

Article

Wettability and Adhesion Work Prediction in the Polymer–Aqueous Solution of Surface Active Agent Systems

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Abstract: The wettability of solids by aqueous solutions of surfactants is very important in many practical applications. Thus, the measured advancing contact angles of aqueous solutions of chosen surfactants on polyethylene (PE) and those taken from the literature on polytetrafluoroethylene (PTFE), poly(methyl methacrylate) (PMMA), and polyamide (nylon 6) were analyzed. Based on the measured values of the contact angles and the literature data of the surface tensions of the studied surfactant solutions, their adsorption at the PE–water interface and the work of adhesion (W_a) were determined. The values of W_a to PE calculated on the basis of the contact angles and surface tensions of these solutions were compared to those determined by applying the new Lifshitz–van der Waals component of the water–PE surface tension. There was a good agreement between the W_a values determined in two different ways. Their contact angles were calculated using the values of PE surface tension, the new Lifshitz–van der Waals component of the water surface tension, and the surface tension of aqueous solutions of the studied surfactants. The contact angle values calculated in such a way were close to the measured values. In the case of PTFE, the same relations were obtained. The values of W_a to PMMA and nylon 6 could be also predicted.

Keywords: surfactants; wettability; adhesion; polymers

1. Introduction

The wetting process plays a very important role in many practical applications of surface active agents [1–3]. Surface active agents (also called surfactants) decrease the high surface tension of water. The decrease of water’s surface tension by surfactants influences its contact angle (θ) on solid surfaces. However, the contact angle depends not only on the change in water’s surface tension under the influence of surfactant, but also on the solid surface tension and solid–solution interface tension [2,4]. The changes of the solid surface tension and solid–solution interface tension as a function of the concentration of surfactants in solution can be quite different from those of water surface tension. These changes depend on the kind of the solid and the surfactant. At the solid–air and solid–solution interfaces, a surfactant layer can be formed in which the packing and orientation of its molecules can be different from those at the solution–air interface. The packing and orientation of surfactant molecules at the solid–air, solid–solution, and solution–air interfaces also influence the work of adhesion of the solution to the solid surface. According to the thermodynamic rule, the difference between the work of adhesion of solution to the solid surface (W_a) and cohesion work (W_c) of solution informs the wetting process [4]. If the solid is not completely wetted by the liquid or solution, W_a depends on the contact angle, being the visual measure of solid wettability. W_a and θ depend on the

components and parameters of the solid and liquid (solution) surface tension [4]. Knowing these components and parameters, it should be possible to predict the wettability of some solids by aqueous solutions of the surfactants and their mixtures. However, in the literature it is difficult to find studies dealing with the possibility of adhesion work and wettability prediction in solid–aqueous solutions of surfactant–air systems.

Many authors have attempted to describe changes of the contact angle of surfactant aqueous solutions on polymeric solids as a function of the solution surface tension [5–10]. Zisman and co-workers [5–8] suggested that there is a linear dependence between the cosine of the contact angle and the surface tension of surfactants aqueous solution. In turn, Bargeman and van Voorst Vader [9] found the linear dependence between the adhesion and surface tension of aqueous solutions of surfactants. The suggestion made by Bargeman and van Voorst Vader was confirmed by numerous studies from our group [11–19]. From these studies, it was also shown that, in contrast to Zisman's suggestion [5], the dependence between the cosine of the contact angle and the surface tension can be described by polynomial or exponential functions of the first order.

Some authors [20,21] have stated that the surface tension of the liquid corresponding to the contact angle equal strictly to zero, called the “critical surface tension of solid wetting” by Zisman [5], is equal to the surface tension of the solid. However, this is possible only in the case when the parameter of interfacial interactions (ϕ) proposed by Girifalco and Good [22] is close to 1. It is difficult to establish the ϕ parameter. Neumann et al. [23–26] found that there is a linear dependence between ϕ and the solid–liquid interface tension, from which it results that $\phi = 1$ if the solid–liquid interface tension is equal to zero. This indicates that in such a case the critical surface tension of solid wetting is equal to the solid surface tension. However, this was not confirmed by our studies [11–19]. In any case, the critical surface tension of solid wetting obtained from the linear dependence between the adhesion and surface tension of surfactant solution for apolar, monopolar, and bipolar polymers is equal to their surface tension. Thus, it is generally not possible to establish the correlation between the wettability of solids and their surface tension from the dependence between the adhesion and surface tension of the surfactant aqueous solution. On the other hand, in the case of the apolar polytetrafluoroethylene (PTFE), the slope of the dependence between the adhesion and surface tension of aqueous solution of anionic, cationic, and nonionic surfactants and their binary and ternary mixtures is equal to -1 [11–19]. The slope of this dependence equal to -1 was also found for some aqueous solutions of surfactant and surfactant mixtures in the presence of short-chain alcohol, but only at alcohol concentrations lower than its critical aggregation concentration [11–19]. From the Young–Dupre equation, it results that if the slope of the linear dependence between the adhesion and surface tension of surfactant solution is equal to -1 , then one constant in this equation is equal to W_a . This means that in such case, W_a does not depend on the kind of surfactants, their mixture, mixtures of surfactants with alcohol, or the surface tension of surfactant solutions. As mentioned above, for PTFE the slope of the linear dependence between the adhesion and surface tension is equal to -1 , so W_a does not depend on the kind of surfactants and their mixture, or on the concentration of surfactant in solution.

