

Phase Relations of *o*- and *p*-Chlorobenzoic Acids in Hydrotrope Solutions

Edésio J. Colônia,[†] Ashok B. Dixit, and Narayan S. Tavare*

Department of Chemical Engineering, University of Bradford, West Yorkshire BD7 1DP, U.K.

The separation of chlorobenzoic acids from their mixtures of *o*- and *p*-components in hydrotrope solutions was investigated. The aqueous solubilities of *o*- and *p*-chlorobenzoic acids in different concentrations of sodium cumene sulfonate and sodium butyl monoglycol sulfate solutions at different temperatures were determined by the mass disappearance method. The ternary solid–liquid-phase equilibrium diagrams for the *o*-chlorobenzoic acid + *p*-chlorobenzoic acids + water system with sodium cumene sulfonate and sodium butyl monoglycol sulfate as hydrotropes, incorporating several hydrotrope *isoplethal* curves and the two-component saturation and eutectic tie lines, were constructed. The sensitivity and feasibility of the proposed process are examined by carrying out solubilization and equilibrium precipitation experiments with the mixtures of various compositions, including the eutectic composition. With both these hydrotropes it was possible to enrich *p*-chlorobenzoic acid significantly in the product crystalline phase from the eutectic composition in a single stage. Highly pure (>99.0%) crystals of chlorobenzoic acid were obtained from precipitation of noneutectic mixtures of *o*- and *p*-chlorobenzoic acids in their primary crystallization region.

Introduction

Hydrotropes are a class of organic compounds that significantly increase the aqueous solubility of certain sparingly soluble compounds. Sharma and co-workers (Jankiraman and Sharma, 1985; Gaikar and Sharma, 1986; Gaikar et al., 1988) used hydrotropes to enhance the rates of multiphase chemical reactions as well as to separate selectively close-boiling compounds by either extractive distillation or liquid–liquid extraction. Tavare and co-workers (Tavare and Gaikar, 1991; Geetha et al., 1991; Raynaud-Lacroze and Tavare, 1993; Colônia and Tavare, 1994; Jadhav et al., 1995; Colônia et al., 1996; Dixit et al., 1996, 1997) exploited the phenomenon of hydrotropy for the separation of isomeric mixtures. For several binary mixtures, they found that the increase in the solubility with the hydrotrope concentration was significantly higher for one of the components and used this observation to selectively precipitate one of the components by controlled dilution with water. This technique avoids the use of inflammable and expensive organic solvents as often used in dilution crystallization, or extreme temperatures and multistage operations required in melt crystallization. They demonstrated its successful application for the separation of *o*- and *p*-chloronitrobenzenes, 1- and 2-naphthols, and *m*- and *p*-aminoacetophenones, in some cases even at eutectic compositions. The specificity in solubilization has been successfully employed not only for the separation of close boiling and both close boiling and close melting components from binary mixtures forming simple eutectics but also for achieving improved quality and purity of pharmaceutical intermediates such as 6-aminopenicillanic acid (Tavare and Jadhav, 1996).

The present study focuses on the separation of *o*- and *p*-chlorobenzoic acid (CBA) through hydrotropy. Chlorobenzoic acids, used as intermediate chemicals, can be

synthesized by the oxidation of a mixture of chlorotoluenes; therefore, the end product will contain an isomeric mixture of CBAs. The melting points of *o*- and *p*-CBAs are 142 °C and 243 °C, respectively. Laddha and Sharma (1978) reported the dissociation extraction method on a laboratory scale to separate selectively *p*-CBA from its mixture with *o*-CBA, while Phatak and Gaikar (1993) determined the solubilities of pure *o*- and *p*-CBAs in various hydrotropes. The scope of this work is to develop the phase relationships for the binary system in hydrotrope solutions of sodium cumene sulfonate (NaCS) and sodium butyl monoglycol sulfate (NaBMGS). This experimental study concerns the determination of relevant solubility data and the construction of ternary-phase equilibrium diagrams for the *o*-CBA + *p*-CBA + water system.

Solubility Data

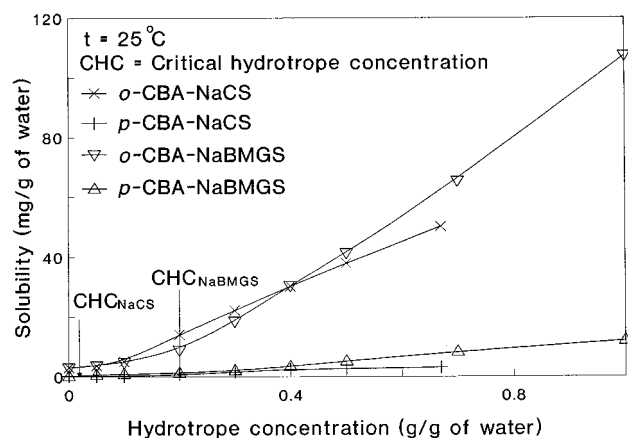
Solubility data may provide a good indication of possible separation of a given solid binary mixture. The solubilities of pure *o*- and *p*-CBAs in aqueous NaCS and NaBMGS solutions were determined by the mass disappearance method developed by Geetha et al. (1991). An excess amount of solid was charged into a known amount of hydrotrope solution contained in a small jacketed vessel (typically 100 mL), and the resulting suspension was magnetically stirred for equilibration at a desired temperature for at least 6 h. The vessel temperature was maintained constant (within ± 0.1 °C) by circulating water from a thermostatic bath. After equilibration, the slurry was filtered through filter paper (Whatman #1), and the residue was dried in an oven overnight and weighed. The solubility was determined as the ratio of the difference in masses between the initial charge and the final residue to the mass of water in the hydrotrope solution. The solubility was calculated as the amount dissolved per unit mass of water, thus requiring evaluation of the amount of water present in the hydrotrope solution of a given concentration. The solubility data (expressed in milligrams of component/per gram of water) were used to construct solubility curves.

