Separation of Styrene- Ethyl Benzene Mixture Through Hydrotropy

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Abstract: The field of separation using hydrotropy has been studied. Solvent extraction and extractive distillation with aqueous solutions of hydrotropes are the novel separation techniques suitable for separation of close boiling mixtures. The present work is concerned with the separation of styrene-ethyl benzene mixture using hydrotropic solutions of urea, nicotinamide and sodium benzoate. The influence of a wide range of hydrotrope concentrations (0 to 3.0 mol/L) and different system temperatures (303 to 333 K) on the separation of styrene and ethyl benzene mixture was studied. The percentage extraction of styrene from the styrene-ethyl benzene mixture increases with an increase in hydrotrope concentration and also with system temperature. A Minimum Hydrotrope Concentration (MHC) was found essential to initiate significant extraction of styrene from the styrene-ethyl benzene mixture. The maximum enhancement factor, which is the ratio of the value in the presence and absence of a hydrotrope was determined. The Setschenow constant, K_s, a measure of the effectiveness of a hydrotrope, was determined for each case.

Keywords: hydrotropy; separation; hydrotropes; hydrophobic; enhanced solubility

1. Introduction

In the manufacture of chemical and pharmaceutical products, a variety of isomeric or closely related mixtures of organic compounds are encountered and this often requires their separation into nearly pure components [1]. In cases of compounds having very close boiling points it is very difficult to separate by conventional methods such as distillation and extraction [2]. Hydrotropy is a unique and unprecedented solubilization technique in which certain chemical components termed as hydrotropes can be used to effect a several fold increase in the solubility of sparingly soluble solutes under normal conditions [3-6].

Hydrotropes are organic salts that when present in aqueous solutions can substantially enhance the solubility of a variety of hydrophobic organic substances in the aqueous phase. These substances include aryl sulfonic acids, their potassium, sodium, calcium, and ammonium salts, sodium and potassium salts of benzoic acids and phenols etc [7, 8]. The first report on extractive separations using hydrotrope solutions was published by Gaikar and Sharma [9]. Several industrial systems of close boiling point substances were separated using hydrotropes such as benzoates, substituted benzoates, substituted benzene sulfonate, and sodium and potassium butyl monoglycol

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sulfates [10]. The effective separation of a near boiling mixture could be due to the formation of molecular structures in the form of complexes at a particular concentration. The high solubilization capacity of the hydrotropes has made them potentially useful in various industrial applications [11-13].

The hydrotropes used in this work are freely soluble in water and practically insoluble in styrene and ethyl benzene mixture. The selectivity in extraction is a strong function of the concentration of the hydrotrope and is higher above the MHC value of the hydrotrope [14-16]. The hydrophobic bulky group on a hydrotrope molecule has an effect on the aggregational behavior, which in turn effect the solubilization of the solute [8, 17-19]. The main property of the hydrotropes is related to the MHC (Minimum Hydrotrope Concentration), which is defined as the concentration at which hydrotropes start to aggregate, i.e., forming new microenvironments with different properties as those of the hydrotropes in relatively diluted solutions. Above MHC, the solubility of the organic compound in aqueous phase increases significantly [20, 21].

Styrene serves as a raw material for the production of rubber and its separation from ethyl benzene has been found to be difficult until now. Styrene is most commonly produced by catalytic dehydrogenation of ethyl benzene. Styrene and ethyl benzene have close boiling point and their separation is difficult and requires huge distillation towers and high return/ reflux ratio. Hence hydrotropy may be used to separate this system effectively.

2. Materials and methods

The chemicals used were checked for purity using gas chromatography. The purity of chemicals was observed to be 99.97%. Hydrotropes such as urea, nicotinamide and sodium benzoate were of high purity grade and procured from SD Fine Chemicals, Mumbai, India with manufacturer's stated purity of 99.9%.