In the case of poly(methyl methacrylate) (PMMA) and polyamide (nylon 6), the slope of the dependence between the adhesion and surface tension of solution was higher than -1 [18]. In such a case it is impossible to establish the W_a values from this dependence. The W_a values should be deduced, among others, on the basis of the van Oss et al. concept [27–31], knowing components and parameters of the solid and solution surface tension. However, if for the calculation of W_a the value of the Lifshitz–van der Waals component of water surface tension equal to 21.8 mN/m is used, there will be some differences between the values of W_a calculated using the van Oss et al. concept [27–31] and those determined from the Young–Dupre equation. The value equal to 21.8 mN/m was calculated from the water–*n*-alkane interface tension. However, the value of the Lifshitz–van der Waals component of the water surface tension determined by us on the basis of the contact angle of water on the PTFE surface was equal to 26.85 mN/m. We used this value for the prediction of θ and W_a of aqueous solutions of a few individual surfactants in PTFE–solution systems [32]. A good agreement between

the calculated and measured contact angle values as well as between the calculated W_a values and those determined from the dependence between the adhesion and surface tension of the surfactant solution was observed.

Therefore, the purpose of the paper was to study the applicability of this value for the prediction of θ and W_a in other polymer–aqueous solutions of surfactants and their mixtures as well as surfactant mixtures in the presence of propanol systems. For this purpose, polytetrafluoroethylene (PTFE), polyethylene (PE), poly(methyl methacrylate) (PMMA) and polyamide (nylon 6) were chosen. Of these polymers, PTFE and PE are apolar, PMMA is monopolar, and nylon 6 is bipolar. For prediction of θ and W_a in the polymer–aqueous surfactant solution systems, the components and parameters of PTFE, PE, PMMA [32], and nylon 6 surface tension determined by us, and the surface tensions of aqueous solutions of surfactants and their mixtures were also applied [11–19]. The calculated values of θ and W_a for PTFE, PMMA, and nylon 6 were compared to the measured ones taken from the literature [11–19]. For this comparison, in the case of PE, the contact angles for aqueous solutions of *p*-(1,1,3,3-tetramethylbutyl)phenoxypolyoxyethylene glycols (Tritons): X-100 (TX-100), X-114 (TX-114), and X-165 (TX-165), dodecyldimethylethylammonium bromide (DDEAB), benzyldimethyldodecylammonium bromide (BDDAB), cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), cetylpyridinium bromide (CPyB), sodium dodecylsulfate (SDS), sodium hexadecylsulfonate (SHS), and sodium *N*-lauryl sarcosinate (SDSa) were measured.

2. Utility Equations for the Data Treatment

The spreading of a liquid or solution over a solid surface depends on the difference between the work of adhesion of the liquid or solution to the solid surface (W_a) and the cohesion work of the liquid or solution (W_c), and can be expressed by the spreading coefficient, $S_{S/L}$ [2,4]:

$$S_{S/L} = W_a - W_c. \quad (1)$$

If $W_a \geq W_c$, then the contact angle of a given liquid or solution is equal to zero.
On the other hand:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}, \quad (2)$$

where γ_{SV} is the solid surface tension and/or the solid/vapor film surface tension, γ_{LV} is the liquid or solution surface tension, and γ_{SL} is the solid–liquid (solution) interface tension.

If γ_{SV} and γ_{SL} are not known and the contact angle (θ) of liquid or solution on the surface of a given solid is higher than or strictly equal to zero, the adhesion work can be calculated from the Young–Dupre equation, which has the form [4]:

$$W_a = \gamma_{LV}(\cos \theta + 1). \quad (3)$$

Equation (3) results from Equation (2) and the Young equation (Equation (4)):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta. \quad (4)$$

Equation (3) can be expressed in a somewhat different form:

$$\gamma_{LV} \cos \theta = -\gamma_{LV} + W_a. \quad (5)$$

In using Equation (5) to calculate the work of adhesion of a liquid or solution to a solid surface, it should be remembered that Harkins and Livingston modified Equation (4) to the following form [4]:

$$\gamma_S - \pi_e - \gamma_{SL} = \gamma_{LV} \cos \theta, \quad (6)$$

where γ_S is the solid surface tension without the vapor film, and π_e is the vapor film pressure around the liquid drop settled on the solid surface.

