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Short Articles

Separation of a Phenol/*o*-Chlorophenol Mixture through Hydrotropy

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A comprehensive study on the effect of hydrotropes such as urea, citric acid, sodium salicylate, and nicotinamide on the separation of phenol from phenol/*o*-chlorophenol mixtures under a wide range of hydrotrope concentrations, (0 to 3.0) mol·L^{-1}, and different system temperatures, (303 to 333) K, has been undertaken. The performance of hydrotropes toward separation of phenol was measured in terms of the Setschenow constant K_S. A Minimum Hydrotrope Concentration (MHC) in the aqueous phase was found essential to initiate significant separation of phenol from the phenol/*o*-chlorophenol mixture. The maximum enhancement factor which is the ratio of the percentage extraction value in the presence and absence of a hydrotrope has been determined for each case.

1. Introduction

Hydrotropy is a potentially attractive technique that can be considered to separate close boiling isomeric/nonisomeric mixtures.

Hydrotropes are a class of chemical compounds used to effect a several-fold increase in the solubility of certain solutes which are sparingly soluble in water under normal conditions.[1−3] This phenomenon termed as hydrotropy can be considered to be a potentially and industrially attractive technique, since the observed increase in solubility is generally higher than that effected by other solubilization methods. Hydrotropes have been used to solubilize various sparingly soluble organic compounds.[5−8] The role of hydrotropes in enhancing rates of heterogeneous reactions has also been brought out.[9−11] The effect of hydrotropes on the solubility and the mass-transfer coefficient of a series of organic esters was studied in our earlier publications.[12,13,17] Easy recovery of dissolved solute, possible reuse of hydrotrope solution, and high selectivity make this method the most effective one particularly at industrial levels.[4,14−16] Data on the effect of hydrotropes on the separation of phenol/*o*-chlorophenol are reported for the first time.

Hydrotropes have been effectively used in the development of extractive separations for the separation of close boiling point mixtures.[18−20] The hydrotropes used in this work are nonreactive and nontoxic and do not produce any significant heat effect when dissolved in water. The easy availability and low cost are two other factors considered in the selection of these hydrotropes.

2. Experimental Section

2.1. Materials. The phenol and *o*-chlorophenol were of 99.9 % purity, and hydrotropes such as urea, citric acid, sodium salicylate, and nicotinamide were of high purity grade and procured from S.D.Fine Chemicals Ltd., Mumbai.

2.2. Apparatus and Procedure. The thermostatic bath method was used for the separation of phenol from phenol/*o*-chlorophenol. For each test, an equal amount of (100 mL) of phenol and *o*-chlorophenol was taken and mixed well to make a single-phase solution using a shaker. Hydrotrope solutions of different concentration were prepared by dilution with distilled water. Approximately 100 mL of the phenol/*o*-chlorophenol mixture was taken, and an equal amount of hydrotrope solution was added and mixed for 3 h. The mixture was then transferred to a separating funnel which was immersed in a bath at constant temperature fitted with a temperature controller that could control the temperature within ± 0.1 °C. The setup was kept overnight for attaining equilibration. After equilibrium was attained, the aqueous phase and organic phase were carefully separated using a separating funnel and analyzed to quantify the concentration using HPLC with the following conditions: LC mode, reversed phase chromatography; Packing material, Silica-C18 (ODS); Mobile phase, MeOH/Water; Interaction, Hydrophobic. All the experiments were conducted in duplicate to check the reproducibility, and the observed deviation was < 2 %.

3. Results and Discussion

Experimental data on the effect of hydrotropes, i.e., urea, citric acid, sodium salicylate, and nicotinamide, on the separation of phenol from phenol/*o*-chlorophenol mixtures are presented in Tables 1 to 4 and are plotted in Figures 1 to 4. The percentage extraction of phenol from phenol/*o*-chlorophenol mixtures in the absence of any hydrotrope at 303 K was found to be 3.6 % (Table 1). Urea is one of the hydrotropes used in this study. It was observed that the percentage extraction of phenol from phenol/*o*-chlorophenol mixtures did not show any appreciable increase until 0.30 mol·L^{-1} of urea was in the aqueous phase. Upon subsequent increase in the concentration of urea above 0.30 mol·L^{-1}, the percentage extraction of phenol from the phenol/*o*-chlorophenol mixture was found to increase significantly. This concentration of urea in the aqueous phase, i.e., 0.30 mol·L^{-1}, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required amount of urea (hydrotrope) concentration in the aqueous phase to initiate a significant increase in the percentage extraction of phenol from the phenol/*o*-chlorophenol mixture. It has been observed that

