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The micelle formation of cationic and anionic surfactants in aqueous medium: Determination of CMC and thermodynamic parameters at different temperatures

L. Tennouga[1,*], A. Mansri[1], K. Medjahed[1], A. Chetouani[2, 3], I. Warad[4]
[1] *Laboratoire d'Application des Electrolytes et des Polyélectrolytes Organiques (LAEPO).*
Université de Tlemcen. Département de Chimie. B. P. 119, Tlemcen 13000, Algeria.
[2] *LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, BP 4808, Oujda,Morocco.*
[3] *Laboratoire de chimie physique, Centre Régionale des Métiers de l'Education*
et de Formation "CRMEF", Région de l'Orientale, 60000 Oujda, Morocco
[4] *Department of Chemistry, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia.*

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[*] *Corresponding author. E-mail: l14_ten@yahoo.fr*

Abstract

In this paper, the micellization of anionic surfactant sodium dodecyl sulphate (SDS) and cationic surfactant N-dodecylpyridinium chloride (DPC) in aqueous solution at various temperatures has been reported using conductivity measurements. The thermodynamic parameters of micellization; the free energy, ΔG^0_{mic}, the enthalpy, ΔH^0_{mic}, and the entropy, ΔS^0_{mic} were calculated from the critical micelle concentration (CMC) at different temperatures. The results show that the CMC of surfactants decreases to reach a minimum and then increases with temperature. Also, the thermodynamic parameters of micellization are discussed.

Keywords: Micellization, Surfactant, Critical micelle concentration (CMC), Thermodynamic parameters, Conductivity.

1. Introduction

Surfactants are extremely versatile chemicals with applications in chemistry, biology, and pharmaceutical science [1]. Surfactants are amphiphilic molecules with polar head groups, which may be anionic, cationic, non-ionic and zwitterionic, and hydrophobic tails, that may be hydrogenated or fluorinated, linear or branched. Recently, some interest has been devoted to the new class of so-called gemini surfactants [2-5]. It is well known that surfactant molecules are associated into micelles above the critical micelle concentration (CMC). The micellization of surfactants has been a topic of considerable interest for many years, with an enormous literature of several thousand papers published year after year in journals of widely differing scopes [6, 7]. The micellar properties of anionic or cationic surfactants are significantly influenced by the presence of various nonelectrolytes in solution [8, 9]. There has recently been much research dealing with the effects of non aqueous polar solvents on the formation of cationic micelles [10-16]. Evans et al. [17] have indicated that the ability of a solvent to form hydrogen bonds is a necessary condition of micelle formation. However, it has been shown in the literature that the unique structure of water (H-bonding) is not a necessary condition for the aggregation process [18-21]. The determination of thermodynamic parameters of micelle formation in aqueous solutions, the Gibbs free energy, ΔG_{mic}, the enthalpy, ΔH_{mic}, and the entropy, ΔSmic is more important, because they quantify the relative importance of hydrophobic interactions, surfactant-water contact and (for ionic surfactants) head-group repulsion. These parameters can be derived from the temperature dependence of the critical micelle concentration (CMC) [22].

In the present work, the micellization behaviour of sodium dodecyl sulphate (SDS) and N-dodecylpyridinium chloride (DPC) in dilute aqueous solutions between 10-50°C are reported by conductivity measurements.

2. Materials and methods

2.1. Apparatus

Our conductimetric measurements were made using a conductivity meter CDM 210 (Radiometer, Meter Lab).

2.2. Products

The cationic surfactant N-dodecylpyridinium chloride (DPC) was provided by Aldrich. Its molecular mass is 283.5 g/mol. Sodium dodecyl sulfate (SDS) was supplied by Aldrich society. Its molecular weight is 288.38 g/mol.

