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Adsorption of sodium bis(2-ethylhexyl) sulfosuccinate and wettability in polytetrafluoroethylene–solution–air system

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Abstract

The role of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) adsorption at water–air and polytetrafluoroethylene–water (PTFE) interfaces in wetting of low energy PTFE was established from measurements of the contact angle of aqueous AOT solutions in PTFE–solution drop–air systems and the aqueous AOT solution surface tension measurements. For calculations of the adsorption at these interfaces the relationship between adhesion tension ($\gamma_{LV}\cos\theta$) and surface tension (γ_{LV}), and the Gibbs and Young equations were taken into account. On the basis of the measurements and calculations the slope of the $\gamma_{LV}\cos\theta$–γ_{LV} curve was found to be constant and equal -1 over the whole range of surfactant concentration in solution. It means that the amount of surfactant adsorbed at the PTFE–water interface, Γ_{SL}, is essentially equal to its amount adsorbed at water–air interface, Γ_{LV}. By extrapolating the linear dependence between $\gamma_{LV}\cos\theta$ and γ_{LV} to $\cos\theta = 1$ the determined value of critical surface tension of PTFE surface wetting, $\gamma_{C,}$ was obtained (23.6 mN/m), and it was higher than the surface tension of PTFE (20.24 mN/m). Using the value of PTFE surface tension and the measured surface tension of aqueous AOT solution in Young equation, the PTFE–solution interface tension, γ_{SL}, was also determined. The shape of the γ_{SL}–log C curve occurred to be similar to the isotherm of AOT adsorption at water–air interface, and a linear dependence existed between the PTFE–solution interfacial tension and polar component of aqueous AOT solution. The dependence was found to be established by the fact that the work of adhesion of AOT solution to the PTFE surface was practically constant amounting 46.31 mJ/m^2 which was close to the work of water adhesion to PTFE surface.

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Keywords: Adsorption; Surface tension; Polytetrafluoroethylene; Surfactant; Sodium bis(2-ethylhexyl) sulfosuccinate

1. Introduction

Wetting of solids by surface active agents is important for many technological applications, such as oil recovery, coating, adhesion, flotation, printing, detergency and cosmetics industry [1]. The addition of surface active agents is needed to achieve a better wettability of a given solid by a water solution. The surface active agents adsorb at water–air and solid–air interfaces reducing the water surface tension and solid–water interface tension to values which cause contact angle decrease in hydrophobic low energetic solid–solution drop–air systems. In the case of polar solid–solution drop–air systems surfactant adsorption at solid–water interface does not always reduce the solid–water interfacial tension [2].

The influence of surfactants on the contact angle in solid–water–air systems was studied by many investigators [2–6], but it was often studied without resorting to adsorption. However, adsorption and wetting are strongly related [3,7].

At solid–water interfaces we are interested in determining: (1) the amount of surfactant adsorbed per area unit of the solid surface, since this is a measure of how much of the surface of the solid has been covered and changed by adsorption, (2) the orientation of the adsorbed surfactant at the interface, since this determines how it will be affected by adsorption, (3) the energy changes in the system, since these parameters may shed light on the mechanism allowing us to predict how a surfactant with a given molecular structure is adsorbed at the water–air and solid–water interfaces [2].

Bernett and Zisman [8,9] showed a straight linear relationship between $\cos\theta$ (θ is the contact angle) and the surface tension of liquids or aqueous surfactant solutions. The

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extrapolation of this relationship to $\cos\theta = 1$ allows us to estimate the liquid surface tension required to give the contact angle of 0°, which Zisman [10] described as the critical surface tension of wetting (γ_C). But Bergman and van Voorst Vader [11] showed a straight linear relationship between the adhesion tension and surface tension of aqueous solutions of several types of surfactants, and that the slope of the lines for low-energy solids, such as PTFE was equal to −1.

For non-polar solids, such as for example PTFE, a variety of approaches, which basically assume adsorption and applicability of the Gibbs and Young equations, give a very good agreement with experimental results of the contact angle in the solid–surface active agent solution drop–air system and the surface tension of the active agent solution when hydrocarbon chain surfactants are used [3].

A thermodynamic analysis of the contact angle and surface tension as a function of the surfactant concentration revealed that the surface excess parameter (Γ_{SL}–Γ_{SV}), which simultaneously measures adsorption to solid–water and water–air interfaces, could be interpreted in terms of solid–water adsorption for non-wettable surfaces under experimental conditions to avoid surfactant deposition at solid–air interfaces, so that $\Gamma_{SV} = 0$ [2,7,12]. These conditions provide direct access to interaction between non-polar PTFE surface and the aqueous phase containing a surfactant.

