Table X. Experimental Distribution Coefficients D_i of Water (i = 1) and 2-Propanol (i = 2) and Separation Factors ($S = D_2/D_1$)^a

system no.	D_2	D_1	S
1	3.647	0.127	28.72
2	3.612	0.128	28.20
3	0.477	0.023	20.74
4	2.442	0.284	8.60
5	1.832	0.283	6.47
6	2.535	0.134	11.53
7	2.398	0.150	15.97
8	0.510	0.019	26.84
9	3.495	0.089	39.27

[a] Composition range: 10 – 20 wt % of 2-propanol in water.

The results are listed in Table X.

Conclusions

A survey of the literature indicates that no LLE data are available for the present ternaries, except the water + 2-propanol + 1,2-dichloroethane system. Our tie-line data are in fair agreement, but the binodal curve compares well with those reported by Izmailov and Franke (*1*).

It appears that ternaries 4–7 represent type IC systems, whereas 1, 2, and 8 are considered type IB systems. Besides, ternaries 3 and 9 seem to be in the IC category rather than IB (*2*).

Unfortunately, in the determination of mutual solubilities for IC systems there is some loss of accuracy up to 50% in weight fraction of dissolved component.

It can be mentioned that no solutropic system was observed among the studied ternaries.

Industrial purposes usually require D_i values higher than 0.2 and separation factors higher than 10 (*3*, *4*). Therefore, the studied solvents may serve as separating agents for 2-propanol, except phenylmethanol, cyclohexanol, and 1-pentanol. The best results were obtained with dibenzyl ether and octanenitrile. Unfortunately, these are toxic and expensive solvents. Outstanding advantages of high-boiling solvents in separating substances from dilute aqueous solutions have recently been reported by some researchers (*5*–*8*). The solute will be the only overhead product if the solvent has a higher boiling point. With higher solvent/solute ratios, the energy consumption of stripping or distillation operations will be quite high if the solvent has a lower boiling point. Therefore, high-boiling solvents like 2-methylbutyl acetate and 1-methylcyclohexanol, showing very low solubility against water, are considered adequate separating agents for 2-propanol.

Glossary

W_i	weight percent of *i*th component
w_i	weight fraction of *i*th component
D_i	distribution coefficient of *i*th component, eq 1
S	separation factor, eq 2

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Equilibrium Diagrams at 20 °C of Water–Tartaric Acid–2-Methyl-1-propanol, Water–Tartaric Acid–1-Pentanol, and Water–Tartaric Acid–3-Methyl-1-butanol Ternary Systems

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The purpose of this work is to study the tartaric acid recovering possibilities from wine distillery wastewater through a liquid–liquid extracting process. 2-Methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol may be suitable as extracting solvents. Water–tartaric acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 20 °C. Partition coefficients are comprised between 0.07 and 0.42. 1-Pentanol seems to be the best solvent to extract tartaric acid from regeneration of ion-exchanging resins.

Introduction

Tartaric acid is extracted from natural substances. It is an organic acid used as an acidulant in the food processing and pharmaceutical industries (*1*). In order to recover tartaric acid from wine distillery wastewater, which is present with a concentration of about 3.4 g/L (*2*, *3*), we considered the possibility of using the liquid–liquid extracting process.

The solvation character of oxygen atoms tied to the carbon chain lends especially to alcohols extracting properties with regard to acids. Thus we have selected 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol.

Experimental Section

Chemicals. The solvents have been obtained with a purity of 98% (mass %) and the tartaric acid with a purity of 99% (mass %). The analysis by the high-performance liquid chromatography method bears out these purities.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device comprising separatory funnels maintained at the constant temperature of 20 ± 0.1 °C in a thermostated vessel. Several tartaric acid solutions at different concentrations were prepared to determine the tie lines.

