

# Densities, Refractive Indexes, and Isobaric Vapor-Liquid Equilibria for the Ternary System Cyclohexane + 2-Butanol + Toluene

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Densities and refractive indexes have been determined experimentally for the binary systems cyclohexane + 2-butanol and cyclohexane + toluene and for the ternary system cyclohexane + 2-butanol + toluene over the whole composition range at 298.15 K. Also, vapor-liquid equilibrium data for the system cyclohexane + 2-butanol + toluene at 740 mmHg have been determined, and the results have been compared with those predicted by using two group-contribution methods, ASOG and UNIFAC.

## Introduction

This paper reports experimental vapor-liquid equilibrium (VLE) data for the system cyclohexane + 2-butanol + toluene at 740 mmHg, which are indispensable for the design of rectification columns. No literature data are available for this system. The data obtained have been compared with those predicted by the methods ASOG (1) and UNIFAC (2, 3).

Previous to the determination of VLE, the densities and refractive indexes of cyclohexane + 2-butanol, cyclohexane + toluene, and cyclohexane + 2-butanol + toluene have been measured at 298.15 K. These data were used to determine the liquid- and vapor-phase compositions of the ternary mixtures.

## Experimental Section

**Apparatus and Procedure.** Binary and ternary mixtures were prepared by weight, and mole fractions  $x_1$  were calculated with an uncertainty of less than 0.0001. Densities  $\rho$  were measured with an Anton Paar DMA-46 vibrating-tube densimeter with a resolution of 0.0001 g cm<sup>-3</sup>. Refractive indexes  $\eta$  have been measured with an Abbe-type Officine-Galileo refractometer with an accuracy of 0.0001.

The VLE measurements were carried out under an atmosphere of argon in a modified Othmer-type ebulliometer with recirculation of both phases (4). The boiling points  $T$  of the mixtures were measured with a Crison digital thermometer with an estimated uncertainty of 0.1 K. Pressure  $P$  was kept constant at 740 ± 0.1 mmHg. Each experiment was continued for 1 h after the boiling point had become stable. The composition of the phases at equilibrium were determined from  $\rho$  and  $\eta$  measurements. The estimated uncertainties of mole fractions are 0.001 for the liquid phase and 0.005 for the vapor phase.

**Materials.** Merck chromatography grade products were used after their purity had been checked by determining their  $\rho$  and  $\eta$  values at 298.15 K and their normal boiling points  $T_b$  (Table I).

## Results

**Densities and Refractive Indexes.** Tables II and III list the direct experimental  $\rho$  and  $\eta$  results as a function of  $x_1$ . The isoline diagram is shown in Figure 1.

Table I. Densities  $\rho$ , Refractive Indexes  $\eta(D)$ , and Normal Boiling Points  $T_b$  of the Pure Components

component	$\rho(298.15 \text{ K})/$ (g cm <sup>-3</sup> )		$\eta(D, 298.15 \text{ K})$		$T_b/K$	
	exptl	lit. (8)	exptl	lit. (8)	exptl	lit. (8)
cyclohexane	0.7739	0.773 89	1.4237	1.423 54	353.95	353.880
2-butanol	0.8026	0.802 41	1.3953	1.395 30	372.55	372.662
toluene	0.8621	0.862 19	1.4944	1.494 13	383.55	383.780

Table II. Experimental Densities  $\rho$  and Refractive Indexes  $\eta(D)$  at 298.15 K as a Function of the Mole Fraction  $x_1$  of Cyclohexane, Coefficients  $A_i$ , Equation 3, and Standard Deviations  $\sigma(V^E)$  and  $\sigma(R^E)$ , Equation 4, for Binary Systems

