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The Effect of Surfactants on Equilibrium Wetting*

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Contact angles Θ_0 of aqueous solutions contacting with hydrophilic and hydrophobic surfaces were studied as affected by various surfactants (alcohols, fatty acids, soaps) under conditions close to thermodynamic equilibrium (in the atmosphere saturated with the solution vapour). The conditions of transitions from limited wetting ($\Theta_0 > 0$) to complete wetting, i. e. spontaneous spreading were also studied. The effect of surfactants adsorption at the solid gas interface was estimated from the isotherms of wetting tension $W = \sigma_{lg}$ Cos Θ_0 (σ_{lg} is the surface tension of the solution) on the basis of equation describing W as a function of concentration. It is shown that adsorption of surfactants at the solid-gas interface markedly affects wetting of hydrophilic materials. For hydrophobic materials the effect is primarily due to adsorption of surfactants at the solid-solution and solution-gas interfaces. It was found that equilibrium wetting is affected by the type of adsorption at the solid surface (physical or chemical adsorption). The influence of hydrocarbon chain length in homological series of alcohols and fatty acids on equilibrium contact angles and on transition to spontaneous spreading was studied as well.

INTRODUCTION

In 1938 A. N. Frumkin developed a theory according to which the equilibrium at the three phases contact line (at the wetting parameter) depends not only on the initial (prior to the contact with the liquid) surface tension at the solid-gas interface, but also on adsorption of the liquid phase components at this interface[1]. The result is that the surface tension on the solid decreases by the value $\Delta\sigma_{sg}$ which depends on specific adsorption Γ_{sg} and then equals

$$\sigma^*_{sg} = \sigma_{sg} - \Delta\sigma_{sg} \tag{1}$$

As long as $\sigma_{sg} > \sigma^*_{sg}$, $\Delta\sigma_{sg} > 0$. If adsorption is physical, reversible, from the Gibbs' equation we get that

$$\Delta\sigma_{sg} + \mathrm{RT} \int_{0}^{P} \Gamma_{sg} \, \mathrm{d}\ln p \tag{2}$$

where R is the gas constant, T is the temperature (K), P is the pressure of the vapour of the adsorbed substances.

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According to Frumkin the equation for the equilibrium contact angle (T. Young's equation) would then look as follows

$$\cos \Theta_o = \frac{\sigma^*_{sg} - \sigma_{sl}}{\sigma_{lg}} = \frac{(\sigma_{sg} - \Delta\sigma_{sg}) - \sigma_{sl}}{\sigma_{lg}} \quad (3)$$

σ_{sl} and σ_{lg} here are surface tensions at the solid-liquid and solid-gas interfaces respectively. The effect of the solution components adsorption on equilibrium contact angles was studied by B. V. Deryagin, L. M. Shcherbakov, A. Adamson and others (see for instance ref. 2. and 3.). The problem, however, was investigated primarily for wetting by pure liquids (one-component).

Our paper deals with the wetting of hydrophilic and hydrophobic surfaces by aqueous solutions of surfactants under conditions close to equilibrium, i. e. in atmosphere saturated with vapours of the wetting liquid. The experiments were carried out with systems where surfactant adsorption on the solid surface was predominantly either physical or chemical (reversible). The principal problem was to analyze the influence of surfactants' adsorption at the solid-gas interface. The method of experimental data processing (the analysis of wetting tension isotherms) made it possible to directly check the principal notion of Frumkin's theory, which states that there exists an adsorption layer in equilibrium with the liquid phase at the solid-gas interface, i. e. with the drop of the wetting liquid. At the same time it has proved possible to elucidate the effect of adsorption at the solid-gas surface on transition from limited wetting ($\Theta_o > 0$) to spontaneous spreading, when no finite contact angle is formed but the drop spreads to form a thin film. These questions are not of pure theoretical interest only, but they are important from the practical point of view of the use of surfactants for controlling wetting in diverse technological processes.

MATERIALS AND TECHNIQUE

The hydrophilic materials used were metals covered by natural oxide film (zinc, cadmium, aluminium) and polymers containing polar groups (lavsan, polycarbonate, polyarylate, etc.). On these materials water forms the contact angle $\Theta_o < 90^0$ (at the interface with air). Polytetrafluorethylene (teflon) was used as a hydrophobic material.

