EFFECT OF HYDROTROPES ON SOLUBILITY AND MASS TRANSFER COEFFICIENT OF 1, 2- DICHLOROETHANE

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Abstract
A comprehensive investigation on the solubility and mass transfer coefficient enhancement of 1,2-dichloroethane through hydrotropy has been undertaken. The solubility and mass transfer coefficient studies were carried out using hydrotropes such as urea, citric acid, nicotinamide and sodium salicylate under the influence of a wide range of hydrotrope concentrations (0 to 3.0 mol/L) and different system temperatures (303 to 333 K). It has been observed that the solubility of 1,2-dichloroethane increases with increase in hydrotrope concentration and also with system temperature. A Minimum Hydrotrope Concentration (MHC) in the aqueous phase was required to initiate significant solubilization of 1,2- dichloroethane. Consequent to the increase in solubilization of 1,2-dichloroethane, the mass transfer coefficient was also found to increase with increase in hydrotrope concentration at 303 K. A threshold value of MHC is to be maintained to have an appreciable enhancement in the mass transfer coefficient. The maximum enhancement factor, which is the ratio of the value in the presence and absence of a hydrotrope, has been determined for all sets of experimentalizations. The performance of hydrotropes was measured in terms of setschenow constant (Ks) and reported for all hydrotropes used in this study.

Key Words: Hydrotropy, Solubilization, Mass transfer co-efficient, Separation.

1. Introduction

Hydrotropes can be used to effect a several fold increase in the solubility of solutes that are sparingly soluble in water under normal conditions. This increase in solubility in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentration. The origin of hydrotropy dates back to 1916 when Neuberg identified this pioneering technique for effecting very large solubility enhancement for a variety of sparingly soluble organic compounds [1-3]. Hydrotropes in general are water-soluble and surface active compounds which can significantly enhance the solubility of organic solutes such as esters, acids, alcohols, aldehydes, ketones, hydrocarbons and fats. Easy recovery of dissolved solute and possible reuse of hydrotrope solutions makes this technique most attractive one particularly at industrial levels [4 - 6]. Aqueous hydrotrope solutions provide safe and effective media for the extraction of natural products and for conducting organic synthetic reactions. They have also been used to increase the rate of heterogeneous reactions, besides being an extraction agent for fragrances [9-10]. Hydrotropes have also been used as intermediates in the in the production of various organic compounds [11-14].

The advantage of certain properties, such as easy recovery of the dissolved solute, possible reuse of hydrotrope solution, absence of emulsification, inexpensive aqueous phase makes this technique superior to other solubilization methods such as micellar solubilization, miscibility, cosolvency, salting-in, etc. Because of the solubilizing effect of these hydrotropes, the mass transfer coefficient of two-phase systems can considerably be enhanced [15-16].

It has been observed that, in many two-phase reaction systems involving a sparingly soluble organic compound like 1,2-dichloroethane, the mass-transfer coefficient was found to be very low solely due to the poor
solubility of solute in the aqueous phase. Since 1,2-dichloroethane serves as raw material/intermediate for a wide variety of chemicals and allied products [17 -18] and its separation from any liquid mixture seems to be difficult, this hydrotropic phenomenon can be effectively used for this system. The hydrotropes used in this work are freely soluble in water and practically insoluble in 1-2 dichloroethane. All are non- reactive and non- toxic and do not produce any temperature effect when dissolved in water [19-20]. The easy availability and cheapness of hydrotropes are the other factors considered in the selection of hydrotropes [21-22]. Data on various aspects of hydrotropic study on the solubility and mass-transfer coefficient for the 1,2- dichloroethane -water system are reported for the first time.

2. Materials and methods

All the chemicals used in this work were manufactured by S.D.Fine Chemicals Pvt. Ltd., Mumbai, with a manufacturer’s stated purity of 0.99 mole fraction. The thermostatic bath method was to determine solubility value. For each solubility test, about 100 ml of 1,2- dichloroethane, previously saturated with distilled, water was taken in a separating funnel and 100 ml of a solution of the hydrotropic of known concentration was added. The separating funnel was sealed to avoid evaporation of mixtures at higher temperatures. The solution of different concentrations of the hydrotropic was prepared by dilution with distilled water. The separating funnel was immersed in a constant-temperature bath fitted with a temperature controller which could control the temperature within ± 0.1 °C. The setup was kept overnight for equilibration. After equilibrium was attained, the aqueous layer was carefully separated from the ester layer and transferred into a beaker. The ester concentration was estimated by the addition of excess NaOH using standardized HCl solution and phenolphthalein as an indicator. All the solubility experiments were conducted in duplicate to check the reproducibility. The observed error was < 2 %.

