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Hydrotropic effect and thermodynamic analysis on the solubility and mass transfer coefficient enhancement of ethylbenzene

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Abstract−Concentrated aqueous solutions of a large number of hydrotropic agents, urea, nicotinamide, and sodium salicylate, have been employed to enhance the aqueous solubilities of poorly water soluble organic compounds. The influence of a wide range of hydrotrope concentrations (0-3.0 mol·L^{-1}) and different system temperatures (303-333 K) on the solubility of ethylbenzene has been studied. The solubility of ethylbenzene increases with increase in hydrotrope concentration and also with system temperature. Consequent to the increase in the solubility of ethylbenzene, the mass transfer coefficient was also found to increase with increase in hydrotrope concentration at 303 K. The enhancement factor, which is the ratio of the value in the presence and absence of a hydrotrope, is reported for both solubility and mass transfer coefficient of ethylbenzene. The Setschenow constant, K_s, a measure of the effectiveness of a hydrotrope, was determined for each case. To ascertain the hydrotropic aggregation behavior of ethylbenzene, thermodynamic parameters such as Gibb's free energy, enthalpy, and entropy of ethylbenzene were determined.

Key words: Ethylbenzene, Hydrotropy, Solubility, Mass Transfer Coefficient, Sodium Salicylate

INTRODUCTION

Hydrotropy is a unique and unprecedented solubilization technique which also facilitates the separation of close boiling and nonisomeric mixtures, besides increasing the rate of heterogeneous reactions [1]. The solubility enhancement in water is probably due to the formation of organized assemblies of hydrotrope molecules at critical concentration [2]. The origin of hydrotropy dates back to 1916 when Neuberg identified this pioneering technique for effecting very large solubility enhancement for a variety of sparingly soluble organic compounds and defined hydrotropes as metal salts of organic acids [3-5]. Hydrotropy is a type of solubilization with the solute dissolved in oriented clusters of hydrotropic agents. Hydrotropes are a class of chemical compounds that cause a several-fold increase in the solubility of sparingly soluble solutes under normal conditions [6,7]. Easy recovery of dissolved solute, possible reuse of hydrotrope solution and absence of emulsion make this technique much superior in industrial levels and considered highly selective. The foremost property of the hydrotrope is related to the MHC (minimum hydrotrope concentration), which is defined as the concentration at which the hydrotrope molecules begin to aggregate, i.e., forming new microenvironment with different traits as those of the hydrotropes in relatively diluted solutions [8,9]. Above MHC, the solubility of organic compound in aqueous phase rises eloquently. Solubility does not show appreciable rise even after the addition of hydrotrope in the aqueous phase, but on subsequent increase in the concentration of hydrotrope, the solubility of the organic compound present in aqueous phase rises significantly [10-12].

In many two phase reaction systems, the mass transfer coefficient has been found to be very low solely due to the poor solubility of the hydrophobic reactant in the aqueous phase [13,14]. Ethylbenzene is used in the manufacture of styrene and as an intermediate for the production of acetophenone, diethylbenzene and ethyl anthraquinone. Ethylbenzene even serves as a constituent of asphalt and naphtha and as an antiknock additive in fuels and gasoline. It is utilized in the coating industry for paints, lacquers, and varnishes. Since its major application in petrochemical industry is to form a two phase liquid system, it has become essential to enhance the solubility and mass transfer coefficient of ethylbenzene to get the maximum rate of output of the desired products made from ethylbenzene. All hydrotropes are surface active, non-reactive, non-toxic and do not produce any temperature effect when dissolved in water [15]. The cheapness and ease of availability are other factors considered in the selection of hydrotropes.

THEORETICAL

1. Thermodynamic Study

Consistent thermodynamic properties like standard Gibbs free energy, standard enthalpy and standard entropy reveal the aggregation behavior of different hydrotropes with respect to ethylbenzene used in this study.

Gibbs energy is the capacity of a system to do non-mechanical work and ΔG measures the non-mechanical work done on it. If Gibbs free energy change (ΔG^o) is negative, then the entropy increases and the reaction is extemporaneous. The calculations are to be done based on MHC as determined in solubility studies.

$$\Delta G^o = RT \ln(X_{MHC}) \tag{1}$$

Where, R is the universal gas constant, i.e., 8.3145 J/mol K, T denoting the temperature and X_{MHC} the solubility of ethylbenzene at MHC in mol·L^{-1}.

