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Enhancement of Solubility and Mass Transfer Coefficient of Cinnamic Acid Through Hydrotropy

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The effect of hydrotropes such as sodium benzoate, sodium salicylate and nicotinamide on the solubility and mass transfer coefficient of cinnamic acid has been investigated. The solubility studies were carried out under a wide range of hydrotrope concentrations (0 to 3.0 mol/L) and different system temperatures (303 K to 333 K). It has been observed that the solubility and mass transfer coefficient of cinnamic acid increases with increase in hydrotrope concentration and also with system temperature. A minimum hydrotrope concentration was essential to initiate significant increase in the solubility and mass transfer coefficient. The maximum enhancement factor, which is the ratio of the solubility of cinnamic acid in the presence and absence of a hydrotrope, has been determined for all sets of experimentations. The solubility of cinnamic acid was almost 15-fold enhanced in 2.5 mol/L aqueous sodium benzoate solution at 333 K compared to that of its solubility in water. The effectiveness of hydrotropes was measured in terms of Setschenow constant K_s and the highest value has been observed as 0.454 for sodium benzoate.

Key Words: Hydrotropy, Solubilization, Mass transfer coefficient, Cinnamic acid.

INTRODUCTION

Cinnamic acid is a phenylacrylic acid obtained from natural source or it can be synthesized chemically. It has wide pharmaceutical and industrial applications. Cinnamic acid and its derivatives are used as significant components in flavours, perfumes, synthetic indigo and pharmaceuticals[1-4]. Since it has ability to deactivate substrate molecules that have been excited by light it is used as optical filters for protecting polymers and organic substances. The poor solubility of cinnamic acid in water can hinder the development of industrial and pharmaceutical processes[5]. Hence the increase in aqueous solubility of cinnamic acid is important to develop effective process for extraction and also for its pharmaceutical applications. There are various research work carried out to study the solubility of cinnamic acid. Recent studies shows that supercritical carbon dioxide is used to increase the solubility of cinnamic acid but their applications are limited due to high pressure involved which adds to the cost of process[6,7]. Among the various methods to enhance the solubility of sparingly soluble organic compounds we have already studied the enhancement of solubility of various organic compounds in hydrotrope solutions and it is reported in our earlier publications[8-12].

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 solubility of sparingly soluble solutes under normal conditions[13]. This increase in solubility in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentrations[14,15]. Hydrotropes 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[16-22]. The solubility enhancement in the organic compounds could be due to the formation of molecular structures in the form of complexes[23,24]. Easy recovery of dissolved solute and possible reuse of hydrotrope solutions makes this one most attractive particularly at industrial levels[25-27].

Besides the advantage of certain properties such as the solvent character being independent of pH, non-flammability, easy availability of hydrotropes, inexpensive aqueous phase makes this method superior to other solubilization methods[28-30]. Hydrotropy is a process which goes beyond other conventional solubilization methods such as miscibility, co-solvency, salting-in *etc.*, since it offers high selectivity and unprecedented increase in solubility and mass transfer coefficient. The problem of emulsification, which is normally encountered with surfactant solution, is not found with hydrotrope solution[31]. To the best of our knowledge the solubility of cinnamic acid in various hydrotrope solutions has not been previously reported. In this research, we report the experimental data of solubility and mass transfer coefficient of cinnamic acid in various hydrotrope solutions that are useful in separation and pharmaceutical applications.

EXPERIMENTAL

All the chemicals used in this work were procured from Himedia Chemicals, Mumbai with a manufacturer's stated purity of 99 %. The experimental setup for the determination of solubility values consists of a thermostatic bath and separating funnel. For each solubility test, an excess amount of cinnamic acid was added to the hydrotrope solution of a known concentration in the separating funnel placed in the thermostatic bath fitted with temperature controller capable of maintaining temperature within ± 0.1 ºC. The separating funnel was sealed to avoid evaporation of the solvent at higher temperatures. The setup was kept overnight for equilibration. After equilibrium was attained, the solution was filtered using Whatman filter paper to remove excess undissolved cinnamic acid. The concentration of the dissolved cinnamic acid in aqueous hydrotrope solutions was analyzed by titrating against standardized sodium hydroxide solution using phenolphthalein solution as an indicator. Blank titration was carried out and necessary correction was done to calculate the dissolved cinnamic acid in aqueous hydrotrope solutions. All the solubility experiments were conducted in duplicate to check the reproducibility. The observed error in the reproducibility of experimental results was less than 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 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 that rotate at a speed of 600 rpm.