Moreover, Schrader [33] suggests that the Young equation should be expressed as follows:

$$\gamma_S - \pi_{e1} - \gamma_{SL} - \pi_{e2} = \gamma_{LV} \cos \theta, \quad (7)$$

where π_{e1} and π_{e2} denote the changes of the solid surface tension and the solid–liquid (solution) interfacial tension, respectively.

From Equation (7), it results that there are five cases of the solid–liquid drop–air system equilibrium: (a) $\pi_{e1} = 0$ and $\pi_{e2} = 0$; (b) $\pi_{e1} = \pi_{e2}$; (c) $\pi_{e1} \neq 0$ and $\pi_{e2} = 0$; (d) $\pi_{e2} \neq 0$ and $\pi_{e1} = 0$; and (e) $\pi_{e1} \neq \pi_{e2}$. Indeed, Schrader [33] assumes that only the first and second cases take place in real three-phase systems. Thus we can state that in the case of aqueous solutions of surface active agents, the latter case of the three-phase equilibrium can be observed. However, in many cases, there is a linear dependence between the adhesion tension ($\gamma_{LV} \cos \theta$) and the surface tension of an aqueous surfactant solution, which can be expressed as:

$$\gamma_{LV} \cos \theta = a\gamma_{LV} + b, \quad (8)$$

where a and b are constants.

The constant a fulfils the expression:

$$a = \frac{\partial(\gamma_{LV} \cos \theta)}{\partial \gamma_{LV}}. \quad (9)$$

According to the Lucassen-Reynders' suggestion [34,35]:

$$\frac{\partial(\gamma_{LV} \cos \theta)}{\partial \gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{LV}}{\Gamma_{SL}}, \quad (10)$$

where Γ_{SV} , Γ_{LV} , and Γ_{SL} are the Gibbs surface excess concentration of surfactant at the solid–air, liquid–air, and solid–liquid interfaces, respectively.

From Equations (9) and (10), it results that:

$$a = \frac{\Gamma_{SV} - \Gamma_{LV}}{\Gamma_{SL}}. \quad (11)$$

If $a = -1$ and $\Gamma_{SV} = 0$, then $\Gamma_{LV} = \Gamma_{SL}$. For $a \neq -1$ and $\Gamma_{SV} = 0$, then $\Gamma_{LV} \neq \Gamma_{SL}$.

On the other hand, from Equations (3) and (13), for $a = -1$ it results that:

$$b = W_a. \quad (12)$$

If the straight linear dependence between the adhesion and surface tension of an aqueous solution of surfactants yields a slope equal to -1 , the work of adhesion does not depend on the surfactant concentration. This should also be determined on the basis of the method of van Oss et al. [27–31]. For this purpose, the following equation can be used:

$$W_a = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+}. \quad (13)$$

For solid–liquid or solution drop–air systems in which the contact angle is in the range from 0° to 180° , we can write:

$$\gamma_{LV}(\cos \theta + 1) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+}, \quad (14)$$

where LW, + and − indicate the Lifshitz–van der Waals component, electron-acceptor, and electron-donor parameters of the acid–base component of the solid and liquid surface tension, respectively.

If liquid and solid surface tension or one of them results only from the Lifshitz–van der Waals intermolecular interactions, Equation (14) assumes the simplest form [27]:

$$\gamma_{LV}(\cos \theta + 1) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}}. \quad (15)$$

In the case when a straight linear dependence between the adhesion and surface tension of the surfactant solution exists and the slope of this relation is different from −1, the adhesion work satisfies the expression:

$$W_a = (1 - a)\gamma_{LV} + b. \quad (16)$$

From Equation (16), it results that in such a case a straight linear dependence takes place between the adhesion work and the surface tension of the aqueous surfactant solution. A slope of the linear dependence between the adhesion and the surface tension different from −1 indicates that the orientation and packing of surfactant molecules in the adsorption layer at the solid–solution and solution–air interfaces is different and that it is possible to form a surface layer of surfactant around the solution drop settled on the solid surface [34]. To test whether the surfactant layer influences the surface tension of the solid, the equation of Neumann et al. can be applied, which has the form [23–26]:

$$\frac{\cos \theta + 1}{2} = \sqrt{\frac{\gamma_S}{\gamma_L}} \exp[-\beta(\gamma_L - \gamma_S)^2], \quad (17)$$

where according to Neumann et al. β is the constant for all systems and its most proper value is equal to $0.000115 \text{ (m}^2/\text{mJ)}^2$.