The change in enthalpy change is the amount of heat evolved or

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absorbed in a reaction carried out at constant pressure. It is denoted by the symbol ΔH. The standard enthalpy (ΔH^o) of aggregation can be found by the van't Hoff equation.

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

The slope in the plot of $\ln(X_{MHC})$ versus T at each temperature gives the value of $\partial \ln X_{MHC}/\partial T$.

Entropy is merely a way to measure the energy that disperses or spreads out in a process (at a specific temperature). Entropy can also be defined as a measure of disorder or randomness of a system. The standard entropy (ΔS^o) of aggregation was calculated from

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

2. Setschenow Constant

Setschenow in 1889, established an empirical formula relating organic compound solubilities in saline aqueous solutions to those in pure water. The Setschenow constant may also referred to as "Salting constant. This salting constant relates the effectiveness of a particular salt or combination of salts to the change in solubility of a given compound. Later, this model which was suggested by Setschenow [16], was modified by Gaikar and Pathak [17], and proposed as an equation:

$$\log[S/S_m] = K_s\,[C_s - C_m] \quad (4)$$

Where, S and S_m are the solubility of ethylbenzene 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.

EXPERIMENTAL

1. Materials

All the chemicals used in this work were manufactured by the Loba Chemie Pvt. Ltd., Mumbai, with a manufacturer's stated purity of 99.9%. The hydrotropes used in this work, urea, nicotinamide, and sodium salicylate, are of analytical grade. Double distilled water was used for the preparation of hydrotropic solutions.

2. Methods

The experimental setup for the determination of solubility values consisted of a thermostatic bath and a separating funnel. The solubility of ethylbenzene was measured at 303, 313, 323, and 333 K. For each solubility test, equal volumes [100 ml] of ethylbenzene and hydrotrope solution of known concentration were taken in a separating funnel of 500 ml volume. The separating funnel was immersed in a constant temperature water bath which could control the temperature within ±1 °C. The set up was kept overnight for attaining equilibration. After equilibrium was attained the aqueous layer was carefully separated from the solute layer and analyzed to quantify the concentration using HPLC (Manufacturer - Varian, Inc. USA; Type - 940lc) with the following conditions: LC mode, normal phase chromatography; packing material, silica gel; mobile phase, n-Hexane/IPE; interaction, adsorption.

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 rpm 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 mass transfer 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 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, 250 ml of the ethylbenzene was added to 250 ml of hydrotrope solution of known concentration. The sample was then agitated for a known time of 600, 1200, 1800, and 2,400 seconds. After the end of fixed time t, the entire mixture was transferred to a separating funnel. After standing for 1 hour, the aqueous layer was carefully separated from the ethylbenzene layer. The concentration of the solubilized ethylbenzene in aqueous hydrotrope solutions at time t was analyzed as done for solubility determinations based on the equation,

$$-\log[1 - C_b/C^*] = [k_L a/2.303] \times [T] + c \quad (5)$$

A plot of $-\log[1 - C_b/C^*]$ versus t was 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 [18,19]. 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

1. Solubility

Experimental data on the effect of hydrotropes, i.e., urea, nicotinamide, sodium salicylate on the solubility of ethylbenzene are plotted in Figs. 1-3. Sodium salicylate is one of the hydrotropes used in this study. The solubility of ethylbenzene in water at 303 K in the absence of any hydrotrope is 1.523×10^{-3} mol·L^{-1} (Fig. 1). It was observed that the solubility of ethylbenzene in water did not show any considerable increase even up to a concentration of 0.30 mol·L^{-1} of sodium salicylate in the aqueous phase. Increasing the concentration of sodium salicylate in a subsequential manner above 0.30 mol·L^{-1}, the solubility of ethylbenzene in water was found to