* Corresponding author. Fax number, 00 44 1274 385700; E-mail, n.s.tavare@bradford.ac.uk.

[†] Deceased.

Table 1. Solubilities of *o*- and *p*-CBA (mg/g of Water) as a Function of Hydrotrope Concentration

hydrotrope concn, g/g of water	solubility (mg/g of water)							
	NaCS		NaBMGS					
	<i>o</i> -CBA <i>t</i> = 25 °C	<i>p</i> -CBA <i>t</i> = 25 °C	<i>t</i> = 15 °C	<i>o</i> -CBA <i>t</i> = 25 °C	<i>t</i> = 35 °C	<i>p</i> -CBA <i>t</i> = 45 °C	<i>t</i> = 25 °C	<i>t</i> = 45 °C
1.00			90.8	107.3	137.8	161	12.0	24.3
0.70			59.5	65.4	88.1	105	8.3	13.8
0.67	50.1	3.04						
0.50	37.9	2.52	40.0	41.3	62.0	79.0	5.1	9.3
0.40	30.2	2.46	29.2	30.6	43.1	47.8	3.4	6.7
0.30	22.2	1.50	16.6	18.6	25.2	38.4	2.0	4.7
0.20	14.0	0.64	8.5	8.9	14.2	18.4	1.2	2.7
0.10	5.0	0.16		4.8			0.8	
0.05	3.6	0.13		3.7			0.6	
0.03	3.2	0.12						
0.00	3.0	0.11		3.0			0.1	

**Figure 1.** Solubility curves at 25 °C: ×, *o*-CBA–NaCS; +, *p*-CBA–NaCS; ∇, *o*-CBA–NaBMGS; Δ, *p*-CBA–NaBMGS.

The amounts of solute in both the solid and solution phases were kept at the same order of magnitude. Generally the undissolved solids were in the range of 25–30% of the solids initially charged into the vessel. The solubility data (with an estimated accuracy within 2%) for pure components (namely *o*- and *p*-CBAs) were determined by this method in two commercially available hydrotropes (NaCS and NaBMGS) at different solution hydrotrope concentrations. All hydrotrope concentrations were expressed in a mass/mass basis. Commercial neat aqueous solution of NaBMGS was supplied either by Hüls (U.K.) Ltd., Milton Keynes or Hydrion, AG., Wettingen, while neat NaCS solution was obtained from Hickson Manro Ltd., Stalybridge. The other hydrotrope concentrations were prepared by diluting commercially available neat solutions with water. The two components, *o*- and *p*-CBAs, were procured from Aldrich Chemicals Co.

Solubility data for pure components in NaCS and NaBMGS hydrotrope solutions are shown in Table 1 and some of them in Figure 1. Solubility curves of *o*- and *p*-CBA in aqueous hydrotrope solutions in Figure 1 were drawn through the data points using polynomial interpolation. Hydrotropes themselves are freely soluble in water and appear to self-aggregate in an aqueous solution as organized assemblies in a stack like fashion and solubilize the solute by a similar associative mechanism above a minimum hydrotrope concentration. Above this threshold called *critical hydrotrope concentration* (CHC), the solubilization rises appreciably and eventually levels off to a plateau, thus resulting in a sigmoidal solubility versus hydrotrope concentration curve. For NaBMGS, the neat and critical hydrotrope concentrations are about 1.0 and 0.2 g/g of water, respectively. The respective values for

