Registry No. Toluene, 108-88-3; 1,4-dioxane, 123-91-1; oxane, 142-68-7; 1,3-dioxolane, 646-06-0; oxolane, 109-99-9.

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Separation of Phenol from Its Mixture with *o*-Cresol by Adductive Crystallization

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A ternary solid–liquid diagram of the system phenol, *o*-cresol, and 2-methyl-2-propanol is prepared. 2-Methyl-2-propanol can be used as an extraneous agent for the separation of phenol from its mixture with *o*-cresol by adductive crystallization in a multistage process. The boiling points of these compounds in the mixture differ by 9 °C and the melting points by 10 °C.

Introduction

The process of extractive or adductive crystallization appears attractive over the conventional separation methods used in the chemical industry for separation of organic isomeric or nonisomeric close boiling components from a mixture (*1–6*). The purpose of the present study was to select a suitable solvent for separation of components from a mixture of phenol–*o*-cresol by adductive crystallization, the boiling point and melting point differences between these two components being 9 and 10 °C, respectively. 2-Methyl-2-propanol is considered as a possible solvent for this system as it is a good solvent for many other separations (*6*). Its suitability was also judged by empirical measurements of enthalpy changes on complex formation for binary mixtures. After the favorable indication a detailed ternary solid–liquid equilibrium diagram was developed and the feasibility of the process demonstrated.

Solvent Selectivity by Calorimetry

In an adductive crystallization process the solvent usually forms a weak molecular compound, having a different melting point, with either one or both of the components to be separated. The data on enthalpy changes on complex formation were determined calorimetrically using the apparatus and procedure similar to those previously reported (*5*). The calorimeter consisted of a standard Dewar flask of ~0.2-L capacity and was mounted in a well-insulated constant-temperature bath with a water circulation pump. The thick and tightly fitting polypropylene lid had three holes, one for the tip of the jacketed buret through which the second liquid component was added, another for a thermometer graduated up to 0.1 °C, and the third for an electrically driven stirrer. The change in temperature was observed at steady state after mixing two components maintained at a constant temperature. Radiation corrections were applied and water equivalents of calorimeter determined repeatedly by the electrical method. All AnalaR grade chemicals were used during this investigation and further purified by conventional methods whenever it was necessary. The results for the two binaries of the present system are reported in Table I and also plotted in Figure 1, indicating that 2-methyl-2-propanol has greater interaction and more complex formation with phenol than *o*-cresol. The adduct-forming system usually showed enthalpy changes more than ~400 J/mol, and therefore the present calorimeter provided sufficient accuracy for the measurement. The working of the calorimeter was tested with the standard system (chloroform–acetone), yielding reasonably precise and comparable data (with less than ±2% error in measurement of enthalpy changes). Using the two-parameter chemical theory of solution (*7*), the apparent activity coefficient and selectivity values were determined and are shown in Figure 2. 2-Methyl-2-propanol appears to be a favorable solvent for separation of the eutectic of phenol and *o*-cresol.

Table I. Enthalpy of Mixing, $-\Delta H$, Data for Binary Systems at 50 °C

phenol (1) + 2-methyl-2-propanol (2)		*o*-cresol (1) + 2-methyl-2-propanol (2)	
x_2	$-\Delta H$, J/mol	x_2	$-\Delta H$, J/mol
0.098	661	0.105	415
0.192	1337	0.207	972
0.298	1904	0.291	1338
0.399	2179	0.396	1509
0.497	2192	0.496	1603
0.585	2049	0.596	1581
0.702	1520	0.682	1323
0.801	874	0.803	945
0.900	418	0.912	518

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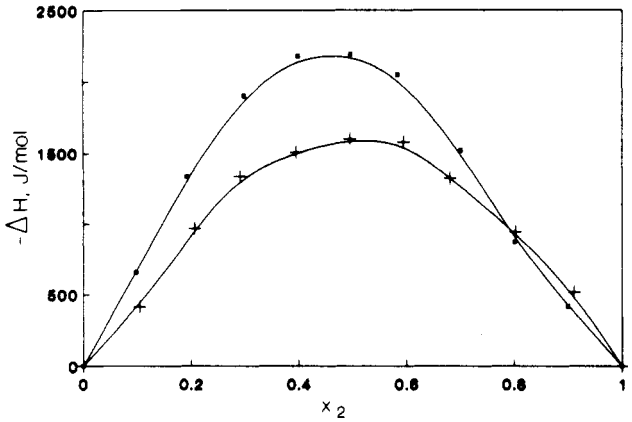

Figure 1. Enthalpy changes on complex formation for the following binaries at 50 °C: (■) phenol (1) + 2-methyl-2-propanol (2) and (+) *o*-cresol (1) + 2-methyl-2-propanol (2).

