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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2011, Vol. 27, No. (4):
Pg. 1671-1677

Separation of 2, 4 / 2,6 - Xylidine Mixture through Hydrotropy

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(Received: September 12, 2011; Accepted: October 22, 2011)

ABSTRACT

The separation of 2,6 - xylidine from 2,4 /2,6 - xylidine mixtures in hydrotrope solutions was carried out. The aqueous solubilities of 2,4 - xylidine and 2,6 -xylidine in different hydrotropic concentrations (0-3.0 mol/L) of sodium cumene sulfonate , citric acid and nicotinamide solutions at different system temperatures (303 to 333 K) were studied. The percentage extraction of 2,6- xylidine from 2,4 /2,6 - xylidine mixture increases with increase in hydrotrope concentration and also with system temperature, and sodium cumene sulfonate were found to be effective for the selective extraction of 2,6- xylidine with a recovery of 90% from the aqueous solution of hydrotropes with high purity. The process was further optimized with respect to concentration of hydrotropes and temperature of extraction. The effectiveness of hydrotropes was measured in terms of Setschnew constant, Ks and reported for all hydrotropes used in this study. The solubility data are also fitted in a polynomial equation as the function of hydrotrope concentration. The solubilized material has been recovered by dilution with distilled water.

Key words: Hydrotropy, Extraction, Enhanced solubility, Separation.

INTRODUCTION

A variety of industrial mixtures having close boiling point isomeric/non- isomeric components present a challenging separation problem, as in most cases usual separation methods cannot be successfully applied[1,2]. These components usually have similar chemical properties, molecular sizes and comparable volatilities. In order to effect a physical separation of these mixtures, it is necessary to invoke some property which depends on molecular structure rather than on molecular size[3].

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[4-7].

Hydrotropic substances are a class of chemical compounds that are freely soluble in water and are effective at significant hydrotrope concentrations in enhancing the aqueous solubility of other substances, because of the possibility of

molecular solution structures probably in the form of stack-type aggregates. The solute will therefore precipitate out on dilution with distilled water from most hydrotropic solutions. This process may be used to recover the solute in pure form and the remaining mother liquor may be used to concentrate the hydrotrope for recycle[8].

The present study focuses on the separation of *2,4/2,6 xylidine* through hydrotropy. Xylidine is the trivial name of dimethylaniline, $(CH_3)_2C_6H_3NH_2$. There are six structural isomers. The names of six compounds indicate methyl group positions relative to the amino on the benzene ring. They can be obtained from coal tar as by-products in the fractional distillation Xylidines and derivatives are widely used as raw materials to produce imaging chemicals like pigments and dyestuffs. The aromatic amine 2,6-xylidine (2,6-dimethylaniline) is used as a chemical intermediate in the production of dyes, pesticides, and pharmaceutical[9]. All of these compounds are also used in the production of antioxidants, agricultural, pharmaceutical, rubber chemicals and other target organic molecules. Therefore, the end product will contain an isomeric mixture of 2,4 xylidine and 2,6 xylidine. The boiling points of 2,4- and2,6- xylidine are 218 °C and 216 °C, respectively[10,11].

Hydrotropes have been effectively used in extractive separations for the separation of close boiling point mixtures[12-16] 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 the other factors considered in the selection of these hydrotropes.

EXPERIMENTAL

Materials

All the chemicals used in this work were manufactured by SD Fine Chemicals., Mumbai with a manufacturer's stated purity of 99.9 %. The hydrotropes used in this work viz., sodium cumene sulfonate, nicotinamide, and citric acid are of analar grade. Double distilled water was used for the preparation of hydrotropic solutions.

