Original Article

INFLUENCE OF PEG-4000 ON THE MICELLIZATION BEHAVIOR OF SDBS AND CPC AT DIFFERENT TEMPERATURES

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ABSTRACT

Objective: The main objective of this research work was to gain a qualitative understanding of polymer-surfactant interactions by comparing the micellar properties of anionic (SDBS) and cationic (CPC) surfactants in aqueous mixtures of PEG-4000.

Methods: Conductivity method was employed to investigate the micellization behavior of two oppositely charged ionic surfactants in polymer solutions at a temperature range between 298.15 K to 308.15K. Thermodynamic parameters of micellization were also derived (ΔG°_m, ΔH°_m and ΔS°_m) to support the findings.

Results: CMC of both the surfactants was directly proportional to the concentration of PEG-4000. Negative values of ΔG°_m suggested that the micellization was a spontaneous process, but these values were inversely proportional to PEG concentration suggesting the origin of London dispersion interactions on increasing polymer concentration in the system.

Conclusion: Comparative study of polymer–surfactant interactions enabled us to evaluate the relative contribution of electrostatic and hydrophobic interactions between surfactant and polymer molecules. Studies showed that the micellization is more favored by CPC-PEG system as compared to SDBS-PEG system.

Keywords: Micellization, Polymer, Surfactant

INTRODUCTION

Micellar properties of surfactants have the majority of applications in pharmaceutical [1], Agriculture [2], Cosmetic industries [3], detergency [4] and corrosion [5]. PEG and surfactants are collectively used as drug delivery vehicles in pharmaceutical industry [6]. Thermodynamic stability of pharmaceutical products is a major issue among the researchers of the current era. Thus, it is important to study the thermodynamics of micellization of ionic surfactants in the presence of industrially acknowledged excipients i.e. PEG [7]. Earlier studies on polymer-surfactant interactions reveals the importance of the formation of association structures [8], modifications in polymer rheology [9] and changes in the micellar

behavior of surfactants [10] in different environments. Our work is on the study of the micellar behavior of ionic surfactants in aqueous mixtures of PEG. As both anionic (SDBS) and cationic surfactant (CPC) contain aromatic rings in their head groups (fig. 1a and 1b) thus due to the presence of extra hydrophobicity in surfactant head group low CMC of these ionic surfactants has been observed. This study will help to understand the role of surfactant head group and it's binding with polymer molecules. The comparison of micellization behavior of ionic surfactants (SDBS and CPC) has not been critically analyzed till now, so we have tried to understand the solution properties of these ionic surfactants in the presence of polymer (PEG-4000) at different temperatures.
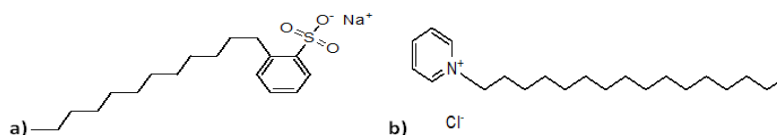

Fig. 1: a) Chemical structure of sodium dodecyl benzene sulfonate, b) Structure of cetyl pyridinium chloride

MATERIALS AND METHODS

Ordinary tap water of conductivity in the range $3-5 \times 10^{-6}$ S cm^{-1} at 25 $^\circ$C was distilled thrice in the presence of alkaline KMnO$_4$. The distillation was carried out through a 750-mm long vertical fractionating column. The middle fraction of the triple distilled water of conductivity $1-4 \times 10^{-7}$ S cm^{-1} and pH in the range 6.8-7.0 at 25 $^\circ$C was collected for use in all experiments. PEG-4000 (Extra Pure) was supplied by Loba chemie Pvt. Ltd. Mumbai and was used without any further purification. CPC of purity>99% was obtained from Loba chemie Pvt. Ltd. Mumbai and was used as received. SDBS was procured from Loba chemie Pvt. Ltd. Mumbai. Pure sample of SDBS was obtained by several re-crystallizations as described in the literature [11]. Aqueous solutions of SDBS and CPC of different concentrations ranging from 0-2 mM for SDBS and 0-3 mM for CPC were made and

added to water as well as different concentrations of PEG-4000 i.e. 0.1%, 0.2%, 0.4%, 0.8%, 1.0% w/v to note the specific conductance (κ) of the above said systems at different temperatures. Conductivity measurements were carried out with the help of a digital conductometer. It was supplied by HANNA instruments Pvt. Ltd. The CMCs were determined precise to±1% from the apparent discontinuity in the plot of specific conductance κ verses concentration of Surfactants.

