Effect of *n*-Alkylamines on Micellization of Aqueous Sodium Dodecyl Sulphate Solutions through Ultrasonic Measurements

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Abstract: Acoustical studies are undertaken in 0.025 m aqueous solution of SDS with the addition of *n*-alkyl amines (ethylamine, diethyl amine and triethyl amine) at various concentrations ranging from 0.01 to 0.05 molar at 303 K. From the measured values of velocity, density, viscosity and observed absorption $(\alpha/f^2)_{obs}$, various other parameters such as compressibility, free length, free volume, relative association, Rao's constant, classical absorption $(\alpha/f^2)_{cl}$, excess absorption $(\alpha/f^2)_{ex}$, volume viscosity and relaxation time are calculated and reported. The results indicate that the addition of amines to the surfactant activates the micellar growth and leads to solubilization of shorter chain amines.

Introduction

Amphiphilic molecules like surfactants exhibit several special properties, such as critical micelle concentration (CMC), aggregation number, size and shape of the micelle and degree of micelle dissociation, because of their ability to undergo co-operative and non co-operative aggregation in aqueous system. Such properties are modified by the addition of substances such as, salts or non electrolytes (alcohols, urea, amine *etc*.)[1-4], these additives can affect in many ways to delicate balance of hydrophilic and hydrophobic interactions of micelle forming surfactants.

Considerable attention has been paid in recent years to the influence of amines on ionic micellar structures, partly because they are the co-surfactants most commonly employed in the preparation of micro emulsions. In the present investigation ultrasonic method is used for obtaining dynamic information and reactions occurring in the aqueous micellar solutions (0.025 m) of sodium dodecyl sulphate in the presence of co-surfactant amines. The second cmc of SDS in water was found to be 0.025 m, which is in agreement with the literature value[5].

Experimental

Sodium dodecyl sulfate (SDS), [$C_{12}H_{25}O_4SNa$] 99% and amines were obtained from Sigma and were used as received**.** The sample solutions containing various concentrations of *n*-alkylamines were prepared by adding 0.01 to 0.05 molar concentrations of ethylamine, diethylamine and triethylamine in 0.025 m aqueous solution of SDS.

The ultrasonic velocity and absorption measurements were carried out using a Pulse echo overlap technique at a fixed frequency of 10 MHz .This is a most widely used techniques for the study of ultrasonic propagation in liquids and solids. The values of density and shear viscosity of different concentrations were measured using specific gravity bottle and Ostwald's viscometer respectively. All the measurements were carried out at 303 K by maintaining the temperature constant by circulating water from a thermostatically controlled (±0.1 °C) water bath.

Results and Discussion

In the present study, the ultrasonic velocity, absorption, density and viscosity measurements were carried out in 0.025m aqueous solution of SDS with addition of amines (ethylamine, diethylamine and triethylamine) at different concentrations**.**

Employing the measured values of velocity (U), density (ρ) and viscosity (η) and ultrasonic absorption, some acoustical parameters can be computed through the following expression[6,7].

Adiabatic compressibility	: $\beta_{ad} = [U^2\rho]^{-1}$	(1)
Free length	: $L_f = K_T [\beta_{ad}]^{1/2}$	(2)
Free volume	: $V_f = [M_{eff} U/ K\eta]^{3/2}$	(3)
Rao's number	: $R = U^{1/3}V$	(4)
Relative association	: $RA = [\rho/\rho_0][U_0/U]^{1/3}$	(5)
Classical absorption	: $(\alpha/f^2)_{cl} = 8\pi^2\eta / 3\rho U^3$	(6)
Excess absorption	: $(\alpha/f^2)_{ex} = (\alpha/f^2)_{ob} - (\alpha/f^2)_{cl}$	(7)
Relaxation time	: $\tau = \beta_0[\eta_v+(4/3)\eta_S]$	(8)
Volume viscosity	: $\eta_v = (4/3)\eta_s[((\alpha/f^2)_{ob}-(\alpha/f^2)_{cl})/(\alpha/f^2)_{cl}]$	(9)

Where, ρ, V ,η_S ,U_0 and K_T are the density, molar volume, shear viscosity, ultrasonic velocity of water and Jacobson constant for different temperatures respectively. Then these parameters are correlated with concentration(c) and are tabulated in the Tables 1 and 2.

From the tables it is observed that ultrasonic velocity increases with increase in concentration. The adiabatic compressibility decreases with increase in concentration. A change of slope is observed between 0.03 and 0.04 molar concentration of amines. The ultrasonic absorption increases with amine concentration and a change of slope is observed above 0.03 molar concentrations.

The above changes can be explained on the basis of effect of co-surfactant on the micellar aggregate. If an additive is surface active to a hydrocarbon/water interface, it will be mainly partitioned near to the micellar palisade layer and will promote the micellar growth[8]. The amines have a high possibility of becoming embedded between the monomers that comprise a micelle. The presence of amine between head groups of similar charge reduces the electrostatic repulsion between the head groups, leading to a decrease in the surface area occupied per surfactant head group[9]. Thus the amine in aqueous SDS should have a tendency to form large micelles above 0.03 molar concentrations, as is indeed indicated by the observed rise in velocity and viscosity on addition of amines to 0.025 m SDS in micellar solutions.

