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Separation of *p*-Cresol from Its Mixture with 2,6-Xylenol by Adductive Crystallization

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A ternary solid–liquid diagram of the system *p*-cresol, 2,6-xylenol, and *tert*-butyl alcohol is prepared. *tert*-Butyl alcohol can be used as an extraneous agent for the separation of *p*-cresol from its mixture with 2,6-xylenol by adductive crystallization in a multistage process, both of these compounds being close-boiling components of the mixture.

Introduction

Separation of organic isomeric or nonisomeric close-boiling components from a mixture is a challenging task in the chemical industry. The process of extractive or adductive crystallization appears attractive over the conventional separation methods (*1–6*). The purpose of the present study was to select a suitable solvent for separation of components from a mixture of *p*-cresol–2,6 xylenol by adductive crystallization, the boiling point difference between these two components being only 0.03 °C. *tert*-Butyl alcohol is considered as a possible solvent for this system. Its suitability was 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.

Sharma and his co-workers (*7–12*) suggested several alternative possibilities for this separation on a laboratory scale. A process of dissociation extraction can be used to carry out this separation on the basis of relative acidity (*7, 8*). Anhydrous piperazine can be used as a crystallizing agent in the process of dissociation extractive crystallization (*10*). Diethanolamine can be used to increase the relative volatility between these two components in order to separate the mixture by extractive distillation process (*12*). For this separation an aqueous solution of lauryl alcohol 7 ethoxylate surfactant can be used in the micelles process (*11*) and an aqueous solution of sodium xylenesulfonates as a hydrotrope in the liquid–liquid extraction process (*9*). All these routes have not yet been commercially exploited.

Selectivity of Solvent

In an adductive crystallization process the solvent usually forms a weak molecular compound, having a different melting point, with either one or both the components to be separated. The data on enthalpy changes on complex formation were determined calorimetrically by 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 the mixing two components were 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. The results for the two binaries of the present system are reported in Table I and also plotted in Figure 1, indicating that *tert*-butyl alcohol has greater interaction and more complex formation with *p*-cresol than 2,6-xylenol. The adduct-forming system usually showed enthalpy changes of more than ~100 cal/mol, and therefore the present calorimeter provided sufficient accuracy for the measurement. From the two-parameter chemical theory of solution (*13*), the apparent activity coefficient and selectivity values were determined and are shown in Figure 2. *tert*-Butyl alcohol appears to be a favorable solvent for separation of the eutectic of *p*-cresol and 2,6-xylenol.

Table I. Heat of Mixing ($-\Delta H$) Data for Binary Systems at 50 °C

p-cresol–*tert*-butyl alcohol		2,6-xylenol–*tert*-butyl alcohol	
mole fraction of *tert*-butyl alcohol	$-\Delta H$, cal/mol	mole fraction of *tert*-butyl alcohol	$-\Delta H$, cal/mol
0.101	107.0		
0.201	230.8	0.197	49.1
0.302	320.6	0.307	109.1
0.409	384.0	0.402	125.2
0.505	386.6	0.497	136.8
0.603	354.8	0.596	115.6
0.677	318.7	0.696	104.5
0.773	262.1	0.800	72.5
0.900	150.0	0.896	5.8

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 careful observation. The temperature at which the last traces of suspended crystals disappeared was determined and the average value of the three repeated readings taken as the equilibrium temperature. The results are tabulated in Table II and represented in Figure 3. The binary system *p*-cresol–2,6-xylenol forms a single eutectic at 5.2 °C and 0.619 mole fraction of *p*-cresol. The solvent *tert*-butyl alcohol forms two eutectics with *p*-cresol (at ~11 and 3 °C and 0.175 and 0.755 mole fractions of *p*-cresol, respectively) and a single eutectic with 2,6-xylenol (at ~20.2 °C and 0.278 mole fraction of 2,6-xylenol). The melting point of *tert*-butyl alcohol (25 °C) is lower than those of *p*-cresol (35

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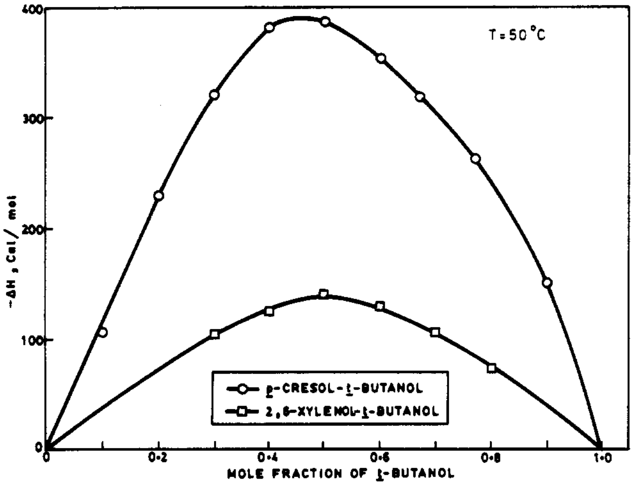

Figure 1. Enthalpy changes on complex formation for the binaries *p*-cresol–*tert*-butyl alcohol and 2,6-xylenol–*tert*-butyl alcohol.