RESULTS AND DISCUSSION

Different plots of conductance vs. concentration of surfactants were obtained from the readings as per w/v concentrations of PEG-4000 and were used to calculate CMC values. The CMCs of both the surfactants (SDBS and CPC) in water at 25 $^\circ$C were in excellent agreement with the literature values [12, 13].

Table 1: CMC values for SDBS and CPC in different concentrations of aqueous PEG at different temperatures

%W/v PEG-4000	CMC (10^3) mM for SDBS				CMC (10^3) mM for CPC			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0	0.0012	0.00123	0.00144	0.00168	0.00098	0.001	0.00102	0.00106
0.10	0.00123	0.00141	0.0015	0.00153	0.00104	0.00106	0.00108	0.00114
0.20	0.00129	0.00135	0.00159	0.00174	0.0011	0.00116	0.00118	0.00124
0.40	0.00126	0.0015	0.00168	0.00176	0.0012	0.00124	0.00132	0.00136
0.80	0.00129	0.00151	0.00171	0.00178	0.00122	0.00127	0.00135	0.00139
1	0.00132	0.00156	0.00174	0.00186	0.00126	0.00131	0.0014	0.00144

Sample size, N=48 and all values are given as mean.

Temperature dependence of CMC

Effect of temperature on CMC of SDBS and CPC is shown in fig.2. CMCs of SDBS and CPC increased linearly with increase in temperature which signified the increase in thermal motions of surfactants and the solvent system. These increased thermal motions were responsible for the disruption of water structure and inhibited the formation of ordered structure of micelles. So CMC was directly proportional to the degree of disruption of ordered micellar structures [12].
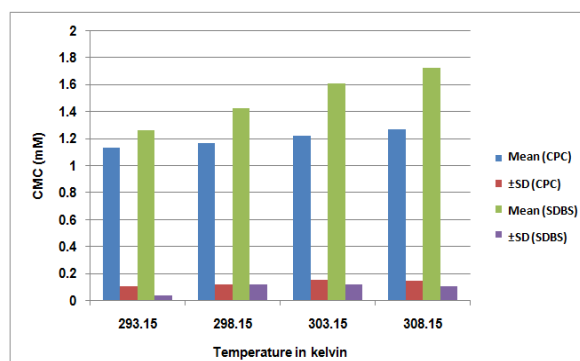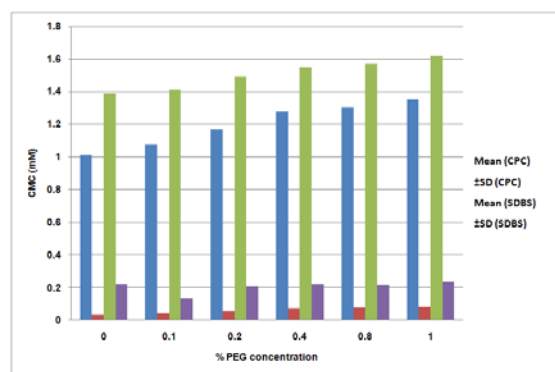

Fig. 2: Temperature dependence of CMC of SDBS and CPC in terms of mean±SD

Sample size, N=48 and errors bars have been omitted for the simple presentation.

The complex behavior of CMC in the case of SDBS was attributed in terms of two forces acting simultaneously. First was the decrease in the degree of hydration of hydrophilic groups (favorable for micellization) and second was a disruption in water structure (Unfavorable for micellization) and second was dominant in both the cases [14]. Micellization of SDBS was more temperature dependent as compared to CPC.

