International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:3, No:9, 2009

Thermodynamic Study for Aggregation Behavior of Hydrotropic Solution

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***Abstract*—**Aggregation behavior of sodium salicylate and sodium cumene sulfonate was studied in aqueous solution at different temperature. Specific conductivity and relative viscosity were measured at different temperature to find minimum hydrotropic concentration. The thermodynamic parameters (free energy, enthalpy and entropy) were evaluated in the temperature range of 30°C-70°C. The free energy decreased with increase in temperature. The aggregation was found to be exothermic in nature and favored by positive value of entropy.

***Keywords*—**Hydrotropes, Enthalpy, Entropy, Free Energy, Minimum Hydrotropic Concentration.

I. INTRODUCTION

HYDROTROPES are mild surface active amphiphilic organic salts with hydrophobic part comparatively smaller than that of a conventional surfactant. Hydrotropes exhibit a higher and often more selective ability to solubilize guest molecules. The self aggregation of the hydrotropes has been considered to be a pre-requisite for a number of applications in various fields such as drug solubilization [1], chemical reactions [2], separation of organic compounds [3], extraction of curcuminoids from turmeric [4],piperine from *Piper nigrum* [5] and boswellic acids from *Boswellia serrata* resins [6]. The studies carried out on individual hydrotropes or surfactant-hydrotrope mixtures support the fact that hydrotropes are capable of forming self-aggregates in the aqueous solutions above a certain minimum concentration known as minimum hydrotrope concentration (MHC), analogous to critical micellar concentration (CMC) for surfactants [7,8]. Since, hydrotropes have poor hydrophobic characteristics, i.e. a shorter hydrocarbon chain length as compared to that of surfactants, they show aggregating tendency at much higher concentrations [9]. Medium and long chain surfactants have been extensively studied for their thermodynamic properties [10,11]. However, similar properties of aqueous hydrotropic solutions have not been explored to the same extent although hydrotropes are routinely used for detergent formulations. The general objective of the present work is to investigate the properties of aqueous solutions of sodium cumene sulfonate (NaCS) with particular emphasis on the effect of temperature.

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II. EXPERIMENTAL

A. Materials

Sodium salicylate (NaSal) was purchased from M/s S. D. Fine Chemicals, Mumbai. Sodium cumene sulfonate (NaCuS) was obtained from M/s National Chemicals, Baroda. All the chemicals were used as such. For preparation of aqueous solution, deionized water from Millipore Elix 3 Century Distillation System, Millipore, USA was used.

B. Methods

i. Conductance

Specific conductivity of hydrotropes in water and aqueous salt solution was made with a digital conductivity meter (HACH, USA) at a temperature of 30 and 35°C. All the measurements were done in constant temperature water bath at equilibrium temperature.

ii. Relative Viscosity

Viscosity of hydrotropic solution was measured using Oswald viscometer. The efflux time was measured at different temperatures ranging from 30°C to 80°C. All the measurements were done in constant temperature water bath. The efflux time was measured after achieving temperature equilibrium.

III. RESULT AND DISCUSSION

A. Conductance

Specific conductivities of NaSal and NaCuS at 30°C and 35°C are shown in Figs. 1 and 2, respectively. In case of NaSal, minimum hydrotropic concentration (MHC) is found to be 0.609 M. MHC of NaCuS is reported in Table I.

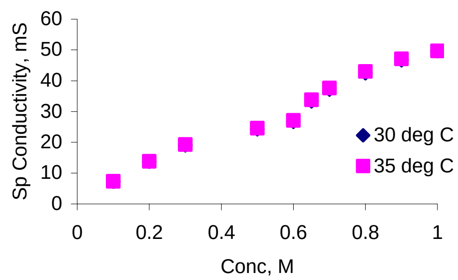

Fig. 1 Specific conductivity versus concentration of NaSal at different temperature

B. *Relative Viscosity*

The relative viscosities for NaSal and NaCuS, in the temperature range of 30°C to 70°C are shown in Figs. 3 and 4, respectively. Unlike NaSal, NaCuS does not show a sharp break at MHC. With increase in temperature the slope of the curve keeps on changing.

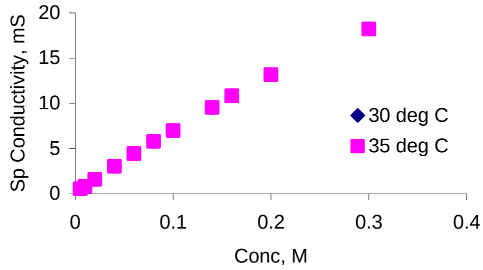

Fig. 2 Specific conductivity versus concentration of NaCuS at different temperature

At 80°C, the change in slope is so negligile that the MHC of NaSal can not be measured. The increase in temperature causes increase in molecular motion causing the poor aggregation of hydrotrope molecules at the interface resulting in negligible change in the slope of the curve. Same is the case with NaCuS. No sharp break in curve was observed at any temperature of NaCuS. The MHCs found are shown in Table II.

