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Wettability of a Glass Surface in the Presence of Two Nonionic Surfactant Mixtures

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Measurements of the advancing contact angle (θ) were carried out for aqueous solution of *p*-(1,1,3,3-tetramethylbutyl)phenoxy(ethylene glycol), Triton X-100 (TX100), and Triton X-165 (TX165) mixtures on glass. The obtained results indicate that the wettability of glass depends on the concentration and composition of the surfactant mixture. The relationship between the contact angle and concentration suggests that the lowest wettability corresponds to the concentration of TX100 and TX165 and their mixture near the critical micelle concentration (CMC). The minimum of the dependence between the contact angle and composition of the mixtures for each concentration at a monomer mole fraction of TX100, α , equals 0.2 and 0.4 points to synergism in the wettability of the glass surface. In contrast to the results of Zisman (Zisman, W. A. In *Contact Angle, Wettability and Adhesion*; Gould, R. F., Ed.; Advances in Chemistry Series 43; American Chemical Society: Washington, DC, 1964; p 1) there was no linear dependence between $\cos \theta$ and the surface tension of aqueous solutions of TX100 and TX165 mixtures for all studied systems, but a linear dependence exists between the adhesional tension and surface tension for glass, practically, in the whole concentration range of surfactants studied, the slopes of which are positive in the range of 0.43–0.67. These positive slopes indicate that the interactions between the water molecules and glass surface might be stronger than those between the surface and surfactant molecules. So, the surface excess of surfactant concentration at the glass–water interface is probably negative, and the possibility for surfactant to adsorb at the glass/water film–water interface is higher than that at the glass–water interface. This conclusion is confirmed by the values of the work of adhesion of “pure” surfactants, aqueous solutions of surfactants, and aqueous solutions of their mixtures to the glass surface and by the negative values of glass–water interfacial tension determined from the Young equation in the range of surfactant concentrations corresponding to their unsaturated monolayer at the water–air interface.

Introduction

The special property of surfactants that makes them so interesting is their amphiphilicity. This property enables them to form a multitude of different structures in solution depending on concentration and surrounding media. Another consequence of their amphiphilicity is their tendency to adsorb at interfaces.¹ The behavior at solid–liquid interfaces is of special importance for many industrial applications such as detergency, wetting, flotation, and dispersion stability.^{2,3}

Nonionic surfactants composed of a polyethylene oxide chain to which a hydrophobic part is attached have widespread industrial and technological applications.^{2–5} One of the most important reasons for their frequent use is that these surfactants are suited for mixing with other surfactants. This seems to be very important because in practical applications nonionic surfactant mixtures are often used because they are usually more effective than a single surfactant.⁵ The effectiveness of mixed surfactant systems, which is called synergism, is related to specific interactions between molecules (ions) of different surfactants, which can enhance or deteriorate the action of a mixture with respect to some property of these systems.^{6,7} Our earlier studies

showed that, even for mixtures of two anionic surfactants, having different hydrophilic heads and a different length of hydrophobic alkyl tails,^{8,9} and also for cationic/nonionic^{10,11} and nonionic/nonionic surfactant mixtures,^{12,13} there is no linear relationship between the surface tension, the critical micelle concentration, the wettability of hydrophobic low energetic solids, and the composition of the mixtures. This deviation and the negative values of intermolecular interactions between surfactants in the mixed monolayer, micelles, at the solid–liquid interface, and the conditions for the existing synergism or antagonism confirmed that there was synergism in the surface tension reduction and contact angle and also micelle formation in the whole composition range of two nonionic surfactants mixtures. From this point of view it is interesting if the synergetic effect is present in the wettability of hydrophilic high energetic solids. Thus, the purpose of our studies was to determine the influence of the concentration and composition of aqueous solutions of mixtures of two nonionic surfactants, *p*-(1,1,3,3-tetramethylbutyl)phenoxy(ethylene glycol), Triton X-100 (TX100), and Triton X-165 (TX165) on the wettability of glass plates. The correlation between the adsorption of the surfactants at the water–air and glass–water interfaces and the advancing contact angle was also investigated.

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2. Experimental Section

2.1. Materials. Triton X-100 (TX100), *p*-(1,1,3,3-tetramethylbutyl)phenoxy-poly(ethylene glycol) [$C_{14}H_{21}(CH_2CH_2O)_xOH$ ($x = 10$), Fluka], and Triton X-165 *p*-(1,1,3,3-tetramethylbutyl)phenoxy-poly(ethylene glycol) [$C_{14}H_{21}(CH_2CH_2O)_xOH$ ($x = 16$), Fluka] were used for the preparation of aqueous solutions. Aqueous solutions of individual surfactants and TX100 and TX165 mixtures at different ratios of TX100 to TX165 were prepared using doubly distilled and deionized water (Destamat Bi18E). The surface tension of water was always controlled before the solution preparation.