NaCS are about 0.67 and 0.02 g/g of water. At 25 °C, although the relative enhancement in solubilities of both components in NaBMGS (i.e., the ratio of solubilities at neat to critical hydrotrope concentration) is the same (about 10 and 12), the absolute increase for *o*-CBA (from 0.009 to 0.107 g/g of water) is significantly higher than that for *p*-CBA (from 0.001 to 0.012 g/g of water). The solubility data in NaBMGS solution as reported in Table 1 also indicate that the absolute enhancements at 45 °C are higher by a factor of about 2 than at 25 °C. The solubilities of *o*- and *p*-CBA in water at 25 °C are 0.0030 and 0.0001 g/g of water, respectively. Slightly lower values (0.0021 and 0.00008 g/g of water for *o*- and *p*-CBA, respectively, were reported at 30 °C by Laddha and Sharma (1978). The values reported by both Osol and Kilpatric (1933) (~0.0021 and 0.00007 g/g of water) and Phatak and Gaikar (1993) (~0.0021 and 0.00008 g/g of water for *o*- and *p*-CBAs, respectively, at 30 °C) were similar to those of Laddha and Sharma (1978). The ratios of the solubilities of two CBAs at 25 °C in neat solution of NaCS and NaBMGS to those in distilled water are 17 and 36 for *o*- and 28 and 109 for *p*-CBA, respectively. Since the absolute enhancements in solubility for the two components are significantly different, both dilution and thermal effects can be exploited to achieve improved performance of the separation process. Trends in solubilities of *o*- and *p*-CBAs in NaBMGS solutions reported in this study and by Phatak and Gaikar (1993) are similar; the precise comparison is, however, difficult. The solubility of the *o*-isomer is much higher (about 1 order of magnitude) than that of the *p*-isomer in most hydrotrope solutions. In their recent studies (Phatak and Gaikar, 1996), *p*-CBA was more soluble than *o*-CBA in aqueous *N,N*-dimethylformamide solutions at high concentrations, indicating perhaps a different kind of solution-phase structure. The absolute enhancement in the *o*-CBA solubility may be attributed to its molecular structure. Generally, the *p*-component has a higher melting point and a lower boiling point than corresponding the *o*-component. The aggregation structure of a hydrotrope in aqueous solution can better accommodate an *o*-component into mobile aggregates than its symmetrically structured *p*-component.

Finally, the surface tension and densities of solutions were determined with a standard tensiometer (Du Nouy Apparatus for surface tension measurement) and density meter (Anton Paar Density meter, DMA55), respectively. The results are reported in Table 2. Measured surface tension values of hydrotrope solutions prepared from commercial solutions over the range of hydrotrope concentration are practically constant (~40 mN/m) and are not influenced by the presence of solutes in the solutions. The

Table 2. Surface Tension, σ , and Density, ρ , at $t = 20\text{ }^{\circ}\text{C}^a$

hydrotrope concn, g/g of water	NaCS		NaCS saturated with <i>o</i> -CBA		NaCS saturated with <i>p</i> -CBA		NaBMGS	
	σ , mN/m	ρ , g/cm ³	σ , mN/m	ρ , g/cm ³	σ , mN/m	ρ , g/cm ³	σ , mN/m	ρ , g/cm ³
1.00							40	1.1890
0.70							39	1.1598
0.67	38	1.1370	38	1.1352	40	1.1366		
0.50	40	1.1126	40	1.1170	39	1.1119	39	1.1264
0.40	41	1.0981	41	1.0991	40	1.0967	40	1.1111
0.30	42	1.0770	41	1.0857	40	1.0767	40	1.0899
0.20	42		38	1.0788	41	1.0542	41	1.0625
0.10			38	1.0557			40	1.0330
0.00	72	0.9982	51	0.9991	52	0.9980		

^a Accuracies: σ , ± 1 mN/m; ρ , $\pm 1 \times 10^{-4}$ g/cm³.

presence of hydrotrope and solutes does reduce the surface tension of water phase (~ 72 mN/m), and significant changes in surface tension values may be expected around and below critical hydrotrope concentrations. Measured densities of hydrotrope solutions appear to show correct trend, and vary with both hydrotrope and solute concentrations, variations with solute concentrations being small compared to hydrotrope concentration.

Ternary-Phase Equilibrium Diagrams

In the present study the two quaternary isothermal systems, viz., *o*-CBA + *p*-CBA + water + hydrotrope, should ideally be represented in a space model as either a tetrahedron or a triangular prism for each hydrotrope. Instead of these elaborate time-consuming constructions, three-component systems on a free hydrotrope basis can conveniently be represented on a ternary diagram [see, for example, Colônia et al. (1993); Raynaud-Lacroze and Tavare (1993); Colônia and Tavare (1994); Tavare and Jadhav (1996)]. The construction of the ternary-phase equilibrium diagram is essential for the prediction of the efficacy of a given hydrotrope as the location of the initial composition and the path followed by the separation process on the ternary-phase diagram decide the quality of the products separated. In addition to solubility data, saturation points with respect to both components were determined. For a data point on a saturation line with respect to both components, at any hydrotrope concentration an excess amount of the mixture of two components (i.e., the amount of each of them was more than the solution could dissolve) was added to the hydrotrope solution of desired concentration. Again, the undissolved solids should account for a reasonable fraction of the dissolved solids. The solution was then stirred at the desired temperature for ~ 24 h using a magnetic stirrer in a similar jacketed glass vessel for equilibration. Undissolved solids were separated by filtration of the entire slurry through (Whatman #1) filter paper, and the residue on the filter paper was dried, weighed, and subsequently used for component analysis. The composition of the dry solids was determined by high-performance liquid chromatography (HPLC). The wavelength of 236 nm was selected using a Cary spectrophotometer over the range 190–350 nm. Dry CBA solids were diluted in methanol for injection in a Varian chromatograph (Model 5020). The column employed was S5 ODS2 (25 cm of length \times 4.6 mm of diameter) supplied by Phase Separation Ltd., Deeside, Clwyd. The mobile phase consisted of 65 vol % methanol and 35% vol water, buffered by means of acidification to 0.5 vol % with a strong H₃PO₄ solution. The standard CBA solutions contained a total of 25 mg of solids/100 mL of methanol. A material balance calculation for both solubilizates was carried out in a few cases by analyzing the mother liquor. The hydrotrope in