The metal plates were polished; the zinc ones underwent additional electrochemical polishing in the mixture of concentrated phosphoric acid, glycerine and water (in proportion 2 : 2 : 1), the current density being 0.5 mA/mm^2. The microrelief of the samples was examined by a microprophilograph with a resolution of 0.1 mcm. Contact angles were measured on plates with the same smoothness. After polishing, the plates were washed with water and kept for two hours in crioscopic benzene in order to eliminate any trace of grease and fatty acids from their surface. Then they were washed with a redistilled water stream and dried in a vacuum chamber. Polymer plates were cleaned by potassium bichromate solution and dried. Such a technique of preparing the samples made possible a high reproducibility of contact angle measurements.

The surfactants used were normal alcohols from methanol to hexanol, fatty acids from acetic to capronic acid and micelle-forming surfactants, namely cation--active cetyltrimethylammonium bromide and anion-active sodium dodecylsulphonate. The alcohols were dried beforehand, the acids were purified by vacuum distillation. The purity of surfactants was controlled by chromatographic analysis. The solvent used was redistilled water of specific conductivity not higher than $1.5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

In order to measure the contact angles we used the technique of sessile drop image projection. A 0.2 ml drop was deposited onto a horisontal plate with the help of a calibrated pipette or a medical syringe. The angles were measured on both sides of the image, from the left and from the right, each figure being averaged from the measurements of 6—7 drops. The mean square deviation was usually ± 1^0, in agreement with the accuracy of the instrument scale.

In order to provide equilibrium at the solid-gas interface the samples were kept in a thermostatic chamber whose hydraulic lock was filled with the solution of the same composition as the drop during the experiments. Before the drop was deposited the sample was kept in the chamber for 30 minutes, the time sufficient for adsorption to reach equilibrium. In all the cases we measured the advancing contact angles Θ_a. In most systems Θ_a became stable (stationary) in 5—10 minutes after the drop was deposited on the sample. Control experiments (varying of the drop volume and the chamber volume, measurements of wetting angles on vertical plates put into the solution) have shown that the angles Θ_a are highly reproducible. Since the measurements were carried out in a vapour-saturated atmosphere we can assume that the contact angles Θ_a are close to the equilibrium angles Θ_o. Most experiments were carried out at 20 ± 5 °C, some in the range 5—60 °C.

The surface tension of the solution was measured by the gas bubble maximum pressure technique.

EXPERIMENTAL RESULTS

A common characteristics of the surfactant effect on wetting is the contact angles isotherm. In our case which concerns the effect of surfactants at the solid-gas interface it is, however, more appropriate to employ another parameter, namely the wetting tension isotherms $W = f(c)$. It would then not necessary to take into account the variations of surface tension of the solution at the interface with gas.

According to (4) the wetting tension, or the adhesion tension (5) equals

$$W = \sigma_{lg} \cos \Theta_o \qquad (4)$$

From the equation (3), we get

$$W = \sigma_{sg}{}^* - \sigma_{sl} \qquad (5)$$

Thus under equilibrium conditions the wetting tension depends on the surface tensions at the solid-gas and solid-liquid interfaces. Accordingly, the dependence of wetting tension on concentration, or wetting isotherm, can be described by the following equation:

$$W = \sigma_{sg}{}^* (c) - \sigma_{sl} (c) = W_o - [\Delta \sigma_{sg} (c) - \Delta \sigma_{sl} (c)] \qquad (6)$$

Here $W_o = (\sigma_{sg} - \sigma_{sl})$ is the wetting tension for the pure solvent (for water in our case); $\Delta\sigma_{sl}(c) = \sigma_{sl} - \sigma_{sl}(c)$ is the variation of surface tension at the solid--solution interface, which depends on specific adsorption of the surfactant Γ_{sl}. As long as $\sigma_{sl} > \sigma_{sl}(c)$, $\Delta\sigma_{sl} > 0$. Thus the shape of the wetting tension isotherms of the initial point (O, W_o) depends on the correlation between $\Delta\sigma_{sg}(c)$ and $\Delta\sigma_{sl}(c)$. Depending on the nature of the solid and the surfactant, different correlations between these two values may exist and therefore different shapes of the isotherms are also possible.

