Effect of hydrotropes on solubility and mass transfer coefficient of lauric acid

Saghadevan Thenesh Kumar*, Dhakshina Gnana Prakash**, and Nagaraja Nagendra Gandhi***,†

*Department of Chemical Engineering, St. Peter's Engineering College, Chennai - 600 054, India
**Department of Chemical Engineering, S S N College of Engineering, Chennai - 603 110, India
***Department of Chemical Engineering, Alagappa College of Technology,
Anna University, Chennai - 600 025, India

Abstract−A comprehensive investigation on the solubility and mass transfer coefficient enhancement of lauric acid through hydrotropy has been undertaken. The solubility and mass transfer studies were carried out using hydrotropes such as sodium cumene sulfonate, sodium p-xylene sulfonate and sodium p-toluene sulfonate under a wide range of hydrotrope concentrations (0 to 3.0 mol/L) and different system temperatures (303 to 333 K). The effectiveness of hydrotropes was measured in terms of Setschnew constant K_s and reported for all hydrotropes used in this study. The solubility data are also fitted in a polynomial equation as the function of hydrotrope concentration.

Key words: Hydrotropy, Solubilization, Mass Transfer Coefficient, Separation

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 solubility of sparingly soluble solutes under normal conditions [1]. This increase in solubility in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentrations [2,3].

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 [4-10].

The solubility enhancement in the organic compounds could be due to the formation of molecular structures in the form of complexes [11-14]. 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. The effect of hydrotropes on the solubility and mass transfer coefficient for a series of organic esters such as butyl acetate, ethyl benzoate, amyl acetate, methyl salicylate and benzyl acetate was studied in our earlier publications [15-20].

It has been observed that, in many two-phase reaction systems involving a sparingly soluble organic compound like lauric acid, the mass transfer coefficient was found to be very low solely due to the poor solubility of lauric acid in the aqueous phase. Since lauric acid serves as raw material/intermediate for a wide variety of chemicals and allied products [21-23] and the separation of lauric acid 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 effectively. Data on various aspects of hydrotropic study on the solubility and mass transfer coefficient for lauric acid-water system are reported for the first time.

EXPERIMENTAL

All the chemicals used in this work were procured from S D Fine-Chem Ltd., Mumbai with a manufacturer's stated purity of 99%.

The experimental setup for the determination of solubility values consisted of a thermostatic bath and a separating funnel. For each solubility test, an excess amount of powdered solid 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 ±0.1 ℃. The setup was kept overnight for equilibration. After equilibrium was attained, the solution was filtered from the remaining solid. The concentration of the dissolved organic acid in aqueous hydrotrope solutions was analyzed by titration using standardized NaOH solutions with phenolphthalein as an indicator. 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 that rotate at a speed of 600 rpm.

For each run, to measure the mass transfer coefficient, an excess amount of powdered solid was added to the aqueous solution of the hydrotrope of known concentration. The sample was then agitated for a known time of 600, 1,200, 1,800 and 2,400 seconds. After the end of fixed time t, the entire mixture was transferred to a separating funnel. After allowing the sample to stand for some time, the solution was filtered from the remaining solid. The concentra-

†To whom correspondence should be addressed.
E-mail: n_nagendra2002@yahoo.com

tion of the solubilized organic acid in aqueous hydrotrope solutions at time t was analyzed in the same way as for solubility determinations. A plot of $-\log[1-C_b/C^*]$ versus t was drawn, where C_b is the concentration of lauric acid at time t and C^* is the equilibrium solubility of lauric 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

1. Solubility

The solubility of lauric acid standard in water is 1.05×10^{-3} mol/L at 303 K, compared to "insoluble" as reported by Dean (1987). Thus, the solubility values in water are in excellent agreement with the earlier reported values [24,25].

