Glossary

A_i	coefficients of eq 1
$\bar{e}(y_1)$	mean error in y_1, $(\sum\|y_{1,\text{exptl}} - y_{1,\text{calcd}}\|/y_{1,\text{exptl}})100/N$
k	parameter in eq 1
N	number of experimental points
s	standard deviation, $\|\sum(\text{exptl} - \text{calcd})^2/N\|^{1/2}$
T	temperature, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ_i	activity coefficient of component *i*
ρ	liquid density, kg m^{-3}

Registry No. $H_3CCOOCH_3$, 79-20-9; ethanol, 64-17-5; 1-propanol, 71-23-8.

Literature Cited

(1) Ortega, J.; Peña, J. A.; de Alfonso, C. *J. Chem. Eng. Data* **1986**, *31*, 339.
(2) Susial, P.; Ortega, J.; de Alfonso, C. *J. Chem. Eng. Data* **1989**, *34*, 247.
(3) Nagata, I.; Ohta, T.; Nakagawa, S. *J. Chem. Eng. Jpn.* **1976**, *9*, 276.
(4) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; Dechema: Frankfurt-Main, FRG, 1977; Vol. 1, part 2a.
(5) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*; Dechema, Frankfurt-Main, FRG, 1982; Vol. 1, Part 2c.
(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry, Vol. 2; Wiley-Interscience: New York, 1986.
(7) Horsley, L. H. *Azeotropic Data*; Advances in Chemistry Series 6; American Chemical Society: Washington, DC, 1952.
(8) Nishi, Y. *J. Chem. Eng. Jpn.* **1972**, *5*, 334.
(9) Perelygin, V. M.; Volkov, A. G. *Izv. Vyssh. Uchebn. Zaved. Pishch. Tekhnol.* **1970**, 124.
(10) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263; **1978**, *24*, 1112.
(11) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(12) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibrium Using UNIFAC. A Group Contribution Method*; Elsevier: Amsterdam, 1977.
(13) Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Kodansha Ltd.: Tokyo, 1979.
(14) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21* (6), 1086.
(15) Skjold-Jorgensen, B.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18* (4), 714.
(16) Fredenslund, Aa.; Gmehling, J.; Michelsen, M. L.; Rasmussen, P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16* (4), 450.

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Equilibrium Diagrams at 25 °C of Water–Oxalic Acid–2-Methyl-1-propanol, Water–Oxalic Acid–1-Pentanol, and Water–Oxalic Acid–3-Methyl-1-butanol Ternary Systems

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The purpose of this work is to study the oxalic acid recovery possibilities from wastewater of the ozonization process of wood sawdust through a liquid-liquid extracting process. 2-Methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol may be suitable as extracting solvents. Water–oxalic acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 25 °C. Partition coefficients are comprised between 0.28 and 0.81. 1-Pentanol is the most selective solvent with regard to oxalic acid.

Introduction

Oxalic acid is principally manufactured from propylene. It is an organic acid used in the metal treatment, coating process, and anodizing industries (*1*). In order to recover oxalic acid from ozonization wastewater of poplar sawdust, which is present at a concentration rate of about 7 g/100 g of wood sawdust dried (*2*), 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 for use in this work.

Experimental Section

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

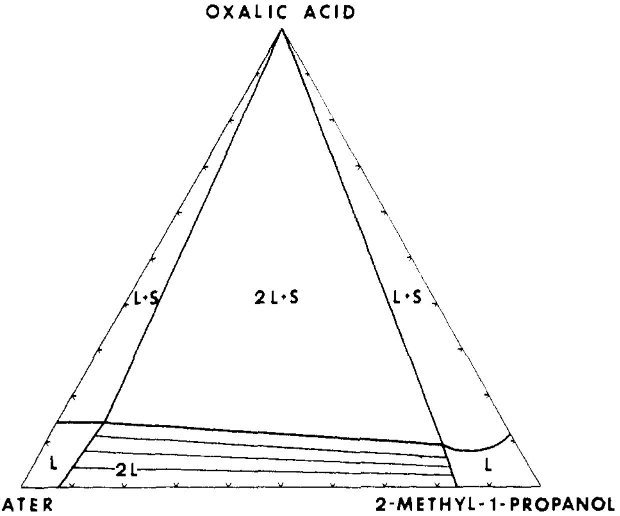

Figure 1. Water–oxalic acid–2-methyl-1-propanol phase diagram with tie lines at 25 °C: S = solid; L = liquid.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device maintained at the constant temperature of 25 ± 0.1 °C in a thermostated vessel. Several oxalic 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 4 h.

