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Liquid−Liquid Equilibria for Water + 2,3-Butanediol + 3-Methyl-1-Butanol with Sodium Sulfate and Sodium Carbonate at 303.15 K

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Liquid−Liquid equilibria at 303.15 K were measured for water + 2,3-butanediol + 3-methyl-1-butanol with and without sodium sulfate and sodium carbonate. Complete phase diagrams were obtained by evaluating the solubility and tie-line results for ternary and quaternary systems. The consistency of the tie-line results was ascertained using Othmer−Tobias plots. The effect of salts on the distribution coefficient and selectivity of 2,3-butanediol was studied. Sodium carbonate was found to have more salting out power. Addition of salt was, therefore, found to improve not only the extracting power of the solvent but also the selectivity of the solvent for 2,3-butanediol.

Introduction

2,3-Butanediol, a value added chemical produced by fermentation, is recovered from fermentation broth by solvent extraction. Othmer *et al.* (1945) suggested the use of solvents like butan-1-ol, butylene glycol diacetate, butyl acetate, and methylvinylcarbinol acetate. Escudero and Cabezas (1994) investigated the extraction of 2,3-butanediol with chlorinated hydrocarbon and phenolic compounds. Sharma *et al.* (1994) investigated extraction using 3-methyl-1-butanol, butan-1-ol, 2-methyl-2-pentanone, tributyl phosphate, and butyl acetate. It has been found that solvents having good extracting power for 2,3-butanediol in aqueous solution usually have a low selectivity which results in extraction of water along with 2,3-butanediol in the solvent phase. Therefore, the possibility of enhancing the selectivity as well as distribution coefficient was investigated.

This work reports the effect of sodium carbonate and sodium sulfate at 303.15 K on the mutual solubility and tie lines for the system water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3). 3-Methyl-1-butanol was used as the extracting solvent and was selected on the basis of earlier studies (Sharma *et al.*, 1994).

Experimental Section

Chemicals. 3-Methyl-1-butanol was of analytical grade and was used without further purification. Anhydrous sodium sulfate and sodium carbonate were of analytical grade. 2,3-Butanediol was obtained from Merk with a purity of 98% and used as such. Double distilled water was used throughout the experimental study.

Procedure. Mutual solubilities and tie lines for water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) at 303.15 K were determined using the procedure of Othmer *et al.* (1941). The temperature was maintained within ±0.5 K of the experimental temperature. A microburet calibrated to ±0.02 cm^3 was used for the titration. Mutual solubility curves of the quaternary water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) + sodium carbonate (s) and water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) + sodium sulfate (s) were determined by the procedure adopted by Swabb and Mongan (1952). A 3 cm^3 volume of the solvent and a known mass of fine dry crystals of the salt were titrated carefully with water and 2,3-butanediol separately. The titrations were so adjusted that the disappearance of the two liquid phases closely coincided with the dissolution of all but a couple of the salt crystals. The solvent side of the solubility curve requires very careful observations of disappearance of the liquid phases to obtain the correct end point. For studies on the water rich side of the solubility curve, 3 cm^3 of solution containing a known mass of 2,3-butanediol, water, and salt was titrated with 3-methyl-1-butanol solvent. The tie-line data for the pseudoternary systems were obtained by the method used for the ternary system. The 2,3-butanediol concentration was determined by a GLC-PE Model Sigma 3B equipped with an FID, using a stainless steel column (2.5m × 1/8 in. O.D.) packed with chromosorb 101 (80/100 mesh) coated with 3% FFAP as described earlier by Sharma *et al.* (1994). The complete compositions of the conjugated layers were obtained from the binodal curve. The mutual solubility points were determined in triplicate, and the average value was considered. The mass fraction was accurate to ±0.0028. The salts were weighed on a precision Mettler AE163 analytical balance with an accuracy of ±0.0001 g.

Table 1. Mutual Solubility Data and Tie Lines for Water (1) + 2,3-Butanediol (2) + 3-Methyl-1-Butanol (3)[a]

w_1	w_2	w_3	w_1	w_2	w_3
0.987		0.013	0.456	0.292	0.252
0.838	0.140	0.022	0.339	0.282	0.379
0.753	0.212	0.035	0.244	0.221	0.535
0.691	0.252	0.056	0.188	0.162	0.650
0.600	0.292	0.108	0.133	0.066	0.801
0.548	0.294	0.158	0.094		0.906

water-rich layer			solvent-rich layer		
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}
0.950	0.032	0.018	0.090	0.020	0.890
0.906	0.076	0.018	0.100	0.029	0.871
0.852	0.128	0.020	0.110	0.040	0.850
0.830	0.149	0.021	0.120	0.060	0.820
0.775	0.195	0.030	0.131	0.080	0.790

[a] w = mass fraction.