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Table 1. Effect of Urea Concentration (C) on the Percentage Extraction (E) of Phenol from a Phenol/*o*-Chlorophenol Mixture at T = 303 K, 313 K, 323 K, and 333 K

	E, %			
C, mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	3.60	4.20	4.72	5.02
0.10	3.60	4.20	5.01	5.54
0.20	3.60	4.20	5.41	6.11
0.30 (MHC)	4.60	5.21	6.60	7.40
0.40	5.10	7.30	9.70	12.40
0.50	6.20	9.80	12.80	14.50
0.60	7.30	11.50	14.67	16.80
0.70	8.10	13.90	18.80	20.90
0.80	9.20	15.60	22.60	25.70
0.90	10.10	19.50	26.60	30.60
1.00	12.20	22.00	30.50	35.40
1.10	14.30	26.90	33.50	40.30
1.20	16.30	28.70	38.90	45.70
1.30	18.70	32.80	44.10	50.90
1.40	20.50	35.50	48.60	56.80
1.50	21.30	37.50	52.80	62.40
1.60	22.40	40.20	55.80	68.70
1.70	23.60	41.60	58.80	73.12
1.80	24.50	43.70	61.20	78.10
1.90	25.40	45.20	64.80	82.70
2.00	26.21	46.23	67.20	87.23
2.20	27.10	48.62	71.51	91.01
2.40 ($C_{\max}$)	28.90	51.13	74.90	95.12
2.60	29.70	51.17	75.10	95.15
2.80	29.90	51.19	75.13	95.15
3.00	29.90	51.19	75.13	95.15

Table 2. Effect of Citric Acid Concentration (C) on the Percentage Extraction (E) of Phenol from a Phenol/*o*-Chlorophenol Mixture at T = 303 K, 313 K, 323 K, and 333 K

	E, %			
C, mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	3.60	4.20	4.72	5.02
0.10	3.63	4.41	5.01	5.44
0.20	3.66	4.92	5.63	6.03
0.30	3.69	5.12	6.21	6.78
0.40 (MHC)	4.99	6.98	9.81	12.32
0.50	5.19	7.53	11.03	15.00
0.60	5.99	8.59	12.34	17.25
0.70	6.88	10.37	14.12	21.12
0.80	8.08	11.62	17.00	25.49
0.90	9.22	13.02	20.50	30.42
1.00	10.50	16.31	25.50	36.00
1.10	11.90	17.94	28.00	42.50
1.20	13.10	20.21	33.50	49.50
1.30	13.80	22.41	37.50	56.50
1.40	14.70	26.50	43.00	62.00
1.50	15.60	29.00	46.50	67.00
1.60	16.40	31.50	49.00	71.00
1.70	17.30	34.00	52.00	73.27
1.80	18.10	35.10	54.00	74.82
1.90	19.15	36.62	55.16	75.32
2.00 ($C_{\max}$)	20.68	38.90	57.71	79.05
2.20	20.90	38.94	57.76	79.38
2.40	21.20	38.99	57.82	79.84
2.60	21.20	38.99	58.03	80.90
2.80	21.20	38.99	58.03	80.90
3.00	21.20	38.99	58.03	80.90

Table 3. Effect of Sodium Salicylate Concentration (C) on the Percentage Extraction (E) of Phenol from a Phenol/*o*-Chlorophenol Mixture at T = 303 K, 313 K, 323 K, and 333 K

