]. Some aqueous phase systems composed of aliphatic alcohols and salts have been introduced by Greve and Kula [6]. Liquid–liquid equilibria for the ternary systems butanols + water + sodium chloride or + potassium chloride also have been obtained by Gomis *et al.* [7].

In this research work, we report LLE data for the ternary systems $\text{H}_2\text{O} + 2$ -butanol + potassium phosphate and $\text{H}_2\text{O} + 2$ -butanol + Na_2CO_3 at 298.15 K. These data have very important applications for large-scale extraction systems and in testing thermodynamic models. An improved regular solution theory incorporating the Fowler–Guggenheim equation is used for the correlation of LLE data [8].

2. Experimental

2.1. Materials

The alcohols and sodium carbonate were obtained from Merck (alcohols GR, min. 99.8% and sodium carbonate GR, min. 99.5%). All chemicals were used without further purification. The stock solutions of sodium carbonate and potassium phosphate salt (pH = 7) were prepared with triply distilled water.

2.2. Apparatus and procedure

The experimental apparatus was described previously [5,9]. 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 within $\pm 0.1\text{ K}$. The binodal curves were determined by the cloud point method. An aqueous sodium carbonate solution or potassium phosphate solution (pH = 7) 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 $\pm 1 \times 10^{-7}\text{ kg}$. For the determination of the tie-lines alcohol, 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 alcohol and salt concentration. The concentration of alcohols was determined using a U-tube vibrating densimeter (Mettler TOLEDO densimeter, DE51). For this purpose the water and alcohol were separated from the salt by an evaporation apparatus. The density of the water + alcohol mixture was determined. The precision of the densimeter was $\pm 1 \times 10^{-5}\text{ g cm}^{-3}$. The temperature of the vibrating tube in the densimeter was controlled to within $\pm 0.05\text{ K}$. To obtain the mass fraction–density curves, various compositions of each alcohol + water solution were prepared by mass and their density was measured at 298.15 K. The density data were fitted to the polynomial equations from which the average relative error in alcohol concentration was within 0.2%. However, taking into account the corresponding error of the separation process of alcohol + water solution from the salt, for known salt + alcohol + water mixtures, a higher error of 0.4% was obtained. From the method of evaporation, the mass of the dried salt could be obtained. However, the concentration

of sodium carbonate and potassium phosphate were measured with a flame photometer (Perkin-Elmer) with an average relative deviation of about 0.2%.

3. Theory

The general equation used in this article for the correlation of LLE data is as follows [8]

$$\frac{\Delta G}{RT} = \left(\sum_i n_i \ln \phi_i \right) + \left(\sum_i n_i V_i \right) \left(\sum_i \sum_j A_{ij} \phi_i \phi_j \right) - \frac{V}{4\pi a^3} \left[\ln(1 + \kappa a) - \kappa a + \frac{(\kappa a)^2}{2} \right] \quad (1)$$

where the first term gives the mixing entropy, the middle term is the original Scatchard-Hildebrand equation, and the last term represents the Fowler-Guggenheim long-range electrostatic term. Here:

$$V = \sum n_i V_i \quad (2)$$

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i} \quad (3)$$

$$\kappa^2 = \frac{4\pi e^2 \sum N_i Z_i^2}{VDKT} \quad (4)$$

We can define the activity a_i and activity coefficient γ_i of species i in the mixture as

$$\frac{\partial \Delta G}{\partial n_i} = \Delta \mu_i = RT \ln a_i = RT \ln x_i \gamma_i \quad (5)$$