Three cases were observed in the systems we studied[6]:

1) With increasing concentration of the solution the wetting tension gradually decreases, i. e. $(dW/dc) < 0$ (Figures 1 and 2).

2) Wetting tension increases with concentration of the solution, i. e. $(dW/dc) > 0$ (Figures 3—5).

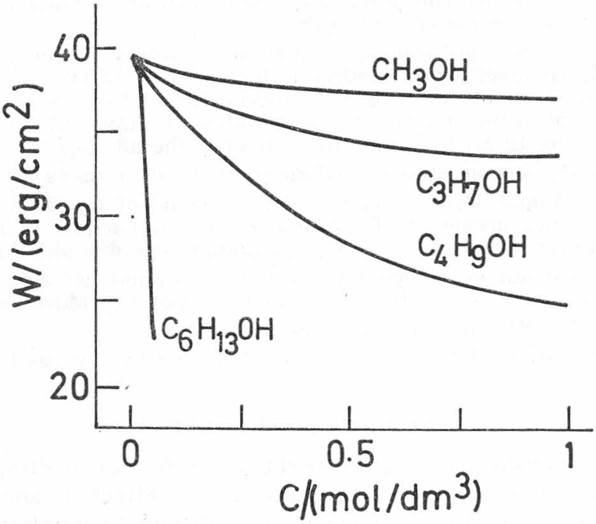

Figure 1. Wetting tension isotherms for aluminium wetted by aqueous solutions of alcohols ($t = 20$ °C).

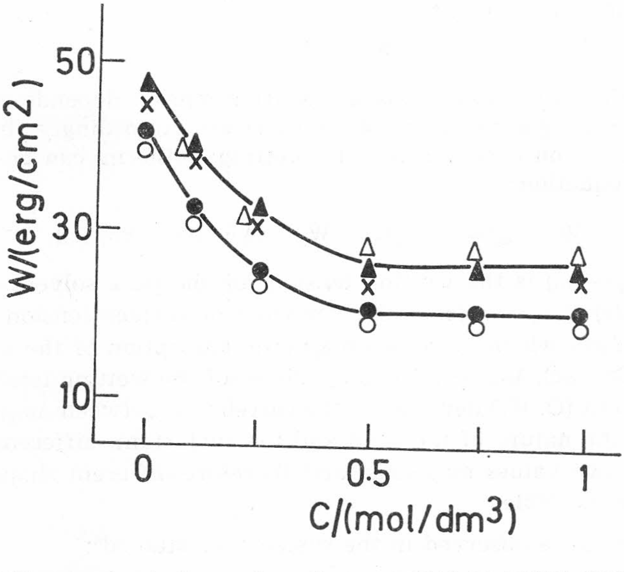

Figure 2. Wetting tension isotherms for polymers wetted by buthyl alcohol solutions.

▲ — polycarbonate

● — polyamide

× — lavsan polyester

○ — cellulose triacetate

△ — polyarylate

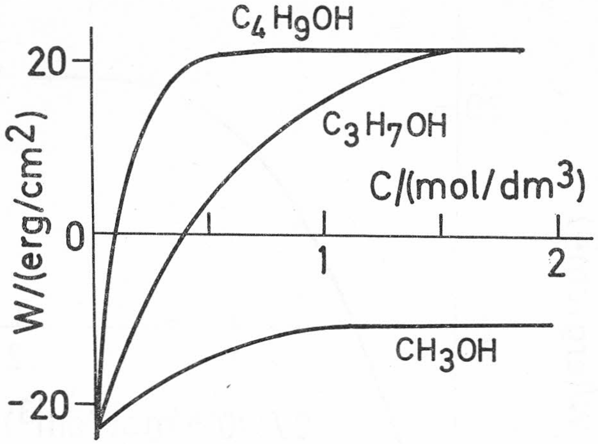

Figure 3. Wetting tension isotherms for teflon wetted by water solutions of alcohols.