	E, %			
C, mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	3.60	4.20	4.62	5.02
0.10	3.62	4.24	4.73	5.23
0.20	3.64	4.36	5.01	5.61
0.30	3.67	4.54	5.68	6.13
0.40	3.71	4.82	6.22	6.86
0.50 (MHC)	5.32	6.71	8.25	9.73
0.60	5.81	7.21	9.31	10.15
0.70	6.44	8.03	10.04	12.48
0.80	7.12	8.84	11.46	17.20
0.90	7.81	10.13	14.73	21.50
1.00	8.54	12.41	18.47	25.00
1.10	9.47	13.92	21.40	28.80
1.20	10.32	15.35	24.00	32.50
1.30	11.25	18.24	26.80	34.50
1.40	12.24	20.70	29.80	37.10
1.50	13.74	24.00	32.00	39.23
1.60	15.21	25.50	33.21	40.71
1.70	16.03	27.20	34.92	42.83
1.80	17.8	27.92	36.07	44.03
1.90 ($C_{\max}$)	19.2	29.83	38.25	46.34
2.00	19.31	29.95	38.29	46.41
2.20	19.36	30.13	38.32	46.43
2.40	19.38	30.14	38.33	46.48
2.60	19.38	30.14	38.33	46.48
2.80	19.38	30.14	38.33	46.48
3.00	19.38	30.14	38.33	46.48

Table 4. Effect of Nicotinamide Concentration (C) on the Percentage Extraction (E) of Phenol from a Phenol/*o*-Chlorophenol Mixture at T = 303 K, 313 K, 323 K, and 333 K

	E, %			
C, mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	3.60	4.20	4.72	5.02
0.10	3.61	4.23	4.77	5.11
0.20	3.62	4.25	4.83	5.23
0.30	3.63	4.27	4.87	5.29
0.40	3.64	4.28	4.93	5.34
0.50 (MHC)	4.65	5.78	6.99	8.92
0.60	4.73	6.32	7.21	11.12
0.70	4.82	6.91	9.54	14.50
0.80	4.93	8.53	11.81	16.30
0.90	5.45	9.17	13.62	19.30
1.00	5.96	10.28	15.55	22.12
1.10	6.17	11.46	17.25	24.60
1.20	7.23	12.52	19.27	26.50
1.30	7.52	13.63	20.17	28.90
1.40	7.71	15.47	22.30	31.00
1.50	8.69	16.23	24.20	33.74
1.60	8.95	17.14	26.30	35.74
1.70	9.24	18.06	27.63	36.94
1.80	9.65	18.98	28.98	37.45
1.90 ($C_{\max}$)	10.91	19.92	30.01	39.58
2.00	11.01	20.12	30.12	40.01
2.20	11.12	20.34	30.21	40.10
2.40	11.19	20.42	30.35	40.15
2.60	11.23	20.42	30.35	40.15
2.80	11.23	20.42	30.35	40.15
3.00	11.23	20.42	30.35	40.15

the MHC of urea in the aqueous phase does not vary even at higher temperatures of (313, 323, and 333) K. A similar trend in the MHC requirement has been observed for other hydrotropes also. Therefore, it is evident that hydrotropic separation is displayed only above the MHC irrespective of the system temperature. Hydrotropy does not seem to be operative below the MHC which may be a characteristic of a particular hydrotrope with respect to each solute.

The percentage extraction varies with the concentration of hydrotropes (Tables 1 to 4). In the present case, a clear increasing trend in the percentage extraction of phenol from the phenol/*o*-chlorophenol mixture was observed above the MHC of urea. This increase in percentage extraction is maintained only up to a certain concentration of urea in the aqueous phase beyond which there is no appreciable increase in the percentage extraction of phenol from the phenol/*o*-chlorophenol mixture. This concentration of urea (hydrotrope) in the aqueous phase is referred to as maximum hydrotrope concentration ($C_{\max}$). From the analysis of the experimental data, it is observed that further increase in the hydrotrope concentra-

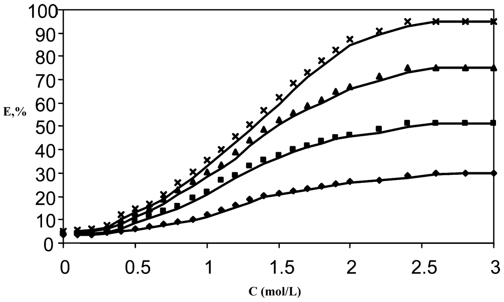

Figure 1. Effect of urea concentration (*C*) on the percentage extraction (*E*) of phenol from a phenol/*o*-chlorophenol mixture at *T* = ◆, 303 K; ■, 313 K; ▲, 323 K; and ×, 333 K.

