



Effect of Hydrotropes on Solubility and Mass Transfer Coefficient of Chlorobenzene

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Abstract

A comprehensive investigation on the solubility and mass transfer coefficient enhancement of chlorobenzene through hydrotropy has been undertaken. The solubility and mass transfer coefficient studies were carried out using hydrotropes such as citric acid, sodium benzoate and urea 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 chlorobenzene 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 chlorobenzene. Consequent to the increase in solubilization of chlorobenzene, 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 experimentations. The performance of hydrotropes was measured in terms of setschenow constant (K_s) and reported for all hydrotropes used in this study.

Keywords: Hydrotropy, hydrophobicity, mass transfer coefficient, solubility.

Introduction

Hydrotropy is a unique and unprecedented solubilization technique in which certain chemical compounds termed as hydrotropes can be used to effect a several fold increase in the aqueous solubility of sparingly soluble solutes under normal conditions. This increase in solubility in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentrations. 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 fats¹⁻⁴.

The solubility enhancement in the organic compounds could be due to the formation of molecular structures in the form of complexes. Previous experimental findings have concluded that hydrotropy is a process which goes beyond conventional solubilization methods such as miscibility, co-solvency, salting-in effect since the solubilization effected by hydrotropy was higher and more selective compared to other solubilization techniques⁵⁻⁶. It has been observed that, in many two-phase reaction systems involving a sparingly soluble organic compound like chlorobenzene, the mass-transfer coefficient was found to be very low solely due to the poor solubility of chlorobenzene in the aqueous phase. Since chlorobenzene serves as raw material/intermediate for a wide variety of chemicals and allied products and the separation of chlorobenzene from any liquid mixture seems to be difficult, this hydrotropic technique can be adapted to increase the solubility as well as to separate such mixtures effectively⁷.

Hydrotropes have been used to increase the rate of heterogeneous reaction and are also used for the separation of liquid mixtures with similar boiling points and narrow melting points through extractive distillation and liquid-liquid extraction⁸. Each hydrotrope has a selective ability toward a particular component in the mixture, which facilitates easy recovery of the hydrotrope solution by controlled dilution with distilled water. The solubility enhancement in the organic compounds could be due to the formation of molecular structures in the form of complexes.⁵ Previous experimental findings have concluded that hydrotropy is a process that goes beyond miscibility or co solvency or the salting-in effect or other conventional solubilization methods because the solubilization effected by hydrotropy was higher and more selective compared to that of other solubilization methods⁹⁻¹¹.

For many binary systems involving a sparingly soluble organic compound such as chlorobenzene, the mass transfer coefficient in the presence of a hydrotrope is probably due to the difference between binary diffusivity (solute + solvent) and the diffusivity of the solute in the solution (solute + solvent + hydrotrope). The hydrotropes used in this work are freely soluble in water and practically insoluble in chlorobenzene. All are non reactive and non toxic and do not produce any significant heat effect when dissolved in water. The easy availability and low cost are two other factors considered in the selection of these hydrotropes.

Material and Methods

Experimental procedure of solubility and mass-transfer coefficient: The experimental setup for the determination of

solubility values consisted of a thermostatic bath and a separating funnel. For each solubility test, about 100 ml of chlorobenzene previously saturated with distilled water was taken in a separating funnel and 100 ml of a solution of the hydrotrope of known concentration was added. The separating funnel was immersed in a constant-temperature bath fitted with a temperature controller which could control the temperature within $\pm 0.1^\circ\text{C}$. The setup was kept overnight for equilibration. After equilibrium was attained, the aqueous layer was carefully separated from the organic layer and transferred into a beaker. Then the aqueous layer was analyzed for chlorobenzene concentration using U-V spectrophotometer, the absorption values of the samples were determined with respective pure hydrotrope solutions as blank. All the solubility experiments were conducted in duplicate to check the reproducibility. The observed error in the reproducibility 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 height 40 cm and of 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 four blades. The baffle is 40 cm high with a diameter of 1.5 cm. There are about four baffles. For each run to measure the mass transfer coefficient, about 250 ml of the chlorobenzene previously saturated with distilled water was added to the hydrotrope 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 t , the entire mixture was transferred to a separating funnel. After allowed to stand for some time, the aqueous layer was carefully separated from the organic layer. The concentration of the solubilized chlorobenzene 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 chlorobenzene at time t and C^* is the equilibrium solubility of chlorobenzene 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., urea, citric acid and sodium benzoate, on the solubility of chlorobenzene are presented in figures 1, 2 and 3. The solubility of chlorobenzene in water at 303 K in the absence of any hydrotrope is 3.99×10^{-3} mol/L. It was observed that the solubility of chlorobenzene in water has not shown any appreciable increase even after the addition of 0.30 mol/L of urea in the aqueous phase. But on subsequent increase in the concentration of urea above 0.30 mol/L, the solubility of chlorobenzene in water was found to increase significantly. This concentration of urea in the aqueous phase, i.e., 0.30 mol/L, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required urea (hydrotrope) concentration

in the aqueous phase above which the solubility of chlorobenzene in water increases significantly. It has been observed that the MHC of urea in the aqueous phase is unaltered even at increased system temperatures. 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 MHC, irrespective of system temperature. Hydrotrope does not seem to be operative below MHC, which may be a characteristic of a particular hydrotrope with respect to each solute. This MHC value assumes greater significance in the context of recovery of hydrotrope solutions. Since hydrotrope appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved chlorobenzene on dilution with water below MHC. The knowledge of MHC values is necessary especially at industrial levels as it ensures ready recovery of the hydrotrope for reuse.

