



Influence of Hydrotrop on Solubility and Mass Transfer Co Efficient Enhancement of Triphenylcarbinole

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Abstract

A broad research of the solubility and mass transfer coefficient enhancement of triphenylcarbinole through hydrotropy has been commenced. The solubility investigations have been carried out with hydrotropes such as potassium acetate, sodium saccharin, and sodium toluene sulfonate, for a wide concentration range from 0 to 3.0 mol/L along with system temperature from 303K to 333 K. The effectiveness of hydrotropes was measured by the determination of Setschenow constant "Ks". The solubility of triphenylcarbinole increases with increasing hydrotrope concentration and also with system temperature. A minimum hydrotrope concentration (MHC) in the aqueous phase was required to initiate significant solubilization of triphenylcarbinole. Consequent to the increase in solubilization of triphenylcarbinole, the mass transfer coefficient was also found to increase with increasing hydrotrope concentration. 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 solubility values in the presence and absence of a hydrotrope, has been determined for all sets of experiments.

Keywords: Hydrotropy, solubilization, enhanced solubility, mass transfer co efficient.

Introduction

Hydrotropy is one of the potentially attractive techniques that can be considered to separate close boiling point isomeric / non isomeric mixtures. The phenomenon of hydrotropy was first reported by Neuberg¹ in 1916 to solubilize sparingly soluble compounds. Hydrotropy as a solubilization phenomenon, hydrotropes are a class of highly water soluble salts / molecules that are characterized by an amphiphilic molecular structure with an ability to dramatically increase the solubility of sparingly soluble organic compounds in water, often by several orders of magnitude². Besides the contamination of the product by hydrotrope is minimal and can be reduced to below an acceptable level, if any, simply by washing with water³

The concentration at which self-association begins is denoted as the Minimum Hydrotrope Concentration (MHC) and is often indicated by changes in solution properties such as density, conductivity, and surface tension⁴. The formation and nature of aggregates of hydrotrope molecules in water are essential to make a strong association between microscopic assembly and the corresponding macroscopic behavior. This hydrotropic phenomenon can be adapted to industrial scale⁵⁻¹⁰.

Hydrotropic solubilization has been claimed to be a collective molecular phenomenon, possibly occurring by the aggregation of a solute with the hydrotrope aggregates and the self-aggregation of hydrotrope molecules in aqueous solutions is considered to be a prerequisite for the enhanced solubility of the

solute and drug solubilization¹¹⁻¹³. A hydrotrope above MHC is expected to form organized loose nano assemblies with distinct hydrophobic regions where the solute can be solubilized¹⁴⁻¹⁶. The solute molecules may also take part in the aggregation process of the hydrotrope, thereby forming co aggregates with the hydrotrope molecules in aqueous solutions. The formation of a stable co aggregate depends on the molecular structure as well as the functional group(s) attached to the carbon skeleton of the solute as it would govern the intercalation of the solute between the hydrotrope molecules. The solubilization of a solute is influenced by its hydrophobic part and also the chain length of an alkyl group of a hydrotrope¹⁷⁻²⁰.

The current work was commenced for the fundamental study of the global character of hydrotropes in the selective solubilization of a triphenylcarbinole. With particular attention on both the theoretical understanding of the mechanistic action and the experimental studies which demonstrate the utility of hydrotropes in the solubilization of a triphenylcarbinole (molecular weight M = 260 and insoluble in water) was selected, for enhancing its solubility using several commercially available hydrotropes. Since triphenylcarbinole serves as a raw material/intermediate. And this makes its separation from any liquid mixture, which has been difficult, until now. Hence, this hydrotropic technique can be adopted to increase the solubility as well as to separate such mixtures effectively.

For many binary systems involving a sparingly soluble organic compound such as triphenylcarbinole, 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. All are nonreactive and nontoxic 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

All the chemicals used in this work were manufactured by the Loba Chemie Pvt. Ltd., Mumbai. With manufacturers stated purity of 99.9%. The hydrotropes used in this work viz., potassium acetate, sodium saccharin and sodium toluene sulfonate are analar grade. Double distilled water was used for the preparation of hydrotropic solutions.

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 triphenylcarbinole was carried out at temperatures of 303, 313, 323 and 333 K.