2.3. Preparation of Solutions

a. Preparation of the N-dodecylpyridinium chloride solution

To prepare a stock solution of DPC with a concentration equal at 0.1 mol/l, 0.7097 g of DPC was dissolved in 25 ml of distilled water, magnetic stirring was carried out for 24 hours before the use.

b. Preparation of the solution of sodium dodecyl sulfate

To prepare a stock solution of sodium dodecyl sulfate with a concentration equal at 0.04801 mol/l, 0.3461 g of SDS was dissolved in 25 ml of distilled water, magnetic stirring was carried out for 24 hours before the use.

3. Results and discussion

To estimate the CMC of the cationic and anionic surfactants two plots of conductivity as a function of the concentration of DPC and SDS in aqueous solutions at different temperatures were made. Indeed, at this concentration CMC value many important properties of surfactants usually change sharply in the solutions. The results are presented in figure 1.

The conductivity variations of the studied surfactants versus its concentration and with various temperatures are show in (Figure 1). In this figure, the breaks in the conductivity according surfactant concentration curves is observed for the all temperatures, these breaks are attributed to the beginning of micelles formation. Also, the CMC was determined by the intersection of the two slopes of each curve. The slope for C<CMC is higher than that for C>CMC. This can be explained by the fact that, beyond the CMC, condensation counter-ions are formed on the micelles, causing a decrease in the number of charge carriers and hence the conductivity decreases slightly compared to the first regime [23-26].

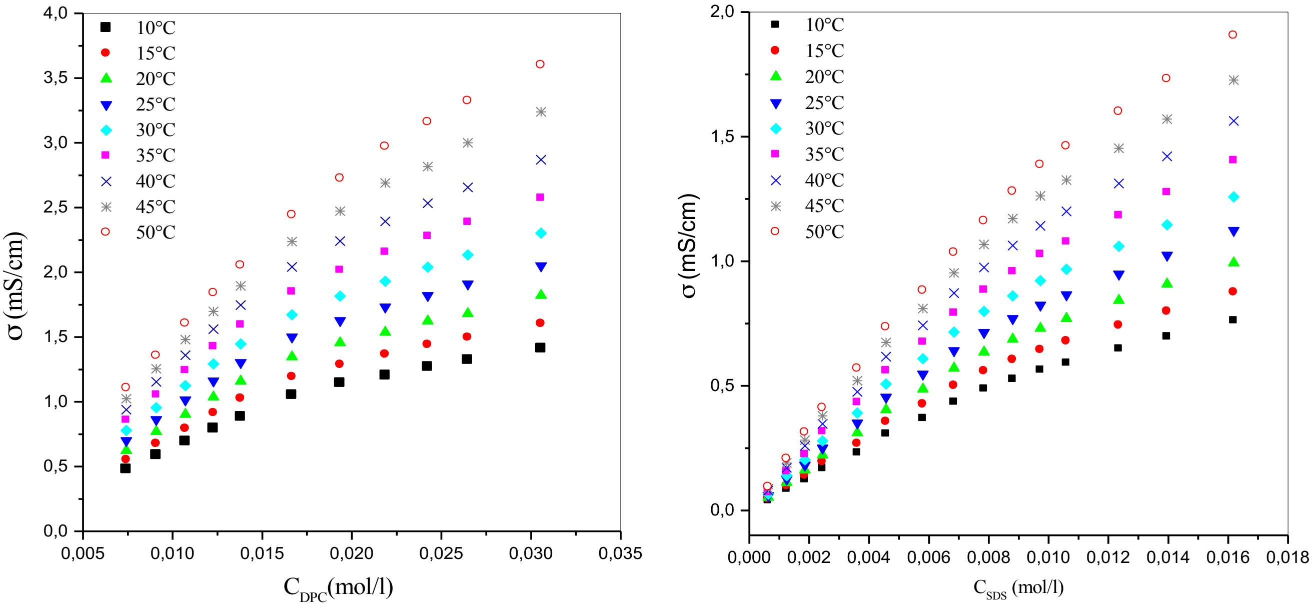

Figure 1: Variation of the conductivity of the surfactants with its concentration at different temperatures: a) DPC; b) SDS

For each temperature, the CMC was determined by the intersection of the two slopes of each curve. The values of CMC and lnCMC are presented in Table 1.