Microscope glass slides (COMEX, Poland) used for contact angle measurements were cleaned many times, washed in double distilled water, and placed in an ultrasonic bath for 15 min. They were then dried and placed in a desiccator filled with a dehydrating agent. The quality of the surface of each plate was controlled by using a polarizing microscope (Nikon, ECLIPSE E 600 POL). Only plates of a good smoothness and purity were used for contact angle measurements.

2.2. Contact Angle Measurements. The measurements of advancing contact angles^{14–17} for aqueous solutions of TX100, TX165, and TX100/TX165 mixtures on glass slides were carried out via the sessile drop method with a telescope–goniometer system, at 25 \times , in a thermostatted measuring chamber at 293 \pm 0.1 K. At the beginning of the experiments, the contact angles of aqueous solutions of surfactant mixtures at different concentrations were determined in the time period from 1 to 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 by the vapor of the solution at a given concentration of surfactant mixtures 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 mixture were carried out immediately after depositing the drop on the glass surface (within about 1–2 min after depositing 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. In the chamber, the saturated vapor of water was present because a vessel with a given solution was placed in it for a few hours at a given temperature. For each system of glass–solution drop–air, at least 30 independent drops were used for determining the average value of the 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 $^\circ$.

2.3. Liquid Surface Tension Measurements. Surface tension measurements were made at 293 K with a Krüss K9 tensiometer under atmospheric pressure by the ring method. The platinum ring was thoroughly cleaned, and the flame was dried before each measurement. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension.

It was then subsequently pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension, γ_{LV} (mN/m). Measurements of the surface tension of pure water at 293 K were performed to calibrate the tensiometer and to check the cleanliness of the glassware. In all cases, more than 10 successive measurements were carried out, and the standard deviation did not exceed ± 0.2 mN/m. The temperature was controlled to within ± 0.1 K.

3. Results and Discussion

3.1. Wettability of a Glass Surface. The measured values of the advancing contact angle (θ) for aqueous solutions of TX100, TX165, and their mixtures on the glass surface are presented in Figure 1. This figure shows the dependence of θ on the logarithm

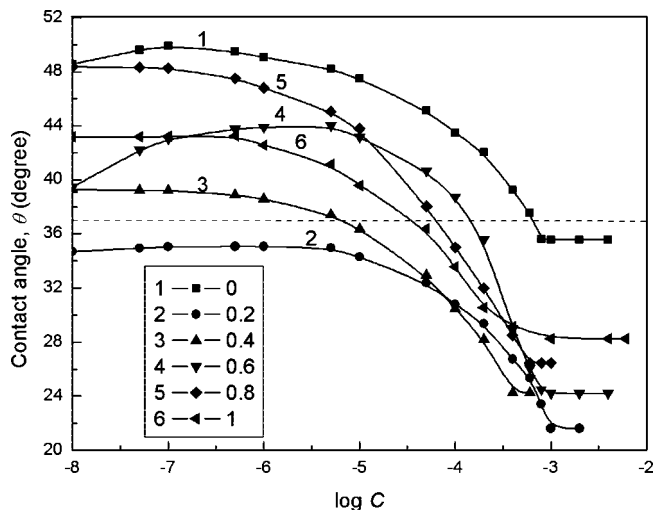


Figure 1. Relationship between the contact angle, θ , and logarithm C for different values of the monomer mole fraction of TX100, α , in TX100 and TX165 mixtures (for glass), where C is the total concentration of the mixture.

of the total concentration of surfactants in aqueous solution (C) for α (α is the mole fraction of TX100 in the mixture) equal to 0, 0.2, 0.4, 0.6, 0.8, and 1. The obtained results indicate that the contact angles, θ , of TX100, TX165, and their mixtures depend on the concentration of the solution, C , and composition, α , of the mixture (Figure 1). The θ – $\log C$ curve for each α value apart from 0.2 (C is the total mixture concentration) has a maximum of θ at C corresponding to the formation of the unsaturated monolayer of adsorption at the water–air interface.¹² For α equal to 0.4, 0.6, and 0.8, a maximum is observed between 10^{-8} and 10^{-5} mol/dm³, because the contact angle of water on the glass surface is equal to 37 $^\circ$ (dashed line in Figure 1). A similar shape of θ – $\log C$ curves was observed by other authors in different systems including the surfaces of mineral oxides and aqueous solutions of surfactants.^{18,19} In the literature, there are few examples of such rather high values of contact angles of water on glass surfaces,^{20,21} but it is worth emphasizing that the value of the contact angle for a given liquid can change significantly with an increase of the environment relative humidity. Also, the method of glass preparation affects significantly the values of the contact angle.

