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Work of adhesion and activity of aqueous solutions of ternary mixtures of hydrocarbon and fluorocarbon nonionic surfactants at the water–air and polymer–water interfaces

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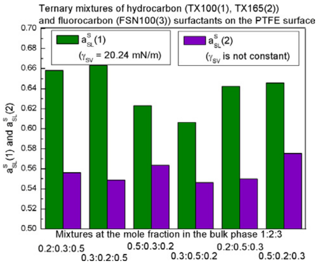
HIGHLIGHTS

- The work of adhesion is not constant for fluorocarbon surfactants.
- The work of adhesion of the fluorocarbon tail to the PTFE surface is different.
- The surface tension of PTFE changes with the total concentration of the mixture.

GRAPHICAL ABSTRACT

Comparison of the values of the activity at the PTFE-water interface ($a^S_{S,SL}$) of aqueous solutions of the ternary surfactant mixtures composed of TX100, TX165 and FSN100 at the total concentration in the bulk phase equal to 10^{-4} M, calculated on the assumption that γ_{SV} for PTFE is equal to 20.24 mN/m, and that γ_{SV} is not constant and is equal to that determined for FSN100 at a given concentration.



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ABSTRACT

The values of the surface tension and contact angle on the polytetrafluoroethylene surface (PTFE) of aqueous solutions of the ternary mixtures of hydrocarbon surfactants, TX100 and TX165, and fluorocarbon FSN100 at different mole fractions of surfactants in the bulk phase were applied for the studies of the correlation between the adsorption of surfactants at the solution–air and polymer–solution interfaces, the work of adhesion determined from the Young–Dupree equation, the parameter of the intermolecular interactions and the spreading coefficient of aqueous solutions of the studied mixtures on the PTFE surface. For this purpose the values of the total mole fraction and activity of surfactants at the polymer–solution interface obtained from the Sprow and Prausnitz equation were compared to those at the solution–air one. Also on the basis of the mole fraction of the particular surfactants at the PTFE–solution and water–air interface and on the assumption of the additivity of the adhesion work, the work of adhesion of the fluorocarbon tail to the PTFE surface as well as the Lifshitz–van der Waals component of the PTFE surface tension were calculated.

1. Introduction

Wetting of solid substrates by liquids is a basic element in many natural and commercial processes, and its understanding has been the subject of intensive investigation over the past decades [1–10]. Some common examples include the spreading of liquid droplets on solids such as in the spraying of paint and agricultural chemicals, the penetration of ink in paper, the liquid absorbency or repellency of fabrics, inbibition of fibers in absorbent media, and the displacement of one fluid (oil) by another (water or a complex solution) over a solid in enhanced oil recovery [11,12]. From a fundamental perspective, a study of wetting behavior is challenging because

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contact angles are the macroscopically observable consequence of interactions on a molecular level. It can be spreading of a liquid over a surface, penetration of a liquid into a porous medium, or displacement of one liquid by another. It can help characterize surfaces and determine solid–liquid interactions [13–15].

In the previous paper [16] the wettability of polytetrafluoroethylene (PTFE) by aqueous solutions of the ternary mixtures of nonionic hydrocarbon, TX100, TX165, and fluorocarbon, FSN100, surfactants at different mole fractions of surfactants in the bulk phase, and the concentration of these mixtures of surfactants at the water–air and PTFE–water interfaces were considered. It was shown that at the concentration of the studied mixtures equal and higher than their critical micelle concentration (CMC), the values of the contact angle, θ, on the PTFE surface are smaller than those of the contact angle for all single surfactants but the values of the surface tension, γ_{LV}, are smaller than those only for the hydrocarbon surfactants, TX100 and TX165. Also the values of the ratio of the surface excess concentration of the mixtures at the water–air and PTFE–water interfaces calculated in different ways and those of the critical surface tension of PTFE wetting suggest the specific interactions and synergetic effect between the hydrocarbon and fluorocarbon surfactant molecules, as well as those of surfactants with water and PTFE surface. In addition, the values of the critical surface tension of wetting of the PTFE surface determined from the relationship between the adhesion and surface tension of the studied mixtures suggest that the PTFE surface tension decreases step by step with the increase of the fluorocarbon surfactant concentration in the mixture. Since in the earlier studies it was proved that the surface tension of PTFE is changed under the influence of the FSN100 film on its surface and depends on the time of solution contact with the polymer surface and its concentration in the bulk phase, it was interesting to determine the concentration and activity of surfactants in the ternary mixtures at the PTFE–solution interface in two different ways, that is on the assumption that the surface tension of PTFE is either constant and/or changing, and to compare these values with those at the water–air interface. Thus, the purpose of the presented studies was to find the correlation between the adsorption of ternary surfactant mixtures studied earlier [16] at the PTFE–solution and solution–air interfaces and the work of adhesion and spreading coefficient of the solutions on the PTFE surface as well as the parameter of the interaction across the interface.