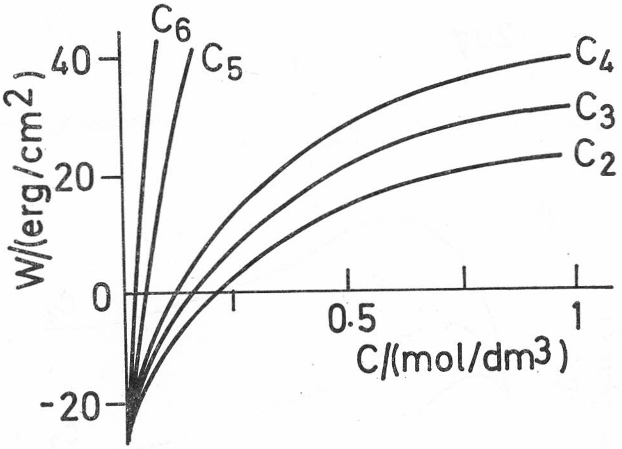

Figure 4. Wetting tension isotherms for teflon wetted by water solutions of fatty acids from acetic acid (C_2) to capronic acid (C_6).

3) At low concentrations the wetting tension grows with concentration but after reaching a maximum starts to fall (Figures 6 and 7).

Let us consider these cases in detail and find out why the wetting tension isotherms may have different shape.

Case I: $(dW/dc) < 0$

It follows from (6) that a condition necessary for the wetting tension to decrease is

$$\Delta \sigma_{sg}(c) > \Delta \sigma_{sl}(c) \qquad (7)$$

In case $\Delta\sigma_{sg}(c) \gg \Delta\sigma_{sl}(c)$ we have

$$W(c) = W_o - \Delta \sigma_{sg}(c) \qquad (8)$$

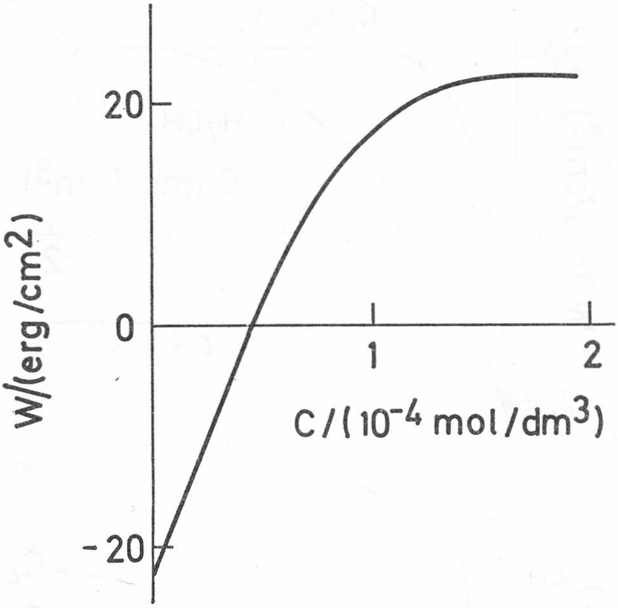

Figure 5. Wetting tension isotherms for teflon wetted by cetyltrimethylammonium bromide aqueous solutions.

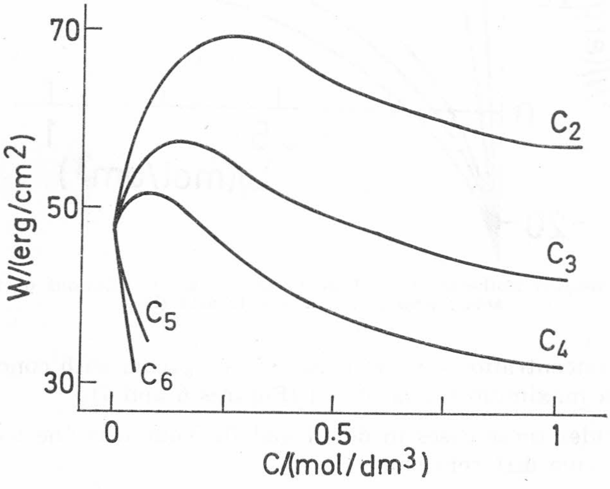

Figure 6. Wetting tension isotherms for zinc wetted by aqueous solutions of acids from acetic acid (C_2) to capronic acid (C_6).

