Unusual S-Shaped Binodal Curves of the System Water + Lithium Chloride + 2-Methyl-2-propanol

V. Gomis,* F. Ruiz, N. Boluda, and M. D. Saquete

Departamento de Ingeniería Química, Universidad de Alicante, Aptdo. 99, Alicante, Spain

Liquid−liquid and liquid−solid equilibrium data of the ternary system water + LiCl + 2-methyl-2-propanol (*tert*-butanol) have been determined experimentally at 25 °C and 40 °C. The system presents a marked salting out effect since a small amount of LiCl can split the completely miscible water + 2-methyl-2-propanol system into two liquid phases in equilibrium. However, when more salt is added, the solubility curve of water in the organic solvent presents an unusual S shape.

Introduction

Liquid−liquid equilibria for ternary systems containing water + salt + organic solvent are of interest for many unit operations. The effect to be investigated here is the salting out effect: the decrease in solubility of an organic solvent in the presence of inorganic salts. The addition of the salt introduces ionic forces that alter the structure of the liquids in equilibrium. The water molecules surround the salt ions and become unavailable for dissolution of the solvent, which is then "salted out" from the aqueous phase.

With respect to the organic phase, the solubility of water in the solvent usually decreases as well when salt is added. As many of the water molecules in the aqueous phase are now unavailable, the organic phase contains less water at equilibrium. The higher the concentration of salt in the aqueous phase, the less the solubility of water in the organic solvent.

Therefore, the usual effects of the addition of salt to a liquid−liquid water + organic solvent system are to decrease both the solubility of the solvent in the aqueous phase and the solubility of water in the organic phase. However, Al-Sahhaf and Kapetanovic[1] and Gomis et al.[2] have shown that the system water + lithium chloride + 1-butanol exhibits an unusual behavior. In the organic phase, the concentration of water drops sharply with increasing LiCl (the usual effect), but thereafter, its concentration stays relatively constant instead of decreasing more and more as in most of the water + salt + solvent systems.

2-Methyl-2-propanol (*tert*-butanol) is the only butanol that is completely miscible with water, and obviously, the decrease in solubility of water in the organic solvent due to the salt is maximal. The system water + lithium chloride + 2-methyl-2-propanol presents a marked salting out effect since a small amount of LiCl can split the completely miscible water + 2-methyl-2-propanol system into two liquid phases in equilibrium. However, as will be shown here, it also leads to an unusual effect: the solubility of water in the organic solvent increases as more salt is added. Both effects cause the organic branch of the solubility curve of the system to have an unusual S shape that has been studied at two different temperatures in this paper, by means of an experimental determination of the liquid−liquid equilibrium data of the ternary system.

Table 1. Tie Line Data as Mass Fraction for Water (1) + Lithium Chloride (2) + 2-Methyl-2-propanol (3) at 25 °C

aqueous phase			organic phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
two liquid phases					
63.7	34.5	1.84	18.0	11.3	70.7
64.8	32.6	2.64	19.8	10.7	69.5
66.6	30.0	3.41	20.6	9.02	70.4
68.7	27.1	4.26	18.4	6.90	74.7
70.4	24.4	5.17	16.8	4.92	78.3
72.4	21.7	5.90	16.1	3.45	80.5
74.1	18.5	7.45	16.3	2.50	81.2
75.3	15.4	9.25	19.0	2.25	78.7
76.0	12.4	11.6	23.5	2.10	74.4
73.9	8.95	17.2	33.3	2.32	64.4
one liquid phase + one solid phase					
54.2	45.8				
				1.56	98.4
			2.20	2.03	95.8
			4.43	4.53	91.0
			6.21	6.10	87.7
			8.36	7.20	84.4
			10.3	7.92	81.8
			12.2	9.40	78.4

Table 2. Tie Line Data as Mass Fraction for Water (1) + Lithium Chloride (2) + 2-Methyl-2-propanol (3) at 40 °C

aqueous phase			organic phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
two liquid phases					
57.5	41.6	0.97	11.5	11.9	76.5
61.6	37.0	1.41	13.9	10.9	75.2
65.4	32.3	2.30	15.6	8.36	76.0
67.4	29.7	2.87	14.6	6.55	78.9
68.6	27.9	3.51	13.1	3.61	83.3
71.4	24.6	4.00	12.6	3.24	84.2
73.7	21.4	4.91	11.4	2.33	86.3
75.3	19.1	5.64	14.6	1.83	83.6
76.8	16.7	6.63	16.4	1.47	82.0
78.7	12.7	8.60	19.6	1.36	79.0
79.4	9.42	11.1	23.3	1.33	75.4
75.7	5.64	18.7	38.7	1.71	59.5

Experimental

The materials and the method used to determine the liquid−liquid and liquid−solid equilibrium at different temperatures are as reported in previous papers where the equilibrium

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* Corresponding author. E-mail: vgomis@ua.es.

