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Separation of Close Boiling Point Mixtures (p-Cresol/m-Cresol, Guaiacol/Alkylphenols, 3-Picoline/4-Picoline, Substituted Anilines) through Dissociation Extractive Crystallization

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Separations of close boiling point mixtures, namely, *m*-/*p*-cresols, 3-/4-picolines, guaiacol/alkylphenols, and substituted anilines, have been successfully accomplished by a novel strategy of dissociation extractive crystallization. *p*-Cresol has been separated in pure form from mixtures with *m*-cresol by reactive crystallization with piperazine and diazabicyclooctane (DABCO) in nearly quantitative yields. Very high values of separation factor were realized for the separations of guaiacol/alkylphenols and 3-/4-picolines. The crystallization of substituted anilines–*p*-toluenesulfonates from an aqueous phase further improved the separation factor, by an order of magnitude over those obtained using a nonaqueous phase. A theory has been developed to predict the separation factor for the crystallization from an aqueous phase.

A variety of industrial mixtures consist of close boiling point isomeric/nonisomeric components. In most cases, the separation of such mixtures cannot be economically realized by the conventional methods of separation. In such cases, the strategy of selective reactions may prove to be useful. Reversible reactions, such as acid–base reactions and chelation, offer many opportunities for realizing the high selectivity that is needed to make such separations economical. Dissociation extraction is one of such methods which exploits the differences between dissociation constants and distribution coefficients of the components of acidic/basic mixtures and has been widely employed for various industrially important mixtures (Anwar et al., 1971a,b, 1973, 1974, 1979; Wadekar and Sharma, 1981a–c; Jagirdar and Sharma, 1980, 1981a,b; Gaikar and Sharma, 1984a,b, 1985).

Gaikar and Sharma (1987) have extended the principle of dissociation extraction, namely, the addition of a neutralizing agent in stoichiometrically deficient amount, i.e., an amount just sufficient to neutralize the stronger component, to develop the process of dissociation extractive crystallization. This selective chemical complexation process based on acid–base reactions has been successfully used to separate 2,6-xylenol/*p*-cresol, piperazine/*N*-methylpiperazine, *N*-methylpiperazine/*N,N'*-dimethylpiperazine, *N*-alkyl-substituted anilines, *o*-/*p*-chloroanilines, *o*-/*p*-cumidines, and 2,4-/2,6-xylidines. Anhydrous piperazine was used for the separation of 2,6-xylenol/*p*-cresol, and aromatic sulfonic acids, such as *p*-toluenesulfonic acid and *p*-xylenesulfonic acid, were used for the basic mixtures. Earlier Jagirdar and Sharma (1981b) and Gaikar and Sharma (1984a) separated various substituted anilines by crystallizing their hydrochloride salts from solutions of these bases in suitable organic solvents by using anhydrous HCl gas. The precipitation of the product of neutralization increased the separation factor several times those realized with conventional processes including dissociation extraction. In this paper, the process of dissociation extractive crystallization has been used to separate "difficult to separate" close boiling point mixtures, such as *m*-/*p*-cresols, 3-/4-picolines, guaiacol/alkylphenols, and substituted anilines. The crystallization of aniline–*p*-toluenesulfonates from aqueous solutions considerably improved the separation of substituted anilines. An attempt has been made to predict the separation factor in such cases.

Previous Studies

The separation of *m*-/*p*-cresols has been a challenging

problem and has attracted the attention of many workers in the course of the last 4 decades. A number of methods have been proposed for separating *m*- and *p*-cresols. Physical methods, such as distillation or even azeotropic or extractive distillation, were unsuccessful owing to the closeness of properties of these isomers (Othmer et al., 1949). A potentially useful method depends on the preferential adduct formation with substances such as oxalic acid (Engel, 1937), phenol (Ludewig and Wilke, 1965), benzylamine (Fleischer and Meier, 1966), urea (Santhanam, 1970; Orlova et al., 1975), benzidine (Savitt and Othmer, 1952), and 2,6-lutidine (Cislak and Otto, 1948). However, the temperatures involved for the adduct formation were very low (−10 to −20 °C) and the recovery was poor (30–60%). In the case of benzidine, a carcinogenic compound is involved. Some chemical methods based on sulfonation–desulfonation or alkylation of mixture with isobutylene followed by fractional distillation of butylated products and then debutylation are other methods, but these are cumbersome and expensive. However, these processes are practiced industrially. The principle of dissociation extractive crystallization can possibly be exploited for the separation of *m*- and *p*-cresols from their mixtures because of the differences in their acidities.