Experimental data representing the average of duplicate determinations on the effect of hydrotropes, i.e., sodium cumene sulfonate, sodium p-xylene sulfonate and sodium p-toluene sulfonate on the solubility of lauric acid are plotted in Figs. 1-3. Sodium cumene
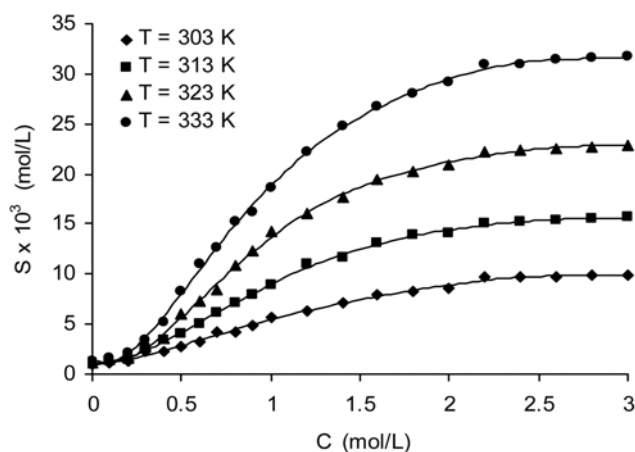

Fig. 1. Effect of Sodium cumene sulfonate concentration (C) on the solubility (S) of lauric acid in water at different temperatures (T).
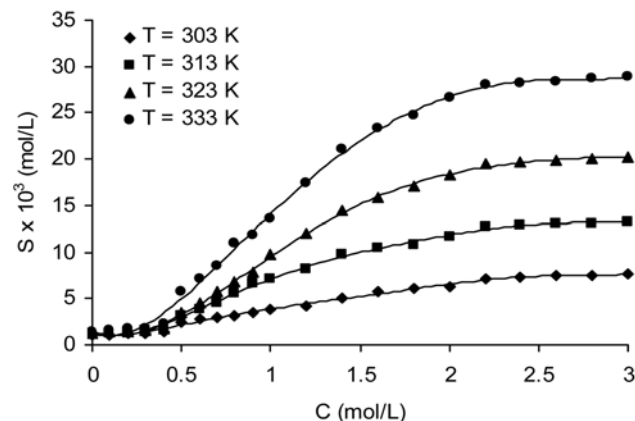

Fig. 2. Effect of Sodium p-xylene sulfonate concentration (C) on the solubility (S) of lauric acid in water at different temperatures (T).

sulfonate is one of the hydrotropes used in this study. The solubility of lauric acid in water at 303 K in the absence of any hydrotrope is 1.05×10^{-3} mol/L (Fig. 1). It has been observed that the solubility of lauric acid in water increases significantly only after the addition of 0.30 mol/L of sodium cumene sulfonate in the aqueous solution. This concentration in referred to as the minimum hydrotrope concentration (MHC).

Therefore, it is evident that hydrotropic solubilization is displayed only above the MHC, irrespective of system temperature. This MHC 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 lauric acid on dilution with water below MHC. A knowledge of MHC values is necessary especially at industrial levels, as it ensures ready recovery of the hydrotrope for reuse. The MHC values remained unaltered even at increased system temperatures.

The solubilization effect varies with concentration of hydrotrope (Fig. 1). In the present case, a clear increasing trend in the solubility of lauric acid was observed above the MHC of sodium cumene sulfonate. This increasing trend is maintained only up to a certain concentration of sodium cumene sulfonate in the aqueous solution, beyond which there is no appreciable increase in the solubility of lauric acid. This concentration of sodium cumene sulfonate (hydrotrope) in the 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 lauric acid even up to 3.00 mol/L of sodium cumene sulfonate in the aqueous solution. Similar to the MHC values, C_{max} values of hydrotropes also remained unaltered at increased system
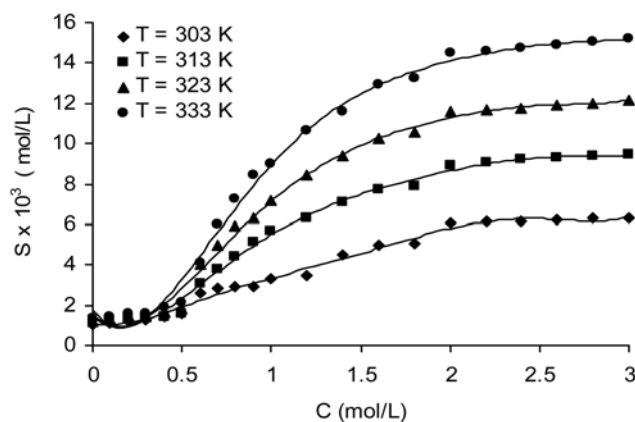

Fig. 3. Effect of Sodium p-toluene sulfonate concentration (C) on the solubility (S) of lauric acid in water at different temperatures (T).

