

Study of Micellar Behaviour and Viscosity of Anionic (SDS & PDS) and Cationic Surfactants (TTAB & HTAB) in (Alkanol + Toluene) Systems

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Abstract: The surface activity of these materials is due to the structural features of their molecules. The solubility and relative size of polar and non polar part in relation to overall molecular structure determine the surface activity of such substances. CMC is probably the simplest method of characterizing the micellar behaviour of surface active agents (solutes). The viscosity of Sodium decyl sulfate (SDS), Potassium decyl sulfate (PDS) surfactants in alkanol increases with increasing surfactant concentration which may be attributed due to the increasing tendency to form aggregates with increasing concentration of surfactant. The viscosity (η) of cationic surfactants tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) have been measured in a (methanol+Toluene) systems at different temperatures. The CMC values for TTAB in these systems at different temperature have been determined from the viscosity vs. concentration plots. The CMC values obtained by viscosity are in close agreement with those obtained from conductance measurements. The values of molar volume and interaction coefficient have been evaluated from the Vand's equation. The plots of $[\log \eta \text{ vs. } 1/T]$ are found to be linear and the values of ΔH^* have been calculated from the slopes of the linear plots. The values of ΔH^* for methanol+10% toluene systems have been calculated. The values of ΔS^* and ΔG^* have been also calculated for the same systems from Eyring's and Gibb's equation respectively at 40°C. Various activation parameters for fluidity of all the surfactants in methanol + Toluene systems were also calculated.

Keywords: Viscosity, CMC, Micelles, Cationic surfactants, anionic surfactants Fluidity, alcohol-water, alcohol-toluene system, activation parameters.

Introduction

When surfactant is dissolved in solvent, its hydrophobic part causes distortion of solvent fluid thus increasing the free energy of the system. Surfactants therefore concentrate at the interface while hydrophilic group (carrying a negative or positive charge) opposes this process. The aggregation number for nonionic surfactants is usually large in comparison to other category with about hundreds or thousands molecules constituting a micelle. The hydrophobic part of the aggregate forms the core of micelle while polar head group remains in contact with water. These general tendencies lead these substances surface active i.e. their molecules absorb at air-water or oil-water interfaces and to surfaces of non polar solids or to molecules such as proteins. Hydrophobic interactions are primarily responsible for this phenomenon. The shape of micelle changes with surfactant concentration. Increasing concentration of surfactant changes the spherical micelles to cylindrical micelles or lamellar micelles or mesomorphic structures.

Above all CMC parameters vary according to whether the solute is monomer or aggregation. Since above the CMC, the activity of monomers rises very slowly, so it is also a measure of the concentration at which the thermodynamic activity of the monomers and therefore, its net surface activity and absorbability to various substrates, level off to a nearly constant value.

The abrupt changes in the concentration depend upon several properties of surface active agent solutions. This was observed first before 1930's by (1-3). McBain and coworkers (4, 5) developed the concept of micelles in solutions. The existence of CMC was established by Bury and his coworkers (6, 7) and Hartley (8).

Like CMC necessary to form micelle, critical temperature is also necessary over which micellar solutions of surfactants can be formed (9-10). In other words, the characteristic solubility behaviour of surfactants is usually observed in aqueous solutions. Very low values of solubility at low temperature show abrupt rise at certain temperature, known as Krafft point (11). The solubility of surfactant at Krafft point is its CMC value at this temperature. For practical purpose, the use of a surfactant is limited to temperature only above the Krafft point. The increase in solubility at high temperature (above Krafft point) is due to the presence of individual surfactant molecules as aggregates i.e. micelles (12). Formation of micelles above Krafft point can be regarded as liquid phase. At the Krafft point, hydrocarbon chain of surfactants passes as they were into liquid state. Adderson and Taylor (13) observed that the CMC of cationic surfactants in water decreases with increase in chain length of alkyl groups and also observed that three factors contribute to the enthalpy changes of micellization, namely those associated with head group aggregation, those with breakdown of hydrocarbon stabilized water structure and changes due to the transfer of the hydrocarbon to micelles. Surface mixed films of cationic surfactants at aqueous solution/air interface has been studied by Paluch and Korchowiec (14).

Eastoe and coworkers (15) reported the properties of solution of asymmetric chain cationic surfactants. Several authors (16, 17) explained the micelle formation of cationic surfactants in organic solvents (chloroform, dimethyl formide, dimethyl sulphoxide,