To show more clearly the influence of the composition of the mixtures of TX100 and TX165 on the glass wettability in Figure 2, the dependence between the contact angle and monomer molar fraction of TX100, α , in the TX100 and TX165 mixture is presented for the total concentrations equal to 10^{-7} (curve 1), 10^{-6} (curve 2), 10^{-5} (curve 3), 10^{-4} (curve 4), and 4×10^{-4} M (curve 5). From Figure 2, it appears that, for each value of α and all shown concentrations (C) corresponding to unsaturated mixed monolayers at the water–air interface or close to the critical micelle concentration (CMC), changes of the contact angle as a function of the mixture composition are observed. The θ – α curves have a clear minimum at α equal to 0.2 and 0.4, which indicates that synergism is present in the glass wettability. In our earlier studies,¹³ because of the similarity of the isotherms of adsorption of TX100, TX165, and their mixtures at the water–air

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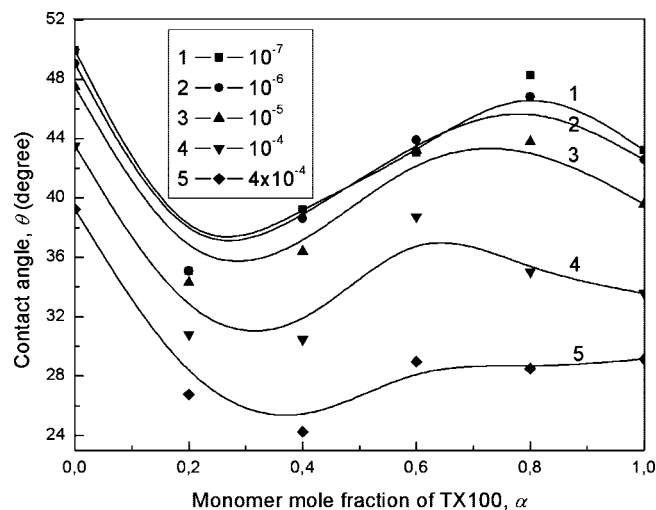


Figure 2. Relationship between the contact angle, θ , and monomer mole fraction of TX100, α , in TX100 and TX165 mixture (for glass) at constant total mixture concentration, C , equal to 10^{-7} (curve 1), 10^{-6} (curve 2), 10^{-5} (curve 3), 10^{-4} (curve 4) and 4×10^{-4} M (curve 5).

interface and the θ – $\log C$ curves for poly(tetrafluoroethylene) (PTFE), we employed Rosen's approach²² to calculate the interaction parameters in the mixed adsorption layers at the solid–solution interface, β^θ , and to show the synergetic effect. In this case, if we compare the values of the contact angles of TX100 and TX165 with the values for mixtures at α equal to 0.2 and 0.4, it is clear that the values of contact angles for these two mixtures are considerably smaller and the synergetic effect is present.

3.2. Adsorption At Water–Air and Glass–Water Interfaces.

Bennett and Zisman^{15,16} carried out contact angle measurements of different liquids and aqueous solutions of surfactants on the polymer surfaces, and from them they found that there was a linear dependence between $\cos \theta$ and the surface tension of liquids for hydrophobic solids such as PTFE even in the case of aqueous solutions of surfactants. According to them, extrapolation of $\cos \theta$ versus γ_{LV} plots to $\cos \theta = 1$ allows us to estimate the critical surface tension of wetting, γ_c . However, from the systems studied by us, it appears from Figure 3 that there is no linear dependence between $\cos \theta$ and the surface tension for both individual surfactants and their mixtures on glass surfaces. Contrary to our earlier studies dealing with PTFE wettability by aqueous solutions of TX100 and TX165 and their mixtures¹³ for glass, it is impossible to express the relationship between $\cos \theta$ and the surface tension of their solutions by one function. A linear relationship exists between the adhesional tension ($\gamma_{LV} \cos \theta$) and surface tension of aqueous solutions of surfactants, γ_{LV} (Figure 4), practically, in the whole range of their concentrations; however, for each surfactant and their mixtures, this relationship is described by a different function. It is interesting that the slope of the $\gamma_{LV} \cos \theta$ – γ_{LV} curves is positive and depends on C and α . The shape of these $\gamma_{LV} \cos \theta$ – γ_{LV} curves is different from the relationship between the adhesional and surface tensions for aqueous solutions of TX100, TX165, and their mixtures on low energetic hydrophobic solid PTFE studied by us earlier,¹³ but it is similar to those obtained by us for mixtures of two cationic surfactants and glass surfaces²³ and for mixtures studied by other researchers for minerals.²²