For each solubility test, an equal volume of triphenylcarbinole was comprehensively mixed with equal volume of hydrotrope solution 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 triphenylcarbinole was taken and added to 100ml of hydrotrope solution of known concentration. The mixture was then made to mix consecutively 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 $\pm 0.1^\circ\text{C}$. The setup was kept overnight for equilibration. After equilibrium was attained, the organic phase was carefully separated and analyzed to determine the concentration using a high-performance liquid chromatography (HPLC). All the solubility trials were conducted in duplicate runs to check their reproducibility. The observed error was $< 2\%$.

Mass transfer Coefficient: 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 at 600 rpm was selected to achieve effective mixing, and was maintained at the same value for all experiments. The vessel used for mass transfer studies had a height of 40 cm and an inner diameter of 15 cm. The turbine impeller had a diameter of 5 cm, width of 1 cm and length of 1.2 cm. It had four blades and rotated at 600 rpm. The baffle has a height of 40 cm, diameter of 1.5 cm and four baffles arranged at 90° to each other. For each run, to measure the mass transfer coefficient, an excess amount of triphenylcarbinole was added to the aqueous solution of the hydrotrope of known concentration. The sample was then

agitated for 600, 1200, 1800 or 2400 s and the mixture was transferred to a separating funnel. After allowing the sample to stand for some time, the solution was filtered. The concentration of the solubilized organic compound triphenylcarbinole in aqueous hydrotrope solutions at time t was analyzed in the same way as done for solubility determinations using HPLC.

Results and Discussion

Hydrotropic extracted triphenylcarbinole been shown in schematic comparative HPLC chromatogram in figure. 1. Experimental data on the effect of hydrotropes, i.e potassium acetate, sodium saccharin and sodium toluene sulfonate on the solubility of triphenylcarbinole is displayed in figure 2–4.

Sodium toluene sulfonate is one of the hydrotropes used in this research. It was observed that the solubility of triphenylcarbinole did not indicate any appreciable increase until 0.30 mol/L of sodium toluene sulfonate. However, upon a subsequent increase in the concentration of sodium toluene sulfonate, i.e., 0.30 mol/L, the solubility of triphenylcarbinole was found to increase significantly. This concentration of sodium toluene sulfonate in the aqueous phase, i.e., 0.30 mol/L, is termed as the Minimum Hydrotrope Concentration (MHC), which is the minimum required amount of sodium toluene sulfonate in the aqueous phase to commence a significant increase in the solubility of triphenylcarbinole. It was observed that the MHC of sodium toluene sulfonate in the aqueous phase does not modify even at increased system temperatures, i.e., 313, 323 and 333 K.

A related tendency in the MHC requirement has also been observed for other hydrotropes. Accordingly, it is manifest that hydrotropic separation is displayed only above MHC, irrespective of the system temperature. Hydrotropey does not seem to be functioning below the MHC, which may be a distinctive of a particular hydrotrope with respect to each solute. The solubility effect changes with concentration of the hydrotropes. In this case, a clear increasing trend in the solubility of triphenylcarbinole was observed above the MHC of sodium toluene sulfonate. This increase is affirmed only up to a certain concentration of sodium toluene sulfonate in the aqueous phase, i.e, 2.20 mol/L further than which there is no appreciable increase in the solubility of triphenylcarbinole. This concentration of sodium toluene sulfonate 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 further increase in the hydrotrope concentration beyond C_{max} does not cause any considerable increase in the solubility up to 3.0 mol/L in the aqueous phase. Similar to the MHC values, the C_{max} values of the hydrotropes also remained unaltered with the increase in system temperature table 1. The maximum enhancement factor of hydrotrope (Φ_s) which is the ratio of the solubility value in the presence and absence of a hydrotrope respectively. It was determined and the highest value of Φ_s

91.96 in the case of sodium toluene sulfonate at a system temperature of 333 K, table 2.

Effectiveness of Hydrotrope: The effectiveness factor for each hydrotrope with respect to the solubility of triphenylcarbinole at different system temperatures was determined by applying the model suggested by Setschenow and later modified by Phatak 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 values of triphenylcarbinole maximum hydrotrope concentration C_s (same as C_{max}) 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, potassium acetate, sodium saccharin, and sodium toluene sulfonate for the solubility triphenylcarbinole different system temperatures are listed in table. 3. The highest value was observed as 0.59 in the case of sodium toluene sulfonate as the hydrotrope at temperature 333K.