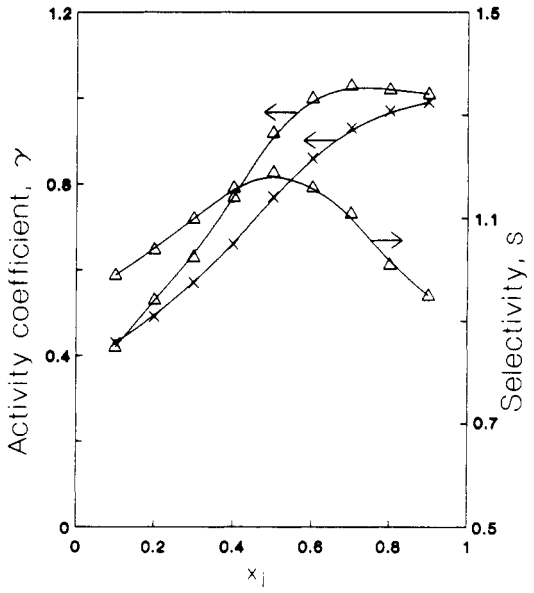

Figure 2. Selectivity, *s*, and activity coefficient, γ, curves with respect to x_1 for the following binaries: activity coefficient curves for (Δ) phenol (1) + 2-methyl-2-propanol (2) and (×) *o*-cresol (1) + 2-methyl-2-propanol (2); (Δ) selectivity curve of phenol (1) + *o*-cresol (2) in 2-methyl-2-propanol.

Table II. Solid–Liquid Equilibrium Data for Three Binary Systems

phenol (1) + 2-methyl-2-propanol (2)		2-methyl-2-propanol (2) + *o*-cresol (2)		*o*-cresol (1) + phenol (2)	
x_1	*t*, °C	x_1	*t*, °C	x_1	*t*, °C
0.000	25.0	0.000	30.8	0.000	40.8
0.105	11.7	0.099	24.8	0.107	33.3
0.126	8.8	0.196	17.5	0.205	27.2
0.150	12.6	0.294	7.5	0.301	21.4
0.198	18.0	0.302	−6.0	0.349	19.2
0.310	23.1	0.474	−21.7	0.397	19.4
0.351	23.4	0.500	−20.7	0.497	19.9
0.403	21.5	0.553	−14.7	0.529	20.0
0.498	15.0	0.600	−13.5	0.588	21.0
0.524	11.8	0.653	−12.5	0.690	22.8
0.535	10.7	0.714	−11.5	0.795	25.1
0.549	12.1	0.725	−11.4	0.896	27.5
0.605	15.3	0.753	−12.5	1.00	30.8
0.670	16.5	0.806	−3.5		
0.700	16.1	0.897	11.5		
0.715	15.5	1.000	25.0		
0.756	13.4				
0.807	21.1				
0.886	30.5				
1.000	40.8				

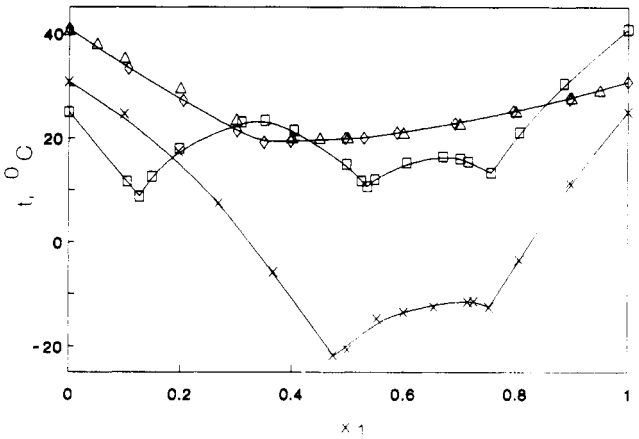

Figure 3. Binary solid–liquid equilibria for the following systems (disappearance temperature, *t* (°C), versus mole fraction, x_1): (□) phenol (1) + 2-methyl-2-propanol (2); (×) 2-methyl-2-propanol (1) + *o*-cresol (2); (◇) *o*-cresol (1) phenol (2); and (Δ) *o*-cresol (1) + phenol (2) (*9*).

