Thermodynamic Study on Hydrotropic Aggregation Behavior of Benzamide†

C. Jayakumar and N. Nagendra Gandhi*

Department of Chemical Engineering, Alagappa College of Technology, Anna University, Chennai - 600 025, India

A comprehensive investigation on the solubility and mass transfer coefficient of benzamide through hydrotropy has been undertaken. This study was carried out using hydrotropes such as nicotinamide, sodium salicylate, resorcinol, and sodium citrate under the influence of a wide range of hydrotrope concentrations [(0 to 3.0) mol·L^{-1}] and different system temperatures [(303 to 333) K]. It has been observed that the solubility of benzamide increases with an 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 benzamide. Consequent to the increase in the solubilization of benzamide, the mass transfer coefficient was also found to increase with increase in hydrotrope concentration at 303 K. A threshold value similar to MHC is to be maintained to have an appreciable enhancement in 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. To ascertain the hydrotropic aggregation behavior of benzamide, thermodynamic parameters such as Gibb's free energy, enthalpy, and entropy of benzamide were determined. The Gibb's free energy decreases with an increase in system temperature. The aggregation of hydrotropes was found to be exothermic in nature and favored by a positive value of entropy.

Introduction

Hydrotropy is a solubilization phenomenon whereby addition of large amounts of a second solute results in an increase in the aqueous solubility of another solute.[1] Neuberg, who identified this pioneering technique, was the first to report hydrotropy, for effecting very large solubility enhancement for a variety of sparingly soluble organic compounds.[2−4] Hydrotropic agents are freely soluble organic compounds that, at a concentration sufficient to induce a stack-type aggregation, considerably enhance the aqueous solubility of organic substances practically insoluble under normal conditions.[5,6] These compounds may be anionic, cationic, or neutral molecules. Since most hydrotropic solutions precipitate the solute (solubilizate) on dilution with water, this phenomenon allows the ready recovery of the hydrotrope for reuse.[7−9] Hydrotropy does seem to be operative above a particular concentration termed critical or minimum hydrotrope concentration. Above this critical concentration, the solubilization rises remarkably and may level off to a plateau thus leading to a sigmoidal solubility profile with hydrotrope concentration.[10−13]

Hydrotropes have many practical applications including separation process, development of pharmaceutical formations, painting and coatings, food, plastic additives, vesicle preparation, selective separation, increase of cloud points of detergent solutions, changes in reaction rate, preparation of drilling well fluids, and separation of water−oil emulsion.[14−17] In detergent formulation, health care, and household purposes, aqueous hydrotrope solutions provide safe and effective media for the extraction of natural products and for conducting organic synthetic reactions.[18−21] The use of hydrotrope solutions in such industrial applications is attractive because of their easy availability, the ready recovery of the dissolved solutes by simple dilution with water or by solvent extraction, and the absence of any fire hazards.[22,23]

It has been observed that, in many two-phase reaction systems involving a sparingly soluble organic compound like benzamide, the mass-transfer coefficient was found to be very low solely due to the poor solubility of solute in the aqueous phase. Since benzamide serves as raw material/intermediate for a wide variety of chemicals and allied products and its separation from any liquid mixture seems to be difficult, this hydrotropic phenomenon can be effectively used for this system. The hydrotropes used in this work are freely soluble in water and practically insoluble in benzamide. All are nonreactive and nontoxic and do not produce any temperature effect when dissolved in water. The easy availability and cheapness of hydrotropes are the other factors considered in the selection of hydrotropes. Data on various aspects of hydrotropic study on the solubility and mass-transfer coefficient for the benzamide−water system are reported for the first time.

Experimental Section

All the chemicals used in this work are manufactured by SD. Fine Chemicals Pvt. Ltd., Mumbai, with a manufacturer's stated purity of 0.99 mol fraction. The thermostatic bath method was to determine solubility values. For each solubility test, about 100 mL of benzamide, 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 sealed to avoid evaporation of mixtures at higher temperatures. The solution of different concentrations of the hydrotrope was prepared by dilution with distilled water. The separating funnel was immersed in a constant-temperature bath fitted with a temperature controller which could control the temperature within ± 0.1 °C. The setup was kept overnight for equilibration. After equilibrium was attained, the aqueous layer was carefully separated from the ester layer and transferred into

† Part of the "Sir John S. Rowlinson Festschrift".

* Corresponding author. Tel.: +91-44-22359180. Fax: +91-44-22352642. E-mail: n_nagendra2002@yahoo.com.