The experimental setup for conducting a single-stage batch wise liquid-liquid extraction consisted of a thermostatic bath and separating funnel. For each test, an equal amount (100 ml) of styrene and ethyl benzene was thoroughly mixed to make a single-phase solution using a shaker. The mixture was pre-saturated with distilled water and organic phase was carefully separated. The hydrotrope solutions of different concentrations were prepared by dilution with distilled water and then the organic phase was added. The mixture was then allowed to settle and was transferred to a separating funnel, which was immersed in a constant temperature bath fitted with a temperature controller. The setup was kept overnight for equilibration. After equilibrium was attained, the aqueous phase was carefully separated and analyzed to determine the concentration using a High-Performance Liquid Chromatography (HPLC). Duplicate runs were conducted and found that the error was <2%.

3. Results and discussion

Experimental data on the effect of hydrotropes, i.e., urea, nicotinamide and sodium benzoate on the percentage extraction of styrene are presented in Tables 1 to 3 and plotted in Figures 1 to 3. Percentage extraction (E) is the ratio of moles of styrene extracted due to the effect of hydrotropes to moles of styrene initially present. Urea is one of the hydrotropes used in this study. It was observed that the percentage extraction of styrene did not show any appreciable increase until 0.30 mol/L of urea was added in the aqueous phase. But upon subsequent increase in the concentration of urea, i.e., 0.40 mol/L, the percentage extraction of styrene was found to increase significantly. This concentration of urea in the aqueous phase, i.e., 0.40 mol/L, is termed the Minimum Hydrotrope Concentration (MHC), which is the minimum required

amount of urea in the aqueous phase to initiate significant increase in the percentage extraction of styrene. It was observed that the MHC of urea in the aqueous phase does not vary even at increased system temperatures, i.e., 313, 323, and 333 K. A similar trend in the MHC requirement has also been observed for other hydrotropes.

Therefore, it is evident that hydrotropic separation is displayed only above MHC, irrespective of the system temperature. Hydrotropy technique 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 effect varies with concentration of the hydrotropes. In this case, a clear increasing trend in the percentage extraction of styrene was observed above the MHC of urea. This increase is maintained only up to a certain concentration of urea in the aqueous phase, i.e., 2.50 mol/L beyond which there is no appreciable increase in the percentage extraction of styrene. This concentration of urea in the aqueous phase is referred to as the maximum hydrotrope concentration (C_{max}). As can be seen from Table 1, the C_{max} values of urea range between 2.50 and 3.0 mol/L. From the analysis of the experimental data, it is observed that further increase in the hydrotrope concentration beyond C_{max} does not cause any appreciable increase in the percentage extraction of styrene in the aqueous phase. Similar to the MHC values, the C_{max} values of the hydrotropes also remained unaltered with the increase in system temperature.

In the concentration range of urea between 0 and 3.00 mol/L, three different regions were obtained (first region, 0.00 to 0.40 mol/L; second region, 0.40 to 2.50 mol/L, and third region, 2.50 to 3.00 mol/L). It was observed that urea was inactive below MHC of 0.40 mol/L, above which an appreciable increase in the percentage extraction of styrene was found up to a C_{max} value of 2.50 mol/L, beyond which there is no further increase in the percentage extraction of styrene. Therefore, urea was found to be an effective hydrotrope in the concentration range between 0.40 and 2.50 mol/L towards styrene. The insignificant separation below MHC may be due to the inability of hydrotropes to form aggregates with the required number of hydrotrope molecules in the aqueous phase. Similarly, the saturation of the separation effect of hydrotropes beyond C_{max} may be due to the non-availability of water molecules to form further aggregates comprising of additional MHC aggregates. It was also observed that the separation effect of urea does not vary linearly with the concentration of urea. The separation effect of urea increases with the increase in hydrotrope concentration and also with system temperature.

A similar trend was observed in the percentage extraction effect of other hydrotropes, namely nicotinamide and sodium benzoate. It was observed that MHC values of hydrotropes used in this work range between 0.40 and 0.50 mol/L, which seem to depend on the hydrophilic nature of the hydrotrope. The C_{max} values of hydrotropes range between 2.2 to 2.5. The maximum enhancement factor (Φ_E), which is the ratio of the percentage extraction value in the presence and absence of a hydrotrope, respectively, was determined and which ranged between 18.64 and 43.96. The highest value of Φ_E (43.96) was observed in the case of sodium benzoate at a system temperature of 333 K.

