Selective Wetting of Heterogeneous Surfaces by Solutions of Surfactants

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Abstract—Selective wetting of dimethyldichlorosilane-modified glass plates by solutions of tetradecyltrimethylammonium bromide (TDTAB), a cationic surfactant, in *p*-xylene has been studied. When surfactant concentrations are lower than the critical micelle concentration (CMC), the contact angles under selective wetting conditions increase with increasing hydrophobic surface fraction. When surfactant concentrations are higher than CMC, contact angles are the same on all substrates studied. The adsorption of the surfactant on hydrophilic and hydrophobic regions of heterogeneous surfaces and the stability of wetting films are taken into account in interpreting the results.

Selective wetting, i.e., wetting in solid–liquid (1)–liquid (2) systems, is important for many natural, biological, and industrial processes [1–3]. However, many features of the mechanisms of selective wetting remain unclear. The effects of the nature of a solid substrate and its surface energy on the stability of wetting films and the contact angles of selective wetting θ_{12} are poorly understood. Surfactants influence selective wetting in a complex manner: on one hand, the interfacial energies of various interfaces decrease as a result of the adsorption of surfactants, as a rule, enhancing wetting. On the other, surfactants have a stabilizing effect on polar–nonpolar phase surfaces and on wetting films, hindering the spreading of drops under selective wetting conditions [4, 5]. The influence of surfactants on the selective wetting of heterogeneous surfaces is virtually unstudied.

This work is a comparative study of the effect of the hydrophobic fraction of a solid surface on its wetting by solutions of surfactants in air and under selective wetting conditions (in an immiscible liquid).

SUBJECTS AND METHODS

The surfactants used were tetradecyltrimethylammonium bromide (TDTAB) (from Merck); the nonpolar liquid was *p*-xylene (chemically pure grade). TDTAB solutions with concentrations c ranging from 10^{-5} to 10^{-2} mol/L were prepared by consecutive dilution of the stock solution with distilled water. Glass plates treated with dimethyldichlorosilane (DMDCS) were used in experiments.

Surface tension isotherms at aqueous TDTAB solution–air and solution–*p*-xylene interfaces were obtained in Wilhelmy's plate equilibration experiments (Fig. 1). The critical micelle concentration (CMC) for TDTAB as derived from the kink on the surface tension isotherm is 4×10^{-3} mol/L, which agrees with the literature [6, 7]. Interfacial tension strongly decreases with
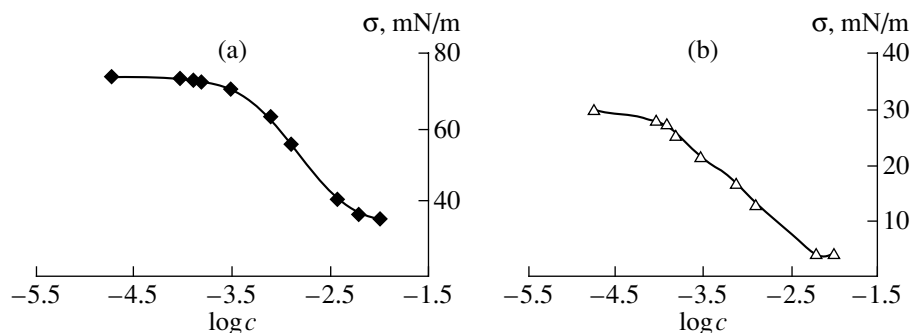

Fig. 1. Surface tension isotherms at (a) aqueous TDTAB solution–air and (b) this solution–*p*-xylene interfaces (*c*, mol/L).

Table 1. Glass modification in solutions of DMDCS in chloroform

DMDCS concentration, vol %	Modification time, s	Water contact angle θ, deg	Hydrophobic surface fraction, X
0.1	5	41	0.20
1	30	66	0.46
1	600	76	0.60

rising TDTAB concentration to acquire a constant value of 4 mN/m near the CMC. This is the lower limit for Wilhelmy's technique. Smaller values cannot be determined because the plate is not equilibrated at the interface.

The starting glass plates were cleaned as follows: they were stored in sulfochromic acid for 1 day, after which they were boiled three rimes with distilled water and dried in air. The contact angle between water and cleaned plates was 5 deg. A horizontal microscope equipped with a digital video camera, which was interfaced with a computer, was used to determine contact angles. Contact angles were determined by digitizing video images of a seating drop. To make the surface fully hydrophobic, cleaned glass plates were treated in DMDCS vapor for 1 day followed by washing with chloroform. As a result of this treatment, hydrophobic methyl groups substituted for hydrophilic silanol groups on the glass surface. The water contact angle at hydrophobic plates was 105 deg.

