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HYDROTROPIC EFFECT ON SOLUBILITY AND MASS TRANSFER COEFFICIENT ENHANCEMENT OF CYCLOHEXENE

Antony Bertie Morais, M.Dhinakaran, C. Jayakumar, N. Nagendra Gandhi*
Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai, India 600 025

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For Correspondence:

Dr. N. Nagendra Gandhi

Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai, India 600 025

E-mail:

n_nagendra2002@yahoo.com

ABSTRACT

In this paper, we have studied the effect of hydrotropes like citric acid, urea and sodium salicylate on cyclohexene under certain parameters viz., concentrations in the range from (0 to 3.0) mol/L and system temperatures ranging from T = (303 to 333) K. We found that all the hydrotrope molecules self-aggregate in aqueous solution to form organized assemblies. We show that hydrotropy is different from salting-in or phase-mixing behavior, which influences the formation of micelle and microemulsion. Hydrotropy is a collective molecular phenomenon, exhibited above the MHC (Minimum Hydrotropic Concentration), which was found essential in the solubility and mass transfer coefficient for cyclohexene - water system. Hydrotropic compounds are seen to be surface active though somewhat less than classical surfactants. All hydrotropes used in this work showed an enhancement in solubility and mass transfer coefficient to variant proportions. The enhancement factor, which is the ratio of value in the presence and absence of a hydrotrope is reported for both solubility and mass transfer coefficient.

INTRODUCTION

Carl Neuberg described the large increase in the solubility in water of a variety of hydrophobic compounds brought about by the addition of certain compounds[1]. These solubility-enhancing molecules were termed hydrotropic agents or hydrotropes, and the phenomenon itself was named hydrotropy[2]. Well, after several publications on hydrotropic research, it has become a unique and unprecedented solubilization technique in which specific chemical components termed as hydrotropes can be used to enhance the solubility of sparingly soluble solutes under standard conditions.

Hydrotropes are widely used in various industries for applications such as drug solubilization, detergent formulation, health care, and household applications besides being an extraction agent for fragrances[3]. Hydrotropes are freely water-soluble organic compounds that are capable of increasing significantly the water solubility of sparingly soluble substances at their relatively high concentrations above the threshold or critical hydrotrope concentration. At the same time, the problem of emulsification, which is normally encountered with conventional surfactant solutions, is not found with hydrotrope solutions. Hydrotrope solutions brought out its vital role in industrial applications, which was found to be much attractive, because of their easy availability, ready recovery of the dissolved solutes by simple dilution with water[4] or by solvent extraction, and absence of any fire risk because of no volatility.

It has been observed that in many two phase reaction systems, the mass transfer coefficient was found to be very low solely due to the poor solubility of the hydrophobic reactant in the aqueous phase[5]. The present investigation focuses on the solubility and mass transfer coefficient enhancement of cyclohexene through hydrotropy. Cyclohexene is a hydrocarbon with the molecular formula C_6H_{10}. This cyclohexene, being a most important intermediate in various industrial processes is generally immiscible in water. It is converted to cyclohexanol, which is dehydrogenated to give cyclohexanone, a precursor to caprolactam. Cyclohexene is also a precursor to adipic acid, maleic acid, dicyclohexyladipate, and cyclohexeneoxide. Solubility and mass transfer coefficient enhancement attempt has been made in order to increase the rate of the reaction. The hydrotropes used in this work are freely soluble in water and practically insoluble in cyclohexene. All hydrotropes are nonreactive, nontoxic and they do not produce any significant heat effect when dissolved in water. Cost effective and easy availability are the other factors considered in the selection of these hydrotropes[6-8].

EXPERIMENTAL SECTION

Materials

All the chemicals used in this work were manufactured by Asahi Chemical Company and SRL, with a manufacture's stated purity of 99.9%. The hydrotropes used in this work viz., citric acid, urea and sodium salicylate, which are of analar grade. Doubly distilled water was used for the preparation of hydrotropic solutions.