The solubilization effect varies with concentration of hydrotropes. In the present case, a clear increasing trend in the solubility of chlorobenzene was observed above 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 chlorobenzene.

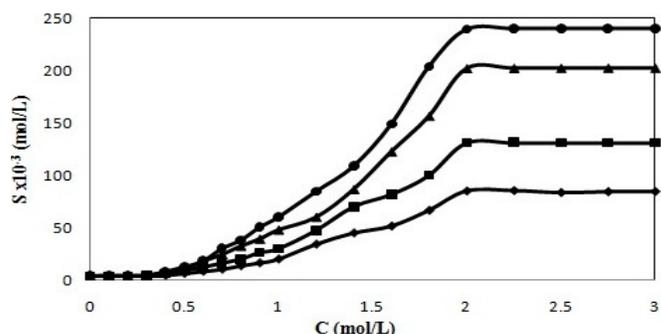


Figure-1

Effect of urea concentration (c) on the solubility (S) of chlorobenzene in water at different temperatures: \blacklozenge , $T = 303$ K; \blacksquare , $T = 313$ K; \blacktriangle , $T = 323$ K; and \bullet , $T = 333$ K

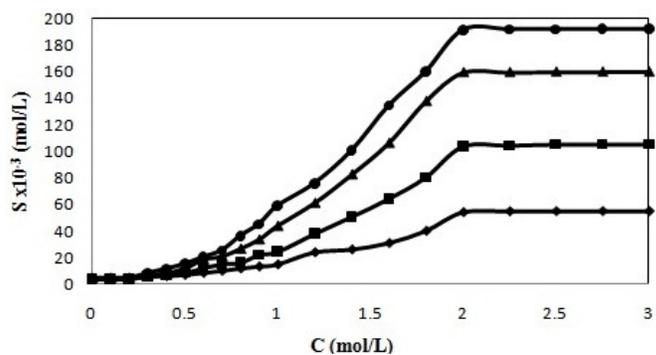


Figure-2

Effect of citric acid concentration (c) on the solubility (S) of chlorobenzene in water at different temperatures: \blacklozenge , $T = 303$ K; \blacksquare , $T = 313$ K; \blacktriangle , $T = 323$ K; and \bullet , $T = 333$ K

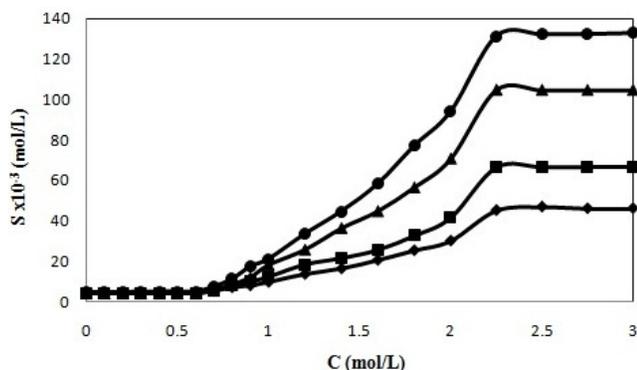


Figure-3

Effect of sodium benzoate concentration (*c*) on the solubility (*S*) of chlorobenzene in water at different temperatures: ♦, *T* = 303 K; ■, *T*= 313 K; ▲, *T* = 323 K; and ●, *T* = 333 K

Table-1
MHC and *C*_{max} values for hydrotropes

Hydrotrope	MHC (mol/L)	<i>C</i> _{max} (mol/L)
Urea	0.30	2.0
Citric acid	0.2	2.0
Sodium benzoate	0.6	2.25

This concentration of urea (hydrotrope) in the aqueous phase is referred to as the maximum hydrotrope concentration (*C*_{max}). The *C*_{max} values of urea, citric acid and sodium benzoate with respect to chlorobenzene are 2.00, 2.00, 2.25 mol/L, respectively. From the analysis of the experimental data, it is observed that further increase in hydrotrope concentration beyond *C*_{max} does not bring any appreciable increase in the solubility of chlorobenzene even up to 3.00 mol/L of urea in the aqueous phase. Similar to the MHC values, the *C*_{max} values of hydrotropes also remained unaltered with increase in system temperature.

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. However, the effect of hydrotrope was found to be predominant at concentrations close to *C*_{max} values of a hydrotrope in most cases. The values of MHC and *C*_{max} of a hydrotrope with respect to chlorobenzene may be useful in determining the recovery of the dissolved chlorobenzene even to an extent of 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.