Results and Discussion

The experimental results, in mass fraction, for the mutual solubility and tie lines of the ternary system water

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Table 2. Mutual Solubility Data for Water (1) + 2,3-Butanediol (2) + 3-Methyl-1-butanol (3) in the Presence of Sodium Sulfate (4) or Sodium Carbonate (5)[a]

w_1	w_2	w_3	w_s
	$w_4 = 0.10$		
0.890		0.011	0.099
0.757	0.140	0.081	0.084
0.696	0.206	0.021	0.077
0.657	0.243	0.027	0.073
0.595	0.286	0.053	0.066
0.553	0.307	0.079	0.061
0.343	0.346	0.279	0.031
0.216	0.326	0.488	0.019
0.180	0.267	0.536	0.017
0.158	0.186	0.642	0.014
0.133	0.146	0.708	0.012
	$w_5 = 0.10$		
0.900		0.010	0.090
0.757	0.151	0.016	0.076
0.682	0.227	0.022	0.068
0.585	0.292	0.064	0.058
0.552	0.322	0.072	0.053
0.540	0.330	0.080	0.050
0.230	0.410	0.319	0.039
0.199	0.395	0.382	0.024
0.162	0.369	0.446	0.023
0.165	0.313	0.504	0.019
0.134	0.249	0.601	0.016
0.108	0.151	0.727	0.014
0.076		0.916	0.076

[a] w = mass fraction.

Table 3. Tie Lines for Water (1) + 2,3-Butanediol (2) + 3-Methyl-1-butanol (3) in the Presence of Sodium Sulfate (4) or Sodium Carbonate (5) (Salt-Free Basis)[a]

water-rich layer			solvent-rich layer		
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}
		$w_4 = 0.10$			
0.970	0.025	0.010	0.090	0.030	0.880
0.952	0.039	0.010	0.095	0.058	0.848
0.928	0.062	0.010	0.110	0.085	0.805
0.897	0.093	0.010	0.115	0.099	0.786
		$w_5 = 0.10$			
0.975	0.021	0.004	0.077	0.031	0.892
0.953	0.041	0.006	0.085	0.072	0.843
0.938	0.052	0.010	0.090	0.098	0.812
0.915	0.075	0.010	0.097	0.125	0.778

[a] w = mass fraction.

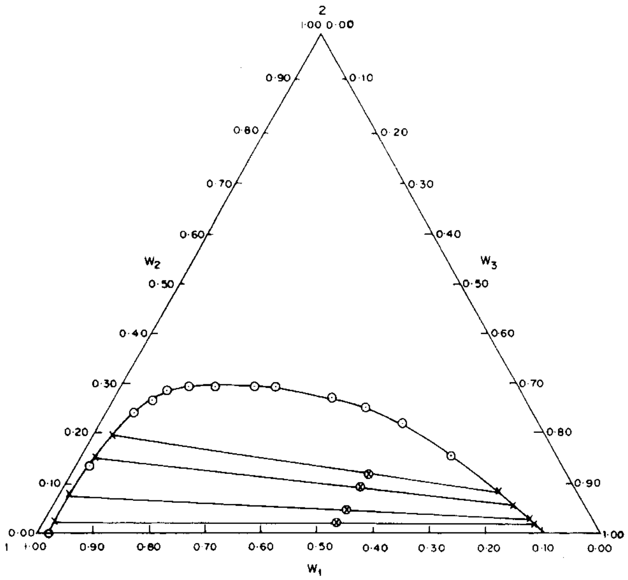

Figure 1. Ternary diagram for experimental liquid–liquid equilibria of water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) without salt at 303.15 K: ○, solubility results; ×, tie-line values; ⊗, overall composition for the tie-line.

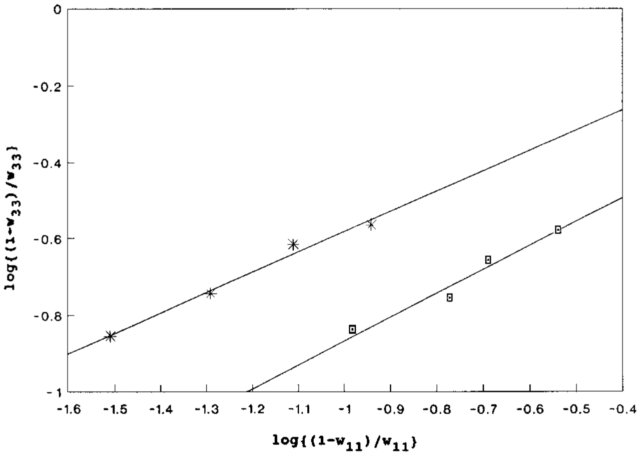

Figure 2. Othmer–Tobias correlation for water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) with and without sodium sulfate (4): ⊡, no salt; ∗, $w_4 = 0.10$.