Effect of PEG on micellization of SDBS and CPC

CMC of SDBS and CPC were directly proportional to PEG concentration. Effect of PEG concentration on micellization of ionic surfactants is given in fig 3 and it showed that the effect was more prominent in case of SDBS

Fig. 3: Effect of PEG on micellization of SDBS and CPC in terms of mean±SD

Sample size, N=48 and errors bars have been omitted for the simple presentation

Thermodynamics of PEG-SDBS and PEG-CPC systems

The CMC data reported in the table 1 was used to calculate the standard enthalpy of micellizationΔH°_m of both surfactants in an aqueous solution of polymer (PEG-4000) from equation 1 [15].

$$\Delta H^o_m = -RT^2 \frac{d \ln CMC}{dT} \text{ ... (1)}$$

Where $\frac{d \ln CMC}{dT}$ the slope of the straight line is obtained by plotting lnCMC against T (Temperature)

The standard entropy of micellization ΔS^o_m and standard free energy of micellization ΔG^o_m were calculated by using the relations (2) and (3) respectively.

$$\Delta S^o_m = \frac{\Delta H^o_m - \Delta G^o_m}{T} \text{ .... (2)}$$

$$\Delta G^o_m = RT \ln cmc \text{ .... (3)}$$

Thermodynamic parameters derived by above relations are presented in the form of tables (2-4) respectively.

Table 2: Change in enthalpy of micellization ΔH °ₘ (kJ mol⁻¹) values for SDBS and CPC in different concentration of aqueous PEG at different temperatures

%W/v PEG-4000	ΔH °ₘ (kJ mol⁻¹) for SDBS				ΔH °ₘ (kJ mol⁻¹) for CPC			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0	-16.676	-17.2497	-17.8331	-18.4262	-3.64385	-3.76921	-3.89669	-4.02629
0.1	-10.2385	-10.5907	-10.9489	-11.3131	-4.20114	-4.34567	-4.49265	-4.64207
0.2	-15.1684	-15.6902	-16.2209	-16.7604	-5.38003	-5.56512	-5.75334	-5.94469
0.4	-15.9472	-16.4958	-17.0537	-17.6209	-6.25884	-6.47416	-6.69313	-6.91574
0.8	-15.5828	-16.1189	-16.6641	-17.2183	-6.46604	-6.68849	-6.91471	-7.14468
1	-16.2616	-16.821	-17.3899	-17.9683	-6.67324	-6.90282	-7.13628	-7.37363
0	-16.676	-17.2497	-17.8331	-18.4262	-3.64385	-3.76921	-3.89669	-4.02629

(*Estimated uncertainty is±0.1 kJ mol⁻¹) Sample size, N=48 and all the values are given as mean

Table 3: Change in Gibb's free energy of micellization ΔG °$_m$ (kJ mol^{-1}) values for SDBS and CPC in different concentration of aqueous PEG at different temperatures

| %W/v PEG-4000	ΔG °$_m$ (kJ mol^{-1}) for SDBS				ΔG °$_m$ (kJ mol^{-1}) for CPC			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0	-16.3916	-16.6099	-16.4912	-16.3683	-16.8852	-17.1231	-17.3603	-17.5481
0.1	-16.3314	-16.2714	-16.3883	-16.6079	-16.7403	-16.9786	-17.2163	-17.3617
0.2	-16.2153	-16.3792	-16.2414	-16.2784	-16.6036	-16.7552	-16.9931	-17.1463
0.4	-16.2726	-16.118	-16.1027	-16.2491	-16.3916	-16.5899	-16.7105	-16.9096
0.8	-16.2153	-16.1015	-16.0581	-16.2201	-16.3513	-16.5306	-16.6539	-16.8537
1	-16.1593	-16.0208	-16.0142	-16.1075	-16.2726	-16.4537	-16.5622	-16.7632

(*Estimated uncertainty is±0.1 kJ mol^{-1}) Sample size, N=48 and all values are given as mean.

Table 4: Change in entropy of micellization ΔS °$_m$ (J K^{-1} mol^{-1}) values for SDBS and CPC in different concentration of aqueous PEG at different temperatures

| %W/v PEG-4000	ΔS °$_m$ (J K^{-1} mol^{-1}) for SDBS				ΔS °$_m$ (J K^{-1} mol^{-1}) for CPC			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0	-0.97014	-2.14568	-4.42645	-6.6783	45.16907	44.7891	44.41245	43.88064
0.1	20.78418	19.05299	17.94286	17.18253	42.77397	42.37117	41.97134	41.27739
0.2	3.571184	2.310678	0.067732	-1.56432	38.28618	37.53161	37.07646	36.35109
0.4	1.110215	-1.2672	-3.13726	-4.45187	34.56495	33.92819	33.04424	32.43189
0.8	2.157579	-0.05825	-1.99901	-3.23921	33.72073	33.01058	32.12649	31.50752
1	3.572794	4.054855	3.754723	3.935274	-2.87985	-3.07767	-3.02739	-2.99975

(*Estimated uncertainty is±5 J K^{-1} mol^{-1}) Sample size, N=48, and all the values are given as mean.