Since the mechanism of surfactants adsorption at water–air and solid–air in relation to the wettability process is not completely explained in some systems, the purpose of our studies was to determine the adsorption properties at water–air and PTFE–water in relation to PTFE wettability by AOT solutions ($C_{20}H_{37}NaO_7S$) which is a double-chained anionic surfactant with a relatively small hydrophilic head, soluble both in polar and non-polar solvents [13,14]. For this purpose measurements of the surface tension of AOT aqueous solutions and the contact angle in the PTFE–drop of aqueous AOT solution–air system were carried out.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (Sigma–Aldrich), (purity ≥ 99%) was used for aqueous solution preparation. For preparation of AOT aqueous solutions doubly distilled and deionized water (Destamat Bi 18E) was used. The surface tension of water ($\gamma_W = 72.8$ mN/m) was always controlled at 293 K by Krüss K9 tensiometer under atmospheric pressure by ring method before the solutions were prepared.

The polytetrafluoroethylene (PTFE) plates used for contact angle measurements were prepared from PTFE homopolymer, obtained as a result of free-radical polymerization of tetrafluoroethylene in the presence of peroxides as initiators by the Nitrogen Industrial Plant in Tarnów (Poland). The plates were cut from a large sheet of PTFE, mechanically polished and cleaned by triple boiling in HCl (1:1) and triple boiling in doubly distilled and deionized water. Their final cleaning in doubly distilled water was performed in an ultrasonic bath for twenty minutes; the plates were then dried by blowing hot air [15]. The quality of the surface of each plate was controlled by a polarizing microscope (Nikon, ECLIPSE E600 POL). Plates of a good smoothness were used for contact angle measurements.

2.2. Contact angle and surface tension measurements

The advancing contact angle for water and aqueous solution of AOT on PTFE plates was measured with sessile drop method by using the telescope–goniometer system at 25× magnification in a thermostated measuring chamber at 293 ± 0.1 K. After settling a drop of aqueous solution of the surfactant at a given concentration in the range from 0 to 10^{-2} M on PTFE plate the contact angle was read immediately on both sides of the drop. 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. The reported contact angle values were the average of at least 10 independent drops. They were exactly reproducible to 1.1° [5].

Surface tension measurements of the AOT aqueous solutions were made by ring method using a Krüss K9 tensiometer, under atmospheric pressure. In all cases, more than five successive measurements were carried out and the standard deviation did not exceed ±0.2 mN/m. The temperature was controlled within ±0.1 K.

3. Results and discussion

3.1. Critical micelle concentration (CMC)

Surface tension, γ_{LV}, values of AOT solutions (Table 1) are presented in Fig. 1 (curve 1), in the form of, γ_{LV} versus log C plots; C is the concentration of AOT.

A curve break [2], occurs at critical micelle concentration (CMC), the concentration at which the monomeric form, in which the surfactant exists in a very dilute solution, aggregates forming a surfactant cluster known as a micelle. The CMC value of AOT in water is in agreement with the reported value [2,13,19], and equals 2.5×10^{-3} mol/dm^3.

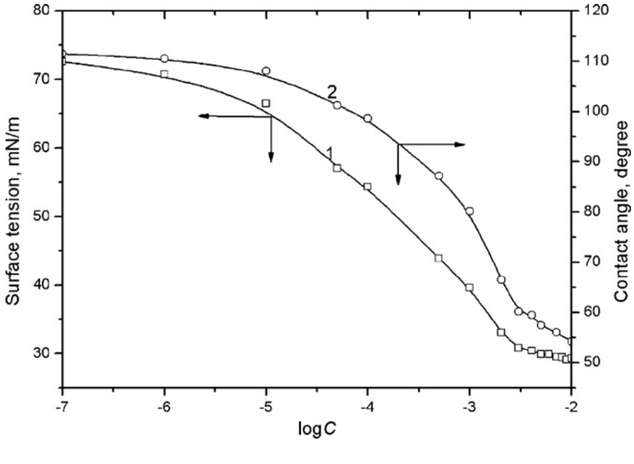

Fig. 1. The relationship between the values of surface tension of aqueous AOT solution (γ_{LV}) (□) and the contact angle, θ (○) and AOT concentration (log C).