Mass-Transfer Coefficient: The mass transfer coefficient of the triphenylcarbinole + water system in the absence of any hydrotrope is $7.3 \times 10^{-4} \text{ s}^{-1}$ at 303 K (Table. REMARK: INCOMPLETE SENTENCE). The effect of different hydrotropes on the mass transfer coefficient of triphenylcarbinole at different hydrotrope concentrations is also

given in the same table. It can be seen that a threshold value of 0.40 mol/L is required to affect significant enhancement in the mass transfer coefficient of triphenylcarbinole + water system, as observed in the case of solubility determinations. The mass transfer coefficient of triphenylcarbinole + water system increases with an increase in sodium toluene sulfonate concentration. A similar trend in the mass transfer coefficient of triphenylcarbinole has been observed for other hydrotropes also, namely, potassium acetate, sodium saccharin.

Conclusion

The solubility of triphenylcarbinole which is practically insoluble in water has been increased to a maximum of 91.96 times in the presence of sodium toluene sulfonate as hydrotrope at a system temperature of 333 K with the corresponding increase in the mass transfer coefficient. This would be much useful in increasing the rate of output of the desired product made from triphenylcarbinole. The MHC and C_{max} values of the hydrotrope with respect to triphenylcarbinole can be used for the recovery of the dissolved triphenylcarbinole 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 solubilized triphenylcarbinole from its solution. Hence sodium toluene sulfonate is found to be the best suitable hydrotrope for the enhancement of solubility and mass transfer coefficient of poorly soluble triphenylcarbinole within the framework of the present investigation.

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

Hydrotropes	MHC, mol/L	C _{max} , mol/L
Potassium acetate	0.5	2.4
Sodium saccharin	0.4	2.4
sodium toluene sulfonate	0.3	2.2

Table - 2
Maximum Enhancement factor

Hydrotropes	Maximum enhancement factor (Φs)			
	T = 303 K	T = 313 K	T = 323 K	T = 333 K
Potassium acetate	18.03	29.98	41.12	55.6
Sodium saccharin	21.08	36.18	54.37	76.02
sodium toluene sulfonate	22.22	29.89	60.91	91.96

Table-3
Setschenow constant

Hydrotrop	303K	313K	323K	333K
Potassium acetate	0.456	0.49	0.5	0.51
Sodium saccharin	0.41	0.43	0.44	0.46
sodium toluene sulfonate	0.43	0.47	0.55	0.59

Table-4
Effect of hydrotrope concentration (C) on the Mass-transfer Coefficient (kLa) of triphenylcarbinol

Hydrotropes	C, mol/L	$10^4 k_{La}, S^{-1}$
Potassium acetate	0	7.3±0.15
	0.2	8.7±0.16
	0.5*	11.8±0.22
	1	17.3±0.35
	1.4	24.2±0.47
	1.8	31.5±0.61
	2.4**	38.4±0.77
Sodium saccharin	0	7.3±0.15
	0.2	7.4±0.16
	0.4*	11.7±0.20
	0.8	23.5±0.47
	1.4	32.7±0.64
	1.8	41.2±0.80
	2.40**	47.3±0.95
sodium toluene sulfonate	0	7.3±0.15
	0.1	9.1±0.16
	0.3*	12.6±0.24
	1.4	23.7±0.45
	1.8	40.6±0.78
	2	48.5±0.97
	2.2**	61.4±0.21

*-MHC: **-C_{max}

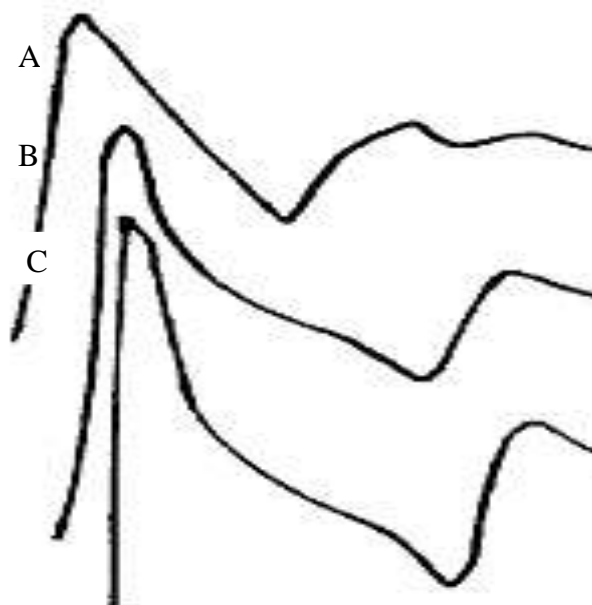


Figure-1
 Comparative HPLC chromatogram A. potassium acetate, B. sodium saccharin C. sodium toluene sulfonate