If the calculated values of solid surface tension are changed as a function of surfactant concentration, it is probable that the surfactant layer influences this tension. In this case, Equations (13) and (14) can be useful for the W_a calculations in the following form:

$$W_a = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} - \pi_e \quad (18)$$

or

$$\gamma_{LV}(\cos \theta + 1) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} - \pi_e. \quad (19)$$

3. Experimental

3.1. Materials

For aqueous solution preparation, *p*-(1,1,3,3-tetramethylbutyl)phenoxy polyoxyethylene glycols (Tritons): X-100 (TX-100), X-114 (TX-114), and X-165 (TX-165), dodecyldimethylethylammonium bromide (DDEAB), and benzyldimethyldodecylammonium bromide (BDDAB) (purity greater than 99%) were bought from Sigma-Aldrich (Poznań, Poland) and used without further purification. Cetyltrimethylammonium bromide (CTAB) (Sigma-Aldrich), tetradecyltrimethylammonium bromide (TTAB) (Sigma-Aldrich), cetylpyridinium bromide (CPyB) (Sigma-Aldrich), sodium dodecylsulfate (SDDS) (Merck, Warsaw, Poland) (purity > 99%), sodium hexadecylsulfonate (SHS) (Sigma Chemical Co., St. Louis, MO, USA) (purity > 99%), and sodium *N*-lauryl sarcosinate (SDSa) (Sigma Chemical Co.) (purity > 99%) were purified before the solution preparation by the method described in the literature [35]. The water used for the preparation of surfactant solutions was doubly-distilled and deionized (Destamat Bi18E).

Polyethylene (PE) was obtained from Mega-Tech, Grodzisk Mazowiecki, Poland. Before the measurements, the PE surface was prepared according to a procedure described earlier [32].

This procedure was repeated twice for each plate. Then, the plates were dried and placed in the desiccator with molecular sieves.

3.2. Methods

Measurements of the advancing contact angle (θ) for aqueous solutions of surfactants on the PE surface were made using the sessile drop method, DSA30E measuring system (Krüss) in a thermostated chamber at 293 K. The quality of PE plates used for studies were checked by the contact angle measurements for water drops. Plates for which θ for water was equal to 100° were used for further studies. This value of θ is included in the range of literature data. For measurement of the θ of surfactant solutions, a drop volume equal to 6 μL was used. The procedure of advancing contact angle measurements was based on that applied by Zisman et al. [5–8]. Thus, before the contact angle measurement, the apparatus chamber was saturated with the vapor of the solution whose contact angle was being measured by placing a cell filled with the given solution in a chamber for 4 or 5 h depending on the solution concentration. The contact angle for a given solution was measured for at least 30 drops, and good reproducibility was found. The standard deviation of contact angle values for most systems did not exceed $\pm 2.0^\circ$. However, the standard deviation of θ values depends on the surfactant solution concentration. Thus, the average value of θ for each surfactant concentration was used for further calculations and considerations.

4. Results and Discussion

4.1. Wettability of PE

The isotherms of the contact angles of aqueous solutions of all studied surfactants on the PE surface (Figures 1–3) were similar to their surface tension isotherms. This indicates that the surfactants' adsorption at the PE–water interface should be comparable to their adsorption at the water–air interface. This was confirmed by the relationship between the adhesion and surface tension of aqueous surfactant solutions (Figure 4). For all surfactants, it was possible to describe this relationship with one linear function:

$$\gamma_{LV} \cos \theta = -1.01(\pm 0.003)\gamma_{LV} + 60.96(\pm 0.29). \quad (20)$$

Equation (20) indicates that the slope of this function is equal to -1 , which confirms that the adsorption of studied surfactants at the PE–water and water–air interfaces was comparable, and that the surfactant molecules at both interfaces were oriented by the hydrophobic tail toward the hydrophobic phase (air or PE).

From Equation (20) it can also be seen that the critical surface tension (γ_c) of PE wetting calculated at θ equal to zero (30.48 mN/m) was lower than its surface tension (33.71 mN/m) [32].

The critical surface tension of PE wetting can be also calculated from the relationship between the cosine of the contact angle ($\cos \theta$) and the surface tension of aqueous surfactant solutions. Taking into account the measured contact angle values (Figures 1–3) as well as the literature data of the surface tension of aqueous solutions of surfactants, the following relationship was obtained (Figure 5):

$$\cos \theta = 4.2547 \times 10^{-4} (\pm 1.0790 \times 10^{-5}) \gamma_{LV}^2 - 0.0690 (\pm 0.0012) \gamma_{LV} + 2.6010 (\pm 0.030). \quad (21)$$

γ_c of PE wetting calculated from Equation (21) was equal to 28.06 mN/m. Comparing the γ_c values for PE determined from Equations (20) and (21) to PE's surface tension, it can be stated that there was no agreement between them.