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Table 1. Effect of the Urea concentration (C) on the percentage extraction (E) of styrene.

SI. No	C, mol/L	E, %			
		303 K	313 K	323 K	333 K
1	0.0	1.17	1.28	1.41	1.56
2	0.1	1.82	2.15	2.21	2.52
3	0.2	2.56	2.87	3.14	3.67
4	0.3	3.20	3.43	3.98	4.56
5	0.4 (MHC)	4.96	5.92	6.45	7.23
6	0.5	6.93	9.46	13.32	16.38
7	0.6	8.84	12.15	18.11	22.14
8	0.7	10.74	15.34	20.67	26.85
9	0.8	13.37	18.10	24.53	31.43
10	0.9	16.21	22.39	26.96	35.26
11	1.0	18.29	24.33	29.82	38.89
12	1.2	22.36	28.79	35.80	45.12
13	1.5	27.22	33.54	41.39	50.19
14	1.8	30.65	37.68	45.13	54.11
15	2.0	32.81	39.35	47.08	55.53
16	2.2	34.24	41.51	50.87	58.25
17	2.5 (C_{max})	35.19	44.16	52.23	62.16
18	2.8	35.76	44.78	52.85	62.78
19	3.0	36.20	45.13	53.27	63.12

Table 2. Effect of the Nicotinamide (C) on the percentage extraction (E) of styrene.

SI. No	C, mol/L	E, %			
		303 K	313 K	323 K	333 K
1	0.0	1.17	1.28	1.41	1.56
2	0.1	1.24	1.45	1.58	1.73
3	0.2	1.43	1.67	1.82	1.99
4	0.3	1.59	1.84	2.49	2.67
5	0.4	1.79	2.12	3.08	3.48
6	0.5 (MHC)	3.67	3.94	4.73	5.14
7	0.6	4.64	5.65	6.48	8.65
8	0.7	5.87	7.75	8.17	11.38
9	0.8	7.32	9.47	10.21	14.63
10	0.9	8.25	11.26	13.34	17.86
11	1.0	9.41	13.43	15.75	21.34
12	1.2	12.94	17.39	20.38	27.81
13	1.5	18.72	23.94	28.49	34.53
14	1.8	20.51	25.31	31.53	38.86
15	2.0	21.46	27.12	34.85	43.22
16	2.2 (C_{max})	21.83	28.65	35.79	44.57
17	2.5	22.56	28.97	36.21	44.91
18	2.8	22.75	29.16	36.73	45.13
19	3.0	23.10	29.33	37.18	45.39

Table 3. Effect of the Sodium benzoate(C) on the percentage extraction (E) of styrene.