(1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) are given in Table 1 and those of the pseudoternary systems, with sodium sulfate and sodium carbonate, are given in Tables 2 and 3. Mutual solubility curves along with tie-lines and mixture compositions for ternary system have been plotted on a triangular diagram and is shown in Figure 1.

The two-phase region has been found to increase on addition of salt which was further found to increase with an increase in the salt concentration. The area of heterogeneity in the presence of $w_s = 0.1$ sodium sulfate is nearly 1.2-fold greater than that of the basic ternary, and with $w_s = 0.1$ sodium carbonate it is 1.5-fold greater, indicating that sodium carbonate has a greater salting out effect than sodium sulfate.

The reliability of measured tie-line compositions was ascertained by the Othmer–Tobias (1941) correlation method by plotting $\log\{(1 - w_{11})/w_{11}\}$ against $\log\{(1 - w_{33})/w_{33}\}$; the equation involved is

$$(1 - w_{33})/w_{33} = K\{(1 - w_{11})/w_{11}\}^n \qquad (1)$$

where w_{11} is the mass fraction of water (1) in the aqueous phase, w_{33} is the mass fraction of solvent (3) in the solvent phase, and K and n are Othmer–Tobias constants. Figures 2 and 3 show, with both the salts, a linear dependency of the plot of $\log\{(1 - w_{11})/w_{11}\}$ against $\log\{(1 - w_{33})/w_{33}\}$, indicating the consistency of the results.

Figures 4 and 5 represent the distribution curves in the presence of sodium sulfate and sodium carbonate, respectively. The curves are obtained by plotting the mass fraction of 2,3-butanediol in the aqueous phase (w_{21}) against the mass fraction of 2,3-butanediol in the solvent phase (w_{23}). The distribution curves clearly indicate that sodium carbonate has more salting out power than sodium sulfate. Addition of sodium carbonate and sodium sulfate at $w_s = 0.10$ salt concentration increases the distribution coefficient from 0.6 to 1.48 and 1.2, respectively.

The selectivity values were also calculated to ascertain their variation on addition of salts. It is found that the presence of salt has a pronounced effect on the selectivity, and this can be observed from Figures 6 and 7, which have $w_{23}/(w_{23} + w_{13})$ on the ordinate and $w_{21}/(w_{21} + w_{11})$ on the abscissa on a salt free basis, where w_{21}, w_{23}, and w_{11} are as described earlier and w_{13} is the mass fraction of water

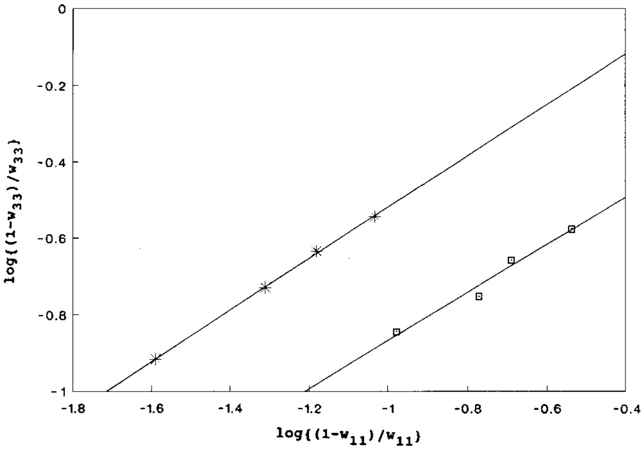

Figure 3. Othmer–Tobias correlation for water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) with and without sodium sulfate (4): ⊡, no salt; ∗, $w_5 = 0.10$.

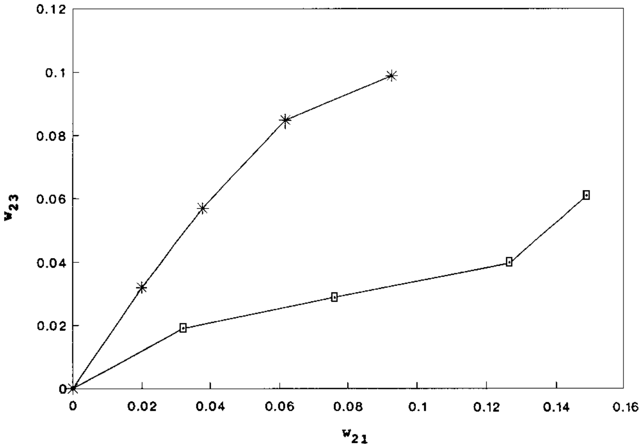

Figure 4. Distribution of 2,3-butanediol (2) between water (1) and 3-methyl-1-butanol (3) with and without sodium sulfate (4): ⊡, no salt; ∗, $w_4 = 0.10$.