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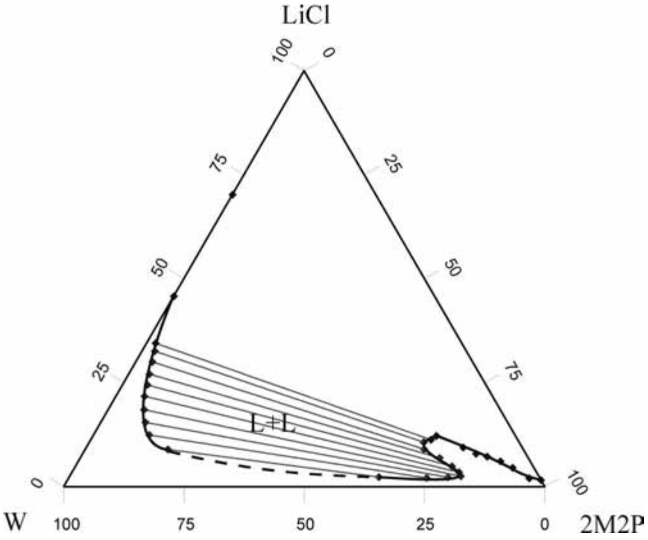

Figure 1. Diagram representing the equilibrium data (% mass) for the ternary system water (W) + lithium chloride (LiCl) + 2-methyl-2-propanol at 25 °C.

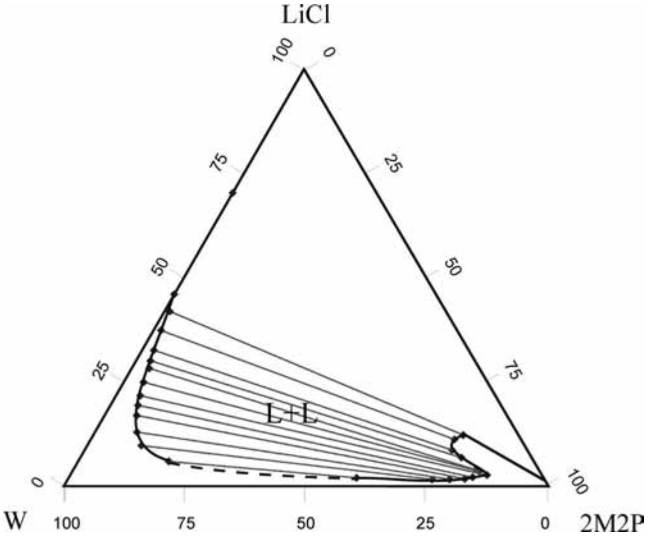

Figure 2. Diagram representing the equilibrium data (% mass) for the ternary system water (W) + lithium chloride (LiCl) + 2-methyl-2-propanol at 40 °C.

data for systems with water + sodium chloride or potassium chloride + 2-methyl-2-propanol (3) and with water + lithium chloride + 1-propanol or 2-propanol (4) were obtained.

Basically, the procedure involved preparing mixtures of known overall composition by mass, stirring intensively, and resetting to constant temperature several times to ensure that equilibrium was reached. After that, samples were taken from both phases and analyzed. The 2-methyl-2-propanol was determined by gas chromatography with a flame ionization detector after mass dilution of the sample by a factor of 5 with water. 2-Propanol was used as the internal standard. Water in the organic phase was determined by the Karl Fischer method and checked by gas chromatography using a thermal conductivity detector. The concentration of salt in both phases was obtained by evaporation of a known mass of sample at 120 °C.

The solid fraction of the samples of both the liquid + liquid + solid heterogeneous zone and the organic liquid + solid zone was colloidal. The separation of the liquid phases from the solid was difficult, and the global mixtures were prepared quite near the solubility curve to increase the amount of liquid. The composition of the colloid cannot be determined because of the interference of the liquid wetting the solid.