To obtain heterogeneous surfaces, cleaned glass plates were placed into a solution of DMDCS in chloroform. The solution concentration and the modification time were varied to achieve the set degree of surface modification (table 1). After exposure to the solu-

tion, plates were cleansed with chloroform and dried in air. The hydrophobic surface fraction was calculated from the Cassie–Baxter relationship [8]:

$$\cos\theta = X\cos\theta_1 + (1 - X)\cos\theta_2. \qquad (1)$$

Here, θ is the water contact angle at a heterogeneous surface in air, θ_1 is the water contact angle at a hydrophobic surface (105 deg, $\cos\theta_1 = -0.259$), θ_2 is the water contact angle at a hydrophilic surface (5 deg, $\cos\theta_2 = 0.996$), and X is the hydrophobic surface fraction of the glass plate. Plates with hydrophobic surface fractions equal to 0.20, 0.46, and 0.60 were obtained as a result of modification (Table 1). The modification of plates was quite uniform; the scatter of the contact angles of water drops at various parts of the surface of a plate did not exceed 3 deg in 10–15 measurements.

RESULTS AND DISCUSSION

Wetting by TDTAB solutions in air (Fig. 2) for glass and hydrophobic glass is described by considerably different isotherms. The contact angles on the unmodified glass plates (Fig. 2, curve *1*) first increase with rising TDTAB concentration as a result of the adsorption of surface-active cations on negatively charged adsorption sites of the glass surface. Then, as the TDTAB concentration increases further, the angles decrease because the solid surface becomes hydrophilic because of the formation of a bilayer or the adsorption of aggregates [9–11]. When hydrophobic glass is wetted, the contact angles decrease with rising concentration to acquire a constant value when $c > $ CMC (Fig. 2, curve *5*). This type of isotherm for wetting of hydrophobic surfaces is characteristic of micelle-forming surfactants [12].

When heterogeneous surfaces are wetted, the contact angles increase with rising hydrophobic surface fraction of glass (considering wetting by TDTAB solutions of identical concentrations) (Fig. 2). The trend of wetting isotherms for heterogeneous surfaces resembles that for hydrophobic glass: the contact angles decrease with rising surfactant concentration and acquire constant values after the CMC is achieved. The adsorption of surfactants on a heterogeneous surface has a complex influence on wetting, because adsorption on hydrophilic regions makes the surface hydrophobic and increases the solid–aqueous solution interfacial energy (σ_{SL}), whereas adsorption on hydrophobic regions adds to the hydrophilicity of the surface and decreases σ_{SL}. Proceeding from the measured contact angles and the solution–air interfacial tension (σ_{LG}), we can use the Young relationship (2) to suggest the direction in which σ_{SL} will change:

$$\sigma_{LG}\cos\theta = \sigma_{SG} - \sigma_{SL}. \qquad (2)$$

Table 2 lists the values of the product ($\sigma_{LG}\cos\theta$) for the TDTAB concentration c equal to 10^{-5} mol/L (the smallest concentration studied), 10^{-3} mol/L (the concentration corresponding to the maximum contact angles for wetting of unmodified glass), and 5×10^{-3} mol/L (close
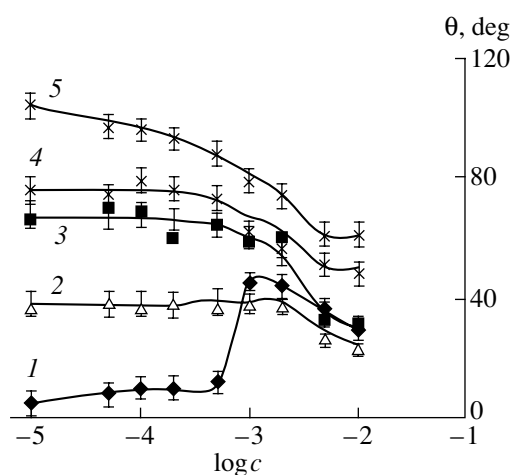

Fig. 2. Wetting of (*1*) glass, (*5*) hydrophobic glass, and (*2–4*) heterogeneous surfaces with the hydrophobic fraction equal to (*2*) 0.20, (*3*) 0.46, (*4*) 0.60 by solutions of TDTAB in air (*c*, mol/L).

