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Reflection of Hydrotropy Technique in the Segregation of 1,1/1,2-Diphenylethane

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Abstract: A thorough study on the aqueous solubility of 1,1/1,2-diphenylethane using different hydrotropes such as diethylnicotinamide, sodium pseudocumene sulfonate and sodium thiocyanate at various concentrations (0-3.0 mol/L) and at different system temperatures (303K to 333K). Consequent to the increase in solubility, the percentage extraction (%E) of 1,1-diphenylethane from 1,1/1,2-diphenylethane mixture also increases with increase in hydrotrope concentration. A Minimum Hydrotrope Concentration (MHC) in the aqueous phase was required to initiate the significance of the %E of 1,1-diphenylethane. Percentage extraction (%E) is the ratio of moles of 1,1-diphenylethane extracted in presence and absence of a hydrotrope. The sensitivity and feasibility of the proposed process were examined by carrying out the experiments involving precipitation of solubilization and equilibrium with the mixtures of various compositions. The Setschenow constant, Ks, a measure of the effectiveness of hydrotrope, has been determined for each case. It is possible to extract 89% of 1,1-diphenylethane from its mixture.

Key words: Hydrotropy · Solubilization · Enhanced solubility · Extraction

INTRODUCTION

A range of industrial mixtures having close boiling point isomeric or non isomeric components present a challenging separation problem, as in most cases conventional separation methods cannot be successfully applied. These components usually have similar chemical properties and molecular sizes and comparable volatilities. A simple technique is employed which involves either solubilization and precipitation i.e., the solubilization of the mixture in a hydrotrope solution and subsequent selective precipitation of a desired component by controlled dilution with water.

Hydrotropy is a unique and unprecedented solubilization technique in which certain chemical components termed as hydrotropes can be used to affect a several fold increase in the solubility of sparingly soluble solutes under normal conditions [1-4].

Hydrotropic substances are a class of chemical compounds that are freely soluble in water. Hydrotropes are much effective at high concentrations which in turn enhance the aqueous solubility of organic compound, because of the possibility of molecular solution structures probably in the form of stack-type aggregates. The solubilised solute will therefore precipitate out on dilution with water from most hydrotropic solutions. This process may be used to recover the solute in a pure form and the remaining mother liquor may be used to concentrate the hydrotrope for recycle [5].

In recent years the aggregation behaviour of common hydrotropes by several techniques have been determined [6, 7]. The self aggregation of the hydrotropes has been considered to be a pre-requisite for a number of applications in various fields such as drug solubilization [8-10], chemical reactions [11], separation of organic compounds [12] extraction of curcuminoids from turmeric [13], piperine from Piper nigrum [14] and boswellic acids from Boswellia serrata resins [15].

The present work was initiated for the fundamental study of the global role of hydrotropes in the selective separation of a component from mixtures via solubilization and precipitation techniques. [16-21] with particular emphasis on both the theoretical understanding of the mechanistic behavior and the experimental studies which demonstrates the utility of hydrotropes in the separation of commercially important mixtures [21-25]. The system 1,1/1,2-diphenylethane (molecular weight M = 182.25) [26] was chosen, for enhancing its solubility using several

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commercially available hydrotropes. Since 1,1-diphenylethane serves as a raw material/intermediate for a wide variety of chemical and petro products and this makes its separation much more superior from any liquid mixture, which has been difficult until now.

The separation of 1,1/1,2-diphenylethane through solubilization and selective precipitation is much important as both these isomers have not only close boiling points, but also close melting points. The boiling points of 1,1/1,2-diphenylethane are 272.6°C and, 284°C respectively. All hydrotropes are non- reactive, non-toxic and do not produce any change in temperature effect when dissolved in water. Cost effective and easy availability are other factors considered in the selection of hydrotropes. This method is separation of 1,1/1,2-diphenylethane using the pioneering technique hydrotropy. Our research deals with eco friendly method of separating isomeric components by using hydrotropy technique and also we made a cost-effective method for separation of 1,1/1,2-diphenylethane.

MATERIALS AND METHODS

Materials: All the chemicals used in this work were manufactured by the Loba Chemie Pvt. Ltd., Mumbai. with a manufacturer's stated purity of 99.9 %. The hydrotropes used in this work viz., diethyl nicotinamide, sodium pseudocumene sulfonate and sodium thiocyanate are of analar grade. Double distilled water was used for the preparation of hydrotropic solutions.

