Colloids and Surfaces A: Physicochem. Eng. Aspects 424 (2013) 81–88

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Determination of CTAB CMC in mixed water + short-chain alcohol solvent by surface tension, conductivity, density and viscosity measurements

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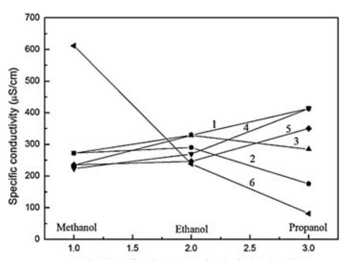
HIGHLIGHTS

- ► Short-chain alcohols form aggregates in the aqueous solutions of their mixture with CTAB.
- ► Ethanol and 1-propanol decrease the CMC of CTAB at their low concentrations.
- ► CTAB forms micelles in the whole range of methanol concentration.
- ► CTAB slightly affects the apparent and partial molar volume of alcohols and water.
- ► The contraction minimum of the sum of alcohol and water volumes exists at their 1:1 ratio.

GRAPHICAL ABSTRACT

Influence of alcohol molecules form on specific conductivity of the aqueous solution of CTAB mixture with methanol, ethanol and propanol. (1) – Conductivity at the critical aggregation concentration of alcohol (CAC). (2) – Conductivity at the constant concentration of alcohols equal to CAC of methanol. (3) – Conductivity at the constant concentration of alcohols equal to CAC of ethanol. (4) – Conductivity at the constant concentration of alcohols equal to CAC of 1-propanol. (5) – Conductivity at the constant concentration of alcohols equal to 1.07 mol/dm^3. (6) – Conductivity in "pure" alcohols.



ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form 1 February 2013
Accepted 4 February 2013
Available online 20 February 2013

Keywords:
Cationic surfactant
Short-chain alcohols
Critical micelle concentration
Apparent molar volume
Partial molar volume
Standard Gibbs free energy of micellization

ABSTRACT

We considered the mutual influence of cetyltrimethylammonium bromide (CTAB) and methanol, ethanol as well as 1-propanol on their behaviour in the aqueous solution. This consideration was based on the surface tension, density, viscosity and conductivity measurements of the aqueous solutions of CTAB and alcohol mixture at 293 K in the whole range of alcohol concentration and in the presence of the surfactant in the monomeric and aggregated forms in the solution. Additionally, the dynamic light scattering measurements were made at the surfactant and alcohol concentration at which the aggregation of their molecules can be expected. CTAB practically does not influence the possibility of the formation of the small aggregates of alcohols and slightly affects the partial and apparent molar volumes of water and alcohols, but alcohols considerably affect the critical micelle concentration (CMC) of CTAB and the degree of counterions bound to its micelles. The mixed micelles of CTAB and methanol are probably formed in the whole range of alcohol concentration but those of CTAB and ethanol or 1-propanol only in their concentration range in which they are present in the monomeric form in the solution.

1. Introduction

Cetyltrimethylammonium bromide (CTAB) is one of the most frequently used surfactants in many industrial processes and everyday life [1]. Therefore, the knowledge of the surface and volumetric properties of CTAB in the presence of different kinds of substrates

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http://dx.doi.org/10.1016/j.colsurfa.2013.02.017

is very important from practical and theoretical points of view. Among the substrates added to the aqueous solution of CTAB, the short-chain alcohols play a very important role [1–3]. Alcohols are organic additives that depending on their concentration should be treated as cosurfactants or cosolvents [1]. However, in the literature there are different opinions concerning the influence of the short-chain alcohols on the CTAB micellization in the whole range of their concentration. According to Rosen [1], they can behave like the water structure breakers, decreasing the dielectric constant of the solvent and increasing the value of critical micelle concentration (CMC), but they can be also incorporated in the micelles, decreasing the repulsive interactions between the ionic heads of the surfactant and reducing the CMC. It should be also mentioned that over a certain concentration, the molecules of alcohol aggregate in the solution.

Li et al. [4] investigated the CTAB–ethanol system in the whole range of ethanol concentration and they stated that the CMC of CTAB increases with the increasing content of alcohol in the solution because of the stronger interactions of CTAB hydrophobic tail with ethanol than with water which makes micellization more difficult. Moreover, ethanol molecules act as solvent structure modifiers, reducing the hydrophobic effect in the solution and therefore increasing the CMC. Li et al. [4,5] also stated that the aggregation number of the micelle decreases with the increasing ethanol content in the solution because of the larger surface area per head group. Anderson et al. [6] investigated the influence of methanol on the CTAB micellization in the wide range of methanol concentration and they also confirmed a considerable increase of the CTAB CMC with the growing concentration of methanol in the solution. When the methanol concentration reaches 60%, the micelles no longer form in the solution. On the contrary, Benito et al. [7] reported that the CMC in the CTAB–1-propanol system determined on the basis of conductometric and spectrophotometric measurements decreases with the increasing concentration of 1-propanol in the solution because the hydroxyl groups of alcohol located between the CTAB polar heads reduce the repulsive interactions between them. Shah et al.[8] and Shah et al. [9] reported that the CMC of CTAB decreases linearly with the increasing content of 1-alkanols in the solution, but they made their measurements only at very low concentrations of alcohols.