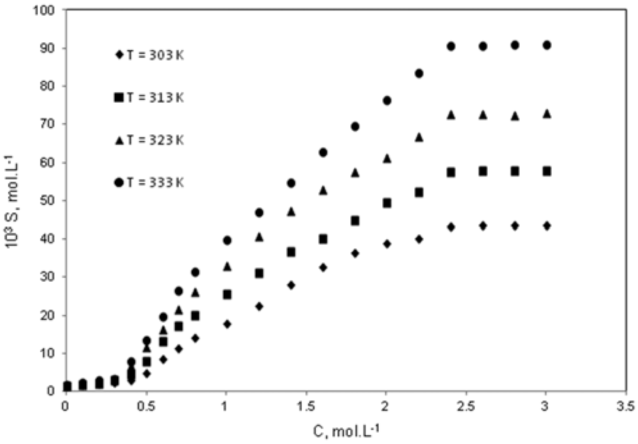

Fig. 1. Effect of sodium salicylate concentration (C) on the solubility (S) of ethylbenzene at different temperatures.

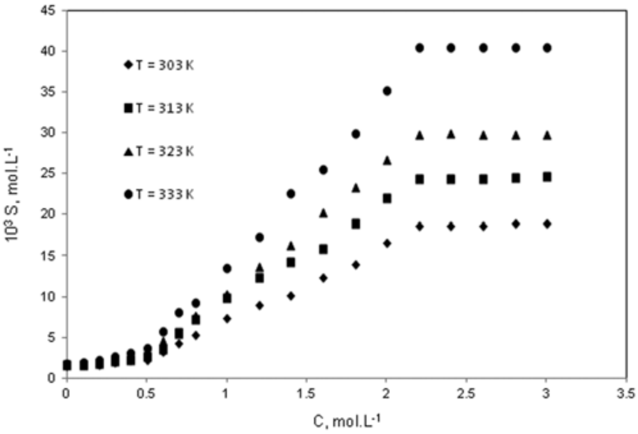

Fig. 2. Effect of urea concentration (C) on the solubility (S) of ethylbenzene at different temperatures.

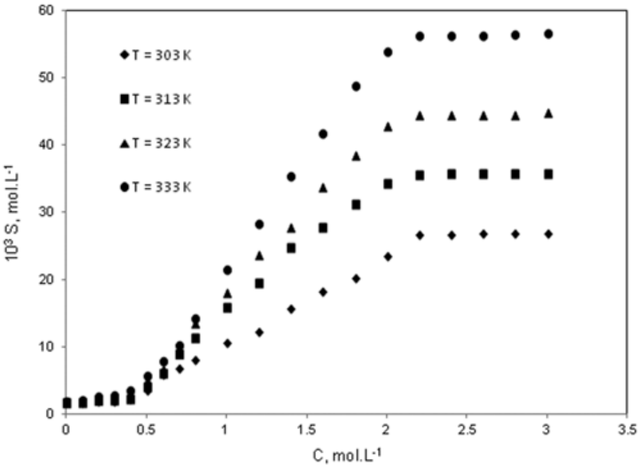

Fig. 3. Effect of nicotinamide concentration (C) on the solubility (S) of ethylbenzene at different temperatures.

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

Hydrotropes	MHC, mol·L^{-1}	C_{max}, mol·L^{-1}
Urea	0.50	2.20
Nicotinamide	0.40	2.20
Sodium salicylate	0.30	2.40

increase significantly. This concentration of sodium salicylate in the aqueous phase, i.e., 0.30 mol·L^{-1} (Table 1), is termed as the minimum hydrotrope concentration (MHC), which is the minimum required sodium salicylate (hydrotrope) concentration in the aqueous phase above which the solubility of ethylbenzene in water increases reasonably. It has been observed that the MHC of sodium salicylate 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. 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 ethylbenzene on dilution with water below MHC. 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 hydrotrope (Fig. 1). In the present case, a clear increasing trend in the solubility of ethylbenzene was observed above MHC of sodium salicylate. This increasing trend was sustained up to a certain concentration of sodium salicylate in the aqueous phase, beyond which there was no appreciable increase in the solubility of ethylbenzene. This concentration of sodium salicylate (hydrotrope) in the aqueous phase is referred to as the maximum hydrotrope concentration (C_{max}). The C_{max} values of urea, nicotinamide, and sodium salicylate with respect to ethylbenzene are 2.20, 2.20, and 2.40 mol·L^{-1} (Table 1), respectively. From the analysis of the experimental data, further increase in the concentration of hydrotrope above C_{max} does not bring any appreciable increase in the solubility of ethylbenzene even up to 3.00 mol·L^{-1} of sodium salicylate 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 the C_{max} value of a hydrotrope in most cases. The values of MHC and C_{max} of a hydrotrope with respect to ethylbenzene may be beneficial in determining the recovery of the dissolved ethylbenzene even to the 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.

