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Liquid−Liquid−Solid Equilibria for the Ternary Systems Butanols + Water + Sodium Chloride or + Potassium Chloride

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Liquid−liquid−solid equilibria for the ternary systems water + sodium choride + 2-butanol, water + sodium choride + 2-methyl-1-propanol, water + sodium choride + 2-methyl-2-propanol, water + potassium chloride + 1-butanol, water + potassium chloride + 2-butanol, water + potassium chloride + 2-methyl-1-propanol, and water + potassium chloride + 2-methyl-2-propanol have been measured at 25 °C.

Introduction

Recently, several thermodynamic models have been developed for the liquid−liquid equilibria of mixtures containing a salt dissolved in a mixed solvent (Dahl and Macedo, 1992; Zerres and Prausnitz, 1994). The application of these models requires the knowledge of the experimental concentrations of all the components in each of the phases. However, most of the experimental studies on liquid−liquid equilibria of water + salt + solvent systems do not contain the concentrations of salt in the organic phase since they are very small. Consequently there are a small number of systems which contain the concentrations of all the components (Santis et al., 1976a,b; Renard et al., 1965, 1968). Results obtained in some studies (Santis et al., 1976a,b) can be inaccurate since in the determination of the tie lines only some components are analyzed in each phase and the remaining components are calculated using material balances. The consequence is that small relative errors in the analysis of one of the components can produce large errors in the compositions of the minor components calculated from material balance.

In this paper liquid−liquid−solid equilibria of seven water + salt + solvent ternary systems have been studied. All the minor components have been analyzed, and the results have been checked with material balance.

Experimental Section

Materials. All chemicals (Merck) were used as supplied. The contents of possible volatile impurities were examined by gas−liquid chromatography; all compounds contained negligible amounts of impurities (2-methyl-2-propanol <1%, 2-methyl-1-propanol <1%, 2-butanol <1%, 1-butanol <0.5%, and 2-propanol <0.3%).

Analytical Methods. Equilibrium measurements were made by preparing mixtures of known overall composition by mass, stirring intensively and allowing the solution to settle for 2 h at a constant temperature of (25.0 ± 0.1) °C. The mixing and settling procedures were repeated several times to ensure that equilibrium was reached. At the end of each experiment, samples were taken from both phases and analyzed.

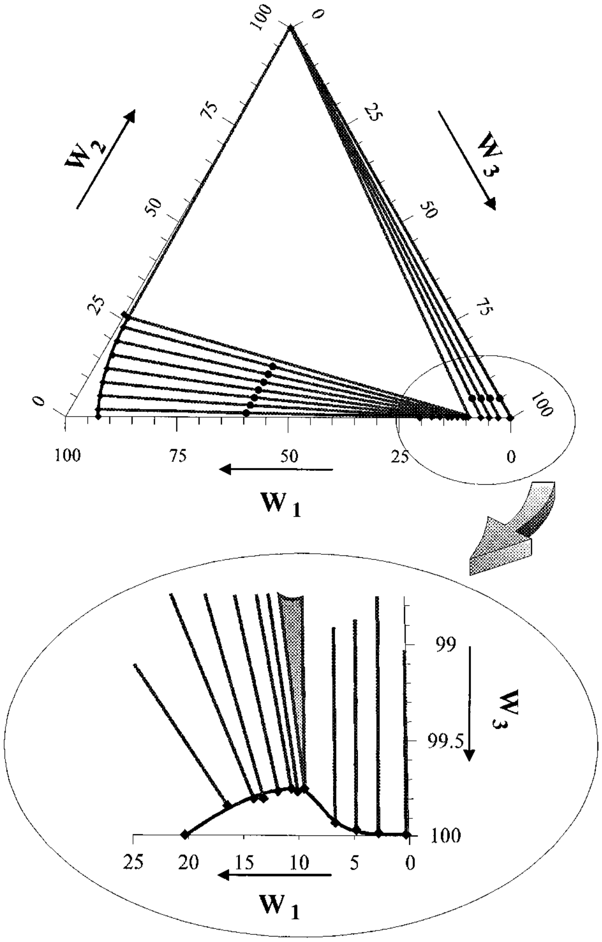

Figure 1. Representation of the equilibrium for water (1) + potassium chloride (2) + 1-butanol (3) at 25 °C.

The concentrations of alcohol (2-methyl-2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol) in the aqueous phase were determined after mass dilution by a factor of 5 of the sample with water, in order to prevent phase separation effects. The analysis was carried out by gas chromatography using a 2 m × 3 mm column packed with Porapack Q 80/100. The column temperature was 210 °C, and detection was carried out using a flame ionization detector. To obtain quantitative results, 2-propanol was used as the internal standard.