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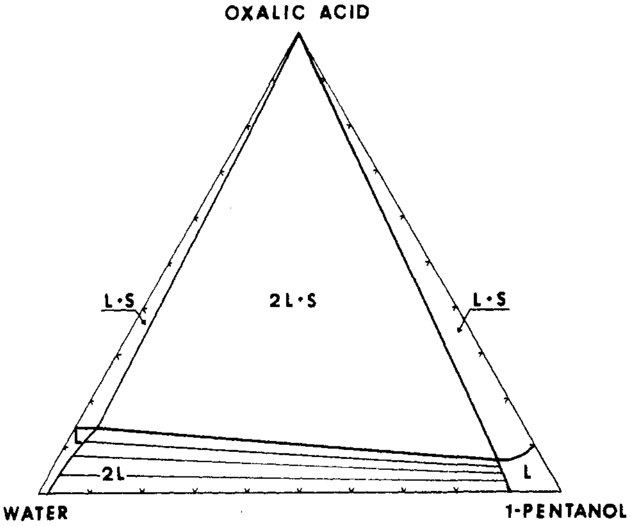

Figure 2. Water-oxalic acid-1-pentanol phase diagram with tie lines at 25 °C: S = solid; L = liquid.

Table I. Ternary Diagram for Water (A)-Oxalic Acid (B)-2-Methyl-1-propanol (C) at 25 °C

(a) Binodal Curve Data, wt %

water	oxalic acid	2-methyl-1-propanol
92.88	0	7.12
91.10	1.13	7.77
89.94	1.97	8.09
88.99	2.80	8.21
88.03	3.66	8.31
87.09	4.41	8.50
86.32	4.86	8.82
85.48	5.43	9.09
78.47	12.50	9.03
76.72	14.19	9.09
14.29	9.19	76.52
14.83	8.02	77.15
14.69	7.93	77.38
15.96	3.49	80.55
16.00	3.03	80.97
15.98	2.08	81.94
15.95	1.54	82.51
16.02	1.01	82.97
16.07	0.51	83.42
16.15	0	83.85

(b) Mutual Solubility Data, wt %

water	oxalic acid	2-methyl-1-propanol
85.84	14.16	0
82.50	14.05	3.45
79.88	14.13	5.99
77.36	14.10	8.54
76.73	14.19	9.08
14.29	9.19	76.52
11.44	8.29	80.27
9.76	8.23	82.01
8.35	7.93	83.72
6.13	8.18	85.69
4.15	8.82	87.03
2.37	9.75	87.88
0.57	11.41	88.02

(c) Tie-Lines Data, wt %

aqueous phase (R)			organic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
91.24	1.10	7.66	16.07	0.50	83.43	0.45
90.31	1.79	7.90	16.07	0.90	83.03	0.50
88.25	3.36	8.39	16.04	1.88	82.08	0.56
86.81	4.51	8.68	15.99	2.57	81.44	0.57
85.32	5.74	8.94	15.91	3.32	80.77	0.58
83.88	6.98	9.14	15.80	4.07	80.13	0.58
82.78	7.97	9.25	15.69	4.69	79.62	0.59
81.46	9.20	9.34	15.54	5.38	79.08	0.58
80.64	9.99	9.37	15.42	5.89	78.69	0.59
79.40	11.24	9.36	15.25	6.52	78.23	0.58
76.72	14.19	9.09	14.29	9.19	76.52	0.65