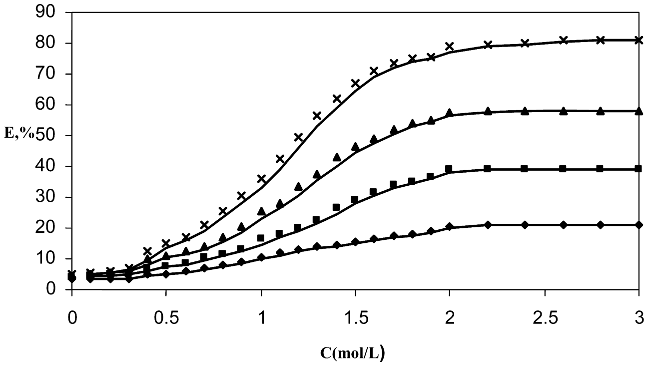

Figure 2. Effect of citric acid concentration (*C*) on the percentage extraction (*E*) of phenol from a phenol/*o*-chlorophenol mixture at *T* = ◆, 303 K; ■, 313 K; ▲, 323 K; ×, 333 K.

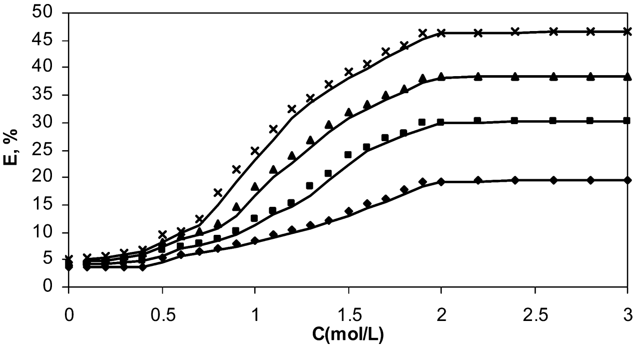

Figure 3. Effect of sodium salicylate concentration (*C*) on the percentage extraction (*E*) of phenol from a phenol/*o*-chlorophenol mixture at *T* = ◆, 303 K; ■, 313 K; ▲, 323 K; ×, 333 K.

tion beyond $C_{\max}$ does not effect any appreciable increase in the percentage extraction of phenol even up to 3.00 mol·L^{-1} urea in the aqueous phase. Similar to the MHC values, $C_{\max}$ values of hydrotropes also remained unaltered with increased system temperature. The MHC and $C_{\max}$ values for hydrotropes are given in Table 5.

It appears that in the concentration range of urea between (0 and 3.00) mol·L^{-1} three different regions, (0 to 0.30) mol·L^{-1}, (0.30 to 2.40) mol·L^{-1}, and (2.40 to 3.00) mol·L^{-1}, were observed. It was inactive below an MHC of 0.30 mol·L^{-1}, above which an appreciable increase in the percentage extraction of phenol was found up to a $C_{\max}$ value of 2.40 mol·L^{-1}, beyond which there is no further increase in the percentage extraction of phenol. Therefore, urea was found to be an effective hydrotrope in the concentration range between (0.30 and 2.40) mol·L^{-1} toward phenol. It has also been observed that the separation effect of urea does not vary linearly with the concentration of the urea. The separation effect of urea increases with an increase in hydrotrope concentration and also with system temperature.