2. Concentration and activity of surfactants at the solution–air and polymer–solution interfaces

On the basis of the values of Γ_{LV} and Γ_{SL} that is the surface excess concentration of surfactants at the solution–air and polymer–solution interface, respectively, which are practically equal to the total concentration at this interface, it is possible to calculate the composition of the surface layer, namely the mole fraction of the surfactant 1 (X^S) forming 1 m^2 surface plane using the following equations [17,18]:

$$\Gamma_{LV}^{W} N A_o^{W} + \Gamma_{LV}^{S} N A_{o,LV}^{S} = 1 \tag{1}$$

$$\Gamma_{SL}^{W} N A_o^{W} + \Gamma_{SL}^{S} N A_{o,SL}^{S} = 1 \tag{2}$$

$$X_{LV}^{S} = \frac{\Gamma_{LV}^{S}}{\Gamma_{LV}^{W} + \Gamma_{LV}^{S}} \tag{3}$$

$$X_{SL}^{S} = \frac{\Gamma_{SL}^{S}}{\Gamma_{SL}^{W} + \Gamma_{SL}^{S}} \tag{4}$$

where Γ_{LV}^{W} and Γ_{SL}^{W} are the Gibbs surface excess concentrations of water at the solution–air and polymer–solution interface, Γ_{LV}^{S} and Γ_{SL}^{S} are the Gibbs surface excess concentrations of the surfactant at the solution–air and polymer–solution interface, N is the Avogadro number, A_o^{W} is the minimal possible area occupied by water molecules at the interface, and $A_{o,LV}^{S}$ and $A_{o,SL}^{S}$ are the minimal possible areas occupied by the surfactant molecules at the interfaces. A_o^{W} is commonly assumed on the basis of adsorption data as equal to 10 Å^2, but it is possible to determine $A_{o,LV}^{S}$ and $A_{o,SL}^{S}$, among others, from the Joos equation of state [19].

It is known that the standard chemical potential can be defined in two different ways. Thus, for the surface region S and bulk B phase, the chemical potential can be expressed by the following equations, respectively [20,21]:

$$\mu_i^S = \mu_i^{S(0)} + RT \ln a_i^S - \gamma_i \omega_i \tag{5a}$$

$$\mu_i^S = \mu_i^{S(0)} + RT \ln x_i^S f_i^S - \gamma_i \omega_i \tag{5b}$$

or

$$\mu_i^S = \mu_i^{S(\Theta)} + RT \ln a_i^{*S} - \gamma_i \omega_i \tag{6a}$$

$$\mu_i^S = \mu_i^{S(\Theta)} + RT \ln x_i^S f_i^{*S} - \gamma_i \omega_i \tag{6b}$$

and

$$\mu_i^B = \mu_i^{B(0)} + RT \ln a_i^B \tag{7a}$$

$$\mu_i^B = \mu_i^{B(0)} + RT \ln x_i^B f_i^B \tag{7b}$$

or

$$\mu_i^B = \mu_i^{B(\Theta)} + RT \ln a_i^{*B} \tag{8a}$$

$$\mu_i^B = \mu_i^{B(\Theta)} + RT \ln x_i^S f_i^{*B} \tag{8b}$$

where T is the temperature, R is the gas constant, a is the activity, f is the activity coefficient and $\mu_i^{(0)}$ is the standard chemical potential if $f_i \to 1$ for $x_i \to 1$, $\mu_i^{(\Theta)}$ is the standard chemical potential if $f_i^* \to 1$ for $x_i \to 0$, γ_i is the surface tension of pure component i and ω_i is the molar surface area of i component. If we assume that for each component of the solution the condition $f_i \to 1$ for $x_i \to 1$ is fulfilled then this is the symmetrical definition of the activity of solution components. However, if only for solute this condition is fulfilled but for the solutes $f_i^* \to 1$ for $x_i \to 0$ then this is the asymmetric definition of activity.

Because in the equilibrium state $\mu_i^B = \mu_i^S$, then on the basis of Eqs. (5a) and (8b) the Sprow and Prausnitz equation [22] can be obtained. This equation for the aqueous solution of surfactants assumes the following forms:

$$\gamma_{LV} = \gamma_W + \frac{RT}{\omega_W} \ln \frac{a_W^S}{a_W^B} \tag{9}$$

and

$$\gamma_{LV} = \gamma_S + \frac{RT}{\omega_S} \ln \frac{a_S^S}{a_S^B} \tag{10}$$

where γ_{LV} is the surface tension of aqueous solution of the surfactant, γ_W is the surface tension of water, γ_S is the “surface tension of surfactant”, ω_W is the molar area of water at the water–air interface, ω_S is the molar area of surfactant at the water–air interface, a_W^S and a_W^B are the activity of water in the surface layer and bulk phase, respectively, and a_S^S and a_S^B are the activity of surfactant in the surface layer and bulk phase, respectively.