Table 3. Compositions (mg of CBA/g of Water) of Saturated Hydrotrope Solutions with Respect to Both *o*- and *p*-CBAs at $t = 25\text{ }^{\circ}\text{C}$

hydrotrope concn, g/g of water	NaCS		NaBMGS	
	<i>o</i> -CBA	<i>p</i> -CBA	<i>o</i> -CBA	<i>p</i> -CBA
1.0			81.5	8.1
0.70			48.6	5.5
0.67	91.2	7.0		
0.50	50.5	3.9	37.0	2.8
0.40	35.6	3.1	26.6	1.7
0.30	23.4	1.8	16.1	1.0
0.20	12.7	0.8	7.7	0.3
0.10	4.7	0.2		

the mother liquor was precipitated with methanol prior to HPLC analysis. The two-component saturation tie line was drawn by joining the water apex with the data points representing solutions saturated with respect to both solutes for different hydrotrope concentrations. The eutectic tie line, on the other hand, was obtained by simply linking up the water apex with any data point representing the simple eutectic composition. Table 3 shows all the compositions (milligrams of component per gram of water) of solutions saturated with respect to both the components of the binary as a function of NaCS and NaBMGS hydrotrope concentrations. The data point representing the composition of solution saturated with respect to two components of the binary system provides a characteristic limit on the solubility of the components in the mixture and is invariant when the temperature and hydrotrope concentration are fixed.

In addition, the solubility data were obtained for binary mixtures of known CBA composition by the crystal disappearance method (Raynaud-Lacroze and Tavare, 1993). In this method, the amount of known hydrotrope solution required just for complete disappearance of the solid crystalline phase by visual observation was determined. The total amount of the hydrotrope solution slowly added to the slurry, up to the disappearance point where no crystal (undissolved solids) could any longer be seen by the naked eye, was used to determine a data point on an *isoplethal* solubility curve. Unless the initial composition happened to be that of the two-component saturation point, the resulting solution was assumed to be saturated with respect to only one of the components. To measure the mass of the hydrotrope solution added in the solution phase during the equilibration step, a near-saturated solution was prepared by adding a known amount of hydrotrope solution to a binary solid CBA mixture and maintained in a magnetically stirred and jacketed vessel (of ~ 100 mL capacity) at a constant temperature (within $\pm 0.1\text{ }^{\circ}\text{C}$) by circulating water from a thermostatic water bath. The remaining small amount of known hydrotrope solution was then added very slowly until the last crystal disappeared and homogeneous solution was achieved. The results of

