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Thermodynamics of micellization of Ionic surfactants (SDS and CTAB) in aqueous mixtures of PEG-4000

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Abstract: Micellization behavior of two oppositely charged surfactants SDS (Anionic) and CTAB (Cationic) in presence of aqueous mixtures of PEG-4000 at a temperature range between 298.15 K to 308.15K is studied using conductivity method. CMC of both the surfactants is directly proportional to concentration of PEG-4000. Negative values of ΔG^0_m show that the micellization is a spontaneous process but it is inversely proportional to PEG concentration and suggest the origin of hydrophobic interactions on increasing polymer concentration in system.

Introduction:

The property of surfactants to solubilize hydrophobic organic compounds makes them a useful in pharmaceutical industry[1], whereas use of polyethylene glycols as solvent and dispersants in pharmaceutical and cosmetic industries is widely known due to their low toxicity and the property to get solubilized in water[2]. As both PEG and surfactants are collectively used in various processes[3], it is necessary to investigate the interaction behavior of these complex systems. In order to maintain thermodynamic stability of pharmaceutical products it is necessary to study thermodynamics of such widely used excipients. The interactions between polymers and surfactants in aqueous media give rise to the formation of association structures, thereby modifying the solution and interfacial properties[4]. Polymer surfactant systems have been extensively studied using viscometry[5], conductivity[6], Surface tension[7], Size exclusion chromatography[8], Isothermal titration calorimetry and Dynamic light scattering techniques[9] etc.

Thermodynamic nature of polymer surfactant interactions expected to yield some useful information in respect of such systems.

Experimental:

Tripled distilled water of conductivity range 1-3x10^{-6} Scm^{-1} and pH in the range 6.8 -7.0 at 25°C was used for all the experiments. PEG-4000 (Extra Pure) was supplied by Loba chemie Pvt. Ltd. and was used without any further purification. CTAB of purity > 98% was obtained from Qualikems Pvt. Ltd. and was recrystallized using ethanol as suggested in literature[10]. SDS (AR Grade) was procured from Loba chemie Pvt. Ltd. Pure sample of SDS was obtained as described in literature[11]. Aqueous solutions of SDS and CTAB of different concentrations ranging from 0-23.07 mM were made and added to the different concentrations of PEG-4000 i.e. .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. The CMCs of both the surfactants (SDS and CTAB) in water at 25°C were in excellent agreement with the literature values[12, 13].

Result and Discussion:

Different plots of conductance vs. concentration of surfactants were obtained from the readings as per w/v concentrations of PEG-4000.

Table1: CMC values for SDS and CTAB in different concentrations of aqueous PEG at different temperatures.

%W/v PEG-4000	CMC (10^3) mM for SDS				CMC (10^3) mM for CTAB			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0.1	0.00575	0.00625	0.00775	0.00876	0.00225	0.00325	0.0045	0.0057
0.2	0.00625	0.0073	0.00805	0.00975	0.00275	0.0035	0.00475	0.00675
0.4	0.0074	0.00775	0.009	0.0103	0.0045	0.005	0.00575	0.00725
0.8	0.0085	0.00875	0.0105	0.0118	0.00525	0.00625	0.00675	0.00875
1	0.0095	0.00995	0.0115	0.01195	0.00675	0.007	0.00775	0.00925

Temperature dependence of CMC: Effect of temperature on CMC of SDS and CTAB is shown in Figures1 and 2.

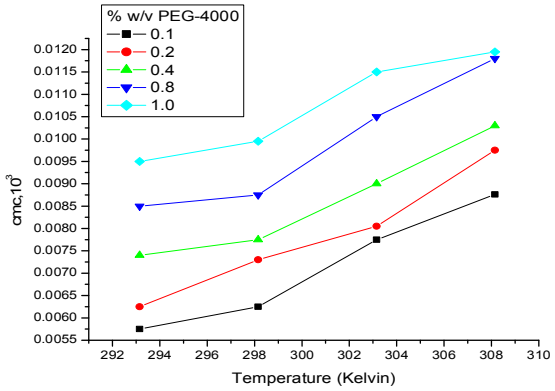

Figure1: Plots of CMC vs. Temperature in aqueous solution for SDS containing different concentrations of PEG.