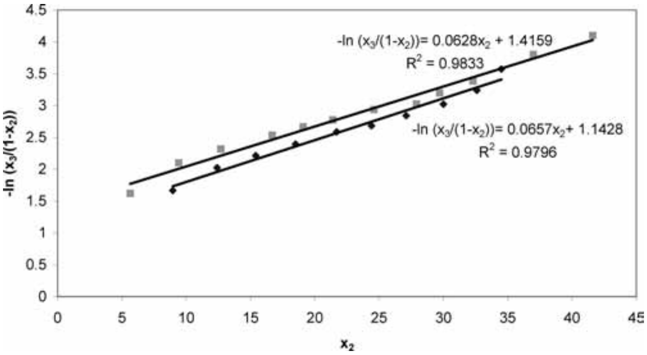

Figure 3. Correlation of the liquid−liquid equilibrium data of the aqueous phase using the Setschenov equation for the system water (1) + lithium chloride (2) + 2-methyl-2-propanol (3). ♦, 25 °C; ■, 40 °C.

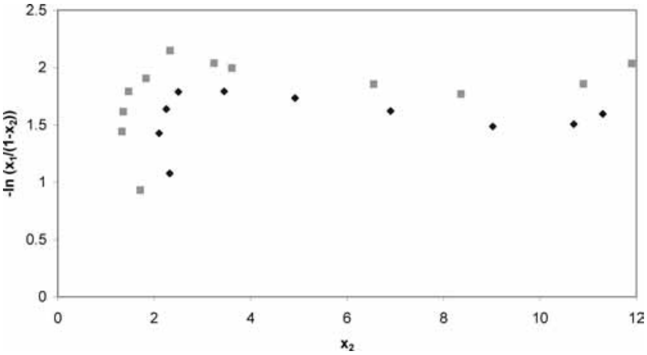

Figure 4. Plot of the liquid−liquid equilibrium data of the organic phase using the Setschenov equation for the system water (1) + lithium chloride (2) + 2-methyl-2-propanol (3). ♦, 25 °C; ■, 40 °C.

The relative precision of the weight fraction measurements was 1 %. The concentration obtained with the relative precision and the known overall composition of the heterogeneous mixture were used to check the mass balance and fit the results following a data reconciliation method.[5] The results reported here correspond to the values obtained by this method.

Results

Tables 1 and 2 present the experimental data obtained at the two different temperatures. The equilibrium of the system was determined initially at 25 °C. As the melting point of 2-methyl-2-propanol is close to that temperature, a second determination of the equilibrium at 40 °C was carried out to study the influence of temperature on the formation of the colloid. No great differences were found between the two determinations.

Figures 1 and 2 are a representation of the equilibrium diagrams for both temperatures. As can be seen, the diagrams are very similar, both having an unusual S-shaped solubility curve in the organic branch. The line of separation between the liquid + liquid + solid and the organic liquid + solid zones has not been drawn since the composition of the solid (the colloid) could not been determined, which could be indicative of a salt with water and 2-methyl-2-propanol in its structure.

Discussion

The Setschenov equation has long been used to correlate the experimental data of the solubility (S) of organic solvents in water as a function of the concentration of salt (C_s)

$$\ln(S_o/S) = k_s C_s \tag{1}$$

where k_s is a constant and S_o is the solubility of the organic solvent in water without salt.

Clearly, the Setschenov equation is not directly applicable to completely miscible binary systems such as water + 2-methyl-2-propanol since S_o is infinite. However, the equation may be rearranged so that S_o appears on its right-hand side

$$-\ln S = k_s C_s - \ln S_o = k_s C_s + b \qquad (2)$$

and the plot of $-\ln S$ against C_s should give a straight line with slope k_s and intercept b.

This equation can be written in terms of the mass or mole fraction free of salt as follows

$$-\ln(x_3/(1 - x_2)) = k_s x_2 + b \qquad (3)$$

where x is the mass or mole fraction of the component in the aqueous phase and the subscripts 2 and 3 denote salt and solvent, respectively

Figure 3 shows how the equilibrium data of the aqueous branch of the solubility curve of the system are perfectly fitted with eq 3 when concentrations are expressed in mass fraction. However, eq 3 applied to the experimental data of the organic branch (substituting x_1 for x_3) does not fit the results as shown in Figure 4. Initially the curves rise sharply and afterward decrease slightly remaining more or less constant and only for high salt concentrations increase again. The competition between water and *tert*-butanol to take part in the solvation of ions in the organic phase could explain this behavior and the unusual S shape of the organic branch of the solubility curve. The relatively dense charge of the Li ion probably induces ionic dipole forces between Li and *tert*-butanol molecules which can solvate the ion. When the concentration of salt in the organic phase is low, the ions are solvated by water which is relatively abundant. As a result, the solubility of water in the solvent decreases with the increase of salt since the organic solvent cannot participate in these solvations. However, as the concentration of salt in the organic phase grows, *tert*-butanol molecules begin to take part in the solvation of ions. These solvations can be sustained by the organic phase, and the solubility of water and salt in the organic phase increases.

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