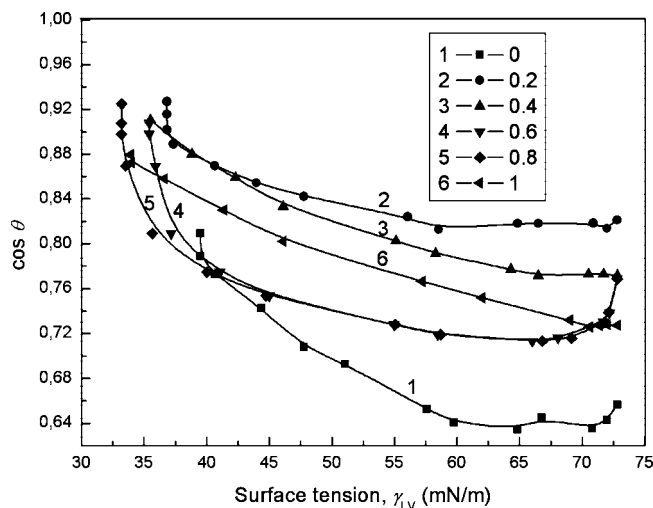


Figure 3. Relationship between the values of $\cos \theta$ and the surface tension (γ_{LV}) of aqueous solutions of TX100 and TX165 mixtures for different values of the monomer mole fraction of TX100 (α).

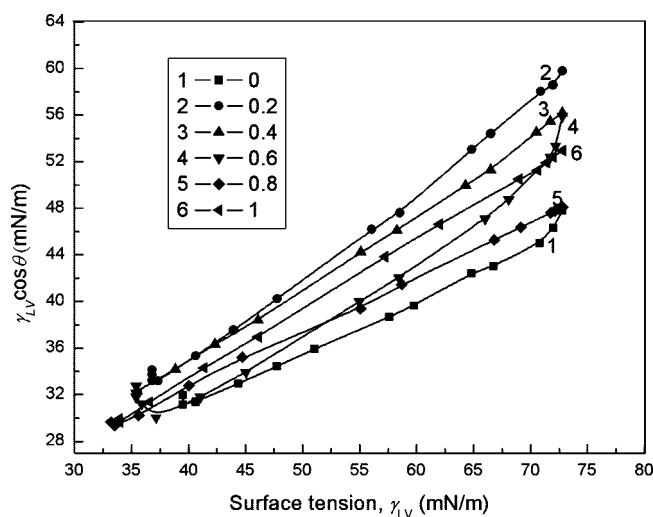


Figure 4. Relationship between the values of $\gamma_{LV} \cos \theta$ and the surface tension (γ_{LV}) of aqueous solutions of TX100 and TX165 mixtures.

Table 1. Values of Lifshitz–van der Waals (γ_s^{LV}) and Acid–Base (γ_s^{AB}) Components of the Glass Surface Tension, and Electron-Acceptor (γ^+) and Electron-Donor (γ^-) Parameters of the Acid–Base Component

	γ_s^{LV}	γ^+	γ^-	γ_s^{AB}	γ_{sv}
glass	28.43	0.74	51.51	12.36	40.79

On the basis of the linear parts of the relationships presented in Figure 4, we estimated the critical surface tension of wetting, γ_c . The values of γ_c for TX100, TX165, and their mixtures are in the range of 23–26 mN/m. These values are smaller than the Lifshitz–van der Waals component of glass surface tension, γ_s^{LV} , which is equal 28.43 mN/m². The values of γ_s^{LV} and other components of the surface tension of glass are presented in Table 1. These values were determined from the values of contact angles measured on a glass surface for water (37°), glycerol (51°), and diiodomethane (42°) on the basis of the Young–Fowkes–Good–van Oss equation.²⁴

From the linear relationship between the adhesional surface tension and the surface tension of aqueous solutions of surfactants,

