

## Wettability of polymeric solids by aqueous solution of surfactants

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Advancing contact angle ( $\theta$ ) measurements were carried out for aqueous solutions of cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyB), sodium dodecyl sulfate (SDS), sodium hexadecyl sulfonate (SHS) and Triton X-100 (TX-100) on polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA). The obtained results indicate that there were only small contact angle changes over the range of surfactant concentrations in the solution, corresponding to the unsaturated surfactant layer at the aqueous solution-air interface. However, when saturation of the surfactant layer was reached a considerable decrease in the contact angle as a function of concentration was observed. The obtained results also indicate that in the range of small concentrations of surfactants the contact angle, with exception of TX-100, does not depend on the type of the surfactant, but in the concentration range corresponding to the saturated layer at solution-air interface, it depends on the type of surfactant. On the basis of the values of contact angle and surface tension of aqueous solution of surfactants a linear dependence between the adhesional tension ( $\chi_V \cos\theta$ ) and surface tension ( $\chi_V$ ) was found. The slope of  $\chi_V \cos\theta$  vs  $\chi_V$  lines for PTFE does not depend on the type of surfactant and is equal -1, which suggests that the surface excess of the surfactant concentration at the PTFE-solution interface is the same as that at the solution-air interface for a given bulk concentration. It was also found that the work of adhesion of aqueous solution of surfactants to PTFE surface does not depend on the type of surfactant and its concentration, which suggests that the Lifshitz-van der Waals forces interact only at solution-air and PTFE-solution interfaces, and that the contribution of these forces in surface tension of aqueous solution of surfactants studied does not depend on the surfactant

concentration. In the case of PMMA the slope of  $\gamma_{LV} \cos\theta$  vs  $\gamma_{LV}$  lines depends on the type of surfactant and is considerable different from -1, which suggests that the surface excess of surfactant concentration for a given bulk concentration at solution-air interface is higher than at PMMA-solution interface. Also the work of adhesion of solution of surfactant to PMMA surface depends on the type of surfactant and its concentration, which suggests that across PMMA-solution interface van der Waals and polar interactions take place. Basing on the dependence between the adhesional tension and surface tension the critical surface tension of PTFE and PMMA wetting was found.

## 1. INTRODUCTION

Wetting of solids by solution of surface active agents is important for many technological applications such as oil recovery, coating, adhesion, printing and detergents. Since water has a high surface tension (72.8 mN/m) [1] it does not spontaneously spread over solids that have surface free energy of less than 72.8 mN/m. Addition of surface active agents to water to modify the interfacial tensions of the system is, therefore, often necessary to enable water to wet a solid surface. Adsorption of a surface active agent at solid/water interface leads to a layer or film formation on the solid surface, which affects its surface tension. The presence of the film of surface active agents changes the contact angle in a solid- liquid drop-air system, which is a measure of wettability.

Zisman and co-workers [2-4] characterized these conditions for low energetic solids by measuring contact angles,  $\theta$ , for different pure liquids and plotting  $\cos\theta$  vs  $\gamma_{LV}$ , ( $\gamma_{LV}$  is the liquid surface tension). Extrapolation of such plots to  $\cos\theta = 1$  ( $\theta = 0^\circ$ ) allows estimation of  $\gamma_c$ , the liquid surface tension required to give a contact angle of zero degree, which Zisman described as the critical tension of wetting. Bernett and Zisman [3,4] showed that there is linear relationship between  $\cos\theta$  and not only surface tension of pure liquids, but also aqueous surfactant solutions.

However, Bargeman and van Voorst Vader [5] found, in contrast to Zisman and co-workers [2-4], that there is a linear relationship for hydrophobic solids, however, between adhesion tension ( $\gamma_{LV} \cos\theta$ ) and surface tension of aqueous solutions of several types of surfactants, and that the slope of the lines for low-energy hydrophobic solids such as paraffin and PTFE was equal to -1. Our studies dealing with the wettability of PTFE by aqueous solution of the mixtures of an anionic surfactant and co-surfactant [6] confirmed conclusions drawn by Bargeman and van Voorst Vader [5]; however, the values of the critical surface tension of wetting determined from extrapolation of the plots  $\gamma_{LV} \cos\theta$  vs  $\gamma_{LV}$  to

the value of adhesional tension equal  $\gamma_{LV}$  ( $\cos\theta = 1$ ;  $\theta = 0^\circ$ ) are considerably higher than their value of  $\gamma_c$  and surface tension of PTFE.