Experimental set up and procedure

The experimental setup for the determination of solubility values consisted of a thermostatic bath and a separating funnel. Measurement of the solubility of cyclohexene was carried out at temperatures which range from 303 - 333 K. For each solubility measurement test, about 100 mL of cyclohexene, was taken in a separating funnel and 100 mL of a solution of the hydrotrope of known concentration was added. The separating funnel was then sealed to avoid evaporation of mixtures at higher temperatures, which in turn being immersed in a constant-temperature bath fitted with a temperature controller, which could control the temperature within $\pm$1 °C. The setup was kept all night to attain equilibration. Subsequently, the aqueous layer was carefully separated from the organic layer, as the attainment of equilibrium being ascertained. The separated aqueous layer was analyzed to quantify the concentration using HPLC with the following conditions: HPLC (Manufacturer - Varian, Inc. USA; Type - 940lc) with the following conditions: LC mode, normal phase chromatography; Packing material, Silica gel; Mobile phase, n-Hexane/IPE; Interaction, Adsorption. All experiments were conducted in duplicate to check the reproducibility, and observed deviation 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 vessel used for mass transfer studies is of 40 cm height and of 15 cm inner diameter. The turbine impeller diameter is 5 cm, the width 1cm, and the length 1.2 cm. It has four blades. The baffle is 40 cm high with a diameter of 1.5 cm. There are about four baffles that rotate at a speed of 600 rpm. For each run, to measure the mass transfer coefficient, 250 ml of the cyclohexene was added to 250 ml of hydrotrope solution of known concentration. The sample was then agitated for a known time of (600, 1200, 1800, and 2400) s. After the end of fixed time t, the entire mixture was transferred to a separating funnel. After allowing to stand for about an hour, the aqueous layer was carefully separated from the cyclohexene layer. The concentration of the solubilized cyclohexene in aqueous hydrotrope solutions at time t was analyzed as done for solubility determinations. A plot of $-\log [1 - C_b / C^*]$ versus t is drawn, where C_b is the concentration of solute at time t and C* is the equilibrium solubility of solute at the same hydrotrope concentration. The slope of the graph gives $k_L a / 2.303$, from which $k_L a$, the mass-transfer coefficient was determined. Duplicate runs were made to check the reproducibility. The observed error was < 2 %.

RESULTS AND DISCUSSION

Solubility

Experimental data on the effect of hydrotropes, i.e., citric acid, urea, and sodium salicylate on the solubility of cyclohexene are plotted in Figures 1-3. The solubility of cyclohexene in water at 303 K in the absence of any hydrotrope is 1.41×10^{-3} mol/L (Figure 2). Citric acid was one of the hydrotropes used in this study. A minimum hydrotrope concentration (MHC) of 0.40 mol/L was found to be required to effect a significant increase in the solubility of cyclohexene in water. The solubility of cyclohexene in water did not show any appreciable increase even after the addition of 0.40 mol/L of citric acid to the aqueous solution. A similar trend in MHC requirement in the aqueous phase has been observed for other hydrotropes also.

Therefore, it is evident that hydrotropic solubilization is displayed only above the MHC, irrespective of system temperature. Since hydrotropy appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved cyclohexene on dilution with water below MHC. The knowledge of MHC values are much necessary especially at industrial levels, as it ensures ready recovery of the hydrotrope to reprocess. The solubilization effect varies with the concentration of hydrotrope (Figure 1). In the present case, a clear increasing trend in the solubility of cyclohexene was observed above the MHC of citric acid. This increasing trend is maintained only up to a certain concentration of citric acid in the aqueous solution, beyond which there is no appreciable increase in the solubility of cyclohexene. This concentration of citric acid in the aqueous phase is referred to as the maximum hydrotrope concentration (C_{max}). From the analysis of the experimental data, it is observed that a further increase in hydrotrope concentration beyond C_{max} does not bring any appreciable increase in the solubility of cyclohexene even up to 3.00 mol/L of citric acid in the aqueous solution. Similar to the MHC values, the C_{max} values of hydrotropes also remained unaltered with increase in system temperature.