Various substituted phenols, namely guaiacol, *p*-cresol, *o*-ethylphenol, and 2,6-xylenol, obtained in a mixture from a variety of low-temperature carbonization tars have very close boiling points. Since their separation by distillation will be difficult, it may be considered by reactive crystallization. These mixtures were earlier separated by Jagirdar and Sharma (1981a) by dissociation extraction.

The base fractions commonly described as commercial 3-picoline are mixtures containing 3-picoline, 4-picoline, and 2,6-lutidine. No process based on straight distillation has been useful for the separation of individual components from the tar base fraction (bp 143–145 °C). Many alternative methods have been proposed and some have been used with a degree of success for the separation of one or the other of the three constituents. 2,6-Lutidine forms a moderately insoluble complex with urea from which the base may be recovered in a state of purity by thermal decomposition, and by this means the bulk of the lutidine can be recovered prior to the separation of the picolines (Riethof, 1943). The separation of 3-/4-picolines is, however, a difficult task. Generally, fractional crystallization of derivatives, such as hydrochlorides (Karpman, 1980), oxalates (Arnold and Hejno, 1956) and borates (Robinson, 1957), has been considered, but this is laborious and may not be suitable for commercial exploitation.

Table I. Separation of m-Cresol (A)/p-Cresol (B)

solvent	feed concn, mol/L		extracting agent[a]	temp, °C	composition of solid, %		% recovery of B
	A	B			A	B	
diisopropyl ether	0.92	0.92	DABCO	-10		100	85
diisopropyl ether + n-heptane (50:50)	0.92	0.92	DABCO	0	0.8	99.2	78
diisopropyl ether	1.05	1.02	PIP	-20		100	70
dibutyl ether	1.05	0.97	PIP	-20		100	91
toluene	2.41	1.33	PIP	-20		100	32

[a] DABCO is diazabicyclooctane; PIP is piperazine.

Complexation with CuCl and fractional distillation of hydrochlorides were other approaches (Coulson and Jones, 1946). We have attempted to utilize dissociation extractive crystallization for the separation of 3-/4-picolines using arylsulfonic acids and oxalic acid.

All the previous work on dissociation extractive crystallization involved precipitation from nonaqueous solvents. However, the crystallization can be carried out from an aqueous phase provided the product of neutralization exhibits limited solubility in the aqueous phase. Such a strategy has proved to be useful for the separation of 2,4,6-trichlorophenol (TCP)/2,6-dichlorophenol/2,4-dichlorophenol using aqueous solutions of monoethanolamine (MEA), where 2,4,6-TCP–MEA salt being sparingly soluble in the aqueous phase precipitated as a solid crystalline product (Gaikar and Sharma, 1984b). A similar strategy has been used in this paper for the separation of cumidines, o-anisidine/m-chloroaniline, and m-/p-toluidines because substituted aniline–toluenesulfonates exhibit limited solubility in the aqueous phase.

Materials and Experimental Section

The organic chemical compounds, m- and p-cresols, guaiacol, 2,6-xylenol, o-ethylphenol, m-chloroaniline, o-anisidine, 3- and 4-picoline, m- and p-toluidine, piperazine, and diazabicyclooctane (DABCO) were of Fluka AR grade. A commercial mixture of cumidines was purified by distillation and found to contain 60% para isomer, 33% ortho isomer, and remaining meta isomer. Different solvents, such as n-heptane, toluene, and diisopropyl ether, were of AR grade. The purity of all organic compounds was checked by gas–liquid chromatography (GLC).

A known weight of a neutralizing agent in stoichiometric deficiency was added to the solution of a synthetic mixture of phenols (or bases) in a proper organic solvent. The mixture was vigorously stirred for 1–4 h at ambient temperature of 30 °C and then slowly cooled to the desired level, if necessary. For mixtures of substituted phenols, piperazine and DABCO were used as the neutralizing agent while for the organic bases anhydrous as well as concentrated aqueous solutions of p-toluenesulfonic acid were used. The crystalline product was separated from the solution, dried, and analyzed on GLC after neutralization and extraction of the liberated organics into an water-immiscible solvent, e.g., toluene.