It is interesting whether the  $\gamma_c$  value is the same for other aqueous solutions of surfactants for PTFE, and whether there is the same divergence between  $\gamma_c$  and surface tension of a higher energy of polymeric solid than PTFE.

Thus, the purpose of our studies was to determine the critical surface tension of wetting of polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) by aqueous solution of two cationic surfactants: cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyB), two anionic surfactants: sodium dodecyl sulfate (SDS), sodium hexadecyl sulfonate (SHS) and nonionic surfactant, Triton X100 as well as the correlation between the adsorption of the surfactants at water-air and PTFE, PMMA-water interfaces and wettability of PTFE and PMMA.

## 2. EXPERIMENTAL

### 2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (Sigma Aldrich) (purity > 99%), hexadecylpyridinium bromide (CPyB) (Sigma Aldrich) (purity > 99%), sodium dodecyl sulphate (SDS), sodium hexadecyl sulfonate (SHS) and Triton X100 purified as described in the literature [7] were used for aqueous solution preparation.

Aqueous solutions of the individual surfactants were prepared using doubly distilled and deionized water (Destamat Bi18E). The surface tension of water was always controlled before solution preparation.

The polytetrafluoroethylene (PTFE), ZA Tarnów (Poland), and polymethyl methacrylate (PMMA) Z. Ch. Oświęcim (Poland) used for contact angle measurements were prepared and cleaned by the procedure described earlier [8,9].

### 2.2. Contact angle measurements

Advancing contact angle measurements for aqueous solutions of CTAB, CPyB, SDS, SHS and Triton X100 on PTFE, PMMA plates were carried using the sessile drop method by the telescope-goniometer system, at 25x, in a thermostated measuring chamber at  $293 \pm 0.1$  K [8]. After settling a drop of aqueous solution of the surfactant at a given concentration on PTFE or PMMA plate the contact angle on both sides of the drop was read immediately. 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 PTFE-solution drop-air, PMMA-solution drop-air and at least 30 independent drops were used for the average value of the advancing contact angle determination. A good reproducibility was found for contact angle measurements. The standard deviation for each set of values was less than  $1.1^\circ$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. PTFE

The measured values of the advancing contact angle ( $\theta$ ) for aqueous solution of CPyB, CTAB, SDS, SHS and TX-100 on the PTFE surface are presented in Figure 1. This figure shows the dependence of  $\theta$  on the logarithm of the concentration of surfactants in aqueous solution ( $C$ ). From this Fig it is seen that in the range of  $\log C$  from -8 to -5,  $\theta$  values are slightly changed. However, if the concentration of surfactant mixtures is close or higher than  $10^{-4}$  M ( $\log C = -4$ ) then a considerable decrease of  $\theta$  as a function of  $\log C$  is observed. In the range of  $\log C$  from -3 to -2 the values of contact angles are almost constant and they are minimal for a given surfactant.

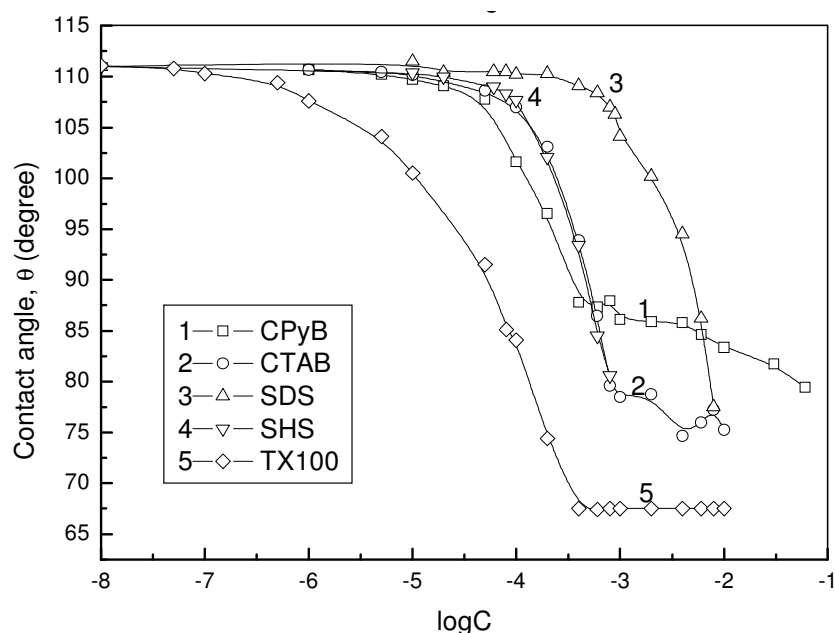


Fig. 1. The relationship between the contact angle,  $\theta$ , for aqueous solution of CPyB (curve 1), CTAB (curve 2), SDS (curve 3), SHS (curve 4) and Triton X100 (curve 5) on PTFE surface and logarithm  $C$  ( $C$  – concentration).

