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## International Journal of Adhesion &amp; Adhesives

journal homepage: [www.elsevier.com/locate/ijadhadh](http://www.elsevier.com/locate/ijadhadh)

# Wettability of polymers by aqueous solution of binary surfactants mixture with regard to adhesion in polymer–solution system II. Critical surface tension of polymers wetting and work of adhesion



Joanna Krawczyk, Katarzyna Szymczyk, Anna Zdziennicka\*, Bronisław Jańczuk

Department of Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

## ARTICLE INFO

## Article history:

Accepted 24 April 2013

Available online 10 May 2013

## Keywords:

Surfactant

Polymer

Interface tension

Contact angle

Wettability

Adhesion work

## ABSTRACT

The values of the surface tension of the aqueous solution of CTAB+TX-100, CTAB+TX-114 and TX-100+TX-114 mixtures and those of the contact angle for the same solutions on PTFE, PMMA and nylon 6 surface were applied for the studies of the correlation between the critical surface tension of PTFE, PMMA and nylon 6 wetting and their surface tension as well as the influence of the kind, concentration and composition of the aqueous solutions of binary mixtures of surfactants and the adhesion to those polymers. From these studies it results that the critical surface tension of PTFE wetting by the investigated solutions is somewhat higher than its surface tension determined from the contact angles for *n*-alkanes. However, the critical surface tension of PMMA and nylon 6 wetting is lower than their surface tension determined by using the van Oss et al. approach to the interfacial tension. The critical surface tension of PMMA and nylon 6 wetting was also compared to their surface tension calculated from the Neumann equation. It was found that there is agreement between these values if the surface tension of these polymers was determined on the basis of the solution surface tension and contact angle data corresponding to the concentration equal or higher than the critical micelle concentration.

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## 1. Introduction

The wettability of solids by the aqueous solutions of the surface active agents mixtures, which plays a highly important role in many technological processes and everyday life, depends on the activity of the adsorbed surface active agents at different interfaces [1,2]. In turn, the number of the adsorbed surface active agents and their activity at the interface depends on the components and parameters of the surface tension of both the given solid and the surface active agents.

In the previous paper [3] the wettability of polytetrafluoroethylene (PTFE), polymethyl methacrylate (PMMA) and nylon 6 by the aqueous solutions of CTAB+TX-100, CTAB+TX-114 and TX+100+TX-114 mixtures was considered. It was deduced that the wettability of these polymers by the aqueous solutions of binary mixtures of the studied surfactants depends on the kind of the mixture, its composition and concentration and there is synergism in the water contact angle reduction in the range of the mixture concentration from 0 to CMC and antagonism above the CMC. It was also deduced that for the PTFE–solution–air system, it is possible to describe the changes of the contact angle as a function

of the logarithm of the surface tension and the logarithm of the polymer–solution interface tension by one second order polynomial function. For this system there is one linear dependence between the contact angle and the sum of these logarithms. In the case of the systems including PMMA and nylon 6 the dependence between the contact angle and the surface tension of the aqueous solution of binary mixtures of surfactants and polymer–solution interface tension is more complicated. Using the contact angle and surface tension data, the relationship between the adsorption at the water–air and polymer–water interfaces was established and discussed in the light of the wettability of the studied polymers.

According to the Young equation [1,2] the wettability of the solid depends on the surface tension of solid and liquid as well as the solid–liquid interface tension and is connected by this equation with the work of adhesion of solution to the solid surface. Thus, the purpose of our paper was to establish and explain the relationship between the critical surface tension of polymers wetting and their surface tension as well as the dependence between the surface tension of polymers and solution, and the work of adhesion of the aqueous solution of the CTAB+TX-100, CTAB+TX-114 and TX-100+TX-114 mixtures to the PTFE, PMMA and nylon 6 surfaces in the light of the parameter of interactions across the polymer–solution interface. In the literature it is difficult to find such considerations for the polymer–aqueous solution of binary surfactants mixture–air systems. For these studies the

\* Corresponding author. Tel.: +48 81 537 56 70; fax: +48 81 533 3348.  
E-mail address: [aniaz@hektor.umcs.lublin.pl](mailto:aniaz@hektor.umcs.lublin.pl) (A. Zdziennicka).

surface tension and contact angle data were taken from our previous papers [3,4].

## 2. Experimental

### 2.1. Materials

The studies presented in this paper are based on the results of the contact angle measurements carried out elsewhere [3]. For these measurements the double distilled and deionized water (Destamat Bi18E), p-(1,1,3,3-tetramethylbutyl)-phenoxy polyoxyethylene glycols, Tritons: Triton X-100 (TX-100) and Triton X-114 (TX-114) and cetyltrimethylammonium bromide (CTAB) (Sigma-Aldrich) were used. For the contact angle measurements the CTAB+TX-100, CTAB+TX-114 and TX-100+TX-114 mixtures at the mole fraction of surfactants in the bulk phase ( $\alpha$ ) ( $\alpha_1$ -TX-100,  $\alpha_2$ -TX-114,  $\alpha_3$ -CTAB) equal to 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1 were prepared. The total concentration of these mixtures in aqueous solution was  $1 \times 10^{-8}$ ,  $5 \times 10^{-8}$ ,  $1 \times 10^{-7}$ ,  $5 \times 10^{-7}$ ,  $1 \times 10^{-6}$ ,  $5 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $4 \times 10^{-4}$ ,  $6 \times 10^{-4}$ ,  $8 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , and  $2 \times 10^{-3}$  M. The details of the solution preparation are described elsewhere [3].

