Liquid−Liquid−Solid Equilibria for Ternary Systems Water + Sodium Chloride + Pentanols

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Liquid−liquid−solid equilibria for the ternary systems water + sodium chloride + 1-pentanol, water + sodium chloride + 2-pentanol, water + sodium chloride + 3-pentanol, water + sodium chloride + 2-methyl-1-butanol, and water + sodium chloride + 2-methyl-2-butanol have been measured at 25 °C. The data obtained have been fitted by the Setschenov equation.

Introduction

Liquid−liquid equilibria for ternary systems containing one salt and two solvents are of interest for many unit operations, for example for extractive crystallization (Weingaertner et al., 1991). On the other hand several thermodynamics models have recently been developed for the liquid−liquid equilibria of mixtures containing salt dissolved in a mixed solvent (Dahl and Macedo, 1992; Zerres and Prausnitz, 1994). The application of these models requires knowledge of the experimental concentrations of all the components in each of the phases. Unfortunately, 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 these are very small.

In this paper liquid−liquid−solid equilibria of five water + sodium chloride + pentanol systems have been determined at 25 °C. The five pentanols studied are as follows: 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, and 2-methyl-2-butanol.

Experimental Section

All chemicals (Merck) were used as supplied. The minimum purities of the alcohols were as follows: 1-pentanol, 98.5%; 2-pentanol, 98%; 3-pentanol, 98%; 2-methyl-1pentanol, 98%; 2-methyl-2-butanol, 99.5%.

The method used in the determination of the liquid−liquid−solid equilibrium at 25 °C was as reported in a previous paper, where the equilibrium data for systems with water, butanols, and sodium chloride (Gomis et al., 1996) were obtained.

The methodology applied in selecting the most appropriate compositions to study was as reported in a previous paper (Gomis et al., 1993). Basically, the procedure consisted of preparing duplicate heterogeneous mixtures of known overall composition by intensive stirring and settling several times at constant temperature to ensure that equilibrium was reached. After that, samples were taken from both phases and analyzed.

1-Pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, and 2-methyl-2-butanol were determined by gas chromatography using a 2 m × 3 mm column packed with Porapack Q 80/100. The detection was carried out with a flame ionization detector after mass dilution of the sample with water by a factor of 5. The glass insert of the chromatograph injector was filled with silica wool so that the salt does not enter into the column. 1-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 the aqueous phase was obtained by evaporation at 105 °C of a known mass of

Table 1. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + 1-Pentanol (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				
				0.002	100.0
Two Liquid Phases + One Solid Phase					
73.5	26.4	0.18	4.84	0.048	95.1
Two Liquid Phases					
73.9	25.9	0.19	4.92	0.048	95.0
76.9	22.9	0.26	5.51	0.039	94.5
79.9	19.8	0.32	6.09	0.035	93.9
82.9	16.6	0.46	6.75	0.029	93.2
86.1	13.2	0.61	7.40	0.026	92.6
89.5	9.70	0.85	8.19	0.018	91.8
92.8	5.99	1.23	9.20	0.013	90.8
96.2	2.04	1.74	9.92	0.006	90.1
97.9		2.11	10.6		89.4

Table 2. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + 2-Pentanol (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				
				0.015	100.0
Two Liquid Phases + One Solid Phase					
73.5	26.2	0.30	4.86	0.025	95.1
Two Liquid Phases					
73.9	25.8	0.32	5.00	0.022	95.0
76.7	22.9	0.44	5.70	0.021	94.3
79.6	19.8	0.59	6.14	0.020	93.8
82.6	16.6	0.83	6.81	0.019	93.2
85.3	13.5	1.15	7.69	0.014	92.3
88.6	9.68	1.71	8.57	0.011	91.4
91.6	5.91	2.45	9.55	0.010	90.4
94.4	2.05	3.58	10.9	0.004	89.1
95.6		4.45	11.5		88.5

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Table 3. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + 3-Pentanol (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				
				0.0047	100.0
Two Liquid Phases + One Solid Phase					
73.5	26.2	0.28	4.08	0.0065	95.9
Two Liquid Phases					
74.1	25.6	0.30	4.23	0.0065	95.8
77.3	22.3	0.47	4.72	0.0052	95.3
79.7	19.6	0.65	5.24	0.0046	94.8
82.7	16.4	0.94	5.70	0.0039	94.3
85.7	13.0	1.36	6.25	0.0031	93.8
88.6	9.43	2.01	6.98	0.0025	93.0
91.3	5.76	2.92	7.55	0.0023	92.5
93.8	1.95	4.26	8.27	0.0008	91.7
94.8		5.16	8.72		91.3