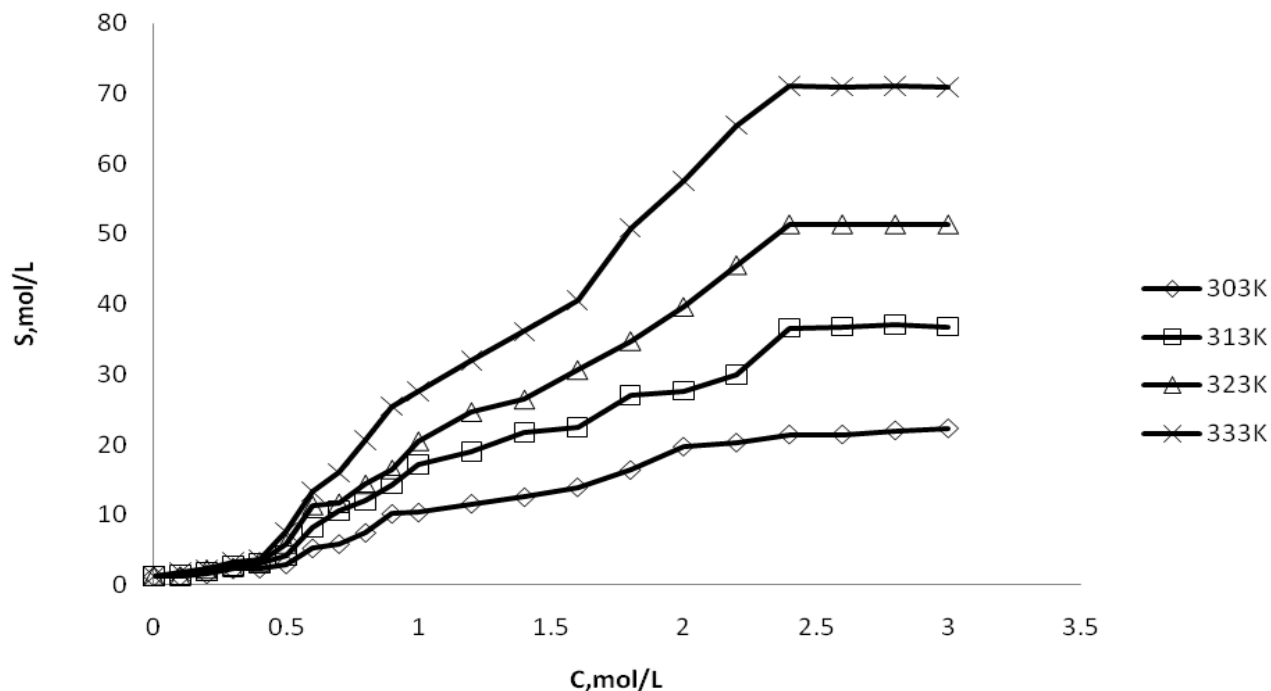


Figure-2
Effect of potassium acetate concentration (C) on solubility of Triphenylcarbinole