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

Hydrotrope	MHC, mol/L	C_{max}, mol/L
Sodium cumene sulfonate	0.30	2.20
Sodium p-xylene sulfonate	0.50	2.20
Sodium p-toluene sulfonate	0.60	2.00

Table 2. Maximum solubilization enhancement factor (φ_s) of lauric acid

Hydrotrope	Maximum enhancement factor for solubility (φ_s)			
	T=303 K	T=313 K	T=323 K	T=333 K
Sodium cumene sulfonate	9.48	14.10	19.05	24.20
Sodium p-xylene sulfonate	7.28	11.90	16.85	22.00
Sodium p-toluene sulfonate	6.04	8.49	10.13	11.60

temperatures.

The unprecedented increase in the solubilization effect of hydrotropes above MHC may be due to the formation of organized aggregates of hydrotrope molecules at this particular concentration. The highest effect of hydrotrope, i.e., sodium cumene sulfonate towards lauric acid may be due to the ability of sodium cumene sulfonate to form a greater number of organized aggregates from and above MHC. This may be due to the presence of a greater number of carbon atoms in the alkyl group of sodium cumene sulfonate and more methyl groups in the sodium cumene sulfonate structure.

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 values of MHC and C_{max} of a hydrotrope with respect to lauric acid may be useful in determining the recovery of the dissolved lauric acid 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 Fig. 1, it can further be observed that, in order to achieve the particular solubility of lauric acid, say 9.00×10^{-3} mol/ L, the sodium cumene sulfonate concentration should be 2.00 mol/L at 303 K, 1.00 mol/L at 313 K, 0.70 mol/L at 323 K and 0.55 mol/L at 333 K in the aqueous solution. Thus, it can be seen that as the system temperature increases, the concentration of sodium cumene sulfonate required in the aqueous phase to achieve a particular solubility of lauric acid decreases. A similar trend has been observed for other systems also.

It has also been observed that the solubilization effect of sodium cumene sulfonate was not a linear function of the concentration of the sodium cumene sulfonate. The solubilization effect of sodium cumene sulfonate increases with increase in hydrotrope concentration and also with system temperature [26].

A similar trend has been observed in the solubilization effect of other hydrotropes namely sodium p-xylene sulfonate and sodium p-toluene sulfonate. 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) and the C_{max} values of hydrotropes range between 2.00 and 2.20 mol/L (Table 1). The highest value of solubilization enhancement factors φ_s, which is the ratio of solubility values in the presence and absence of a hydrotrope, has been observed in the case of sodium cumene sulfonate as 24.20 at a system temperature of 333 K (Table 2).

2. Mass Transfer Coefficient

The mass transfer coefficient of lauric acid+water system in the absence of any hydrotrope was determined as 3.88×10^{-4} s^{-1} at 303 K (Table 3). The effect of different hydrotropes on the mass transfer coefficient of lauric acid at different hydrotrope concentrations

is also given in the same table. It can be seen that a threshold value of 0.30 mol/L is required to effect significant enhancement in the mass transfer coefficient of lauric acid+water system, as observed in the case of solubility determinations. The mass transfer coefficient of lauric acid+water system increases with increase in sodium cumene

Table 3. Effect of hydrotrope concentration (C) on the mass transfer coefficient (k_{La}) of lauric acid

Hydrotrope	C, mol/L	k_{La}, 10^4 s^{-1}	Enhancement factor for mass transfer coefficient (φ_{mtc})
Sodium cumene sulfonate	0.00	3.88	-
	0.20	4.00	1.03
	0.30 (MHC)	7.76	2.00
	0.40	8.15	2.10
	0.60	9.70	2.50
	0.80	12.00	3.09
	1.00	16.00	4.12
	1.20	18.90	4.87
	1.40	23.00	5.93
	1.60	25.40	6.55
	1.80	28.30	7.29
	2.00	29.60	7.63
	2.20 (C_{max})	39.70	10.23
	2.40	40.12	10.34
	2.60	40.40	10.41
	2.80	41.00	10.57
	3.00	41.40	10.67
Sodium p-xylene sulfonate	0.00	3.88	-
	0.20	3.90	1.01
	0.40	4.27	1.10
	0.50 (MHC)	8.23	2.12
	0.60	9.40	2.42
	0.80	10.98	2.83
	1.00	13.70	3.53
	1.20	16.34	4.21
	1.40	19.44	5.01
	1.60	21.46	5.53
	1.80	26.30	6.78
	2.00	27.20	7.01
	2.20 (C_{max})	36.40	9.38
	2.40	36.63	9.44
	2.60	36.90	9.51
	2.80	37.52	9.67
	3.00	37.99	9.79

