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Received for review November 23, 1987. Revised May 31, 1988. Accepted July 19, 1988. Financial support from STATOIL, Norway is gratefully acknowledged.

Equilibrium Diagrams at 19 °C of Water–Malic Acid–2-Methyl-1-propanol, Water–Malic Acid–1-Pentanol, and Water–Malic Acid–3-Methyl-1-butanol Ternary Systems

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The purpose of this work is to study the malic 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–malic acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 19 °C. Partition coefficients are comprised between 0.18 and 0.75. 3-Methyl-1-butanol is the most selective solvent with regard to malic acid.

Introduction

Malic acid is a costly product that 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 malic acid from wine distillery wastewater, which is present with a concentration rate of about 3.4 g/L (*2*), we considered the possibility of using the liquid–liquid extracting process.

Previous works about malic acid extraction by different solvents (methyl isobutyl ketone, methylisobutylcarbinol, *n*-octyl alcohol, oleoyl alcohol, 2-methyl-1-propanol and ether) show fairly weak values for the partition coefficient, located between 0.018 and 0.12 (*3*–*5*).

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. Solvents, with a minimum purity of 98%, have been obtained from Prolabo. Malic acid (Prolabo) had a purity of 99%.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device maintained at the constant temperature of 19 ± 0.1 °C in a thermostated vessel. Several malic acid solutions at different concentrations were prepared to determine the tie lines. The solutions were mixed in glass-stoppered separatory funnels and then added to the solvent and shaken for 30 min. 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 waiting for another 30 min, malic acid, present in the phases in equilibrium, was neutralized with standard sodium hydroxide (0.1 or 1.0 N) and phenolphthalein used as indicator. The error induced when titrating and weighing is less than 1%.

The cloud-point method was used to determine liquid–liquid solubility isotherms. Solubility points were obtained with a relative accuracy of 1%. Solid–liquid saturation curves were determined from saturated solutions, malic acid being titrated with standard sodium hydroxide (1.0 N).

Results and Discussion

Figures 1–3 were set at 19 °C from the data of Tables I–III. These figures represent solubility isotherms and tie-line curves of water–malic acid ternary systems with successive solvents:

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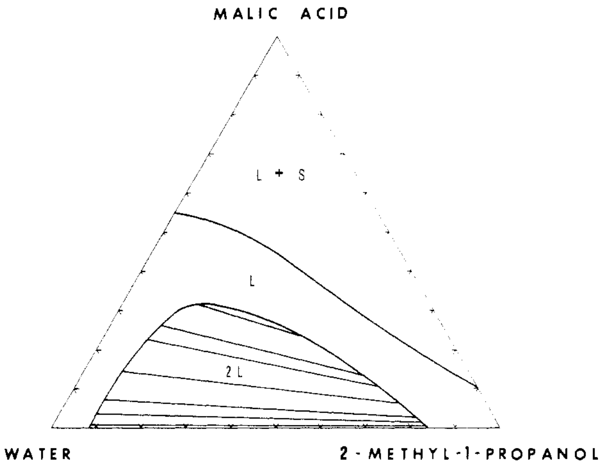

Figure 1. Water-malic acid-2-methyl-1-propanol phase diagram with tie lines at 19 °C. S = solid; L = liquid.

Table I. Ternary Diagram for Water (A)-Malic Acid (B)-2-Methyl-1-propanol (C) at 19 °C

water	malic acid	2-methyl-1-propanol
(a) Binodal Curve Data, wt %		
91.77	0	8.23
90.91	0.46	8.63
90.68	0.92	8.40
86.86	4.57	8.57
82.33	9.15	8.52
76.05	15.21	8.74
72.93	18.23	8.84
62.25	26.68	11.07
56.47	30.06	13.47
49.64	31.59	18.77
47.68	31.79	20.53
46.84	31.01	22.15
41.70	29.00	29.30
38.43	26.39	35.18
33.73	24.62	41.65
31.78	22.74	45.48
29.27	20.75	49.98
27.12	18.22	54.66
25.41	16.47	58.12
23.50	13.77	62.73
22.82	13.12	64.06
20.30	7.97	71.73
18.93	5.67	75.40
18.17	4.09	77.74
16.22	0.84	82.94
16.16	0.42	83.42
16.43	0	83.57
(b) Mutual Solubility Data, wt %		
45.22	54.78	0
29.12	46.02	24.86
18.98	33.16	47.86
9.00	19.88	71.12
0	11.69	88.31

(c) Tie-Line Data, wt %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
91.2	0.36	8.44	16.2	0.13	83.67	0.36
90.9	0.73	8.37	16.4	0.25	83.35	0.34
87.8	3.61	8.59	16.6	1.31	82.09	0.36
84.2	7.31	8.49	17.5	2.79	79.71	0.38
76.5	14.83	8.67	19.5	6.27	74.23	0.42
67.1	22.79	10.11	22.0	10.48	67.52	0.46
62.9	26.06	11.04	24.1	13.37	62.53	0.51
50.8	31.50	17.70	32.8	23.52	43.68	0.75

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 (*6*).