$x_1$	$\rho/(g \text{ cm}^{-3})$	$\eta(D)$	$x_1$	$\rho/(g \text{ cm}^{-3})$	$\eta(D)$
Cyclohexane (1) + Toluene (3)			Cyclohexane (1) + 2-Butanol (2)		
0.0000	0.8621	1.4944	0.0000	0.8026	1.3953
0.0342	0.8585	1.4918	0.0245	0.8014	1.3958
0.0990	0.8518	1.4866	0.0356	0.8009	1.3959
0.1893	0.8427	1.4797	0.1771	0.7943	1.3993
0.1935	0.8424	1.4795	0.2980	0.7890	1.4022
0.2123	0.8404	1.4779	0.3440	0.7874	1.4030
0.3248	0.8294	1.4692	0.3799	0.7860	1.4043
0.3637	0.8259	1.4664	0.5668	0.7802	1.4096
0.3987	0.8226	1.4638	0.6007	0.7793	1.4106
0.4421	0.8186	1.4606	0.6873	0.7772	1.4131
0.5919	0.8052	1.4499	0.7077	0.7769	1.4138
0.5932	0.8051	1.4498	0.7952	0.7754	1.4166
0.6417	0.8010	1.4465	0.8815	0.7742	1.4193
0.6914	0.7968	1.4431	0.9457	0.7736	1.4214
0.7270	0.7940	1.4408	1.0000	0.7739	1.4237
0.7969	0.7886	1.4363			
0.7994	0.7883	1.4360			
0.8508	0.7845	1.4328			
0.9213	0.7793	1.4284			
0.9717	0.7757	1.4254			
1.0000	0.7739	1.4237			

	$V^E$	$R^E$	$V^E$	$R^E$
	Cyclohexane (1) + Toluene (3)		Cyclohexane (1) + 2-Butanol (2)	
$A_0$	2.3028	2.0180	2.6031	0.0015
$A_1$	0.5462	-0.0258	0.6096	0.1534
$A_2$	-0.1179	-0.0941	-0.4232	0.0554
$A_3$	-0.1786	-0.0639	0.8078	0.0263
$A_4$	0.3121	-0.0014	1.1620	-0.2121
$\sigma/(\text{cm}^3 \text{ mol}^{-1})$	0.0086	0.0024	0.0092	0.0023

The densities  $\rho$  and refractive indexes  $\eta$  of the mixtures were used to calculate the excess molar volumes  $V^E$

$$V^E = \sum_i x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

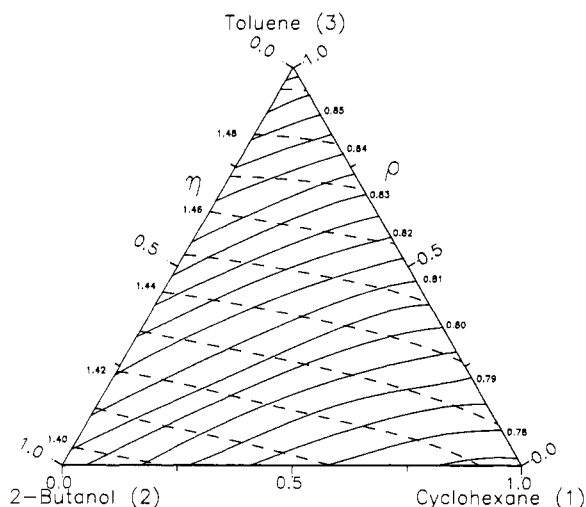
and the excess molar refractions  $R^E$

$$R^E = \frac{\sum_i x_i M_i}{\rho} \frac{\eta^2 - 1}{\eta^2 + 2} - \sum_i x_i \frac{M_i}{\rho_i} \frac{\eta_i^2 - 1}{\eta_i^2 + 2} \quad (2)$$

where  $R^E$  represents the excess molar refractions,  $M_i$  the molar

**Table III. Experimental Densities  $\rho$  and Refractive Indexes  $\eta(D)$  for the Ternary System Cyclohexane (1) + 2-Butanol (2) + Toluene (3) at 298.15 K as a Function of Mole Fractions  $x_1$  and  $x_2$** 