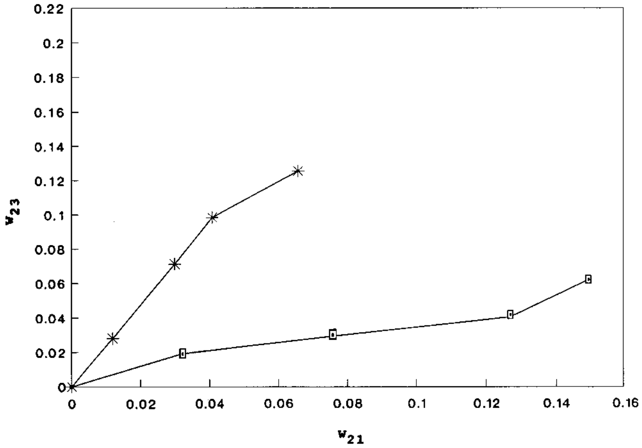

Figure 5. Distribution of 2,3-butanediol (2) between water (1) and 3-methyl-1-butanol (3) with and without sodium sulfate (5): ⊡, no salt; ∗, $w_5 = 0.10$.

in the solvent phase. The selectivity has been found to increase from 6.59 to 18.84 and 12.93 with sodium carbonate and sodium sulfate, respectively, at $w_s = 0.10$ salt concentration. Observation also indicates that the greater salting out effect in the case of sodium carbonate is due to the carbonate ion. This is probably because the size of the carbonate ion is smaller than that of the sulfate ion. Moreover, the solubility of sodium carbonate in water is greater than that of sodium sulfate. It has been shown by Glasstone (1956) that the smaller the size of the ion and the greater the charge it carries, the greater is the salting out effect. The hydration or solvation number of salts, defined as the number of moles of solvent carried per mole of salt, is also one of the factors responsible for the salting out effect (Glasstone, 1956) which is apparent as sodium carbonate has a solvation number of 19.1 while sodium sulfate has a solvation number of 18.2 (Hinton and Amis, 1971).

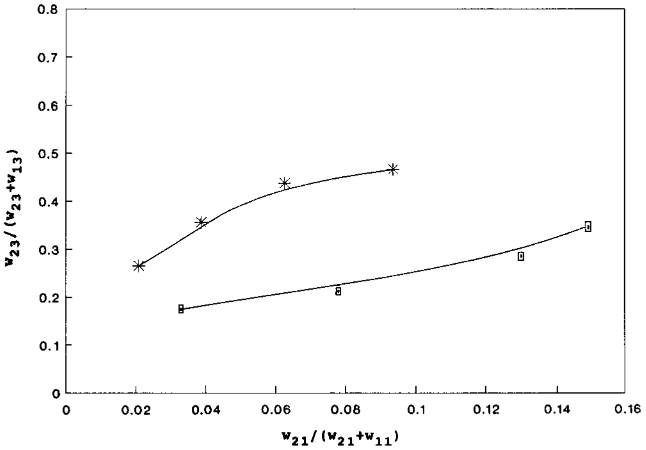

Figure 6. Selectivity diagram for water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) with and without sodium sulfate (4): ⊡, no salt; ∗, $w_4 = 0.10$.

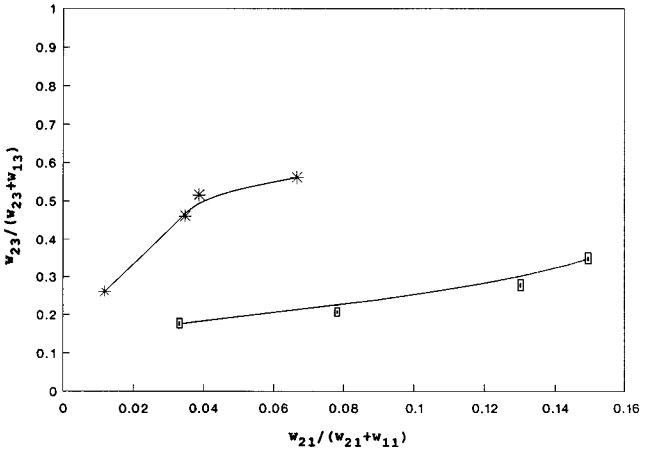

Figure 7. Selectivity diagram for water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) with and without sodium sulfate (5): ⊡, no salt; ∗, $w_5 = 0.10$.

Conclusions

The addition of sodium carbonate and sodium sulfate improved 2,3-butanediol extraction from the aqueous phase with 3-methyl-1-butanol. This improvement results from the salting out effect which modifies the phase equilibria of the system water + 2,3-butanediol + 3-methyl-1-butanol, increasing the distribution coefficient for 2,3-butanediol and selectivity of the solvent which have a direct effect on the amount of solvent and the number of equilibrium stages required for extraction. The results obtained in this investigation indicate an improved extraction for value added chemicals such as 2,3-butanediol using salts.

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