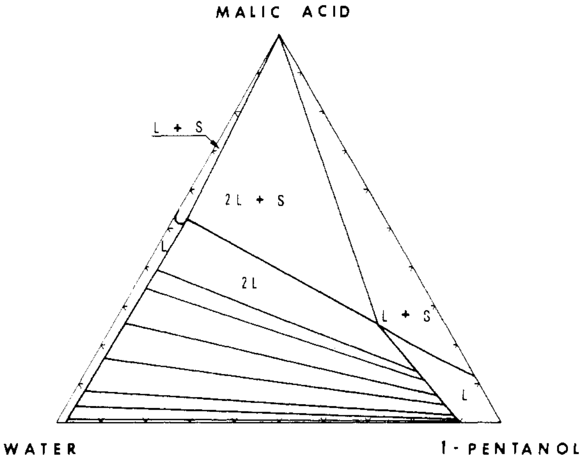

Figure 2. Water-malic acid-1-pentanol phase diagram with tie lines at 19 °C. S = solid; L = liquid.

Table II. Ternary Diagram for Water (A)-Malic Acid (B)-1-Pentanol (C) at 19 °C

water	malic acid	1-pentanol
(a) Binodal Curve Data, wt %		
97.96	0	2.04
96.90	0.49	2.61
96.28	0.97	2.75
92.79	4.88	2.33
87.94	9.77	2.29
78.32	19.56	2.12
68.94	29.26	1.80
58.47	38.98	2.55
53.54	43.80	2.66
52.35	44.93	2.72
49.27	47.83	2.90
13.86	24.92	61.22
13.50	20.82	65.68
13.33	17.48	69.19
12.51	13.12	74.37
11.71	8.83	79.46
10.48	5.82	83.70
10.95	4.46	84.59
9.99	0.90	89.11
10.00	0.45	89.55
9.84	0	90.16
(b) Mutual Solubility Data (wt %)		
45.22	54.78	0
46.87	52.19	0.94
47.00	50.90	2.10
14.05	24.42	61.54
12.85	22.30	64.86
10.49	21.21	68.31
7.49	17.76	74.75
4.87	15.11	80.02
0	12.20	87.80

(c) Tie-Line Data, wt %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
97.7	0.41	1.89	9.7	0.09	90.21	0.22
97.2	0.85	1.95	9.8	0.19	90.01	0.22
93.5	4.17	2.33	9.9	0.94	90.10	0.23
89.3	8.28	2.42	10.0	1.98	88.02	0.24
81.1	16.71	2.19	10.3	4.16	85.54	0.25
71.9	25.45	2.65	11.1	6.90	82.00	0.27
62.6	34.50	2.90	12.0	10.90	77.10	0.32
57.9	39.12	2.98	12.1	12.81	75.09	0.33
44.9	52.01	3.09	14.5	22.84	62.66	0.44
44.5	52.39	3.11	15.1	25.09	59.81	0.48

The partition coefficient (m) is defined as the ratio of acid concentration (wt %) in organic phase to acid concentration (wt %) in aqueous phase. Malic acid partition coefficients between water and successively 2-methyl-1-propanol, 1-pen-

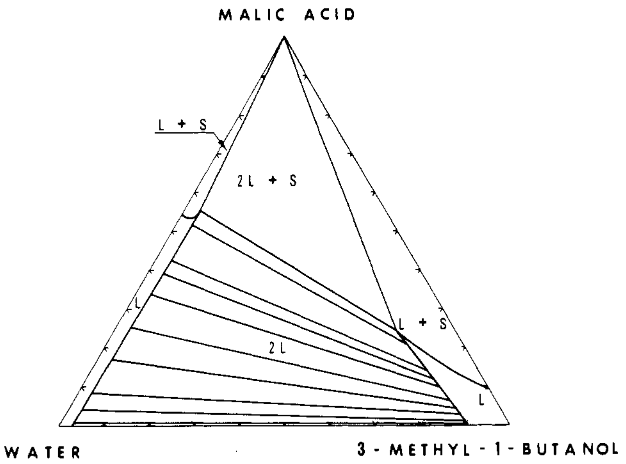

Figure 3. Water-malic acid-3-methyl-1-butanol phase diagram with tie lines at 19 °C. S = solid; L = liquid.

