



Cationic and anionic surfactants interaction in water and methanol–water mixed solvent media



Ajaya Bhattarai*, Kavita Pathak, Bikash Dev

Department of Chemistry, M. M. A. M. C., Tribhuvan University, Biratnagar, Nepal

ARTICLE INFO

Article history:

Received 25 May 2016

Received in revised form 6 December 2016

Accepted 7 December 2016

Available online 18 December 2016

Keywords:

Cationic surfactant

Methanol

Micelle

Surface tension

Conductivity

Solvent parameters

Solvophobic effect

ABSTRACT

The micellar properties between dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS) in water and 0.10, 0.20, and 0.30 volume fractions of methanol in methanol–water mixed solvent media have been studied by conductivity and surface tension measurements at 293.15 K. The concentration of dodecyltrimethylammonium bromide varied from 0.0001 to 0.03 mol·L⁻¹ in the presence of ~0.01 mol·L⁻¹ sodium dodecylsulfate and the concentration of sodium dodecylsulfate varied from 0.001 to 0.015 mol·L⁻¹ in the presence of ~0.005 mol·L⁻¹ dodecyltrimethylammonium bromide. Hence, the concentrations of cationic rich (DTAB–SDS) and anionic rich (SDS–DTAB) solutions have been taken in the ratio of 3:1. The critical micelle concentrations (cmc) of DTAB–SDS and SDS–DTAB solutions have been determined by conductivity and surface tension measurements at 293.15 K.

The physicochemical properties such as Gibb's free energy of micellization (ΔG_m^0), free energy of surfactant tail transfer ($\Delta G_{\text{trans}}^0$), maximum surface excess concentration (Γ_{max}), area occupied by surfactant molecule (A_{min}), surface pressure at the cmc (π_{cmc}), packing parameters (P) and standard free energy interfacial adsorption (ΔG_{ads}^0) are calculated in water, 0.10, 0.20 and 0.30 volume fractions of methanol–water at 293.15 K. Addition of methanol significantly affects the physicochemical properties between DTAB and SDS. With increasing concentration of methanol, the cohesive force and the dielectric constant decrease that affects the micellization and other physicochemical properties.

The micellization between DTAB and SDS have been assessed in terms of different solvent parameters. The ratio of the solvent surface tension to the limiting surface tension at the cmc has been used as the solvophobic effect.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications because surfactant mixtures enhance the performance of applications when compared to the use of single surfactants. When mixing surfactants, especially oppositely charged ones, new properties may appear. Aqueous mixtures of anionic and cationic surfactants exhibit many unique properties that arise from the strongly electrostatic interactions between the oppositely charged head groups [1]. It has been well-known for a long time that among the various types of binary surfactant systems, anionic/cationic binary systems exhibits the strongest synergisms in both such as reduction in surface tension and in mixed micelle formation [2].

Interaction between cationic and anionic surfactants in aqueous solution leads to various systems of great importance for both basic science and technological applications [3]. Cationic and anionic surfactant

mixtures are important for a wide range of applications in industries such as enhanced oil recovery, detergency, waste water treatment and pharmaceutical applications [4]. On mixing of the two anionic and cationic surfactants together can produce interesting microstructures not formed by the pure components (e.g. vesicles and/or rodlike micelles) and can dramatically decrease the concentration at which liquid crystalline phases form [5].

The formations of aggregations and their dependence on environmental factors (temperatures and additives etc), their thermodynamics of formation, counterion binding, aggregation numbers and so forth, are important physicochemical aspects that need detailed and intensive attention for understanding both the fundamental and application prospects [6,7]. Changing the solvent quality provides the opportunity to study the role of the co-solvent or solvophobic effect and the increasing use of surfactants in applications which require water free or water poor media makes this type of research more interesting. In recent years, however, many authors have turned their attention to micelle formation and aggregation process of micelles in solvent systems constituted by mixtures of water with some organic solvents having properties similar to water such as ethanol, formamide and glycerol, which have been

* Corresponding author.