The experimental setup for the determination of the mass-transfer coefficient consisted of a vessel provided with baffles and a turbine impeller run by a motor to agitate the mixture. The speed of the impeller in rpm was selected in such a way to get effective mixing, which was maintained at the same value for all experimentations. The experimental procedure used for the determination of the mass transfer coefficient is a well-adopted one. The vessel used for mass transfer studies is of height 40 cm and inner diameter 15 cm. The turbine impeller diameter is 5 cm, the width is 1 cm, and the length is 1.2 cm. It has 4 blades. The baffle is 40 cm high with a diameter of 1.5 cm. There are about 4 baffles that rotate at a speed of 600 rpm.

For each run to measure the mass-transfer coefficient, 250 ml of the 1,2- dichloroethane previously saturated with distilled water was added to the hydrotropic solution of known concentration. The sample was then agitated for a known time of (600, 1200, 1800, and 2400) seconds. After the end of fixed time, the entire mixture was transferred to a separating funnel. After allowing to stand for 1 hr, the aqueous layer was carefully separated from the 1,2-dichloroethane layer. The concentration of the solubilized 1,2- dichloroethane in aqueous hydrotropic solutions at time t was analyzed as done for solubility determinations. A plot of – log (1 - Cα / Cα*) versus t is drawn, where Cα is the concentration of solute at time t and Cα* is the equilibrium solubility of solute at the same hydrotropic concentration. The slope of the graph gives kαa / 2.303, from which kαa, the mass-transfer coefficient was determined. Duplicate runs were made to check the reproducibility. The observed error was < 2 %.

3. Results and Discussion

3.1. Solubility

The solubility of the 1,2-dichloroethane standard in the absence of any hydrotropic in water is 3.57 x 10⁻¹ mol/L at 303 K, compared to 3.60 x 10⁻¹ mol/L as reported by Dean (1987). Thus, the solubility value in water is in excellent agreement with earlier reported value.

Experimental data representing the average of duplicate determinations on the effect of hydrotropes, i.e., urea, citric acid, nicotinamide and sodium salicylate on the solubility of 1,2-dichloroethane are presented in Fig 1 to Fig 4. It has been observed that the solubility values increase significantly only after the addition of 0.30 mol/L of urea in the aqueous phase. This concentration in referred to as the Minimum Hydrotropic Concentration (MHC).

Therefore, it is evident that hydrotropic solubilization is displayed only above the MHC, irrespective of system temperature. Hydrotropy does not seem to be operative below the MHC, which may be a characteristic of a particular hydrotropic with respect to each solute. This MHC value assumes greater significance in the context of recovery of hydrotropic solutions. Since hydrotropy appears to operate only at significant concentrations of hydrotropic in water, most hydrotropic solutions release the dissolved solute on dilution with water below MHC. The knowledge of MHC values is necessary especially at industrial levels, as it ensures ready recovery of hydrotropic for reuse. The MHC values remained unaltered even at increased system temperatures.

The solubilization effect varies with concentration of hydrotropes. In the present case, a clear increasing trend in the solubility of 1,2-dichloroethane was observed above the MHC of urea. This increasing trend is maintained only up to a certain concentration of urea in the aqueous phase, beyond which there is no appreciable increase in the solubility of 1,2-dichloroethane. This concentration of urea (hydrotrope) in the aqueous phase is referred to as the maximum hydrotropic concentration (Cmax). From the analysis of the experimental data, it is observed that further increase in the hydrotropic concentration beyond Cmax does not bring any appreciable
increase in the solubility of 1,2-dichloroethane even up to 3.00 mol/L of urea in the aqueous phase. Similar to the MHC values, the $C_{\text{max}}$ values of hydrotropes also remained unaltered with an increase in system temperature.

The knowledge of MHC and $C_{\text{max}}$ values of each hydrotrope with respect to a particular solute assumes greater significance in this study since it indicates the beginning and saturation of the solubilization effect of hydrotropes. The MHC and $C_{\text{max}}$ values of a hydrotrope with respect to 1,2-dichloroethane may be useful in determining the recovery of the solute even to an extent of the calculated amount from hydrotrope solutions at any concentration between MHC and $C_{\text{max}}$ by simple dilution with distilled water. This is the unique advantage of the hydrotrropic solubilization technique.