10.1021/je100533u © 2010 American Chemical Society
Published on Web 08/31/2010

Table 1. Effect of Nicotinamide Concentration (*c*) on the Solubility (*S*) of Benzamide in Water

C	$10^3 S$/mol·L^{-1}			
mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	1.25	1.98	2.69	3.24
0.10	1.52	2.36	2.74	3.46
0.20	1.98	2.57	3.12	3.83
0.30	2.16	2.62	3.58	4.45
0.40 (MHC)	3.21	3.85	4.46	4.98
0.50	6.27	8.51	11.23	16.35
0.60	8.45	11.35	17.36	21.45
0.70	10.39	15.46	22.58	27.21
0.80	13.14	18.73	25.25	35.54
0.90	15.32	20.15	31.49	38.78
1.00	18.58	23.86	35.68	43.45
1.10	20.78	26.24	38.92	46.67
1.20	22.56	30.47	40.65	49.34
1.30	24.85	33.83	42.17	53.78
1.40	26.13	35.26	46.28	55.29
1.50	27.46	37.72	48.76	58.73
1.60	30.24	39.15	50.95	61.45
1.70	31.26	40.31	52.49	64.62
1.80	34.79	43.65	56.32	66.19
1.90	35.71	45.29	57.18	68.84
2.00	38.64	46.76	58.59	72.91
2.20	40.38	49.53	62.84	73.46
2.40 (c_{max})	41.26	50.42	63.94	74.81
2.60	41.27	50.43	62.95	73.84
2.80	41.28	50.44	62.96	73.85
3.00	41.28	50.45	62.96	73.86

Table 2. Effect of Sodium Salicylate Concentration (*c*) on the Solubility (*S*) of Benzamide in Water

c	$10^3 S$/mol·L^{-1}			
mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	1.25	1.98	2.69	3.24
0.10	1.48	2.32	2.72	3.26
0.20	1.81	2.43	2.81	3.29
0.30	2.16	2.58	3.12	3.39
0.40 (MHC)	3.16	3.72	4.25	4.83
0.50	5.24	7.65	10.36	14.35
0.60	6.83	10.39	13.52	18.49
0.70	8.58	12.45	17.86	23.68
0.80	10.62	14.75	19.35	27.54
0.90	11.53	16.68	22.74	29.96
1.00	12.98	18.76	24.59	32.75
1.10	14.74	20.38	27.45	35.28
1.20	15.73	22.87	30.18	38.42
1.30	17.19	24.35	32.74	40.93
1.40	18.47	26.52	35.85	44.76
1.50	19.71	28.68	36.36	46.54
1.60	21.34	30.19	38.64	48.78
1.70	23.75	32.78	41.51	52.19
1.80	24.93	35.46	44.92	53.47
1.90	26.54	36.29	45.85	56.18
2.00	28.72	38.58	48.19	58.26
2.20	30.95	39.62	50.54	61.45
2.40 (c_{max})	31.42	40.24	51.76	62.85
2.60	31.43	40.25	51.77	62.86
2.80	31.44	40.26	51.78	62.87
3.00	31.45	40.26	51.79	62.87

Table 3. Effect of Resorcinol Concentration (*c*) on the Solubility (*S*) of Benzamide in Water

c	$10^3 S$/mol·L^{-1}			
mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	1.25	1.98	2.69	3.24
0.10	1.42	2.36	3.14	3.57
0.20	1.38	2.57	3.25	3.82
0.30	1.92	2.69	3.39	4.09
0.40	2.23	2.82	3.51	4.18
0.50	3.73	4.34	5.12	5.84
0.60 (MHC)	6.34	9.67	12.9	16.56
0.70	8.45	11.29	16.84	21.87
0.80	9.62	13.54	18.65	25.32
0.90	11.27	15.85	22.16	28.15
1.00	12.78	17.09	24.87	30.94
1.10	14.52	18.48	26.25	34.68
1.20	16.45	20.34	29.56	36.75
1.30	17.26	21.73	30.67	38.61
1.40	18.58	23.14	32.53	41.74
1.50	19.25	24.59	34.83	43.75
1.60	20.39	25.62	35.42	45.69
1.70	21.81	27.64	36.96	46.87
1.80	22.59	29.38	37.75	47.25
1.90	23.28	31.26	38.69	48.62
2.00	24.12	32.39	40.73	49.35
2.20 (c_{max})	25.25	33.82	41.35	50.15
2.40	25.26	33.83	41.36	50.16
2.60	25.27	33.84	41.37	50.17
2.80	25.28	33.85	41.38	50.18
3.00	25.29	33.86	41.39	50.19

Table 4. Effect of Sodium Citrate Concentration (*c*) on the Solubility (*S*) of Benzamide in Water

C	$10^3 S$/mol·L^{-1}			
mol·L^{-1}	T = 303 K	T = 313 K	T = 323 K	T = 333 K
0.00	1.25	1.98	2.69	3.24
0.10	1.31	2.17	2.93	3.45
0.20	1.52	2.35	3.16	3.87
0.30	1.69	2.48	3.26	3.96
0.40	1.92	2.63	3.39	4.05
0.50	2.16	2.79	3.51	4.18
0.60 (MHC)	3.38	5.31	6.03	6.84
0.70	4.53	6.75	10.34	12.47
0.80	5.61	8.94	12.61	17.24
0.90	6.19	9.56	14.83	20.51
1.00	7.83	11.45	16.76	23.08
1.10	8.29	13.73	18.29	26.69
1.20	9.52	14.65	21.42	28.25
1.30	10.87	17.49	22.39	31.62
1.40	11.65	18.95	24.35	33.18
1.50	12.68	19.52	26.48	35.85
1.60	13.35	21.18	29.75	37.16
1.70	14.06	23.35	30.24	40.25
1.80	14.57	24.23	31.36	42.63
1.90	15.18	25.92	33.76	43.22
2.00	15.52	26.56	35.17	44.39
2.20 (c_{max})	16.44	27.62	36.25	45.53
2.40	16.45	27.63	36.26	45.54
2.60	16.46	27.65	36.27	45.55
2.80	16.47	27.66	36.28	45.56
3.00	16.48	27.67	36.29	45.57

a beaker. The solute concentration was estimated by the addition of excess NaOH using a standardized HCl solution and phenolphthalein as an indicator. All the solubility experiments were conducted in duplicate to check the reproducibility. The observed error 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 speed of the impeller in revolutions per minute was selected in such a way to get effective mixing, which was maintained at the same value for all experiments.