For each run, to measure the mass transfer coefficient, an excess amount of cinnamic acid was added to the aqueous solution of the hydrotrope of known concentration. The sample was then agitated for a known time of 600, 1200, 1800 and 2400 sec. After the end of fixed time *t*, the mixture was allowed to stand for some time. Then the solution was filtered from the remaining solid. The concentration of the solubilized cinnamic acid in aqueous hydrotrope solutions at time *t* was analyzed in the same way as done for solubility determinations. A plot of $-\log [1-C_b/C^*]$ *versus* *t* is drawn, where C_b is the concentration of cinnamic acid at time *t* and C^* is the equilibrium solubility of cinnamic acid at the same hydrotrope concentration. The slope of the graph gives $k_La/2.303$, from which k_La, the mass transfer coefficient was determined. Duplicate runs were made to check the reproducibility. The observed error was < 2 %.

RESULTS AND DISCUSSION

Solubility: The solubility of cinnamic acid in water at 303 K is 3.02×10^{-3} mol/L, which is in excellent agreement with the earlier reported values[32,33]. Experimental data representing the average of duplicate determinations on the effect of hydrotropes, *i.e.*, sodium benzoate, sodium salicylate and nicotinamide on the solubility of cinnamic acid are plotted in Figs. 1-3. It has been observed that the solubility of cinnamic acid in water increases significantly only after the addition of 0.40 mol/L of sodium benzoate in the aqueous solution. This concentration is referred to as the minimum hydrotrope concentration (MHC)[34].

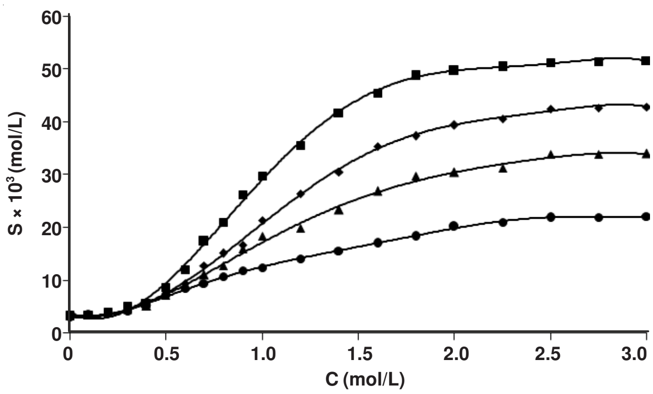

Fig. 1. Effect of sodium benzoate concentration (C) on the solubility (S) of cinnamic acid in water at different temperatures T=303K (●), 313 K (▲), 323 K (◆) and 333 K (■)

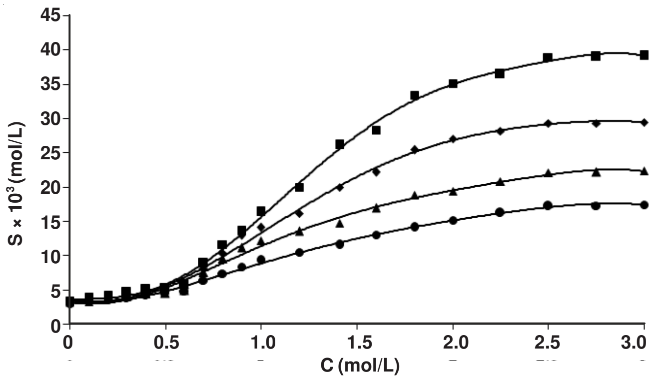

Fig. 2. Effect of sodium salicylate concentration (C) on the solubility (S) of cinnamic acid in water at different temperatures T=303 K (●), 313 K (▲), 323 K (◆) and 333K (■)

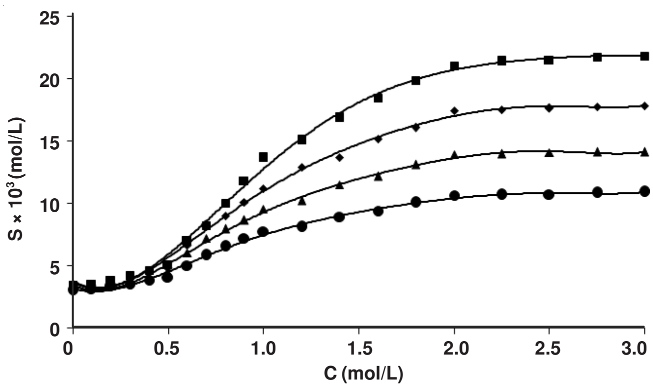

Fig. 3. Effect of nicotinamide concentration (C) on the solubility (S) of cinnamic acid in water at different temperatures T = 303 K (●), 313 K (▲), 323K (◆) and 333K (■)