From the experimental data plotted in fig 1, it can further be observed that, in order to achieve the particular solubility of say $6 \times 10^{-3}$ mol/L, the urea concentration required should be 1.80 mol/L at 303 K, 1.40 mol/L at 313 K, and 0.90 mol/L at 333K in the aqueous phase. Thus it can be seen that as the system temperature increases, the concentration of urea required in the aqueous phase to achieve a particular solubility of 1,2-dichloroethane decreases. A similar trend has been observed for other systems also.

In the concentration range of urea between 0.00 and 3.00 mol/L, three different regions of urea as hydrotrope were observed. It was inactive below MHC values of 0.30 mol/L, above which an appreciable increase in the solubility of 1,2-dichloroethane was found up to 2.40 mol/L. Therefore, urea was found to be an effective hydrotrope in the concentration range between 0.30 and 2.40 mol/L towards 1,2-dichloroethane. It has also been observed that the solubilization effect of urea was not a linear function of the concentration of the urea solution. The solubilization effect of urea increases with increase in hydrotrope concentration and also with system temperature.
Table 1: MHC and $C_{\text{max}}$ values of hydrotropes.

| Hydrotropes      | MHC (mol/L) | $C_{\text{max}}$ (mol/L) |
|------------------|-------------|--------------------------|
| Urea             | 0.30        | 2.40                     |
| Citric acid      | 0.40        | 2.40                     |
| Nicotinamide     | 0.50        | 2.20                     |
| Sodium Salicylate| 0.60        | 2.40                     |

Table 2: Maximum enhancement factor for solubility ($\phi_s$) 1,2-Dichloroethane.

| Hydrotropes    | $\phi_s$ T = 303 K | $\phi_s$ T = 313 K | $\phi_s$ T = 323 K | $\phi_s$ T = 333 K |
|----------------|-------------------|-------------------|-------------------|-------------------|
| Urea           | 9.57              | 10.56             | 11.01             | 12.02             |
| Citric acid    | 8.88              | 9.20              | 10.14             | 11.44             |
| Nicotinamide   | 10.07             | 10.77             | 11.78             | 13.01             |
| Sodium Salicylate| 7.86               | 8.41              | 9.38              | 10.61             |

Table 3: Effect of hydrotrope concentration (C) on the mass transfer coefficient ($k_{La}$) of 1,2- Dichloroethane at 303 K.

| Hydrotropes   | C (mol/L) | $k_{La}$ ($10^5$ s$^{-1}$) | Enhancement Factor for Mass Transfer Coefficient ($\phi_{mtc}$) |
|---------------|-----------|-----------------------------|---------------------------------------------------------------|
| Urea          | 0.00      | 2.45                        | -                                                             |
|               | 0.20      | 3.16                        | 1.28                                                          |
|               | 0.60      | 7.59                        | 3.09                                                          |
|               | 0.80      | 13.68                       | 5.58                                                          |
|               | 1.00      | 22.14                       | 9.04                                                          |
|               | 1.20      | 35.82                       | 14.62                                                         |
|               | 1.40      | 51.61                       | 21.06                                                         |
|               | 1.60      | 55.73                       | 22.75                                                         |
|               | 1.80      | 58.56                       | 23.90                                                         |
|               | 2.00      | 59.62                       | 24.33                                                         |
|               | 2.20      | 60.76                       | 24.80                                                         |
|               | 2.40($C_{\text{max}}$) | 61.28                     | 25.01                                                         |
|               | 2.60      | 62.15                       | 25.49                                                         |
|               | 2.80      | 63.67                       | 25.98                                                         |
|               | 3.00      | 63.89                       | 26.07                                                         |
| Citric acid   | 0.00      | 2.45                        | -                                                             |
|               | 0.20      | 3.06                        | 1.25                                                          |
|               | 0.40(MHC) | 7.21                        | 2.94                                                          |
|               | 0.60      | 12.59                       | 5.14                                                          |
|               | 0.80      | 20.67                       | 8.43                                                          |
|               | 1.00      | 28.48                       | 11.62                                                         |
|               | 1.20      | 35.54                       | 14.58                                                         |
|               | 1.40      | 38.15                       | 15.57                                                         |
|               | 1.60      | 43.27                       | 17.66                                                         |
|               | 1.80      | 49.18                       | 20.07                                                         |
|               | 2.00      | 50.34                       | 20.55                                                         |
|               | 2.20      | 51.42                       | 20.99                                                         |
|               | 2.40($C_{\text{max}}$) | 52.63                     | 21.48                                                         |
|               | 2.60      | 53.19                       | 21.71                                                         |
|               | 2.80      | 53.45                       | 21.82                                                         |
|               | 3.00      | 53.86                       | 21.98                                                         |
| Nicotinamide  | 0.00      | 2.45                        | -                                                             |
|               | 0.20      | 2.89                        | 1.17                                                          |
|               | 0.40      | 6.31                        | 2.57                                                          |
|               | 0.60(MHC) | 9.52                        | 3.88                                                          |
|               | 0.80      | 15.34                       | 6.26                                                          |
A similar trend has been observed in the solubilization effect of other hydrotropes namely citric acid, nicotinamide and sodium salicylate. It has also been observed that the MHC values of hydrotrope used in this work range between 0.30 and 0.60 mol/L table (1) which seem to depend on the hydrophilicity of a hydrotrope. The $C_{\text{max}}$ values of hydrotropes range between 2.20 and 2.40 mol/L table (1) in most cases. The highest value of solubilization enhancement factors $\phi_s$, which is the ratio of solubility values in the presence and absence of a hydrotrope has been observed in the case of urea as 12.02 at a system temperature of 333 K table (2).