Table 1: Variation of CMC and lnCMC as a function of temperature

Temperature (K)	CMC (mol/l)		lnCMC (mol/l)	
	DPC	SDS	DPC	SDS
283,16	0,01720	0,00824	-4,06284	-4,06284
288,16	0,01602	0,00806	-4,13391	-4,13391
293,16	0,01566	0,00794	-4,15664	-4,15664
298,16	0,01527	0,00776	-4,18186	-4,18186
303,16	0,01560	0,00776	-4,16048	-4,16048
308,16	0,01597	0,00784	-4,13704	-4,13704
313,16	0,01611	0,00816	-4,12831	-4,12831
318,16	0,01735	0,00833	-4,05416	-4,78789
323,16	0,01802	0,00853	-4,01627	-4,76416

From Table 1, the CMC is plotted as a function of temperature (Figure 2).

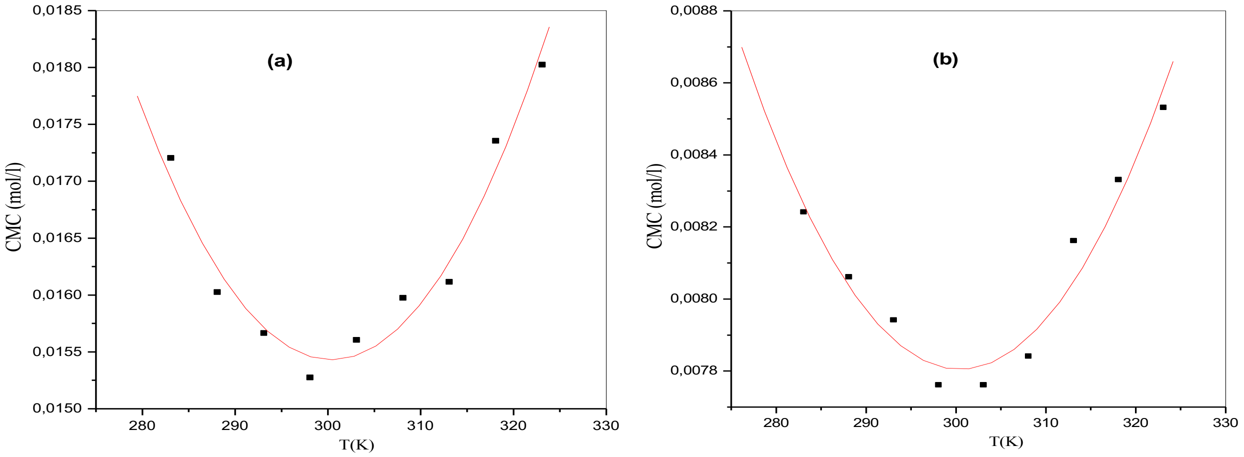

Figure 2: CMC variation of surfactants with temperature: a) DPC; b) SDS

This behavior of the CMC is justified by the forces responsible for the micellization of surfactant molecules:

- *The hydrophobic interactions between the tails:* these forces, promote micellization, but the temperature has a major effect on these forces, because at low temperatures the alkyl chains of surfactant takes conformations so they minimize the volume occupied by these molecules, which minimizes the hydrophobic interactions between the tails (which explains the large values of CMC at low temperature).
- *The electrostatic repulsion between the ionic heads*: these forces, disadvantage micellization. For a pure electrolyte, when the temperature increases the conductivity also increases as the distance between the ion and the cons-ion increases and consequently the electrostatic field of the ions increases, and in the case of repulsion between the surfactant heads increase which explains large values of CMC high temperature.

