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Effect of polymers and temperature on critical micelle concentration of some gemini and monomeric surfactants

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Abstract

Effect of polymers on the physicochemical properties of cationic gemini (16-4-16 MEA, 2Br⁻) and monomeric surfactants (cetyldiethylethanolammonium bromide, (CDEEAB) and cetyldimethylethanolammonium bromide (CDMEAB)) have been studied by conductivity measurements. The critical micelle concentration (cmc) value increases by increasing percentage and molecular mass of polymers (poly (ethylene glycol), PEG-X, where X = 400, 600) while it decreases with higher molecular mass (X = 4000, 6000, 20,000). Thermodynamic parameters (standard Gibb's energy (ΔG_m°), enthalpy (ΔH_m°), and entropy (ΔS_m°), of micellization) have also been investigated. Hydrophobic interactions and the ability to form hydrogen bonds play a role in the polymer-surfactant association. This associative behavior was shown to depend significantly on the polymer and surfactant concentrations. The enthalpies of micellization are much more exothermic for the gemini surfactants than for the monomeric surfactants. All of the surfactants exhibited the enthalpy-entropy compensation phenomenon.

Keywords: Polymers; monomeric surfactants; critical micelle concentration; gemini surfactant.

1. Introduction

Polymers have tremendous application in various fields [1-3]. The interaction between polymers and surfactants in aqueous solutions has played a significant role in the field of technological applications and in fundamental research [4-5]. The polymer-surfactants molecules influence the solution and interfacial properties are controlled by the state of their occurrence in aqueous solutions, namely whether they form mixed aggregates in solution and, if so, the nature of their microstructures [6].

It is well known that solutions of mixtures of certain polymers and surfactant can exhibit molecular interactions that may affect the rheological and physicochemical properties of the solution [7]. These interactions also display features that depend on the polymer and surfactant electrical charges, hydrophobicity of the polymer and nonpolar tail of the surfactant, the structural confirmation and the flexibility of the polymers [8-9].

The polymer/surfactant interactions have become a major topic in colloidal research over the past few decades. Much of the interest in this area has stemmed from the numerous possible industrial applications such as pharmaceutical products, thickening agents, coatings, and cosmetic formulations [10-12]. The interactions of water-soluble polymers and ionic surfactants in aqueous solution are of interest from the fundamental standpoint of special structure and dynamics of polymer/surfactant association and can be used in the process of enhanced oil recovery [13-14]. The ability of surfactants to aggregate and form micelles adds a particular dimension to their interactions with water-soluble polymers [15-22].

Gemini surfactants are surface-active agents having two head groups and two tail group linked by a spacer. Gemini are considerably more surface active than conventional monomeric surfactants [23-26]. These surfactants, because of their unique solution properties such as very low CMC, high detergency, high solubilization and high surface wetting capability, possess a wide range of applications such as in mining, petroleum, chemical, pharmaceutical and biochemical research. Gemini are also utilized as catalysts in several organic and inorganic reactions. They are also used as preservatives, anticorrosives and antimicrobial agents [27-30]. Currently, gemini surfactants have also attracted attention as potential gene delivery agents [31-32].

Recently, Janczuk et al. [33] have studied the adsorption properties of nonionic (Triton X-100, 114, 165), anionic (sodium dodecylsulfate) and cationic (tetradecyltrimethylammonium bromide) surfactants at polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE) -water and solution-air interfaces. They observed that the adsorption of surfactants at the PTFE, PMMA-solution and nylon 6-solution interface is lower than that at the

