Conductometric and Spectrofluorimetric Studies of Cationic Gemini Surfactant in Aqueous Solutions

Halide Akbaş[1]and İkbal Sarıkaya[2]

***Abstract*—**The critical micelle concentration (cmc) of the cationic gemini surfactant was evaluated using the conductivity measurements. The conductivity as a function of surfactant concentration was measured at different temperatures and the data were used the find cmc and degree of counterion dissociation of the micelle (α). Thermodynamic parameters were also obtained from the temperature dependence of the cmc values. The micelle aggregation numbers (N_{agg}) of cationic gemini surfactant in aqueous medium has been obtained using steady state fluorescence quenching technique. The micropolarity of the systems was also evaluated from the ratio of intensity of peaks (I_1/I_3) of the pyrene fluorescence emission spectrum.

***Keywords*—** cationic gemini surfactant, critical micelle concentration, krafft temperature, aggregation number.

I. Introduction

Surfactants are amphiphilic compounds containing both hydrophobic groups (their tails) and hydrophilic groups (their heads) [1]-[3]. A special class of surfactants, the so-called geminis, are constructed by connecting any two identical or different conventional monomeric amphiphilic moieties with a spacer group [4],[5]. The potential applications of gemini surfactants are in detergents, cosmetics, chemical industry, biological and biomedical fields [6]. Constantly growing interest in the investigation and synthesis of novel dimeric surfactants is a consequence of their superior properties in comparison to conventional surfactants [7]. They are usually much more efficient than the corresponding monomeric surfactants. The critical micelle concentration of a gemini surfactant is typically 10–30 times lower than that of a regular monomeric surfactant with the same hydrocarbon chain length [8]. In view of all these features, they are used in many applications. Therefore, it is important to understand their behavior with other surfactants [9].

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II. Materials and Methods

A. Materials

3-(dimethylamino)-1-propylamine, 1,6 dibromohexane, decanoyl chloride, acetone, chloroform, pyrene, cetylpyridinium chloride.

B.Methods

Synthesis of cationic gemini surfactant

The gemini surfactant was synthesized and purified in our laboratory. The synthesis of the gemini surfactant was realized two steps.

Docanoyl chloride (0.3 mol) was added slowly to 3-(dimethylamino)-1-propylamine (0.3 mol) in chloroform, under dry, under inert atmosphere of nitrogen. The first step product was formed after 24 h. We obtained $C_9H_{19}CONH(CH_2)_3N(CH_3)_2$ colorless, viscous liquid. After first step the cationic gemini surfactant was synthesized by refluxing 1,6dibromohexane with $C_9H_{19}CONH(CH_2)_3N(CH_3)_2$ (molar ratio 1:2) in dry acetone with continuous stirring at 80°C for 24 h. At the end of the two steps we obtained (Fig. 1) cationic gemini surfactant. All the synthesized compounds were characterized with FT-IR, ^1H and ^{13}C NMR.

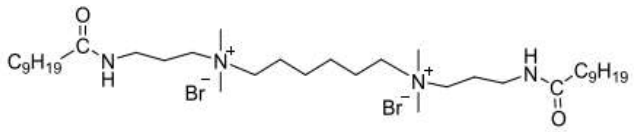

Fig.1 Cationic gemini surfactant

Determination of cmc by conductivity measurements

The conductivity of single and mixed surfactant solutions was measured by a WTW Terminal 740 with cell constant 0.433 cm^{-1} in doubly distilled water at five different temperature (from 303,15K to 323,15K). Conductivity measurements were used to determine the CMC and the α value of the single and mixed surfactant solutions. The conductivity was measured by addition of stock solution successively in pure water. The binary solutions were prepared by mixing the gemini and conventional surfactant

solutions in 1:4;2:3;3:2 and 4:1 ratios. The cmc values were obtained at the break point of the specific conductivity ~ surfactant concentration isotherms.

Determination of Aggregation Number by Fluorescence measurements

The micellar aggregation numbers (N_{agg}) of surfactant solutions were determined using steady-state fluorescence measurements at excitation wavelength of 335 nm. Cetylpyridinium chloride monohydrate was used as a quencher and pyrene as probe. Emission spectra of solutions were recorded in the range 350–450 nm. I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, for the first vibronic peak in the pyrene emission spectra. Aggregation number values were determined by keeping [C_{Surf}] at ten times of cationic gemini surfactant's CMC. The surfactant solution was added and the pyrene concentration was kept at constant 2×10^{-6} M concentration. As the quencher concentration was varied from 0 to 9.10^{-5} M. All the fluorescence measurements were carried out at 25 °C. The micelle aggregation number can be calculated by using the following equation [10]. T The plots give straight lines in all the cases, and the values of N_{agg} are obtained from the slope.