CMC values determined at various temperatures were used to calculate the thermodynamic parameters. The free energy of micellization ΔG^0_{mic} is obtained using relation:

$$\Delta G^0_{mic} = RTlnCMC \qquad (1)$$

From the temperature dependence of the CMC, the enthalpy of micellization ΔH^0_{mic} is obtained through the van't Hoff relation:

$$\Delta H^0_{mic} = -RT^2 dlnCMC/dT \qquad (2)$$

Entropy of micellization ΔS^0_{mic} is obtained from the relationship:

$$\Delta G^0_{\text{mic}} = \Delta H^0_{\text{mic}} - T\,\Delta S^0_{\text{mic}} \tag{3}$$

Where R is the gas constant and T is the absolute temperature.

The CMC dependence on temperature is often [17-20] expressed as a symmetrical parabolic curve according to equation (4):

$$\ln\text{CMC} = A + BT + CT^2 \tag{4}$$

where the constants A, B and C are determined by the regression analysis of least squares. The enthalpy of micelles is then calculated numerically by substituting equation (4) into equation (2):

$$\Delta H^0_{\text{mic}} = -RT^2[B + 2CT] \tag{5}$$

The entropy, ΔS^0_{mic}, for the micellization can be calculated by the equation:

$$\Delta S^0_{\text{mic}} = \frac{\Delta H^0_{\text{mic}} - \Delta G^0_{\text{mic}}}{T} \tag{6}$$

The values of thermodynamic parameters ΔG^0_{mic}, ΔH^0_{mic} and ΔS^0_{mic} for the studied surfactants are listed in Table 2.

Table 2: Thermodynamic parameters as a function of temperature

Temperature (K)	ΔG^0_{mic} (J/mol)		ΔH^0_{mic} (J./mol)		ΔS^0_{mic} (J/mol.K^{-1})		$-T\,\Delta S^0_{\text{mic}}$ (J/mol)	
	DPC	SDS	DPC	SDS	DPC	SDS	DPC	SDS
283.16	-9571.60	-11305.33	7345.24	4142.58	59.72	54.528	-16904.51	-15440.15
288.16	-9911.01	-11557.92	5401.55	3053.59	53.11	50.679	-15305.97	-14603.66
293;16	-10138.42	-11795.05	3308.06	1880.62	45.84	46.619	-13439.73	-13899.92
298;16	-10373.90	-12053.10	1060.76	621.42	38.32	42.481	-11427.75	-12666.13
303;16	-10493.94	-12255.23	-134.30	-726.23	30.15	38.002	-9142.65	-11520.68
308;16	-10606.92	-12431.05	-3911.14	-2164.57	21.70	33.288	-6688.70	-10258.03
313;16	-10756.27	-12528.53	-6643.73	-3695.84	13.10	28.177	-4105.36	-8823.90
318;16	-10746.57	-12673.98	-9546.06	-5322.26	3.70	23.079	-1178.52	-7342.81
323.16	-10813.21	-12809.35	-12622.1	-7046.07	5.66	17.807	-1830.78	-5754.51

From Table 2, we plotted the thermodynamic parameters as a function of temperature (Figure 3).

Figure 3 shows the variation of thermodynamic parameters of the studied surfactants versus temperature. The results also show that the ΔG^0_{mic} is negative and remains practically constant in the temperature range. The negative value is like with reported by [27-28]. From the results presented in Table 2 it can be generalized that the micellization is exothermic for the two surfactants in the all temperature range studied (ΔG^0_{mic} is negative). The entropy of micellization though positive in all temperature range, decreases with increase in temperature, indicating that the micellization process is endothermic. This is due to the fact that the head group is more hydrated than the hydrophobic tail with increase in temperature which leads to an overall ordering of the system hence, the lowering of the entropy with increase in temperature [29].

The variation of ΔH^0_{mic} with temperature for the surfactants investigated shows two behavior:

(i) The values of ΔH^0_{mic} were positive and decreased with the temperature range [283.16 - 298.16 K], indicating that the micellization process becomes endothermic.