solution–air interface. Wang and his research group [34] have observed the interactions of cationic ammonium gemini surfactant ($C_{12-6-C_{12}} Br^+$) and single-chain surfactant dodecyltrimethylammonium bromide (DTAB) with anionic polyelectrolytes poly(sodium styrenesulfonates) (NaPSS) and poly(sodium acrylates) (NaPAA) with different molar masses by microcalorimetry, turbidity and steady-state fluorescence measurements. They observed that polyelectrolytes show a remarkable interaction with the cationic surfactants. Compared with DTAB, $C_{12-6-C_{12}} Br^+$ can bind to NaPSS and NaPAA at a very low concentration and has stronger interactions with NaPSS and NaPAA. Larson et al. [35] have focused the effect of sodium *n*-dodecyl sulfate (SDS), *n*-dodecyl trimethylammonium chloride (DTAC) of *n*-dodecyl ammonium chloride (DAC) and its headgroup size, charge and structures of poly(ethylene oxide) (PEO) -micelle interaction. They observed that direct electrostatic interactions between the polymer and micelle are most responsible for the preference for interaction with anionic micelles. The synthesis and physicochemical behavior of alkanediethylethanolammonium bromide and alkanedimethylethanolammonium bromide ($R = C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}$) have been studied by Palepu et. al. [36]. Their micellar properties in binary aquo-organic solvent mixtures [37-38] as well as studies on their mixed surfactant systems have also been reported [39-40]. Significant contributions were also made by Manna [41] and Oliveira et al. [42] in this context.

Our research group studied the effect of polymers on micellar properties of surfactants [43] and observed acidic hydrolysis of hydroxamic acid in single and mixed systems [44]. To our knowledge, studies of the effects of polymer–surfactant mixture on the physicochemical behavior of cationic gemini and monomeric surfactants in presence of polymers have not been reported, previously. In the present work, two series of combinations of PEG polymers with cationic surfactants of: (i) monomeric i.e. cetyldiethylethanolammonium bromide and cetyldimethylethanolammonium bromide and (ii) gemini surfactant (16-4-16 MEA, $2Br^+$) [Scheme 1] head groups have been selected. The choice of these surfactants is based on the fact that the alkanol amine surfactants are considered to be having amine and hydroxyl groups and gemini surfactants having bis(hydroxyethylammonium) head groups. Hence it is expected that the micellar behavior of both kinds of surfactants with polymers would be quite different from each other. The aim of the present work is to study the effect of a series of polymer with different molecular mass (PEG-400, PEG-600, PEG-4000, PEG-6000 and PEG-20,000) on the micellization of

cationic gemini (C_{16} -4- C_{16} MEA, $2Br^-$) and monomeric surfactants (cetyldiethylethanolammonium bromide (CDEEAB), cetyldimethylethanolammonium bromide (CDMEAB)).

2. Experimental

2.1 Materials

The gemini surfactant was synthesized and the purity of the surfactant was checked using 1H NMR, as previously reported [45a-46]. Cationic surfactants cetyldiethylethanolammonium bromide (CDEEAB) and cetyldimethylethanolammonium bromide (CDMEAB) were prepared in the laboratory of Prof. R M. Palepu, St. Francis Xavier University, Canada. The purity of these surfactants was checked employing conductometric titration of bromide ion with a standard silver nitrate solution. In all the cases surfactants were found to be >99.5% pure [45b]. Polyethylene glycols i.e. PEG-400, PEG-600 were obtained from Sigma-Aldrich and PEG-4000, PEG-6000 and PEG-20,000 were purchased from Merck and used without further purification. The purity of samples are given in Table 1. All the solutions were prepared in triple distilled water.

2.2 Conductivity Method

Conductivity of aqueous solutions of surfactants were measured using a Systronics direct reading conductivity meter (Type 304 and 306). The conductometer was calibrated with KCl solutions of appropriate concentration range. A concentrated solution of surfactant was progressively added to 10 mL of medium in a thermostat container (having a temperature accuracy of $\pm 0.01^\circ C$) using a micropipette. Measurements were taken thorough mixing and allowing time for thermal equilibration. The fitting of experimental specific conductivity data vs surfactant concentration was performed with the program Table Curve, using a Levenberg-Marquardt procedure.