Methods: The experimental setup for conducting a single-stage batch wise liquid-liquid extraction consisted of a thermostatic bath and a separating funnel. Measurement of the solubility of 1,1-diphenylethane was carried out at temperatures of 303, 313, 323 and 333 K. For each solubility test, an equal volume (100mL) of 1,1/1,2-diphenylethane was thoroughly mixed to make a single-phase solution using a mechanical shaker. The hydrotrope solutions of different known concentrations were prepared by dilution with distilled water. Following to this, 100 ml of 1,1/1,2-diphenylethane mixture was taken and added to 100ml of hydrotrope solution of known concentration. The mixture was then made to mix continuously for three hours. The mixture was then allowed to settle and was transferred to a separating funnel, which was immersed in a thermostatic bath with a temperature controller within ± 0.1°C. The setup was kept overnight for equilibration. After equilibrium was attained, the organic phase containing 1,1-diphenylethane was carefully separated and analyzed to determine the concentration using a high-performance liquid chromatography (HPLC). All the solubility experiments were conducted in duplicate runs to check their reproducibility. The %E has been calculated from these solubility data. The observed error was <2%.

RESULTS AND DISCUSSION

Experimental data on the effect of hydrotropes, i.e., diethyl nicotinamide, sodium pseudocumene sulfonate and sodium thiocyanate on the percentage extractions (%E) of 1,1-diphenylethane are presented in Figs. 1-3. Percentage extraction (%E)) is the ratio of extraction of 1,1-diphenylethane in the presence and absence of hydrotrope, respectively.

Sodium thio cyanate is one of the hydrotropes used in this study. It was observed that the %E of 1,1-diphenylethane did not show any appreciable increase until 0.40 mol/L of sodium thiocyanate, however, upon subsequent increase in the concentration of sodium thiocyanate, i.e., 0.40 mol/L, the %E of 1,1-diphenylethane was found to increase significantly. This concentration of sodium thiocyanate in the aqueous phase, i.e., 0.40 mol/L, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required amount of sodium thiocyanate in the aqueous phase to initiate significant increase in the percentage extraction of 1,1-diphenylethane. At this point only the hydrotropes starts for self aggregation, It was observed that the MHC of sodium thiocyanate 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 the MHC, irrespective of the system temperature. Hydrotrope does not seem to be operative below the MHC, which may be a characteristic of a particular hydrotropes 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 1,1-diphenylethane. was observed above the MHC of sodium thiocyanate. This increase is maintained only up to a certain concentration of sodium thiocyanate in the aqueous phase, i.e, 2.50 mol/L beyond which there is no appreciable increase in the percentage extraction of 1,1-diphenylethane. This concentration of sodium thiocyanate in the aqueous phase is referred to as the maximum hydrotrope

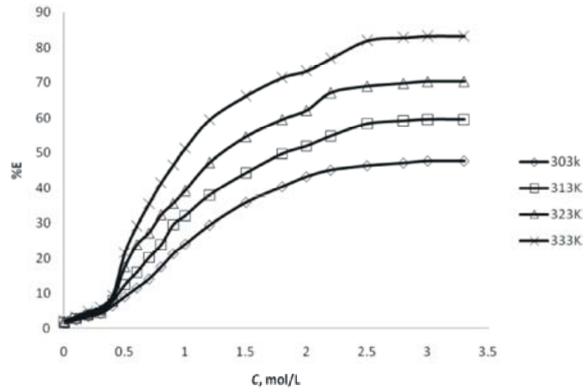

Fig. 1: Effect of diethylnicotinamide concentration (C) on percentage extraction(%E) of 1,1-diphenylethane

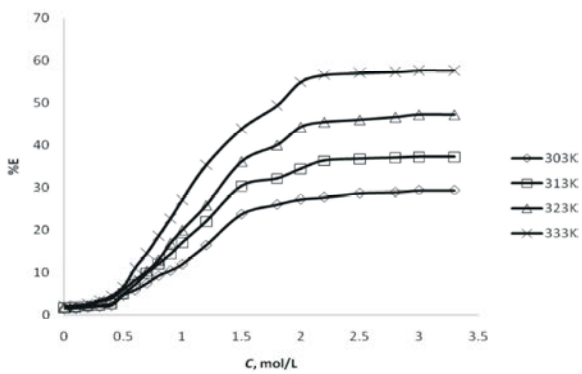

Fig. 2: Effect of sodium pseudocumene sulfonate concentration (*C*) on percentage extraction(%E) of 1,1-diphenylethane