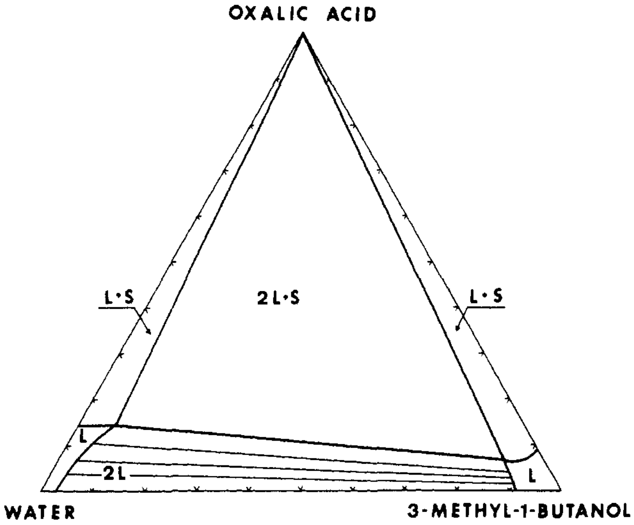

Figure 3. Water-oxalic acid-3-methyl-1-butanol phase diagram with tie lines at 25 °C: S = solid; L = liquid.

Table II. Ternary Diagram for Water (A)-Oxalic Acid (B)-1-Pentanol (C) at 25 °C

(a) Binodal Curve Data, wt %

water	oxalic acid	1-pentanol
98.08	0	1.92
96.78	1.14	2.08
95.66	2.20	2.14
94.16	3.56	2.28
92.42	4.96	2.62
90.83	6.11	3.06
89.46	7.41	3.13
85.26	11.60	3.14
81.77	13.54	4.69
81.95	13.90	4.15
8.91	6.52	84.57
9.51	3.34	87.15
9.45	2.71	87.84
9.56	2.19	88.25
9.57	1.49	88.94
9.69	0.83	89.48
9.74	0.35	89.91
9.75	0	90.25

(b) Mutual Solubility Data, wt %

water	oxalic acid	1-pentanol
85.84	14.16	0
85.07	14.07	0.86
84.34	13.93	1.73
83.43	14.01	2.56
82.64	13.91	3.45
81.95	13.90	4.15
8.91	6.52	84.57
7.83	7.35	84.82
5.93	7.07	87.00
4.11	7.29	88.60
0.50	9.98	89.52

(c) Tie-Line Data, wt %

aqueous phase (R)			organic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
96.65	1.23	2.12	9.67	1.00	89.33	0.81
95.19	2.59	2.22	9.62	1.58	88.80	0.61
93.65	4.00	2.35	9.55	2.24	88.21	0.56
92.26	5.24	2.50	9.49	2.80	87.71	0.53
90.65	6.67	2.68	9.41	3.47	87.12	0.52
89.04	8.05	2.91	9.33	4.02	86.65	0.50
87.36	9.48	3.16	9.23	4.70	86.07	0.50
85.24	11.24	3.52	9.10	5.48	85.42	0.49
84.22	12.07	3.71	9.03	5.87	85.10	0.49
81.95	13.90	4.15	8.91	6.52	84.57	0.47

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

Table III. Ternary Diagram for Water (A)-Oxalic Acid (B)- 3-Methyl-1-butanol (C) at 25 °C

(a) Binodal Curve Data, wt %

water	oxalic acid	3-methyl-1-butanol
97.05	0	2.95
95.70	1.30	3.00
94.59	2.37	3.04
93.77	3.17	3.06
92.53	4.31	3.16
91.62	5.17	3.21
91.32	5.45	3.23
90.70	6.02	3.28
89.68	6.83	3.49
87.04	8.61	4.35
85.20	9.91	4.89
79.58	13.34	7.08
78.36	14.05	7.59
7.55	6.23	86.22
7.85	5.42	86.73
8.14	4.58	87.28
8.48	3.09	88.43
8.53	2.72	88.75
8.58	2.40	89.02
8.66	2.08	89.26
8.72	1.74	89.54
8.73	1.25	90.02
8.76	0.39	90.85
8.80	0	91.20

(b) Mutual Solubility Data, wt %

water	oxalic acid	3-methyl-1-butanol
85.84	14.16	0
83.02	14.00	2.98
80.42	14.02	5.56
78.36	14.05	7.59
7.58	6.09	86.33
7.15	6.21	86.64
5.30	6.29	88.41
3.39	6.72	89.89
2.12	7.43	90.45
0.70	8.72	90.58