E-mail address: bkajaya@yahoo.com (B. Dev).

most widely studied [8,9]. In the past two decades, many investigations have been carried out on various systems [10–12].

Zana et al. [13] investigated the Kraft temperature, cmc, micelle ionization degree of cetyltrimethylammonium in presence of an anionic dimeric (Gemini) surfactant through electrical conductivity; however, the thermodynamic properties were not calculated. Bhattarai et al. [14,15] have explained the influence of concentration, temperature and solvent composition of the binary mixtures of CTAB–SDS surfactant systems in water and methanol–water mixed solvent media and also the thermodynamic properties were calculated [15].

Aslanzadeh and Yousefi [16] have studied the effect of cosolvent (ethanol) on nanostructures of mixed cationic and anionic surfactants. Similarly, catanionic micelles were studied in the mixtures of cetyltrimethylammonium bromide (CTAB) and sodium-dodecyl sulfate (SDS) by Yousefi et al. [17]. Study of the variations in the self-diffusion coefficient and viscosity with the changing concentration of CTAB to SDS in the cationic-rich and anionic-rich regions revealed a phase transitions nanostructures from microstructures (vesicles) to nanostructures (mixed micelle) [18].

As far as we know, there is very little work in the literature that deals with the studies of anionic and cationic surfactant mixtures in non-aqueous solvents [19–21] and few works have been done on the effect of medium [14,15,22]. In this work, we have reported the results for conductance and surface tension measurements on SDS–DTAB and DTAB–SDS in water and methanol–water mixed solvent media at 293.15 K. The cmc has been calculated by using the data extracted from conductometry and tensiometry plots. The thermodynamic parameters and surface properties have also been studied.

The obtained results based on the literature data for individual SDS and DTAB aqueous solution as well as the aqueous solutions of methanol have been compared with the mixed surfactants systems. This study would provide valuable information towards the extent of interactions of the surfactant systems studied. This article intends to discuss minutely about the effect of methanol–water system on micellization between DTAB and SDS at 293.15 K.

The results have been analyzed in terms of the solvent parameters, viz., permittivity (D), Reichardt's parameter ($E_T(30)$), Gordon parameter (G), viscosity (η_0) and Hildebrand parameter (δ). The solvophobic effect can be described from the ratio of solvent surface tension to the limiting surface tension at the cmc.

2. Experimental

2.1. Materials

Methanol (E. Merck, India, 99% pure) was first distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.7911 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $0.5944 \text{ mPa}\cdot\text{s}$ at 293.15 K; these values are in good agreement with those found in the literature [23].

DTAB and SDS were purchased from Merck Specialities Private Limited (Mumbai, India). DTAB was recrystallized several times until no minimum in the surface tension-concentration plot was observed and its cmc 15.38 mM agreed with the literature value [24] at 293.15 K.

SDS was recrystallized several times for purification. The minimum in the surface tension-concentration plot was observed. The aqueous solutions of purified and unpurified samples of sodium dodecylsulfate exhibited minimum in the surface tension versus $\log C$ plot (C , concentration of sodium dodecylsulfate). The minimum in the plot of γ versus $\log C$ for sodium dodecylsulfate is considered due to the presence of highly surface-active dodecyl alcohol molecules [25]. Dodecyl alcohol may be present as impurity in the supplied sample of sodium dodecylsulfate or it may be produced in the sodium dodecylsulfate solution by its hydrolysis. The cmc of sodium dodecylsulfate is taken to be the concentration of sodium dodecylsulfate corresponding to the minimum in the plot of γ versus $\log C$ and it is equal to $8.10 \text{ mmol kg}^{-1}$ in

the absence of any added electrolyte at 25 °C. This value is in good agreement with the cmc values of sodium dodecylsulfate obtained from conductance ($8.10 \text{ mmol kg}^{-1}$) [26].

DTAB and SDS were kept in desiccators and used after drying for 1 h. All solutions were prepared in double-distilled water with a specific conductance of $<0.5 \mu\text{S}/\text{cm}$ at 293.15 K. To make the ratio of 3:1 of DTAB and SDS, first of all, $0.01 \text{ mol}\cdot\text{L}^{-1}$ SDS was dissolved in 250 ml volumetric flask with water and the volume make up of the SDS solution was done after 24 h at constant temperature 293.15 K in thermostat [27].