$x_1$	$x_2$	$\rho/(\text{g cm}^{-3})$	$\eta(D)$	$x_1$	$x_2$	$\rho/(\text{g cm}^{-3})$	$\eta(D)$	$x_1$	$x_2$	$\rho/(\text{g cm}^{-3})$	$\eta(D)$
0.0213	0.4927	0.8297	1.4454	0.6097	0.2411	0.7878	1.4254	0.0668	0.7306	0.8112	1.4178
0.1753	0.4152	0.8173	1.4392	0.5278	0.3431	0.7886	1.4214	0.0622	0.7492	0.8107	1.4163
0.2619	0.3717	0.8113	1.4366	0.5047	0.3718	0.7890	1.4203	0.0440	0.8227	0.8084	1.4102
0.2966	0.3542	0.8089	1.4356	0.4747	0.4092	0.7895	1.4189	0.0281	0.8867	0.8063	1.4048
0.3991	0.3025	0.8023	1.4330	0.4440	0.4473	0.7900	1.4174	0.0099	0.9603	0.8039	1.3987
0.5243	0.2395	0.7951	1.4309	0.3994	0.5029	0.7909	1.4152	0.7172	0.2828	0.7767	1.4136
0.5802	0.2113	0.7921	1.4299	0.3332	0.5853	0.7924	1.4120	0.6973	0.2749	0.7788	1.4157
0.6958	0.1531	0.7862	1.4278	0.2991	0.6277	0.7933	1.4103	0.6696	0.2640	0.7817	1.4185
0.7129	0.1445	0.7853	1.4274	0.2688	0.6654	0.7942	1.4087	0.6423	0.2532	0.7844	1.4213
0.7303	0.1358	0.7845	1.4272	0.1750	0.7822	0.7968	1.4039	0.6191	0.2441	0.7869	1.4238
0.8016	0.0998	0.7812	1.4260	0.1493	0.8141	0.7976	1.4026	0.6067	0.2392	0.7882	1.4251
0.8956	0.0525	0.7773	1.4247	0.1348	0.8322	0.7981	1.4019	0.5669	0.2236	0.7925	1.4294
0.9419	0.0292	0.7755	1.4241	0.0670	0.9166	0.8004	1.3988	0.5243	0.2067	0.7974	1.4341
0.9452	0.0276	0.7754	1.4241	0.0422	0.9474	0.8012	1.3976	0.4743	0.1866	0.8031	1.4397
0.0464	0.8203	0.8082	1.4102	0.2437	0.0177	0.8360	1.4743	0.4361	0.1720	0.8075	1.4440
0.0938	0.7795	0.8055	1.4106	0.2251	0.0925	0.8326	1.4683	0.3865	0.1524	0.8133	1.4496
0.1272	0.7507	0.8035	1.4108	0.2041	0.1775	0.8294	1.4618	0.3721	0.1467	0.8151	1.4513
0.1971	0.6907	0.7998	1.4114	0.1905	0.2323	0.8274	1.4576	0.3546	0.1399	0.8171	1.4533
0.2044	0.6844	0.7994	1.4115	0.1817	0.2677	0.8261	1.4548	0.3261	0.1286	0.8207	1.4567
0.2917	0.6093	0.7950	1.4123	0.1677	0.3241	0.8241	1.4504	0.2639	0.1041	0.8282	1.4639
0.3555	0.5544	0.7920	1.4130	0.1605	0.3532	0.8232	1.4482	0.2402	0.0947	0.8311	1.4667
0.4247	0.4949	0.7890	1.4138	0.1530	0.3835	0.8222	1.4458	0.1916	0.0756	0.8373	1.4725
0.4884	0.4400	0.7864	1.4146	0.1467	0.4088	0.8214	1.4438	0.1715	0.0676	0.8399	1.4749
0.5535	0.3841	0.7841	1.4156	0.1395	0.4378	0.8203	1.4414	0.1230	0.0485	0.8458	1.4805
0.6088	0.3365	0.7822	1.4164	0.1305	0.4731	0.8192	1.4386	0.1117	0.0440	0.8474	1.4819
0.6272	0.3207	0.7816	1.4167	0.1240	0.5000	0.8183	1.4364	0.0942	0.0371	0.8496	1.4840
0.7119	0.2478	0.7790	1.4181	0.1215	0.5104	0.8181	1.4356	0.0727	0.0287	0.8525	1.4867
0.7743	0.0362	0.7874	1.4339	0.1064	0.5711	0.8161	1.4307	0.0543	0.0214	0.8549	1.4889
0.7191	0.1050	0.7874	1.4309	0.1055	0.5746	0.8160	1.4304	0.0367	0.0144	0.8573	1.4909
0.6638	0.1737	0.7874	1.4280	0.0789	0.6822	0.8127	1.4218				

**Figure 1.** Composition diagram at 298.15 K for the system cyclohexane + 2-butanol + toluene, showing constant density  $\rho$  (—) and refractive index  $\eta$  (---) contours.

mass,  $\rho_i$  the density, and  $\eta_i$  the refractive index of component  $i$ .