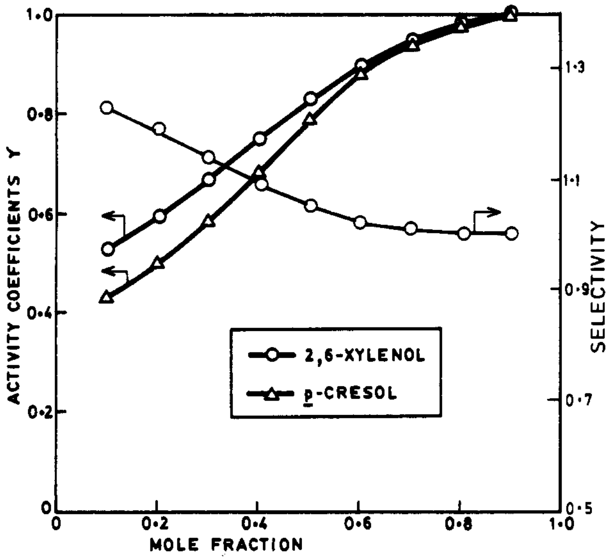

Figure 2. Selectivity and activity coefficient curves for the binaries *p*-cresol–*tert*-butyl alcohol and 2,6-xylenol–*tert*-butyl alcohol.

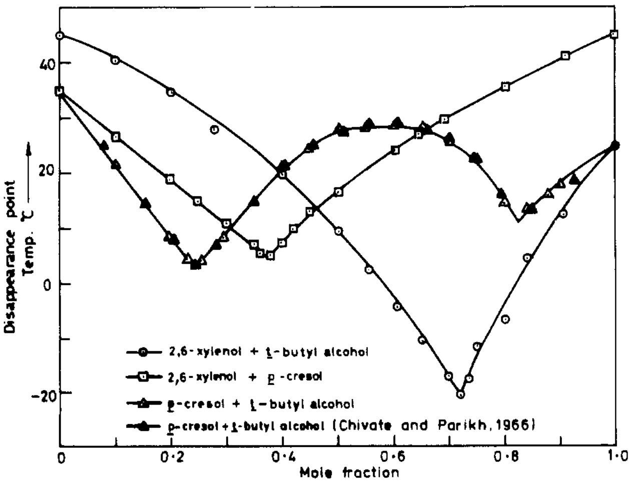

Figure 3. Binary solid–liquid equilibria for the systems *p*-cresol–*tert*-butyl alcohol, 2,6-xylenol–*tert*-butyl alcohol, and *p*-cresol–2,6-xylenol.

°C) and 2,6-xylenol (45.6 °C). The boiling point of *tert*-butyl alcohol (83 °C) is much lower than those of the other two close-boiling components (202 °C).

In order to judge clearly the effectiveness of *tert*-butyl alcohol 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 a composition triangle. Figure 4 shows 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 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.

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

p-cresol–*tert*-butyl alcohol		*tert*-butyl alcohol–2,6-xylenol		2,6-xylenol–*p*-cresol	
mol % *p*-cresol	temp, °C	mol % *tert*-butyl alcohol	temp, °C	mol % 2,6-xylenol	temp, °C
0.00	25.0	0.0	45.0	0.00	34.7
10.01	18.2	10.12	40.5	10.09	26.5
11.96	15.9	20.08	34.6	19.94	19.1
15.08	13.6	30.36	27.8	25.03	15.1
19.98	14.4	40.09	19.5	30.03	10.8
24.99	22.5	49.75	9.5	35.23	7.2
30.13	25.2	55.35	2.7	36.11	5.6
34.79	28.0	60.55	−3.9	38.12	5.2
40.16	28.6	64.94	−10.5	39.77	7.5
44.70	28.1	70.14	−17.0	42.07	10.2
49.91	27.7	72.23	−20.2	45.09	12.8
54.83	25.0	72.74	−17.7	49.92	16.6
60.33	20.1	72.93	−21.8	60.03	23.9
64.96	15.2	74.77	−20.2	69.08	29.7
70.00	9.5	75.15	−11.7	80.12	35.6
71.80	7.0	75.97	−17.0	90.72	41.2
75.02	4.1	78.00	−9.0	100.0	45.0
76.84	4.6	79.97	−6.7		
79.91	8.0	80.00	−8.2		
89.97	21.7	84.06	4.6		
100.0	34.7	85.00	6.5		
		90.43	12.5		
		100.0	25.0		