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{agg}[Q]}{[S] - CMC}$$

where [S] is the total surfactant concentration, [Q] is the quencher concentration, and I and I_0 are the fluorescence intensities of pyrene in the absence and presence of quencher, respectively.

III. Results and Discussion

The critical micelle concentration (cmc) and degree of counterion values (α) of cationic gemini surfactant estimated through conductometric experiments, at all the studied temperatures (298.15K, 303.15K, 308.15K, 313.15K, 318.5K, 323.15K) are listed in Table 1. The change of the slope in specific conductivity vs. concentration plot demonstrates that the molecular aggregates or micelles start to form at the concentration corresponding to the break point [11]. An increase in the cmc values can be seen with increasing temperature. As can be seen, the cmc values for the cationic gemini surfactant, were much lower than that DTAB .α is obtained as the ratio of the slope of the linear plot in the post-micellar region to that in the pre-micellar. Various thermodynamic parameters viz., Gibbs energy of micellization (ΔG^o_{mic}), enthalpy of micellization (ΔH^o_{mic}) and entropy of micellization (ΔS^o_{mic}) of the cationic gemini surfactant are calculated from experimental data of conductivity. The ΔG^o_{mic} values are found to be negative in all the cases and listed in Table I. Micellization is affected by temperature as the by temperature as the hydrophobic and hydrophilic interactions change with temperature. The critical micelle concentration versus temperature studies have been performed to obtain information on the interactions. As the temperature increases the degree of hydration of the hydrophilic group decreases, which favors micellization; however, an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group and this is unfavorable to micellization.

TABLE I
VALUES OF EXPERIMENTAL CRITICAL MICELLE CONCENTRATIONS (CMC), MICELLAR DISSOCIATION DEGREE (α) AND THERMODYNAMIC PARAMETERS, OBTAINED FROM EXPERIMENTAL DATA OF CONDUCTIVITY.

Temp.(K)	298.15	303.15	308.15	313.15	318.15	323.15
CMC (mmol/L)	0.96	0.99	1.04	1.11	1.17	1.24
α	0.28	0.30	0.31	0.33	0.35	0.36
ΔG^o_{mic} (kJ/mol)	-46.76	-46.82	-47.08	-47.18	-47.11	-47.10
$\Delta G^o_{m,tail}$ (kJ/mol)	-23.38	-23.41	-23.54	-23.59	-23.55	-23.55
ΔH^o_{mic} (kJ/mol)	-13.73	-14.01	-14.39	-14.75	-15.03	-15.35
ΔS^o_{mic} (kJ/mol)	0.111	0.108	0.106	0.104	0.101	0.100

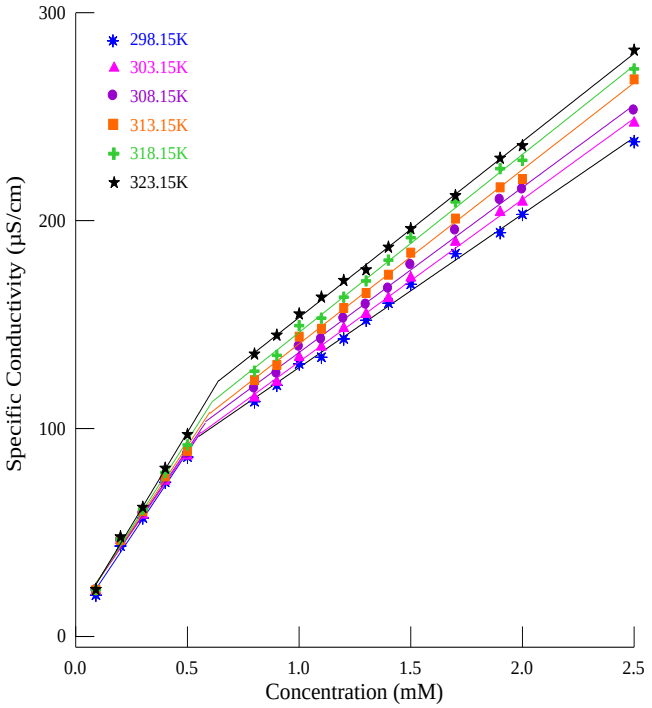

Fig.2 Plots for determination of cmc values of cationic gemini surfactant solutions at different temperature.

