

Effect of Viscosity of cationic surfactants [tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB)] on Critical Micelle Concentration and Various Activation Parameters in (Methanol+ Water) and (Methanol+ Toluene) Systems

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Abstract

The viscosity (η) of cationic surfactants tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) have been measured in both (methanol+ water) and (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 so obtained are in complete agreement with those obtained from conductance measurements. The values of molar volume and interaction coefficient have been evaluated from the Vand's equation. The values of molar volume and interaction coefficient increase with increase in temperature and number of carbon atom in hydrophobic chain of the surfactant. 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 both the surfactants in methanol + water systems were also calculated.

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

Introduction

Surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase. The aggregation of monomers of surface active agents in some solvents forms particles of colloidal dimensions, called micelles. 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 adsorb 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 enesomorphic 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. Micelle formation of cationic surfactants in alkanols and alkanol+water systems has been reported by many workers (1-3). Bahadur and Chand (4) have studied the effect of additives on dodecylammonium chloride. Conductometric and Fluometric investigation on the mixed micellar systems of cationic surfactants in aqueous media were studied by Moore and coworkers (5). The CMC of TTAB and HTAB in aqueous buffered and unbuffered systems have been reported by Fuguet and coworkers (6). Szymczyk and coworkers (7) measured the surface tension and conductivity of a system containing mixture of CTAB and CPyB. Micelle formation of cationic surfactants in aqueous (8) and non-aqueous media i.e. solvents of low dielectric constants e.g. benzene, xylene, toluene etc. (9) has been reviewed. Adderson and Taylor (10) 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 (11).

Eastoe and coworkers (12) reported the properties of solution of asymmetric chain cationic surfactants. Several authors (13, 14) 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 (15) studied the unusual behaviour of CMC for binary mixture of alkytrimethylammonium bromide due to the chain length difference. Hato and Shinoda (16) 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 (17). Moroi and coworkers (18) 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 15-45⁰C was reported by Kiraly and Dekany (19). 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). Lawrence and Pearson (20) too concluded that as the chain length of alcohol increases, the tendency to penetrate into the micelle increases.

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 $\pm 0.0002 \text{ g cm}^{-1}$ 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:

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

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) In Methanol + water Systems

The viscosity (η) of cationic surfactants tetradecyltrimethylammonium bromide (TTAB) and hexa deecyltrimethylammonium bromide (HTAB) have been measured in 0.5M methanol+water systems at different temperatures (35-50°C). The CMC values for TTAB in 0.5M methanol + water system at different temperature have been determined from the viscosity vs. concentration plots (Fig.1). The CMC values so obtained are in complete agreement with those obtained from conductance measurements.

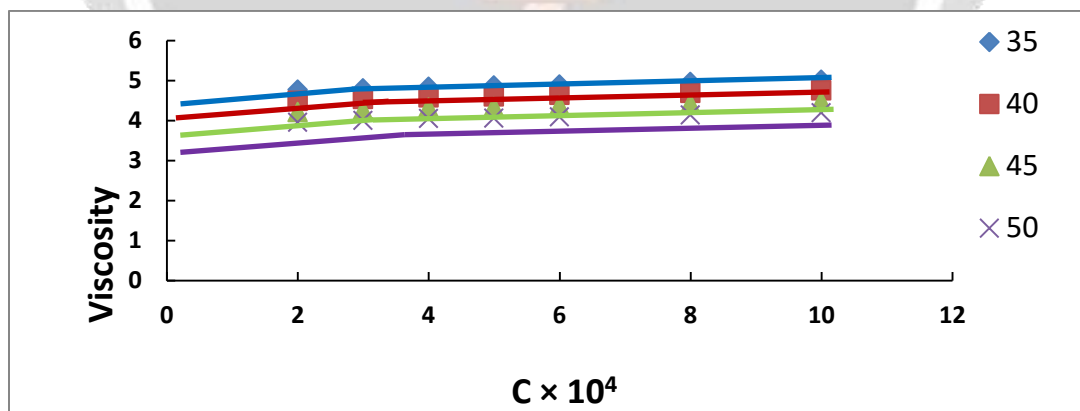


Fig.1: Plots of viscosity (η) vs. molar concentration (C) for TTAB in 0.5M methanol+ water systems at different temperature.