Results and Discussion

When the solution of two phenolic (or basic) components A and B (A being the weaker component), in a suitable organic solvent, is contacted with a neutralizing agent C, taken in a stoichiometric deficiency, the competition for C between A and B leads to the following key equilibrium reaction based on their relative acidic/basic strengths:

$$A–C + B \rightleftharpoons A + B–C \qquad (1)$$
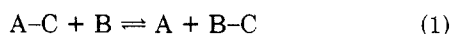
However, if complex B–C is sparingly soluble, the crys-

tallization of B–C will shift the equilibrium to the right. This continuous precipitation (removal) of the product will be manifested into high values of separation factor. The solvent used for the process plays an important role, both from the point of selectivity and of yield. It is necessary to use a solvent with the following characteristics:

(a) The weaker component must be considerably soluble in the solvent.

(b) The precipitated product should be essentially insoluble in the solvent.

(c) The neutralizing agent must be soluble in the solvent.

The selected neutralizing agent must be able to interact with the desired compound selectively, and the product of neutralization must be a solid. The formation of a liquid product leads to the distribution of the weaker component between the initial solvent and the newly formed liquid phase, resulting in unfavorable separations. This results in a decrease in the separation factor. It is difficult to predict a priori the separation factor in nonaqueous phases because of our inability to predict relative strengths of acidic/basic components in the organic phase.

The separation factor is defined as

(a) for solid–liquid systems

$$\alpha = \frac{[B–C]_{solid}}{[A–C]_{solid}} \Big/ \frac{[B]_{raffinate}}{[A]_{raffinate}} \qquad (2a)$$

(b) for liquid–liquid–solid systems

$$\alpha = \frac{[BH^+]_{solid} + V_a[BH^+]_a + V_a[B]_a}{[AH^+]_{solid} + V_a[AH^+]_a + V_a[A]_a} \Big/ \frac{V_s[B]_s}{V_s[A]_s} \qquad (2b)$$

Separation of m-/p-Cresols. Table I gives the results of preferential crystallization of p-cresol–base complex from solutions in different solvents. Both the selected organic bases, piperazine and DABCO were effective in isolating almost pure p-cresol from the mixtures in the form of a solid crystalline complex. The values of the separation factor approach infinity as 100% p-cresol–base complex crystallized. Both the bases were dibasic, and thus 1 mol of the base could react with 2 mol of p-cresol. The solvent plays an important role in this separation. The use of aliphatic solvents, like n-heptane, was not successful because of low solubility of m-cresol in n-heptane. The yield of p-cresol was very impressive with some aliphatic polar solvents, but relatively lower temperatures were required to increase the yield. However, with aromatic solvents, like toluene, the yield decreased drastically even at lower temperatures because of substantial solubility of complexes in the aromatic solvents. The importance of a suitable solvent has not been recognized by previous workers for crystallizing the adducts of either m-cresol or p-cresol with various compounds. In the absence of a proper solvent, the highly polar nature of m-cresol can reduce the recovery of p-cresol–base complex and can also affect the selectivity. Conventional dissociation extraction gives a separation factor close to unity

Table II. Separation of Guaiacol/Alkylphenols (Extracting Agent: Piperazine)[a]

system	solvent	initial concn, mol/L		final concn, mol/L		α^b
		A	B	A	B	
guaiacol (A)	diisopropyl ether	0.4	0.1	0.04	0.08	52
p-cresol (B)		0.25	0.25	0.09	0.22	16
guaiacol (A)	n-heptane	0.45	0.05	0.004	0.026	109
2,6-xylenol (B)		0.35	0.15	0.01	0.08	34
		0.25	0.25	0.02	0.17	24
guaiacol (A)	n-heptane	0.45	0.05	0.002	0.01	56
o-ethylphenol (B)		0.35	0.15	0.008	0.03	12

[a] Temperature: 0–5 °C. [b] α is separation factor.