The experimental procedure used for the determination of the transport coefficient is a well-adopted one. 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 4 blades. The baffle is 40 cm high with a diameter of 1.5 cm. There are 4 baffles that rotate at a speed of 600 rpm. For each run to measure the mass-transfer coefficient, 250 mL of the benzamide 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) s. After the end of fixed time *t*, the

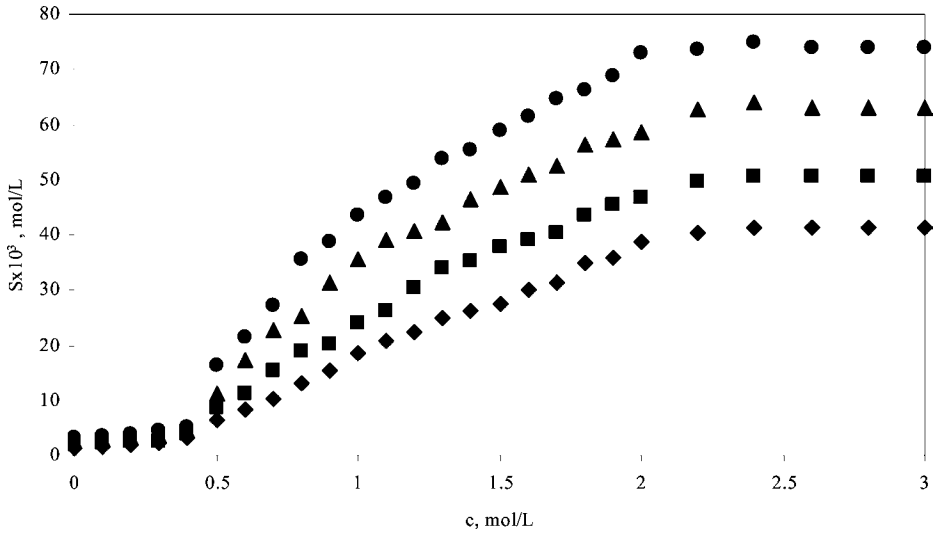

Figure 1. Effect of nicotinamide concentration (c) on the solubility (S) of benzamide in water at different temperatures: ◆, $T = 303$ K; ■, $T = 313$ K; ▲, $T = 323$ K; ●, $T = 333$ K.

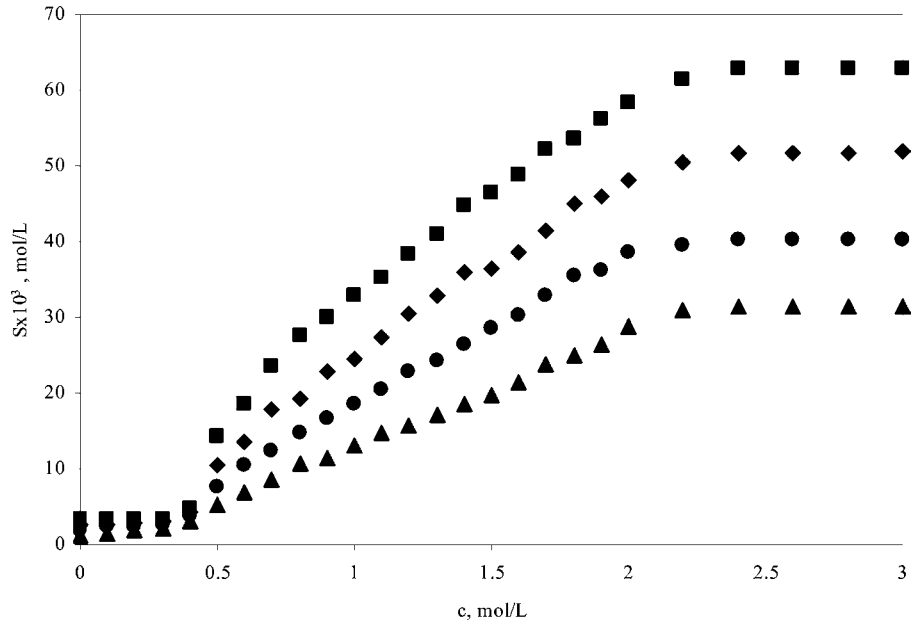

Figure 2. Effect of sodium salicylate concentration (c) on the solubility (S) of benzamide in water at different temperatures: ▲, $T = 303$ K; ●, $T = 313$ K; ◆, $T = 323$ K; ■, $T = 333$ K.