From the experimental data plotted in Fig. 1, as the temperature increases, the concentration of sodium salicylate hydrotrope required in the aqueous phase to achieve a particular solubility of ethylbenzene is considerably decreased.

In the concentration range of sodium salicylate between 0.00 and 3.00 mol/L, three different regions (Region # 1: Concentration=0.00 mol·L^{-1} to 0.30 mol·L^{-1}, Region # 2: Concentration=0.30 mol·L^{-1} to 2.40 mol·L^{-1}, Region # 3: Concentration=2.40 mol·L^{-1} to 3.00 mol·L^{-1}) were observed. The increase in solubility was found inactive below MHC of 0.30 mol·L^{-1}, above which shows unprecedented increase in the solubility of ethylbenzene till C_{max} of 2.40 mol·L^{-1}, and beyond which there is no further solubilization effect of hydrotrope. Therefore, sodium salicylate was found to be an effective hydrotrope in Region # 2, towards ethylbenzene. Also, the solubilization effect of sodium salicylate was not a linear function of the concentration of the sodium salicylate solution. A similar trend in the solubilizing effect of sodium salicylate was observed at increased system temperatures, 303, 313, 323, 333 K, with the values of MHC, and C_{max} remaining unaltered even at higher temperatures. The solubilization effect of sodium salicylate increases with increase in hydrotrope concentration and also with system temperature. The enhancement factor, widely referred to as *Φ* factor, resembles the increase in solubility in terms of folds. The maximum enhancement factor values enumerated for solubility (Φ_s) for the ethylbenzene+water system in the presence of various hydrotropes at 303, 313, 323 and 333 K (Table 2) were calculated using the equation,

$$\Phi_s = S_{max}/S_o \qquad (6)$$

Where,

S_{max}=the maximum solubility value in the presence of hydrotropes at different system temperatures

S_o=the solubility value in the absence of a hydrotrope at different system temperatures

The maximum solubilization enhancement factor (Φ_s) was affected by various hydrotropes for ethylbenzene range between 12.227 and 52.561. The highest value of Φ_s has been observed to be 52.561 folds, in case of sodium salicylate at a system temperature of 333 K (Table 2). A similar trend has been observed in the solubilization effect of other hydrotropes, namely, urea, and nicotinamide.

2. Mass-transfer Coefficient

This section is concerned with a study on the effect of hydrotropes on the mass-transfer coefficient of ethylbenzene in water in the presence of hydrotropes. For this purpose, an agitated vessel was used. The mass-transfer coefficient of the ethylbenzene+water system in the absence of any hydrotrope was determined as 1.05×

Table 2. Maximum enhancement factor for solubility (Φ_s) of ethylbenzene

Hydrotropes	Temperature, K	10^3, S_o mol·L^{-1}	10^3, S_{max} mol·L^{-1}	Φ_s
Urea	303	1.523	18.622	12.227
	313	1.546	24.369	15.763
	323	1.628	29.725	18.259
	333	1.723	40.512	23.512
Nicotinamide	303	1.523	26.625	17.482
	313	1.546	35.509	22.968
	323	1.628	44.369	27.254
	333	1.723	56.154	32.591
Sodium salicylate	303	1.523	43.325	28.447
	313	1.546	57.541	37.219
	323	1.628	72.623	44.609
	333	1.723	90.562	52.561

Table 3. Effect of hydrotrope concentration (C) on the mass-transfer coefficient (k_La) of ethylbenzene