According to the rule of polarities levelling, which was first suggested by P. A. Rehbinder[4], the correlation $\Delta\sigma_{sg}(c) \gg \Delta\sigma_{sl}(c)$ may be observed in case of, say, wetting of hydrophilic surfaces by water solutions of alcohols. In these systems adsorption should occur primarily at the interface between the polar (solid) phase and the non-polar one(gas), so that the surface active molecules in the adsorption layer would be orientated with their polar groups towards

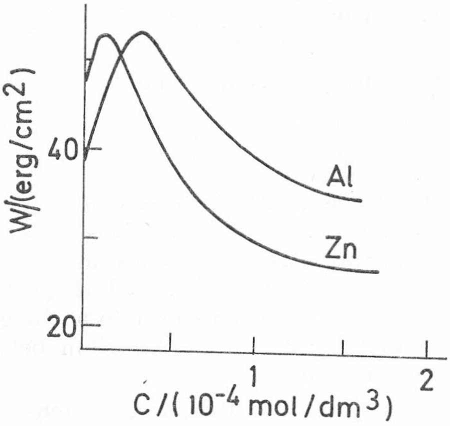

Figure 7. Wetting tension isotherms for aluminium and zinc wetted by cetyltrimethylammonium bromide aqueous solutions.

the hydrophilic solid, whereas their non-polar parts (hydrocarbon chains) would be turned to the gas phase. At the interface between two polar phases (solid-solution) adsorption of alcohols must be rather low, while it can be neglected if we consider the problem of surfactants influence on equilibrium contact angles in the first approximation.

Thus the wetting tension isotherms of the first type directly indicate that adsorption of surfactants at the solid-gas interface affects considerably the equilibrium contact angles.

In order to estimate $\Delta\sigma_{sg}(c)$ let us use Langmuir's equation:

$$\Gamma_{sg} = \Gamma_{\infty(sg)} \frac{p}{A + p} \tag{9}$$

where $\Gamma_{\infty(sg)}$ is the ultimate specific adsorption, $A = 1/K_{sg}$, K_{sg} is the contact of the adsorption-desorption equilibrium at the solid-gas interface and p is the pressure of gas. Substitution of Γ_{sg} into (2) gives

$$\Delta\sigma_{sg} = RT\,\Gamma_{\infty} \ln(1 + p/A) \tag{10}$$

According to Konovalov's first law, the partial pressure of the solution vapour grows with concentration of the solution. In first approximation this correlation at low concentrations can be described by a linear equation:

$$p = \alpha c \tag{11}$$

where c is the concentration and α is a factor depending on the heat of evaporation of the substance and on the temperature.

Therefore we can obtain

$$\Delta\sigma_{sg}(\mathrm{c}) = \mathrm{RT}\,\Gamma_{\infty(sg)} \ln(1 + \frac{\alpha}{A}\mathrm{c}) \tag{13}$$

As a final result the wetting isotherm of the first type can be described by the equation

$$W(c) = W_0 - RT\,\Gamma_{\infty(sg)} \ln\left(1 + \frac{\alpha}{A} c\right) \tag{14}$$

The initial slope of the wetting tension isotherm

$$\left(\frac{dW}{dc}\right)_{c \to 0} = -RT\,\Gamma_{\infty(sg)} \frac{\alpha}{A} \tag{15}$$

For surfactants belonging to one homological series $\Gamma_{\infty(sg)} = \text{const}$. Therefore the slope of the $W = f(c)$ isotherm which characterizes the effectiveness of surfactants influence on equilibrium wetting angles in determined by the ratio between the two parameters (α/A), one of the which (α) refers to the dynamic equilibrium between evaporation and condensation at the gas-solution interface, while the other (A) — to the dynamic equilibrium between adsorption and desorption at the solid-gas boundary.

This theoretical analysis shows that the wetting tension of alcohol solutions contacting with hydrophilic solids must decrease with increasing concentration of the solution. Since the parameter A is dependent on the hydrocarbon chain length more than α (at least for lower homologues), the initial slope of the isotherms must gradually increase in its absolute value by transition to higher homologues.