Therefore, it is evident that hydrotropy was operational above the minimum hydrotrope concentration of sodium benzoate (0.40 mol/L), sodium salicylate (0.6 mol/L) and nicotinamide (0.5 mol/L) irrespective of system temperature. This minimum hydrotrope concentration value assumes greater significance in the context of recovery of hydrotrope solutions. Since hydrotropy appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved cinnamic acid on dilution with water below minimum hydrotrope concentration. The knowledge of minimum hydrotrope concentration values is necessary especially at industrial levels, as it ensures ready recovery of the hydrotrope for reuse. The minimum hydrotrope concentration 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 cinnamic acid was observed above the minimum hydrotrope concentration of sodium benzoate. This increasing trend is maintained only up to a certain concentration of sodium benzoate in the aqueous solution, beyond which there is no appreciable increase in the solubility of cinnamic acid. This concentration of sodium benzoate (hydrotrope) in aqueous solution is referred to as the maximum hydrotrope concentration (C_{max}). 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 cinnamic acid even up to 3 mol/L of sodium benzoate in the aqueous solution. Similar to the minimum hydrotrope concentration values, C_{max} values of hydrotropes also remained unaltered at increased system temperatures.

The knowledge of minimum hydrotrope concentration 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 values of minimum hydrotrope concentration and C_{max} of a hydrotrope with respect to cinnamic acid may be useful in determining the recovery of the dissolved cinnamic acid even to an extent of the calculated amount from hydrotrope solutions at any concentration between minimum hydrotrope concentration 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 Fig. 1, it can further be observed that, in order to achieve the particular solubility of cinnamic acid, say 12.5×10^{-3} mol/L, the sodium benzoate concentration should be 1.00 mol/L at 303 K, 0.80 mol/L at 313 K, 0.70 mol/L at 323 K and 0.60 mol/L at 333 K in the aqueous solution approximately. Thus it can be seen that as the system temperature increases, the concentration of sodium benzoate required in the aqueous phase to achieve a particular solubility of cinnamic acid decreases. A similar trend has been observed for other systems also. It has also been observed that the solubilization effect of sodium benzoate was not a linear function of the concentration of the sodium benzoate. The solubilization effect of sodium benzoate increases with increase in hydrotrope concentration and also with system temperature[35].

A similar trend has been observed in the solubilization effect of other hydrotropes namely sodium salicylate and nicotinamide. It has also been observed that the minimum hydrotrope concentration values of hydrotrope used in this work range between 0.40 and 0.60 mol/L (Table-1), which seem to depend on the hydrophilicity of a hydrotrope. As can be seen from Table-1, C_{max} values of sodium benzoate, sodium salicylate and nicotinamide are 2.50, 2.50 and 2.00 mol/L respectively. The maximum solubilization enhancement factor (ϕ_s), which is the ratio of solubility values in the presence and absence of a hydrotrope, ranges between 3.52 and 14.84. The lowest value of ϕ_s (3.52) was observed in the presence of nicotinamide at a system temperature of 303 K. The highest value of fs (14.84) has been observed in the case of sodium benzoate at a system temperature of 333 K (Table-2).

TABLE-1
MINIMUM HYDROTROPE CONCENTRATION (MHC) AND C_{max} VALUES FOR HYDROTROPES

Hydrotrope	MHC (mol/L)	C_{max} (mol/L)
Sodium benzoate	0.40	2.50
Sodium salicylate	0.60	2.50
Nicotinamide	0.50	2.00

TABLE- 2
MAXIMUM SOLUBILIZATION ENHANCEMENT FACTOR (ϕ_s) OF CINNAMIC ACID

Hydrotrope	Maximum enhancement factor for solubility (ϕ_s)			
	Temperature (K)			
	303	313	323	333
Sodium benzoate	7.23	10.52	12.65	14.84
Sodium salicylate	5.71	6.86	8.72	11.25
Nicotinamide	3.52	4.33	4.18	6.38