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Table I. Ternary Diagram for Water (A)–Tartaric Acid (B)–2-Methyl-1-propanol (C) at 20 °C

(a) Binodal Curve Data, mass %

water	tartaric acid	2-methyl-1-propanol
93.3	0.0	6.7
92.2	1.0	6.8
91.1	2.1	6.8
88.6	4.5	6.9
83.4	9.7	6.9
78.5	14.6	6.9
73.6	19.2	7.2
68.7	24.1	7.2
64.0	28.7	7.3
59.4	33.3	7.3
55.0	37.6	7.4
51.1	41.4	7.5
46.0	46.4	7.6
42.8	49.3	7.9
38.8	53.1	8.1
17.9	22.8	59.3
17.3	19.7	63.0
17.2	16.1	66.7
17.1	8.2	74.7
16.8	3.8	79.4
16.6	1.7	81.7
16.5	0.3	83.2
16.1	0.1	83.8
16.0	0.0	84.0

(b) Mutual Solubility Data, mass %

water	tartaric acid	2-methyl-1-propanol
42.8	57.2	0
42.7	56.3	1.0
42.8	54.2	3.0
41.5	52.5	6.0
39.3	52.9	7.8
15.0	20.0	65.0
12.1	17.1	70.8
7.9	13.0	79.1
7.0	11.8	81.2
0	3.9	96.1

(c) Tie-Line Data, mass %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
91.1	2.1	6.8	16.5	0.3	83.2	0.14
88.6	4.5	6.9	16.5	0.8	82.7	0.18
73.6	19.2	7.2	16.8	3.8	79.4	0.20
68.7	24.1	7.2	16.8	5.1	78.1	0.21
59.4	33.3	7.3	17.1	8.2	74.7	0.25
55.0	37.6	7.4	17.1	10.6	72.3	0.28
46.0	46.4	7.6	17.2	16.1	66.7	0.35
42.8	49.3	7.9	17.3	19.7	63.0	0.40
38.8	53.1	8.1	17.9	22.8	59.3	0.43

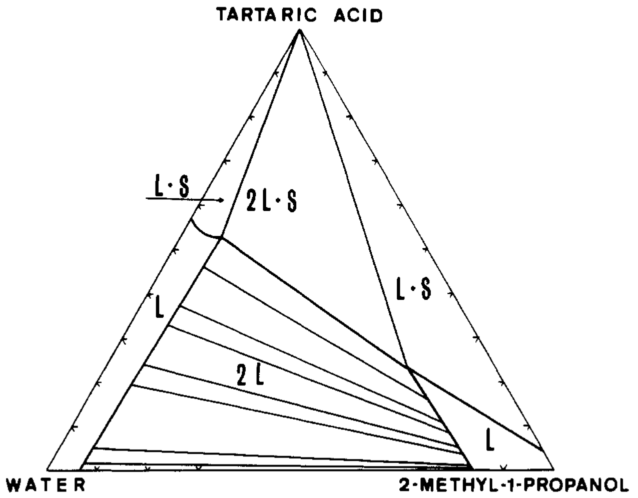

Figure 1. Water–tartaric acid–2-methyl-1-propanol phase diagram with tie lines at 20 °C: S = solid; L = liquid.

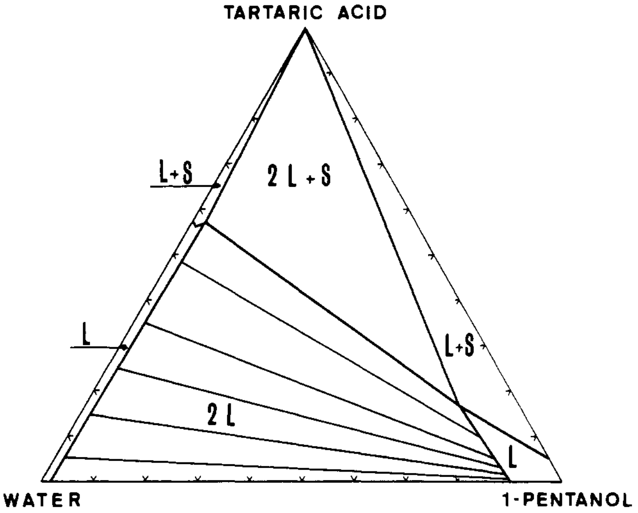

Figure 2. Water–tartaric acid–1-pentanol phase diagram with tie lines at 20 °C: S = solid; L = liquid.