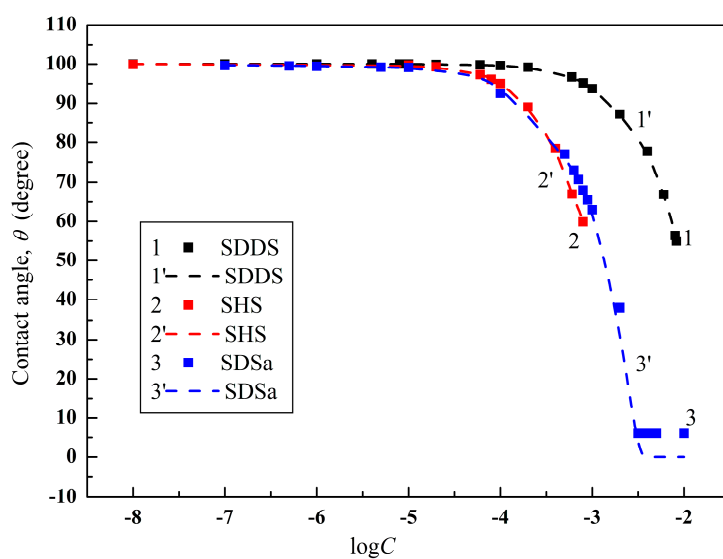


Figure 1. A plot of the contact angles of aqueous solutions of sodium dodecylsulfate (SDDS), sodium hexadecylsulfonate (SHS) and sodium *N*-lauryl sarcosinate (SDSa) (θ) on the polyethylene (PE) surface vs. the logarithm of surfactant concentration (C). Points 1–3 correspond to the measured θ values and dotted lines 1'–3' to those calculated from Equation (15).

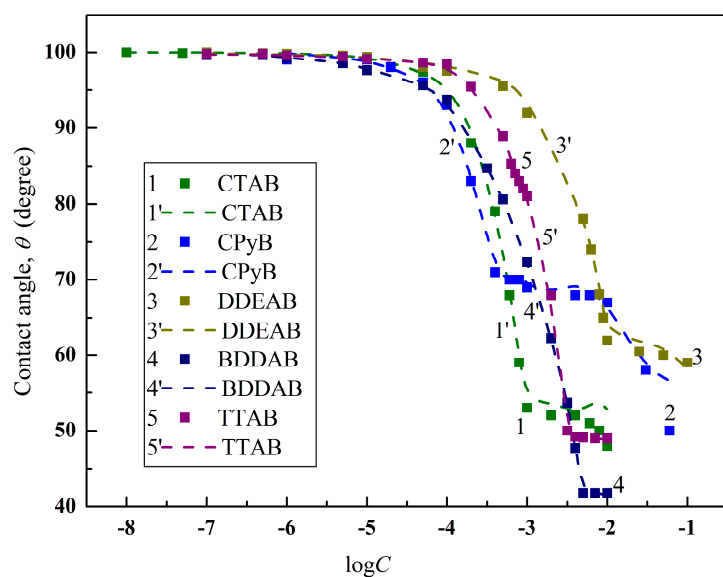


Figure 2. A plot of the contact angle of the aqueous solution of cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyB), dodecylmethylethylammonium bromide (DDEAB), benzyldimethyldodecylammonium bromide (BDDAB), and tetradecyltrimethylammonium bromide (TTAB) (θ) on the PE surface vs. the logarithm of surfactant concentration (C). Points 1–5 correspond to the measured θ values and dotted lines 1'–5' to those calculated from Equation (15).

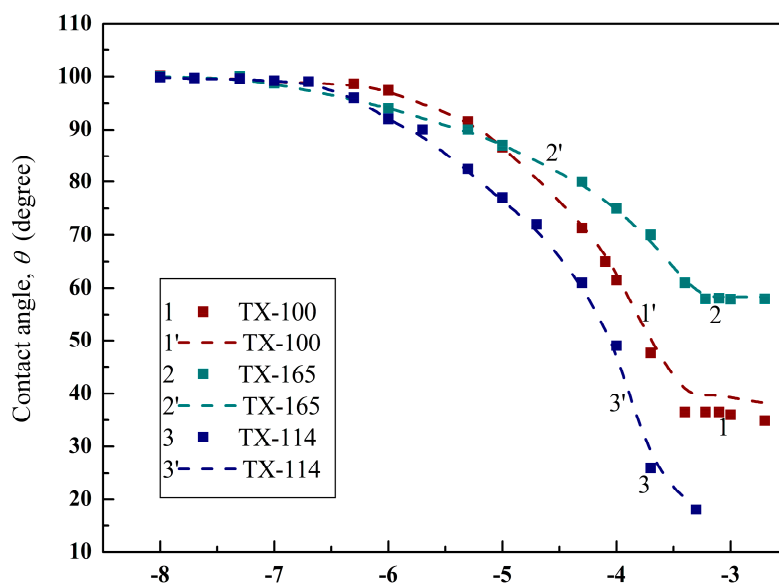


Figure 3. A plot of the contact angles of aqueous solutions of *p*-(1,1,3,3-tetramethylbutyl) phenoxypolyoxyethylene glycols (Tritons) X-100 (TX-100), X-165 (TX-165), and X-114 (TX-114) (θ) on the PE surface vs. the logarithm of surfactant concentration (C). Points 1–3 correspond to the measured θ values and dotted lines 1'–3' to those calculated from Equation (15).