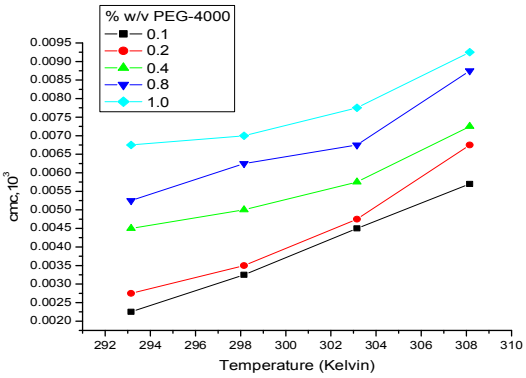

Figure2: Plots of CMC vs. Temperature in aqueous solution for CTAB containing different concentrations of PEG.

CMCs of SDS and CTAB increase linearly with increase in temperature which signifies the increase in thermal motions of surfactants and the solvent system. These increased thermal motions are responsible for the disruption of water structure and inhibits the formation of ordered structure of micelles. So CMC is directly proportional to degree of disruption of ordered micellar structures.[14]

Thermodynamics of PEG-SDS and PEG-CTAB Systems:

The CMC data reported in the table 1 was used to calculate the standard enthalpy of micellization ΔH°_{m} of surfactants in aqueous solution of polymer (PEG-4000) from the equation 1. [15]

$$\Delta H^{o}_{m} = -RT^{2}\frac{d\ln CMC}{dT} \quad (1)$$

Where $\frac{d\ln CMC}{dT}$ the slope of straight line is 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.

$$\Delta S^{o}_{m} = \frac{\Delta H^{o}_{m} - \Delta G^{o}_{m}}{T} \quad (2)$$

$$\Delta G^{o}_{m} = RT\ln cmc \quad (3)$$

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

Table 2: Change in enthalpy of micellization ΔH^{0}_{m} (kJ mol^{-1}) values for SDS and CTAB in different concentration of aqueous PEG at different temperatures.

%W/v PEG-4000	ΔH^{0}_{m} (kJ mol^{-1}) for SDS				ΔH^{0}_{m} (kJ mol^{-1}) for CTAB			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0.1	-21.12	-21.8466	-22.5855	-23.3367	-44.4978	-46.0287	-47.5854	-49.168
0.2	-20.4627	-21.1667	-21.8826	-22.6104	-42.8545	-44.3288	-45.8281	-47.3523
0.4	-16.3116	-16.8727	-17.4434	-18.0235	-22.4418	-23.2139	-23.999	-24.7972
0.8	-16.6688	-17.2423	-17.8254	-18.4183	-17.7977	-18.41	-19.0326	-19.6656
1	-11.9032	-12.3127	-12.7292	-13.1525	-10.0599	-10.406	-10.7579	-11.1157

Table 3: Change in Gibb's free energy of micellization ΔG^{0}_{m} (kJ mol^{-1}) values for SDS and CTAB in different concentration of aqueous PEG at different temperatures.

%W/v PEG-4000	ΔG^{0}_{m} (kJ mol^{-1}) for SDS				ΔG^{0}_{m} (kJ mol^{-1}) for CTAB			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0.1	-12.5727	-12.5804	-12.2492	-12.1374	-14.8595	-14.2014	-13.6194	-13.2384
0.2	-12.3695	-12.1955	-12.1535	-12.8631	-14.3704	-14.0177	-13.4831	-12.8052
0.4	-11.9578	-12.0472	-11.8724	-11.7225	-13.1701	-13.1336	-13.0016	-12.6221
0.8	-11.62	-11.7464	-11.4839	-11.3742	-12.7944	-12.5804	-12.5974	-12.4513
1	-11.349	-11.4278	-11.2546	-11.3419	-12.1819	-12.2995	-12.2492	-12.2911

Table 4: Change in entropy of micellization ΔS^0_m (J $K^{-1}mol^{-1}$) values for SDS and CTAB in different concentration of aqueous PEG at different temperatures.

