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Surface and volumetric properties of *n*-octyl-β-D-glucopyranoside and rhamnolipid mixture

Diana Mańko, Anna Zdziennicka *, Bronisław Jańczuk

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

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ABSTRACT

The measurements of surface tension, density and viscosity of aqueous solutions of *n*-octyl-β-D-glucopyranoside (*OGP*) and rhamnolipid (*RL*) were performed at constant concentration of *OGP* or *RL*. The measured values of the surface tension were compared to those calculated from the Joos equation as well as to the hypothetical one. The obtained results were analyzed with regard to adsorption at the water-air interface and micellization of *OGP* in the presence of *RL* and vice versa. On the basis of this analysis, the Gibbs surface excess concentration of the particular surfactants at the water-air interface, the Gibbs surface free energy of adsorption and micellization, the composition of the surface layer, the apparent and partial molar volumes of *OGP* and *RL* were determined. The Gibbs surface free energy of adsorption was calculated on the basis of the critical micelle concentration (CMC) and the surface tension values at this concentration as well as by using the Langmuir equation. The composition of the surface layer was compared to that of hypothetical one. In turn, apparent and partial molar volumes were discussed in the light of the volume of surfactant molecules on the basis of the length and angle of the bonds. From the obtained results it was deduced that there is a strong synergism in the reduction of water surface tension by the *OGP* and *RL* mixture as well as in the CMC. The adsorption of *RL* increases in the presence of *OGP* but *OGP* decreases in the presence of *RL*.

1. Introduction

Surfactants are amphiphilic compounds which are widely applied in many industries and everyday life [1–3]. Commercially available surface active agents are mainly chemically synthesized or derived from petroleum feedstock [4]. The increasing pollution of the environment by synthetic surface active agents has become a significant problem and that is why natural surfactants are intensively studied. These compounds are biodegradable, less toxic than classical ones and very often have better physicochemical properties. Among natural surfactants these of microbial origin are of a special interest. These secondary metabolites of microorganisms have high surface and interface activity, low values of critical micelle concentration, very good cleaning, wetting, emulsifying and foaming properties and they are stable even at extremes of pH, salinity and temperature. One of the most interesting biosurfactant which can be used in many industries, medicine, pharmacy, enhanced oil recovery and in the remediation and bioremediation of soil and water is rhamnolipid (*RL*) [5–13]. It is typically produced by *Pseudomonas aeruginosa* as a mixture of different homologues formed by one or two rhamnose molecules linked to one or two residues of 3-hydroxydecanoic acid groups [14,15]. Two major types of rhamnolipids are monorhamnolipid and dirhamnolipid [7,8,16]. However, our previous studies show that monorhamnolipid is probably synthesized with the highest efficiency [17].

Other ecological friendly surfactants are those produced from renewable resources like sugar-based ones [1,2,18]. Among them these based on glucosides are often used. *N*-octyl-β-D-glucopyranoside (*OGP*) is a nonionic surfactant which is composed of one molecule of glucose as a hydrophilic head linked glycosidically with the straight, alkyl chain. This surfactant is very important in the term of membrane research and it can be used for solubilization, crystallization and extraction of a large number of membrane proteins because it does not cause protein denaturation [19,20]. Moreover, it is no-irritating but mild for skin, mucous membranes and eyes and therefore it is very attractive for personal care products [21–23].

The application of both mentioned surfactants is connected with their surface and volumetric properties. However, in the literature there is not consistency regarding the reduction of the water surface tension as well as the micellization processes [8,17,22,24–27]. In the case of *RL* it is probably connected with the fact that the rhamnolipids are a mixture of different homologues [11,17]. Our previous studies showed that *RL* is very effective in the reduction of water surface tension and forms micelles at very low concentration despite the fact that it is an anionic surfactant [17]. Despite the nonionic character *OGP* [24] is no very effective in the reduction of the water surface tension in the range of its low concentration. However, both surfactants reduced

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* Corresponding author.
E-mail address: aniaz@hektor.umcs.lublin.pl (A. Zdziennicka).

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high water surface tension to the value lower than 30 mN/m which is difficult to obtain using classical nonionic surfactants [1,28]. Because the *RL* molecule has the ═CO groups these groups can form hydrogen bonds between them and —OH groups in *OGP*. It seems that the mixture of these surfactants should show a synergetic effect both in the reduction of water surface tension and in the micellization process. It is known that from the practical point of view the aqueous solutions of surfactant mixture are more useful than those of single surfactants because of the mentioned effect [1].

In the literature it is difficult to find information about the surface and volumetric properties of rhamnolipid mixtures, especially with such compounds like sugar-based surfactants. Therefore, the aim of the research was to investigate the adsorption and the micellization process of the mixtures of biosurfactant and sugar-based surfactant.

2. Material and methods

2.1. Materials

N-octyl-β-D-glucopyranoside (*OGP*) (Fig. 1a) (Sigma-Aldrich) (purity >98%) and R-95 Rhamnolipid (*RL*) (Fig. 1b) (Sigma-Aldrich) were used without further purification. The aqueous solutions of *OGP* and *RL* mixture were prepared using doubly distilled and deionized water (Destamat Bi18E) 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 series of the aqueous solutions of *OGP* and *RL* mixture at the constant *OGP* concentration (C_{OGP}) (1×10^{-5}, 1×10^{-4}, 1×10^{-3}, 5×10^{-3} and 1×10^{-2} M) or *RL* (C_{RL}) (0.00625, 1, 5 and 30 mg/dm^3) were prepared. At the constant *OGP* the concentration of *RL* was changed in the range from 0.0002 to 40 mg/dm^3 while at the constant *RL* the concentration of *OGP* was changed in the range from 1×10^{-7} to 5×10^{-2} M.

