J. Chem. Thermodynamics 77 (2014) 54–62

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamic analysis of unimer-micelle and sphere-to-rod micellar transitions of aqueous solutions of sodium dodecylbenzenesulfonate

Artur J.M. Valente [a], J.J. López Cascales [b], Antonio J. Fernández Romero [c,*]

[a] Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[b] Grupo de Bioinformática y Macromoléculas (BIOMAC), Universidad Politécnica de Cartagena, Aulario II, Campus de Alfonso XIII, Cartagena, Murcia 30203, Spain
[c] Grupo de Materiales Avanzados para la Producción y Almacenamiento de Energía, Universidad Politécnica de Cartagena, Aulario II, Campus de Alfonso XIII, Cartagena, Murcia 30203, Spain

ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form 25 April 2014
Accepted 1 May 2014
Available online 10 May 2014

Keywords:
Sodium dodecylbenzenesulfonate
Electrical conductivity
Critical micelle concentration
Transition micellar concentration
Sphere-to-rod transition
Micellization thermodynamics

ABSTRACT

Temperature dependence of specific conductivity of sodium dodecylbenzenesulfonate (NaDBS) aqueous solutions was analyzed. Two breaks on the plot appeared for all temperature, which suggest two micellar transitions. This has been corroborated by surface tension measurements. The first transition concentration occurs at the critical micelle concentration (CMC), whilst the second critical concentration (so-called transition micellar concentration, TMC) is due to a sphere-to-rod micelles transition. The dependence of CMC and TMC on the temperature allows the computation of the corresponding thermodynamic functions: Gibbs free energy, enthalpy and entropy changes. For the CMC, enthalpy and entropy increments were found that decrease with the temperature values. However, an anomalous behavior was obtained for the TMC, where both ΔS^0 and ΔH^0 values raised with the temperature increase. However, for both transitions, an (enthalpy + entropy) compensation is observed. These results will be compared with similar systems reported in the literature.

1. Introduction

It is well known that amphiphilic molecules form aggregates in aqueous solution when concentration is higher than its critical micelle concentration (CMC). Many experimental magnitudes can be studied to detect the CMC in aqueous solution, such as conductivity, viscosity, refractive index or surface tension [1–3].

Moreover, it has been frequently reported that a second change of the physicochemical properties of the surfactant solutions appears at concentrations above the first CMC. This second change has been determined for numerous surfactants by different experimental methods and it has been termed as the second CMC or second transition micellar concentration (TMC hereafter) [4–10]. Conductivity measurements have been considered one of the most straightforward methods to obtain information about the second CMC, due to its high sensitivity and reproducibility [4]. Several authors have interpreted this second CMC as due to structural micellar changes, most likely a sphere to rod-like transition.

Formation of different micelle shapes aggregates has been previously proposed for sodium dodecylbenzenesulfonate (NaDBS), or other alkyl-benzenesulfonates solutions: also spherical micelles, ellipsoid, rodlike, wormlike, and bilayer structures [11–15] molecular dynamic [11] and NMR studies [12] have shown evidence of NaDBS micelle shape transformations from spherical to more complex micellar aggregates. Also, species accompanying NaDBS can dramatically affect the structural micellar transition from spherical to rod-like or other micellar structures [16,17].

Recently we used electrical conductivity, viscosimetry and cyclic voltammetric measurements to demonstrate a second micellar transition occurring in NaDBS aqueous medium, at concentrations around 0.1 M. [15] Furthermore, we observed how the structural micellar transition of the NaDBS surfactant influences the potentiodynamic polymerization and the final morphology of polypyrrole/DBS synthesized using (monomer + NaDBS) aqueous solutions.

Temperature dependence of CMC for aqueous solutions of ionic and nonionic surfactants has been frequently reported, usually obtaining a concave-shaped with a minimum at a characteristic temperature, labeled as T^*. Hence, Gibbs free energy, enthalpy and entropy changes of micellization, as a function of temperature, have been estimated [5,10,20,21].