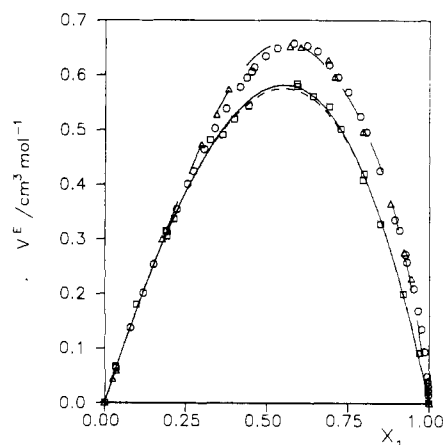
The excess properties  $Y^E$  ( $Y = V$  or  $R$ ) were fitted by the least-squares technique, all experimental points  $Y_{\text{exp}}^E$  being equally weighted, to the following equation:

$$Y^E/(\text{cm}^3 \text{ mol}^{-1}) = x_1(1 - x_1) \sum A_k (2x_1 - 1)^k \quad (3)$$

The values of the coefficients  $A_k$  and the standard deviations  $\sigma(Y^E)$  appear in Table II. The standard deviations were calculated by means of the equation

$$\sigma(Y^E) = [\sum (Y_{\text{exp}}^E - Y^E)^2 / (N - p)]^{1/2} \quad (4)$$

where  $N$  is the number of the experimental points and  $p$  the number of the coefficients  $A_k$ . Our experimental  $V^E$  values for the binary systems and their adjustments to eq 3 with respect to those reported by Marsh and French (5) for 2-butanol +

**Figure 2.** Excess molar volumes  $V^E$  at 298.15 K for systems of cyclohexane (1) + 2-butanol (2) [ $\Delta$ ] experimental value, this work; (O) experimental value, Marsh and French (5); (---) curve calculated from the coefficients given in Table II] and cyclohexane (1) + toluene (2) [ $\square$ ] experimental value, this work; (---) curve calculated from the coefficients given in Table II, (---) curve calculated from the coefficients proposed by Watson et al. (6)], as a function of the mole fraction  $x_1$  of cyclohexane.

cyclohexane and Watson et al. (6) for toluene + cyclohexane are plotted in Figure 2. Figure 3 shows experimental  $R^E$  values for the binary systems.

**Isobaric Vapor-Liquid Equilibria.** The equilibrium temperature and composition results for the system cyclohexane + 2-butanol + toluene are shown in Table IV. Figure 4 shows the composition distribution in a triangular diagram.

#### Prediction of the Vapor-Liquid Equilibria of the Ternary System

Prediction of the vapor-liquid equilibria for the ternary system cyclohexane + 2-butanol + toluene at 740 mmHg has been carried out by the methods ASOG and UNIFAC. In all of the calculations, the nonideality of the vapor phase was taken into account in terms of the second virial coefficients estimated by

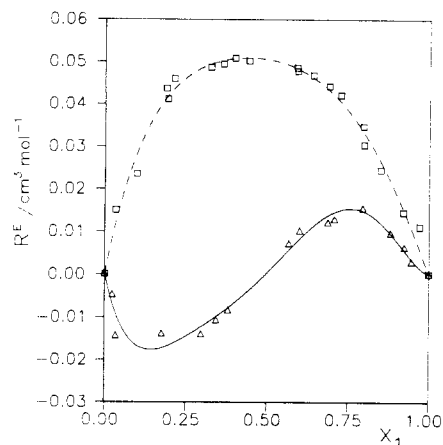
**Table IV. Experimental Liquid-Vapor Equilibrium Temperatures  $T$ , Liquid-Phase  $x_i$  and Vapor-Phase  $y_i$  Mole Fractions for Cyclohexane (1) + 2-Butanol (2) + Toluene (3) at 740 mmHg**