entire mixture was transferred to a separating funnel. After allowing to stand for 1 h, the aqueous layer was carefully separated from the benzamide layer. The concentration of the solubilized benzamide 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. The solubility of the benzamide standard in the absence of any hydrotrope in water is $1.25 \cdot 10^{-3}$ mol·L^{-1} at 303 K, compared to $1.29 \cdot 10^{-3}$ mol·L^{-1} as reported by Dean (1987). Thus, the solubility values in water are in excellent agreement with earlier reported values.[24,25]

Experimental data representing the average of duplicate determinations on the effect of hydrotropes, i.e., nicotinamide, sodium salicylate, resorcinol, and sodium citrate, on the solubility of benzamide are presented in Tables 1 to 4 and are plotted in Figures 1 to 4. Nicotinamide is one of the hydrotropes used in this study. It has been observed that the solubility values increase significantly only after the addition of 0.40 mol·L^{-1} of nicotinamide in the aqueous phase. This concentration is 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. Hydrotropy 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 hydrotropy appears to operate only at significant concentrations of hydrotrope in water, most hydrotropic solutions release the dissolved solute on dilution with distilled water below MHC. The knowledge of MHC values is necessary especially at industrial levels, as it ensures ready recovery of hydrotrope for reuse. The MHC values remained unaltered even at increased system temperatures.

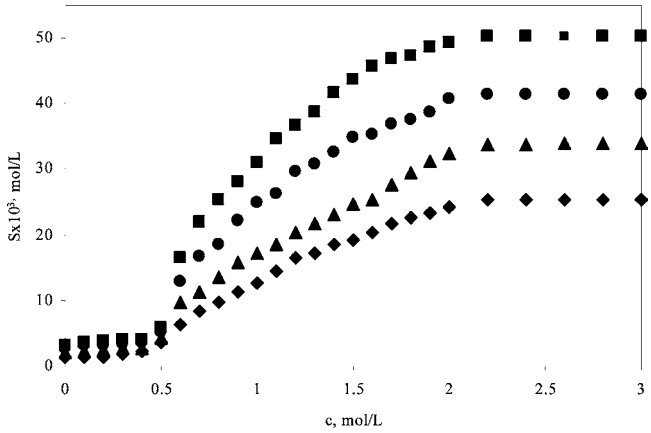

Figure 3. Effect of sodium benzoate concentration (c) on the solubility (S) of benzamide in water at different temperatures: ◆, $T = 303$ K; ▲, $T = 313$ K; ●, $T = 323$ K; ■, $T = 333$ K.

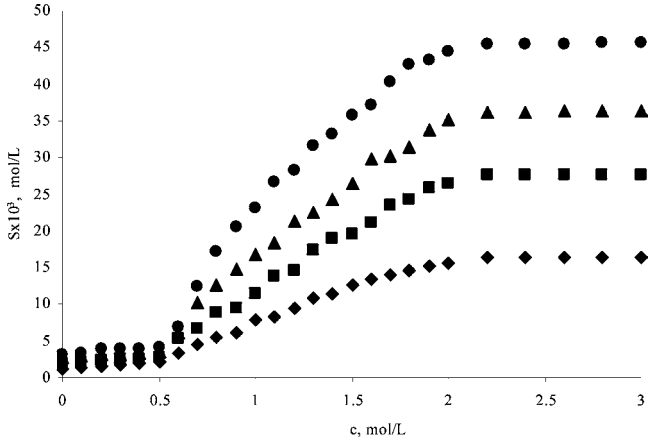

Figure 4. Effect of sodium citrate concentration (c) on the solubility (S) of benzamide in water at different temperatures: ◆, $T = 303$ K; ■, $T = 313$ K; ▲, $T = 323$ K; ●, $T = 333$ K.

The solubilization effect varies with concentration of hydrotropes (Table 1). In the present case, a clear increasing trend in the solubility of benzamide was observed above the MHC of nicotinamide. This increasing trend is maintained only up to a certain concentration of nicotinamide in the aqueous phase, beyond which there is no appreciable increase in the solubility of benzamide.This concentration of nicotinamide (hydrotrope) 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 benzamide even up to 3.00 mol·L^{-1} of nicotinamide in the aqueous phase. Similar to the MHC values, the c_{max} values of hydrotropes also remained unaltered with an 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. The values of MHC and c_{max} of a hydrotrope with respect to benzamide 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 say

Table 5. MHC and C_{max} Values of Hydrotropes

hydrotropes	MHC / mol·L^{-1}	c_{max} / mol·L^{-1}
nicotinamide	0.40	2.40
sodium salycilate	0.40	2.40
resorcinol	0.50	2.20
sodium citrate	0.60	2.20

Table 6. Maximum Enhancement Factor for Solubility (ϕ_s) of Benzamide

	maximum enhancement factor for solubility (ϕ_S)			
hydrotropes	$T = 303$ K	$T = 313$ K	$T = 323$ K	$T = 333$ K
nicotinamide	12.85	13.09	14.34	15.02
sodium salycilate	9.94	10.82	12.18	13.01
resorcinol	6.77	7.79	8.07	8.58
sodium citrate	4.71	5.12	6.81	7.95

$35 \cdot 10^{-3}$ mol·L^{-1}, the nicotinamide concentration should be 1.90 mol·L^{-1} at 303 K, 1.40 mol·L^{-1} at 313 K, 1.00 mol·L^{-1} at 323 K, and 0.80 mol·L^{-1} at 333 K in the aqueous phase. Thus, it can be seen that as the system temperature increases the concentration of nicotinamide required in the aqueous phase to achieve a particular solubility of benzamide decreases. A similar trend has been observed for other systems also.