Table 3. Continued

Hydrotrope	C, mol/L	k_{La}, 10^4 s^{-1}	Enhancement factor for mass transfer coefficient (φ_{mtc})
Sodium p-toluene sulfonate	0.00	3.88	-
	0.20	3.89	1.00
	0.40	4.00	1.03
	0.60 (MHC)	8.19	2.11
	0.80	9.66	2.49
	1.00	12.42	3.20
	1.20	13.35	3.44
	1.40	16.80	4.33
	1.60	17.93	4.62
	1.80	18.93	4.88
	2.00 (C_{max})	26.60	6.86
	2.20	26.81	6.91
	2.40	27.20	7.01
	2.60	27.60	7.11
	2.80	27.90	7.19
	3.00	28.20	7.27

sulfonate concentration. The maximum enhancement factor for mass transfer coefficient of lauric acid+water system in the presence of sodium cumene sulfonate was found to be 10.23 (Table 3). A similar trend in the mass transfer coefficient enhancement (φ_{mtc}) of lauric

acid has been observed for other hydrotropes also, namely sodium p-xylene sulfonate and sodium p-toluene sulfonate. The highest value of φ_{mtc} (10.23) has been observed in the presence of sodium cumene sulfonate as hydrotrope at C_{max} of 2.20 mol/L.

3. Effectiveness of Hydrotropes

The effectiveness factor of each hydrotrope with respect to lauric 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 (1992), as given by the equation

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

Where S and S_m are the solubility of lauric 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 cumene sulfonate, sodium p-xylene sulfonate and sodium p-toluene sulfonate for lauric acid+water system at different system temperatures, are listed in Table 4. The highest value has been observed as 0.965 in the case of sodium cumene sulfonate as hydrotrope at 333 K.

Since the exponential relation may not be valid at lower and higher hydrotrope concentrations, the data have been fitted in a polynomial equation of the form

$$S=a\,C_s^6+b\,C_s^5+c\,C_s^4+d\,C_s^3+e\,C_s^2+f\,C_s+g \qquad (2)$$

Table 4. Setschenow constant (K_s) of hydrotropes with respect to lauric acid

Hydrotrope	Setschenow constant (K_s)			
	T=303 K	T=313 K	T=323 K	T=333 K
Sodium cumene sulfonate	0.627	0.791	0.895	0.965
Sodium p-xylene sulfonate	0.466	0.608	0.748	0.693
Sodium p-toluene sulfonate	0.356	0.460	0.501	0.548

Table 5. Correlation constants for polynomial Eq. (2)

T, K	Correlation constants							Variance in correlation
	A	b	c	d	e	f	g	
				Sodium cumene sulfonate				
303	0.140	−1.431	5.746	−11.555	11.102	0.421	1.011	0.030
313	0.083	−1.153	6.299	−16.740	19.614	−0.204	1.105	0.031
323	0.403	−4.758	22.118	−50.263	52.449	−7.692	1.424	0.088
333	0.796	−8.480	35.738	−74.287	71.852	−8.218	1.460	0.111
				Sodium p-xylene sulfonate				
303	0.294	−2.784	10.058	−17.454	14.528	−1.827	1.066	0.028
313	0.326	−3.532	15.034	−31.642	32.042	−6.454	1.333	0.046
323	−0.085	0.353	1.847	−13.545	25.466	−5.977	1.433	0.066
333	0.357	−3.702	16.336	−39.330	48.159	−9.271	1.559	0.197
				Sodium p-toluene sulfonate				
303	0.364	−3.254	11.025	−17.869	14.081	−2.105	1.094	0.042
313	0.294	−3.179	13.572	−28.636	29.015	−6.975	1.388	0.064
323	0.332	−3.639	15.954	−34.940	36.689	−8.763	1.505	0.101
333	0.359	−4.207	19.549	−44.805	48.525	−12.255	1.771	0.172

which gives a better fit for the solubility data. The values of correlation constants "a-g" are reported in Table 5 along with the variance of the fit. The solid curves in Figs. 1-3 are from these polynomial equations.