The amount of water in the organic phase was determined by the Karl Fischer method using a Mettler DL 18 Karl Fischer titrator.

The concentration of salt in the aqueous phase was determinated from the mass of the solid residue obtained by evaporation at 105 °C of a known mass of the sample.

The salt concentration in the organic phase was determinated by two methods. If the concentration of salt was >0.1%, chloride was determined by titration with silver nitrate. An equivalent amount of sodium or potassium was

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Table 1. Tie Line Data as Mass Fraction w for Water (1) + Sodium Chloride (2) + 2-Butanol (3) at 25 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
74.1	25.9				
			0.31	0.0011	99.7
			2.51	0.0026	97.5
			4.63	0.017	95.4
			6.66	0.051	93.3
Two Liquid Phases + One Solid Phase					
73.0	25.3	1.72	8.07	0.11	91.8
Two Liquid Phases					
75.6	22.8	1.62	9.57	0.11	90.3
78.2	19.4	2.42	11.2	0.12	88.7
80.5	15.9	3.55	13.4	0.13	86.4
82.8	12.4	4.85	15.3	0.14	84.5
84.2	8.98	6.87	18.4	0.16	81.4
85.2	5.21	9.62	20.9	0.15	78.9
84.3	1.73	13.9	27.6	0.13	72.3
81.6		18.4	35.1		64.9

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

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
74.1	25.9				
			0.13	0.0034	99.9
			2.83	0.017	97.2
			4.86	0.043	95.1
Two Liquid Phases + One Solid Phase					
73.2	25.9	0.94	6.51	0.093	93.4
Two Liquid Phases					
74.7	24.3	1.00	6.89	0.088	93.0
77.8	20.7	1.49	7.57	0.088	92.3
80.7	17.4	1.99	8.91	0.089	91.0
83.4	13.8	2.84	9.36	0.089	90.6
85.9	10.4	3.73	10.9	0.083	89.0
88.1	6.88	5.06	12.4	0.069	87.6
89.7	3.38	6.88	13.6	0.041	86.3
91.9		8.12	16.7		83.3

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

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
74.1	25.9				
			8.42	0.047	91.5
Two Liquid Phases + One Solid Phase					
72.9	24.6	2.56	12.1	0.26	87.7
Two Liquid Phases					
74.0	22.8	3.20	12.5	0.26	87.3
75.0	21.3	3.76	14.3	0.30	85.4
75.8	19.6	4.63	16.4	0.36	83.2
76.9	17.7	5.40	16.8	0.41	82.8
77.6	15.9	6.52	18.9	0.51	80.6
77.7	14.4	7.82	22.0	0.58	77.5
78.4	12.4	9.16	24.1	0.71	75.2

assumed to be present. If the concentration of salt was <0.1%, sodium or potassium was measured by atomic emission spectrometry, using a 2100 Perkin-Elmer spectrometer. The analysis was carried out on an aliquot of the sample which was treated with water. The mass proportion of water/sample was in the range 40/1 to 70/1. Alcohol was added to the resultant solution until the appearance of two liquid phases, to ensure that the aqueous phase which was analyzed was saturated with alcohol. The sodium and potassium chloride aqueous standards were also saturated with each one of the alcohols analyzed.

Table 4. Tie Line Data as Mass Fraction w for Water (1) + Potassium Chloride (2) + 1-Butanol (3) at 25 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
73.8	26.2				
			0.28	0.0020	99.7
			2.77	0.0088	97.2
			4.77	0.023	95.2
			6.65	0.050	93.3
Two Liquid Phases + One Solid Phase					
73.4	25.3	1.27	9.39	0.19	90.4
Two Liquid Phases					
75.6	22.9	1.54	10.0	0.18	89.8
78.7	19.3	1.96	10.6	0.19	89.2
81.5	15.8	2.62	11.8	0.18	88.0
84.4	12.3	3.24	13.1	0.15	86.7
87.1	8.77	4.10	14.0	0.15	85.9
89.4	5.34	5.23	16.4	0.12	83.5
91.8	1.78	6.44	18.1	0.055	81.9
92.5		7.46	20.3		79.7

Table 5. Tie Line Data as Mass Fraction w for Water (1) + Potassium Chloride (2) + 2-Butanol (3) at 25 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
73.8	26.2				
			0.27	0.00023	99.7
			2.62	0.0078	97.4
			5.26	0.019	94.7
			7.26	0.032	92.7
			8.79	0.047	91.2
Two Liquid Phases + One Solid Phase					
72.9	24.7	2.47	11.2	0.16	88.6
Two Liquid Phases					
74.3	22.9	2.80	11.6	0.16	88.2
76.8	19.4	3.82	13.1	0.18	86.7
79.3	15.7	5.01	14.4	0.20	85.4
81.3	12.2	6.49	16.4	0.21	83.4
83.0	8.65	8.37	18.7	0.22	81.0
84.2	5.09	10.7	22.6	0.22	77.2
83.8	1.68	14.5	28.9	0.14	71.0
81.6		18.4	35.1		64.9

