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Adsorption and wetting properties of cationic, anionic and nonionic surfactants in the glass-aqueous solution of surfactant-air system

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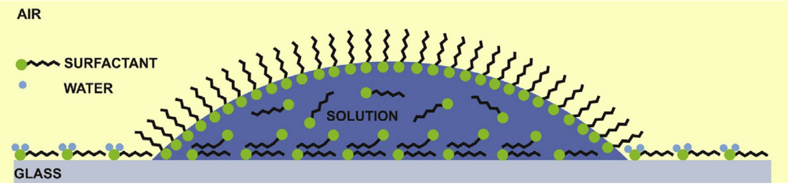
HIGHLIGHTS

- Surface free energy of glass somewhat differs from that of quartz.
- Surfactant molecules are not oriented perpendicularly to glass surface.
- Surfactant tendency to adsorb at glass–water and water–air interfaces does not differ.
- Adhesion of surfactant solution to glass depends on surfactant layer pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

The measurements of the advancing contact angle for water, formamide, glycerol, diiodomethane and aqueous solutions of Triton X-100 (TX-100), Triton X-165 (TX-165), sodium decylsulfate (SDS), sodium dodecylsulfate (SDDS), hexadecyltrimethylammonium bromide (CTAB) and hexadecylpyridinium bromide (CPyB) on the glass surface were carried out. Using the values of the contact angle of these liquids and solutions, the glass surface free energy as well as its components and parameters were determined. This energy, its components and parameters were used for interpretation of the glass wettability by the surfactants solutions in the light of the surfactants adsorption in the three-phase systems and the adhesion of the solution to the glass surface. It appeared that the surface free energy of glass determined from the contact angle of aqueous solution of surfactants on its surface is useful for the determination of the Gibbs surface excess concentration of surfactant at the glass–air and glass–solution interfaces and consequently, the Gibbs standard free energy of surfactant adsorption at these interfaces. It also appeared that by using the Neumann et al. and van Oss et al. equations, it is possible to predict the work of adhesion of aqueous solution of surfactant to the glass surface.

1. Introduction

According to van Oss et al. [1] glass belongs to bipolar solids whose surface free energy results from the Lifshitz–van der Waals and Lewis acid–base intermolecular interactions, The glass surface properties strongly depend on the density of –OH groups [2–4]. In turn, the density of –OH groups on the glass surface depends on the kind of the commercial glass [2]. It has been found that the surface density of –OH groups is dependent on the surface silicon concentration [2]. Thus the SiOH groups play an important role in the adsorption of organic substances such as surfactants [5–7]. The adsorption of surfactants at both the glass–water and at the water–air interfaces largely influences wetting behavior of the aqueous solutions of surfactants on the glass surface [8]. Wettability of the glass surface is important not only from theoretical but also practical points of view. Glass can be treated as a highly

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energetic solid [9,10] so, water should spread completely on its surface. On the other hand, a water drop settled on a high energy solid surface would spread over the surface in two stages [11]. In the first one, a water film is formed on the solid surface as a result of water vapor adsorption or water molecules diffusion from the drop. Thickness of this film depends on the nature of the solid and liquid. The second stage is the actual spreading process. The film formation occurs at the cost of solid surface free energy [12–14], which can be decreased to such a level that, despite theoretical circumstances of complete wetting of the solid, the liquid drop forms a finite contact angle. Such a situation can appear in the case of glass during its wetting by water. This was confirmed by the studies of the glass wettability by apolar and polar liquids [8,9]. It has been proved that temperature treatment and the presence of molecular sieves influence the values of contact angle particularly of polar liquids [9]. Thus the kind of glass and environmental conditions are very important in the studies of its wettability by aqueous solutions of surfactants. As results from the Young equation [15] wettability of solids depends on the solid–air, solid–liquid and liquid–air interfaces tension. The adsorption of surfactants at these three interfaces influences the contact angle value which is a visual measure of solid wettability. The addition of surfactants to water decreases its surface tension [16]. But the solid–water interface tension can decrease, increase or not change due to the surfactant addition [16]. It depends on the structure of the surface layer of surfactants at the solid–water interface. In the case of the bipolar solids such as glass, it is very difficult to establish the changes of the solid–water interface tension under the influence of surfactant adsorption at this interface. Therefore in the literature it is difficult to find the interpretation of the contact angle of aqueous solution of surfactants on the glass surface on the basis of the glass–air, glass–water and water–air interfaces tension changes as a function of surfactants concentration. For such interpretation of contact angle, the glass surface free energy as well as the Lifshitz–van der Waals component and electron-donor and electron-acceptor parameters of the acid–base component should be known. Therefore the purpose of our studies was to determine these components and parameters of the surface free energy of microscope glass slides and the total surface free energy of glass in the presence of surfactants. Then to discuss wettability of glass and the work of adhesion of aqueous solution of some nonionic, anionic and cationic surfactants to the glass surface on the basis of glass–air, glass–water and water–air interfaces free energy changes under the influence of surfactants adsorption at these interfaces were taken into account.