The shape of the curves in Figure 1 is similar to the shape of the isotherms of adsorption of CPyB and CTAB at water-air interface [10]. The biggest changes of contact angle occur in the concentration range of solutions corresponding to the saturated monolayer of adsorption at water-air interface, and the minimal values of contact angles are attained for aqueous solution at a concentration higher than the critical micelle concentration (CMC) [10].

Zisman and Bernett [3,4] carried out measurements of the contact angle of different liquids and aqueous solution of the surfactants on the surface polymers, and on this basis they found that there is linear dependence between  $\cos\theta$  and surface tension of liquids for hydrophobic solids, e.g. PTFE, even in the case of aqueous solutions of surfactants. According to them extrapolation of  $\cos\theta$  versus  $\gamma$  plots to  $\cos\theta = 0$  allows us to estimate the critical surface tension of wetting,  $\gamma_c$ . However, in the systems studied by us, as seen in Figure 2, there is no linear dependence between  $\cos\theta$  of all surfactants and the values of their surface tension.

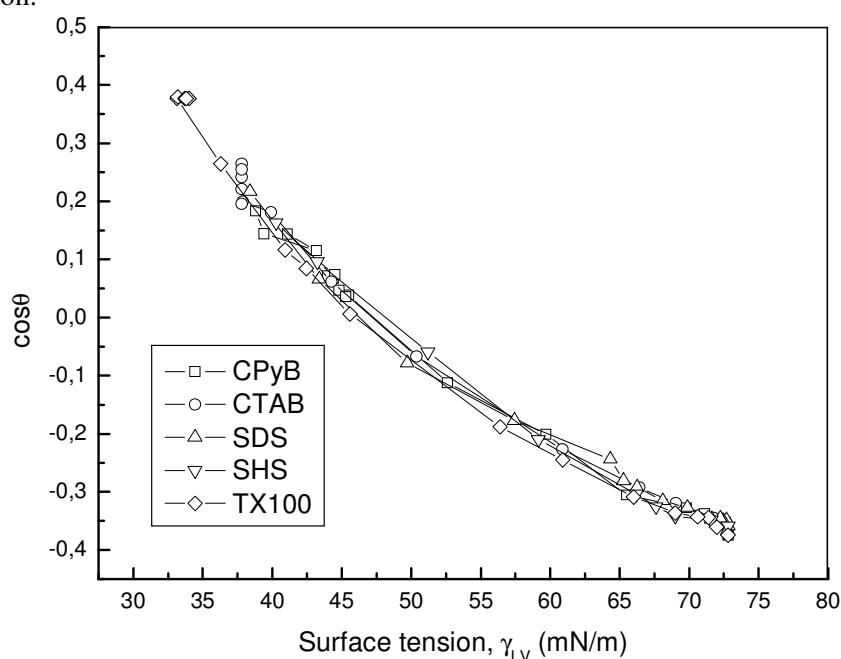


Fig. 2. The relationship between the values of  $\cos\theta$  for PTFE and the surface tension ( $\gamma_{LV}$ ) of aqueous solution of CPyB, ( $\square$ ) CTAB ( $\circ$ ), SDS ( $\triangle$ ), SHS ( $\nabla$ ) and Triton X100 ( $\diamond$ ).

Bargeman and van Vorst Vander [5] found that for hydrophobic solids linear dependence is between the adhesional tension ( $\gamma_{LV} \cos\theta$ ) and surface tension of aqueous solutions of surfactants.

In Figure 3 the dependence between the adhesional tension and surface tension of aqueous solutions of cationic, anionic and nonionic surfactants is presented. From this figure it results that for all investigated surfactants there exists linear relationship between the adhesional tension and surface tension. For each surfactant nearly the same constants in the linear relationships were found. Therefore, it was possible to establish a general expression to describe the changes of the adhesion tension as a function of the surface tension for all surfactants. This expression is:

$$\gamma_{LV} \cos\theta = -\gamma_{LV} + 47.26 \quad (1)$$

From this equation we can determine the relation between adsorption of surfactants at water-air and solid-water interfaces and the critical surface tension of PTFE wetting by aqueous solutions of surfactants.