For ternary systems water (1) + alcohol (2) + salt (3), the activity expression of the three components are as follows:

$$\ln a_1 = 1 + \ln \phi_1 - \frac{V_1}{V_x} + V_1 [A_{12} \phi_2 (1 - \phi_1) + A_{13} \phi_3 (1 - \phi_1) - A_{23} \phi_2 \phi_3] + \left(\frac{\bar{V}_1}{8\pi a^3 N_0} \right) \left[1 + \kappa a - \frac{1}{(1 + \kappa a)} - 2 \ln(1 + \kappa a) \right] \quad (6)$$

$$\ln a_2 = 1 + \ln \phi_2 - \frac{V_2}{V_x} + V_2 [A_{12} \phi_1 (1 - \phi_2) + A_{23} \phi_3 (1 - \phi_2) - A_{13} \phi_1 \phi_3] + \left(\frac{\bar{V}_2}{8\pi a^3 N_0} \right) \left[1 + \kappa a - \frac{1}{(1 + \kappa a)} - 2 \ln(1 + \kappa a) \right] \quad (7)$$

$$\ln a_3 = \ln\left(\frac{\phi_3 V_1}{V_3}\right) - V_3\left(\frac{1}{V_x} + \frac{1}{V_1}\right) + V_3[A_{13}\phi_1(1 - \phi_3) + A_{23}\phi_2(1 - \phi_3) - A_{12}\phi_1\phi_2] - A_{13}V_3 - \frac{e^2\kappa\left(\sum_i v_i Z_i^2\right)}{2\left(\sum_i v_i\right)DKT(1 + \kappa a)} \quad (8)$$

where $V_x = x_1V_1 + x_2V_2 + x_3V_3$. The V_1 , V_2 and V_3 are volume parameters and A_{12} , A_{13} and A_{23} are interaction parameters of components. In these equations, the pure liquid state is taken as the reference state for water and organic substances, and the infinite dilution state is taken for ions of electrolytes. In order to calculate the activities of three components from equations (6), (7) and (8), we need six parameters V_1 , V_2 , V_3 , A_{12} , A_{13} and A_{23} . The five parameters other than $V_1 = 18.05 \text{ cm}^3 \text{ mol}^{-1}$ come from the corresponding binary systems and experimental

Table 1. Solubility data as mass fraction for H₂O (1) + 2-butanol (2) + K₂HPO₄/KH₂PO₄ (3) system at 298.15 K.

100w ₁	100w ₂	100w ₃
74.8	1.8	23.4
76.8	2.2	21.0
80.4	3.4	16.2
81.9	4.5	13.6
83.2	5.2	11.6
85.0	7.1	7.9
85.4	8.1	6.5
85.7	8.8	5.5
85.9	10.3	3.8
85.8	11.1	3.1
85.9	11.3	2.8
85.5	13.2	1.3
84.4	15.0	0.6
83.3	16.4	0.3
82.2	17.6	0.2

Table 2. Solubility data as mass fraction for H₂O (1) + 2-butanol (2) + Na₂CO₃ (3) system at 298.15 K.

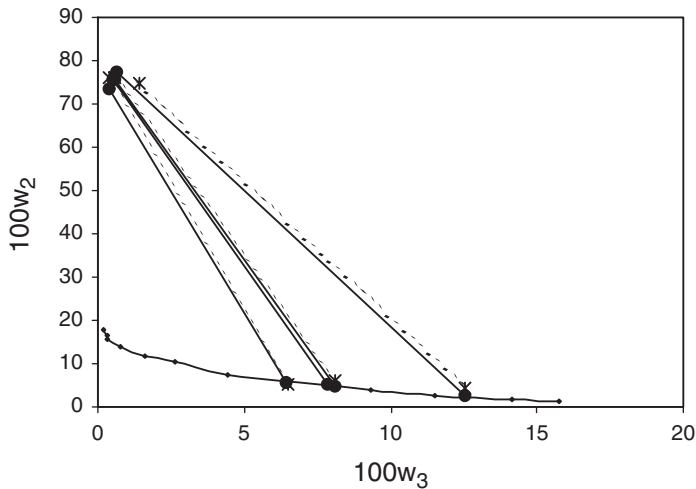
100w ₁	100w ₂	100w ₃
82.8	1.4	15.8
83.9	1.9	14.2
86.0	2.5	11.5
86.9	3.7	9.4
88.1	5.7	6.2
88.0	7.5	4.5
87.0	10.4	2.6
86.6	11.8	1.6
85.4	13.8	0.8
84.1	15.5	0.4
83.0	16.7	0.3
82.0	17.8	0.2

Table 3. Tie-line data as mass fraction for H₂O (1) + 2-butanol (2) + K₂HPO₄/KH₂PO₄ (3) system at 298.15 K.