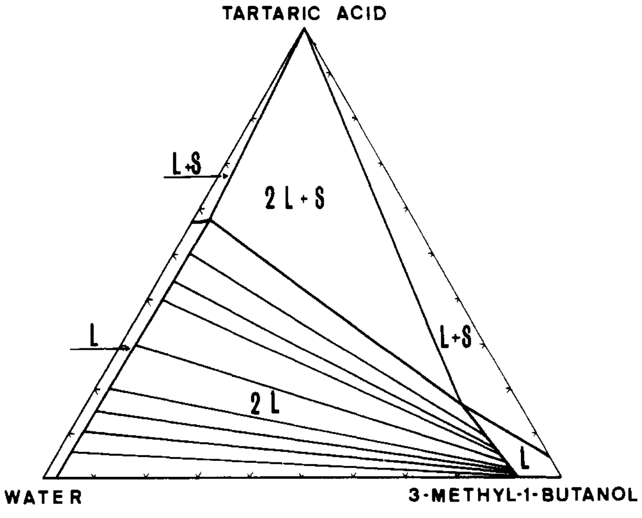

Figure 3. Water–tartaric acid–3-methyl-1-butanol phase diagram with tie lines at 20 °C: S = solid; L = liquid.

The solutions were mixed in glass-stoppered separatory funnels and then added to the solvent and shaken for 3 h. That the times allowed for the acid solute distribution equilibrium point and the amount of shaking were sufficient to establish equilibrium was proved by showing that increasing each did not alter the results. After decantation and after another 30 min had passed, tartaric acid, present in the phases in equilibrium, was neutralized with standard sodium hydroxide (0.1 or 1.0 M) and phenolphtalein used as indicator.

The amount of water in each phase at equilibrium was determined by the Karl-Fisher method. The error induced on tie-line compositions based upon five readings is less than 1% ($X \pm 0.01X$). Solid–liquid saturation curves were determined from saturated solutions, tartaric acid being titrated with standard sodium hydroxide (0.1 or 1.0 M).

Results and Discussion

Figures 1–3 were set at 20 °C from the data of Tables I–III. These figures represent solubility isotherms and tie-line curves of water–tartaric acid ternary systems with successive solvents: 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol. The three figures present a zone showing the solid phase, which corresponds to the type 4 classification proposed by Treybal

Table II. Ternary Diagram for Water (A)–Tartaric Acid (B)–1-Pentanol (C) at 20 °C

(a) Binodal Curve Data, mass %

water	tartaric acid	1-pentanol
98.2	0.0	1.8
93.5	4.7	1.8
88.4	9.7	1.9
82.9	14.9	2.2
77.8	20.0	2.2
73.3	24.6	2.1
66.9	30.9	2.2
62.9	34.8	2.3
57.4	40.3	2.3
52.5	45.3	2.2
49.6	48.2	2.2
45.7	52.1	2.2
40.0	57.7	2.3
11.8	16.5	71.7
11.6	12.9	75.5
11.3	9.8	78.9
11.2	8.6	80.2
10.9	6.7	82.4
10.9	5.2	83.9
10.5	4.2	85.3
10.4	2.9	86.7
10.3	2.2	87.5
10.1	1.6	88.3
9.9	1.0	89.1
9.8	0.4	89.8
9.8	0.0	90.2

(b) Mutual Solubility Data, mass %

water	tartaric acid	1-pentanol
42.8	57.2	0.0
42.7	56.1	1.2
41.7	56.5	1.8
40.5	57.5	2.0
9.9	15.0	75.1
7.1	12.9	80.8
3.7	9.3	87.0
2.6	7.2	90.2
0.0	5.5	94.5