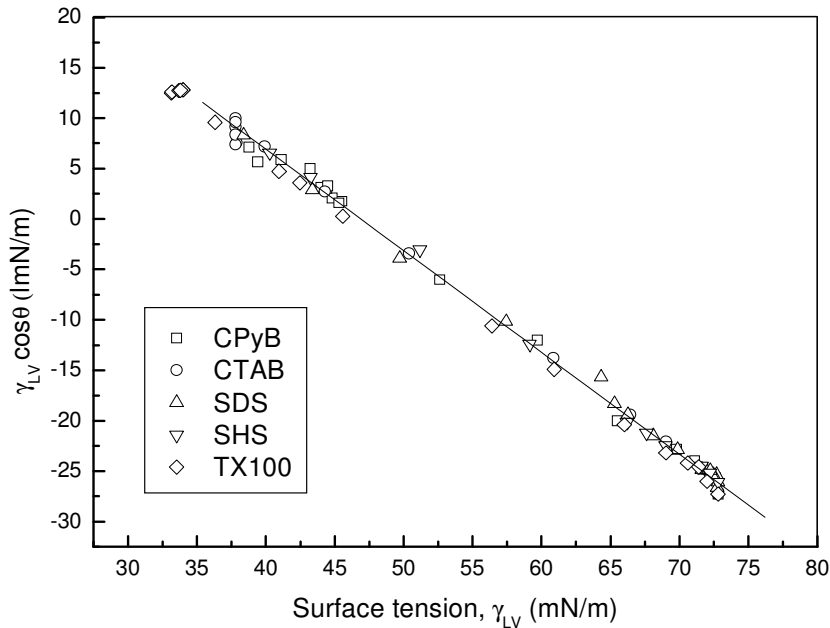


Fig. 3. The relationship between the values of  $\gamma_{LV} \cos\theta$  for PTFE and the surface tension ( $\gamma_{LV}$ ) of aqueous solution of CPyB, (□) CTAB (○), SDS (△), SHS (▽) and Triton X100 (◇).

A direct method to investigate relative adsorption to interfaces in wetting studies was developed by Lucassen-Reynders [11]. By combining the Young and Gibbs equations it was shown that:

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

where  $\Gamma_{SV}$ ,  $\Gamma_{SL}$ , and  $\Gamma_{LV}$  represent the surface excess of surfactants at polymer-air, polymer-water and water-air interfaces, respectively.

Assuming that  $\Gamma_{SV} \approx 0$  it is possible to establish from Eq. (2) the ratio of  $\Gamma_{SL}$  to  $\Gamma_{LV}$  by plotting  $\chi_{LV} \cos \theta$  vs  $\chi_{LV}$ . Thus, the constants -1 in Eqs (1) indicate that in the case of PTFE for all surfactants at a given concentration in the bulk phase the concentration excess at water-air interface is the same as that at PTFE-water interface. So, adsorption of surfactants at water-air and PTFE-water is the same, and the orientation of the CTAB, CPyB, SDS, SHS and TX-100 molecules at both interfaces in the saturated monolayer should also be the same (the hydrocarbon chain directed to air and PTFE, respectively).

From Eq. (1) it is also possible to determine the critical surface tension of PTFE wetting. The obtained value of  $\gamma_C$  is equal to 23.44 mN/m and is higher than that obtained by Bargeman and van Voorst Vander (20.3) [5]. This value of critical surface tension of PTFE wetting is higher than its surface tension determined on the basis of contact angle measured for *n*-alkanes (20.24 mN/m) [12].

On the basis of contact angle measurements for ethanol-water series of solutions Dann [13] stated that at PTFE-water interface some polar interactions are present, such as electrostatic or resulting from hydrogen bonding, so probably the critical surface tensions of wetting determined in the two ways mentioned above are different. On the other hand it is known from the literature [14] that the presence of the water film on the PTFE surface in the PTFE-water drop system in some cases cannot be excluded.

If the polar interactions across PTFE-solution interface influence the critical tension of PTFE wetting, the work of adhesion of aqueous solution of surfactant to PTFE surface should depend on the concentration of surfactant.

The work of adhesion of liquid to solid,  $W_A$ , is defined by equation [2]:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (3)$$

where  $\gamma_{SV}$  is the surface tension of solid in the presence of liquid vapor and  $\gamma_{SL}$  is the solid-liquid interface tension.