Experimental set up and procedure

The experimental setup for conducting a single-stage batch wise liquid-liquid extraction consisted of a thermostatic bath and separating funnel. The thermostatic bath method was used for the separation of 2,6 xylidine from 2,4-xylidine and 2,6 xylidine mixture. For each test, an equal amount of (100 mL) of 2, 4-xylidine and 2,6 xylidine was taken and mixed well to make a single phase solution using a shaker. Hydrotrope solutions of different concentration (0- 3mol/L) were prepared by dilution with distilled water. Approximately 100 mL of 2,4/ 2,6 xylidine mixture was taken, and an equal amount of hydrotrope solution was added and mixed for 3 h at 600rpm. The mixture was then transferred to a separating funnel which was immersed in a constant temperature bath fitted with a temperature controller. The setup was kept overnight for attaining equilibration. After equilibrium was attained, the aqueous phase was carefully separated and analyzed to determine the concentration using a High-Performance Liquid Chromatography (HPLC). Column poroshell 120 EC-C18, 3.0mm x 150mm, 2.7 µm Mobile phase: (A) Mono ammonium phosphate, disodium hydrogen phosphate, water-mixture (B) Methanol, Injection Volume: 1 µl. Duplicate runs were conducted and error was found to be <2%. . The thermostatic bath method used for the determination of % extraction of 2,6 xylidine values consisted of a thermostatic bath and a separating funnel and was carried out at temperatures of 303, 313, 323, and 333 K.

RESULTS AND DISCUSSION

Extracted 2, 6 xylidine has been shown in schematic comparative HPLC chromatograms in Fig.1.

Polynomial equation of experimental data on the effect of hydrotropes on the separation of 2, 4/ 2,6 xylidine at different temperatures are plotted in Figs.2 to 4.

Percentage extraction %*E* is the ratio of moles of 2,6 xylidine extracted in the presence of hydrotrops to that in the absence of hydrotrops . It was observed that sodium cumene sulfonate is one of the hydrotropes used in this study. %E of 2,6

xylidine in water at 303 K in the absence of any hydrotrope is 1.5 (Fig.2). The percentage extraction %E of 2,6 xylidine has not shown any appreciable increase until 0.4 mol/L sodium cumene sulfonate was added in the aqueous phase. But on subsequent increase in the concentration of sodium cumene sulfonate i.e 0.5 mol/L, the percentage extraction %E of 2,6 xylidine in aqueous phase increases significantly. This concentration i.e 0.50 mol/ L of hydrotrope required to effect a significant increase in the % extraction of 2,6 xylidine in water is termed as Minimum Hydrotrope Concentration (MHC). It was observed that the MHC of sodium cumene sulfonate in the aqueous phase does not vary even at increased system temperatures, i.e., 313, 323, and 333 K.

Since hydrotropy appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved 2,6 xylidine on dilution with water below the MHC. The knowledge of MHC values is necessary especially at industrial levels, as it ensures ready recovery of the hydrotrope for reuse.

The percentage extraction varies with different concentration of the hydrotropes. In this case, a clear increasing trend in the percentage extraction of 2,6 xylidine was observed above the MHC of sodium cumene sulfonate. This increase is maintained only up to a certain concentration of sodium cumene sulfonate i.e 2.50 mol/ L beyond which there is no appreciable increase in the percentage extraction of 2,6 xylidine. This concentration of sodium cumene sulfonate in the aqueous phase is referred to as the maximum hydrotrope concentration (C_{max}). C_{max} values of nicotinamide and citric acid with respect to 2,6 xylidine are 2.90, 2.70 mol/L, respectively (Table 1). The curves are drawn using polynomial interpolations.

Table 1: MHC and C_{max} values for Hydrotropes

Hydrotrope	MHC mol/L	C_{max} mol/L
Citric acid	0.6	2.7
Nicotinamide	0.5	2.9
Sodium cumune sulfonate	0.4	2.5

Table 2: Enhancement factor (Φs) values of hydrotropy

Hydrotrope	Φs			
	303K	313K	323K	333K
Citric acid	31.00	34.29	36.26	39.09
Nicotinamide	19.26	21.76	24.52	27.28
Sodiumcumune sulfonate	25.21	32.23	38.00	42.14

Table 3: Setschenow constants (Ks) values

Temperature	Ks		
K	Citric acid	Nicotinamide	Sodium cumune sulfonate
303	0.365	0.439	0.440
313	0.377	0.458	0.507
323	0.384	0.431	0.532
333	0.393	0.445	0.541

From the analysis of the experimental data, it was observed that a further increase in the hydrotrope concentration beyond C_{max} did not bring any appreciable increase in the %E of 2,6 xylidine even at concentrations of up to 2.50 mol/L of sodium cumene sulfonate in the aqueous solution. Similar to MHC values, the C_{max} values of hydrotropes remained unaltered with an increase in system temperature.