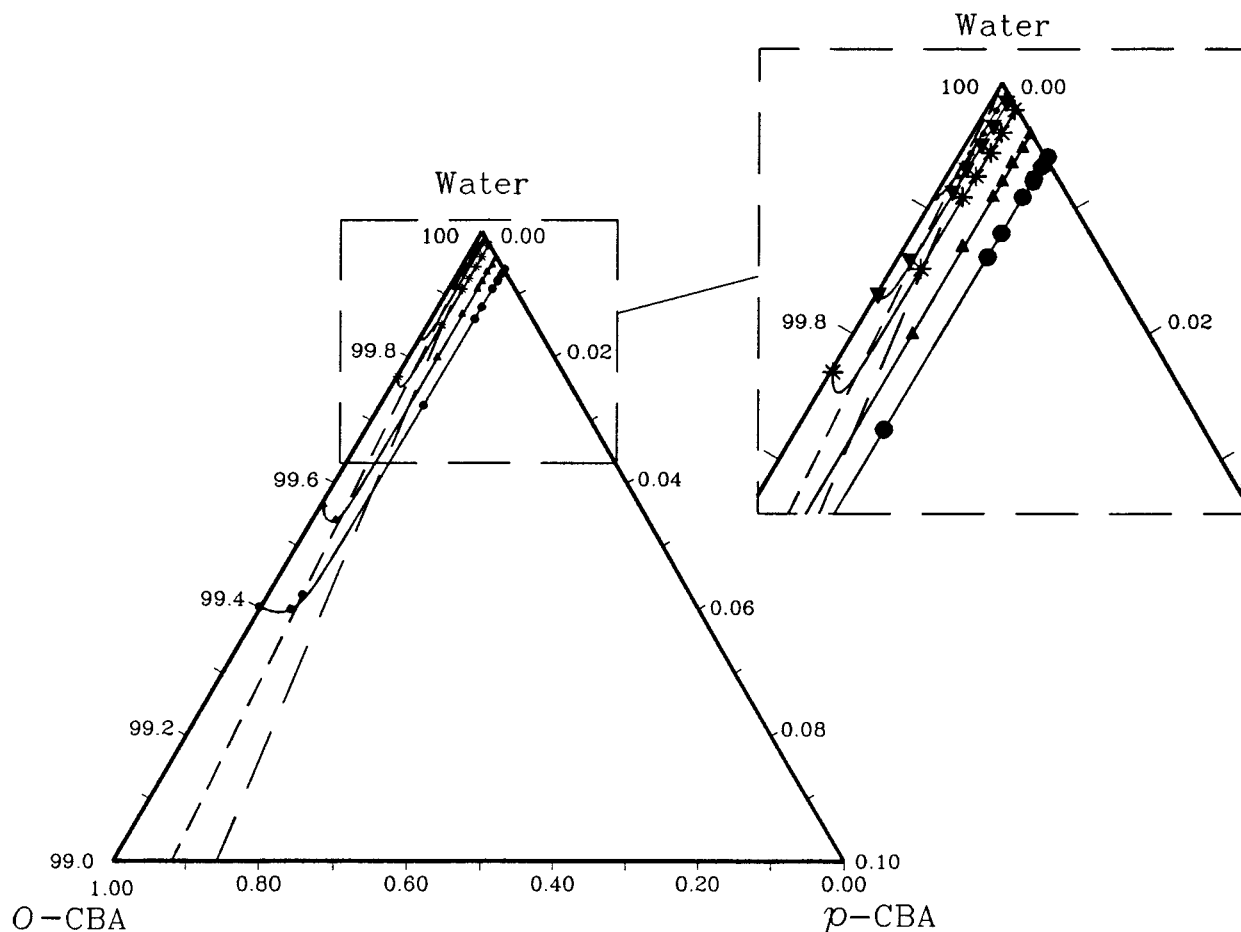


Figure 2. Ternary-phase equilibrium diagram for the system *o*-*p*-CBA–water with NaCS hydrotrope (all components in mol %), c_H = hydrotrope concentration, g/g of water: ○, c_H = 0.2 g/g of water; ▼, c_H = 0.3 g/g of water; *, c_H = 0.4 g/g of water; ▲, c_H = 0.5 g/g of water; ●, c_H = 0.67 g/g of water; ---, eutectic tie line; — — —, two-component saturation tie line.

Table 4. Solubilities (mg of CBA/g of Water) of *o*- and *p*-CBA Mixtures as a Function of Hydrotrope Concentration at $t = 25\text{ }^\circ\text{C}$

hydrotrope	hydrotrope concn, g/g of water															
	1.0		0.7		0.67		0.5		0.4		0.3		0.2		0.0	
	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>
NaCS					50.5	0.0	37.7	0.0	20.2	0.0	13.5	0.0	10.4	0.0	2.1	0.0
					43.6	4.8	14.6	3.7	7.4	1.8	6.2	1.5	2.5	0.6	0.24	0.06
					19.9	5.0	8.0	3.5	3.4	2.2	2.0	1.3	1.02	0.68	0.12	0.08
					12.3	5.3	4.8	3.2	1.3	2.0	1.2	1.8	0.4	0.6	0.044	0.066
					7.3	4.9	3.3	3.3	0.5	2.2	0.4	1.6	0.16	0.64	0.018	0.072
					5.2	5.2	2.3	3.5	0.2	2.0	0.2	1.5	0.0	0.6	0.0	0.08
					3.4	5.0	1.4	3.4	0.0	2.1	0.0	1.3				
					2.2	5.1	0.8	3.4								
					1.3	5.0	0.4	3.3								
					0.6	5.2	0.0	3.2								
				0.0	5.2											
NaBMGS	107.3	0.0	65.4	0.0			41.3	0.0	30.6	0.0	18.6	0.0	8.9	0.0	3.0	0.0
	86.1	15.4	58.1	4.2			39.0	2.8	28.1	1.3	16.5	1.0	2.4	0.9	0.0	0.1
	27.5	10.4	11.8	6.1			22.8	2.1	5.4	1.7	4.5	0.7	1.9	0.5		
	24.1	10.3	10.1	3.0			9.6	3.1	4.3	2.1	3.4	0.9	0.0	1.2		
	0.0	12.0	9.1	3.0			0.0	5.1	0.0	2.0	0.0	2.0				
			0.0	8.3												

such measurements at $25\text{ }^\circ\text{C}$ for the binary mixtures at different hydrotrope concentrations (namely, 0.67, 0.5, 0.4, 0.3, 0.2 g/g of water for NaCS and 1.0, 0.7, 0.5, 0.4, 0.3, 0.2 g/g of water for NaBMGS) are reported in Table 4. The solubility was initially calculated in milligrams of solute per gram of water. The solubility data obtained by this method were slightly less than those obtained by the mass disappearance method under otherwise similar conditions. These data were then converted into mol % (i.e., in the form

of relative concentrations of solute 1–solute 2–water, all in mol %) using molecular weights of all species to construct the hydrotrope *isoplethal* solubility curves of the saturating component in the binary mixture, i.e., hydrotrope *isopleths* for CBA equilibrium concentrations in the ternary-phase equilibrium diagrams. These *isopleths* have a threshold or characteristic point, usually at minimum, as represented by the two-component saturation data point. This point splits the *isopleths* into two primary parts, each being a

