Journal of Molecular Liquids 199 (2014) 196–201

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Influence of the propanol on the behaviour of binary mixture of nonionic surfactants at the water–air interface

Diana Mańko, Anna Zdziennicka *, Katarzyna Szymczyk, Bronisław Jańczuk

Department of Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form 29 August 2014
Accepted 1 September 2014
Available online 9 September 2014

Keywords:
Adsorption
Nonionic surfactants
Propanol
Standard Gibbs free energy of adsorption
Surface tension

ABSTRACT

The influence of propanol on the behaviour of mixed nonionic/nonionic surfactant solutions, that is p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycols) Triton X-100 (TX-100) and Triton X-165 (TX-165) at the water–air interface was studied by measuring the surface tension. The obtained results of the surface tension measurements were compared with those calculated from the von Szyszkowski and Connors equations. It appeared that using the Connors equation, it is possible to describe the dependence between the surface tension of studied solutions as a function of propanol concentration. However, in the case of the Szyszkowski equation it was possible to describe this dependence with good accuracy only in the range of propanol concentration from 0 to that corresponding to the propanol molecules aggregation (CAC). The constant *b* in the Szyszkowski equation is equal to that in the Langmuir one and allows calculating the values of the standard Gibbs free energy of propanol adsorption which is nearly the same as those determined from the Gu and Zhu equation. The standard Gibbs free energy of adsorption of propanol and surfactant mixture indicates that propanol decreases the surfactant mixture adsorption to a larger extent than vice versa which is confirmed by the comparison of the surface layer composition. At the concentration of propanol higher than its CAC, the surface tension of the solution in the presence and absence of surfactants mixture is the same which suggests that the adsorption of surfactants is very small or practically close to zero.

1. Introduction

Choice of surfactant systems is a critical step for many applications, from laundering to tertiary oil recovery. In general, nonionic surfactants have widespread industrial and technological applications [1–4]. Among them nonionic surfactants, those of polyethylene glycol ethers, $C_{14}H_{21}O(C_2H_4O)_xH$, known as Tritons, play the most important role [5]. Tritons have different numbers of ethylene oxide groups ($(CH_2CH_2)O$) incorporated in their molecules whose increase leads to a progressive change in their properties [5]. They are widely applied as commercial detergents, emulsifiers, wetting agents, as well as excellent, inert chemical detergents. They are also used in molecular biology and biochemistry and to lyse cell membranes as well as for isolation of membrane proteins retaining their native state [6,7]. Commercial surfactants are rather not pure compounds with a single general structure but a mixture of isomers or homologues. In most practical applications different kinds of surfactants are deliberately mixed because the mixture of surfactants exhibits synergism in the surface tension reduction and is characterized by better wetting, foaming or emulsifying properties. The surface and volumetric properties of various individual Tritons were intensively studied [8–18], however, it is possible to find only a few such studies dealing with the mixtures of two or more Tritons [19]. In the earlier studies Szymczyk and Jańczuk [19] showed that the maximal effectiveness and efficiency of adsorption of Triton X-100 and Triton X-165 are observed at different compositions of their mixtures and that the mixtures exhibited synergism in the surface tension reduction. If the water surface tension reduction, even by the surfactants mixture, is not sufficient, it is necessary to modify the mixture properties by adding different types of additives. Short-chain alcohols belong to the most commonly used organic additives [5]. The adsorption behaviour of such complicated systems as the mixture of two surfactants with alcohol is difficult to explain although such systems are very important from the practical point of view. In the literature there can be found papers correlated with the influence of alcohols on the behaviour of single surfactants [20–29], also Tritons [30–32], at different interfaces, but such kinds of data lack in the systems including the alcohol and Tritons mixture.

The changes of the surface tension of solutions are important from both scientific and practical points of view in many processes because they provide information on the structure, composition and energy of the surface region. So, it is interesting whether it is possible to apply the same equations as in the case of solutions of individual surfactants or mixtures of surfactant with alcohol to predict the surface tension of mixture of two Tritons with alcohol. It is also interesting how propanol, which has the greatest activity of the short-chain alcohols, changes the

---

* Corresponding author. Tel.: +48 81 537 5649; fax: +48 81 533 3348.
E-mail address: aniaz@hektor.umcs.lublin.pl (A. Zdziennicka).

http://dx.doi.org/10.1016/j.molliq.2014.09.002
0167-7322/

adsorption properties of two Triton mixtures and vice versa. In the literature it is possible to find different opinions dealing with this problem for the mixtures of single surfactants with short chain alcohols and these opinions are rather based on the surface tension data in the low range of alcohol concentrations [20–29]. Thus, the purpose of our studies was to establish the mutual influence of TX-100 and TX-165 mixture and propanol on their adsorption at the water–air interface and whether it is possible to describe the changes of the surface tension of aqueous solutions of this mixture of surface active agents as a function of propanol concentration by using the Szyszkowski [5] and Connors [33,34] equations.

2. Experimental

2.1. Materials

Triton X-100 (TX-100) p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycol) and Triton X-165 (TX-165) p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycol) were purchased from Sigma-Aldrich and used without any further purification. Propanol (99.5% purity, Sigma-Aldrich) was purified by the standard method [35]. For the solution preparation doubly distilled and deionised water (Destamat Bi18E) was used and its purity was controlled by the surface tension measurements. The series of the aqueous solutions of the TX-100 and TX-165 mixture with propanol were prepared. The mole fraction of alcohol in the solution (X_2) was in the range from 0 to 1 and the mole fraction of TX-100 in the mixture with TX-165 (α) in the bulk phase was equal to 0.8.