CONCLUSIONS

The solubility of lauric acid, which is practically insoluble in water, has been increased to a maximum of 24.20 times in the presence of sodium cumene sulfonate 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 lauric acid. The MHC and C_{max} values of the hydrotrope with respect to lauric acid can be used for the recovery of the dissolved lauric acid 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 lauric acid from its solution. The solubility data fitted in a polynomial equation give a better fit.

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APPENDIX

Table 1. Effect of sodium cumene sulfonate concentration (C) on the solubility (S) of lauric acid in water

C, mol/L	10^3 S, mol/L			
	T=303 K	T=313 K	T=323 K	T=333 K
0.00	1.05	1.11	1.20	1.31
0.10	1.12	1.30	1.45	1.70
0.20	1.22	1.48	1.63	2.10
0.30 (MHC)	2.22	2.66	2.89	3.43
0.40	2.34	3.41	3.53	5.24
0.50	2.80	4.00	6.00	8.30
0.60	3.28	5.07	7.30	11.00
0.70	4.18	6.19	8.40	12.60
0.80	4.28	7.14	10.80	15.30
0.90	4.80	8.00	12.30	16.20
1.00	5.60	8.96	14.30	18.70
1.20	6.24	11.02	16.10	22.20
1.40	7.20	11.66	17.70	24.80
1.60	7.93	13.08	19.40	26.80
1.80	8.25	13.89	20.30	28.00
2.00	8.62	14.13	20.90	29.19
2.20 (C_{max})	9.67	15.14	22.21	30.88
2.40	9.71	15.22	22.38	31.00
2.60	9.80	15.43	22.53	31.40
2.80	9.90	15.55	22.71	31.58
3.00	9.95	15.65	22.86	31.70

Table 2. Effect of sodium p-xylene sulfonate concentration (C) on the solubility (S) of lauric acid in water

C, mol/L	10^3 S, mol/L			
	T=303 K	T=313 K	T=323 K	T=333 K
0.00	1.05	1.11	1.20	1.31
0.10	1.10	1.25	1.38	1.53
0.20	1.18	1.35	1.44	1.68
0.30	1.30	1.50	1.49	1.79
0.40	1.44	1.73	1.66	2.25
0.50 (MHC)	2.46	3.15	3.48	5.70
0.60	2.70	3.89	4.50	7.10
0.70	3.00	4.50	5.70	8.50
0.80	3.20	5.60	6.80	11.00
0.90	3.53	6.54	7.80	11.80
1.00	3.77	7.20	9.70	13.60
1.20	4.24	8.26	12.10	17.50
1.40	5.07	9.74	14.40	21.00
1.60	5.71	10.40	15.90	23.30
1.80	6.11	10.80	17.00	24.80
2.00	6.20	11.72	18.20	26.67
2.20 (C_{max})	7.20	12.77	19.46	28.08
2.40	7.23	12.89	19.69	28.29
2.60	7.46	13.00	19.87	28.46
2.80	7.51	13.10	20.06	28.65
3.00	7.64	13.21	20.22	28.82

Table 3. Effect of sodium p-toluene sulfonate concentration (C) on the solubility (S) of lauric acid in water

C, mol/L	10^3 S, mol/L			
	T=303 K	T=313 K	T=323 K	T=333 K
0.00	1.05	1.11	1.20	1.31
0.10	1.08	1.22	1.28	1.42
0.20	1.22	1.33	1.40	1.56
0.30	1.30	1.36	1.45	1.60
0.40	1.38	1.42	1.64	1.91
0.50	1.57	1.61	1.84	2.10
0.60 (MHC)	2.60	3.10	4.00	4.10
0.70	2.87	3.80	4.93	6.00
0.80	2.90	4.45	5.92	7.26
0.90	2.90	5.11	6.29	8.40
1.00	3.28	5.64	7.15	9.02
1.20	3.50	6.34	8.45	10.64
1.40	4.50	7.09	9.37	11.56
1.60	5.00	7.75	10.24	12.90
1.80	5.03	7.88	10.58	13.24
2.00 (C_{max})	6.04	8.94	11.60	14.48
2.20	6.12	9.05	11.66	14.59
2.40	6.16	9.19	11.72	14.71
2.60	6.20	9.27	11.89	14.89
2.80	6.28	9.34	11.99	15.03
3.00	6.34	9.42	12.16	15.19