Solid–Liquid Equilibrium Data

In the first stage binary solid–liquid diagrams for each pair were constructed by the disappearance point method (*1*). The apparatus used for disappearance points consisted of a large freezing tube (25-mm diameter and 300-mm length) enclosed in an air jacket, a hand stirrer, and a calibrated thermometer with an accuracy of ±0.1 °C. The entire assembly of the air-jacketed freezing tube containing ~20 g of solidified mixture of known composition along with the hand stirrer and thermometer was immersed in a constant-temperature water bath. The contents of the tube were warmed slowly, stirred continuously, and illuminated by an electric bulb for a careful observation. The temperature at which the last traces of suspended crystals disappeared was determined. Although the readings were quite reproducible, the average value of the three repeated readings was taken as the equilibrium temperature. The results are tabulated in Table II and presented in Figure 3. The binary system phenol–*o*-cresol forms a simple eutectic at 19.2 °C and 0.651 mole fraction of phenol. The solvent 2-methyl-2-propanol forms three eutectics with phenol (at 13.4, 10.7, and 8.8 °C and 0.756, 0.535, and 0.127 mole fraction of phenol, respectively) and two eutectics with *o*-cresol (at −21.7 and −12.5 °C and 0.526 and 0.247 mole fraction of *o*-cresol). The melting point of 2-methyl-2-propanol (25 °C) is lower than those of phenol (40.8 °C) and *o*-cresol (30.8 °C). The boiling point of 2-methyl-2-propanol (83 °C) is much lower than those of the other two components (phenol 181 °C and *o*-cresol 190 °C).

In order to judge clearly the effectiveness of 2-methyl-2-propanol as a suitable extraneous agent for this separation, a ternary equilibrium diagram showing the primary and binary crystallization regions was constructed from several vertical sections of a triangular solid prism covering the whole range of the composition triangle. For a vertical section with fixed amounts of two components, the disappearance point temperature of ternary mixtures lying on such a vertical section was determined at various amounts of the third component. The characteristic (or minimum) points in a plot of the disappearance point against the amount of the third component for all the vertical sections are reported in Table III and were used to define the binary crystallization curves as shown in Figure 4. In the present case the ternary system consists of six components (viz., three original components and three binary compounds) as depicted by six regions (viz., E_1AE_2, E_2ABE_3, E_3BDCE_4, E_4CE_5, E_5CDE_6, and E_6DBAE_1). The primary crystallization regions E_1AE_2, E_4CE_5, and E_6DBAE_1 are of phenol, 2-methyl-2-propanol, and *o*-cresol, while the binary crystallization regions E_2ABE_3, E_3BDCE_4, and E_5CDE_6 represent the

Table III. Disappearance Point Temperatures, t, on the Binodal Curves for the Ternary System Phenol (1) + o-Cresol (2) + 2-Methyl-2-propanol (3)

x_1	x_2	x_3	t, °C
0.651	0.349		19.2
0.756		0.244	13.4
0.535		0.465	10.7
0.126		0.874	8.8
	0.526	0.474	−21.7
	0.247	0.753	−12.5
0.458	0.249	0.293	−4.5
0.386	0.209	0.405	−6.8
0.105	0.057	0.838	4.9
0.667	0.103	0.230	4.8
0.464	0.072	0.476	1.2
0.110	0.015	0.875	8.3
0.336	0.293	0.350	−17.6
0.093	0.077	0.830	1.9
0.281	0.339	0.380	−21.2
0.077	0.093	0.830	−0.6
0.216	0.404	0.380	−18.8
0.084	0.156	0.760	−8.0
0.140	0.430	0.430	−21.5
0.055	0.165	0.780	−9.2
0.089	0.436	0.475	−23.7
0.048	0.232	0.720	−20.8
0.037	0.483	0.480	−26.0
0.015	0.210	0.775	−16.2
0.613	0.320	0.067	12.4
0.633	0.145	0.222	2.5
0.574	0.225	0.201	−1.7
0.045	0.379	0.576	−14.0
0.350	0.258	0.392	−12.4
0.600	0.159	0.241	22.0
0.040	0.283	0.677	−14.6
0.400	0.177	0.423	−3.3
0.670	0.097	0.233	6.1
0.385	0.300	0.315	−13.2
0.475	0.270	0.255	−8.1
0.585	0.195	0.220	−0.6
0.405	0.135	0.440	0.0
0.112	0.037	0.850	7.3