(c) Tie-Line Data, mass %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
93.5	4.7	1.8	9.8	0.4	89.8	0.09
82.9	14.9	2.2	10.1	1.6	88.3	0.11
73.3	24.6	2.1	10.4	2.9	86.7	0.12
62.7	34.8	2.5	10.9	5.2	83.9	0.15
52.5	45.3	2.2	11.2	8.6	80.2	0.19
49.6	48.2	2.2	11.4	9.8	78.8	0.20
40.0	57.7	2.3	11.7	16.5	71.8	0.29

Table III. Ternary Diagrams for Water (A)–Tartaric Acid (B)–3-Methyl-1-butanol (C) at 20 °C

(a) Binodal Curve Data, mass %

water	tartaric acid	3-methyl-1-butanol
97.5	0.0	2.5
94.5	2.9	2.6
91.4	6.0	2.6
87.6	9.8	2.6
82.3	15.0	2.7
77.6	19.6	2.8
72.4	24.8	2.8
67.9	29.1	3.0
62.2	34.8	3.0
57.1	39.9	3.0
52.6	44.3	3.1
47.2	50.0	2.8
39.6	57.4	3.0
11.1	15.9	73.0
10.9	8.5	80.6
10.4	6.6	83.0
10.1	5.3	84.6
10.0	4.3	85.7
9.9	3.2	86.9
9.8	2.4	87.8
9.6	1.8	88.6
9.4	1.2	89.4
9.3	0.8	89.9
9.3	0.4	90.3
9.0	0.2	90.8
8.8	0	91.2

(b) Mutual Solubility Data, mass %

water	tartaric acid	3-methyl-1-butanol
42.8	57.2	0.0
42.1	56.6	1.3
41.4	57.2	1.4
40.1	57.0	2.9
9.2	14.8	76.0
6.3	11.7	82.0
6.2	10.9	82.9
4.3	8.6	87.1
2.9	6.5	90.6
0.0	3.9	96.1

(c) Tie-Line Data, mass %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
91.4	6.0	2.6	9.3	0.4	90.3	0.07
87.6	9.8	2.6	9.3	0.8	89.9	0.08
82.3	15.0	2.7	9.4	1.2	89.4	0.08
77.6	19.6	2.8	9.6	1.8	88.6	0.09
67.9	29.1	3.0	9.9	3.2	86.9	0.11
57.1	39.9	3.0	10.1	5.3	84.6	0.11
52.6	44.3	3.1	10.4	6.6	83.0	0.15
47.2	49.9	2.9	10.9	8.5	80.6	0.17
39.6	57.4	3.0	11.1	15.9	73.0	0.28

(*4*). The partition coefficient (m) is defined as the ratio of acid concentration (mass percent) in the organic phase to acid concentration (mass percent) in the aqueous phase. Tartaric acid partition coefficients between water and successively 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol for different acid concentrations at 20 °C are indicated in Tables I–III. 2-Methyl-1-propanol presents the most important partition coefficients ($0.15 < m < 0.44$), whereas 3-methyl-1-butanol presents the lowest partition coefficients ($0.07 < m < 0.28$).

2-Methyl-1-propanol, which presents the best partition coefficient (Table Ic), is the most soluble in water (Figure 1). 1-Pentanol seems to be the best solvent to extract tartaric acid from effluents resulting from the regeneration of ion-exchanging resins.

Glossary

X_A	mass percent of water in one phase
X_B	mass percent of tartaric acid in one phase
X_C	mass percent of alcohol in one phase
X_{BR}	mass percent of tartaric acid in aqueous phase
X_{BE}	mass percent of tartaric acid in alcoholic phase
X_{AR}	mass percent of water in aqueous phase
X_{AE}	mass percent of water in alcoholic phase
m	partition coefficient

Registry No. Tartaric acid, 87-69-4; water, 7732-18-5; 2-methyl-1-propanol, 78-83-1; 1-pentanol, 71-41-0; 3-methyl-1-butanol, 123-51-3.

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