In the concentration range of sodium cumene sulfonate between 0 and 2.50 mol/L, three different regions were obtained. It was observed that sodium cumene sulfonate was inactive below MHC of 0.40 mol/L, above which an appreciable increase in the percentage extraction of 2,6 xylidine 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 2,6 xylidine. Therefore, sodium cumene sulfonate was found to be an effective hydrotrope in the concentration range between 0.40 and 2.50 mol/L towards 2,6 xylidine. 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 sodium cumene sulfonate does not vary linearly with the concentration of sodium cumene sulfonate. The separation effect of sodium cumene sulfonate increases with the increase in hydrotrope concentration and also with system temperature. A similar trend was observed in the separation effect

Correlation constants for polynomial equation

Table 4: Effect of the citric acid

A	B	C	D	E	F	Temp K
1.8706	17.681	-60.929	86.351	21.83	2.9988	303
-3.4074	31.426	-104.24	140.52	37.01	3.7384	313
-4.2938	39.648	-131.46	176.43	46.324	4.1679	323
-5.5678	49.811	-159.05	205.26	53.57	4.7002	333

Table 5: Effect of the Nicotinamide

A	B	C	D	E	F	Temp K
-0.8744	10.839	-47.797	82.467	-20.866	2.8669	303
-0.0612	3.4233	-23.596	50.941	-13.288	2.5607	313
-0.5848	7.2781	-32.079	55.395	-15.063	2.3757	323
-0.8744	10.839	-47.797	82.467	-20.866	2.8669	333

Table 6: Effect of the sodium cumune sulfonate concentration

A	B	C	D	E	F	Temp K
-1.0734	8.7551	-26.444	34.529	-2.0751	1.2234	303
1.5387	14.69	-52.614	80.148	-20.893	2.5611	313
-1.3314	14.452	-58.628	98.143	-25.586	2.8983	323
-3.1355	30.046	-106.5	157.73	-42.837	3.7275	333

of other hydrotropes, namely nicotinamide, and citric acid Fig 3 to 4. The highest value of enhancement factors Ös , which is the ratio of the percentage extraction value in the presence and absence of a hydrotrope, respectively, has been observed in the case of sodium cumene sulfonate as 42.14 at a system temperature of 333 K (Table 2).

Effectiveness of hydrotrope

The effectiveness factor for each hydrotrope with respect to the percentage extraction of 2,6 xylidine at different system temperatures was determined by applying the model suggested by Setschenow and later modified by Phatak and Gaikar is given by the equation:

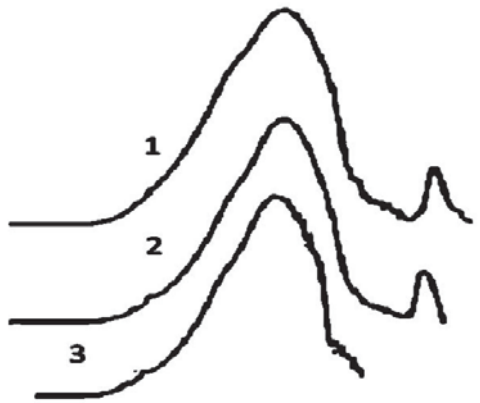
$$log\ (E/E_m) = Ks(C_s - C_m) \quad ...(1)$$

where *E* and *E*m are percentage extraction of 2,6 xylidine 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, nicotinamide and citric acid for percentage extractions of 2,6 xylidine at different system temperatures are listed in Table. 3. The highest value was observed as 0.541 in the case of sodium cumene sulfonate as the hydrotrope.

Since the exponential relation may not be valid at lower and higher hydrotrope concentrations, the data have been fitted in a polynomial equation of the form

$$Y = Ax^5 + Bx^4 + Cx^3 + Dx^2 + Ex + F \quad ...(2)$$

which give a better fit for the solubility data. The values of correlation constants "A-F" are reported in Table 4 to 6. The solid curves in Figs.2-4 are from these polynomial equations.