The extrapolated values of viscosity for zero surfactant concentration are in close agreement with the corresponding values of pure solvents and the values of hexadecyltrimethylammonium bromide are higher than the values of tetradecyltrimethyl ammonium bromide (TTAB) in Table-1.

The plots of Vand's equation i.e. $[1/C \text{ vs. } 1/\log(\eta/\eta_0)]$ (Fig.2 for HTAB) and Moulik's equations i.e. $[(\eta/\eta_0)^2 \text{ vs. } C^2]$ (Fig.3 for HTAB) are linear in concentration range above the CMC.

The values of molar volume (V) and interaction coefficient (-Q) have been evaluated from the Vand's equation and the values are given in Table-2. The values of molar volume and interaction coefficient increase with increase in temperature and number of carbon atom (Table-2) in hydrophobic chain of the surfactant.

The values of constants M and K^1 have been calculated from Moulik's equation and the values are given in Table-2. The values of M and K^1 are similar to that of V and K^1 values increase with increase in temperature and number of carbon atom in hydrophobic chain of the surfactant (Table-2).

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 tetradecyltrimethyl ammonium bromide (TTAB) are higher than the values of hexadecyltrimethylammonium bromide (Table-3). The values of ΔS^* and ΔG^* have been calculated from Eyring's and Gibbs equation respectively at 40°C. The value of ΔS^* and ΔG^* have been calculated from the equations (xx and xxi) and values are given in Table-3.

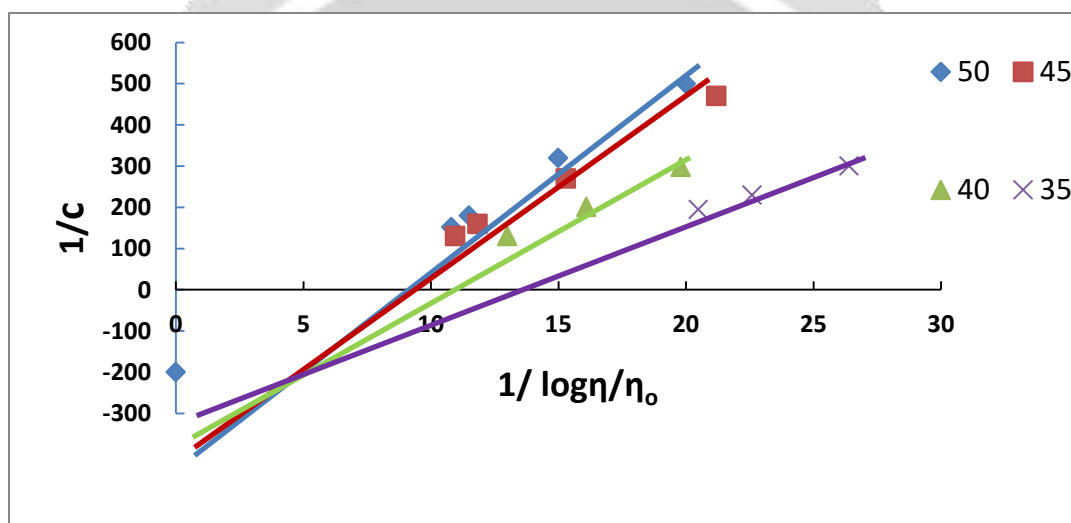


Fig.2: Plots of $1/C$ vs. $1/(\log \eta/\eta_0)$ for HTAB in 0.5M methanol+water systems at different temperature.