Table 6. Tie Line Data as Mass Fraction w for Water (1) + Potassium Chloride (2) + 2-Methyl-1-propanol (3) at 25 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
73.8	26.2				
			0.49	0.0012	99.5
			2.77	0.0052	97.2
			4.82	0.019	95.2
			6.65	0.045	93.3
Two Liquid Phases + One Solid Phase					
73.4	25.3	1.30	8.89	0.088	91.0
Two Liquid Phases					
75.7	22.7	1.67	8.82	0.087	91.1
78.6	19.2	2.20	9.75	0.088	90.2
81.5	15.7	2.85	10.6	0.088	89.4
83.8	12.2	4.04	11.9	0.088	88.0
86.4	8.64	4.97	12.8	0.073	87.1
88.6	5.17	6.23	14.1	0.053	85.8
90.5	1.73	7.91	16.2	0.018	83.7
91.9		8.12	16.7		83.3

Experimental Methods. The methodology applied in selecting the most appropriate compositions to study was as reported in a previous paper (Gomis et al., 1993). After each determination the material balance for each component was checked. The differences between compositions

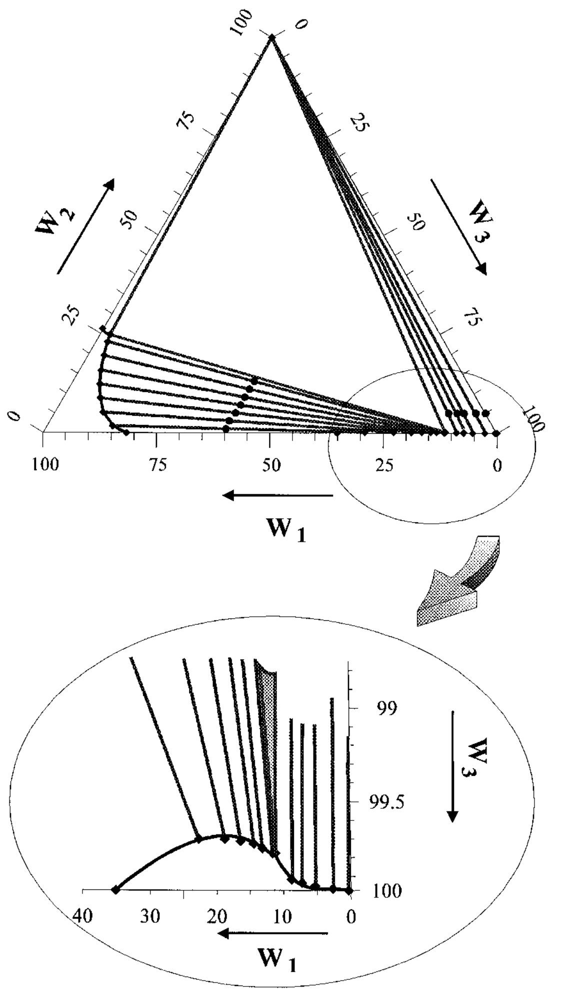

Figure 2. Representation of the equilibrium for water (1) + potassium chloride (2) + 2-butanol (3) at 25 °C.

Table 7. Tie Line Data as Mass Fraction *w* for Water (1) + Potassium Chloride (2) + 2-Methyl-2-propanol (3) at 25 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
73.8	26.2				
			11.0	0.071	89.0
			15.2	0.28	84.5
Two Liquid Phases + One Solid Phase					
72.3	22.8	4.95	17.6	0.54	81.9
Two Liquid Phases					
73.7	19.1	7.29	20.1	0.71	79.2
74.5	17.6	7.88	21.8	0.81	77.4
74.9	15.9	9.25	24.1	0.94	75.0
74.9	13.5	11.6	25.4	1.07	73.5
74.7	12.1	13.2	27.7	1.25	71.1
73.8	10.2	15.9	32.0	1.64	66.3

analyzed and compositions calculated from the material balances were negligible. Duplicates of each heterogeneous mixture were prepared and analyzed. The relative accuracy of the mass fraction measurements of each of the components was approximately 1%.