formamide, N-methyl acetamide) on the basis of factors like dielectric constant of the medium and hydrogen bonding capability. Akisada and coworkers (18) studied the unusual behaviour of CMC for binary mixture of alkyltrimethylammonium bromide due to the chain length difference. Hato and Shinoda (19) have determined CMC, Krafft point, solubilization etc, of bivalent metal alkyl sulfates. The associative interactions and surface tension in ionic surfactant solution at concentrations is much lower than the CMC was reported by Nikolov and coworkers (20). Moroi and coworkers (21) have also reported CMC of binary mixtures of mono and bivalent metal alkyl sulfates in aqueous solutions. Despite these findings on micellar aggregation of bivalent metal alkyl sulfates in aqueous media, not much is known about their solution properties in polar organic solvents. Some investigation comments on the absence of surfactants micelles in alkanol and suggest that surfactants behave like electrolytes in alkanol. Thermometric titration study on the micelle formation of sodium decylsulfate in water at 15-45°C was reported by Kiraly and Dekany (22). Lawrence and Pearson (23) too concluded that as the chain length of alcohol increases, the tendency to penetrate into the micelle increases. Various techniques have been used to determine the CMC of different metal soaps in aqueous- alkanol systems. These also throw light on the change in the nature of solvent as well as on the nature of micelles from alcomicelles to hydromicelles (alkanol+water mixture) and alcomicelles to oleomicelles (alkanol+benzene mixture).

Materials and Methods

The surface active agents were procured from various organizations. Cationic surfactants tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) used were of high degree of purity (checked by observing no minima in γ vs. $\log C$ plots). The CMC of these surfactants in water were found closer to the literature value (1). Most of the chemicals used in the study were A.R grade, except a few which were laboratory chemicals of high grade purity. These were used after proper purification. The purity of organic liquids was checked by measuring physical constants like boiling point, density, refractive index and viscosity. Triple distilled water and pyrex glass assembly were used throughout the experiment. Fresh solutions of surfactants were employed for all measurements.

Ostwald viscometer was used for measuring the viscosity of solutions. The densities of the solutions were determined with a dilatometer using the relation:

$$D = \frac{\text{weight of solution}}{\text{weight of water}} \times \text{density of water}$$

The dilatometer volume was about 15 ml which allowed an accuracy of about $\pm 0.0002 \text{ g cm}^{-3}$ in data. The accuracy and reproducibility of the data was verified by measuring the densities of pure solvents. The viscosities of the solutions were calculated by the simple relation (i):

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \times \frac{d_1}{d_2} \quad \dots\dots (i)$$

where η_1 , η_2 , t_1 , t_2 , and d_1 , d_2 are coefficients of viscosity, flow time and density of the surfactant solutions and the corresponding solvents respectively. Several equations have been applied in order to test their validity for different surfactants-solvents systems.

Vand's equation:

$$\frac{1}{C} = \left[\frac{0.921}{V} \right]^{-1} \times \left[\frac{1}{\log \frac{\eta}{\eta_0}} \right] + Q.V \quad \dots\dots(ii)$$

Moulik's equation:

$$\left(\frac{\eta}{\eta_0} \right)^2 = M + K^1.C^2 \quad \dots\dots(iii)$$

where $\frac{\eta}{\eta_0}$ represents the ratio of viscosity of solution to the viscosity of solvent, Q and V are the interaction coefficient and molar volume of solute respectively, C being the concentration in mole litre⁻¹, M and K¹ are constants.

Arrhenius's equation:

$$\frac{1}{\eta} = A \exp. \frac{-E_\phi}{RT} \quad \dots\dots(iv)$$

where E_ϕ is the activation energy of viscous flow and A is the constant.

Eyring's equation:

$$\frac{1}{\eta} = \frac{V}{h.N} \exp. \left[-\frac{\Delta G^*}{RT} \right] \quad \dots\dots (v)$$

$$= \frac{V}{h.N} \exp. \left[-\frac{\Delta H^*}{RT} \right]. \exp. \left[\frac{\Delta S^*}{R} \right] \quad \dots\dots(vi)$$

The Arrhenius activation energy (E_ϕ) has been taken as equal to the Eyring energy of activation (ΔH^*) and A has been equated with $\frac{V}{h.N} \exp. \left[\frac{\Delta S^*}{R} \right]$ to obtain the entropy of activation (ΔS^*), V is the molar volume of the solvent, R is the gas constant, h and N are planck's constant and Avogadro's number respectively. Gibbs energy of activation (ΔG^*) is then calculated from Gibb's equation.

Results and Discussion

(i) Anionic surfactants in (Alkanol +Toluene) Systems

The viscosity of PDS in 10% methanol+ toluene mixture has been measured at different temperatures (30-45°C). The results (Table-1) show that the extrapolated values of viscosity for zero surfactant concentration are in close agreement with the corresponding values of solvents at different temperatures. In methanol+toluene system too, the plots of viscosity vs. surfactant concentration

show a break corresponding to the CMC of PDS in these solvent mixtures. The plots of $[1/C \text{ vs. } 1/\log(\eta/\eta_0)]$ and $[(\eta/\eta_0)^2 \text{ vs. } C^2]$ are also found linear for all these systems, in the concentration range above the CMC. The values of molar volume (V), interaction coefficient ($-Q$) and M calculated as above are recorded in **Table-1**. The plots of $\log \eta \text{ vs. } 1/T$ are also linear and the values of enthalpy (ΔH^*) have also been calculated. From the Eyring's equation the values of entropy of activation (ΔS^*) and the Gibbs energy of activation (ΔG^*) from Gibb's equation have also been calculated and are reported in **Table-2**.