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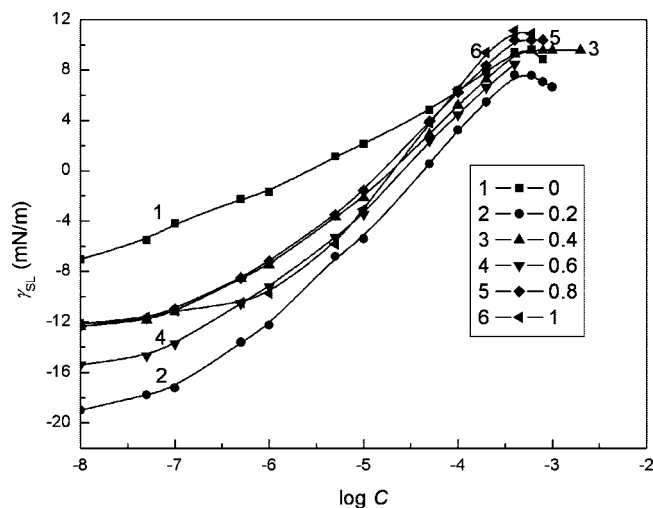


Figure 5. Relationship between the interfacial tension of the glass–aqueous solutions of TX100 and TX165 mixtures (γ_{SL}) and logarithm C for TX100 and TX165 mixtures for different values of the monomer mole fraction of TX100 (α).

we can determine not only the critical surface tension of glass wetting but also the relation between the adsorption of surfactants at liquid–air and solid–liquid interfaces.

A direct method to investigate relative adsorption at interfaces in wetting studies was developed by Lucassen-Reynders.²⁵ By combining the Young and Gibbs equations, it was shown that

$$\frac{d(\gamma_{LV} \cos \theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (1)$$

where Γ_{SV} , Γ_{SL} , and Γ_{LV} represent the surface excess concentration of surfactants at the solid–air, solid–liquid, and liquid–air interface, respectively.

Assuming that $\Gamma_{SV} \approx 0$, it is possible to establish from eq 1 the ratio of Γ_{SL} to Γ_{LV} by plotting $\gamma_{LV} \cos \theta$ versus γ_{LV} . However, the positive slopes of the curves in Figure 4 suggest that the surface excess concentration of surfactants at the glass–air interface is greater than zero and than the surface excess concentration of surfactants at the glass–water interface, or that $\Gamma_{SL} < 0$. If we assume that Γ_{SV} is greater than zero, we must take into account that there is the motion of surfactant molecules from the droplet on the solid surface, which is difficult to prove. On the other hand, if we assume that $\Gamma_{SV} = 0$ then there is the negative adsorption of surfactant molecules on the glass surface.

Some investigators¹⁸ stated that the adsorption of nonionic polyoxyethylene surfactants initially proceeds via hydrogen bonding between their ethylene oxide groups and an adsorbent surface. In particular, for glass such as quartz (100% SiO_2), the interaction of polyoxyethylene nonionic surfactant molecules with the SiO_2 surface is schematically represented as $-\text{SiOH} \cdots \text{O}(\text{OCH}_2\text{CH}_2)_n$.

At low concentration, these surfactants are adsorbed on the SiO_2 surface as individual molecules with hydrocarbon radicals oriented at a certain angle to the surface. This concentration range corresponds to the hydrophobization of the SiO_2 surface. At later stages of adsorption, hydrophobic interactions between hydrocarbon radicals of nonionic surfactant molecules adsorbed on the solid surface and present in the solution bulk take place.¹⁹ The increase of the contact angles of nonionic surfactants with an increase of their concentration is associated with the formation of adsorption layers on the SiO_2 surface where the surfactant molecules are oriented by the hydrocarbon chains predominantly toward the solution. A decrease in the contact angles indicates

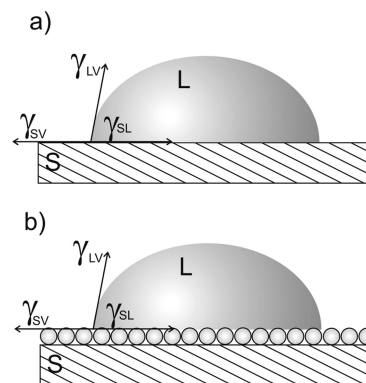


Figure 6. Scheme of the equilibrium state of the system glass–water drop–air: (a) without a water film on the glass surface and (b) with a water film on the glass surface.

the formation of the second adsorption layer where the surfactant molecules are oriented by the hydrophilic groups toward the solution.¹⁹

However, González-Martin et al.²⁶ stated that molecules of TX100 do not adsorb from aqueous solution at the calcium fluoride–water interface. It means that the mechanism of adsorption of nonionic polyoxyethylene surfactants at hydrophilic solid–water interfaces is not completely explained.

If it is possible that at the glass–water interface an initial monolayer of surfactant is formed and followed by a bilayer with a different orientation of its molecules, then the glass–aqueous solution of surfactant interface tension should go through the maximum as a function of surfactant concentration. This tension can be calculated from the Young equation^{22,27}

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2)$$

where γ_{LV} is the surface tension of the liquid, γ_{SV} is the surface tension of the solid in the presence of liquid vapor, and γ_{SL} is the solid–liquid interface tension.