In the concentration range of nicotinamide between (0.00 and 3.00) mol·L^{-1}, three different regions of nicotinamide as hydrotrope were observed. It was inactive below MHC values of 0.40 mol·L^{-1}, above which an appreciable increase in the solubility of benzamide was found up to 2.40 mol·L^{-1} and beyond which there is no further increase in the solubility even up to 3.00 mol·L^{-1}. Hence nicotinamide was found to be an effective hydrotrope in the concentration range between (0.40 and 2.40) mol·L^{-1} toward benzamide. It has also been observed that the solubilization effect of nicotinamide was not a linear function of the concentration of the nicotinamide solution. The solubilization effect of nicotinamide increases with increase in hydrotrope concentration and also with system temperature.

A similar trend has been observed in the solubilization effect of other hydrotropes, namely, sodium salicylate, resorcinol, and sodium citrate. It has also been observed that the MHC values of hydrotrope used in this work range between (0.40 and 0.60) mol·L^{-1} (Table 5) which seem to depend on the hydrophilicity of a hydrotrope. The c_{max} values of hydrotropes range between (2.20 and 2.40) mol·L^{-1} (Table 5) in most cases. 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 nicotinamide as 15.02 at a system temperature of 333 K (Table 6).

Mass-Transfer Coefficient. The mass-transfer coefficient of the benzamide + water system in the absence of any hydrotrope was determined to be $1.13 \cdot 10^{-5}$ s^{-1} at 303 K (Table 7). The effect of different hydrotropes on the mass-transfer coefficient of benzamide at different hydrotrope concentrations is also given in the same table. It can be seen that a threshold value of 0.40 mol·L^{-1} is required to effect significant enhancement in the mass transfer coefficient of the benzamide + water system, as was observed in the case of solubility determinations. The mass-transfer coefficient of the benzamide + water system increases with an increase in nicotinamide concentration. The maximum enhancement factor for the mass-transfer coefficient of the benzamide + water system in the presence of nicotinamide was found to be 26.78 (Table 7). A similar trend in the mass-transfer coefficient enhancement (ϕ_{mtc}) of benzamide has been observed for other hydrotropes also, namely, sodium salicylate, resorcinol, and sodium citrate. The highest value of ϕ_{mtc} (32.87) has been observed in the presence of nicotinamide

Table 7. Effect of Hydrotrope Concentration (*c*) on the Mass Transfer Coefficient (k_La) of Benzamide at 303 K

hydrotropes	*c* / mol·L^{-1}	k_La / 10^5 s^{-1}	enhancement factor for mass transfer coefficient (ϕ_{mtc})
nicotinamide	0.00	1.13	–
	0.20	3.48	3.08
	0.40 (MHC)	5.32	4.71
	0.60	9.76	8.64
	0.80	11.28	9.98
	1.00	15.84	14.02
	1.20	18.72	16.57
	1.40	20.46	18.12
	1.60	21.52	19.04
	1.80	23.17	20.50
	2.00	25.35	22.43
	2.20	28.94	25.61
	2.40 (c_{max})	30.26	26.78
	2.60	32.42	28.69
	2.80	35.56	31.47
	3.00	37.14	32.87
sodium salycilate	0.00	1.13	–
	0.20	2.94	2.61
	0.40 (MHC)	4.86	4.30
	0.60	7.51	6.65
	0.80	10.24	9.06
	1.00	13.46	11.91
	1.20	17.89	15.83
	1.40	19.37	17.14
	1.60	20.69	18.31
	1.80	22.14	19.59
	2.00	24.35	21.54
	2.20	26.18	23.17
	2.40 (c_{max})	28.67	25.37
	2.60	30.19	26.72
	2.80	33.45	29.60
	3.00	34.82	30.81
resorcinol	0.00	1.13	–
	0.20	2.29	2.02
	0.40	3.65	3.23
	0.60 (MHC)	5.92	5.23
	0.80	8.38	7.41
	1.00	10.47	9.27
	1.20	14.86	13.15
	1.40	16.35	14.47
	1.60	18.64	16.49
	1.80	21.52	19.04
	2.00	23.76	21.02
	2.20 (c_{max})	25.74	22.78
	2.40	26.29	23.26
	2.60	28.15	24.91
	2.80	31.93	28.26
	3.00	32.87	29.09
sodium citrate	0.00	1.13	–
	0.20	2.64	2.34
	0.40	3.75	3.32
	0.60 (MHC)	4.52	4.00
	0.80	6.48	5.73
	1.00	8.73	7.72
	1.20	10.56	9.35
	1.40	12.86	11.38
	1.60	14.27	12.62
	1.80	16.53	14.63
	2.00	19.65	17.39
	2.20 (c_{max})	21.56	19.08
	2.40	23.62	20.90
	2.60	26.49	23.44
	2.80	28.78	25.47
	3.00	30.82	27.26

as hydrotrope at *c* of 3.00 mol·L^{-1}. The effect of different hydrotropes on the mass transfer coefficient (k_La) of benzamide 303 K is presented in Figure 8.