$0.03 \text{ mol}\cdot\text{L}^{-1}$ DTAB was dissolved in 100 ml volumetric flask by $0.01 \text{ mol}\cdot\text{L}^{-1}$ SDS solution which was acted as the solvent here and the volume make up was done in the next day at constant temperature 293.15 K in the thermostat by the same $0.01 \text{ mol}\cdot\text{L}^{-1}$ SDS solution.

Similarly, to make the ratio of 3:1 of SDS and DTAB, $0.005 \text{ mol}\cdot\text{L}^{-1}$ DTAB was dissolved in 250 ml volumetric flask with water and the volume make up of the DTAB solution was done after 24 h at constant temperature 293.15 K in the thermostat. $0.015 \text{ mol}\cdot\text{L}^{-1}$ SDS was dissolved in 100 ml volumetric flask by $0.005 \text{ mol}\cdot\text{L}^{-1}$ DTAB solution which was acted as the solvent here and the volume make up was done in the next day at constant temperature 293.15 K in the thermostat by the same $0.005 \text{ mol}\cdot\text{L}^{-1}$ DTAB solution.

The methanol–water mixtures were prepared up to 0.3 volume fractions of methanol at 293.15 K by maintaining at constant temperature in the thermostat. The mixed solvents were used after 24 h to make the solutions of DTAB and SDS surfactants. Further, DTAB–SDS and SDS–DTAB solutions were prepared at constant temperature of 293.15 K. The reasons for limiting from water up to 0.3 volume fractions of methanol were due to the formation of precipitate on mixing DTAB rich with SDS (DTAB–SDS) and SDS rich with DTAB (SDS–DTAB) in 0.4 volume fraction of methanol and then higher volume fraction of methanol. Also, it was not possible to get the critical micelle concentration for DTAB–SDS and SDS–DTAB in methanol because of the linear variation of the plot between specific conductance versus concentration.

2.2. Apparatus and procedure

2.2.1. Conductance measurement

The specific conductance measurements of freshly prepared solutions were carried out on a Pye-Unicam PW 9509 conductivity meter with a dip-type cell having a cell constant of 1.15 cm^{-1} with an uncertainty of 0.01%. The cell was calibrated using aqueous potassium chloride solution (0.1 Demal and 0.01 Demal) [28] at 293.15 K.

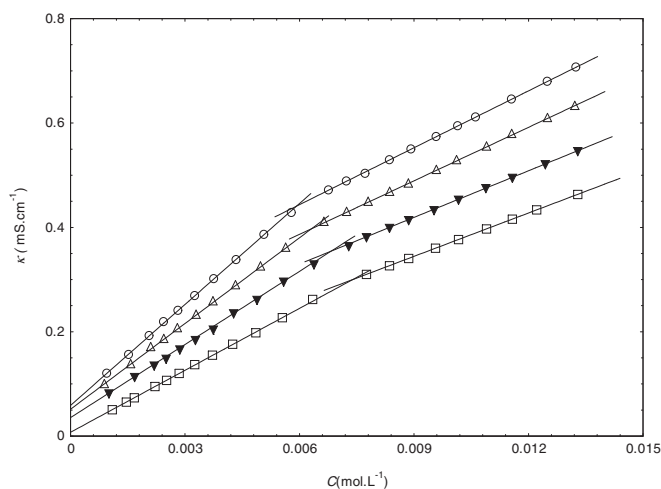


Fig. 1. Concentration dependence of the conductance for SDS–DTAB in pure water (open circle) and (triangles, 0.10 volume fraction of methanol; closed inverted triangles, 0.20 volume fraction of methanol; squares, 0.30 volume fraction of methanol) at 293.15 K.

Download English Version:

<https://daneshyari.com/en/article/5409134>

Download Persian Version:

<https://daneshyari.com/article/5409134>

[Daneshyari.com](https://daneshyari.com)