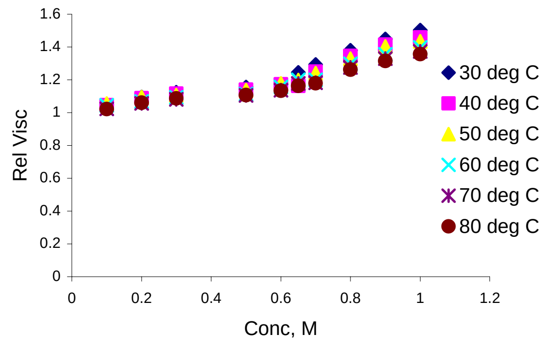

Fig. 3 Relative viscosity versus concentration of NaSal at different temperature

The high values of MHC suggest that the self aggregation of hydrotropes molecules might not be as cooperative as with micellar surfactants [12]. Also, the MHC of a hydrotrope is considered as a measure of the stability of its micellar form relative to its monomeric form. The lower the MHC, the greater is the stability. Increase in temperature causes increase in MHC, thus decreasing stability.

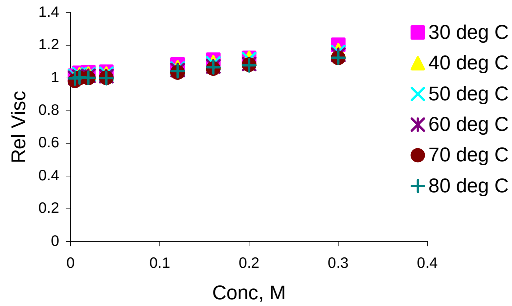

Fig. 4 Relative viscosity versus concentration of NaCuS at different temperature

C. *Aggregation Characteristics at Different Temperature*

The change in enthalpy, entropy and free energy accompanying the aggregation of NaSal and NaCuS were further determined by the standard equations. The calculation is based on the MHC found using relative viscosity in case of NaSal and for NaCuS, it is MHC using conductance. Using the charged pseudo-phase model, the standard free energy (ΔG^o) of aggregation per mole of hydrotropes is given by

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

Fig. 5 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 I and II.

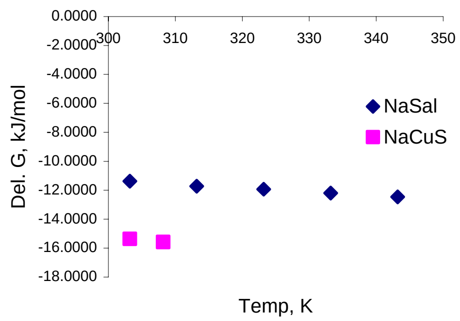

Fig. 5 Standard gibbs free energy versus temperature

The standard enthalpy (ΔH^o) of aggregation can be found by the Van't Hoff equation,

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

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 Fig. 6. The values of enthalpy are negative which indicates the aggregation behaviour of exothermic nature. Similar results were reported for cationic surfactants viz.

tetradecyltrimethylammonium bromide ($C_{14}TABr$) and tetradecyltriphenylphosphonium bromide ($C_{14}TPBr$) [13].

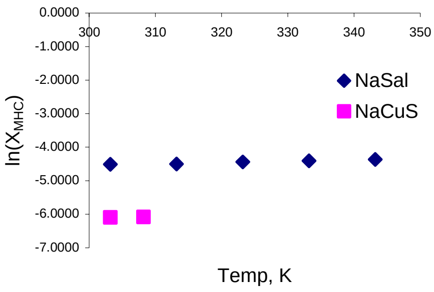

Fig. 6 ln(X_{MHC}) versus temperature

The standard entropy (ΔS^o) of aggregation was calculated from

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

The entropy change in all cases is positive which confirms that aggregation of hydrotropes is favored entropically. However, the values are decreasing with increasing temperature as seen from Table I and II. The reason might be: self aggregation becomes poor at higher temperature because of enhanced molecular motion at increased temperature [14].

TABLE I
THE MHC, STANDARD GIBBS FREE ENERGY, STANDARD ENTHALPY AND ENTROPY FOR NACUS AT DIFFERENT TEMPERATURE

Temperature, K	MHC, M (by conductance)	ΔG^o, kJ/mol	ΔH^o, kJ/mol	ΔS^o, kJ/mol
303.2	0.1254	-15.3675	-2.2936	0.0431
308.2	0.1273	-15.5825	-2.3699	0.0429

TABLE II
THE MHC, STANDARD GIBBS FREE ENERGY, STANDARD ENTHALPY AND ENTROPY FOR NASAL AT DIFFERENT TEMPERATURE

Temperature, K	MHC, M (by relative viscosity)	ΔG^o, kJ/mol	ΔH^o, kJ/mol	ΔS^o, kJ/mol
303.2	0.6167	-11.374	-2.9573	0.0473
313.2	0.623	-11.723	-3.1556	0.0475
323.2	0.6625	-11.934	-3.3604	0.0473
333.2	0.6875	-12.2019	-3.5715	0.0473
343.2	0.714	-12.4615	-3.7891	0.0474

IV. CONCLUSION

Relative viscosity is one of the properties found useful in case of sodium salicylate to study thermodynamic stability. From the data obtained by this study, it is found that sodium salicylate gives self aggregation at higher minimum concentration compared to micellar surfactants. However, the aggregation is stable upto 70 °C. In case of sodium cumene sulfonate, relative viscosity does not provide clear indication of minimum hydrotropic concentration. Conductivity measurement provided minimum hydrotropic concentration of sodium cumene sulfonate at 30°C and 35°C and, hence, stability information.

NOMENCLATURE

R: Universal gas constant (8.31451 J/(mol.K)
T: Temperature (K)
X_{MHC}: Minimum hydrotropic concentration in mole fraction unit

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