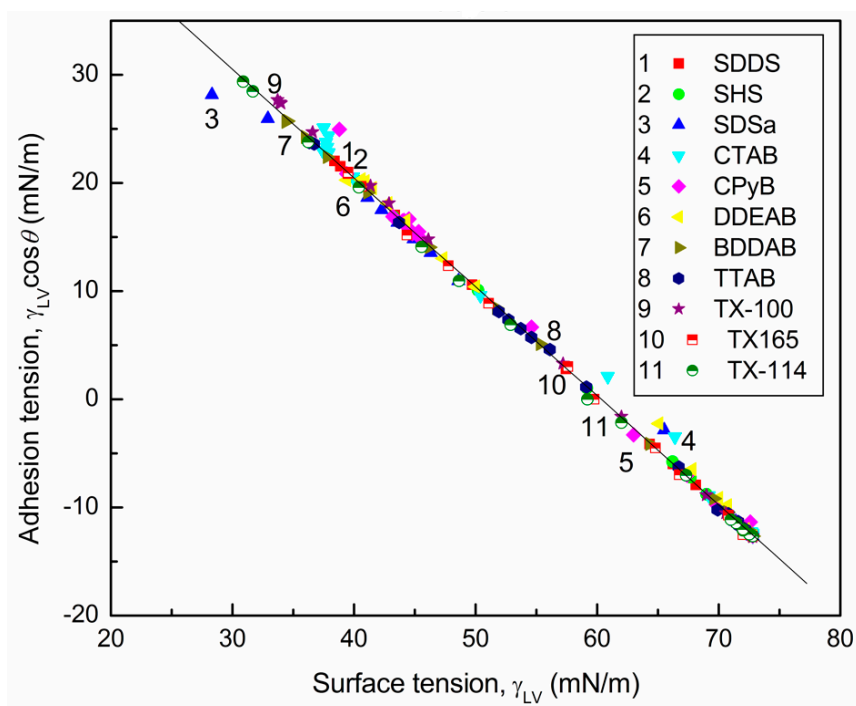


Figure 4. A plot of the adhesion tension ($\gamma_{LV} \cos \theta$) of the aqueous solutions of SDDS, SHS, SDSa, CTAB, CPyB, DDEAB, BDDAB, TTAB, TX-100, TX-165, and TX-114 for the PE surface vs. the surface tension (γ_{LV}).

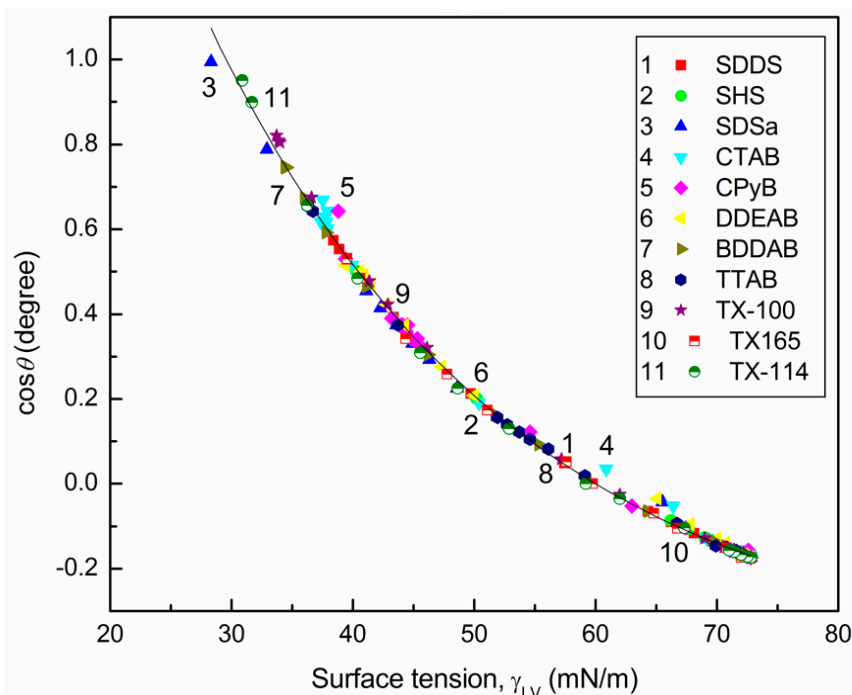


Figure 5. A plot of the cosine of the contact angle ($\cos\theta$) of the aqueous solutions of SDDS, SHS, SDSa, CTAB, CPyB, DDEAB, BDDAB, TTAB, TX-100, TX-165, and TX-114 for the PE surface vs. the surface tension (γ_{LV}).