2.2. Methods

The equilibrium surface tension (γ_{LV}) measurements of the aqueous solutions of the TX-100 and TX-165 mixture with propanol were carried out at 293 K under atmospheric pressure by means of Krüss K9 tensiometer according to the platinum ring detachment method (du Noüy's ring method). The tensiometer was calibrated by using the procedure of Huh and Mason [36]. The platinum ring was carefully cleaned with distilled water and heated to red colour 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 propanol and surfactant mixture 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) to ±0.063 mN/m (calculated for 10 γ_{LV} values), respectively.

3. Results and discussion

3.1. Surface tension isotherms

The surface tension isotherms of the aqueous solutions of the TX-100 and TX-165 mixture with propanol (Fig. 1) can be divided into two parts: in the first part there is a strong influence of the concentration of the TX-100 and TX-165 mixture and in the second part the surface tension values are the same for each concentration of the surfactant mixtures. The inflection points dividing the isotherm of the surface tension into two parts correspond to the values of the mole fraction of propanol in the bulk phase (X_2) equal to: 0.065; 0.078; 0.087; 0.097 and 0.11 (Fig. S1) for the TX-100 and TX-165 mixture concentration equal to 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 2×10^{-4} and 6×10^{-4} M, respectively. Thus, at the surfactant mixture concentration corresponding to the unsaturated monolayer at the water–air interface in the absence of propanol [19], the inflection points correspond to X_2 at which propanol aggregation occurs (CAC) in the absence of surfactants [28,37]. At the surfactant mixture concentration corresponding to the saturated monolayer at the water–air interface these points correspond to X_2 somewhat higher than propanol CAC. These inflection points occurring on the isotherm of the surface tension of the aqueous solutions of TX-100 and TX-165 with propanol (Fig. S1) can also suggest that in these solutions alcohol molecules can aggregate, however, it is not excluded that the mixed aggregates of propanol and Tritons are formed. Because the surface tension values of the studied solutions above the inflection points practically do not depend on the Tritons mixture concentration, it is difficult to state that in this range of propanol concentration the micelles of surfactants are formed.

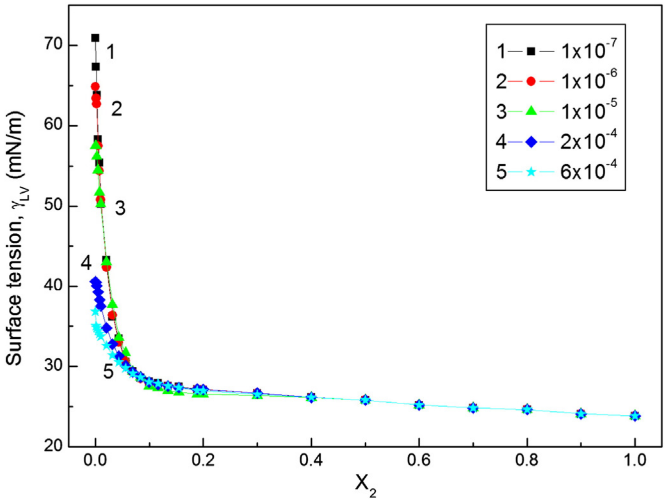

Fig. 1. The plot of the surface tension (γ_{LV}) of the aqueous solutions of TX-100 and TX-165 mixtures with propanol vs. the propanol mole fraction (X_2). Curves 1–5 correspond to the total surfactant mixture concentration equal to 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 2×10^{-4} and 6×10^{-4} M, respectively.

To explain the effect of the mutual influence of alcohol and TX-100 and TX-165 mixtures on the surface tension of the water, the contribution of the propanol and surfactant mixtures to reduction of this tension should be considered. Taking into account the changes of the surface tension of aqueous solution of propanol as a function of its concentration, it can be stated that the influence of surfactant mixtures is evident only in the range of propanol concentration in which it is present in the monomeric form in the solution [28,37]. On the other hand, in this region of propanol concentration the surface tension of the aqueous solution of TX-100 and TX-165 mixtures with propanol is close to that of the solution in the absence of surfactants if their concentration corresponds to the unsaturated monolayer at the water–air interface in the absence of alcohol (Figs. S2 and S3) [19]. Thus, the influence of surfactant mixture on the propanol adsorption is not evident from the surface tension isotherm (Figs. S2 and S3). In the case when the concentration of TX-100 and TX-165 mixtures corresponds to the saturated monolayer of this mixture in the absence of alcohol, considerable influence of surfactant on the surface tension of solution is evident because big differences between the surface tension of alcohol solution and the mixtures with surfactants are observed (Figs. S4–S6, curves 1 and 2). To explain more clearly the contribution of both propanol and the TX-100 and TX-165 mixture to the water surface tension reduction the hypothetical surface tension of the studied solutions was calculated on the assumption that each component of the solution is adsorbed at the water–air interface independently.

It can be stated, at the first approximation that the independent adsorption of surfactants and propanol takes place only at the concentration of the surfactant mixture equal to 1×10^{-7} (Fig. S2). With the increase of the surfactant mixture concentration the mutual influence of propanol and surfactants also increases (Figs. S3–S6). It is interesting that at the concentration of surfactant mixture corresponding to the saturated monolayer at the water–air interface in the absence of alcohol