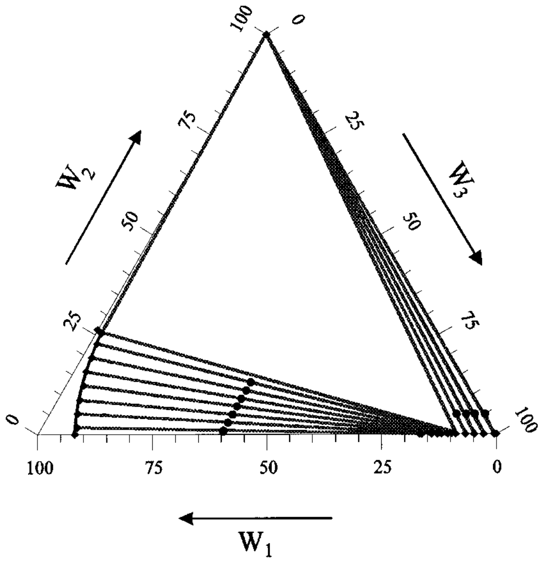

Figure 3. Representation of the equilibrium for water (1) + potassium chloride (2) + 2-methyl-1-propanol (3) at 25 °C.

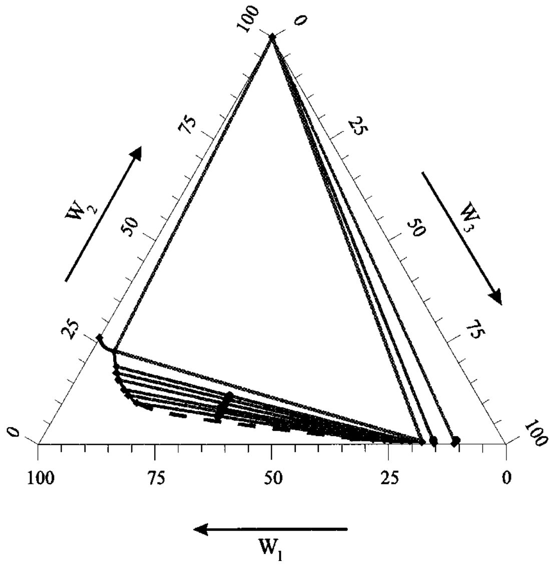

Figure 4. Representation of the equilibrium for water (1) + potassium chloride (2) + 2-methyl-2-propanol (3) at 25 °C.

Results

The results obtained are given in Tables 1−7. The ternary equilibrium diagrams of the systems with potassium chloride are represented in Figures 1−4. Similar diagrams are obtained for the systems with sodium chloride. Four of these systems had been determined previously: the systems water + sodium chloride + 2-butanol, water + sodium chloride + 2-methyl-1-propanol, and water + sodium chloride + 2-methyl-2-propanol by De Santis et al. (1976) and the systems water + potassium chloride + 1-butanol by Li et al. (1995). Shown in Figure 5 is an example for the system water + sodium chloride + 2-methyl-1-propanol. The most significant differences in the results of this work and the previous ones are in the composition of the water in the organic phase which had been obtained from the material balances in the previous works. In this paper, these compositions have been obtained by analysis and the material balance has been used to check the results. In this way, there is little influence of the small relative errors of the analyzed compositions on the calculation of the other compositions.

Similar to the systems water + sodium chloride + 1-propanol, water + sodium chloride + 2-propanol, and water + potassium chloride + 1-propanol (Gomis et al., 1994) all the water + salt + butanol systems present a region with three phases: liquid−liquid−solid.

As 2-methyl-2-propanol is the only butanol which is completely miscible in water, the shapes of the equilibrium

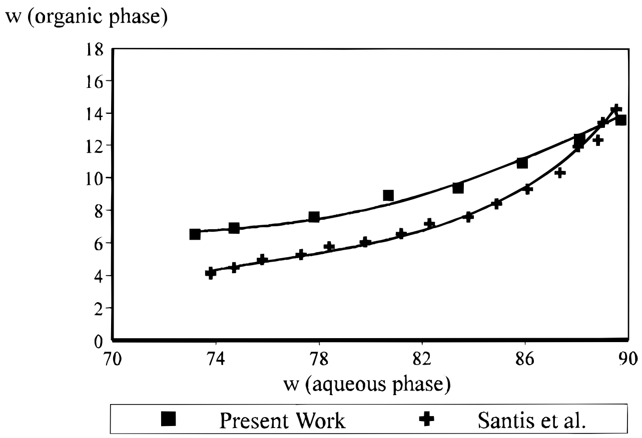

Figure 5. Distribution curve of water (as mass fraction *w*) for the system water + sodium chloride + 2-methyl-1-propanol.

diagrams are similar to those for propanol (which is also completely miscible) and different from those for the other butanols which are partially miscible in water.

The size of the heterogeneous region is in the same order as the solubilities of water in each one of the alcohols: 1-butanol the most immiscible, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol.

There are no significant differences between the systems containing sodium chloride and potassium chloride. This is to be expected as the solubilities of sodium chloride and potassium chloride in water are similar.

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