(ii) The formation of micelles becomes increasingly exothermic and became larger in magnitude as the temperature increased T > 298.16K.

From the results of these investigated of cationic and anionic surfactants, we note that the micelle formation is entropy-controlled at low temperatures T< 298.16 K and enthalpy-controlled at high temperatures T > 298.16 K [29]. Indeed, the large changes in entropy and enthalpy with increasing temperature result in moderate decrease in ΔG^0_{mic}. The thermodynamic parameters for the SDS follow the same behavior as the DPC but with respectful values, because both are polar surfactants, even if they have opposite charges they follow the same behavior.

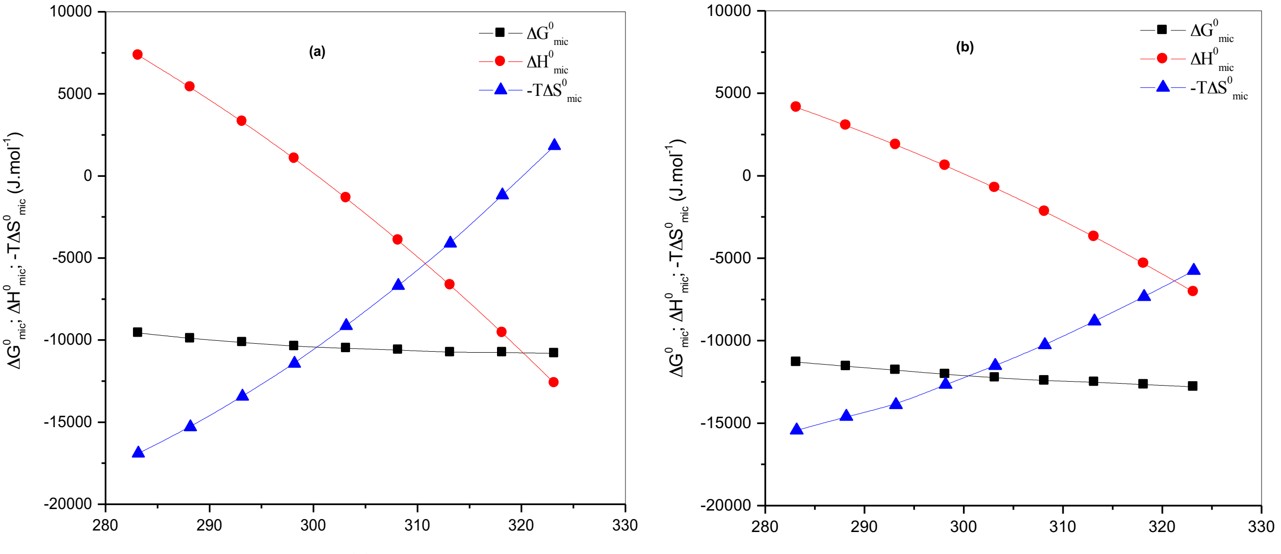

Figure 3: Thermodynamic parameters variation as a function of temperature for studied surfactants: a) DPC; b) SDS

Conclusion

The micellization behavior of cationic DPC and anionic SDS in water has been investigated by conductometric method in the temperature range of 283.16 – 323.16 K. The conductivity is a useful technique for the determination of the thermodynamics parameters of micellization of surfactants, and in probing the effects of their structures on the properties of the aggregates formed. The temperature dependence of the CMC and the micellization process have been determined for DPC and SDS by measuring the concentration dependence of the conductivity at different temperatures. The obtained results have been used to estimate the thermodynamic parameters of micellization. Experimental data indicate that the CMC of surfactants decreases to reach a minimum (T= 298.16 K) and then increases with temperature. ΔG^0_{mic} is negative and remains practically constant indicate that the micellization process is exothermic in nature

ΔH^0_{mic} were positive and decreased with the temperature range [283.16 - 298.16 K], indicating that the micellization process becomes endothermic and the formation of micelles becomes increasingly exothermic as the temperature increased T > 298.16 K.

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