2.2. Measurements

The equilibrium surface tension (γ_{LV}) of the aqueous solution of *OGP* and *RL* mixture was measured by the Krüss K9 tensiometer according to the platinum ring detachment method. Before the surface tension measurements the tensiometer was calibrated 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 [29]. The ring was cleaned with distilled water and heated to red colour before each measurement. In all cases more than 10 successive measurements were carried out. The standard deviation depending on the surfactant 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 concentration.

The density of the aqueous solutions of *OGP* and *RL* mixture was measured with a U-tube densitometer (DMA 5000 Anton Paar). The precision of the density and temperature measurements given by the manufacturer is ±0.000001 g/m^3 and ±0.01 K. Uncertainty was calculated to be equal to 0.01%.

All the dynamic viscosity measurements of the aqueous solutions of *OGP* and *RL* mixture were performed with the Anton Paar viscosimeter (AMVn) with the precision of 0.0001 mPa·s and uncertainty 0.3%. The densitometer and viscosimeter were calibrated regularly with distilled and deionized water.

All the experiments were done at 293 K within ±0.1 K.

3. Results and discussion

The literature reports that rhamnolipids produced by *P. aeruginosa*, grown with different carbon sources, can be mixtures of 4–28 different homologues [11,17]. Our investigations [17] showed that in R-95 Rhamnolipid used by us the monorhamnolipid is a dominant form. Therefore, in all our considerations we took into account the molar concentration of rhamnolipid determined on the basis of monorhamnolipid molecular weight equal to 504.

3.1. Surface tension isotherms

The shape of the surface tension (γ_{LV}) isotherms of aqueous solution of the *OGP* and *RL* mixture depends whether they were obtained at constant concentration of *OGP* or *RL*. From this shape it results that the influence of *RL* on the *OGP* adsorption is greater than the reverse (Fig. 2a and b). It follows from Fig. 2a that the inflection point on the γ_{LV} isotherms at the constant *OGP* concentration (C_{OGP}) is changed to lower concentration of *RL* with the C_{OGP} increase. However, the inflection point on the γ_{LV} isotherms at the constant *RL* concentration (C_{RL}) (Fig. 2b) is changed to a smaller extent than in Fig. 2a. Moreover, the inflection points correspond to the minimum of the solution γ_{LV}. It means that *RL* behaves as some 'impurity' of *OGP*. To confirm different influence of *OGP* and *RL* on their mutual adsorption, the solution surface tension was calculated on the basis of the γ_{LV} of aqueous solution of single *OGP* and *RL* (Figs. S1–S9) [17,24]. If we assume that there is independent adsorption of *OGP* and *RL* at the water-air interface then:

$$\gamma_{LV} = \gamma_W - \Pi_{OGP} - \Pi_{RL} \tag{1}$$

where γ_{LV} is the surface tension of aqueous solution of *OGP* and *RL* mixture, γ_W is the water surface tension equal to 72.8 mN/m, Π_{OGP} and Π_{RL} are the differences between the water and aqueous solution of OGP or RL surface tension, respectively. For γ_{LV} calculations the Π_{OGP} and Π_{RL} values corresponding to the *OGP* and *RL* concentrations in their individual solutions the same as in the mixture of these surfactants were used.

Comparing the measured γ_{LV} values of aqueous solution of *OGP* and *RL* mixture at $C_{OGP} = 1 \times 10^{-5}$ M (Fig. S1), which corresponds to the unsaturated surface layer at the water-air interface in the absence of *RL* to those calculated from Eq. (1), it can be stated that there is independent adsorption of *OGP* and *RL* at this interface in the whole range of C_{RL} or that the decrease of γ_{LV} is equal to the sum of the water surface tension reduction by single components of the mixture. It is interesting that there is agreement between the values of γ_{LV} measured and calculated from Eq. (1) in the range of C_{RL} corresponding to its unsaturated monolayer at the water-air interface in the absence of *OGP* (from 0 to 1.984×10^{-6} M) [17] at the $C_{OGP} = 5 \times 10^{-2}$ (Fig. S5), which is higher than *OGP* CMC (2.24×10^{-2} M) in the absence of *RL* [24]. However, in

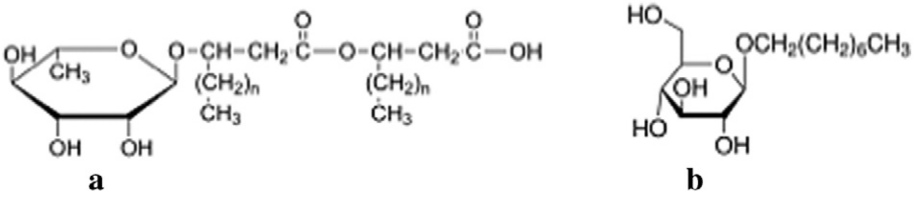

Fig. 1. The structure of rhamnolipid (a) and *n*-octyl-β-D-glucopyranoside (b).