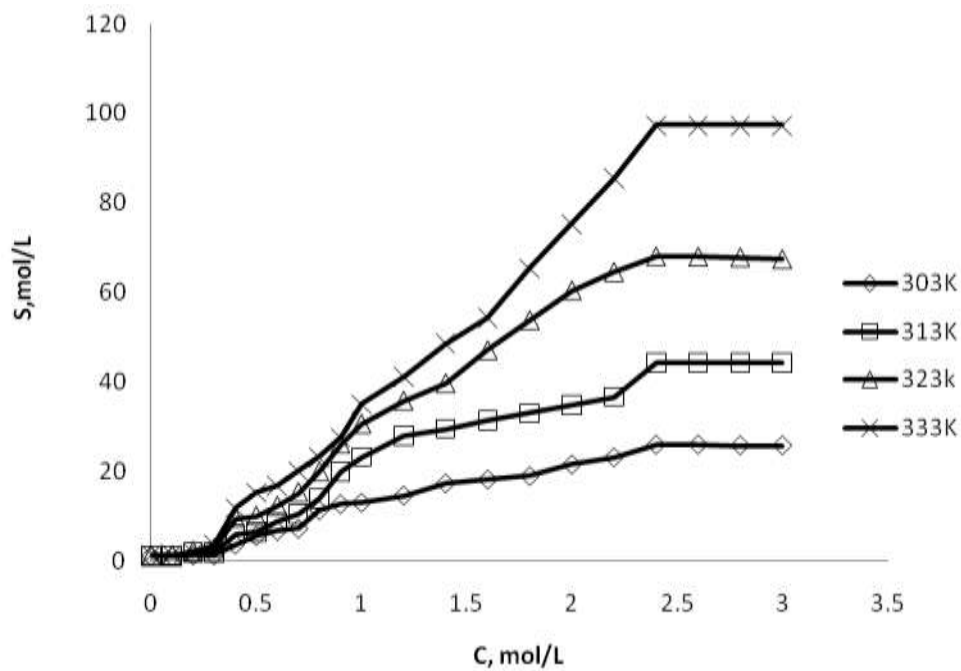


Figure-3
Effect of Sodium saccharin concentration (C) on solubility of Triphenylcarbinole

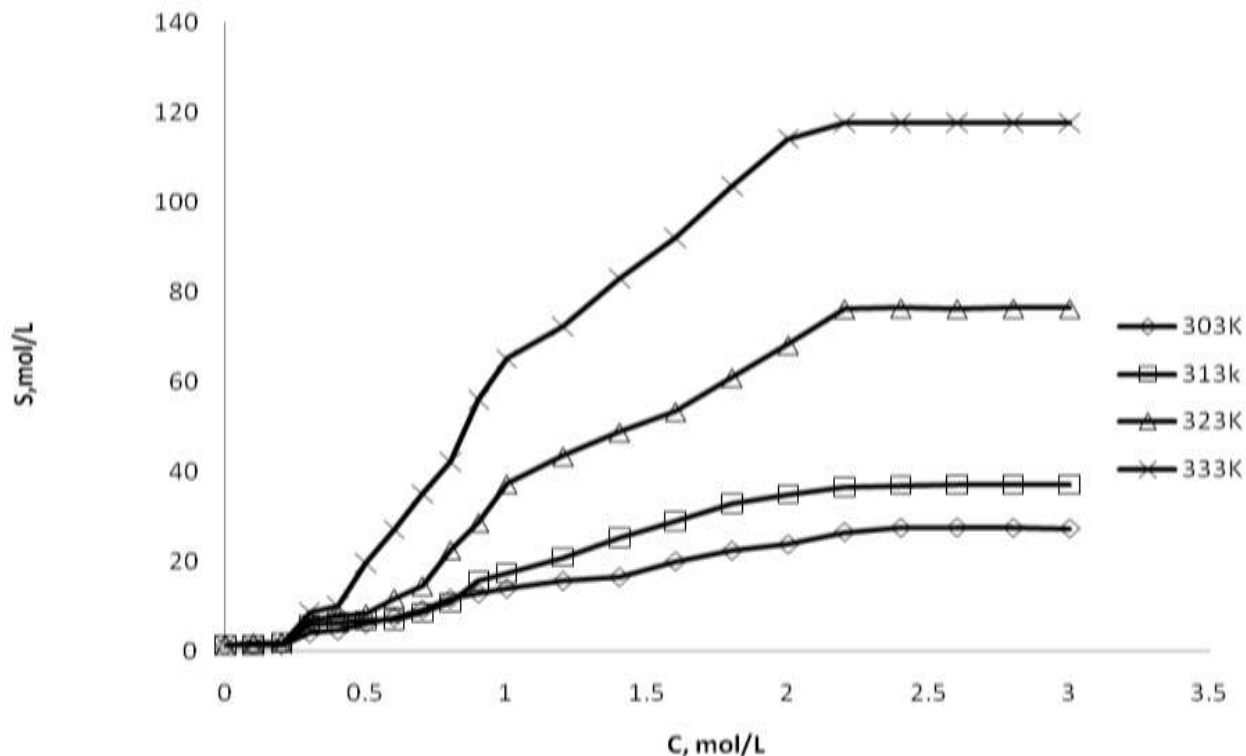


Figure-4
Effect of sodium toluene sulfonate concentration (C) on solubility of Triphenylcarbinole

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