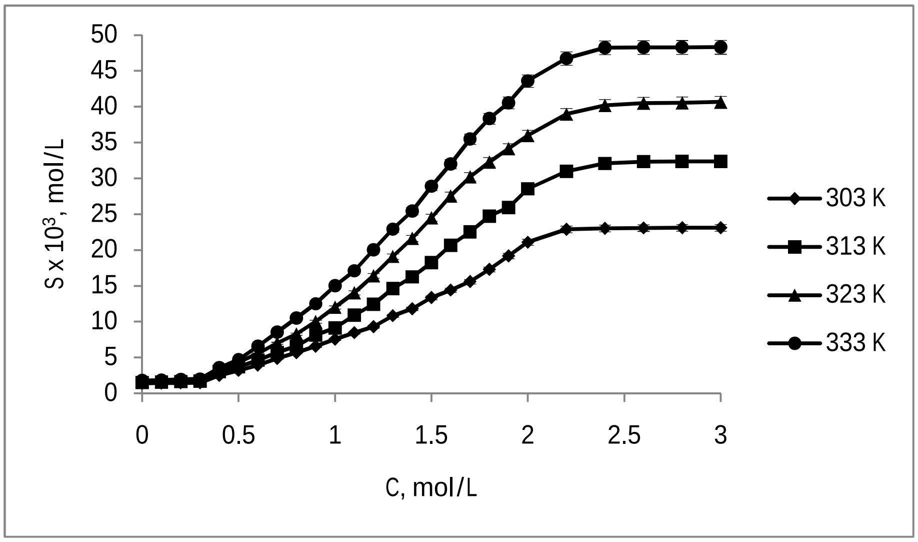

Fig. 1. Effect of citric acid concentration (C) on the solubility (S) of cyclohexene at different temperatures

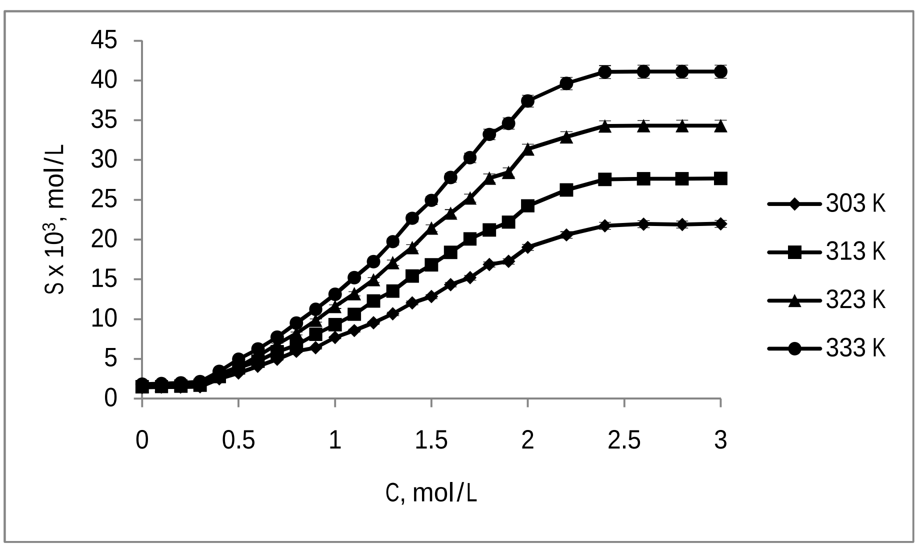

Fig. 2. Effect of urea concentration (C) on the solubility (S) of cyclohexene at different temperatures