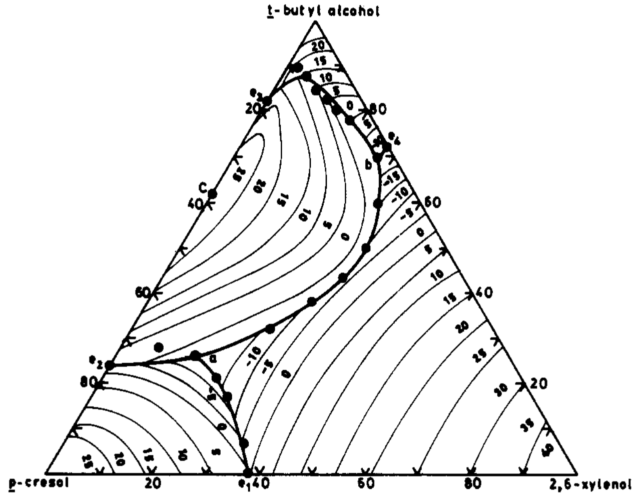

Figure 4. Isotherms of the ternary system *p*-cresol–2,6-xylenol–*tert*-butyl alcohol.

Feasibility Study

Feasibility studies were performed in a phase separation apparatus (*14*). After the equilibration in the apparatus, quick filtration in order to avoid a shift in equilibrium composition and

Table III. Results from Feasibility Studies (Figure 5)

run no.	temp, °C	crystallization stages	purity of *p*-cresol, %	recovery of *p*-cresol, %
1	13.0	I	76.3	65.0
2	13.5	I	77.4	45.5
3	4.0	I	69.7	77.4
4	7.5	I	74.6	54.0
5	17.0	II	90.4	50.5
6	11.5	I	11.6	14.1
7	9.5	I	22.1	16.7
8	14.0	I	90.9	39.4

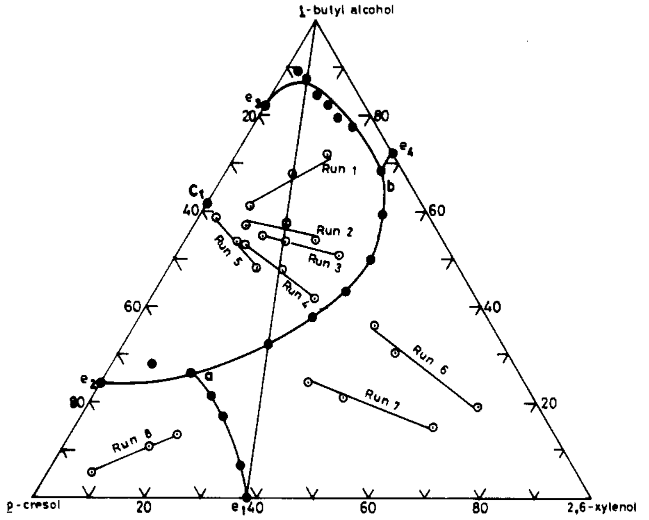

Figure 5. Feasibility runs of the ternary system *p*-cresol–2,6-xylenol–*tert*-butyl alcohol.

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 *p*-cresol and 2,6-xylenol and the requisite amount of *tert*-butyl alcohol 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, and 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 III. All the conodes in the primary crystallization region converge toward the point corresponding to molecular addition components of *p*-cresol and *tert*-butyl alcohol. As indicated in Figure 5 and Table III, the recovery of *p*-cresol in the solid phase from its eutectic mixture is in the range from 45 to 77% and the purity is from 70 to 90%. Recrystallization may yield higher purity. All the runs were performed over the temperature range from 4 to 17 °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. *tert*-Butyl alcohol appears to be a suitable solvent for separation of *p*-cresol from its mixture with 2,6-xylenol. A ternary phase diagram for this system was constructed. With multistage crystallization, reasonable purity of *p*-cresol can be achieved.

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