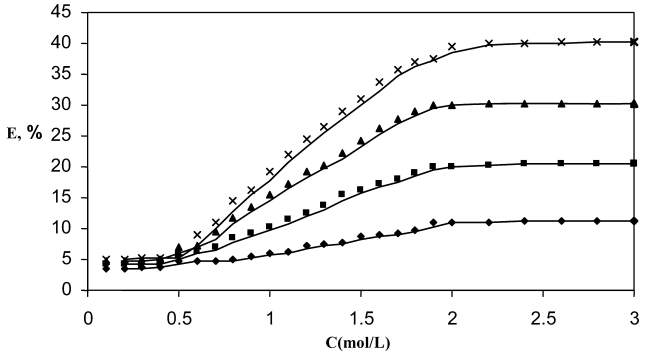

Figure 4. Effect of nicotinamide concentration (*C*) on the percentage extraction (*E*) of phenol from a phenol/*o*-chlorophenol mixture at *T* = ◆, 303 K; ■, 313 K; ▲, 323 K; ×, 333 K.

Table 5. MHC and $C_{\max}$ Values for Hydrotropes

	C, mol·L^{-1}	
hydrotrope	MHC	$C_{\max}$
urea	0.30	2.40
citric acid	0.40	2.00
sodium salicylate	0.50	1.90
nicotinamide	0.50	1.90

Table 6. Maximum Enhancement Factor $Ø_{\mathrm{E}}$ for Percentage Extraction of Phenol

	$Ø_{\mathrm{E}}$			
hydrotrope	*T* = 303 K	*T* = 313 K	*T* = 323 K	*T* = 333 K
urea	6.28	9.87	11.35	12.85
citric acid	4.14	5.57	5.88	6.42
sodium salicylate	3.61	4.45	4.64	4.76
nicotinamide	2.35	3.45	4.29	4.44

A similar trend has been observed in the separation effect of other hydrotropes, namely, citric acid, sodium salicylate, and nicotinamide. It has also been observed that the MHC values of the hydrotropes used in this work range between (0.30 and 0.50) mol·L^{-1}, which seem to depend on the hydrophilic nature of the hydrotrope.

The maximum enhancement factor ($Ø_{\mathrm{E}}$) which is the ratio of the percentage extraction at $C_{\max}$ and MHC values of a hydrotrope have been determined which range between 2.35 and 12.85 (Table 6). The highest value of $Ø_{\mathrm{E}}$ (12.85) has been observed in the case of urea at a system temperature of 333 K. This ratio indicates the optimum separation of a mixture by extraction.

4. Effectiveness of Hydrotropes

The effectiveness factor of each hydrotrope at different system temperatures has been determined by analyzing the experimental percentage extraction data for each case, applying the model suggested by Setschenow and later modified by Pathak and Gaikar applicable for separation studies as follows.

$$\log[E/E_{\mathrm{m}}] = K_{\mathrm{s}}[C_{\mathrm{s}} - C_{\mathrm{m}}] \qquad (1)$$

where *E* and E_{m} are the percentage extraction values of phenol at any hydrotrope concentration (C_{S}) and Minimum Hydrotrope Concentration (MHC), respectively. The Setschenow constant (K_{S}) can be considered as the best measure of the effectiveness of a hydrotrope at any given condition of hydrotrope concentration and system temperature. The Setschenow constant values

Table 7. Setschenow Constant (K_S) of Hydrotropes with Respect to Phenol

	K_S			
temperature (K)	urea	citric acid	sodium salicylate	nicotinamide
303	0.382	0.380	0.376	0.264
313	0.472	0.466	0.442	0.383
323	0.502	0.481	0.475	0.451
333	0.528	0.505	0.484	0.459

of hydrotropes, namely urea, citric acid, sodium salicylate, and nicotinamide, at different system temperatures are listed in Table 7. The highest value has been observed as 0.528 in the case of urea at 333 K.

5. Conclusions

The separation of phenol from phenol/*o*-chlorophenol mixtures which is found to be difficult can be carried out effectively using this technique. The MHC and C_{max} values of hydrotropes with respect to phenol can be used for the recovery of the dissolved phenol and hydrotrope solutions at any hydrotrope concentration between the MHC and C_{max} by simple dilution with distilled water. This will eliminate the huge cost and energy normally involved in the separation of the solubilized phenol from its mixture. The unprecedented increase in the separation effect of hydrotropes is attributed to the formation of organized aggregates of hydrotrope molecules at a critical concentration corresponding to the MHC.

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