Introducing Eqs (3) to Young equation:

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

we obtain:

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

Taking into account in Eq. (5) the measured values of the contact angle for aqueous solution of surfactants on PTFE surface and literature data of their surface tension, the values of the work of adhesion of solution to PTFE surface were calculated and they are presented in Figure 4.

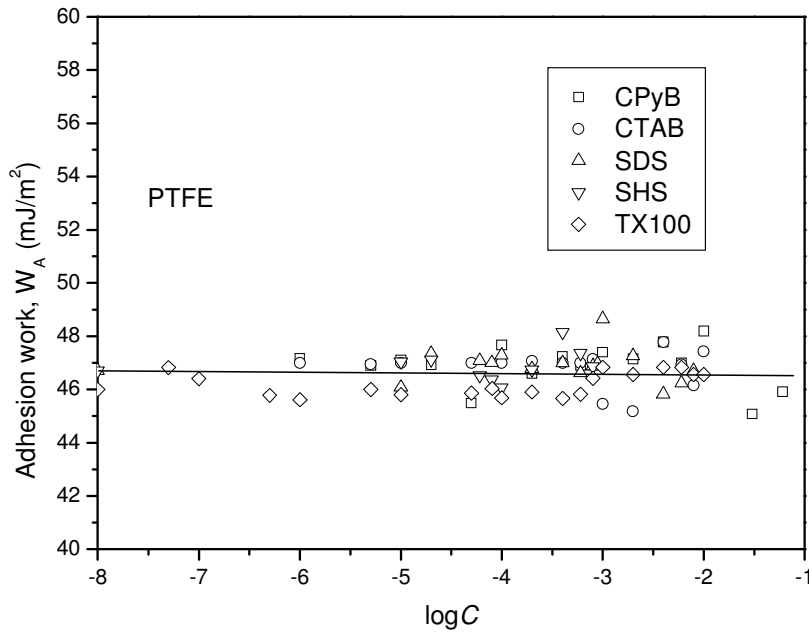


Fig. 4. The relationship between the work of adhesion ( $W_A$ ) of surfactant solution to PTFE and logarithm  $C$  for aqueous solution of CPyB, ( $\square$ ) CTAB ( $\circ$ ), SDS ( $\triangle$ ), SHS ( $\nabla$ ) and Triton X100 ( $\diamond$ ).

From this figure it results that the  $W_A$  does not depend on the type of surfactants and their concentration in solution. The average value of  $W_A$  is close to  $46.8 \text{ mJ/m}^2$ . This value is close to the work of adhesion of water to PTFE surface ( $27.47 \text{ mJ/m}^2$ ) [15]. On the other hand, the adhesion work according to approach of van Oss et al. [16] to liquid-liquid and solid-liquid interfaces the adhesion work fulfils the equation:

$$W_A = 2\sqrt{\gamma_L^{LW} \cdot \gamma_S^{LW}} + 2\sqrt{\gamma_L^- \cdot \gamma_S^+} + 2\sqrt{\gamma_L^+ \cdot \gamma_S^-} \quad (6)$$



where  $\gamma^{\text{LW}}$  is the Lifshitz-van der Waals component of the liquid and solid surface tension, and  $\gamma^{\ddagger}$  and  $\gamma$  are the electron-acceptor and electron-donor parameters of the acid-base component of a solid and a liquid surface tension. Indexes L and S refer to liquid and solid, respectively. If we assume that the surface tension of PTFE results only from Lifshitz-van der Waals interactions then:

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

Introducing into Eq. (7) the value of PTFE surface tension equal to 20.24 mN/m equal to its Lifshitz-van der Waals component and the value of the work of adhesion obtained from Eqs (5) we can determine the  $\gamma_L^{\text{LW}}$ . Thus determined  $\gamma_L^{\text{LW}}$  is equal to 27.05 mN/m. This value is close to the value of the Lifshitz-van der Waals component of the water surface tension proposed by Della Volpe and Siboni [17]. It means that any surfactant studied here does not influence the work of adhesion of solution to PTFE surface and suggests that the PTFE-solution interface tension is different than zero for the contact angle equal zero and probably therefore the critical surface tension of PTFE of wetting is higher than its surface tension [18].

### 3.2. PMMA

In the case of PMMA the contact angle (Fig. 5) for aqueous solution of surfactants on its surface changes in the function of surfactant concentration in the same way as that of PTFE (Fig. 2). Over the range of surfactant concentrations in the solution, corresponding to the unsaturated surfactant layer at aqueous solution-air interface, almost constant values of the contact angle are observed. However, when saturation of the surfactant layer was attained [10] a considerable decrease in the contact angle as a function of surfactant concentration takes place. In the range of low surfactant concentrations, with exception of TX-100, there are small differences between the values of the contact angle among the surfactants studied.