Table III. Separation of Picolines

solvent	temp, °C	extractant (E) (4-picoline:E molar ratio)	initial concn, mol/L		final concn, mol/L		α
			3-	4-	3-	4-	
toluene + n-heptane (50:50)	30	oxalic acid (1:0.5)	0.64	0.70	0.53	0.45	2.5
	0	oxalic acid (1:0.5)	0.64	0.70	0.55	0.37	5.8
	0	oxalic acid (1:1)	0.64	0.70	0.59	0.18	34
toluene	20	oxalic acid (1:0.5)	0.67	0.63	0.65	0.46	12
	0	oxalic acid (1:0.5)	0.67	0.63	0.56	0.12	24
	0	oxalic acid (1:1)	0.67	0.63	0.55	0.07	45
n-heptane	20	p-TSA	0.35	0.36	0.34	0.17	38
	-10	p-TSA	0.35	0.36	0.345	0.13	122

Table IV. Separation of Cumidines (Solvent: Toluene)

concn of p-TSA, mol/L	initial concn, mol/L			final concn, mol/L			composition of ppt, % w/w			α of o/p
	o-	m-	p-	o-	m-	p-	o-	m-	p-	
3.0	0.32	0.07	0.59	0.30	0.04	0.10	2.1	2.9	95.0	73.5
2.0	0.32	0.07	0.59	0.28	0.06	0.06	7.9	2.1	90.0	61.8
1.0	0.32	0.07	0.59	0.30	0.06	0.08	2.0	0.3	97.7	95.6
solid p-TSA	0.32	0.07	0.59	0.17	0.03	0.5	4.1	0.8	95.1	9.7

because of the very small difference in the acidities of two cresols, which further gets cancelled by the adverse distribution coefficient ratio in any solvent (Anwar et al., 1977). Although m-cresol is a stronger acid than p-cresol in the aqueous phase (pK_a 10.1 and 10.28, respectively), p-cresol reacts preferentially with the organic base in the nonaqueous phases. Such a reversal in acidity/basicity was observed earlier in crystallization (Gaikar and Sharma, 1987) and in reactive distillation of organic acids in the presence of bases (Mahapatra et al., 1988). Dissociation extractive crystallization, therefore, seems to be an elegant method of separation which gives pure p-cresol in a single stage with almost 85–90% yield. The organic bases can be recovered from the precipitated complex by thermal treatment. This method is potentially attractive for industrial exploitation.

Separation of Guaiacol/Alkylphenols. Table II gives separation factors for guaiacol/2,6-xylenol, guaiacol/o-ethylphenol, and guaiacol/p-cresol, using anhydrous piperazine as the neutralizing agent. In all cases, the temperature was maintained below 5 °C, and n-heptane and diisopropyl ether were used as solvents. The crystalline product mainly consisted of guaiacol–piperazine complex. The values of the separation factor (11–109) were higher, at least by a factor of 2–5, than those realized with the conventional dissociation extraction even with the best solvent (6–42) (Jagirdar and Sharma, 1981a,b; Gaikar and Sharma, 1985).

Separation of Picolines. Table III gives separation factors for 3-/4-picolines which are very difficult to separate because of close boiling points. Unlike the earlier attempts to separate these isomers by fractional crystallization of their derivatives, the process of dissociation extractive crystallization exploits simultaneous reaction

and crystallization of the product. 4-Picoline was found to react preferentially with the acids. Oxalic acid and p-toluenesulfonic acid were used to neutralize picolines. The values of the separation factor, exceeding 100, are very attractive, and this method of separation has potential for industrial exploitation.

Separation of Substituted Anilines. Unlike our previous work (Gaikar and Sharma, 1987) on separation of substituted anilines by dissociation extractive crystallization from nonaqueous inert solvents, this work deals with crystallization from an aqueous phase. Separations of cumidines, o-anisidine/m-chloroaniline, and m-/p-toluidines were considered using concentrated aqueous solutions of p-toluenesulfonic acid. In these cases, the key equilibrium reaction occurs in the aqueous phase, and therefore it is possible to predict which component will react with p-TSA and crystallize out of solution.

(a) **Cumidines.** p-Cumidine is the strongest base of the three isomers and p-cumidine–p-TSA salt finds limited solubility (0.03 M) in the aqueous phase. Therefore, the precipitated solid was enriched in p-cumidine, while o-cumidine was enriched in the organic phase. The separation factors reported in Table IV are considerably higher, by almost an order of magnitude than those when anhydrous p-TSA was used. The presence of an aqueous phase requires the transfer of cumidines to the aqueous phase and reaction with simultaneous removal by crystallization with p-TSA. This continuous transfer and removal of product increases the separation factor from 9 in nonaqueous phases to 95 in the case of crystallization from an aqueous phase. The organic solvent used in this process must not have high solubility for the precipitated complex and should retain the weaker component in the organic phase.

