Colloids and Surfaces A: Physicochem. Eng. Aspects 454 (2014) 65–73

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Behavior of cetyltrimethylammonium bromide and Triton X-100 mixture at solution–air interface in presence of short-chain alcohols

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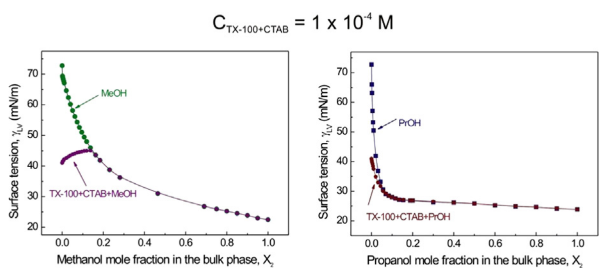
HIGHLIGHTS

- Mutual influence of CTAB + TX-100 mixture and alcohol on their adsorption was found.
- Synergetic effect in water surface tension reduction by studied mixture was found.
- ΔG^0_{ads} of alcohol and CTAB + TX-100 mixture was determined by using different methods.
- Composition of the mixed CTAB + TX-100 + alcohol monolayer was deduced.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 4 April 2014
Accepted 7 April 2014
Available online 16 April 2014

Keywords:
Alcohol
Adsorption
CTAB
Triton X-100
Methanol
Propanol

ABSTRACT

Surface tension measurements of the aqueous solutions of cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) mixture with methanol or propanol in the whole range of alcohol concentration and in the range of surfactant mixture concentration from 1×10^{-6} to 1×10^{-3} M were carried out. Based on the obtained results, the surface excess concentration values of this mixture and alcohols were calculated from the equation of Gibbs adsorption isotherm as well as from the Guggenheim-Adam one. Applying these surface excess concentration values, the composition of the mixed surface layer was established and compared with the hypothetic monolayer determined from the surface excess concentration values of the surfactant mixture and alcohols on the assumption that their adsorption was independent. The composition of the TX-100 and CTAB mixture was also calculated from the Rosen et al. concept on the assumption that water+alcohol was a mixed solvent and compared to the composition of the mixed monolayer formed from the independent adsorption of TX-100 and CTAB. From this comparison it results that there is a synergism in the reduction of the water surface tension at a certain composition of the surfactant mixture in the presence of alcohols. This synergism was confirmed by the standard free energy of the surfactant mixture adsorption calculated from both the Langmuir equation and the excess Gibbs free energy of TX-100 and CTAB mixing in the monolayer in the presence of methanol or propanol.

1. Introduction

Water is a solvent which has a wide application not only in household but also in different industrial processes. In many of them, particularly when the wetting process of the hydrophobic solids is required, the high water surface tension is a disadvantageous property and must be reduced. For this reason, surface active agents are usually added to water [1–4]. Moreover, in practice, mixtures of surfactants are often used because of possible synergetic effect in the water surface tension reduction in comparison to single surface active agents at the same concentration [1,5–7]. Unfortunately, even the application of the surfactant mixture sometimes

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http://dx.doi.org/10.1016/j.colsurfa.2014.04.023
0927-7757/

seems to be not sufficient and for that reason various organic and inorganic substances are added to the product [1]. One of the most important groups of organic additives, which can modify the surface and volumetric properties of aqueous solutions of surfactants are the short-chain alcohols [1,8–14]. At their low concentration they behave as cosurfactants while at higher concentration they should be treated rather as cosolvents [1]. Moreover, the mixed water+alcohol solvents are incredibly important from a practical point of view because they have the antiseptic and disinfecting properties, so they are applied in a large variety of products like cosmetics, cleaning agents and drugs [15,16]. In the literature there is a lot of data concerning the adsorption of single surfactant solutions [1] or mixtures of one surfactant with a short-chain alcohol [8–14,17–19], but there is a lack of information dealing with the multicomponent surfactant mixtures with alcohols and such systems are usually applied.

On the other hand, there is no agreement concerning the mutual influence of alcohol and surfactants on their adsorption [1,10,13,14]. Some authors suggest that, for example, propanol, at its low concentration, causes the increase of the surfactant adsorption at the water–air interface [17]. Others did not report the increase of surfactant adsorption at low alcohol concentration but they stated that at low surfactant concentration, the surfactant causes the alcohol adsorption increase [8,17,18]. From these facts it results that despite a lot of data, the mutual influence of the short-chain alcohol and surfactant on their adsorption at the water–air interface has not been entirely explained yet.

In our previous paper [19], we described the adsorption process of the mixture of two classical surfactants which are widely applied in everyday life, industry and laboratories: cationic cetyltrimethylammonium bromide (CTAB) and nonionic Triton X-100 (TX-100) with ethanol. We found, among other things, that the mole fraction of TX-100 in the mixture with CTAB is higher at the solution–air interface than in the bulk phase and TX-100 is more capable of adsorbing at that interface than CTAB. At very low ethanol concentration, there is a synergism in the reduction of water surface tension and the molecular interaction parameter for formation of the mixed monolayer takes a negative value.