In contrast to Zisman [2] there is no linear dependence between  $\cos\theta$  and surface tension of solutions (Figure 6), however, such a type of dependence was obtained between the adhesional tension and surface tension of solution (Fig. 7). In the case of PMMA, It is impossible to describe the dependence between the adhesional tension and surface tension by one equation because the slope of the lines strongly depends on the type of surfactant, and they are different for cationic, anionic and non-ionic surfactants.

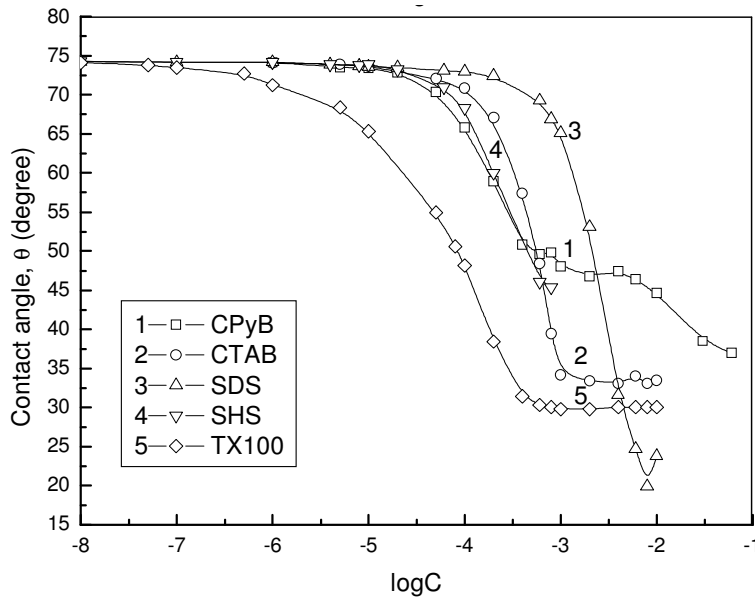


Fig. 5. The relationship between the contact angle,  $\theta$ , for aqueous solution of CPyB (curve 1), CTAB (curve 2), SDS (curve 3), SHS (curve 4) and Triton X100 (curve 5) on PMMA surface and logarithm  $C$  ( $C$  – concentration).

The equations describing the relationships between the adhesional tension and surface tension for the mentioned surfactants have the forms, respectively:

$$\chi_{LV} \cos \theta = -0,34 \chi_{LV} + 44,39 \quad (8a)$$

$$\chi_{LV} \cos \theta = -0,72 \chi_{LV} + 72,68 \quad (8b)$$

$$\chi_{LV} \cos \theta = -0,24 \chi_{LV} + 37,29 \quad (8c)$$

From Eqs (8a) it is seen that the adsorption of CPyB and CTAB at water-air interface is almost three times higher than that at PMMA-water interface because the constant value in Eq. (8a) is equal to -0.34. The lowest adsorption of surfactants at PMMA-water interface than at water-air interface probably results from parallel orientation of surfactants in the monolayer at PMMA-water interface. The value of critical surface tensions of PMMA wetting calculated from Eq. (8a) is equal to 33.13 mN/m and is lower than its surface tension (39.21 mN/m) and lower than even the Lifshitz-van der Waals components of PMMA surface tension [19].