The plates ( $30 \times 50 \text{ mm}^2$ ) used for the contact angle measurements were prepared from polytetrafluoroethylene (PTFE), polymethyl methacrylate (PMMA) and nylon 6. The procedure of preparation and cleaning of PTFE, PMMA and nylon 6 plates is described in detail elsewhere [3].

### 2.2. Contact angle measurements

The measurements of the advancing contact angles of the aqueous solutions of binary surfactants mixture at concentration and composition mentioned above on PTFE, PMMA and nylon 6 plates in the presence of saturated vapour of water were carried out using the sessile drop method by the DSA 30 measuring system, in a thermostated chamber at  $293 \pm 0.1$  K.

The contact angle for aqueous solution of binary surfactants mixture at given concentration and composition on each polymer (PTFE, PMMA and nylon 6) was measured for at least 30 independent drops ( $2 \mu\text{l}$ ). The average value from obtained at least 30 results was treated as the advancing contact angle in the PTFE (PMMA, nylon 6)-solution drop-air system for the solution at a given concentration and composition. Good reproducibility was found for the contact angle measurements. The standard deviation for each set of values was less than  $\pm 1.1^\circ$ . The details of the contact angle measurements were described earlier [3].

## 3. Discussion

### 3.1. PTFE

Combining the relationship between the work of adhesion ( $W_a$ ) and the surface tension of the phases being in contact [5,6]:

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (1)$$

(where  $\gamma_{LV}$  is the surface tension of the liquid,  $\gamma_{SV}$  is the surface tension of the solid and  $\gamma_{SL}$  is the solid-liquid interface tension) with the Young equation [1,5,6]:

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

(where  $\theta$  is the contact angle) we obtain the Young-Dupre equation [5,6]:

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

From Eq. (3) it results that

$$\gamma_{LV} \cos \theta = -\gamma_{LV} + W_a \quad (4)$$

or

$$\cos \theta = -1 + W_a \frac{1}{\gamma_{LV}} \quad (5)$$

If there are linear dependencies between the adhesion tension ( $\gamma_{LV} \cos \theta$ ) and the surface tension and between  $\cos \theta$  and the reciprocal of the surface tension (Fig. 1), and the slope of the first dependence is equal to  $-1$  and the second one crosses  $\cos \theta$  at  $-1$ , then the adsorption of the surface active agents at the water-air and solid-water interfaces is the same [6]. From Eqs. (4) and (5) it is possible to determine the work of adhesion of the aqueous solution of surface active agents to the solid surface and the value of the surface tension for which the contact angle is strictly equal to zero. Zisman [7] called such value the critical surface tension of solid wetting.

Taking into account all our obtained values of the contact angle of aqueous solution of the binary surfactants mixture on PTFE surface and the values of their surface tension the relationship between the adhesion and surface tension was plotted [3]. It appeared that this relationship is linear and for the aqueous solutions of the CTAB+TX-100, CTAB+TX-114 and TX-100+TX-114 mixtures at all concentration and composition studied can be described by one equation and we established that it has the form

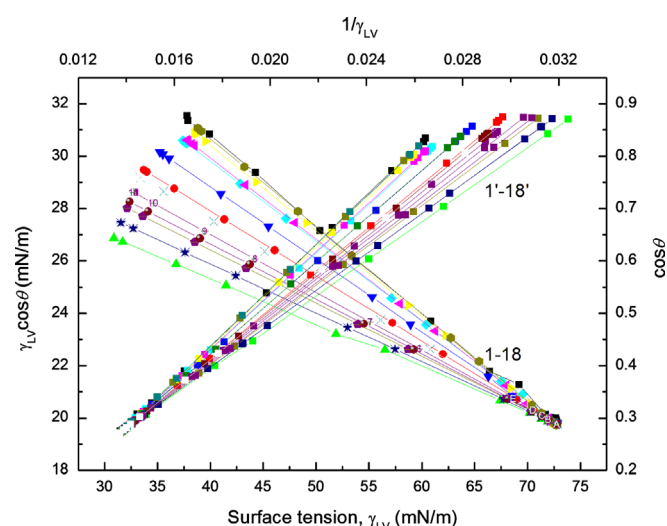
$$\gamma_{LV} \cos \theta = -(1.004632 \pm 0.001141) \gamma_{LV} + (46.691866 \pm 0.061719) \quad (6)$$

Assuming the contact angle equal to zero the surface tension of solution was calculated from this equation, which according to Zisman [7] was equal to critical surface tension of PTFE wetting.

Because the slope of line described by Eq. (6) is close to  $-1$  thus the value  $46.691866 \pm 0.061719$  in this equation is equal to the work of adhesion of all aqueous solutions of binary surfactants mixture.

We also found that for all aqueous solutions of the binary surfactants mixture the dependence between  $\cos \theta$  and  $1/\gamma_{LV}$  can be described by one linear equation which has a form

$$\cos \theta = (46.770683 \pm 0.051914) \frac{1}{\gamma_{LV}} - (1.006082 \pm 0.001171) \quad (7)$$



**Fig. 1.** A plot of the adhesion tension ( $\gamma_{LV} \cos \theta$ ) vs. the surface tension ( $\gamma_{LV}$ ) (curves 1–18) and  $\cos \theta$  vs. the reciprocal of the surface tension (curves 1'–18') of the aqueous solutions of TX-100 (curves 1 and 1'), TX-114 (curves 2 and 2'), CTAB (curves 3 and 3'), and the aqueous solutions of CTAB+TX-100 (curves 4–8 and 4'–8'), CTAB+TX-114 (curves 9–13 and 9'–13') and TX-100+TX-114 (curves 14–18 and 14'–18') at the different mole fractions of surfactants in the mixture in the bulk phase for the PTFE surface.

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