Mass transfer coefficient: The mass transfer coefficient of cinnamic acid + water system in the absence of any hydrotrope was determined as 1.14×10^{-4} s^{-1} at 303 K (Table-3). The effect of different hydrotropes on the mass transfer coefficient of cinnamic acid 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 effect significant enhancement in the mass transfer coefficient of cinnamic acid + water system, as observed in the case of solubility determinations. The mass-transfer coefficient of cinnamic acid + water system increases with increase in sodium benzoate concentration. Beyond a C_{max} of 2.50 mol/L there is no appreciable increase in the mass transfer coefficient of cinnamic acid, as observed in the case of solubility determinations. The maximum enhancement factor for mass transfer coefficient of cinnamic acid + water system in the presence of sodium benzoate was found to be 9.26 (Table-3). A similar trend in the mass transfer coefficient enhancement (ϕ_{mtc}) of cinnamic acid has been observed for other hydrotropes also namely sodium salicylate and nicotinamide. The reported mass transfer coefficient enhancement (ϕ_{mtc}) of cinnamic acid of hydrotrope solutions are 9.26 for sodium benzoate, 6.34 for sodium salicylate and 2.99 for nicotinamide at their maximum hydrotrope concentrations. The highest value of ϕ_{mtc} (9.26) has been observed in the presence of sodium benzoate as hydrotrope at C_{max} of 2.50 mol/L.

Effectiveness of hydrotropes: The effectiveness factor of each hydrotrope with respect to cinnamic acid at different system temperatures has been determined by analyzing the experimental solubility data for each case applying the model suggested by Setschenow (1951) and later modified by Pathak and Gaikar[16], as given by the equation:

TABLE-3
EFFECT OF HYDROTROPE CONCENTRATION (C) ON THE MASS TRANSFER COEFFICIENT (k_La) OF CINNAMIC ACID

Hydrotrope	C (mol/L)	$k_La \times 10^4$ (s^{-1})	Enhancement factor for mass transfer coefficient (ϕ_{mtc})
Sodium benzoate	0	1.14	-
	0.2	1.72	1.51
	0.4 (MHC)	1.86	1.63
	0.6	3.71	3.25
	0.8	4.23	3.71
	1.0	5.09	4.46
	1.2	5.82	5.11
	1.4	6.73	5.90
	1.6	7.90	6.93
	1.8	8.34	7.32
	2.00	9.21	8.08
	2.25	9.85	8.64
	2.50 (C_{max})	10.56	9.26
	2.75	10.74	9.42
	3.00	10.89	9.55
Sodium salicylate	0	1.14	-
	0.2	1.38	1.21
	0.4	1.62	1.42
	0.6 (MHC)	1.87	1.64
	0.8	2.66	2.33
	1.0	3.01	2.64
	1.2	3.62	3.78
	1.4	4.41	3.87
	1.6	5.02	4.40
	1.8	5.68	4.98
	2.00	6.18	5.42
	2.25	6.65	5.83
	2.50 (C_{max})	7.23	6.34
	2.75	7.39	6.48
	3.00	7.57	6.64
Nicotinamide	0	1.14	-
	0.2	1.17	1.03
	0.4	1.21	1.06
	0.5 (MHC)	1.26	1.11
	0.6	1.84	1.61
	0.8	2.05	1.80
	1.0	2.38	2.09
	1.2	2.64	2.32
	1.4	2.81	2.46
	1.6	3.11	2.72
	1.8	3.35	2.94
	2.00 (C_{max})	3.41	2.99
	2.25	3.48	3.05
	2.50	3.51	3.07
	2.75	3.58	3.14
	3.00	3.62	3.17

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

where, S and S_m are the solubility of cinnamic acid at any hydrotrope concentration C_s and the minimum hydrotrope concentration C_m, 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 sodium benzoate, sodium salicylate and nicotinamide for cinnamic acid + water system at different system temperatures are listed in Table-4. The highest value has been observed as 0.454 in the case of sodium benzoate as hydrotrope at 333 K. The order of effectiveness of various hydrotropes based on K_s values is given by sodium benzoate > sodium salicylate > nicotinamide.

TABLE- 4
SETSCHENOW CONSTANT (K_s) OF HYDROTROPES WITH RESPECT TO CINNAMIC ACID

Hydrotrope	Setschenow constant (K_s)			
	Temperature (K)			
	303	313	323	333
Sodium benzoate	0.304	0.390	0.430	0.454
Sodium salicylate	0.287	0.343	0.393	0.436
Nicotinamide	0.278	0.331	0.372	0.412

Conclusion

The solubility of cinnamic acid, which is practically insoluble in water, has been increased to a maximum of almost 15 times in the presence of sodium benzoate as hydrotrope. The mass transfer coefficient was also found to increase to a maximum value of 10.56×10^{-4} s^{-1} and with an enhancement factor of about 9.26 times in the presence of sodium benzoate as hydrotrope. This would be useful in increasing the rate of output of the desired product made from cinnamic acid. The minimum hydrotrope concentration and C_{max} values of the hydrotrope with respect to cinnamic acid can be used for the recovery of the dissolved cinnamic acid and hydrotrope solutions at any hydrotrope concentration between the minimum hydrotrope concentration 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 cinnamic acid 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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