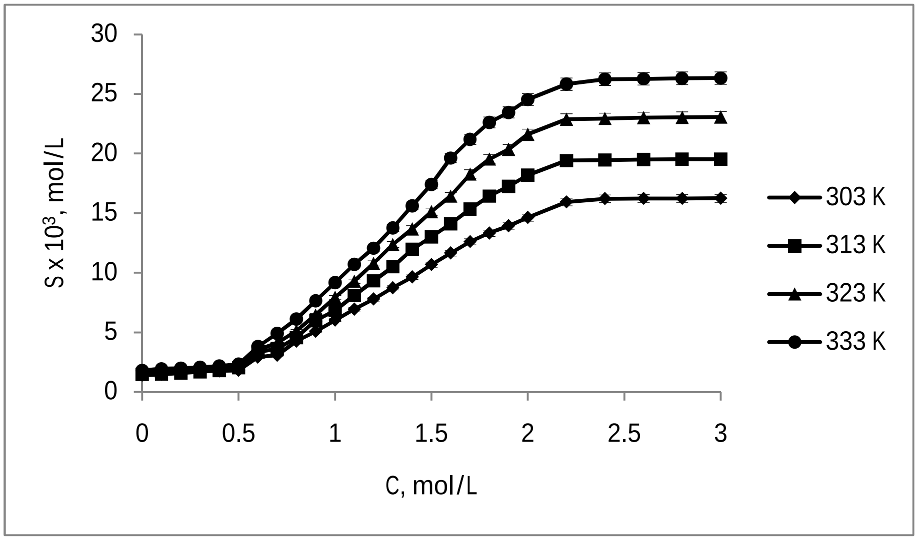

Fig. 3. Effect of sodium salicylate concentration (C) on the solubility (S) of cyclohexene at different temperatures

The knowledge of MHC and C_{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_{max} values of a hydrotrope with respect to cyclohexene 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_{max} by simple dilution with distilled water. This is the unique advantage of the hydrotropic solubilization technique.

From the experimental data plotted in Figure 1, it can further be observed that, to achieve the particular solubility of cyclohexene, say 15 x 10^{-3} mol/L, the citric acid concentration should be 2.20 mol/L at 303 K, 1.70 mol/L at 313 K, 1.50 mol/L at 323 K, and 1.40 mol/L at 333 K in the aqueous solution. Thus, it can be seen that, as the system temperature increases, the concentration of citric acid required in the aqueous phase to achieve a particular solubility of cyclohexene decreases. A similar trend has been observed for other systems also. It has also been observed that the solubilization effect of citric acid was not a linear function of the concentration of the citric acid. The solubilization effect of citric acid increases with the increase in hydrotrope concentration and also with system temperature.

A similar trend has been observed in the solubilization effect of other hydrotropes, namely, urea and sodium salicylate. It has also been observed that the MHC values of hydrotrope used in this work range between (0.20 and 0.40) mol/L and the C_{max} values of hydrotropes range between (2.20 and 2.40) mol/L (Table 1). The highest value of solubilisation enhancement factors Φ_s, which is the ratio of solubility values in the presence and the absence of a hydrotrope, has been observed in the case of citric acid as 26.800 at a system temperature of 333 K (Table 2).

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

Hydrotropes	MHC, mol/L	C_{max}, mol/L
Citric Acid	0.4	2.4
Urea	0.4	2.4
Sodium Salicylate	0.2	2.2

Table 2. Maximum enhancement factor for solubility (Φ_s) of cyclohexene

Hydrotropes	Maximum enhancement factor for solubility (Φ_s)			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
Citric Acid	16.326	21.245	24.669	26.800
Urea	14.993	18.628	21.419	22.560
Sodium Salicylate	11.069	13.204	13.951	14.350