The break pronounced above 0.03 m concentration, is an indicative of specific interaction between the amine and the anionic surfactant head group at the micellar interface.

Table 1. Ultrasonic velocity and related parameters of n-alkylamines in the micellar solution of sodium dodecyl sulphate at 303 K

Conc. moles/ L	U ms^{-1}	ρ kgm^{-3}	ηx10^3 Nsm^{-2}	β_{ad} x 10^{10} N^{-1}m^2	L_f Å	V_f x 10^8 m^3 mol^{-1}	R x10^3	RA x10^3
ethylamine in 0.025 m aqueous solution of SDS
0.01	1513.4	994.1	0.7752	4.3918	0.4191	2.3752	203.49	997.59
0.02	1514.4	994.5	0.7798	4.3843	0.4187	2.3572	203.57	997.77
0.03	1514.9	994.7	0.7855	4.3805	0.4185	2.3334	203.64	997.85
0.04	1515.4	994.9	0.7930	4.3768	0.4184	2.3201	203.70	997.92
0.05	1516.8	995.1	0.8140	4.3679	0.4179	2.2146	203.71	997.81
diethylamine in 0.025 m aqueous solution of SDS
0.01	1506.3	993.8	0.7838	4.4349	0.4211	2.3205	203.33	998.76
0.02	1507.0	994.5	0.7885	4.4269	0.4208	2.3029	203.37	999.35
0.03	1507.1	994.9	0.7891	4.4246	0.4206	2.3017	203.45	999.82
0.04	1507.4	995.3	0.7915	4.4213	0.4205	2.2933	203.53	1000.10
0.05	1509.1	996.9	0.7993	4.4045	0.4197	2.2649	203.65	1001.29
triethylamine in 0.025 m aqueous solution of SDS
0.01	1507.3	993.9	0.7777	4.4285	0.4208	2.3508	203.55	998.75
0.02	1508.4	994.8	0.7949	4.4176	0.4203	2.2796	203.53	999.37
0.03	1509.2	995.5	0.8002	4.4102	0.4200	2.2608	203.64	999.89
0.04	1509.9	996.0	0.8080	4.4034	0.4196	2.2317	203.79	1000.30
0.05	1510.2	996.5	0.8124	4.4000	0.4195	2.2162	203.96	1000.62

Table 2. Ultrasonic absorption and related parameters of *n*-alkylamines in the micellar solution of sodium dodecyl sulphate at 303 K

Conc. moles/ L.	x10^{15} Npm^{-1}s^2			η_v x10^2 Nsm^{-2}	τx10^{11} sec
	$(\alpha/f^2)_{ob}$	$(\alpha/f^2)_{class}$	$(\alpha/f^2)_{exc.}$		
ethylamine in 0.025 m aqueous solution of SDS
0.01	23.884	5.914	17.969	3.139	1.840
0.02	24.861	5.935	18.925	3.314	1.920
0.03	24.952	5.972	18.980	3.327	1.929
0.04	25.382	6.021	19.360	3.398	1.965
0.05	26.689	6.175	20.514	3.604	2.068
diethylamine in 0.025 m aqueous solution of SDS
0.01	25.987	6.067	19.919	3.430	1.973
0.02	26.173	6.089	20.084	3.466	1.992
0.03	26.546	6.090	20.455	3.532	2.021
0.04	26.706	6.156	20.550	3.556	2.038
0.05	27.378	6.133	21.244	3.690	2.097
triethylamine in 0.025 m aqueous solution of SDS
0.01	28.454	6.002	22.451	3.874	2.165
0.02	29.020	6.113	22.906	3.965	2.216
0.03	29.675	6.148	23.526	4.080	2.270
0.04	30.279	6.195	24.083	4.186	2.321
0.05	31.233	6.223	25.009	4.350	2.396

Since, the number density of micelles is high and therefore, the distance between them is decreased with a necessary consequence that counter ions stay in the vicinity of the micellar surface and neutralize the micellar surface charge. It is also clear that in order to reduce the repulsive forces at the micellar surface, the counter ions must be bound firmly to the head group. These two interrelated factors are possibly responsible for the decrease in compressibility and free length and an increase in ultrasonic absorption.

However, it is reported earlier[10] that C_4-C_{10}-*n*-alkylamines are solubilized in micelles by electrostatic and hydrophobic effects with the amine group being left on the surface micelle. This dissociation into $-NH_3^+$ and CH^- may affect the electrostatic interactions with anionic SDS. Thus the amine head group has the ability to sit deeper in the SDS micelle, relieving the requirement of the surfactant tails to reach the center of micelle at a shorter alkyl chain length of additive. This supports the idea that a co-surfactant with the ability to bear a charge opposite to that of a surfactant head group is more effective in the growth of micelle. The variation in the other parameters with concentration also supports the same.

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