The values of γ_{SL} calculated from eq 2 on the assumption that $\gamma_{SV} = 40.79$ mN/m (Table 1) are presented in Figure 5. The value of γ_{SV} similar to the value of the contact angle of water on the glass surface depends on the relative humidity and also on the method of glass preparation. In the literature, we can find values of γ_{SV} for glass in the range of 44.6–64.2 mN/m.^{20,21,28}

The obtained results indicate that γ_{SL} values of TX100, TX165, and their mixtures depend on the concentration of the solution, C , and composition, α , of the mixture. It is interesting that the values of the glass–aqueous solution interfacial tension increase in the range of surfactants and their mixture concentrations from 0 to CMC and any maximal value is not observed. Such changes of the glass–solution interfacial tension as a function of $\log C$ do not confirm the formation of a bilayer of surfactant molecules at glass–solution interface. Moreover, using in the Young equation the value of $\gamma_{SV} = 40.79$ mN/m, negative values of γ_{SL} were obtained for concentrations of surfactants corresponding to their unsaturated adsorption monolayer at water–air interface.¹² The negative values of γ_{SL} indicate that the glass is soluble in the aqueous surfactant solution, which is difficult to understand. There are two possibilities of negative values of glass–solution interface tension. The first one deals with the not proper value of γ_{SV} for glass used in the calculation, and the second one is related to the change of the glass–solution interface for glass/water film–solution interfaces (Figure 6b). In the second case, it is possible that surfactant molecules are soluble in the water film. Shown in Figure 7 are the values of γ_{SL} calculated for mixtures of surfactants at a monomer mole fraction of TX100,

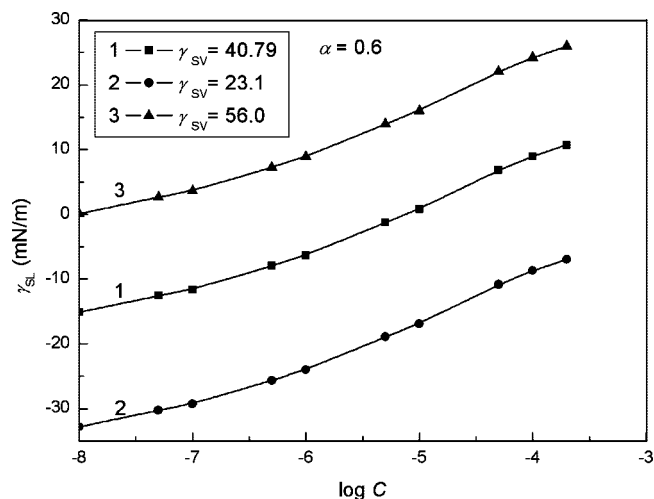


Figure 7. Relationship between the interfacial tension of glass-aqueous solutions of TX100 and TX165 mixtures (γ_{SL}) at α equal to 0.6 and logarithm C for different values of γ_{SV} equal to 40.79 (curve 1), 23.1 (curve 2), and 56.0 (curve 3) mN/m.

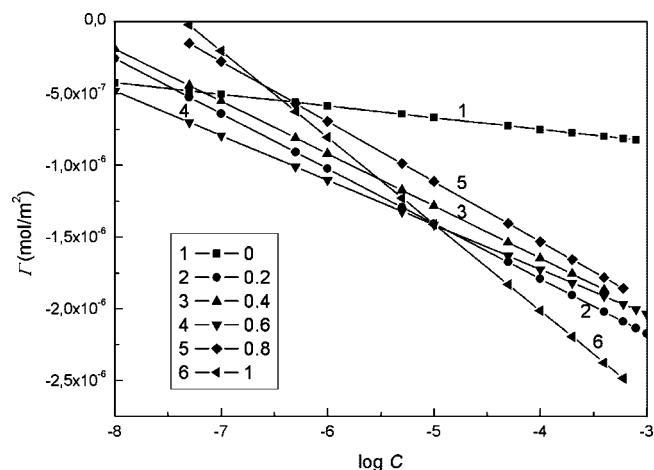


Figure 8. Relationship between the values of the surface excess concentration of surfactants (Γ) at the glass-water interface and logarithm C for different values of the monomer mole fraction of TX100, α , in TX100 and TX165 mixtures, where C is the total concentration of the mixture.