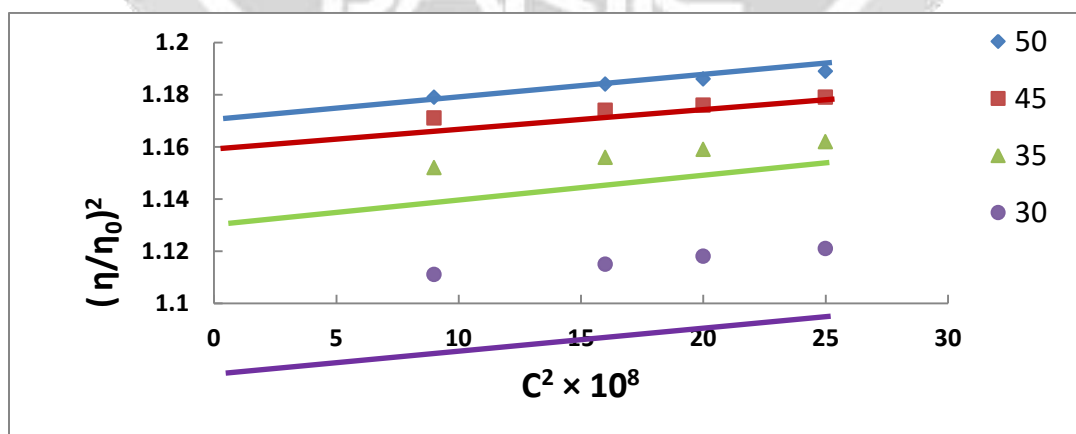


Fig.3: Plots of $(\eta/\eta_0)^2$ vs. C^2 for HTAB in 0.5M methanol+water systems at different temperature.

(ii) In Methanol + 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.4). 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.

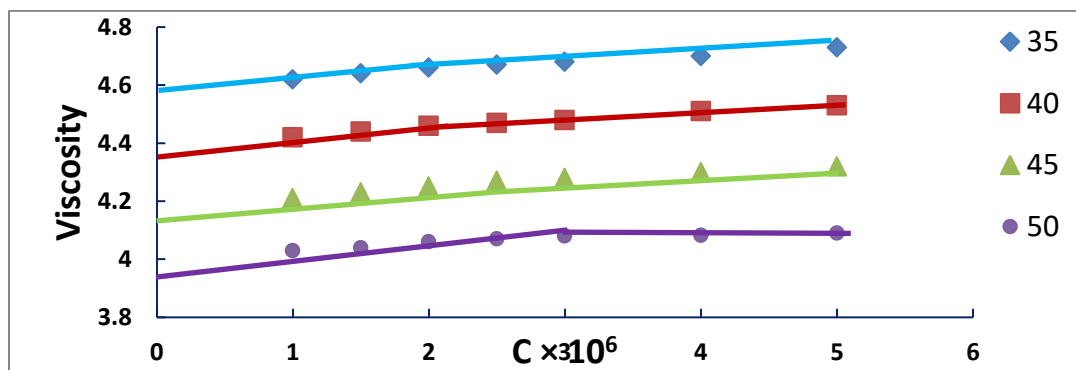


Fig.4: Plots of viscosity (η) vs. molar concentration (C) for TTAB in methanol+10% toluene systems at different temperature.

The plots of Vand's equation i.e. $[1/C \text{ vs. } 1/\log(\eta/\eta_0)]$ and Moulik'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.

TABLE-1

Experimental and extrapolated values of viscosity (η) of cationic surfactants in 0.5M methanol+water systems a different temperatures.

Surfactant	System	Experimental	Extrapolated
TTAB	0.5M Methanol+Water		
	35°C	4.836	4.778
	40°C	4.510	4.218
	45°C	4.213	4.127
	50°C	3.974	3.896
HTAB	0.5M Methanol+Water		
	35°C	6.524	6.446
	40°C	6.325	6.258
	45°C	6.127	6.096
	50°C	5.863	5.765

TABLE-2

Various activation parameters for fluidity of cationic surfactants in 0.5M methanol+water systems.

Temp. °C	Tested conc. limits in m/l	Valid zone in m/l	\bar{V}	$-Q$	M	$K^1 \times 10^2$

TTAB						
35	0.010-0.002	0.010-0.005	4.420	19.223	1.090	4.00
40	0.010-0.002	0.010-0.005	5.709	18.385	1.100	4.50
45	0.010-0.002	0.010-0.005	6.333	18.150	1.105	5.00
50	0.010-0.002	0.010-0.005	7.272	17.875	1.115	5.50
HTAB						
35	0.005-0.0008	0.005-0.003	22.09	8.591	1.100	20.00
40	0.005-0.0008	0.005-0.003	33.15	7.236	1.140	25.00
45	0.005-0.0008	0.005-0.003	40.51	6.412	1.155	30.00
50	0.005-0.0008	0.005-0.003	44.64	6.196	1.170	35.00

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 ^o C	4.550	4.573
	40 ^o C	4.353	4.356
	45 ^o C	4.141	4.178
	50 ^o C	3.957	4.018
HTAB	Methanol+10% Toluene		
	35 ^o C	6.226	6.278
	40 ^o C	6.159	6.198
	45 ^o C	6.054	6.085
	50 ^o C	5.796	5.810

TABLE-4

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

Temp. ^o C	Tested conc. limits in m/l	Valid zone in m/l	∇	-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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