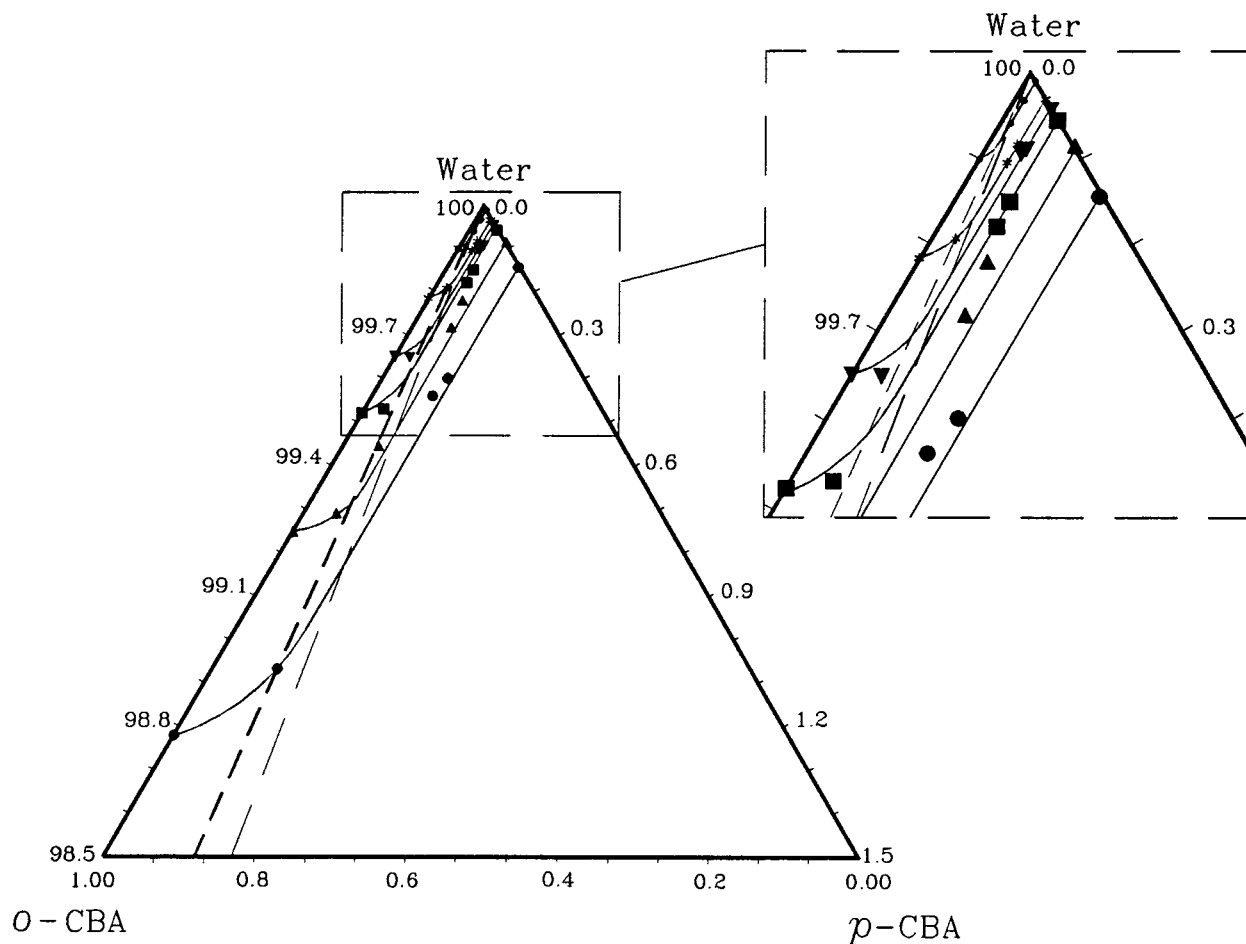


Figure 3. Ternary-phase equilibrium diagram for the system *o*-*p*-CBA-water with NaBMGS hydrotrope (all components in mol %), c_H = hydrotrope concentration, g/g of water: •, c_H = 0.2 g/g of water; *, c_H = 0.3 g/g of water; ▼, c_H = 0.4 g/g of water; ■, c_H = 0.5 g/g of water; ▲, c_H = 0.7 g/g of water; ●, c_H = 1.0 g/g of water; ---, eutectic tie line; - · - ·, two-component saturation tie line.