Table 4. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + 2-Methyl-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					
74.1	25.9				
				0.002	100.0
Two Liquid Phases + One Solid Phase					
73.4	26.4	0.20	4.03	0.028	95.9
Two Liquid Phases					
74.6	25.2	0.24	4.17	0.028	95.8
77.0	22.7	0.30	4.61	0.025	95.4
80.0	19.6	0.43	5.04	0.021	94.9
83.0	16.4	0.60	5.52	0.018	94.5
86.1	13.1	0.83	5.98	0.017	94.0
89.4	9.55	1.08	6.70	0.011	93.3
92.5	5.86	1.59	7.26	0.007	92.7
95.7	2.02	2.28	7.94	0.002	92.1
97.2		2.79	8.49		91.5

Table 5. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + 2-Methyl-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				
				0.002	100.0
Two Liquid Phases + One Solid Phase					
73.2	26.1	0.72	7.32	0.028	92.7
Two Liquid Phases					
75.8	23.3	0.97	8.25	0.025	91.7
78.5	20.2	1.35	9.37	0.020	90.6
81.4	16.9	1.67	10.2	0.018	89.8
83.7	13.5	2.80	12.1	0.017	87.9
86.0	10.0	3.99	13.8	0.011	86.2
87.9	6.05	6.02	15.0	0.007	85.0
89.4	2.14	8.49	18.7	0.002	81.3
89.8		10.2	21.3		78.7

sample. The salt concentration in the organic phase was determined 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 10/1 to 50/1. More pentanol 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 chloride aqueous standards were also saturated with each one of the alcohols analyzed.

The relative accuracy of the mass fraction measurements was 1% for all components except for sodium chloride in the organic phase which was 5%. The concentrations obtained with the value of accuracy and the known overall composition of the heterogeneous mixture were used to check the mass balance and fit the results following a method of data reconciliation (Gomis et al., 1997). The results reported correspond to the values obtained using this method.

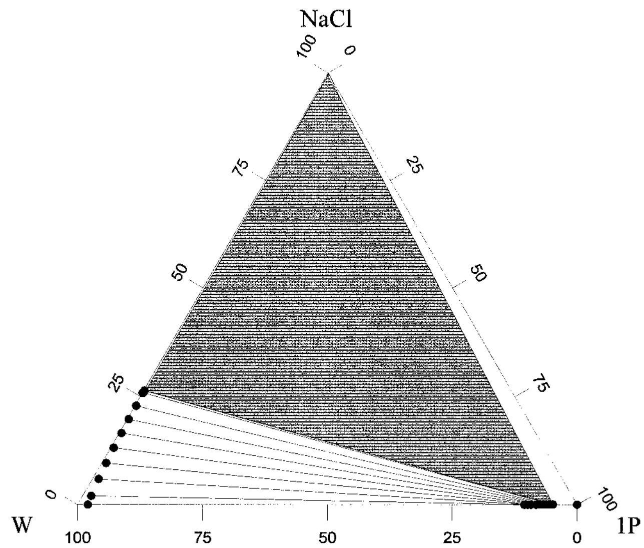

Figure 1. Representation of the equilibrium data (% mass) for the ternary system water (W) + sodium chloride (NaCl) + 1-pentanol (1P).

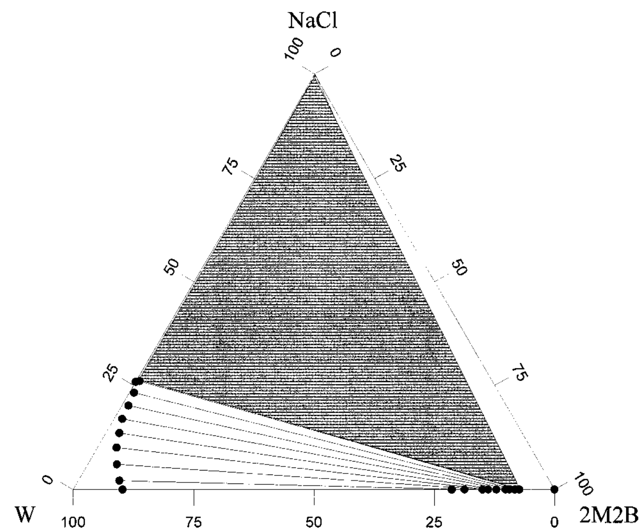

Figure 2. Representation of the equilibrium data (% mass) for the ternary system water (W) + sodium chloride (NaCl) + 2-methyl-2-butanol (2M2B).