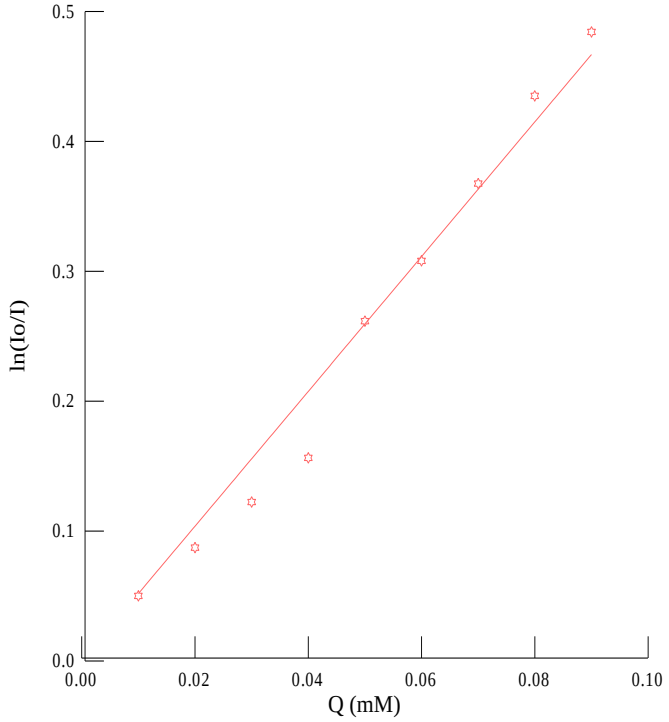

Fig.3 Plots for determination of aggregation number of cationic gemini surfactant.

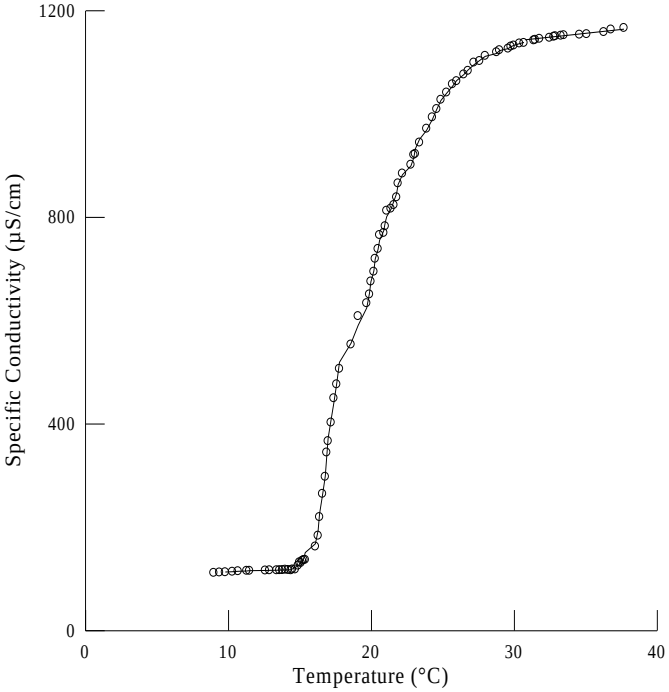

Fig.4 Plots for determination of Krafft Temperature of cationic gemini surfactant solution (%1w/v)

The entropy change is positive in all cases. However, it decreases with increasing temperature. Fig. 3 shows the relationship between Q and $\ln(I_0/I)$ for cationic gemini surfactant. The concentrations of the surfactants used are all 10×cmc. The plots give straight lines in all the cases, and the values of N_{agg} are obtained from the slope of each straight line. The aggregation number of cationic gemini surfactant is found to be 34 and Krafft temperature is found to be 29.6°C.

IV. CONCULUSION

Gemini surfactants are superior in their properties and show better performance over the conventional surfactants. enthalpy of micellization (ΔH^o_{mic}) values become more negative with the rise in temperature, whereas entropy of micellization (ΔS^o_{mic}) values remain roughly constant for most of the systems. The micellization process is exothermic in nature and its magnitude is strongly depend on the temperatures.

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