Hydrotropes	C, mol·L^{-1}	10^5 k_La, s^{-1}	Enhancement factor for mass-transfer coefficient, Φ_{mtc}
Urea	0.00	1.05	-
	0.30	1.21	1.14
	0.40	1.36	1.30
	0.50	1.55	1.48
	0.60	2.15	2.05
	1.00	2.99	2.85
	1.40	5.84	5.56
	1.80	7.09	6.75
	2.20	10.51	10.01
	2.40	10.52	10.02
Nicotinamide	0.00	1.05	-
	0.30	1.24	1.18
	0.40	1.35	1.29
	0.50	2.62	2.50
	0.60	3.87	3.69
	1.00	7.23	6.88
	1.40	10.57	10.07
	1.80	15.79	15.04
	2.20	18.82	17.90
	2.40	18.84	17.94
Sodium salicylate	0.00	1.05	-
	0.30	2.89	2.75
	0.40	2.92	2.78
	0.50	3.26	3.10
	0.60	4.58	4.36
	1.00	9.76	9.30
	1.40	16.28	15.50
	1.80	22.85	21.76
	2.20	25.39	24.18
	2.40	28.87	27.50

Table 4. Effect of minimum hydrotrope concentration (MHC), standard gibbs free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) of ethylbenzene

Hydrotropes	Temperature, K	MHC (by solubility), 10^3 S, mol·L^{-1}	ΔG^o, kJ·mol^{-1}	ΔH^o, kJ·mol^{-1}	ΔS^o, kJ·mol^{-1}·K
Urea	303	2.251	−15.359	−12.901	0.0081
	313	2.564	−15.527	−13.766	0.0056
	323	3.312	−15.335	−14.660	0.0021
	333	3.627	−16.083	−15.582	0.0015
Nicotinamide	303	2.232	−15.38	−12.366	0.0099
	313	2.241	−15.877	−13.196	0.0086
	323	2.869	−15.721	−14.053	0.0052
	333	3.522	−15.64	−14.936	0.0021
Sodium salicylate	303	2.451	−15.144	−7.633	0.0248
	313	3.024	−15.097	−8.146	0.0222
	323	3.205	−15.423	−8.674	0.0209
	333	3.351	−15.778	−9.220	0.0197

10^{-5} s^{-1} (Table 3). The effect of different hydrotropes on the mass-transfer coefficient of ethylbenzene at different hydrotrope concentrations is also given in the same table. It can be seen that a threshold value, i.e., 0.30 mol·L^{-1}, which is nothing but MHC of sodium salicylate for ethylbenzene, is to be maintained to have significant enhancement in the mass-transfer coefficient of ethylbenzene+water system as observed in the case of solubility determinations. The mass-transfer coefficient of the ethylbenzene+water system increases with increase in sodium salicylate concentration. As observed in the case of solubility determinations, there is no considerable increase in the mass-transfer coefficient of ethylbenzene, further beyond the maximum hydrotrope concentration of 2.40 mol·L^{-1}. The maximum enhancement factor for the mass transfer coefficient (Φ_{mtc}, ratio between the mass transfer coefficient (k_La) values in the presence and absence of hydrotropes) of the ethylbenzene+water system in the presence of sodium salicylate was found to be 27.50 (Table 3). These observations suggest that an increase in mass-transfer coefficient is found to occur upon increased solubilization. A similar trend in mass-transfer enhancement (Φ_{mtc}) of ethylbenzene has been observed for other hydrotropes, namely, urea and nicotinamide.

3. Aggregation Characteristics of Hydrotropes

The change in enthalpy, entropy and free energy accompanying the aggregation of hydrotropes such as urea, nicotinamide and sodium salicylate under a wide range of hydrotrope concentrations [(0.00 to 3.00) mol·L^{-1}] and different system temperatures (303 to 333 K) have been determined and presented in Table 4. The calculations are based on Eqs. (1), (2) and (3).

Fig. 4 shows the relationship between the standard free energy of both the hydrotropes and the temperature. The general trend of Gibbs free energy was found to be decreased with increase in temperature, by observing the first and the last value of the Gibbs free energy corresponding to initial and final temperature as reported in Table 4. With reference to standard enthalpy calculation, 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 (Fig. 5). The values of enthalpy are negative, which indicates the aggregation behavior of exothermic nature. Regarding entropy change, in all cases it is positive, which confirms that aggregation of hydrotropes is favored entropically. However, the values decrease with increasing temperature as seen from Table 4. This may be because self-aggregation becomes poor at higher temperature due to enhanced molecular motion at increased temperature.