However, there are few papers where a thermodynamic analysis of the second transition concentration (TMC) of surfactants with

---

* Corresponding author. Tel.: +34 968325580; fax. +34 968 325931.
E-mail address: antonioj.fernandez@upct.es (A.J. Fernández Romero).

http://dx.doi.org/10.1016/j.jct.2014.05.001
0021-9614/

temperature was carried out. Gonzalez *et al.* have reported different surfactants exhibiting two micellar transitions. They showed that CMC values *vs.* temperature form a concave curve, while TMC values show a convex curve [8–10]. However, no thermodynamic analysis involving the computation of ΔS^0 and ΔH^0, as a function of temperature, for both micellar transitions has been reported, to the best of our knowledge.

The aim of this paper is to investigate how the CMC and TMC values of NaDBS change with the temperature and, from here, to analyze how thermodynamic parameters are modified with temperature change. We present for the first time a comprehensive thermodynamic analysis, including the Gibbs free energy, enthalpy and entropy changes, for the two micellar transitions for aqueous solutions of sodium dodecylbenzenesulfonate. This thermodynamic analysis demonstrates that ΔS^0 and ΔH^0 values diminish with temperature for the CMC, while ΔS^0 and ΔH^0 increase with the temperature for the TMC. This opposite behavior has been corroborated by the results obtained for dodecyldimethylbenzylammonium bromide ($C_{12}BBr$) surfactant, which exhibited two micellar transitions too, when ΔS^0 and ΔH^0 were calculated by us from the CMC and TMC values previously reported [8]. Moreover, thermodynamic parameters of the two surfactants were calculated using the charged pseudo-phase separation model of micellization and the Muller's treatment for both micellar transitions resulting in good agreement.

We have also found for the TMC of NaDBS and $C_{12}BBr$ surfactants a linear relationship between enthalpic and the entropic contributions, as it was reported frequently for the CMC of different surfactants [18,19,22–25]. All of thermodynamic results obtained are discussed for a better understanding of the ΔS^0 and ΔH^0 variation with the temperature and the stability differences between spherical and non-spherical micelles.

2. Experimental

2.1. Reagents

Sodium dodecylbenzenesulfonate (Aldrich, with 0.98 mass fraction purity) was used as received. This compound is a mixture of different isomers, prevailing the p-dodecylbenzenesulfonate. A total of 26 different concentrations of NaDBS solutions were prepared ranging between $(1.05 \cdot 10^{-4}$ and $2.35 \cdot 10^{-1})\ \mathrm{mol \cdot Kg^{-1}}$. Solutions were freshly prepared previous to the measurements. To obtain a good solution free of bubbles a JP Selecta Ultrasonic was used. Millipore water with resistivity of >18 MΩ cm was used.

2.2. Apparatus and procedure

Direct current (DC) Conductivities have been measured with a Crison M-Basic 30 Conductivity Meter. A dip type cell with platinum electrodes was used and calibrated with a standard solution (12.88 or 1.413) $\mathrm{mS \cdot cm^{-1}}$ at $T = 298.15$ K and $P = 1.01 \cdot 10^5$ Pa.

The solutions were prepared by weight using an analytical balance with an uncertainty of ±0.1 mg and the molalities calculated found to be uncertain to $\pm 0.0002\ \mathrm{mol \cdot kg^{-1}}$. The specific conductance of the solution was measured after each addition and corresponds to the average of three independent measurements. Specific conductance values and their standard deviation are listed in SM1 and SM2 tables, in supplementary material. Temperature control was carried out with a Julabo EH F-25 thermostat. Temperature was changed between (283.15 and 313.15) K, in steps of $T = 5$ K. The temperature has been controlled within ±0.02 K. Previous to carrying out each measure we wait 15 min to obtain a stable value.