4.2. Prediction of the Contact Angles of Aqueous Solutions of Surface Active Agents on PTFE and PE Surfaces

PTFE and PE are hydrophobic solids [27,36] whose surface tensions result only from Lifshitz–van der Waals intermolecular interactions. Thus, the contact angles of aqueous surfactant solutions and their mixtures can be calculated from Equation (15). As mentioned above, this equation is satisfied for the three-phase systems for which the film pressure behind and under the drop settled on the solid surface is equal to zero. A straight linear dependence between the adhesion and surface tension with slope equal to -1 indicates that Equation (15) should be satisfied in the case of the PTFE (PE)–solution drop–air systems. Moreover, the contact angle values should only depend on the PTFE or PE surface tension, the surface tension of the aqueous surfactant solution, and the Lifshitz–van der Waals component of the water surface tension.

Therefore, using the values of PTFE and PE surface tension determined by us [32] as well as the surface tensions of aqueous surfactant solutions [11–19,37] and the Lifshitz–van der Waals component of the water surface tension equal to 26.85 mN/m, the contact angles of surfactant solutions on these polymers was calculated from Equation (15). It appeared that there was very good agreement between the values calculated from Equation (15) and the measured values of contact angle for the aqueous solutions of surfactant and their binary and ternary mixtures on PTFE (Figures S1–S16) and the aqueous solutions of individual surfactants measured by us. This means that the value of the Lifshitz–van der Waals component of the water surface tension determined by us is more useful for the prediction of the surfactant solution contact angles on hydrophobic polymers than the method proposed by van Oss et al. [27–31]. This probably results from the fact that the surface tension of the surfactant tail (when surfactant molecules are oriented with their tails toward the air phase) is close to the surface tension of hydrocarbons, being the hydrophobic part of surfactant molecules. The surface tension of most such hydrocarbons is close to 26.85 mN/m (and corresponds to the Lifshitz–van der Waals component of water surface tension). This is likely why there was good agreement between the calculated and measured values of θ . However, it must be stressed that in the range of alcohol concentrations in which alcohol is in solution in the aggregated form, there are great discrepancies

between the calculated and measured values of the contact angle (Figure S16) [37]. This results from the fact that the Lifshitz–van der Waals component of the alcohol surface tension is considerably lower than that of water as determined by us [32].

The agreement between the calculated and measured values of the contact angles of aqueous solutions of hydrocarbon surfactants on apolar polymeric solids also indicates that the adsorption of these surfactants at the water–air interface only causes a reduction of the acid–base component of the water surface tension. This is consistent with the fact that the minimal surface tensions of aqueous solutions of hydrocarbon surfactants were not lower than those of the Lifshitz–van der Waals components of the water surface tension determined by us, and in many cases were similar [2,35].

4.3. Prediction of Adhesion Work of Surfactant Solutions to the Polymer Surface

The linear dependence between the adhesion and surface tension of the aqueous surfactant solutions and their mixtures for PTFE and PE at a slope equal to -1 could be described by one equation for many surfactants. This indicates that the adhesion of these solutions to the PTFE (Figure S17) and PE surface (Figure 4) does not depend on the kind of surfactant or the composition and concentration of surfactant mixtures. The constant b in the linear equation is equal to the adhesion work. The values of adhesion work can also be calculated from Equation (15). From the right side of this equation, it could be obtained that the adhesion work of aqueous surfactant solutions and their mixture was equal to 46.6 mJ/m^2 (for PTFE) and 60.2 mJ/m^2 (for PE) if for the calculation of this work the surface tension of PTFE equal to 20.24 mN/m and PE 33.71 mN/m , as well as the Lifshitz–van der Waals component of water surface tension equal to 26.85 mN/m , were taken into account. These values of adhesion work were close to those obtained from the dependence between the adhesion and surface tension of the surfactant solutions (46.67 mJ/m^2 for PTFE and 60.96 mJ/m^2 for PE). This shows that the adhesion work of aqueous surfactant solutions can be predicted from the surface tension of hydrophobic polymers and the Lifshitz–van der Waals component of water surface tension, determined by us as equal to 26.85 mN/m . It is known that the half value of adhesion work is equal to the critical surface tension of solid wetting if there is a linear dependence between the adhesion and the surface tension at a slope equal to -1 . It follows from our studies that for any case, the critical surface tension of solid wetting is equal to the solid's surface tension. In the case of hydrophobic solids, it can be explained based on Equation (15). It was found that this equation was satisfied for the hydrophobic polymer–aqueous surfactant solutions and their binary and ternary mixtures–air systems. Thus, the values of critical surface tension of PTFE and PE wetting were equal to the geometric mean of the surface tension of polymers and the Lifshitz–van der Waals component of the water surface tension. As the surface tension of PTFE and PE is different from 26.85 mN/m , the critical surface tension of PTFE and PE wetting is different from their surface tension. In the case of PTFE, its surface tension is lower than the Lifshitz–van der Waals component of water surface tension. Therefore, the critical surface tension of PTFE wetting (23.34 mN/m) is higher than its surface tension (20.24 mN/m). In the case of PE, the critical surface tension of its wetting (30.48 mN/m) is lower than its surface tension (33.71 mN/m). This indicates that the critical surface tension of a hydrophobic solid's wetting is close to that of a solid only if its surface tension is close to 26.85 mN/m .