From the above tables and fig. it is observed that micellization is a spontaneous process. Negative values of change in free energy of micellization (Figs. 4 and 5) confirm the stability of PEG-Surfactant systems.
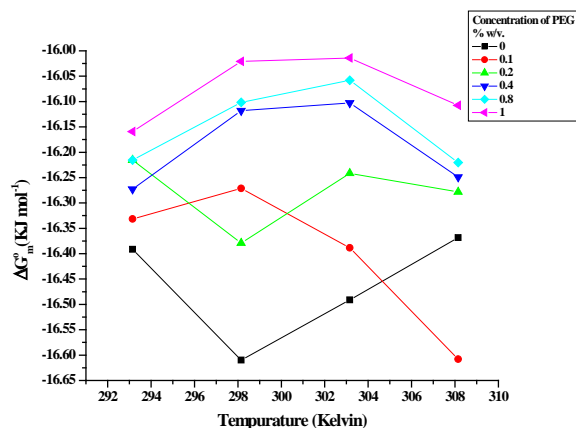
Fig. 4: Effect of temperature and PEG concentration on change in free energy of micellization ΔG °$_m$ (kJ mol^{-1}) of SDBS in terms of mean values

Sample size, N=24 and errors bars have been omitted for the simple presentation

The negative values of ΔG °$_m$ for both the surfactants showed the spontaneity of the reaction mixtures and increase in ΔG °$_m$ on the increase in polymer concentration revealed the presence of electrostatic interaction between the surfactant head group and polymer whereas ΔG °$_m$ was inversely proportional to a temperature which revealed the increase in hydrophobic interactions. ΔH °$_m$ values were more negative in case of SDBS which showed stronger London dispersion forces in SDBS–polymer system. ΔS °$_m$ values were negative in aqueous SDBS but became positive on the addition of PEG and decreased with increase in PEG concentration, this behavior confirmed that the micellization of SDBS was entropically favored at low PEG concentrations and reverse behavior was seen on increasing PEG concentration in the system.
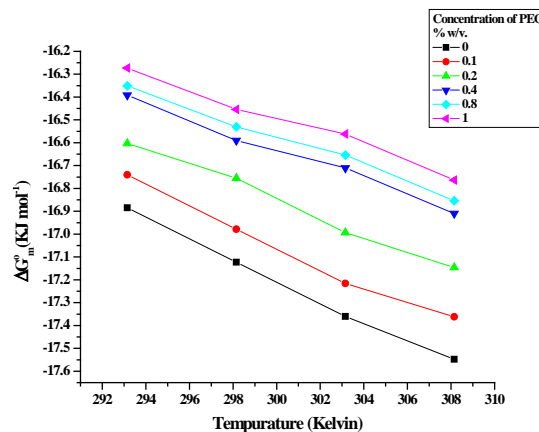
Fig. 5: Effect of temperature and PEG concentration on change in free energy of micellization ΔG °$_m$ (kJ mol^{-1}) of CPC in terms of mean values

Sample size, N=24 and errors bars have been omitted for the simple presentation

In the case of CPC high ΔS °$_m$ values confirmed that the micellization was an entropy driven process, and a decrease in entropy was observed in both the cases which showed a decrease in hydrophobic interactions on increasing polymer concentrations in both the systems.

CONCLUSION

Comparison between the thermodynamics behavior of these two systems revealed the importance of surfactant head group and alkyl chain of surfactant with respect to polymer concentration. At lower surfactant concentration specific binding with polymer takes place. On increasing polymer concentration spontaneity of both the system increases and dominance of London dispersion interactions was seen in both the systems. Micellization was more entropy driven in case of CPC but a decrease in hydrophobic interactions was observed due to extra hydrophobicity provided by surfactant head groups.

CONFLICTS OF INTERESTS

There is no conflict of interest between the authors hence, there is nothing to declare.

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