3. Results and Discussion

3.1 Physicochemical properties

The physicochemical properties (CMC and α) for every surfactant were analyzed with and without the addition of polymers in aqueous solution. The % (w/v) of PEG used were 1, 3 and 5. Figure 1 shows the curve of specific conductivity vs concentration for the surfactants CDEEAB in the presence of 1% (w/v) PEG-400 at 300 K. The CMC values can be determined by the intersection of the two straight lines above and below the inflection point and

as can be seen in Table 2. Table 2 also shows the degree of micellar ionization from the micelles, α , measured as the ratio between the post-micellization slope and pre-micellization slope [47-49].

The conductivity data were fitted to the integral form of the Boltzmann sigmoidal function as proposed by Carpena et. al. [50] for the analysis of specific conductivity-concentration data for solutions of ionic surfactants:

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln \left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right) \quad (1)$$

where $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition, i.e. the CMC and Δx is the width of the transition. The degree of micellar ionization (α) value can also be deduced by the ratio A_2/A_1 . This equation can carefully represent the conductivity vs C data set, since it is the integral of the Boltzmann sigmoid. Before applying the fitting procedure one should ensure that only one transition is present, by simply looking at the plot. The fitting was performed by introducing the equation into a commercial program (see Experimental section) and using reasonable estimates of the parameters as starting point. Care should be taken to avoid obtaining any unreasonable value for the parameters. A good idea is to estimate the maximum value of slope for the premicellar region and the minimum slope for the postmicellar region, by a simple linear fitting. If, by any reason, the non linear fitting could give values substantially exceeding the estimated maximum slope for the premicellar region or lower than the minimum slope for postmicellar region, the fit should be discarded since it does not give “physical” values in agreement with the real behavior shown by experimental data points.

We thus obtained the results by applying both the classical and the non linear fitting method. The results are very similar for both methods (i.e. Classical and the non linear fitting method) and are shown in Table 2.

Critical micelle concentration of the 16-4-16 MEA, $2Br^-$ gemini surfactant is 10-100 times lower than the monomer surfactants [51-52] (shown in Table 2). For 16-4-16 MEA, $2Br^-$ hydrogen bonding can take place with water and among the head groups through oxygen atom of $-C_2H_4OH$ groups. This is likely to provide additional hydration at the head group level resulting in screening of repulsive Coulombic forces between charged heads and

also enforcing a connection among head groups, helping 16-4-16 MEA, 2Br⁻ surfactant to form aggregates at a lower concentration than those of monomeric surfactants. The monomeric surfactants have both the ammonium and hydroxyl groups in ethanol moiety that makes them versatile intermediates for countless industrial applications, particularly in textile, pharmaceutical and household industries [53-54]. If this holds, both monomeric and gemini surfactants having ammonium and ethanol groups in their polar headgroup could be applied in several fields of industrial applications, particularly in textile, pharmaceutical and household industries [53-54].

Table 2 summarizes the variation of CMC and α with polymer composition. The data clearly indicate that the increase in percentage of polymers leads to higher CMC and α value. Figures 2 and 3 show that the CMC values of cationic surfactants increase with increasing percentage of polymer in solution (PEG-400, PEG-600, PEG-4000, PEG-6000, PEG-20000) and temperatures but CMC values decrease with higher molecular mass of polymers.

The polymers (PEG-400 to PEG-20000) form hydrogen bonds with water molecules. The favorable hydrogen bonding ability of these polymers (400 and 600) lead to a poorer contribution to the hydrophobic interactions, which is driving force for micellization and hence the higher CMC values. The increase in the number of repeating units does not have any significant influence of the CMC shown in Figure 2. This might be due to the process of demicellization within the wrapped cavity of higher PEGs.

The effect of the molar mass of PEG on the CMC of cationic monomeric surfactants is not linear and in general is giving only moderate CMC modifications. The process of micellization is controlled by two effects: (i) hydrophobic repulsion between surfactant tails and water, which favors the micellization, and (ii) the repulsive force between surfactant charged headgroups.

They indicate that surfactant-polymer systems are formed in the aqueous solution. The initial rise in conductivity with the polymer content could be related to the ionization effect produced by polymer incorporation into micelles in the aqueous solution. It is well established that micellization process is often facilitated by the presence of a polymer, leading to a lowered critical micelle concentration, with surfactant aggregates closely resembling the micelles formed in the absence of polymer [55].