1.Sodium cumene sulfonate , 2.Nicotinamide, 3.Citric acid

Fig. 1: Comparative HPLC chromatogram for extraction of 2,6 xylidine

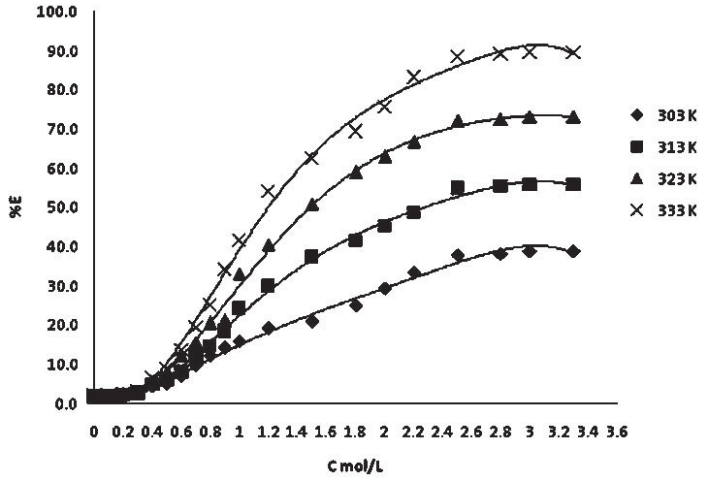


Fig. 2: Effect of sodium cumene sulfonate concentration (*C*) on the %E of 2,6-xylidine at different temperatures (T)

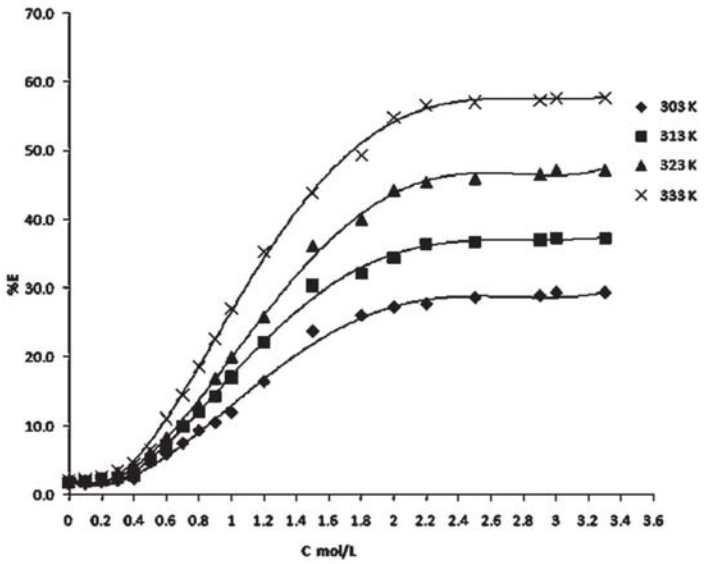


Fig. 3: Effect of Nicotinamide concentration (*C*) on the %E of 2,6-xylidine at different temperatures (T)

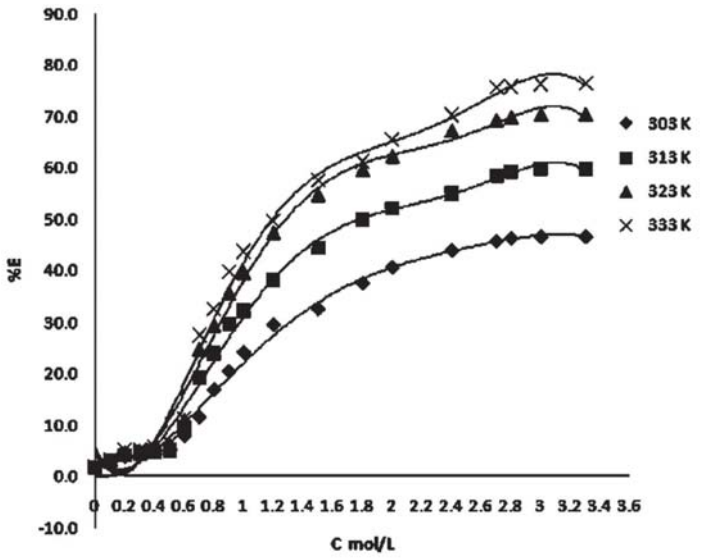


Fig. 4: Effect of citric acid concentration (*C*) on the %E of 2,6-xylidine at different temperatures (T)

CONCLUSIONS

The separation of 2,6 xylidine from2,4 / 2,6 xylidine 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 2,6 xylidine (90%) was observed in the case of sodium cumene sulfonate as hydrotrope at a temperature of 333 K. This unique technique will eliminate the huge cost and energy normally involved in the separation of 2,6 xylidine from its mixture with 2,4 xylidine. The unprecedented 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.

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