Table V. Separation of p-Toluidine (A)/m-Toluidine (B) (Temperature: 0-5 °C)

extractant (molar ratio)	solvent	initial concn, mol/L		final concn, mol/L		α
		A	B	A	B	
98% H_2SO_4 (1:1)	toluene	0.4	0.6	0.11	0.5	13.2
98% H_2SO_4 (1:0.5)	toluene	0.4	0.6	0.21	0.55	9.9
98% H_2SO_4 (1:1)	n-heptane	0.1	0.15	0.003	0.025	7.8
oxalic acid (1:1)	toluene	0.4	0.6	0.09	0.4	6.9
HCl gas (1:1)	toluene	0.4	0.6	0.07	0.44	12.9
H_3PO_4 (100%) (1:1)	n-heptane	0.1	0.15	0.009	0.13	65.7
p-TSA (3.52 M)	toluene	0.4	0.6	0.16	0.47	5.4 (6.1[a])
p-TSA (3.52 M)	toluene	0.9	0.1	0.1	0.06	12.1 (120[a])
HCl (3 M)	toluene	0.4	0.6	0.19	0.44	3.0[b]
H_2SO_4 (2 M) (1:1)	toluene	0.2	0.3	0.037	0.18	6.6[c]

[a] Predicted values. [b] Dissociation extraction. [c] Temperature, 30 °C.

Table VI. Separation of m-Chloroaniline and o-Anisidine: Comparison of Values of Separation Factor Obtained from Theory and Experiments

system	solvent (distribution coeff.)	extracting agent, mol/L	initial concn, mol/L		α	
			B	A	exptl	predicted
o-anisidine (B)	toluene	p-TSA (3.5 M)	0.9	0.1	107	161
m-chloroaniline (A)	$D_B = 30.2$		0.7	0.3	65	39
	$D_A = 67.6$		0.3	0.7	3.3	4.1
			0.1	0.9	1.11	
	diisopropyl ether		0.9	0.1	100	159
	$D_B = 14.33$		0.7	0.3	59.4	38.8
	$D_A = 75.5$		0.3	0.7	16.6	4.1
			0.1	0.9	2	
		p-TSA (2 M)	0.09	0.39	19	0.5
			0.19	0.28	23.6	8.7
			0.11	0.44	10.7	0.8

(b) m-/p-Toluidines. The boiling points of m-toluidine and p-toluidine are 203 and 201 °C, respectively. This mixture is expected to be amenable to separation by dissociation extractive crystallization because of the different pK_a values of the components (4.62 and 4.98, respectively). The values of the separation factor are reported in Table V for different crystallizing agents. Dissociation extraction was also carried out using an aqueous solution of hydrochloric acid for comparison ($\alpha \sim 3$). From these values ($\alpha \sim 6$-65), it is evident that reactive crystallization is an efficient method of separation. Phosphoric acid, in particular, has given excellent results with a separation factor as high as 65. Aqueous solutions of p-TSA were used since the solubilities of p-toluenesulfonates of m- and p-toluidines in the aqueous phase are 0.09 and 0.08 M, respectively. The values of the separation factor in these cases were predicted by using the theoretical method described below.

Theory of Dissociation Extractive Crystallization

Liquid–Liquid–Solid Systems. When crystallization takes place from the aqueous phase, it should be possible to predict the extent of separation as the relative strengths of acids and bases become known in the aqueous phase. An attempt has been made to develop a theoretical method and to predict the separation factor in some of the cases.

Let A and B be two organic bases taken in a suitable solvent. When this solution is put into contact with an aqueous solution containing a neutralizing agent at a concentration of N (mole/liter), the following equilibria will be established:

1. Distribution of both components between the organic phase and the aqueous phase according to their distribution coefficients:
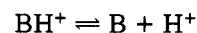
$$D_A = [A]_s/[A]_a \qquad (3a)$$

$$D_B = [B]_s/[B]_a \qquad (3b)$$

2. Dissociation of both bases in the aqueous phase according to their pK_a values:
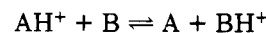
$$AH^+ \rightleftharpoons A + H^+$$

$$K_A = \frac{[A]_a[H^+]_a}{[AH^+]_a} \qquad (4a)$$

$$BH^+ \rightleftharpoons B + H^+$$
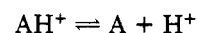
$$K_B = \frac{[B]_a[H^+]_a}{[BH^+]_a} \qquad (4b)$$

3. Competition between A and B for neutralization leading to the key equilibrium reaction:

$$AH^+ + B \rightleftharpoons A + BH^+$$

$$K = \frac{[BH^+]_a[A]_a}{[AH^+]_a[B]_a} \qquad (5a)$$

$$K = K_A/K_B \qquad (5b)$$

4. The precipitation of complexes AH^+ and BH^+ will not appear in the above-mentioned equilibria directly, but it is related through the mass balance equations. If both AH^+ and BH^+ have precipitated, then it can be assumed that $[AH^+]_a$ and $[BH^+]_a$ correspond to saturation solubilities of complexes AH^+ and BH^+, respectively.