SI. No	C, mol/L	E, %			
		303 K	313 K	323 K	333 K
1	0.0	1.17	1.28	1.41	1.56
2	0.1	1.26	1.37	1.54	1.68
3	0.2	1.48	1.59	1.76	1.89
4	0.3	1.83	1.98	2.21	2.43
5	0.4	2.24	2.56	2.98	3.14
6	0.5 (MHC)	3.92	4.63	6.04	6.76
7	0.6	5.41	6.18	9.38	10.53
8	0.7	7.58	9.35	12.12	14.94
9	0.8	9.46	11.21	15.86	19.37
10	0.9	10.93	14.32	16.49	26.53
11	1.0	12.34	18.78	25.66	32.17
12	1.2	14.78	23.15	31.39	41.80
13	1.5	16.11	28.94	39.50	48.47
14	1.8	19.33	32.28	45.63	53.72
15	2.0	22.71	35.14	48.77	58.53
16	2.2	25.88	37.72	51.84	64.46
17	2.5 (C_{max})	29.27	42.49	55.95	68.58
18	2.8	29.56	42.83	56.31	69.10
19	3.0	30.13	43.26	56.79	69.45
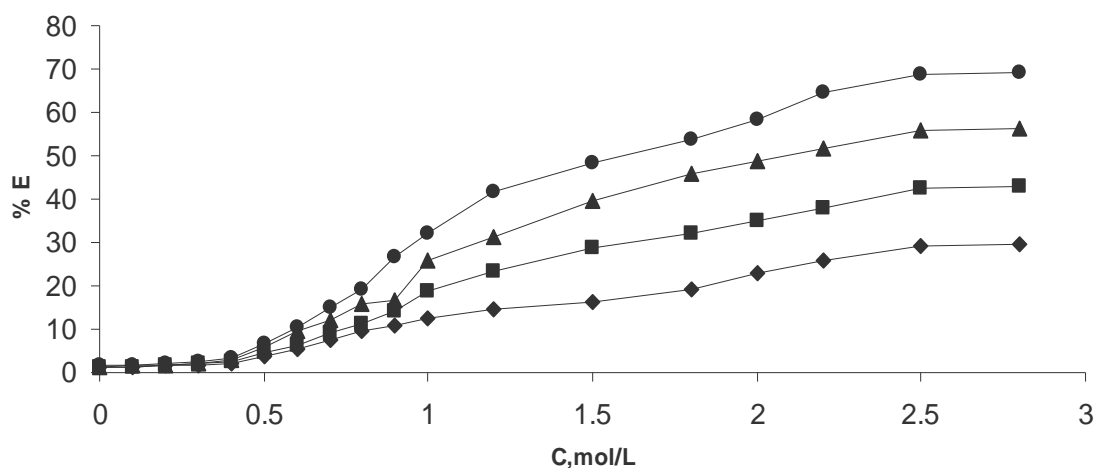
Figure1. Effect of urea Concentration (C) on percentage extraction (%E) of styrene at
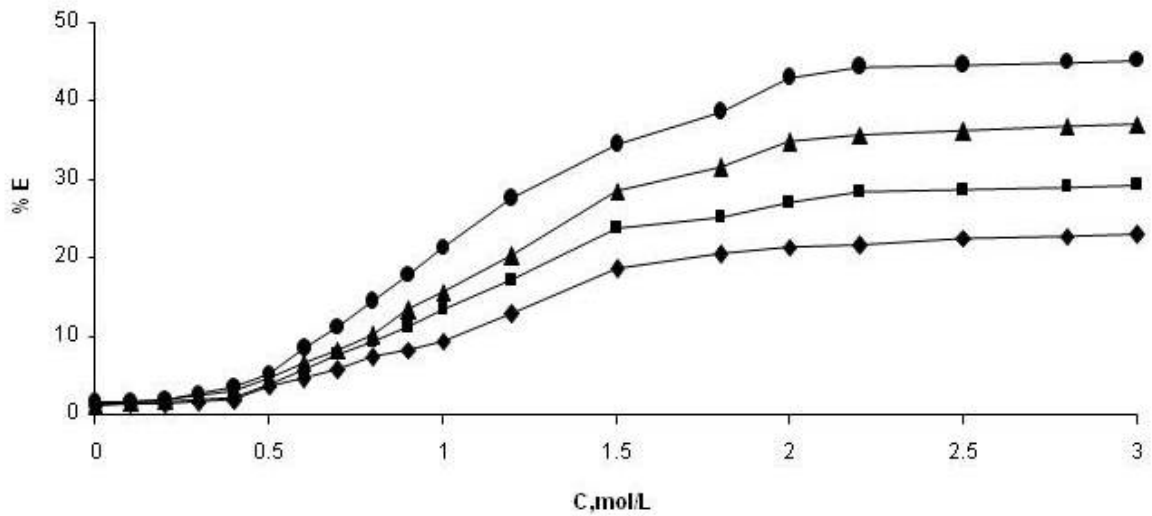—◆— 303 K —■— 313 K —▲— 323 K —●— 333 K