Aggregation Characteristics of Hydrotropes. The change in enthalpy, entropy, and free energy accompanying the aggregation of hydrotropes such as nicotinamide, sodium salicylate, resorcinol, and sodium citrate under a wide range of hydrotrope concentrations [(0 to 3.0) mol·L^{-1}] and different system temperatures [(303 to 333) K] have been determined and presented in Table 8. The calculations are based on MHC as determined in solubility studies.

Table 8. Effect of Minimum Hydrotrope Concentration (MHC), Standard Gibbs Free Energy ($\Delta G°$), Standard Enthalpy ($\Delta H°$), and Entropy ($\Delta S°$) of Benzamide

hydrotropes	*T* / K	MHC (by solubility), 10^3S / mol·L^{-1}	$\Delta G°$ / kJ·mol^{-1}	$\Delta H°$ / kJ·mol^{-1}	$\Delta S°$ / kJ·mol^{-1}
nicotinamide	303	3.21	−14.464	−11.374	0.010
	313	3.85	−14.478	−11.892	0.082
	323	4.46	−14.536	−14.664	0.058
	333	4.98	−14.478	−14.460	0.037
sodium salycilate	303	3.16	−14.504	−10.687	0.012
	313	3.72	−14.558	−11.404	0.010
	323	4.25	−14.666	−12.144	0.078
	333	4.83	−14.765	−12.907	0.055
resorcinol	303	3.73	−14.086	−11.526	0.084
	313	4.34	−14.157	−12.299	0.594
	323	5.12	−14.165	−13.098	0.033
	333	5.84	−14.239	−13.922	0.009
sodium citrate	303	3.49	−14.253	−12.594	0.054
	313	4.52	−14.051	−13.439	0.019
	323	5.32	−14.062	−14.312	0.019
	333	5.73	−14.292	−15.212	0.002

$$\Delta G° = RT \ln(X_{MHC}) \quad (1)$$

where X_{MHC} = solubility of benzamide at MHC in mol·L^{-1}.

Figures 5 and 6 shows the relationship between the standard free energy of both the hydrotropes and the temperature. The free energy decreases with increase in temperature as reported in Table 8.

The standard enthalpy ($\Delta H°$) of aggregation can be found by the Van't Hoff equation

$$\Delta H° = -RT^2(\partial \ln X_{MHC}/\partial T) \quad (2)$$

The slope in the plot of $\ln(X_{MHC})$ versus *T* at each temperature was taken as ($\partial \ln X_{MHC}/\partial T$). A linear plot was observed for both the hydrotropes as shown in Figure 7. The values of enthalpy are negative which indicates the aggregation behavior of exothermic nature.

The standard entropy ($\Delta S°$) of aggregation was calculated from

$$\Delta S° = [(\Delta H° - \Delta G°)/T] \quad (3)$$

The entropy change in all cases is positive which confirms that aggregation of hydrotropes is favored entropically. However, the values decrease with increasing temperature as seen from Table 8. This may be due to the fact that self-aggregation becomes poor at higher temperature because of enhanced molecular motion at increased temperatures.

Effectiveness of Hydrotropes. The effectiveness factor of each hydrotrope with respect to benzamide 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 (1992), as given by[26] the equation

$$\log[S/S_m] = K_s[c_s - c_m] \quad (4)$$

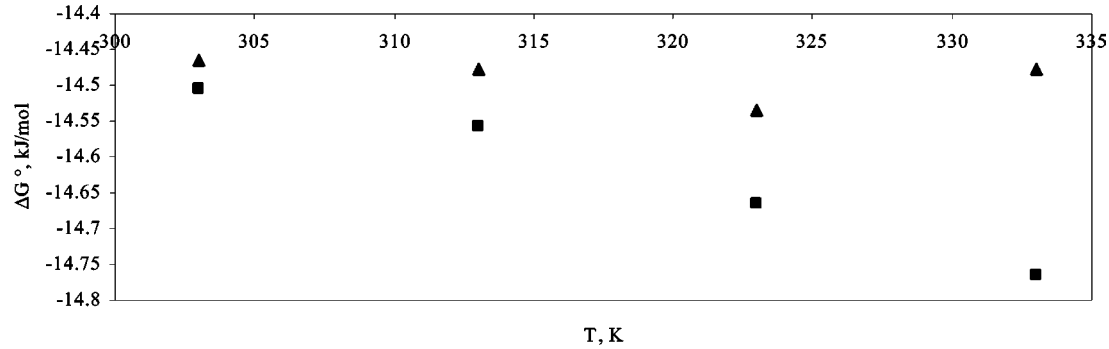

Figure 5. Temperature (T) versus standard Gibbs free energy ($\Delta G°$): ▲, nicotinamide; ■, sodium salycilate.