This is confirmed by the observation that an increase in the weight percentage of polymer in aqueous mixture results in a less abrupt change in conductivity, going from the premicellar to the postmicellar surfactant concentration range as compared to that in pure water, as given in Table 2.

3.2 Effect of Temperature

The critical micelle concentrations of each surfactant with polymers were determined at different temperature (300-320 K) for evaluation of thermodynamic parameters of micellization. At a given polymer concentration the CMC and the degree of micellar ionization increase with temperature (Tables 3-5). The effect of temperature on the micellization is usually discussed in terms of two opposite factors. The increase in temperature results in (i) favoring micellization due to the reduction of the degree of hydration of the head groups and (ii) inhibiting micellization due to the breaking the water structure surrounding the hydrophobic groups. It seems clear that the second effect is dominant in the temperature range studied. Moreover, the degree of micellar ionization (α) of monomeric and gemini surfactants becomes larger with an increase in PEG concentration and temperatures. The values of degree of micellar ionization (α) obtained at different percentages of polymers at varying temperature are presented in Tables 3, 4 and 5. This increase in the value of α , as mentioned above, could be attributed to the Columbic and thermal forces [56]. The former force attracts surfactant headgroups while the latter disperses the surfactant headgroups. The thermal forces predominated the Coulombic forces, and this led to an increase in the separation between the counterions and the headgroups, hence increased α value.

On the basis of the phase separation model of Koshinuma and Sasaki [57] for ionic surfactants to calculate Gibb's energy of micellization (ΔG_m), it is necessary to consider not only the transfer of surfactant molecules from the bulk to the micellar phase but also the transfer of $(1-\alpha)$ moles of counter-ions, where α is the degree of micellar ionization which is equal to $1-\beta$. Hence the temperature dependence of the CMC in surfactant-polymer solution was analyzed to provide information on the thermodynamic parameters of micellization. The standard Gibb's energy of micellization (ΔG_m°) is calculated through combination with the values of the CMC and degree of micellar ionization (α).

$$\Delta G_m^\circ = RT \ln a_s + (1 - \alpha) RT \ln a_{Br^-} \quad (1)$$

Where a_{Br^-} is the activity of the bromide counter-ion. Equation 1 can be written as:

$$\text{For monomeric surfactants [58], } \Delta G_m^\circ = (2 - \alpha) RT \ln a_{\pm CMC} \quad (2)$$

$$\text{For gemini surfactant [59], } \Delta G_m^\circ = 2(1.5 - \alpha) RT \ln a_{\pm CMC} \quad (3)$$

with $a_{\pm CMC}$ as the mean activity of the counter-ions at the CMC. It should be noted that, in most of the thermodynamics of ionic surfactants, the $a_{\pm CMC}$ is replaced by X_{CMC} that is,

$$\Delta G_m^\circ = (2 - \alpha) RT \ln X_{CMC} \quad (4)$$

$$\Delta G_m^\circ = 2(1.5 - \alpha) RT \ln X_{CMC} \quad (5)$$

X_{CMC} is the CMC value on the mole fraction scale and α is the degree of micellar ionization, evaluated by conductometry from the ratio of the slope of the postmicellar and premicellar of the plot of specific conductance vs concentration of the surfactant solution [57-59]. ΔG_m° values are given in Tables 3, 4 and 5. The negative values of standard Gibb's energy are obtained since thermodynamically stable micelles are formed spontaneously; further ΔG_m° become more negative at higher temperatures, indicating a larger driving force for micellization [60]. The Gibb's energy decreased with increase in temperature. The aggregation was found to be exothermic in nature and favored by positive value of entropy. ΔG_m° in each case is negative and becomes more negative as the polymer content in the mixture is increased, indicating that aggregation becomes more favorable at higher polymer content.