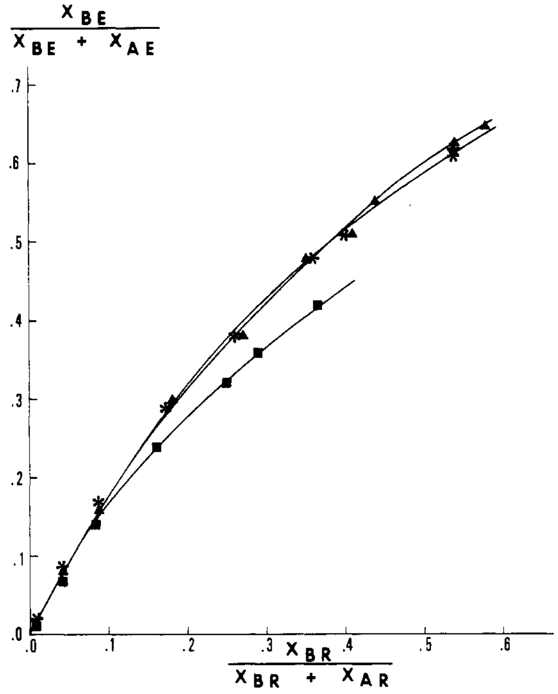

Figure 4. Selectivity diagrams at 19 °C for the systems (■) water-malic acid-2-methyl-1-propanol, (*) water-malic acid-1-pentanol, and (▲) water-malic acid-3-methyl-1-butanol.

tanol, and 3-methyl-1-butanol for different acid concentrations at 19 °C are indicated in Tables I-III. 2-Methyl-1-propanol presents the most important partition coefficients ($0.36 < m < 0.75$), whatever the concentration of the acid solution may be, whereas 3-methyl-1-butanol presents the lowest partition coefficients ($0.18 < m < 0.45$).

Figure 4 represents the selectivity curve of the three solvants versus malic acid in aqueous solution form. We carried out on the abcissa the weight fraction of solute in raffinate on a solvent-free basis and on the ordinate the weight fraction of solute in extract on a solvent-free basis. Figure 4 allows one to compare the diagrams of alcohol selectivity with regard to malic acid in water at 19 °C. (It shows that the three solvents have a selectivity of about the same value.)

2-Methyl-1-propanol, which presents the best partition coefficient (Table Ic) is the least selective (Figure 4) and the most soluble in water (Figure 1). 3-Methyl-1-butanol seems to be the best solvent to extract malic acid from effluents resulting from the regeneration of ion-exchanging resins.

Table III. Ternary Diagram for Water (A)-Malic Acid (B)-3-Methyl-1-butanol (C) at 19 °C

water	malic acid	3-methyl-1-butanol
(a) Binodal Curve Data, wt %		
97.39	0	2.61
96.83	0.49	2.68
96.42	0.97	2.61
92.48	4.87	2.65
87.57	9.73	2.70
77.74	19.44	2.82
67.95	29.12	2.93
57.97	38.64	3.39
53.03	43.49	3.48
49.32	47.34	3.34
48.22	48.22	3.56
45.71	50.58	3.71
43.91	53.67	2.42
13.02	24.16	62.82
11.89	19.58	68.53
11.82	15.87	72.31
11.00	13.35	75.65
11.02	8.90	80.08
10.27	5.83	83.90
10.00	4.50	85.50
9.82	2.71	87.47
9.55	0.90	89.55
9.52	0	90.48
(b) Mutual Solubility Data, wt %		
45.22	54.78	0
45.26	53.77	0.98
42.00	54.64	3.36
11.51	21.56	66.93
10.40	19.55	70.05
7.24	16.26	76.51
5.10	13.31	81.59
0	9.11	90.89

(c) Tie-Line Data, wt %

aqueous phase (R)			alcoholic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
96.6	0.48	3.40	9.3	0.09	90.61	0.18
96.2	0.79	3.01	9.4	0.17	90.43	0.22
92.9	4.18	2.92	9.6	0.83	89.57	0.20
88.7	8.31	2.99	9.8	1.84	88.36	0.22
79.9	16.95	3.15	9.9	4.20	85.90	0.25
71.5	26.25	2.25	10.0	6.05	83.95	0.23
62.9	33.92	3.18	10.5	9.60	79.90	0.28
57.2	39.23	3.57	11.0	11.47	77.53	0.29
54.0	42.46	3.54	11.2	13.79	75.01	0.32
44.6	51.83	3.57	12.3	20.62	67.08	0.40
40.9	55.49	3.61	13.4	24.76	61.84	0.45

Glossary

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

Registry No. Malic acid, 6915-15-7; 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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Received for review December 2, 1987. Revised May 16, 1988. Accepted August 7, 1988.