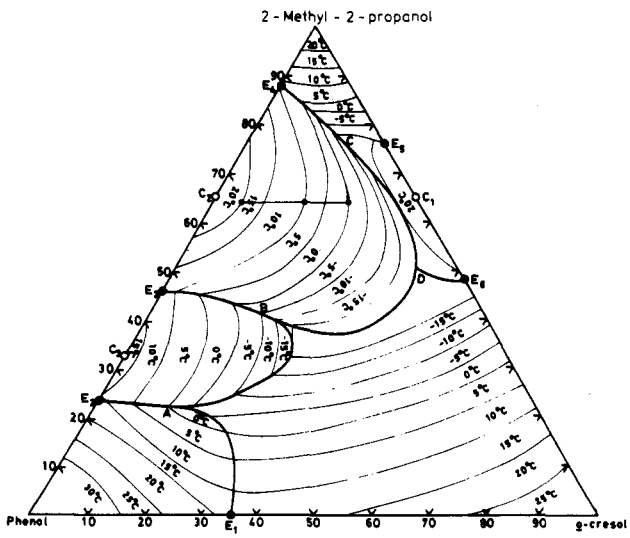

Figure 4. Isotherms of the ternary system phenol–o-cresol–2-methyl-2-propanol.

complex formation between pairs phenol–2-propanol (C_3), phenol–2-methyl-2-propanol (C_2), and o-cresol–2-methyl-2-propanol (C_1), respectively. The shape of these regions is dictated by the mutual interactions among these six components.

The binary crystallization region E_3BDCE_4 appears dominant for the adduct formation between phenol–2-methyl-2-propanol, thus covering a range of solvent-free phenol concentration of 10–90 mol %. The other smaller region forming the adduct between phenol-2-methyl-2-propanol, E_2ABE_3, covers the range of solvent-free phenol concentration from 35 to 100 mol %. The solid phase obtained on crystallization of the feed having the compositions in these two regions contains the phenol–2-methyl-2-propanol adduct. The solvent 2-methyl-2-propanol can easily be recovered by distillation. Also shown in Figure 4 are the isothermal lines constructed from data on compositions of mixtures having the same disappearance point temperature. This diagram is the contour diagram of the equilibrium surface of the ternary system in the triangular prism with temperature as the vertical axis. The isotherms are drawn for a difference of 5 °C. In all the major regions high-temperature isotherms are spread over a large area as compared to low-temperature isotherms, indicating that the slope of the surface at lower temperature is steeper than that at high temperature. For an illustration purpose, the crystallization behavior at points X, Y, and Z on the conode parallel to the base of the triangle having 65 mol % 2-methyl-2-propanol can be considered to indicate the sensitivity of separation to the temperature changes. Point X represents a mixture of 85 mol % phenol and 15 mol % o-cresol on a solvent-free concentration basis and has a disappearance point of 20 °C. If this mixture is cooled to 10 °C (point Y), the melt composition on a solvent-free basis would be equal to 55 mol % phenol and 45 mol % o-cresol. Should this mixture be further cooled to 0 °C (point Z), the solvent-free melt composition would reach 38 mol % phenol and 62 mol % o-cresol. This indicates that the separation of phenol is less sensitive to temperature changes as o-cresol concentration increases.

Table IV. Results from Feasibility Studies (Figure 5)

run	t, °C	crystallizn stages	purity of phenol, mol %	recovery of phenol, mol %
1	6.5	I	74.9	83.6
2	15.5	II	83.5	46.6
3	2.0	I	69.8	85.9
4	0.0	I	63.6	90.9
5	−10.0	I	63.0	86.7
6	1.0	I	31.1	68.0
7	11.0	I	23.1	53.6
8	19.5	I	91.8	73.3

Feasibility Study

Feasibility studies were performed in a phase separation apparatus (*8*). After the equilibration in the apparatus, quick filtration in order to avoid a shift in equilibrium composition and efficient separation to recover the last traces of the entrained melt for accurate analysis of the product crystals were achieved. In a typical run a mixture of known quantity of the eutectic of phenol and o-cresol and the requisite amount of 2-methyl-2-propanol were charged into the apparatus for equilibration. At the end of the run, the mother liquor was filtered, the retained solid phase was melted by circulating an alcohol–water mixture in the jacket, and the melt was subsequently filtered. The components in both the phases were analyzed on a gas–liquid chromatograph (Chemito Model No. 3800) using a stainless steel column packed with 10 wt % carbowax and 2 wt % orthophosphoric acid on chromosorb WAW 80/100 mesh. A calibration curve with the help of synthetic samples of known compositions was constructed and used to determine the precise compositions of unknown samples with an estimated error of less than 2%. A correction for entrained liquid in the solid phase can be applied with the help of a material balance calculation based on melt composition.