(a) mass balance for component A

$$V_s[A]_{s,i} = V_s[A]_s + V_a[AH^+]_a + V_a[A]_a + [AH^+]_{solid} \qquad (6a)$$

(b) mass balance for component B

$$V_s[B]_{s,i} = V_s[B]_s + V_a[BH^+]_a + V_a[B]_a + [BH^+]_{solid} \qquad (6b)$$

(c) mass balance for neutralizing agent

$$V_aN = V_a[AH^+]_a + V_a[BH^+]_a + [AH^+]_s + [BH^+]_{solid}$$

$$(6c)$$

Let

$$[AH^+]_a = S_A \qquad (7a)$$

$$[BH^+]_a = S_B \qquad (7b)$$

which can be determined separately. It is also assumed that the salts are in undissociated form and have no solubility in the organic phase. If (3)–(7) are solved simultaneously with mass balance equations for the neutralizing agent and both of the components, one gets the separation factor as follows:

$$\alpha = \frac{[B]_{s,i}}{[A]_{s,i}}P \times$$

$$\frac{N(P+1) + [B]_{s,i}\left(\dfrac{1}{D_B} + \dfrac{P}{D_A} - \dfrac{N[A]_{s,i}}{[B]_{s,i}}\right)}{N + [B]_{s,i}\left(\dfrac{1}{D_B} + \dfrac{P}{D_A}\right)} \quad (8)$$

where

$$P = \frac{K_A}{K_B}\frac{D_A}{D_B}\frac{S_A}{S_B} \qquad (9)$$

Equation 8 shows that the separation factor is a strong function of the initial composition. At a lower percentage of the stronger component, the separation factor decreases and the separation factor is mainly governed by the dissociation constants, distribution coefficients of components, and the solubilities of the complexes in the aqueous phase. The theory has been tested for the separation of o-anisidine (pK_a 4.43) and m-chloroaniline (pK_a 3.44) mixtures using concentrated aqueous solutions of p-TSA (Table VI). The product was a solid phase which mainly consisted of o-anisidine–p-TSA complex, although the solubility of the p-toluenesulfonate of o-anisidine (0.4 M) was higher than that of m-chloroaniline–p-TSA (0.07 M). The separation factors (10–107) were significantly higher than those realized using conventional dissociation extraction ($\alpha \sim 15$) (Wadekar and Sharma, 1981a–c). The predicted and the experimental values are compared in Table VI. Although these values do not match very well, the trend in the separation factors is the same; i.e., the separation factor decreases at a lower percentage of the stronger component. The difference between the predicted and the experimental values also decreased at a lower concentration of the stronger component. This indicates that the complexes should have solubility in the organic phase which reduces the separation factor. This theory, therefore, can be further improved by considering the distribution of the complexes between two phases and the dissociation of the complexes in the aqueous phase which was assumed to be negligible in the above theoretical method.

Conclusions

The separation of close boiling point mixtures, such as m-/p-cresols, guaiacol/alkylphenols, 3-/4-picolines, and substituted anilines can be successfully accomplished through dissociation extractive crystallization. p-Cresol can be isolated from the mixtures in almost pure form with 90% yield. A liquid–liquid–solid reactive crystallization

process gives higher selectivity than the crystallization from nonaqueous phases. A theory has been proposed to predict the separation factor for liquid–liquid–solid crystallization which has been tested for the separation of anilines.