The isotherms $W = f(c)$ may also be used for evaluation of surfactants adsorption at the solid-gas interface. In fact, according to Gibbs' equation

$$\Gamma_{sg} = -\frac{p}{RT} \times \frac{d\,\sigma_{sg}}{dp} \tag{16}$$

On the other hand, $p = \alpha c$, and $dp = \alpha dc$. Accordingly,

$$\Gamma_{sg} = -\frac{c}{RT} \times \frac{d\,\sigma_{sg}}{dc} \tag{17}$$

Since in the system under consideration $d\sigma_{sg}/dc = dW/dc$, we obtain:

$$\Gamma_{sg} = -\frac{c}{RT} \times \frac{dW}{dc} \tag{18}$$

In this manner the adsorption isotherm $\Gamma_{sg} = f(c)$ can be calculated from the experimental isotherm $W = f(c)$.

The experimental results (Figures 1 and 2) are consistent with the above conclusions. In aqueous solutions of alcohols contacting with hydrophilic materials, the wetting tension has always decreased with increasing concentration[6,7]. As the hydrocarbon chain length of the alcohol molecule grows, the absolute value of the initial slope of the isotherms grows also. These results appear to directly confirm the basic notion of Frumkin's theory, which states that in order to determine the equilibrium conditions of wetting it is necessary to take into consideration the adsorption of the liquid phase components at the solid-gas interface.

Adsorption of alcohols at the solid-gas interface influences also the conditions of transition from limited wetting ($\Theta > 0$) to spontaneous spreading when a drop spreads to form a thin film. The transition took place when the alcohol concentration c_{spr} was rather high.

This threshold concentration sharply decreases with the growing molecular weight of alcohols:

ALCOHOL	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
c_{spr}, mol/dm^3	30	20	10	1

Calculation of the adsorption isotherm $\Gamma_{sg} = f(c)$ according to (18) from, say, the data on zinc wetting by buthyl alcohol solutions has shown that $\Gamma_{\infty(sg)} \approx 6 \times 10^{-10}$ mol/cm^2. Therefore that the adsorption monolayer at the solid-gas surface, in case of spontaneous spreading, (complete wetting) is close to being saturated. At the same time the monolayer, which forms at the liquid-gas interface at the solution concentration c_{spr}, is also saturated too. The surface active molecules in these monolayers are orientated in such a way that in the vicinity of the wetting perimetre their similar hydrocarbon radicals are turned towards each other. This fact contributes to the strong decrease in surface tension at the solid-solution boundary.

Case II: dW/dc > 0

Follows from the equation (6) we see that, the wetting isotherms can belong to this type provided the inequality $\Delta\sigma_{sl}(c) > \Delta\sigma_{sg}(c)$ is fulfilled. According to the rule of polarities levelling this inequality can be true in the case of contact of water solutions of surfactants with hydrophobic materials. In such systems the amphiphilic surface active molecules are adsorbed for the most part at the interface between the non-polar solid and the polar liquid, their hydrocarbon chains orientated towards the solid. If $\Delta\sigma_{sl}(c) \gg \Delta\sigma_{sg}(c)$, the equation of the wetting tension isotherm (6) is transformed into

$$W(c) = W_o + \Delta\,\sigma_{sl}(c) \qquad (19)$$

As far as $\Delta\sigma_{sl} > 0$, the wetting tension must increase with concentration. In the manner similar to the used to analyze the case I it can be shown that the initial slope of the isotherms $(dW/dc)_{c\to 0}$ must grow with elongation of the hydrocarbon chain of the members of one homological series.

These conclusions can be confirmed by the data on the contacts of water solutions of alcohols, fatty acids and micelle-forming surfactants with teflon (Figures 3—5).

Thus in the case when solutions of surfactants are different in their chemical nature and are in contact with the hydrophobic solid surface, the adsorption of surfactants at the solid-gas interface is insignificant, whereas the main role is played by adsorption at the solid-solution and the solution-gas interfaces.

The contact of surfactant solutions with teflon involves at sufficiently high concentrations the effect of inversion, i. e. transition from non-wetting ($\Theta_o > 90^0$) to limited wetting ($90^0 > \Theta_o > 0$). However, even at ultimate concentrations no complete wetting (spontaneous spreading) took place, probably because of the following. In the above discusion of case I we have shown that complete wetting by a solution of a surfactant takes place after monolayers close to being saturated are formed at the solid-gas and liquid-gas interfaces, the similar hydrocarbon radicals facing each other. As long as adsorption of surfactants at the solid-gas interface in case of contact with teflon is negligible, this condition cannot be fulfilled.