α , equal to 0.6 for different values of γ_{SV} . Curve 1 in Figure 7 represents the values of γ_{SL} calculated for $\gamma_{SV} = 40.79$ mN/m (Table 1). Curves 2 and 3 in this figure represent γ_{SL} values calculated on the basis of γ_{SV} equal to the critical surface tension of wetting (23.1 mN/m) and of the minimal value of γ_{SV} at which all values of γ_{SL} are positive (56.0 mN/m), respectively. The value of $\gamma_{SV} = 23.1$ mN/m seems to be too low taking into account the value of water surface tension (72.8 mN/m);¹² however, the value of 56.0 mN/m in the conditions in which measurements of contact angles of solutions on glass surfaces were carried out is too high as the glass surface tension in the presence of water film. So, the most suitable value of γ_{SV} to calculations of γ_{SL} is that equal to 40.79 mN/m. If we take into account this value, it is clear that the adsorption of aqueous solutions of TX100, TX165, and their mixtures takes place not at the glass-water interface but at the glass/water film-water interface (Figure 6b).

The values of the glass surface tension, surface tension of water, and their parameters and components also indicate that the interactions between water molecules and the glass surface are considerably higher than those between this surface and

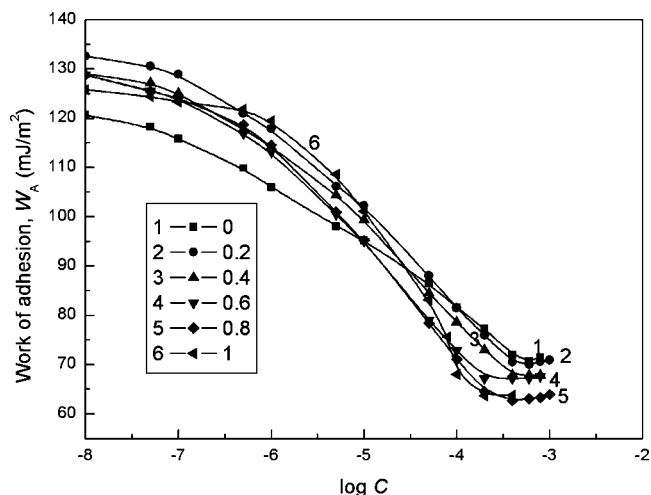


Figure 9. Relationship between the work of adhesion (W_A) calculated from eq 5 and logarithm C for the mixtures of TX100 and TX165 for α equal to 0, 0.2, 0.4, 0.6, 0.8, and 1.

the surfactant molecules.²⁴ If this situation takes place, then it is difficult for the surfactant molecules to destroy the thick film of water on the glass surface, and the adsorption of surfactant molecules takes place at the glass/water film-water interface (Figure 6b). Taking into account this fact and eq 1 developed by Lucassen-Reynders,²⁵ the adsorption of surfactants and their mixtures at the glass-water interface probably becomes negative. If this suggestion is true, then the all changes of the values of the contact angle may be explained by the ability of the molecules of a single surfactant and their mixtures to destroy the water film on the glass surface, which is considered by some authors as icelike.²⁹ On the other hand, in the literature, it is noted that there are the clathrate-like water structures around the polyoxyethylene oxide headgroup, including hydrogen bonding to the ether oxygen, so the water film on the glass surface may exist not only from the stronger interaction between water molecules and this surface but also from the adsorption of surfactant-water structures.³⁰

Knowing the values of γ_{SL} (Figure 5), it is possible to calculate the value of the surface excess concentration of surfactants at the glass-water interface using the Gibbs equation.²⁷

For a dilute solution (10^{-2} mol/dm³ or less) containing nonionic surfactant, the Gibbs equation can be written in the form

$$\Gamma = -\frac{C}{RT} \frac{d\gamma_{SL}}{dC} = -\frac{1}{RT} \frac{d\gamma_{SL}}{d \ln C} = -\frac{1}{2.303RT} \frac{d\gamma_{SL}}{d \log C} \quad (3)$$

where C represents the concentration of surfactant and γ_{SL} represents the glass-water interface tension.

The values of the surface excess concentration of surfactants at the glass-water interface calculated from eq 3 are presented in Figure 8. From this figure, it shows that for all investigated systems including the aqueous solution of a single surfactant and their mixtures the values of the surface excess concentration of surfactants at the glass-water interface are negative, which confirms the above conclusion that the adsorption at the

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glass–water interface is negative. It is interesting that the changes of these negative values for each system are linear.

Negative adsorption at the glass–water interface is also confirmed by the values of the work of adhesion of solutions to glass surface.