In the concentration range of urea between 0.00 and 3.00 mol/L, three different regions were observed. It was inactive below MHC of 0.30 mol/L, above which an appreciable increase in the solubility of chlorobenzene was found up to *C*_{max} of 2.00 mol/L, beyond which there is no further solubilization effect of hydrotrope. Therefore urea was found to be an effective

hydrotrope in the concentration range between 0.30 and 2.00 mol/L towards chlorobenzene. It has also been observed that the solubilization effect of urea was not a linear function of the concentration of the citric acid solution. A similar trend in the solubilizing effect of citric acid and sodium benzoate were observed at increased system temperatures, viz., 303, 313, 323, 333 K with the values of MHC, and *C*_{max} remained unaltered even at higher temperatures. The solubilization effect of urea increases with increase in hydrotrope concentration and also with system temperature. The maximum enhancement factor values observed for the chlorobenzene in water system for urea at 303, 313, 323 and 333 K are 21.28, 32.08, 46.24 and 53.98 respectively.

A similar trend has been observed in the solubilization effect of other hydrotropes, namely, citric acid and sodium benzoate. It has also been observed that the MHC values of hydrotrope used in this work range between 0.30, 0.20 and 0.60 mol/L which seem to depend on the hydrophilicity of a hydrotrope. The *C*_{max} values of hydrotropes range between 2.00 and 2.25 mol/L in most cases. The highest value of solubilization enhancement factors which is the ratio of solubility values in the presence and absence of a hydrotrope has been observed in the case of urea as 53.98 at a system temperature of 333 K.

Enhancement Factor: Enhancement factor is defined as the ratio of solubility of the system in the presence of hydrotrope to the solubility in the absence of hydrotrope.

$$\text{Enhancement factor} = \frac{\text{Solubility value in the presence of hydrotrope}}{\text{Solubility value in the absence of hydrotrope}}$$

Table-2
Maximum solubilization enhancement factor (*φ*_s) of chlorobenzene

Hydrotrope	Maximum enhancement factor for solubility (<i>φ</i> _s)			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
Urea	21.28	32.08	46.24	53.98
Citric acid	13.60	25.30	36.48	43.11

Mass Transfer Coefficient: The mass transfer coefficient of chlorobenzene in water system in the absence of any hydrotrope was determined to be 7.96 x 10⁻⁵ s⁻¹ at 303K. The mass transfer coefficient of chlorobenzene in water system increases with increase in citric acid concentration. The maximum enhancement factor for mass transfer coefficient of chlorobenzene in water system in the presence of urea was found to be 9.73. A similar trend in the mass-transfer coefficient enhancement of chlorobenzene has been observed for other hydrotropes also namely citric acid and sodium benzoate illustrated in table-3.

Table-3
Effect of hydrotrope concentration (c) on the mass transfer coefficient (k_1a) of chlorobenzene

Hydrotrope	C, mol/L	(k_1a), $10^{-5} s^{-1}$	Enhancement factor for mass transfer coefficient
Urea	00	7.96	00
	0.3 MHC	8.02	1.00
	0.5	8.78	1.10
	1.0	13.73	1.72
	1.5	43.34	5.44
	2.0 C_{max}	65.86	8.27
	2.5	72.37	9.09
Citric acid	00	7.96	00
	0.2 MHC	7.98	1.00
	0.5	8.12	1.02
	1.0	17.56	2.21
	1.5	53.07	6.66
	2.0 C_{max}	67.83	8.52
	2.5	62.15	7.81
Sodium benzoate	00	7.96	00
	0.6MHC	8.02	1.00
	1.0	16.96	2.13
	1.5	31.25	3.92
	2.25 C_{max}	42.34	5.32
	2.5	56.21	7.06
	3.0	55.92	7.02

Effectiveness of Hydrotropes: The effectiveness factor of each hydrotrope with respect to chlorobenzene at different system temperatures has been determined by analyzing the experimental solubility data for each case applying the model suggested by Setschenow and later modified by Pathak and Gaikar as given by the equation log

$$[S/S_m] = K_s[C_s - C_m] \quad (1)$$

Where S and S_m are the solubility of chlorobenzene at any hydrotrope concentration C_s and the 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 citric acid, urea and sodium benzoate for chlorobenzene - water system at different system temperatures. The highest value has been observed as 0.9996 in the case of urea as hydrotrope at 333K.

Table- 4
Setschenow constant (K_s) of hydrotropes with respect to chlorobenzene

Hydrotrope	T = 303 K	T = 313 K	T = 323 K	T = 333 K
Urea	0.7768	0.8770	0.9703	0.9996
Citric acid	0.6232	0.7767	0.8613	0.9017
Sodium benzoate	0.6307	0.7227	0.8293	0.8714

Conclusion

The solubility of chlorobenzene, which is practically insoluble in water, has been increased to a maximum of 53.98 times 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 chlorobenzene. The MHC and C_{max} values of the hydrotrope with respect to chlorobenzene can be used for the recovery of the dissolved chlorobenzene and hydrotrope solutions at any hydrotrope concentration between the 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 chlorobenzene 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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