Mass -Transfer coefficient

This section is concerned with a study on the effect of hydrotropes on the mass-transfer coefficient of cyclohexene in water in the presence of hydrotropes. For this purpose, an agitated vessel was used. The mass-transfer coefficient of the cyclohexene + water system in the absence of any hydrotrope has been determined as 2.20 x 10^{-5} s^{-1} (Table 3). The effect of different hydrotropes on the mass-transfer coefficient of cyclohexene at different hydrotrope concentrations is also given in the same table. It can be seen that a threshold value, i.e., 0.40 mol/L, which is nothing but MHC of citric acid for cyclohexene, is to be maintained to have significant enhancement in the mass-transfer coefficient of cyclohexene + water system as observed in the case of solubility determinations. The mass-transfer coefficient of the cyclohexene + water system increases with increase in citric acid concentration. Beyond C_{max} of 2.40 mol/L, there is no appreciable increase in the mass-transfer coefficient of cyclohexene, as observed in the case of solubility determinations. The maximum enhancement in the mass transfer coefficient of the cyclohexene + water system in the presence of citric acid was found to be 23.105 (Table 3). These observations suggest the fact that increase in mass-transfer coefficient is found to occur upon increased solubilization. A similar trend in mass-transfer enhancement (Φ_{mtc}) of cyclohexene has been observed for other hydrotropes, namely, urea and sodium salicylate.

Table 3. Effect of hydrotrope concentration (C) on the mass-transfer coefficient (k_La) of cyclohexene

Hydrotropes	C, mol/L	10^5 k_La, s^{-1}	Enhancement factor for mass-transfer coefficient, Φ_{mtc}
Citric Acid	0.00	0.95	-
	0.10	1.71	1.800
	0.40	3.17	3.337
	0.50	5.90	6.211
	1.00	9.47	9.968
	1.50	14.00	14.737
	2.00	16.60	17.474
	2.20	19.47	20.495
	2.40	21.95	23.105
Urea	0.00	0.95	-
	0.10	1.52	1.600
	0.40	2.73	2.904
	0.50	4.80	5.106
	1.00	7.86	8.085
	1.50	12.00	12.766
	2.00	15.30	16.277
	2.20	17.08	18.170
	2.40	18.64	19.830
Sodium Salicylate	0.00	0.95	-
	0.10	1.41	1.484
	0.20	2.22	2.337
	0.50	3.45	3.632
	1.00	6.06	6.379
	1.50	11.10	11.684
	2.00	13.20	13.895
	2.20	14.45	15.211

EFFECTIVENESS OF HYDROTROPE

The effectiveness factor of each hydrotrope with respect to cyclohexene at different system temperatures was determined by analyzing the experimental solubility data for each case, applying the model suggested by Setschenow[9] and later modified by Gaikar and Sharma (1986) as given by the equation below:

$$\log [S/S_m] = K_s [C_s - C_m]$$

where S and S_m are the solubility values of cyclohexene at any hydrotrope concentration (C_s) and the minimum hydrotrope concentration (C_m) (the same as MHC), respectively. The Setschenow constant (K_s) can be considered to be a measure of the effectiveness of a hydrotrope in any given conditions of hydrotrope concentration and system temperature. The Setschenow constant values of the hydrotropes citric acid, urea, and sodium salicylate, for the cyclohexene + water system at different system temperatures are listed in Table 4. The highest value observed was 0.56537, in the case of citric acid as the hydrotrope at 333 K.

Table 4. Setschenow constant [K_s] values of hydrotropes with respect to cyclohexene

Temperature, K	Setschenow constant, K_s		
	Citric Acid	Urea	Sodium Salicylate
303	0.48295	0.46966	0.49649
313	0.51240	0.49976	0.54331
323	0.53835	0.52248	0.55209
333	0.56537	0.53906	0.55555

CONCLUSIONS

The solubility of cyclohexene, which is practically insoluble in water, has been increased to a maximum value of 26.800 in the presence of citric acid as hydrotrope with corresponding increase in mass-transfer coefficient. This would be very useful in increasing the rate of output of the desired product made from cyclohexene. The separation of cyclohexene from any liquid mixture 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 cyclohexene can be used for the recovery of the dissolved cyclohexene and hydrotrope solutions at any hydrotrope concentration between 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 cyclohexene from its solution.

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