saturation curve with respect to the primary component and undersaturated with respect to the other component of the binary mixture. Naturally, the primary component will precipitate out first in the region as the solution will be supersaturated with respect to this component. The locus of such two-component saturation points for different hydrotrope concentrations is referred to as a two-component saturation tie line. This two-component saturation curve divides the hydrotrope *isoplethal* solubility curves into two sections. Also plotted in these ternary diagrams are the eutectic tie lines, representing the locus of the points (solutions) whose solubilizate composition is that of the simple binary eutectics. Thus, the single- and two-component equilibrium compositions (pure and binary mixtures) for different hydrotrope concentrations together with eutectic and two-component saturation tie lines are all the data used for the construction of the two ternary diagrams with each apex representing one of the three components, namely, *o*-CBA, *p*-CBA, and water, as shown in Figures 2 and 3. For the sake of clarity, only the enlarged triangular sections of the water apex of the ternary diagrams depicting several hydrotrope *isoplethal* solubility curves are shown. In addition, further corresponding enlargements of the water apex are also drawn in Figures 2 and 3. In these ternary-phase equilibrium diagrams, the smooth *isoplethal* solubility curves (six for NaBMGS and five for NaCS) were constructed through the data points. The intersections of the *isoplethal* curves with the two axes represent the solubilities of pure *o*- and

p-CBAs in the hydrotrope of the specified concentration. From the ternary diagram it is evident that, for a given hydrotrope concentration, the saturation concentration of *o*-CBA was significantly higher than that of *p*-CBA. Also, the solubility of *o*-CBA augments rapidly with an increase in the hydrotrope concentration as compared to *p*-CBA. The solubility of *p*-CBA is much more influenced by the presence of *o*-CBA in the solution phase. The eutectic tie line is the locus of the data points with relative compositions of *o*- and *p*-CBAs identical to the eutectic composition, i.e., 86% *o*-CBA. The two-component saturation tie line is the locus of the hydrotrope solutions of different strengths saturated with respect to both *o*- and *p*-CBAs. This tie line is very important as it divides the ternary-phase diagram into two primary crystallization regions, and depending upon the initial composition of the mixture, one of the two components would selectively precipitate out on dilution with water. Thus, if the initial composition of the mixture lies on the left-hand side of the two-component saturation tie line in the *o*-CBA primary crystallization region of the ternary-phase diagram, then *o*-CBA would primarily precipitate out and similarly *p*-CBA from the *p*-CBA primary crystallization region on the right-hand side of the two-component saturation tie line. For the present system, both NaCS and NaBMGS were influential in shifting the two-component saturation tie line away from the eutectic tie line, thus providing the possibility of separation of the eutectic composition.

Table 5. Feasibility Results from Equilibrium Precipitation Experiments

hydrotrope	precipitation of	starting solute composition	product recovery, %	product purity, %
NaBMGS	<i>o</i> -CBA	100% <i>o</i> -CBA	50–80% <i>o</i> -CBA	99%+ <i>o</i> -CBA
		97% <i>o</i> -CBA	45–75% <i>o</i> -CBA	95%+ <i>o</i> -CBA
	<i>p</i> -CBA	100% <i>p</i> -CBA	60–95% <i>p</i> -CBA _o	99%+ <i>p</i> -CBA
		14% <i>p</i> -CBA	~80% <i>p</i> -CBA	~70% <i>p</i> -CBA
		(eutectic composition)		
		42% <i>p</i> -CBA	65–95% <i>p</i> -CBA	~100% <i>p</i> -CBA
NaCS	<i>p</i> -CBA	(industrial reactor product)		
		60% <i>p</i> -CBA	~83% <i>p</i> -CBA	~100% <i>p</i> -CBA
		(Laddha and Sharma, 1978)		
		90% <i>p</i> -CBA	~23% <i>p</i> -CBA	~100% <i>p</i> -CBA
		14% <i>p</i> -CBA	~73% <i>p</i> -CBA	~80% <i>p</i> -CBA
		(eutectic composition)		
<i>p</i> -CBA	42% <i>p</i> -CBA	~65% <i>p</i> -CBA	~95% <i>p</i> -CBA	
	(industrial reactor product)			
	50% <i>p</i> -CBA	~75% <i>p</i> -CBA	~100% <i>p</i> -CBA	
		(equimolar in 50% NaCS)		

Separation Feasibility

The equilibrium phase relations (in the form of solubility curves and ternary diagrams) indicate the possibility of separation of components from any mixture. A simple technique consisting of solubilization and equilibrium precipitation was employed for the separation of a mixture. It involved a complete solubilization of the mixture to be separated in a neat hydrotrope solution and subsequent selective equilibrium precipitation of the desired component performed in a single-stage batch operation by dilution with water. The separation performance depends not only on the starting composition but also on the process conditions. To achieve optimal performance in terms of recovery and purity for their *o*- and *p*-chloronitrobenzenes system with NaBMGS, Geetha et al. (1991) indicated that the amount of diluent water used should be about twice the mass of the initial neat hydrotrope solution. A large number of separation feasibility experiments were carried out with mixtures of various compositions as shown in Table 5 using neat NaBMGS and NaCS solutions (except the experiment with equimolar composition). The precipitation was effected by adding drop-by-drop an amount of diluent water almost equal to twice the mass of hydrotrope solution to the hydrotrope solutions containing binary CBA mixtures. The product precipitate was analyzed by HPLC. Purity with respect to an isomer in a solid phase is the ratio of its weight to the total weight of the solid mixture, while recovery is the ratio of its weight in the precipitated solids to its weight in the original solid mixture. The results in Table 5 do indicate that pure CBA components can be precipitated from their respective primary crystallization regions at a reasonable level of recoveries. The precipitation experiments with the eutectic composition provide significant enrichment with respect to *p*-CBA in the solid phase for both the hydrotropes. The experimental results confirm that both NaBMGS and NaCS hydrotropes can be used for the purpose of separation of binary solid mixtures.