$T/K$	$x_1$	$x_2$	$y_1$	$y_2$
369.65	0.019	0.925	0.057	0.867
367.05	0.054	0.852	0.092	0.806
366.05	0.064	0.806	0.168	0.691
364.45	0.102	0.725	0.205	0.632
362.25	0.128	0.652	0.269	0.538
361.65	0.159	0.565	0.278	0.511
360.65	0.203	0.492	0.382	0.389
360.95	0.207	0.439	0.350	0.408
361.05	0.203	0.399	0.370	0.374
362.25	0.171	0.366	0.331	0.373
360.45	0.228	0.336	0.372	0.343
361.25	0.194	0.399	0.361	0.375
361.95	0.172	0.386	0.341	0.374
362.75	0.126	0.481	0.301	0.430
363.85	0.105	0.540	0.243	0.486
368.55	0.021	0.904	0.092	0.811
366.95	0.049	0.874	0.121	0.785
365.85	0.075	0.859	0.175	0.750
362.95	0.110	0.831	0.278	0.658
359.75	0.185	0.764	0.401	0.544
357.15	0.261	0.685	0.487	0.462
357.45	0.215	0.688	0.482	0.434
351.85	0.962	0.017	0.932	0.056
350.35	0.896	0.083	0.840	0.152
350.05	0.814	0.156	0.808	0.181
350.65	0.673	0.275	0.747	0.231
351.95	0.526	0.397	0.669	0.288
353.85	0.381	0.516	0.598	0.335
355.45	0.351	0.479	0.532	0.367
357.95	0.263	0.493	0.434	0.409
360.65	0.193	0.422	0.362	0.403
352.15	0.883	0.073	0.893	0.083
351.75	0.798	0.099	0.833	0.118
352.55	0.694	0.152	0.770	0.144
353.15	0.548	0.288	0.704	0.204
353.95	0.561	0.206	0.665	0.220
352.05	0.715	0.146	0.798	0.126
356.45	0.366	0.333	0.521	0.315
357.95	0.280	0.492	0.467	0.371
378.25	0.002	0.052	0.037	0.100
374.85	0.056	0.064	0.092	0.177
370.35	0.097	0.122	0.189	0.236
366.55	0.141	0.183	0.255	0.315
363.85	0.180	0.239	0.340	0.309
361.75	0.276	0.177	0.434	0.261
358.95	0.410	0.131	0.539	0.221
356.45	0.439	0.154	0.580	0.248
354.35	0.641	0.103	0.691	0.186
362.65	0.144	0.435	0.285	0.423
355.75	0.487	0.198	0.615	0.230
371.15	0.013	0.218	0.079	0.336
369.45	0.004	0.299	0.084	0.395
365.85	0.058	0.475	0.133	0.501
366.45	0.019	0.613	0.081	0.597
367.05	0.002	0.724	0.056	0.667
353.55	0.854	0.062	0.853	0.096
355.25	0.804	0.040	0.854	0.066
356.55	0.745	0.018	0.810	0.067
358.55	0.630	0.044	0.761	0.068
370.75	0.008	0.974	0.024	0.949
367.05	0.054	0.852	0.115	0.789