Case III: at low concentrations $dW/dc > 0$
at high concentrations $dW/dc < 0$.

This case appears to be the most difficult one for discussion. From the equation (6) we see that this phenomena can be observed if at low concentrations $\Delta\sigma_{sl}(c) > \Delta\sigma_{sg}(c)$, but at higher concentrations of the surfactant solution the inequality changes its sign, i. e. $\Delta\sigma_{sl}(c) < \Delta\sigma_{sg}(c)$. The above considered wetting tension isotherms of types I and II were observed in systems where adsorption of surfactants at solid surface is primarly physical (reversible). In case III the surfactants used were capable of chemisorption at the solid-solution interface. The results typical in this respect were obtained for the contact of fatty acids (lower homologues) and micelle-forming surfactants with hydrophilic surfaces of metals covered by oxide film (Figures 6 and 7).

At low concentrations the wetting tension grows, but after a certain maximum is reached, it gradually falls. The initial slope of the isotherms dW/dc decreases with elogation of the hydrocarbon chain of the acids. For the higher homologues, beginning from valeric acid, even at low concentrations the wetting tension only decreases.

The increase in wetting tension at low concentrations can be attributed to chemical adsorption of fatty acids at the metal oxide surface with formation of a layer of a corresponding salt. The result is a noticeable decrease in surface tension at the solid-solution interface. However, after a saturated adsorption layer is formed the further increase in the solution concentration can no more decrease the σ_{sl}, and the surfactant adsorption at the solid-gas interface starts to play the principal part. As a result the wetting tension begins to fall. In the homological series of fatty acids, the degree of dissociation falls with increasing molecular weight. Therefore acetic acid displays the sharpest increase in the wetting tension, whereas the higher homologues with very low degree of dissociation can only decrease the wetting tension with the increase of their concentration.

CONCLUSION

In wetting of hydrophilic materials by aqueous solutions of alcohols and fatty acids the equilibrium contact angles essentially depend on adsorption of the surface active molecules at the solid-gas interface, thus confirming the theoretical notions of phase equilibrium in wetting suggested by Frumkin. This also applies to the adsorption of surface active molecules at the solid-gas interface and also to the transition from limited wetting ($\Theta_0 > 0$) to complete wetting, i. e. spontaneous spreading into a thin film.

For hydrophobic materials the role adsorption of surfactants at the solid-gas surface is negligible, while the adsorption is of principle importance at the solid-solution and solution-gas interfaces.

The effect of surfactants on equilibrium contact angles depends also on the nature of adsorption at the surface of the solid (physical or chemical adsorption).

The analysis of wetting tension isotherms makes possible the calculation of the adsorption isotherms for solid-gas interface adsorbing surface active substances.

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SAŽETAK

Utjecaj tenzida na ravnotežno kvašenje

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Proučavani su kutovi dodira Θ_0, vodenih otopina s hidrofilnim i hidrofobnim površinama u ovisnosti o različitim tenzidima (alkoholi, masne kiseline, sapuni) u uvjetima bliskim termodinamičkoj ravnoteži (u atmosferi zasićenoj parama otopine). Isto su tako razmatrani uvjeti prijelaza od graničnog kvašenja ($\Theta_0 > 0$) do potpunog kvašenja. Učinak adsorpcije tenzida na granici faza čvrsto/plinovito određen je iz izoterme napetosti kvašenja $W = \sigma_{lg} \cos \Theta_0$ (σ_{lg} je površinska napetost otopine) na osnovi jednadžbe otopine koja opisuje W kao funkciju koncentracije. Pokazano je da adsorpcija tenzida na granici faza čvrsto/plinovito značajno utječe na kvašenje hidrofilnih materijala. Za hidrofobne materijale učinak se prvenstveno osniva na adsorpciji tenzida na granici faza čvrsto/tekuće i tekuće/plinovito. Ravnotežno kvašenje ovisi o tipu adsorpcije na čvrstoj površini (fizička i kemijska adsorpcija). Isto tako je proučavan utjecaj duljine ugljikovodičnih lanaca u homolognom nizu alkohola i masnih kiselina na ravnotežni kontaktni kut i na prijelaz k spontanom širenju.

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