For this purpose the advancing contact angle for water, glycerol, formamide, diiodomethane and aqueous solutions of p-(1,1,3,3-tetramethylbuthyl)phenoxypolyethylene glycols - Triton X-100 (TX-100) and Triton X-165 (TX-165), sodium dodecylsulfate (SDDS), sodium decylsulfate (SDS), hexadecyltrimethylammonium bromide known as cetyltrimethylammonium bromide (CTAB) and hexadecylpyridinium bromide known as cetylpyridinium bromide (CPyB) was measured.

2. Experimental methods

2.1. Materials

Doubly distilled and deionized water (Destamat Bi18E), SDDS, SDS, CTAB, CPyB, TX-100, TX-165, diiodomethane, glycerol and formamide were used in our investigations (Table 1). Of these CTAB, CPyB, SDDS and SDS were purified by the method described in the literature [17].

Microscope glass slides (Glass Processing Plants, Cracow, Poland) (SiO_2 70–74.5%, Na_2O 10–11%, CaO 8–10.5%, Al_2O_3 0.5–1%) used for contact angle measurements were cleaned with soapy water, washed many times in doubly distilled water and placed in an ultrasonic bath for 15 min. This procedure was repeated twice for the same plate. Then they were dried and placed in the desiccator filled with a dehydrating agent (molecular sieves 0.4 nm + 0.5 nm). The quality of the surface of each plate was controlled by a polarizing microscope (Nikon, ECLIPSE E 600 POL). The best glass slides chosen were additionally imaged with the Contour GT (Veeco, USA) profilometer (Fig. 1 as an example). All the images were obtained in open air at room temperature. The images from the profilometer were analyzed using the Vision for Profiles Software. From the obtained images, the values of R_A (the average roughness as calculated over the entire measured array), R_q (the root-mean-squared roughness calculated over the entire measured array) and R_t (max profile height) were determined, for example for Fig. 1 they are: $R_A = 0.39$ nm, $R_q = 0.52$ nm and $R_t = 30.07$ nm. The plates of such and even better parameters were used for contact angle measurements.

2.2. Contact angle measurements

The measurements of advancing contact angle [17–21] of the aqueous solutions of CTAB, CPyB, SDDS, SDS, TX-100, TX-165, water, formamide, glycerol and diiodomethane on the glass slides were carried out by the sessile drop method using the DSA 30 measuring system (Krüss) in a thermostated measuring chamber at 293 ± 0.1 K. Before the contact angle measurements of a given series of solutions, the vessel with water was inserted into the chamber and kept for 24 h. Then the contact angle of water was measured for 1–10 min after the drop was deposited on the glass surface. Then instead of the vessel with water, the one with solution at a given concentration of surfactants was placed in the chamber to stay there for one hour before measurements of its contact angles on the glass surface. The vessel with solution was changed depending on the surfactant concentration. In each case the saturated water vapor was obtained at 293 K for each surfactant concentration. According to Zhuravlev [22] we assumed, at first approximation, that in such conditions, the glass surface is fully hydroxylated and the density of the OH groups should be close to five groups per nm^2 [22]. For each system the glass–solution drop-air contact angle was tested for 1–10 min after the drop was deposited on the glass surface, and the influence of the solution added to the deposited drop was studied. It appeared that the contact angle values in the chamber saturated with the vapor of solution at a given concentration of surfactant were constant in this period of time. The addition of liquid to the deposited drop did not change the contact angle, either. Therefore the contact angle measurements on both sides of the solution drop at a given concentration of surfactant were conducted out immediately after depositing the drop on the glass surface (within about 1–2 min after the drop deposition). The measurements were repeated several times by settling other drops on the same plate. Next a new plate was placed in the chamber and the above procedure was repeated. For each system of glass–solution drop-air at least 30 independent drops were used for determining the average value of advancing contact angle. A good reproducibility of contact angle measurements was found. The standard deviation for each set of values was less than 1.1°.

3. Results and discussion

3.1. Glass surface free energy

The surface free energy of glass (γ_{SV}) and its components as well as parameters can be useful for discussion of the surfactant adsorption at the glass–water interface. In the literature it is