The prediction of the wetting of monopolar and bipolar polymers by aqueous surfactant solutions and their mixtures, as well as the prediction of the work of adhesion of these solutions to the polymers' surfaces is more complicated than for the apolar polymers. For these polymers, in many cases the dependence between the adhesion and surface tension is linear but its slope is higher than -1 and depends on the kind of surfactant [16,18]. If the constant a in Equation (8) is not equal to -1 , then the constant $b \neq W_a$. On the other hand, when $a \neq -1$, then according to Equation (10), $\Gamma_{SL} \neq \Gamma_{LV}$. However, if $a \neq -1$, Equation (8) can be written in the form:

$$W_a = (a + 1)\gamma_L + b. \quad (22)$$

It results from Equation (22) that if there is a linear dependence between the adhesion and surface tension of the aqueous surfactant solution and if $a \neq -1$, then linear dependence exists between the adhesion work and surface tension of the surfactant solution. In this case, it is impossible to predict based on the constant b .

Indeed, the components and parameters of solution and polymer surface tension must be known for this prediction.

Taking into account the components and parameters of PMMA and nylon 6 (determined by us) and the surface tension of aqueous surfactant solutions and their mixtures, and given that the Lifshitz–van der Waals component of water surface tension is equal to 26.85 mN/m, the works of adhesion of the aqueous surfactant solutions to PMMA and nylon 6 surfaces were calculated using Equation (13).

For calculation according to the suggestion of van Oss et al. [27–31] it was assumed that the values of electron-acceptor and electron-donor parameters of surfactant solutions were the same. Moreover, it was proved that the obtained results were different from those calculated from the Young–Dupre equation. This indicates that the values of film pressure around or under the solution drop settled on the PMMA and nylon 6 surface could not be neglected. Thus, it was assumed that the influence of this film on the PMMA and nylon 6 surface tension could be evident from the data calculated from Equation (17). The discrepancies between the values of PMMA and nylon 6 surface tension calculated from Equation (17) for water and the aqueous surfactant solutions at a given concentration were assumed to be equal to π_e in Equation (18). The values of adhesion work calculated from this equation were close to those calculated from the Young–Dupre equation (Figures S18–S32). This indicates that a part of the adhesion work of aqueous surfactant solutions was connected with the surfactants' layer formation at the polymer–air and polymer–water interfaces, which have different properties from layer formed at the water–air interface.

5. Conclusions

Measurements of the contact angle of aqueous solutions of several anionic, cationic, and nonionic surfactants on the PE surface were performed. The obtained values of the contact angle of aqueous solutions of several anionic, cationic, and nonionic surfactants on PE were measured here, and the contact angles of the aqueous surfactant solutions and their mixtures as well as the mixtures of surfactants in the presence of alcohol on PTFE, PMMA, and nylon 6 surfaces were taken into account for the analysis of the wetting process in light of components and parameters of the surface tension of polymers, water, and solution. As follows from the analysis, it was possible to predict the contact angle values of aqueous solutions of hydrocarbon surfactants and their multicomponent mixtures on apolar polymers using the polymer surface tension, the Lifshitz–van der Waals component of water, and surfactant solution surface tension. This analysis of the wetting process of apolar polymers based on the relationship between the adhesion and surface tension of surfactant solutions proved that there was similar adsorption at the polymer–solution and solution–air interfaces. It was also proved that the constant b in the linear dependence between the adhesion and surface tension was equal to the work of adhesion of the surfactant solutions to apolar polymers. This work was predicted on the basis of polymer surface tension and the Lifshitz–van der Waals component of water surface tension determined by us. The analysis of the wetting process of monopolar PMMA and bipolar nylon 6 showed that the adsorption of surfactants at these polymer–solution and solution–air interfaces was different. The analysis also revealed that the constant b in the linear dependence between the adhesion and surface tension of surfactant solutions was not equal to the work of adhesion. Furthermore, the work of adhesion of surfactant solutions to PMMA and nylon 6 surfaces could be determined not only by applying the Young–Dupre equation, but also the equations of Neumann et al. and van Oss et al. It should also be mentioned that the $b/2$ values obtained from the dependence between the adhesion and surface tension were equal to the critical surface tension of polymer wetting. This proved that in any case, the value of this tension was equal to the surface tension of the polymer. Upon analyzing

the adhesion work of the surfactant solution to the hydrophobic polymers, it was proved agreement between the critical surface tension of polymer wetting and its surface tension exists only in the case when the surface tension of the solid is equal to 26.85 mN/m.

Supplementary Materials: The supplementary figures available online at <http://www.mdpi.com/2504-5377/2/2/21/s1>.

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