However, it seems that the behavior of the surfactant mixture at the solution–air interface in the presence of a short-chain alcohol depends strongly on the number of carbon atoms in its chain. It is known that the surface and volumetric properties of methanol are considerably different from those of ethanol and propanol [17]. Therefore it is interesting whether these differences are reflected in the behavior of TX-100 and CTAB mixture at the water–air interface. For that reason, in this paper the surface properties of the mixture of TX-100 and CTAB with methanol as well as propanol were investigated. Our investigations were based on the surface tension measurements of the studied solutions and the analysis of the composition of the mixed surface layer at the water–air interface as well as the efficiency of the surfactant mixture and alcohols in the adsorption process.

2. Experimental

2.1. Materials

P-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycol) (Triton X-100 or TX-100) obtained from Fluka and cetyltrimethylammonium bromide (CTAB) purchased from Sigma–Aldrich were used without any further purification. Methanol (99.9% purity) purchased from Sigma–Aldrich was also used without any further purification. Propanol (99.5% purity) obtained from Sigma–Aldrich was purified by the standard method [20]. All the solutions were prepared by using doubly distilled and deionised water (Destamat

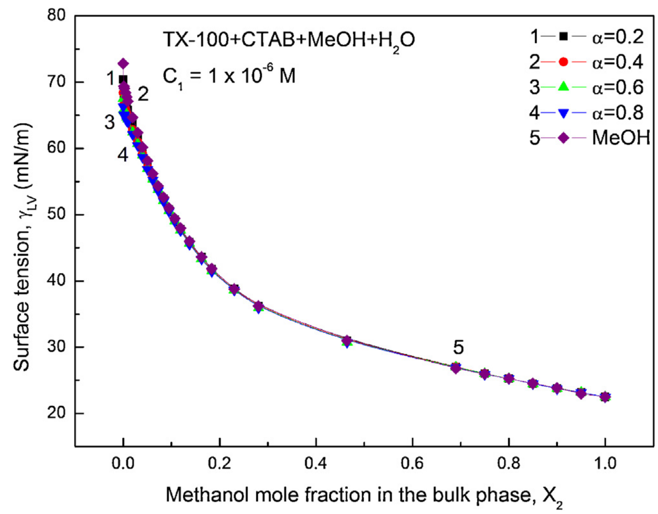

Fig. 1. A plot of the surface tension (γ_{LV}) of the aqueous solutions of the TX-100 and CTAB mixture with methanol vs. methanol mole fraction in the bulk phase (X_2) at the constant total concentration of the TX-100 and CTAB mixture equal to 1×10^{-6} M. Curves 1–4 correspond to the TX-100 mole fraction in the mixture with CTAB in the bulk phase (α) equal to 0.2; 0.4; 0.6 and 0.8, respectively. Curve 5 corresponds to the aqueous solutions of methanol [22].

Bi18E) and its purity was controlled before the preparation of the solutions by the surface tension measurements. The series of the aqueous solutions of the TX-100 and CTAB mixture with methanol as well as propanol in the whole range of alcohol concentration at the constant total concentration of the surfactant mixture (C_1) equal to 1×10^{-6}, 1×10^{-5}, 1×10^{-4} and 1×10^{-3} M were made. The mole fraction of TX-100 in the mixture with CTAB (α) in the bulk phase was equal to 0.2; 0.4; 0.6 and 0.8, respectively and the mole fraction of alcohol (X_2) was in the range from 0 to 1.

2.2. Methods

The equilibrium surface tension (γ_{LV}) measurements of the aqueous solutions of the TX-100 and CTAB mixture with methanol or propanol were carried out by means of Krüss K9 tensiometer according to the platinum ring detachment method (du Noüy's ring method) at 293 K under atmospheric pressure. The tensiometer was calibrated by using the procedure of Huh and Mason [21]. The platinum ring was carefully cleaned with distilled water and heated to the red color using the Bunsen burner before each measurement. The temperature was controlled by a jacketed vessel connected with the thermostatic water bath with the accuracy ±0.1 K. More than 10 successful measurements were performed for each solution. The root-mean-square deviation of the obtained γ_{LV} data depending on the surfactant concentration was in the range from ±0.1 to ±0.2 mN/m and the standard uncertainty (standard deviation of the mean) was in the range from ±0.025 mN/m (calculated for 16 γ_{LV} values for each surfactant mixture concentration in the range of its low concentration) to ±0.063 mN/m (calculated for 10 γ_{LV} values for each surfactant mixture concentration in the range of its high concentration), respectively.

3. Results and discussion

3.1. Surface tension isotherms

The isotherm of the surface tension (γ_{LV}) of the aqueous solutions of the TX-100 and CTAB mixture with methanol (Figs. 1–4) or propanol (Figs. 5–8) can be divided in two parts – the one where the surfactant influence on the solution surface tension is observed and