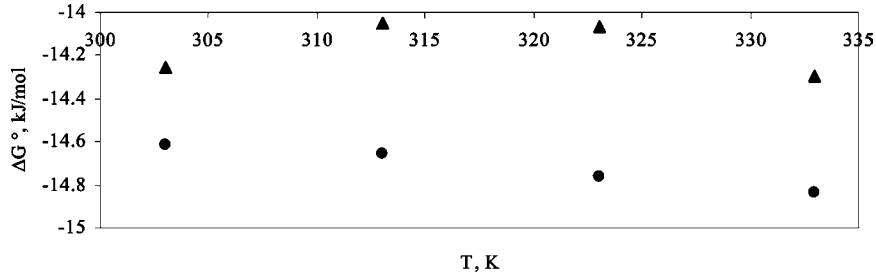

Figure 6. Temperature (T) versus standard Gibbs free energy ($\Delta G°$): ●, resorcinol; ▲, sodium citrate.

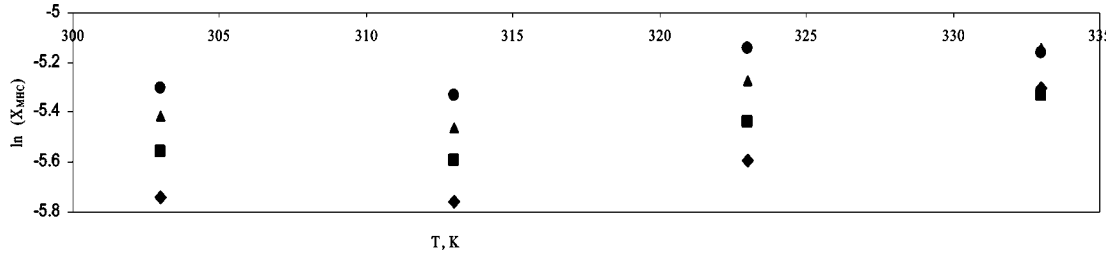

Figure 7. Temperature (T) versus ln(X_{MHC}): ◆, nicotinamide; ■, sodium salycilate; ▲, resorcinol; ●, sodium citrate.

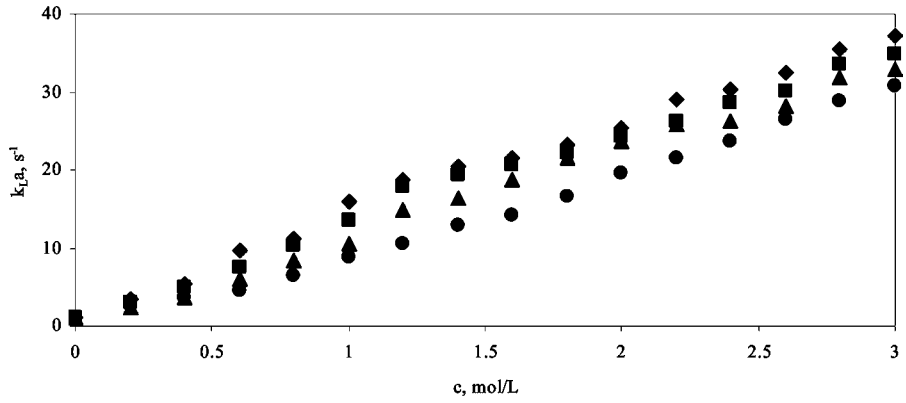

Figure 8. Effect of hydrotrope concentration (c) on the mass transfer coefficient ($k_L a$) of benzamide in water at 303 K: ◆, nicotinamide; ■, sodium salycilate; ▲, resorcinol; ●, sodium citrate.

where S and S_m are the solubility of benzamide 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, nicotinamide, sodium salicylate, resorcinol, and sodium citrate, for the benzamide + water system at different system temperatures are listed in Table 9. The highest value has been observed as 0.588 in the case of nicotinamide as hydrotrope at 333 K.

Table 9. Setschenow Constant (k_s) of Hydrotropes with Respect to Benzamide

	setschenow constant (k_s)			
hydrotropes	T = 303 K	T = 313 K	T = 323 K	T = 333 K
nicotinamide	0.554	0.559	0.578	0.588
sodium salycilate	0.498	0.517	0.542	0.557
resorcinol	0.489	0.525	0.534	0.549
sodium citrate	0.421	0.491	0.521	0.563

Conclusions

The solubility of benzamide which is practically insoluble in water has been increased to a maximum enhancement factor

value of 15.02 in the presence of nicotinamide 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 benzamide. Solubility is found useful in the case of hydrotropes to study thermodynamic stability. From the data obtained by this study, it is found that hydrotrope concentration gives self-aggregation at higher minimum concentration compared to micellar surfactants.The MHC and c_{max} values of the hydrotrope with respect to benzamide can be used for the recovery of the dissolved benzamide 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 solute 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.