Conclusions

Solubility data for binary mixtures of *o*- and *p*-CBAs having different compositions were determined in aqueous solutions of NaCS and NaBMGS at different hydrotrope concentrations. Two ternary-phase equilibrium diagrams for the system *o*-CBA + *p*-CBA + water at 25 °C were constructed. Several hydrotrope *isoplethal* curves and two-component saturation and eutectic tie lines were included in these diagrams. Solubilization–equilibrium precipitation experiments confirmed the promising potential of hydrotropes for the purpose of separation of binary solid mixtures even at the eutectic composition.

Acknowledgment

The experimental work reported in this paper was performed at Department of Chemical Engineering, UMIST, Manchester, M60 1QD, England. Free supplies of hydrotropes from Hüls (U.K.) Ltd., Hydrior AG., and Hickson Manro Ltd. are appreciated.

Literature Cited

- Colônia, E. J.; Tavare, N. S. Separation of eutectics through hydrotropy. *Proceedings of the 1994 IChemE Research Event*; University College London: London, 1994; pp 749–751.
- Colônia, E. J.; Raynaud-Lacroze, P. O.; Tavare, N. S. Separation of isomers: Hydrotropy and precipitation. In Rojkowski, Z. H., Ed.; *Industrial Crystallization '93*; Politechnika: Warszawska: Warsaw Poland, 1993; pp 3-153-3-159.
- Colônia, E. J.; Dixit, A. B.; Tavare, N. S. Separation of *o*- and *p*-chlorobenzoic acids: hydrotropy and precipitation. *J. Cryst. Growth* **1996**, *166*, 976–980.
- Dixit, A. B.; Colônia, E. J.; Tavare, N. S. Selective precipitation of *p*-chlorobenzoic acid. In Biscans, B., Garside, J., Eds.; *Proceedings of the 13th Symposium on Industrial Crystallization*; PROGEP: Toulouse, **1996**; Vol. 1, pp 135–140.
- Dixit, A. B.; Colônia, E. J.; Tavare, N. S. Use of a hydrotrope in selective precipitation of *o*- or *p*-chlorobenzoic acids. *Proceedings of the 1997 IChemE Jubilee Research Event*; University of Nottingham, 1997; Vol 2, pp 1141–1144.
- Gaikar, V. G.; Sharma, M. M. Extractive separations with hydrotropes. *Solvent Extr. Ion Exch.* **1986**, *4*, 839–836.
- Gaikar, V. G.; Mahapatra, A.; Sharma, M. M. New strategies in extractive distillations: use of aqueous solution of hydrotrope and organic bases as solvent for organic acids. *Sep. Sci. Technol.* **1988**, *23*, 429–436.
- Geetha, K. K.; Tavare, N. S.; Gaikar, V. G. Separation of *o*- and *p*-chloronitrobenzenes through hydrotropy. *Chem. Eng. Commun.* **1991**, *102*, 211–224.
- Jadhav, V. K.; Dixit, B. A.; Tavare, N. S. Solubilities of *m*- and *p*-aminoacetophenones in hydrotrope solutions. *J. Chem. Eng. Data* **1995**, *40*, 669–673.
- Janakiraman, B.; Sharma, M. M. Enhancing rates of multiphase reactions through hydrotropy. *Chem. Eng. Sci.* **1985**, *40*, 2156–2158.
- Laddha, S. S.; Sharma, M. M. Separation of close boiling organic acids and bases by dissociation extraction: Chlorophenols, *N*-alkylphenols, chlorobenzoic acids. *J. Appl. Chem. Technol. Biotechnol.* **1978**, *28*, 69–78.
- Osol, A.; Kilpatrick, M. The salting-out and salting-in of weak acids. The activity coefficients of the molecules of ortho, meta, and para chlorobenzoic acids in aqueous salt solutions. *J. Am. Chem. Soc.* **1933**, *55*, 4430–4440.
- Phatak P. V.; Gaikar V. G. Solubility of *o*- and *p*-chlorobenzoic acids in hydrotrope solutions. *J. Chem. Eng. Data* **1993**, *38*, 217–220.
- Phatak P. V.; Gaikar V. G. Solubility of *o*- and *p*-chlorobenzoic acids and *o*- and *p*-nitroanilines in *N,N*-dimethylformamide + water. *J. Chem. Eng. Data* **1996**, *41*, 1052–1054.
- Raynaud-Lacroze, P. O.; Tavare, N. S. Separation of 2-Naphthol: Hydrotropy and Precipitation. *Ind. Eng. Chem. Res.* **1993**, *32*, 685–691.
- Tavare, N. S.; Gaikar, V. G. Precipitation of salicylic acid: Hydrotropy and reaction. *Ind. Eng. Chem. Res.* **1991**, *30*, 722–728.
- Tavare, N. S.; Jadhav, V. K. Solubilities of 6-aminopenicillanic acid and phenoxyacetic acid in hydrotrope solutions. *J. Chem. Eng. Data* **1996**, *41*, 1196–1202.