Figure 2. Effect of nicotinamide Concentration (C) on percentage extraction (%E) of styrene at
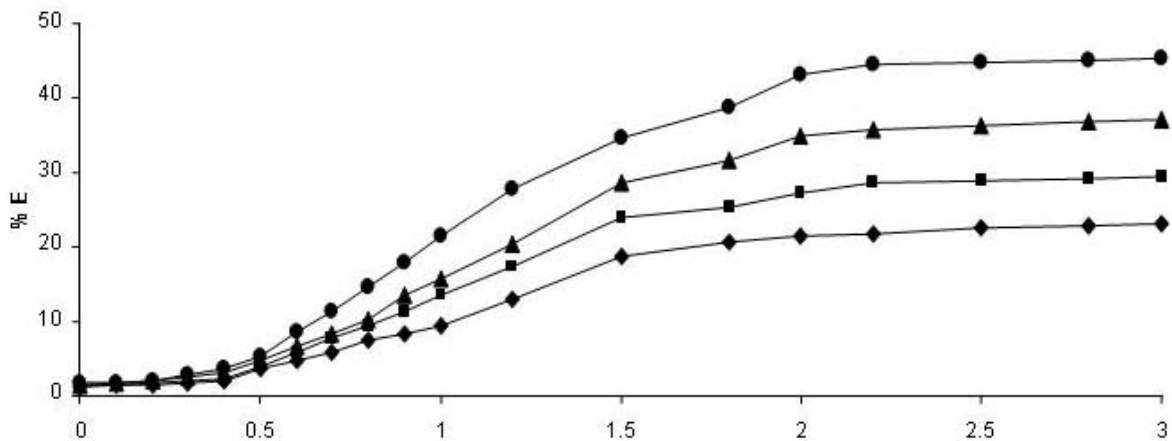◆ 303 K ■ 313 K ▲ 323 K ● 333 K

Figure3. Effect of sodium benzoate Concentration (C) on percentage extraction (%E) of styrene at

◆ 303 K ■ 313 K ▲ 323 K ● 333 K

3.1. Effectiveness of hydrotrope

The effectiveness factor for each hydrotrope with respect to the percentage extraction of styrene at different system temperatures were determined by applying the model suggested by Setschenow and later modified by Phatak and Gaikar [22] is given by the equation:

$$\log (E/E_m) = K_s (C_s - C_m)$$

where E and E_m are percentage extraction of styrene at any hydrotrope concentration, C_s, and minimum hydrotrope concentration C_m, same as MHC respectively. The Setschenow constant (K_s) can be considered as a measure of the effectiveness of a hydrotrope at any given conditions of hydrotrope concentration and system temperature. The Setschenow

constant values of hydrotropes, namely, urea, nicotinamide and sodium benzoate for percentage extractions of styrene at different system temperatures are listed in Table. 4. The highest value was observed as 0.552 in the case of nicotinamide as the hydrotrope.

4. Conclusions

The separation of styrene/ethyl benzene mixture, which is found to be difficult by conventional methods until now has been carried out effectively using hydrotropy technique. The highest percentage extraction of styrene (69.45) was observed in the case of sodium benzoate as hydrotrope at a temperature of 333 K. This unique technique will eliminate the huge cost and energy normally involved in the separation of styrene from its mixture with ethyl benzene. The unprecedent increase in the percentage extraction by the effect of hydrotropes is attributed to the formation of organized aggregates of hydrotrope molecules at a critical concentration.

Table 4. Setschenow constants, K_s, of hydrotropes with respect to styrene.

Temperature, T (K)	K_s		
	Urea	Nicotinamide	Sodium benzoate
303	0.407	0.455	0.437
313	0.416	0.508	0.481
323	0.433	0.517	0.483
333	0.445	0.552	0.503

Table 5. Enhancement factor (Φ_E) for percentage extraction of Styrene.

Hydrotrope	Enhancement factor for separation, Φ_E			
	T=303 K	T=313 K	T=323 K	T=333 K
Urea	30.05	34.50	37.04	39.84
Nicotinamide	18.64	22.46	25.38	28.54
Sodium benzoate	25.02	33.20	39.69	43.96

Notations

C Concentration of hydrotrope, mol/L
C_{max} Maximum Hydrotrope Concentration, mol/L
C_s any hydrotrope concentration, mol/L
E Percentage extraction at any hydrotrope concentration
$\%E$ Percentage extraction
E_m Percentage extraction at minimum hydrotrope concentration, C_m
k_s Setschenow constant
MHC   Minimum Hydrotrope Concentration, mol/L

T Temperature, K
Φ_E Maximum enhancement factor for separation.

Subscripts and Superscripts

max   Maximum
m   Minimum
E   Enhancement

Reference

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