

<i>R</i>	molar refraction, cm ³ mol ⁻¹
<i>T</i>	temperature, K
<i>V</i>	molar volume, cm ³ mol ⁻¹
<i>x</i>	liquid-phase mole fraction
<i>y</i>	vapor-phase mole fraction
<i>Y</i>	property <i>V</i> or <i>R</i>

Greek Letters

η	refractive index for sodium D light
ρ	density, g cm ⁻³
σ	standard deviation, eq 4, or root mean square deviation, eqs 5-6

Superscripts

<i>E</i>	excess property
----------	-----------------

Subscripts

<i>i</i>	component <i>i</i>
----------	--------------------

Registry No. Cyclohexane, 110-82-7; 2-butanol, 78-92-2; toluene, 108-88-3.

Literature Cited

- (1) Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Elsevier: Tokyo, 1979.
- (2) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
- (3) Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118.
- (4) Ocón, J.; Espantoso, J. *An. Quim.* **1958**, *54B*, 413.
- (5) Marsh, K. N.; French, H. T. *Int. DATA Ser., Sel. Data Mixtures* **1984**, 239.
- (6) Watson, A. E. P.; McLure, I. A.; Bennett, J. E.; Benson, G. C. *J. Phys. Chem.* **1965**, *69*, 2753.
- (7) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
- (8) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry, Vol. II; Wiley: New York, 1986.

Received for review September 19, 1990. Revised July 5, 1991. Accepted August 7, 1991.

Solubility of Itaconic and Kojic Acids

Irena Křivánková,[†] Maĵa Marčičšínová,[‡] and Otakar Söhnel^{*†}

Research Institute of Inorganic Chemistry, Revoluční 86, 400 60 Ústí n.L., Czechoslovakia, and Research Institute of Biochemistry and Spirit, Miletičova 23, 824 62 Bratislava, Czechoslovakia

The solubility of itaconic acid in water and kojic acid in water, acetone, and *N,N*-dimethylformamide, respectively, was determined from 0.5 to 69 °C. The metastable zone width for the aqueous solutions of both compounds was determined by the polythermic method.

Introduction

Itaconic acid, C₅H₆O₄ (methylene succinic acid), and kojic acid, C₈H₆O₄ (5-hydroxy-2-(hydroxymethyl)pyran-4-one), have found numerous practical applications in the food industry (1), pharmaceutical industry (2), cosmetics (3), etc. Despite the practical significance of both compounds, there have been few physical property data reported, and in the case of solubilities very few data are available (4). This lack of basic data prevents optimization and the correct handling of crystallization generally used in the isolation and purification process for these compounds.

Therefore, the solubility of itaconic acid in water and kojic acid in water, acetone, and *N,N*-dimethylformamide (DMF) and the metastable zone width of aqueous solutions of both compounds were experimentally determined.

Experimental Section

Solubility was determined by the "last crystal disappearance" method (5). This method is based on sequentially adding weighted amounts of a solid compound to a stirred solution (the initial weight of solvent is known precisely, about 250 g) kept at a constant temperature. When the solid increment completely dissolves, the next portion of solid is introduced. This procedure is repeated until the last increment remains partially

Table I. Solubility of Itaconic Acid in Water

<i>t</i> /°C	<i>x</i> × 10 ²	<i>t</i> /°C	<i>x</i> × 10 ²
0.5	0.413	46	3.346
9	0.632	50	3.998
19	0.987	56	5.032
25	1.298	60	5.865
35	1.995	65	7.041

Table II. Solubility of Kojic Acid in Water

<i>t</i> /°C	<i>x</i> × 10 ²	<i>t</i> /°C	<i>x</i> × 10 ²
1.5	0.164	50.5	1.938
15	0.290	54	2.350
25	0.554	60	3.164
36	0.904	65	4.222
44	1.399	69.2	5.449

undissolved, even after approximately 8 h. The increment weight is gradually decreased when the solution saturation is approached, which is indicated by the lengthening time necessary for each increment to completely dissolve. The last portion being added is approximately 0.01 g.

The solution in which the last increment remains undissolved is regarded as saturated. The solubility calculated from the total solid mass introduced and the initial solvent mass is expressed in the molar fraction, *x*.

The magnetically stirred measuring vessel equipped with thermometer and tightly closed by a rubber stopper (in the case of acetone, by a reflux condenser) was placed in a constant-temperature water bath (±0.1 °C). The presence of solid in the solution was indicated visually as "bright sparkles" appearing in a light beam passed through the solution.

The metastable zone width was determined by the polythermal method (6). A solution saturated at a required temperature was cooled (using a preprogrammed linear cooling of the water bath) at a rate of 5 or 20 K·h⁻¹ until the first crystals appeared while under constant stirring by a magnetic stirrer. The difference between the saturation temperature and the

* To whom correspondence should be addressed.

[†] Research Institute of Inorganic Chemistry.

[‡] Research Institute of Biochemistry and Spirit.