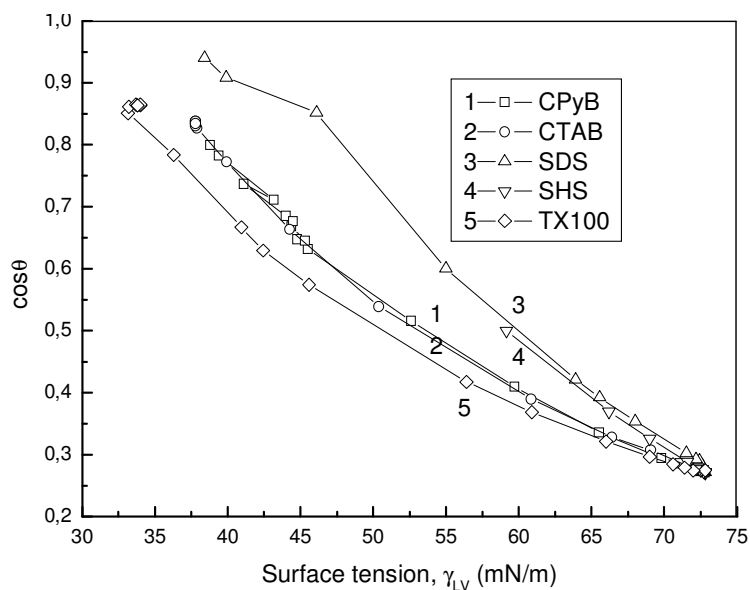


Fig. 6. The relationship between the values of  $\cos\theta$  for PMMA and the surface tension ( $\gamma_{LV}$ ) of aqueous solution of CPyB (curve 1), CTAB (curve 2), SDS (curve 3), SHS (curve 4) and Triton X100 (curve 5).

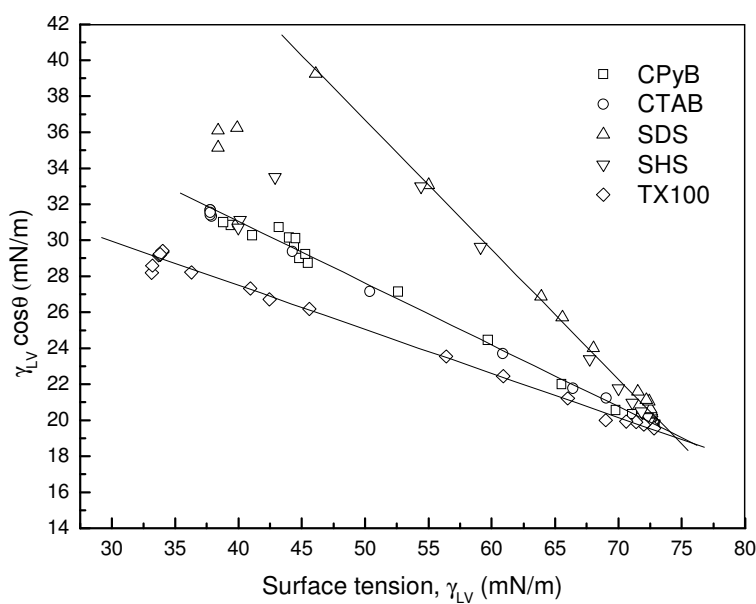


Fig. 7. The relationship between the values of  $\gamma_{LV} \cos\theta$  for PMMA and the surface tension ( $\gamma_{LV}$ ) of aqueous solution of CPyB, ( $\square$ ) CTAB ( $\circ$ ), SDS ( $\triangle$ ), SHS ( $\nabla$ ) and Triton X100 ( $\diamond$ ).

In the case of anionic surfactants, SDS and SHS, a straight relationship between adhesion tension and solution surface tension is obtained in the concentration range of the surfactants from 0 to  $C$  close to CMC [20,21]. However, the points corresponding to CMC or a little higher do not fulfil this relationship. The slope of  $\gamma_{LV} \cos\theta$  vs.  $\gamma_{LV}$  curves is also negative, but its value is equal -0.72 (Eq. (8b)). This means that in the concentration range of the surfactant in the bulk phase lower than CMC, its concentration at PMMA-solution interface is smaller than at solution-air interface. At PMMA-aqueous solution interface there are Lewis acid-base intermolecular interactions, however, the interactions between PMMA and water molecules are stronger than between PMMA and anionic surfactant ions or molecules [19]. It is therefore more difficult for molecules or ions of surfactants to remove water molecules from PMMA-solution interface than from solution-air interface. Probably for this reason the adsorption of the studied surfactants at PMMA solution interface is lower than at solution-air interface. The critical surface tension of PMMA wetting calculated from Eq. (8b) is equal to 42.26 mN/m and is somewhat higher than its surface tension [19].

For non-ionic surfactant, TX-100, we also observed a negative slope which is the smallest among all studied surfactants (Eq. (8c)). It means that the tendency of TX-100 to adsorb at PMMA-water interface is lower than that of cationic and anionic surfactants. Of course the surface excess of TX-100 concentration at PMMA-water interface is lower than at water-air interface. The critical surface tension of PMMA wetting determined from Eq. (8c) is equal to 30.08 mN/m. This value is lower than even Lifshitz-van der Waals component of the PMMA surface tension [19].