Literature Cited

(1) Neuberg, C. Hydrotropy. *Biochem. Z.* **1916**, *Z 76*, 107–108.
(2) Saleh, A. M.; Ebian, A. R.; Etman, M. A. Solubilization of Water by Hydrotropic Salts. *J. Pharm. Sci.* **1986**, *75*, 644–647.
(3) Dhara, D.; Chatterji, P. R. Effect of Hydrotropes on the Volume Phase Transition in Poly (N-isopropylacrylamide) Hydrogel. *Langmuir* **1999**, *15*, 93–9350.
(4) Gaikar, V. G.; Pathak, P. V. Selective Solubilisation of Isomers in Hydrotrope Solution o-/p- Chlorobenzoic acids and o-/*p*-Nitro Anilines. *Sep. Sci. Technol.* **1999**, *34*, 439–459.
(5) Friberg, S. E.; Brancewicz, C. O/W Microemulsions and Hydrotropes: The Coupling Action of a Hydrotrope. *Langmuir* **1994**, *10*, 2945–2949.
(6) Agarwal, M.; Gaikar, V. G. Extractive Separation Using Hydrotropes. *Sep. Technol.* **1992**, *2*, 79–84.
(7) Laxman, M.; Sharma, M. M. Reduction of Isophorone with Borohydride: Change in Regio Selectivity with Hydrotropes. *Synth. Commun.* **1990**, *20*, 111–117.
(8) Srinivas, V.; Balasubramanian, D. When Does the Switch from Hydrotropy to Micellar Behavior Occur? *Langmuir* **1998**, *14*, 6658–6661.
(9) Kumar, M. D.; Gandhi, N. N. Effect of Hydrotropes on the Solubility and Mass Transfer Coefficient of Methyl Salicylate. *J. Chem. Eng. Data* **2000**, *45*, 419–423.
(10) Gandhi, N. N.; Kumar, M. D.; Sathyamurthy, N. Effect of Hydrotropes on Solubility and Mass-Transfer Coefficient of Butyl Acetate. *J. Chem. Eng. Data* **1998**, *43*, 695–699.
(11) Nagendra Gandhi, N. N.; Dharmendira Kumar, M.; Sathyamurthy, N. Solubility and Mass Transfer Coefficient Enhancement of Ethyl Benzoate through Hydrotropy. *Hung. J. Ind. Chem.* **1998**, *26*, 63–68.
(12) Nagendra Gandhi, N.; Dharmendira Kumar, M. Effect of Hydrotropes on Solubility and Mass Transfer Coefficient of Amyl Acetate. *Bioprocess Eng.* **2000**, *23*, 31–36.
(13) Meyyappan, N.; Gandhi, N. N. Solubility and Mass Transfer Coefficient Enhancement of Benzyl Acetate in Water through Hydrotropy. *J. Chem. Eng. Data* **2004**, *49*, 1290–1294.
(14) Meyyappan, N.; Gandhi, N. N. Solubility and Mass Transfer Coefficient Enhancement of Benzyl Benzoate in Water through Hydrotropy. *J. Chem. Eng. Data* **2005**, *50*, 796–800.
(15) Gaikar, V. G.; Pathak, P. V. Solubility o- and p-Chlorobenzoic Acid in Hydrotrope Solutions. *J. Chem. Eng. Data* **1993**, *38*, 217–220.
(16) Tanford, C. *The Hydrophobic Effect: Formation of Micelles andBiological Membranes*, 2nd ed.; John Wiley & Sons: New York, 1980.
(17) Dandekar, D. V.; Jayaprakasha, G. K.; Patil, B. S. Hydrotropic Extraction of Bioactive Limonin from Sour Orange (Citrus Aurantium L.) Seeds. *Food Chem.* **2008**, *109*, 515–520.
(18) Gaikar, V. G.; Sharma, M. M. Extractive Separation with Hydrotropes. *Solvent Extr. Ion Exch.* **1986**, *4*, 839–846.
(19) Wagle, V. B.; Kothari, P. S.; Gaikar, V. G. Effect of Temperature on Aggregation Behaviour of Aqueous Solution of Sodium Cumene Sulfonate. *J. Mol. Liq.* **2007**, *133*, 68–76.
(20) Gaikar, V. G.; Sharma, M. M. Separation with Hydrotropes. *Sep. Technol.* **1993**, *3*, 3–11.
(21) Balasubramanian, D.; Srinivas, V.; Gaikar, V. G.; Sharma, M. M. Aggregation behavior of hydrotropic compounds in aqueous solution. *J. Phys. Chem.* **1989**, *93*, 3865–3870.
(22) Bhat, M. B.; Gaikar, V. G. Characterization of Interaction between Butyl Benzene Sulfonates and Cetyl Trimethylammonium Bromide in a Mixed Aggregate Systems. *Langmuir* **1999**, *15*, 4740–4751.
(23) Huerta-Diaz, M. A.; Rodriguez, S. Solubility measurements and determination of Setschenow constants for the pesticide carbaryl in seawater and other electrolyte solutions. *Can. J. Chem.* **1992**, *70*, 2864–2868.
(24) John, A. D. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1987.
(25) Perry, R. H. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1997.
(26) Gaikar, V. G.; Sharma, M. M. Extractive Separation with Hydrotropes. *Solvent Extr. Ion Exch.* **1986**, *4*, 839–846.

Received for review May 21, 2010. Accepted August 13, 2010.

JE100533U