Nomenclature

$[A]_s$, $[B]_s$ = concentrations in the organic phase of components A and B, respectively, mol/L

$[A]_{s,i}$, $[B]_{s,i}$ = initial concentrations in the organic phase of components A and B, respectively, mol/L

$[A]_a$, $[B]_a$ = concentrations in the aqueous phase of components A and B, respectively, mol/L

D_A, D_B = distribution coefficients of components A and B, respectively

$[AH^+]_a$, $[BH^+]_a$ = concentrations of protonated bases in the aqueous phase, in dissolved form, of A and B, respectively, mol/L

K_A, K_B = acid dissociation constants of components in the aqueous phase as defined by (4a) and (4b)

K = equilibrium constant for the reaction and defined by (5a) and (5b)

S_A, S_B = solubilities of complexes (protonated bases) of A and B with neutralizing agent in the aqueous phase, mol/L

N = initial concentration of the neutralizing agent in the aqueous phase, mol/L

Registry No. m-Cresol, 108-39-4; p-cresol, 106-44-5; guaiacol, 90-05-1; 3-picoline, 108-99-6; 4-picoline, 108-89-4; o-cumidine, 643-28-7; m-cumidine, 5369-16-4; p-cumidine, 99-88-7; p-toluidine, 106-49-0; m-toluidine, 108-44-1; 2,6-xylenol, 576-26-1; o-ethylphenol, 90-00-6; m-chloroaniline, 108-42-9; o-anisidine, 90-04-0.

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The Use of Basic Polymer Sorbents for the Recovery of Acetic Acid from Dilute Aqueous Solution

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Measurements were made of uptakes of acetic acid and water from aqueous solution onto basic polymer sorbents. Sorption equilibria were interpreted through a chemical complexation model, yielding sorption affinities and saturation capacities for acetic acid. Basicity scales, such as pK_a and Gutmann donor number (DN), based upon the monomeric functional group chemistry were shown to explain the trends in sorption affinities. Solvent leaching was investigated as a means of regenerating the sorbents. It was found that regeneration can be improved by using solvents of high donicity. Aqueous ammonia proved to be effective for regenerating moderately strong base sorbents.

Carboxylic acids are already major commercial chemicals and are potentially even more important as intermediates and products from fermentation of biomass. There are also situations where it is desirable to remove or recover carboxylic acids from effluent streams. In both of these cases, the carboxylic acids are usually encountered in relatively dilute, and often complex, aqueous solutions.

Because of dilution, adsorption is an attractive recovery method. For biological systems, adsorption has the added advantage of minimizing contamination and avoiding heating of the medium. Adsorbents containing basic groups can provide selective uptake of carboxylic acids from complex solutions. Also, for dilute solutions, the capacities of basic adsorbents can exceed those of high-surface-area carbons (Kuo et al., 1987).

This work has therefore focused on the properties of weak-base ion-exchange resins that affect the sorption and recovery of carboxylic acids from aqueous solution. The aim is to understand how exchanger properties such as functional group basicity and matrix chemistry affect sorption affinity, imbibition of liquid due to swelling, and regeneration by leaching. Acetic acid was used as a prototype carboxylic acid solute. The ultimate goal is to define the optimal basicity and structural chemistry of a basic polymer sorbent for the recovery of carboxylic acids from dilute aqueous solution.

The sorbents investigated in this work are listed in Table I. [Since the materials considered exhibit both surface and bulk uptake mechanisms, i.e., both adsorption and absorption, they are referred to as "sorbents".] Most of these sorbents are commercially available; a few are experimental. In gel sorbents, solution uptake is accomplished primarily by swelling. Macroreticular sorbents are highly cross-linked and macroporous, with pore sizes on the order of 0.01–0.1 μm; solution uptake is primarily by pore filling.

Experimental Equipment and Procedures

All sorbents were purified by Soxhlet extraction with methanol for at least 24 h. They were then dried in a vacuum oven at 18–36 kPa and 45–50 °C for 2–4 days. After extraction and before drying, Bio-Rad AG-2X8 was converted to the hydroxide form by equilibration with 1 N NaOH and was then washed with water.

Glacial acetic acid (Mallinckrodt Co., Analytical Grade, minimum 99.7% assay) was used. Karl Fischer grade methanol (J.T. Baker Chemical Co.) was employed in the solvent-leaching experiments. All other chemicals were of analytical grade. Water used in sorption, leaching, and titration experiments was distilled and further purified with a Milli-Q system (Millipore Corp.).

Carbon, hydrogen, and nitrogen contents were analyzed with a Perkin-Elmer Model 240 elemental analyzer (Perkin-Elmer Corp.). Samples were thoroughly dried before submission for analysis by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley.

Titrations of the sorbents were conducted in the following manner. Milli-Q purified distilled water was boiled for 20 min in order to eliminate absorbed CO_2 and was

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