To show more clearly the influence of the polar interactions across PMMA-water interface on the values of the contact angle, the values of the work of solution adhesion to PMMA surface were calculated from Eq. (5) and they are presented in Figure (8). It appears from this figure that in the range of surfactant concentrations from  $1 \times 10^{-8}$  to  $10^{-5}$  M the  $W_A$  is almost constant and does not depend on the type of surfactant. However, above  $10^{-5}$  M the changes of  $W_A$  depend on the type of surfactant and its concentration. It is interesting that for anionic surfactants the maximum of  $W_A$  is observed at a concentration close to CMC for SDS [22] or close to its maximal solubility in water (SHS) [23].

According to Eq. (6) the  $W_A$  for PMMA-solution system results from apolar (Lifshitz-van der Waals) and polar (electron-acceptor and electron-donor) interactions. Taking into account the value of  $\gamma_L^{LW}$  (27.05 mN/m) for aqueous solutions of the surfactants studied, which was determined for PTFE-solution system and the  $\gamma_S^{LW}$  value (36.68 mN/m) [19], it is possible to determine from Eq. (6) the values of the component of the work of adhesion resulting from polar

interactions across PMMA-solution interface. In Figure 8, line A divides the work of adhesion into two components: apolar ( $63 \text{ mJ/m}^2$ ) and polar (the difference between total work of adhesion and  $63 \text{ mJ/m}^2$ ).

It is seen from Figure 8 that for cationic and non-ionic surfactant the polar interactions decrease in the range of concentrations corresponding to the saturated monolayer at water-air interface [10], however, in case of anionic surfactant an increase of these interactions is observed. For TX-100 at a concentration higher than that of CMC [24] the work of adhesion of solution to PMMA surface practically results only from apolar interactions. In the case of cationic and non-ionic surfactants their presence in water decreases the contribution of polar interaction in the work of adhesion. This fact confirms the conclusion that PMMA-water interactions are stronger than PMMA-surfactant interactions, therefore the excess of surfactant concentration at PMMA-solution interface is lower than at solution-air interface. However, in the case of anionic surfactant the polar interactions increase at a concentration higher than that of CMC. It is therefore probably that the points corresponding to the adhesional tension in Figure 7 do not fit in with the straight line. Of course, the problem considered here has been not completely solved yet, and additional studies are needed.

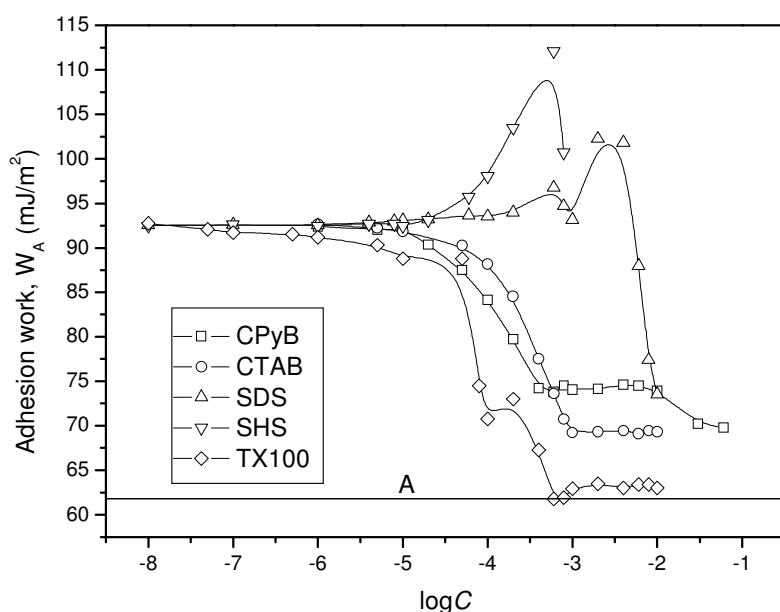


Fig. 8. The relationship between the work of adhesion ( $W_A$ ) of surfactant solution to PMMA and logarithm  $C$  for aqueous solution of CPyB, ( $\square$ ) CTAB ( $\circ$ ), SDS ( $\Delta$ ), SHS ( $\nabla$ ) and Triton X100 ( $\diamond$ ). Line A corresponds to the apolar component of the adhesion work of the surfactant solution to PMMA surface.

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## CURRICULA VITAE



**Wiesław Wójcik** is Full Professor at the Faculty of Chemistry of the Maria Curie-Skłodowska University (Lublin, Poland). His research work is largely concentrated on physicochemistry of the surface and interface phenomena strictly connected with flotation of ores and minerals. He published over 150 papers in the most prestigious scientific journals. He has been invited to the Technical University of Nova Scotia (Halifax, Canada).



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