Nazir et al. [10] studied the influence of the short-chain alcohols on the CTAB micellization by measuring the specific conductivity of the solutions but only at four concentrations of alcohol equal to 5, 10, 15 and 20 wt%. On the basis of the obtained results, they stated that there is the maximum of CTAB CMC shifted from 15 to 5% in the series of alcohols from methanol to 1-propanol and that the increase of the CMC from the value for the aqueous solutions of CTAB in the absence of alcohol to the maximum results from the decrease of the dielectric constant of the solution. Furthermore, the structure of the hydrogen bonds in the short-chain alcohols is not as strong as in water, so it diminishes the entropy effect which favours the micellization. Over a certain concentration of alcohol, the CMC of CTAB decreases with the increasing alcohol concentration which is caused by the penetration of alcohol molecules into the CTAB micelle and that effect rises from methanol to 1-propanol. However, Nazir et al. [10] did not take into account the range of the alcohol concentration in which the other authors found the minimum of CMC [11,12].

To sum up, in the literature it is possible to find many studies concerning the influence of the short-chain alcohols on the CTAB CMC but only in the narrow range of the low alcohol concentration or in its wider range but with the number of the experimental points which do not guarantee the proper determination of real changes of CMC as a function of alcohol concentration. Moreover, the conclusions were usually made on the basis of the measurements of only one physicochemical property of the solution. For this reason we studied the influence of methanol, ethanol and 1-propanol on the CTAB CMC in the whole range of alcohol concentration and we particularly focused on the range in which they occur in the monomeric form in the solution [13]. Our studies were based on the surface tension, density, viscosity, specific conductivity and dynamic light scattering measurements.

2. Material and methods

2.1. Materials

Doubly distilled and deionized water (Destamat Bi18E) was used. Cetyltrimethylammonium bromide (CTAB) (Sigma–Aldrich) (purity >98%) was purified by the method described in the literature [14]. The solubility of CTAB in water at 293 K is equal to 3 g/dm^3 (≈0.008 M). Methanol (99% purity), ethanol (99% purity) and 1-propanol (99% purity) were obtained from Sigma–Aldrich and purified by fractional distillation in the presence of magnesium and iodine as an activator [15] and kept over molecular sieves. The aqueous solutions of CTAB and alcohol mixture were prepared using doubly distilled and deionized water (Milli-Q system) which had an internal specific resistance of 18.2 MΩ. The purity of water was additionally controlled by the surface tension measurements before preparing the solutions. The alcohol mole fraction (X_2) changed from 0 to 1.

2.2. Measurements

The equilibrium surface tension (γ_{LV}) of the aqueous solution of CTAB and alcohol mixture was measured by the Krüss K9 tensiometer according to the platinum ring detachment method (du Nouy's method). Before the surface tension measurements the tensiometer was calibrated by using water (γ_{LV} = 72.8 mN/m) and methanol (γ_{LV} = 22.5 mN/m). The measured surface tension values were corrected according to the procedure of Harkins and Jordan [16]. The ring was cleaned with distilled water and heated to red colour with a Bunsen burner before each measurement. In all cases more than 10 successive measurements were carried out. The standard deviation depending on the region of alcohol concentration was in the range from ±0.1 to ±0.25 mN/m. The measurement temperature was controlled by a jacketed vessel joined to a thermostatic water bath with the accuracy ±0.01 K. The uncertainty of the surface tension measurements was equal from 0.3 to 0.7% depending on the range of surfactant and alcohol concentration.

- All the experiments were done at 293 K within ±0.1 K.
- The density of the aqueous solutions of CTAB and alcohol mixture was measured with a U-tube densitometer (DMA 5000 Anton Paar) at the constant temperature 293 K.
- The precision of the density and temperature measurements given by the manufacturer is ±0.000001 g/m^3 and ±0.001 K. Uncertainty was calculated to be equal to 0.01%. The densitometer was calibrated regularly with distilled and deionized water.
- All the viscosity measurements of the aqueous solutions of CTAB and alcohol mixture were performed with the Anton Paar viscosimeter (AMVn) at 293 ± 0.01 K with the precision of 0.0001 mPa s and uncertainty 0.3%. The densitometer and viscosimeter were calibrated regularly with distilled and deionized water and methanol.
- The specific conductivity measurements of the aqueous solutions of CTAB and alcohol mixture were made by the conductometer, Mettler Toledo, joined with the thermostat LAUDA RE 415S with the temperature precision ±0.01 K. The uncertainty of the conductivity measurements was ±0.5%. All the density, viscosity and conductivity measurements were made for 3 samples of four sets.