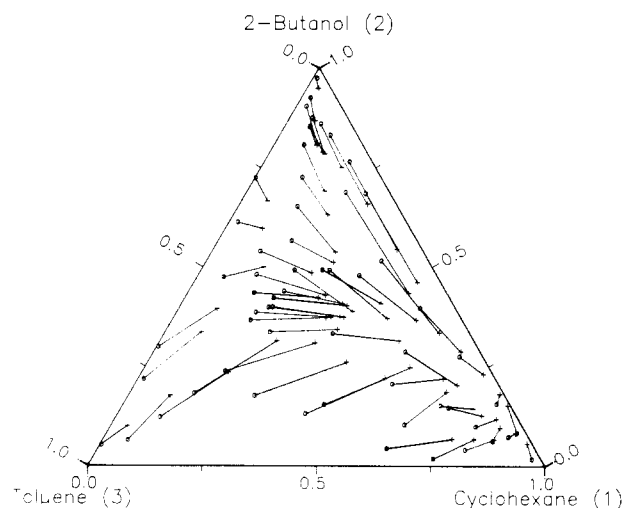
the method of Hayden and O'Connell (7). The group interaction parameters were those published by Gmehling et al. (3) for the UNIFAC method and by Kojima and Tochigi (1) for the ASOG-KT model. The experimental data are compared with the calculated ones, and root mean square deviations for temperature  $\sigma(T)$  and composition of the vapor phase  $\sigma(y_i)$  were determined (Table V).

$$\sigma(T) = [\sum(T_{\text{exp}} - T_{\text{cal}})^2/N]^{1/2} \quad (5)$$

$$\sigma(y_i) = [\sum(y_{i,\text{exp}} - y_{i,\text{cal}})^2/N]^{1/2} \quad (6)$$



**Figure 3. Excess molar refraction  $R^E$  at 298.15 K for mixtures of cyclohexane (1) + 2-butanol (2) ( $\Delta$ ) and cyclohexane (1) + toluene (2) ( $\square$ ) as a function of the mole fraction  $x_1$  of cyclohexane. The curves were calculated from the coefficients given in Table II.**



**Figure 4. Composition (mole fractions  $x_i$ ) diagram for cyclohexane (1) + 2-butanol (2) + toluene (3) at 740 mmHg: (O) liquid phase; (+) vapor phase.**

**Table V. Root Mean Square Deviations between the Experimental and Calculated Temperatures  $\sigma(T)$ , Equation 5, and Vapor-Phase Compositions  $\sigma(y_i)$ , Equation 6, of the Ternary Mixtures Cyclohexane (1) + 2-Butanol (2) + Toluene (3) and Those Calculated by UNIFAC and ASOG Methods**

method	$\sigma(T)/K$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(y_3)$
UNIFAC (2, 3)	1.54	0.049	0.055	0.021
ASOG (1)	0.76	0.040	0.043	0.018

## Conclusions

The excess volumes of the two binary systems and of the ternary system are positive in the whole range of compositions. On the contrary, the excess refractions present positive and negative values.

The vapor-liquid equilibrium measurements at 740 mmHg for cyclohexane + 2-butanol + toluene shows the absence of a ternary azeotrope in this system. The ASOG method yields better results than UNIFAC, both for prediction of the vapor-phase composition and equilibrium temperature.

## List of Symbols

$A_k$	parameters, eq 3
$M$	molar mass, $\text{g mol}^{-1}$
$N$	number of experimental points
$P$	pressure, mmHg
$p$	number of coefficients $A_k$ , eq 4

<i>R</i>	molar refraction, cm <sup>3</sup> mol <sup>-1</sup>
<i>T</i>	temperature, K
<i>V</i>	molar volume, cm <sup>3</sup> mol <sup>-1</sup>
<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**

$\eta$	refractive index for sodium D light
$\rho$	density, g cm <sup>-3</sup>
$\sigma$	standard deviation, eq 4, or root mean square deviation, eqs 5-6

**Superscripts**

<i>E</i>	excess property
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**Subscripts**

<i>i</i>	component <i>i</i>
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Registry No. Cyclohexane, 110-82-7; 2-butanol, 78-92-2; toluene, 108-88-3.

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## Solubility of Itaconic and Kojic Acids

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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, C<sub>5</sub>H<sub>6</sub>O<sub>4</sub> (methylene succinic acid), and kojic acid, C<sub>8</sub>H<sub>6</sub>O<sub>4</sub> (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 <sup>2</sup>	<i>t</i> /°C	<i>x</i> × 10 <sup>2</sup>
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 <sup>2</sup>	<i>t</i> /°C	<i>x</i> × 10 <sup>2</sup>
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<sup>-1</sup> until the first crystals appeared while under constant stirring by a magnetic stirrer. The difference between the saturation temperature and the

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