### 3.2. Mass-transfer coefficient

The mass-transfer coefficient of 1,2-dichloroethane + water system in the absence of any hydrotrope was determined to be $2.45 \times 10^{-5}$ s$^{-1}$ at 303 K table (3) The effect of different hydrotropes on the mass-transfer coefficient of 1,2-dichloroethane at different hydrotrope concentrations is also given in the same table. It can be seen that a threshold value of 0.30 mol/L of urea is required to effect significant enhancement in the mass transfer coefficient of the 1,2-dichloroethane + water system, as observed in the case of solubility determinations. The mass-transfer coefficient of 1,2-dichloroethane + water system increases with increase in urea concentration. The maximum enhancement factor for mass-transfer coefficient of 1,2-dichloroethane + water system in the presence of urea was found to be 25.01 table (3). A similar trend in the mass-transfer coefficient enhancement ($\phi_{\text{mtc}}$) of 1,2-dichloroethane has been observed for other hydrotropes also namely urea, nicotinamide and sodium salicylate.

### 3.3. Effectiveness of hydrotropes

The effectiveness factor of each hydrotrope with respect to 1,2-dichloroethane at different system temperatures has been determined by analyzing the experimental solubility data for each case applying the model suggested by

| Hydrotropes      | Setschenow Constant $(K_s)$ |
|------------------|-----------------------------|
|                  | $T = 303$ K | $T = 313$ K | $T = 323$ K | $T = 333$ K |
| Urea             | 0.467        | 0.487        | 0.494        | 0.514        |
| Citric acid      | 0.474        | 0.481        | 0.503        | 0.529        |
| Nicotinamide     | 0.590        | 0.607        | 0.630        | 0.655        |
| Sodium Salicylate| 0.559        | 0.578        | 0.607        | 0.641        |
setschenow (1951) and later modified by Pathak and Gaikar (1992), as given by the equation.

\[
\log \left( \frac{S}{S_m} \right) = K_c [C_N - C_{N_m}]
\]

where \( S \) and \( S_m \) are the solubilities of 1,2-dichloroethane at any hydrotrope concentration \( C_N \), and the minimum hydrotrope concentration \( C_{N_m} \) (same as MHC) respectively. The setschenow constant \( K_c \) 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, citric acid, and nicotinamide and sodium salicylate for 1,2-dichloroethane + water system at different system temperatures are listed in table (4). The highest value has been observed as 0.540 in the case of urea as hydrotrope at 333 K.

4. Conclusions

The solubility of 1,2-dichloroethane, which is practically insoluble in water has been increased to a maximum value of 12.02 in the presence of urea as hydrotrope with a corresponding increase in the mass transfer coefficient. This would be useful in increasing the rate of output of the desired product made from 1,2-dichloro ethane. The MHC and \( C_{N_{\text{max}}} \) values of the hydrotrope with respect to 1,2-dichloroethane can be used for the recovery of the dissolved 1,2-dichloroethane and hydrotrope solutions at any hydrotrope concentration between the MHC and \( C_{N_{\text{max}}} \) by simple dilution with distilled water. This will eliminate the huge cost and energy normally involved in the separation of the solubilized solute from its solution. The unprecedented increase in the solubilizing effect of hydrotropes is attributed to the formation of organized aggregates of hydrotrope molecules at a particular concentration

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