Table 6. Setschenov Constants (K_s) and Correlation Coefficients (R^2) for the Systems Water + Sodium Chloride + Pentanols

	aqueous phase		organic phase	
alcohol	K_s	R^2	K'_s	R^2
1-pentanol	0.0821	0.9995	0.0287	0.9942
2-pentanol	0.0910	0.9997	0.0317	0.9967
3-pentanol	0.0967	0.9970	0.0274	0.9922
2-methyl-1-butanol	0.0858	0.9986	0.0274	0.9960
2-methyl-2-butanol	0.0897	0.9954	0.0418	0.9859

Results

Tables 1−5 present the experimental data obtained for each one of the systems. The representation of these data

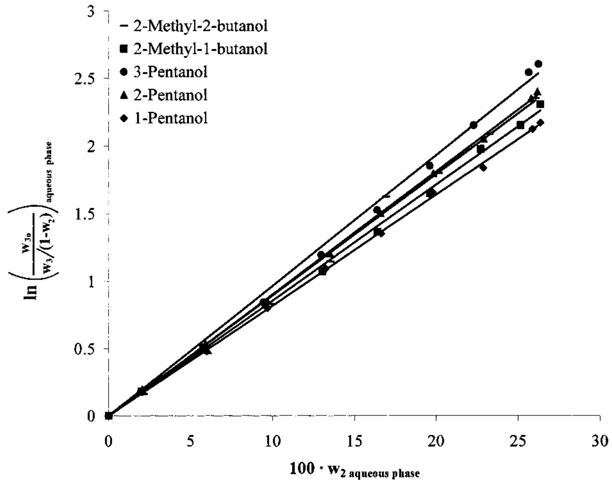

Figure 3. Correlation of the liquid−liquid equilibrium data of the aqueous phase with the Setschenov equation (water (1) + NaCl (2) + pentanols (3)).

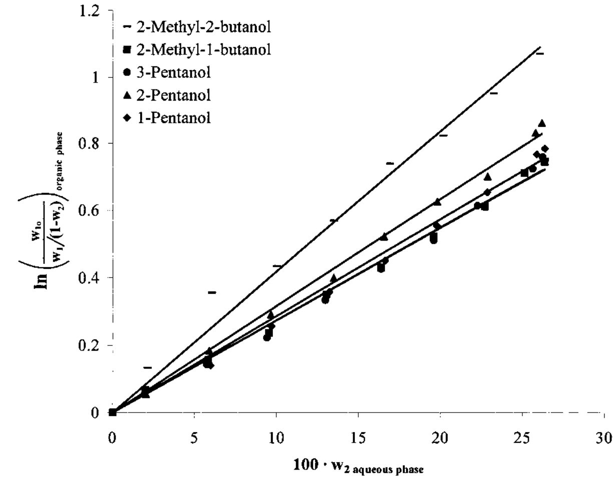

Figure 4. Correlation of the liquid−liquid equilibrium data of the organic phase with the Setschenov equation (water (1) + NaCl (2) + pentanols (3)).

gives similar equilibrium diagrams for all of them. As examples Figures 1 and 2 show the representation of the equilibrium diagrams of the systems water + sodium chloride + 1-pentanol and water + sodium chloride + 2-methyl-2-butanol.

Figure 3 represents the application of the Setschenov equation on a weight fraction and free salt scale (Gomis et al., 1999) to the aqueous phase

$$\ln\left(\frac{w_{3o}}{w_3/(1-w_2)}\right)_{\text{aqueous phase}} = K_s w_{2\ \text{aqueous}}$$

and Figure 4 to the organic phase

$$\ln\left(\frac{w_{1o}}{w_1/(1-w_2)}\right)_{\text{organic phase}} = K'_s w_{2\ \text{aqueous}}$$

where w_{1o} and w_{3o} represent the mass fraction solubilities without salt of water in the organic solvent and of the solvent in water, respectively. K_s and K'_s are constants which measure the magnitude of the salting out effect: the decrease in solubility by the presence of salt.

As can be seen in Table 6, the equilibrium data obtained are almost perfectly fitted by the equation. The values of K_s of the aqueous phase are very similar for all of the pentanols. For the organic phases the K'_s are also similar except for 2-methyl-2-butanol which presents the most important decrease in solubility of water.

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