%W/v PEG-4000	ΔS^0_m (J $K^{-1}mol^{-1}$) for SDS				ΔS^0_m (J $K^{-1}mol^{-1}$) for CTAB			
	Temperature (Kelvin)				Temperature (Kelvin)			
	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
0.1	-29.1569	-31.0789	-34.0961	-36.3442	-101.103	-106.749	-112.044	-116.598
0.2	-27.6078	-30.0895	-32.0931	-34.8766	-97.1656	-101.664	-106.696	-112.111
0.4	-14.8516	-16.1849	-18.3771	-20.4479	-31.6278	-33.8095	-36.2772	-39.5101
0.8	-17.2225	-18.4333	-20.9189	-22.8592	-17.0673	-19.5524	-21.2278	-23.4118
1	-1.89073	-2.96807	-4.86428	-5.87596	7.238674	6.351007	4.919481	3.814381

From the above tables and figures it is observed that micellization is a spontaneous process. Negative values of change in free energy of micellization (Figures 3 and 4) confirm the stability of PEG- Surfactant systems.

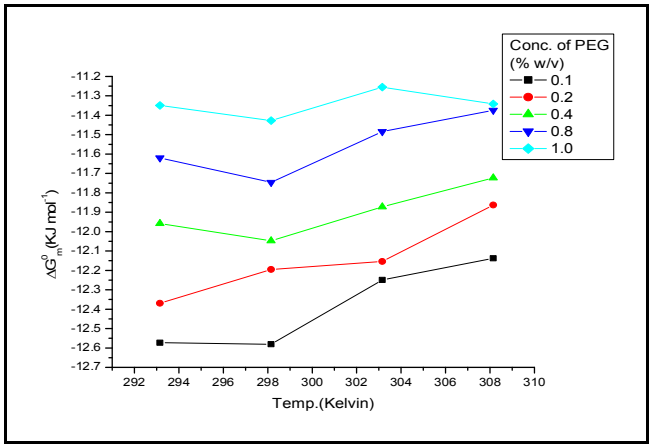

Figure 3: Plot of ΔG^0_m (kJ mol^{-1}) for SDS vs. Temperature in aqueous solutions of P EG-4000.

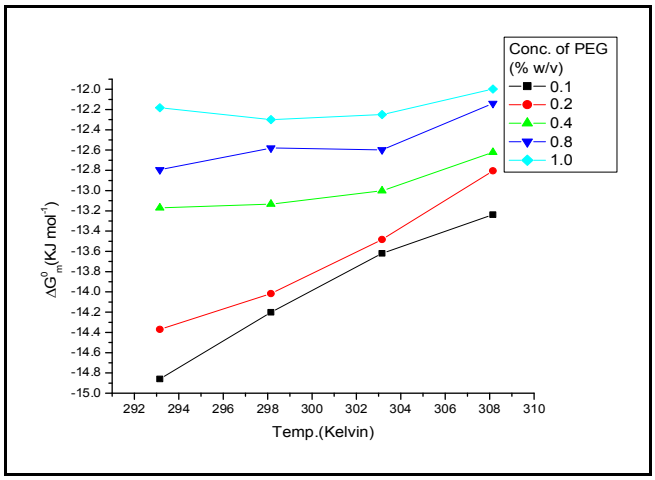

Figure 4: Plot of ΔG^0_m (kJ mol^{-1}) for CTAB vs. Temperature in aqueous solutions of P EG-4000.

Decrease in ΔG^0_m values on increasing concentration of PEG in the system is due to presence of hydrophobic interactions in both the systems[16, 17]. Entropy of micellization starts changing its sign and shows that micellization is entropy driven process. In case of SDS it remains negative but in case of CTAB it becomes positive in the end which shows the dominance of hydrophobic interaction over electrostatic interaction in CTAB-PEG system. Compensation by enthalpy –entropy is more in case of PEG-CTAB system as compared to PEG-SDS system[18]. At lower PEG concentrations electrostatic interactions dominate and at higher PEG concentrations Hydrophobic interactions take charge because of disruption of water structure in the later part of both the systems.

A large change in both ΔH^0_m and ΔS^0_m values can be seen to compensate the effect of each other giving rise to relatively small changes in the magnitude of ΔG^0_m value with polymer concentration.

Conclusion:

Comparison between the thermodynamics behavior of these two systems reveal 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. Extra hydrophobicity provided by the polymer results in disruption in water structure and shows the dominance of hydrophobic interactions. Stronger intermolecular interactions in CTAB- PEG system is due to cooperative binding by CTAB micelles. Whereas SDS- PEG system shows similar behavior but the compensation due to entropy-enthalpy is less in this case.

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