Surface tension values of NaDBS aqueous solutions, in the concentration range $(2.6 \cdot 10^{-4}$ to $0.19)\ \mathrm{mol \cdot kg^{-1}}$, were measured by the du Nouy ring method based on force measurements, using a Lauda-Brinkman tensiometer TD 3. The uncertainty of the surface tension measurements is $(\pm 0.04)\ \mathrm{mN \cdot m^{-1}}$. The measurements were carried out over the temperature range from (298.15 to 313.15) K and atmospheric pressure. The sample under measurement was kept thermostated in a double-jacketed glass cell by means of Thermo Scientific Phoenix II B5 thermostat bath, equipped with a Pt100 probe. The temperature has been controlled within ±0.02 K. All solutions were prepared in Millipore-Q water. Surface tension data shown in figure 3 are average values of, at least, 5 independent measurements. Experimental surface tensions of water, γ_0, at different temperatures are: $\gamma_0 = 72.0\ (\pm 0.1)\ \mathrm{mN \cdot m^{-1}}$ ($T = 298.15$ K), $\gamma_0 = 71.1\ (\pm 0.2)\ \mathrm{mN \cdot m^{-1}}$ ($T = 303.15$ K), $\gamma_0 = 70.3\ (\pm 0.2)\ \mathrm{mN \cdot m^{-1}}$ ($T = 308.15$ K) and $\gamma_0 = 69.4\ (\pm 0.2)\ \mathrm{mN \cdot m^{-1}}$ ($T = 313.15$ K), respectively. These values are in close agreement with those reported by Vargaftik *et al.* [26]. Experimental relative surface tension values and their standard deviation are listed in table SM3, in supplementary material.

3. Results

The NaDBS specific electrical conductance shows three different linear regimes as a function of surfactant concentration, for seven different temperatures, ranging between (283 and 313) K (figure 1). The first slope change occurring at lower NaDBS concentrations are attributed to the critical micelle concentration (CMC). At $T = 298.15$ K the CMC appears at $4.2 \cdot 10^{-3}\ \mathrm{mol \cdot Kg^{-1}}$.

A second slope change appears at *ca.* 0.1 M, which may be assigned to a second micelle transition (TMC), where a structural transition of the micellar aggregates occurs, probably from spherical to rod-like or more complexes micellar aggregates, such as it has been previously reported for this surfactant [11–15].

CMC and TMC values were calculated by using the interception of the data regression lines method at pre- and post-break regions. The fitting of a straightline equation to experimental data, at different concentrations range, led to regression coefficients higher than 0.998. Figure 2 shows the dependence of CMC and TMC molar fractions on the temperature. As can be seen, variation of CMC values with temperature shows a concave-shape curve, as it has been observed frequently for different surfactants [8,9,18,28]. However, temperature dependence of TMC values shows a convex-shaped curve. A similar behavior has been reported for the second breaks observed for different surfactants [8,9].

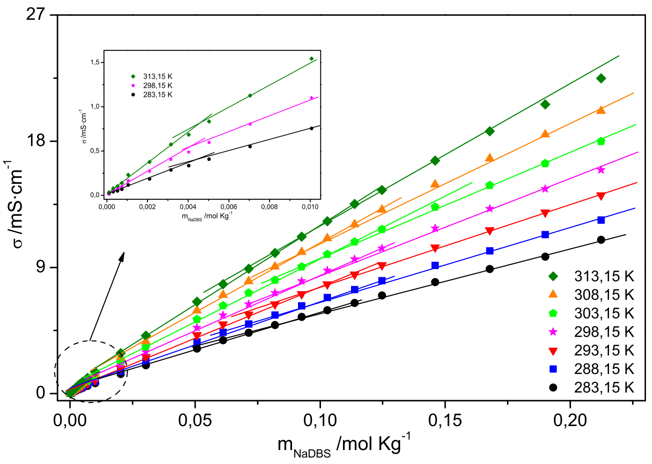

FIGURE 1. Specific conductivity *vs.* NaDBS concentration at different temperatures.