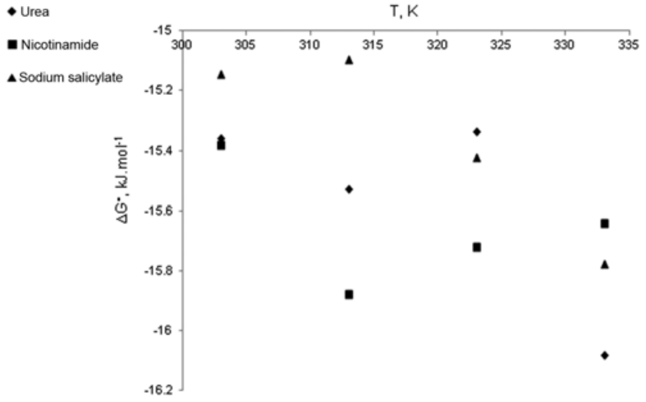

Fig. 4. Temperature (T) versus standard Gibbs free energy (ΔG°).

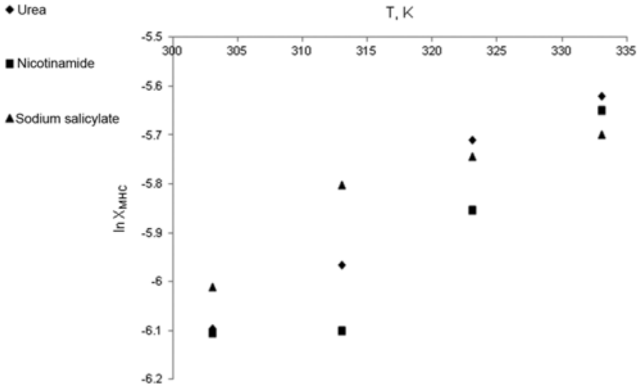

Fig. 5. Temperature (T) versus ln(X_{MHC}).

Table 5. Setschenow constant [K_s] values of hydrotropes with respect to ethylbenzene

Temperature, K	Setschenow constant, K_s		
	Urea	Nicotinamide	Sodium salicylate
303	0.540	0.598	0.594
313	0.575	0.667	0.609
323	0.561	0.661	0.645
333	0.616	0.668	0.682

4. Effectiveness of Hydrotropes

The Setschenow constant values for hydrotropes urea, nicotinamide and sodium salicylate for ethylbenzene - water system at different system temperatures are calculated in order to ascertain the effect of hydrotropes. The obtained values are presented in Table 5. The highest value observed was 0.682 in the case of sodium salicylate as hydrotrope at 333 K.

CONCLUSIONS

The solubility of ethylbenzene, which is practically insoluble in water, has been increased by a maximum enhancement factor of 52.561, with the corresponding increase in the mass transfer coefficient of ethylbenzene has been increased to a maximum value of 28.87 in the presence of sodium salicylate as hydrotrope at 303 K. This would be much useful in increasing the rate of output of the desired product made from ethylbenzene. 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 ethylbenzene can be used for the recovery of the dissolved ethylbenzene 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 solubilized ethylbenzene from its solution. Hence sodium salicylate is found to be the best suitable hydrotrope as it is more effective for the enhancement of solubility and mass transfer coefficient of poorly soluble ethylbenzene within the framework of the present investigation.

NOMENCLATURE

C : concentration [mol·L^{-1}]
C_{max} : maximum hydrotrope concentration [mol·L^{-1}]
k_La : mass transfer coefficient [s^{-1}]
K_s : Setschenow constant [-]
S : solubility [mol·L^{-1}]
T : temperature [K]
t : time [s]
Φ_s : maximum enhancement factor for solubility [-]
Φ_{mtc} : enhancement factor for mass-transfer coefficient [-]
ΔG^o : Gibbs free energy [kJ·mol^{-1}]
ΔH^o : standard enthalpy change [kJ·mol^{-1}]
ΔS^o : standard entropy change [kJ·mol^{-1}·K]

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