3.3. Work of Adhesion. The work of adhesion of liquid to solid, W_A , is defined by the following equation:³¹

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (4)$$

Introducing eq 4 into the Young equation (eq 2), we obtain

$$W_A = \gamma_{LV}(\cos \theta + 1) \quad (5)$$

Taking into account eq 5, the measured values of the contact angles for aqueous solutions of surfactants on glass surfaces, and the data of their surface tension,¹² the values of the work of adhesion of solutions to the glass surface were calculated, and they are presented in Figure 9. From this figure, we can see that not only for TX100 and TX165 but also for their mixtures the values of the work of adhesion depend on the concentrations of surfactants and the composition of their mixtures in aqueous solution and they are in the range of 62–133 mJ/m². For solutions at very low concentrations of surfactant, their work of adhesion to the glass surface is close to the work of adhesion of water (131 mJ/m²). The values of W_A for all systems decreasing with increasing surfactant concentration in a bulk phase confirm the conclusion that the highest interactions are between the glass surface and water molecules. Of course, at higher concentrations of surfactant, some destruction of the water film on the glass surface probably could be observed.

To explain more clearly the influence of the water film on the adsorption and adhesion of aqueous surfactant solutions to the glass surface, we have measured the values of surface tension and contact angle of pure TX100 and TX165 not only on a glass surface but also on PTFE and poly(methyl methacrylate) (PMMA).

Next, taking into account the following equation²⁴

$$\gamma_{LV}(\cos \theta + 1) = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (6)$$

the components and parameters of pure TX100 and TX165 surface tension were calculated. For calculation of the Lifshitz–van der Waals component of the PTFE surface tension equal to its total surface tension (20.24 mJ/m²), the Lifshitz–van der Waals component of the PMMA surface tension (36.66 mJ/m²), the electron-acceptor and electron-donor parameters of the PMMA surface tension ($\gamma_S^+ = 0.16$, $\gamma_S^- = 10.02$), the surface tension of pure TX100 and TX165 (37.0 and 35.9 mN/m, respectively), and the measured contact angles of pure TX100 and TX165 on PTFE (83° and 70°) and PMMA (31.2° and 39.4°) surfaces were used.

The values of γ_L^{LW} calculated from eq 6 for TX100 and TX165 are equal to 21.30 and 27.7 mN/m, respectively, and the values of γ_L^+ and γ_L^- for TX100 are equal 1.43 and 49.1 mJ/m²,

respectively. Unfortunately, it was impossible to determine the values of γ_L^+ and γ_L^- for TX165 because eq 6 for PMMA does not have the solution. We probably cannot solve this equation for TX165 because in this way we calculate some approximate and generalized values. If we consider separately the effects of hydrocarbon chains and polar headgroups, then maybe eq 6 will have the solution for TX165.

Taking into account the values of the components and parameters of the surface tension of TX100, glass, and water, it is possible to calculate from eq 7 the work of adhesion of TX100 to glass and to water and of water to the glass surface. Equation 7 has the form:²⁴

$$W_A = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (7)$$

which can be obtained by introducing into eq 4 the expression for solid–liquid interfacial tension proposed by van Oss et al.³²

From the calculations, it appears that the work of adhesion of TX100 to water (125.9 mJ/m²) is higher than its work of adhesion to glass (78.4 mJ/m²) and that the work of adhesion of water to glass (131 mJ/m²) is higher than that of TX100 to the glass surface. It means that the probability of TX100 adsorption on the glass/water film surface is higher than that on a “pure” glass surface, which confirms the above-mentioned conclusions.

Conclusions

The results of contact angle measurements and the calculations of glass–solution interfacial tension and work of adhesion of aqueous solutions to glass surface suggest the following:

- (i) The wettability of glass depends on the concentration and composition of the aqueous solution of two nonionic surfactant mixtures, and the minimum is observed on the curves presenting the relationship between the contact angle and monomer mole fraction of TX100 at a mole fraction of TX100 equal 0.2 and 0.4, indicating that synergism occurs in contact angle reduction.
- (ii) For glass, there is a linear dependence between the adhesional tension and surface tension of aqueous solutions of TX100 and TX165 mixtures, and the positive slopes indicate that adsorption of the surfactants and their mixtures at the glass–water interface probably becomes negative because of the presence of a water film on this surface.
- (iii) The values of the critical surface tension of wetting of glass are smaller than the Lifshitz–van der Waals component of glass surface tension.
- (iv) The work of adhesion of aqueous solutions of surfactants and their mixtures to the glass surface depends on the concentration and composition of the surfactants.
- (v) The values of the work of adhesion of pure surfactant to water and to glass and of water to glass indicate that the probability of nonionic surfactant adsorption on the glass/water film surface is higher than that on a “pure” glass surface.

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