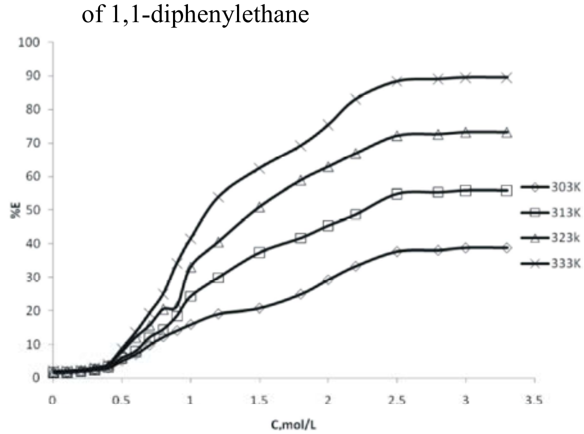

Fig. 3: Effect of sodium thiocyante concentration (*C*) on percentage extraction(%E) of 1,1-diphenylethane

concentration (C_{max}). 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 even up to 3.0 mol/L in the aqueous phase, because of insufficient water molecule may not dissolve further solute. Similar to the MHC values, the C_{max} values of the hydrotropes also

Table 1: MHC and C_{max} values of hydrotropes

S.No	Hydrotropes	MHC, mol/L	Cmax, mol/L
1	Diethylnicotinamide	0.6	2.7
2	Sodium pseudocumene sulfonate	0.5	2.9
3	Sodium thiocyanate	0.4	2.5

Table 2: Effectiveness of hydrotrop (φ)

S.No	Hydrotropes	303K	313K	323K	333K
1	Siethylnicotinamide	30.65	33.89	35.72	39.09
2	Sodium pseudocumene sulfonate	17.86	22.17	24.67	28.13
3	Sodium thiocyanate	24.82	32.32	38.03	41.74

Table 3: Setschenow constant [K_s] values of hydrotropes with respect to 1,1-diphenylethane

S.No	Hydrotropes	303K	313K	323K	333K
1	Diethylnicotinamide	0.37	0.38	0.39	0.41
2	Sodium pseudocumene sulfonate	0.44	0.46	0.43	0.45
3	Sodium thiocyanate	0.44	0.51	0.53	0.54

remained unaltered with the increase in system temperature. (Table 1) The maximum Effectiveness of hydrotrope (φ) which is the ratio of the percentage extraction value in the presence and absence of a hydrotrope, respectively was determined and the highest value of(φ) 41.74 case of sodium thiocyanate 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 1,1-diphenylethane at different system temperatures was determined by applying the model suggested by Setschenow[27] and later modified by Phatak and Gaikar[28] as given by the equation:

$$\log (E/Em) = Ks(Cs - C\,m) \qquad 1$$

where E and Em is the %E values of 1,1-diphenylethane maximum hydrotrope concentration Cs (same as Cmax) and the minimum hydrotrope concentration Cm (same as MHC) respectively. The Setschenow constant (Ks) 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, diethyl nicotinamide, sodium pseudo cumene sulfonate and sodium thiocyanate for percentage extractions of 1,1-diphenylethane different system temperatures are listed in Table 3. The highest value was observed as 0.54 in the case of sodium thiocyanate as the hydrotrope at temperature 333K.

CONCLUSIONS

Selective solubilization of isomeric mixtures of 1,1/1,2-diphenylethane were determined in aqueous solutions of several hydrotropes at different hydrotrope concentrations and temperatures. The MHC and Cmax values of hydrotropes with respect to 1,1-diphenylethane can be used for the recovery of the dissolved 1,1-diphenylethane and hydrotrope solutions at any hydrotrope concentration between MHC and Cmax by simple dilution with distilled water. It was possible to extract 89% of the material and the process was optimized with respect to concentration of hydrotrope solution and temperature required for the extraction of 1,1-diphenylethane. From the data obtained by this study, it is found that hydrotrope concentration gives self-aggregation at higher minimum concentration. These sigmoidal-type solubility variations are influenced by molecular structures. The differences in solubilities with hydrotrope concentration and temperature can be employed for the separation of closely related compounds. This will eliminate the huge cost and energy normally involved in the separation of solubilised 1,1-diphenylethane from its solution. Hence sodium thiocyante is found to be the best suitable hydrotrope for the enhancement of solubility of poorly soluble 1,1-diphenylethane within the framework of the present investigation.

Notation:

C [mol/L]	Concentration of hydrotrope
Cmax [mol/L]	Maximum hydrotrope concentration
Cs [mol/L]	Maximum hydrotrope concentration
Ks [–]	Setschenow constant
E [-]	%E of 1,1-diphenylethane at any hydrotrope concentration
E_m [-]	%E of 1,1-diphenylethane at maximum hydrotrope Concentration
C_m [mol/L]	Minimum hydrotrope concentration
MHC [mol/L]	Minimum hydrotrope concentration
T [K]	Temperature
Φ [–]	Maximum enhancement factor

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