The results of phase separation studies are depicted in Figure 5 and Table IV. All the conodes in the primary crystallization region converge toward the point corresponding to molecular addition components of phenol and 2-methyl-2-propanol. As indicated in Figure 5 and Table IV the recovery of phenol in the

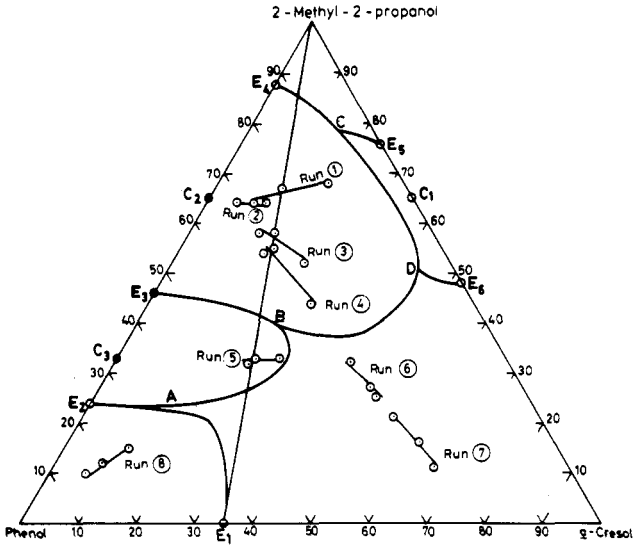

Figure 5. Feasibility runs of the ternary system phenol–*o*-cresol–2-methyl-2-propanol.

solid phase from its eutectic mixture is in the range from 84 to 91 mol % and the purity from 63 to 75 mol %. Recrystallization may yield higher purity. The resulting solid-phase composition from the ternary mixture in run 1 was used in run 2 for the second crystallization at 15.5 °C; the purity of phenol in the solid phase improved from 74.9 to 83.6 mol %. Figure 5 shows that 2-methyl-2-propanol forms two adducts with phenol over the different concentration range. The feasibility runs in a larger region denoted by E_3BDCE_4 yield better results for separation of phenol from eutectic mixtures than those in a smaller region denoted by E_2ABE_3. Runs 6 and 7 performed in the *o*-cresol-rich region yielded low phenol purity in the solid phase (<30 mol %) while the purity of phenol in the solid phase obtained from run 8 in the phenol-rich region was >90 mol %. All the runs were performed over the temperature range from −10 to +20 °C and would require reasonable refrigeration duty.

Conclusions

Enthalpy changes on complex formation were used to calculate the selectivity of a solvent for a given pair of close boiling organic components. 2-Methyl-2-propanol appears to be a suitable solvent for separation of phenol from its mixture with *o*-cresol. A ternary phase diagram for this system was constructed. Using multistage crystallization, a reasonable purity of phenol can be achieved.

Registry No. Phenol, 108-95-2; *o*-cresol, 95-48-7; 2-methyl-2-propanol, 75-65-0.

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Solvent Effects on the Dissociation of Nitrobenzoic Acids in Water + *N,N*-Dimethylformamide at 25 °C

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The dissociation constants and molar conductivities at infinite dilution of benzoic and 2-, 3-, and 4-nitrobenzoic acids have been determined in *N,N*-dimethylformamide + water mixtures at 25 °C. The experimental data have been analyzed by means of the Lee and Wheaton equation. The results are compared with previous findings for these acids in some other water–cosolvent mixtures.

Introduction

The binary mixtures of *N,N*-dimethylformamide (DMF) with water (W) are nonideal and show extrema in various excess thermodynamic functions (*1–3*). The present paper is on the study of the dissociation of benzoic and 2-, 3-, and 4-nitrobenzoic acids in binary mixtures of *N,N*-dimethylformamide with water ranging in composition from 0% to 50% (wt/wt). The molar conductances of the dilute solutions of the acids have been measured at 25 °C. The conductance–concentration data have been analyzed for the derivation of pK_a and Λ_0 values. The finished results are compared with those previously found for other water–cosolvent mixtures (*4*, *5*). Finally the solvent effect on the ionization of these acids has been discussed in terms of the free energy change on the transfer of the respective carboxylate ion from water to water–cosolvent mixtures.

Experimental Section

The acids were the same as those used in previous studies (*4*, *5*). DMF was from E. Merck and was further purified as detailed earlier (*6*).

Conductance measurements were carried out using an autobalance precision bridge (Wayne Kerr, B641) at 1592 Hz in the same way as described elsewhere (*4–6*). Two different cells with cell constants 0.876 and 1.013 ± 0.0015 cm^{-1} were used. The cells were calibrated following the method of Fuoss and co-workers (*7*) using aqueous KCl solutions in the concentration range (2–30) × 10^{-4} mol dm^{-3}. The reproducibility of the conductance measurements was better than ±0.5%. The conductance data are given in Table II. The accuracy of molar conductances is ±0.2%. No solvent corrections were

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