Bottom phase			Top phase		
100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃
79.3	3.8	16.9	23.8	75.7	0.5
80.3	4.5	15.2	24.0	75.5	0.5
83.6	5.9	10.5	25.7	73.9	0.4
82.9	7.7	9.4	28.4	71.2	0.4
84.6	8.2	7.2	28.6	71.0	0.4

Table 4. Tie-line data as mass fraction for H₂O (1) + 2-butanol (2) + Na₂CO₃ (3) system at 298.15 K.

Bottom phase			Top phase		
100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃
84.9	2.5	12.6	22.0	77.3	0.7
87.0	4.9	8.1	23.6	75.8	0.6
87.0	5.1	7.9	23.6	75.9	0.5
88.0	5.6	6.4	26.0	73.6	0.4

Figure 1. Equilibrium phase diagram for H₂O (1) + 2-butanol (2) + Na₂CO₃ (3) at 298.15 K. Solid lines: experimental data; dash lines: model.

data of ternary system. The two parameters V_3 and A_{13} come from the mean ionic activity coefficient data for water (1) + salt (3) binary system. The two parameters V_2 and A_{12} for system water (1) + alcohol (2) come from the VLE data. The parameter A_{23} for these systems is iterated from one set of conjugated LLE data of ternary system.

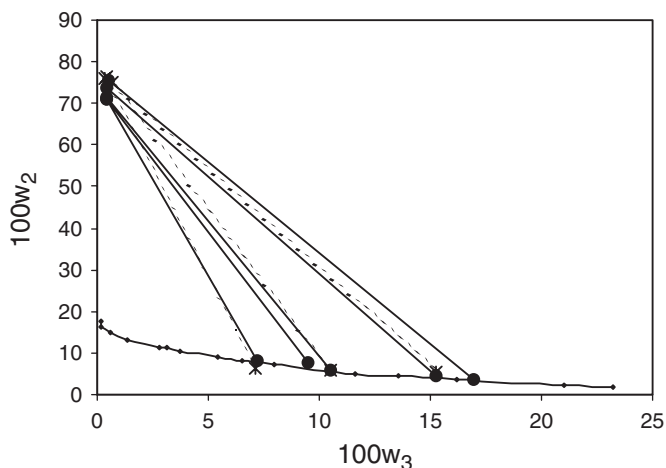


Figure 2. Equilibrium phase diagram for H₂O (1) + 2-butanol (2) + K₂HPO₄/KH₂PO₄ (3) at 298.15 K. Solid lines: experimental data; dash lines: model.

Table 5. Correlated volume (cm³ mol⁻¹) and interaction parameters (mol cm⁻³) for two ternary systems at 298.15 K

System	V_2	V_3	A_{12}	A_{13}	A_{23}
H ₂ O (1) + 2-butanol (2) + Na ₂ CO ₃ (3)	63.91	26.40	0.081	0.021	0.22
H ₂ O (1) + 2-butanol (2) + K ₂ HPO ₄ /KH ₂ PO ₄ (3)	63.91	65.32	0.081	0.036	0.088

4. Results and discussion

The experimental equilibrium compositions and solubility data of the ternary systems H₂O + 2-butanol + potassium phosphate and H₂O + 2-butanol + Na₂CO₃ at 298.15 K systems are given in tables 1–4. In these tables w_1 , w_2 and w_3 are the mass fraction for the water, alcohol and salt. Since the binary system of 2-butanol and water are not completely miscible at all concentrations, the solubility data in tables 1 and 2 show only one part of the binodal curves of these systems. The experimental equilibrium composition data of tables 3 and 4 are shown in figures 1 and 2 as tie lines.

The parameters V_2 , V_3 , A_{12} , A_{13} and A_{23} for the systems H₂O (1) + 2-butanol (2) + potassium phosphate (3) and H₂O (1) + 2-butanol (2) + Na₂CO₃ (3) are given in table 5. The correlated accuracies with these parameters in term of average absolute deviation are less than 1%. Experimental and calculated tie-lines using optimal values of parameters are presented in figures 1 and 2.

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