TABLE-1

Experimental extrapolated and various viscosity parameters of potassium decylsulfate (PDS) in 10% methanol+toluene systems at different temperature.

Temp.	Experimental (η)	Extraploated (η)	V^-	$-Q$	M
30°C	4.771	4.770	2.162	39.420	1.009
35°C	4.532	4.530	2.302	39.098	1.014
40°C	4.334	4.331	2.674	39.442	1.020
45°C	4.122	4.122	4.148	39.994	1.028

TABLE-2

Activation parameters for fluidity of sodium decylsulfate (SDS) in 10% methanol+toluene system at 40°C.

Conc. of surfactant (mol.litre ⁻¹)	$-\Delta H^*$ kcal mol ⁻¹	$-\Delta S^* \times 10^3$ kcal mol ⁻¹	ΔG^* kcal mol ⁻¹
0.0050	2.118	14.110	2.280
0.0040	1.988	13.922	2.272
0.0030	1.840	13.516	2.262
0.0020	1.790	13.120	2.258
0.0015	1.776	12.992	2.251
0.0010	1.695	12.648	2.248

(ii) Cationic Surfactants in (Alkanol +Toluene) Systems

The viscosity of tetradecyltrimethylammonium bromide has been measured in methanol+10% toluene systems at different temperatures (35-50°C). The CMC has been determined from the intersection of viscosity vs. concentration plots (a representative set of curve is given in **Fig.1**). The CMC values are in complete agreement with conductance measurement. The extrapolated values of viscosity for zero surfactant concentration are in close agreement with the corresponding values of pure solvent and are reported in **Table-3**. The plots of Vand's equation i.e. $[1/C \text{ vs. } 1/\log(\eta/\eta_0)]$ and Mouluk's equations i.e. $[(\eta/\eta_0)^2 \text{ vs. } C^2]$ are linear in concentration range above the CMC. The values of V , $-Q$, and K^1 have been calculated. The values of ΔH^* for methanol+10% toluene systems have been calculated from the linear plots of $[\log \eta \text{ vs. } 1/T]$ and the values are given in **Table 4**. The values of ΔS^* and ΔG^* have been also calculated for the same systems from Eyring's and Gibb's equation respectively at 40°C and the values are given in Table-4 in methanol+10% toluene systems at different temperature.

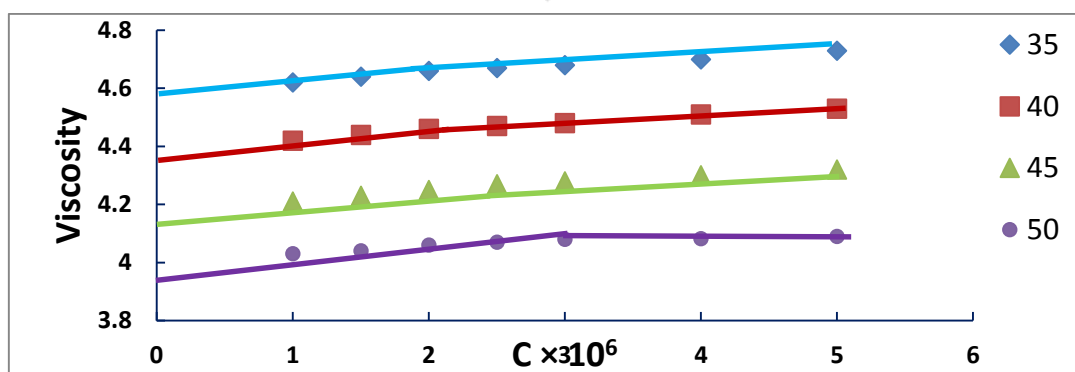


Fig.4: Plots of viscosity (η) vs. molar concentration (C) for TTAB in methanol+10% toluene systems at different temperature.

TABLE-3

Experimental and extrapolated values of viscosity (η) of cationic surfactants in and methanol+10% toluene systems at different temperatures.

Surfactant	System	Experimental	Extrapolated
TTAB	Methanol+10% Toluene		
	35°C	4.550	4.573
	40°C	4.353	4.356
	45°C	4.141	4.178
	50°C	3.957	4.018
HTAB	Methanol+10% Toluene		
	35°C	6.226	6.278
	40°C	6.159	6.198
	45°C	6.054	6.085
	50°C	5.796	5.810

TABLE-4

Various activation parameters for fluidity of cationic surfactant (TTAB) in methanol+10% toluene systems.

Temp. °C	Tested conc. limits in m/l	Valid zone in m/l	Ψ	-Q	M	$K^1 \times 10^2$
TTAB						
35	0.005-0.0005	0.005-0.0025	6.815	48.42	1.044	9.00
40	0.005-0.0005	0.005-0.0025	8.842	45.24	1.052	10.00
45	0.005-0.0005	0.005-0.0025	11.328	41.49	1.060	12.00
50	0.005-0.0005	0.005-0.0025	13.355	31.69	1.067	13.00

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