Table III. Solubility of Kojic Acid in Acetone and DMF

$t/^\circ\text{C}$	$x \times 10^2$		$t/^\circ\text{C}$	$x \times 10^2$	
	acetone	DMF		acetone	DMF
1.5	0.0048	0.183	36		0.353
12		0.234	40	0.0175	
15	0.0072		50	0.0227	0.445
23	0.0106		57	0.0260	
25		0.309	60		0.524
30.5	0.0136				

Table IV. Constants of Equation 1 Describing Solubility in Water

compd	temp range/ $^\circ\text{C}$	A	B	C
itaconic acid	0.5-65	-13.516	-969.28	6.018
kojic acid	1.5-69	-118.29	3493.72	42.146

Table V. Metastable Zone Width of Aqueous Solutions

compd	rate/($\text{K}\cdot\text{h}^{-1}$)	$t_{\text{sat}}^a/^\circ\text{C}$	$\Delta t_{\text{max}}/^\circ\text{C}$
itaconic acid	5	34.4	9.2
		50.1	6.1
		58.6	4.6
	20	63.7	4.5
		34.4	11.2
		50.1	9.0
kojic acid	10	58.6	6.1
		63.7	5.7
		36.0	13.5
		50.5	12.0
		65.0	8.5

^a t_{sat} = temperature at which the solution is saturated.

temperature at which the first crystals appeared was taken as the metastable zone width. Then the temperature was raised above the saturation temperature, and when all crystals dissolved, the solution cooling was started again. This procedure was repeated three times for each combination of the saturation temperature and the cooling rate. The difference among individual values was less than 0.5 K for each combination employed. Reported values represent an arithmetic average of respective values.

The itaconic (fy Ulajne, Latvia) and kojic (our own product) acids used for experiments contained a minimum 99.5% of pure substance. Purity was determined by isotachopheresis and spectrophotometry in the case of itaconic and kojic acid, respectively. Distilled water, acetone containing 0.3% water, and AnalaR grade *N,N*-dimethylformamide were used as solvents.

Results

The measured solubilities are given in Tables I-III. The solubility of itaconic and kojic acids in water were correlated according to the equation (7)

$$\log x = A + B/T + C \log T \quad (1)$$

where A , B , and C are adjustable constants, T is absolute temperature, and x represents the mole fraction of dissolved compound. Constants of this equation determined by the least-squares method are listed in Table IV. The standard deviation of $\log x$ in this correlation was 0.0155 and 0.0179 for itaconic and kojic acid, respectively.

The metastable zone width of aqueous solution for both acids expressed as the temperature difference Δt_{max} together with the saturation temperature t_{sat} is reported in Table V.

Registry No. DMF, 68-12-2; MeCOMe, 67-64-1; itaconic acid, 97-65-4; kojic acid, 501-30-4.

Literature Cited

- (1) Sanei Seiyaku Jpn. Patent KK J5 6024484, 1981.
- (2) Sanei Seiyaku Jpn. Patent KK J5 5154916, 1980.
- (3) Sansho seiyaku Jpn. Patent KK J5 6079616, 1981.
- (4) *Bellsteins Handbuch Der organischen Chemie, Vierte Auflage, Zweites und Drittes Ergänzungswerk*; Springer Verlag: Berlin, 1952, 1961.
- (5) Nývlt, J. *Solid-liquid Equilibria*; Elsevier: Amsterdam, 1977.
- (6) Nývlt, J.; Söhnel, O.; Matuchová, M.; Broul, M. *Kinetics of Industrial Crystallization*; Elsevier: Amsterdam, 1985.
- (7) Broul, M.; Nývlt, J.; Söhnel, O. *Solubility in Inorganic Two-Component Systems*; Academia: Prague, 1981.

Received for review October 29, 1990. Revised April 15, 1991. Accepted June 25, 1991.

Equilibrium Diagram of the Ternary System Water-Malic Acid-Tributyl Phosphate and the Influence of Temperature

Freddy Smaghe, Jian Xu, Muhammad Falzal,[†] Guy Malmay, and Jacques Molinier*

Laboratoire de Chimie des Procédés, Département Génie Chimique, Ecole Nationale Supérieure de Chimie de Toulouse, 118 Route de Narbonne, 31077 Toulouse Cedex, France

In this work the possibility of recovery of malic acid from wastewater by solvent extraction was studied. Tributyl phosphate mixed with dodecane was chosen as solvent. Equilibrium diagrams at 25, 35, and 45 $^\circ\text{C}$ were established in order to know the property of tributyl phosphate as solvent and the influence of temperature. It was found that tributyl phosphate was a very selective solvent for extracting malic acid from wastewater since it gave high selectivities which were between 1.3 and 17.4.

Introduction

Malic acid, $\text{C}_4\text{H}_6\text{O}_5$, is increasingly used in food and nonfood applications because of its pleasant tartness, flavor-retention characteristics, high water solubility, and chelating and buffering properties. Malic acid also is a reactive intermediate in chemical synthesis (1).

The processing of grape must using ion-exchange resins produces large quantities of pollutant effluent involving organic materials which are constituted principally of malic acid and tartaric acid.

In order to reduce the industrial pollution and waste effluent, malic acid can be recovered from effluent by the technique of liquid-liquid extraction.

Previous studies on liquid-liquid extraction of malic acid from

[†]Permanent address: Department of Chemical Engineering, Faculty of Engineering, Sriwijaya University, Jalan Sriwijaya Negara, Palembang 30139, Indonesia.