From the temperature dependence of the CMC, the standard enthalpy change for the micellization process, ΔH_m° , can be obtained from the Gibbs-Helmholtz equation (7 & 8):

$$[\partial (\Delta G_m^\circ / T) / \partial (1/T)] = \Delta H_m^\circ \quad (6)$$

$$\Delta H_m^\circ = - (2 - \alpha) RT^2 [\partial \ln X_{CMC} / \partial T] \quad (7)$$

$$\Delta H_m^\circ = -2(1.5 - \alpha) RT^2 [\partial \ln X_{CMC} / \partial T] \quad (8)$$

The slope in the plot of $\ln X_{CMC}$ versus T at each temperature was taken as $(\partial \ln X_{CMC} / \partial T)$. A linear plot was observed as shown in Figure S1 (supporting information). The negative value of ΔH_m° indicates that the mobilization process in the absence and presence of polymers is exothermic. The variation of ΔH_m° , with temperature and concentration of polymers may be due to a change in the hydration of the head groups during micellization. The interaction enthalpy change may include the following main contributions: electrostatic interaction of the surfactant micelle like aggregates with the polymers, hydrophobic interaction between the surfactant molecules and the hydrophobic moieties of the polymers, the morphological change caused by the interaction of the surfactant aggregates with the polymers, and the phase separation caused by the binding of the surfactant aggregates with the polymers.

The variation of ΔH_m° with temperature in all the systems investigated is shown in Figure 4. In all cases the formation of micelles becomes increasingly exothermic with increase in temperature.

The entropy change associated with the micellization process, ΔS_m° , is obtained by the use of the following relationship:

$$\Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ) / T \quad (9)$$

The entropy change in all cases is positive which confirms that aggregation of surfactant is favored entropically. However, the values are decreasing with increasing temperature as seen from Tables 3, 4 and 5. The reason might be that self aggregation becomes poorer at higher temperature because of enhanced molecular motion at increased temperature [61]. Tables 3, 4 and 5 show that the values of entropy of gemini surfactant are greater than the both monomeric surfactants (CDEEAB and CDMEAB). The positive values of standard entropy of micelle formation are due to the melting of flickering clusters around the hydrocarbon tails of the surfactant monomer and the increased randomness of the hydrocarbon chains in the micellar core. An increase in positive value of ΔS_m° on addition of polymer content is also in favor of more aggregation at higher polymer content.

The increase in entropy of micellization in an aqueous medium can be explained from two aspects. First the iceberg formation [62] of the water molecules surrounding the surfactant molecules would increase the system order, here the micellization process by removing the surfactant molecules from the aqueous medium to the micelle

would certainly increase the entropy of the system simply due to the rupture of iceberg. Second the degree of rotational freedom of the hydrophobic chain of surfactant molecules in the non-polar interior of the micelle is much larger than that in the aqueous medium; in other words, the configurational entropy of hydrophobic chain of surfactant molecules is increased when the surfactant molecules are removed from the aqueous medium to the micelle.

The enthalpy-entropy compensation plots for the micellization process of monomeric surfactants in all the polymers showed a good correlation between ΔS_m° and ΔH_m° values in different compositions (1% - 5% w/v) (Figures 5 and 6). The nature of these plots clearly indicates that the change in ΔH_m° is effectively balanced by a corresponding change in ΔS_m° . As a consequence the magnitude of the Gibb's energy term may change a little. In the present study the apparent compensation temperature, T_c values (300–320 K), are larger than the value in Lumrys range (270-300 K) [63].

4. Conclusion

The physicochemical behaviors of cationic monomeric and gemini surfactants were studied in polymer solution at 300-320 K by conductivity method. It was found that the CMC and degree of micellar ionization (α) values increased with increasing polymer percentage and temperature. Thermodynamic parameters of micellization were calculated from the temperature dependence of CMC values. The values of ΔG_m° and ΔH_m° are negative in all cases and increase with increasing polymer content and temperature. The values of entropy of the micellization ΔS_m° are positive in all cases. Entropy–enthalpy compensation plays an important role in the micellization process. The use of polymer/surfactant couples for surface modification presents a rich opportunity for producing unique reaction medium. The structure and properties of polymer play an important role in determining chemical reactivity.

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