(c) Tie-Line Data, wt %

aqueous phase (R)			organic phase (E)			
X_A	X_B	X_C	X_A	X_B	X_C	m
96.24	0.74	3.02	8.79	0.21	91.00	0.28
95.61	1.42	2.97	8.79	0.43	90.78	0.30
94.34	2.71	2.95	8.76	0.99	90.25	0.37
92.88	4.07	3.05	8.71	1.59	89.70	0.39
91.37	5.36	3.27	8.65	2.12	89.23	0.40
89.65	6.73	3.62	8.56	2.70	88.74	0.40
88.03	7.94	4.03	8.47	3.16	88.37	0.40
86.16	9.25	4.59	8.37	3.62	88.01	0.39
84.45	10.39	5.16	8.26	4.08	87.66	0.39
82.29	11.75	5.96	8.13	4.55	87.32	0.39
78.36	14.05	7.59	7.55	6.23	86.22	0.44

did not alter the results. After decantation and waiting for 2 h, oxalic 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 amount of water in each phase at equilibrium was determined by the Karl-Fischer method. The error induced when a sample was titrated and weighed is less than 1%. Solid-liquid saturation curves were determined from saturated solutions, oxalic acid being titrated with standard sodium hydroxide (0.1 or 1.0 N).

Results and Discussion

Figures 1-3 are plots of the data in Tables I-III for experimental conditions at 25 °C. These figures represent solubility isotherms and tie-line curves of water-oxalic acid ternary systems with successive solvants: 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 (*3*).

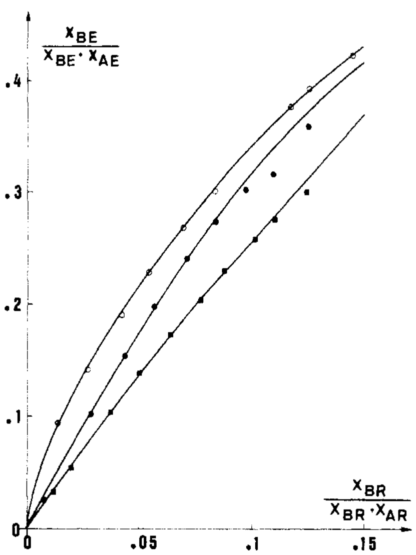

Figure 4. Selectivity diagrams at 25 °C for the systems (■) water-oxalic acid-2-methyl-1-propanol, (○) water-oxalic acid-1-pentanol, and (●) water-oxalic acid-3-methyl-1-butanol.

The partition coefficient (m) is defined as the ratio of acid concentration (wt %) in the organic phase to acid concentration (wt %) in the aqueous phase. Oxalic acid partition coefficients between water and successively 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol for different acid concentrations at 25 °C are indicated in Tables I-III.

1-Pentanol has the most significant coefficients ($0.47 < m < 0.81$), whereas 3-methyl-1-butanol has the lowest partition coefficients ($0.28 < m < 0.44$).

Figure 4 represents the selectivity curve of the solvents versus oxalic acid in aqueous solution form. We carried out on the abscissa 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. 1-Pentanol seems to be the best solvent to extract oxalic acid from effluents resulting from the ozonization process of wood sawdust.

1-Pentanol was chosen as a solvent, taking into consideration its weak solubility in the water phase and the appropriate value of its partition coefficient to extract the solute.

Glossary

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

Registry No. Oxalic acid, 144-62-7; 2-methyl-1-propanol, 78-83-1; 1-pentanol, 71-41-0; 3-methyl-1-butanol, 123-51-3.

Literature Cited

(1) Bernales, C. A.; Bushman, S. E.; Kraljic, J. *Encyclopedia Chemical Technology*, 3rd ed.; Kirk-Othmer, Ed.; Wiley: New York, 1981; Vol. 16, p 630.
(2) Euphrosine-Moy; et al. International Conference on U.V. and Ozone Treatment of Water and Other Liquids, Berlin, 1989.
(3) Treybal, R. E. Liquid Extraction, 3rd ed.; McGraw-Hill: New York, 1963; p 21.

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