Table 2. Worksheet for the calculation of the product $(\sigma_{LG}\cos\theta)$ for wetting of solid surfaces by TDTAB solutions

c, mol/L	$(\sigma_{LG}\cos\theta)$, mJ/m^2				
	glass	$X = 0.20$	$X = 0.46$	$X = 0.60$	hydrophobic glass
10^{-5}	72	57	29	17	-17
10^{-3}	39	43	30	22	11
5×10^{-3}	30	32	31	31	18

to the CMC). As c varies from 10^{-5} mol/L to the CMC, $(\sigma_{LG}\cos\theta)$ decreases for glass and heterogeneous surfaces with the hydrophobic surface mole fraction X equal to 0.20. For a surface with $X = 0.46$, $(\sigma_{LG}\cos\theta)$ remains constant, whereas for a surface with $X = 0.60$ and hydrophobic glass, $(\sigma_{LG}\cos\theta)$ increases. σ_{SG} either decreases or remains unchanged during wetting; therefore, the difference $(\sigma_{SG} - \sigma_{SL})$ can rise only when σ_{SL} decreases. From this, we can infer that TDTAB is adsorbed on these regions of supports with high hydrophobic fractions. The difference $(\sigma_{SG} - \sigma_{SL})$ decreases in response to either a decrease in σ_{SG} or an increase in σ_{SL}. These changes in the surface energy are observed in cases where TDTAB is preferentially adsorbed on hydrophilic regions. Thus, for small hydrophobic surface fractions X, surfactants are adsorbed on hydrophilic regions, and for large X values, on hydrophobic ones. Apparently, adsorption on hydrophilic regions, whose interaction energy is close to chemisorption [10], is preferable to physisorption on nonpolar regions.

When drops of aqueous solutions of TDTAB are applied to solid surfaces in p-xylene rather than in air, it is first necessary to gain data on TDTAB distribution in the water–p-xylene system. The distribution of surfactants in this two-phase system was studied by the scintillating phase method [13, 14]. It was found that the TDTAB distribution coefficient in the two-phase system for TDTAB concentrations lower than the CMC ($K_{OW} = c_O/c_W = 1.8 \times 10^{-3}$, where c_O and c_W are the TDTAB concentrations in organic and water phases, respectively). Micellation in an aqueous solution decreases the tendency of surfactants toward transfer to the organic phase, and K_{OW} decreases about twofold. This small K_{OW} value means that the test compound prefers to concentrate in the aqueous phase; its concentration in the organic phase is low. Therefore, the mass transfer of surfactants from the aqueous to organic phase and subsequent adsorption on the solid surface can be ignored; i.e., it can be taken that the solid–p-xylene interfacial energy does not change upon addition of a surfactant to an aqueous solution.

When drops of TDTAB solutions are applied to glass immersed in p-xylene, contact angles increase in the same concentration range as in air (Fig. 3, curve 1). In the case of selective wetting, however, contact angles change more sharply, from wetting to nonwetting. As the TDTAB concentration rises, the contact angles

remain greater than 90 deg, rather than decreasing as in air.

When applied to hydrophobic glass immersed into p-xylene, TDTAB drops roll across the surface without sticking to it, regardless of the solution concentration. The drops deformed with rising surfactant concentration; their shapes differed strongly from a spherical segment (Fig. 4). Macroscopic contact angles decrease only insignificantly with rising TDTAB concentration (Fig. 3, curve 5). However, autoradiography [14] does not show TDTAB traces on hydrophobic glass in the case of selective wetting. Therefore, we can infer that a stable film is conserved between a drop and a hydrophobic surface, keeping the drop of an aqueous solution of the surfactant from contact with the surface. This p-xylene film on the hydrophobic glass surface is stable; it is not destroyed on the approach of drops of water or aqueous solutions of surfactants. Low interfacial tensions are characteristic of the hydrophobic glass–p-xylene interface, and the replacement of this interface by the hydrophobic glass–aqueous surfactant solution interface is thermodynamically unprofitable, leading to a rise in the interfacial energy.

Changes in the product $\sigma_{L1L2}\cos\theta_{12} = \sigma_{SL1} - \sigma_{SL2}$ (where L1 stands for p-xylene and L2 for aqueous solution) were calculated for the selective wetting of heterogeneous surfaces (Table 3). A decrease in $(\sigma_{L1L2}\cos\theta_{12})$ is possible when σ_{SL2} increases. A rise in
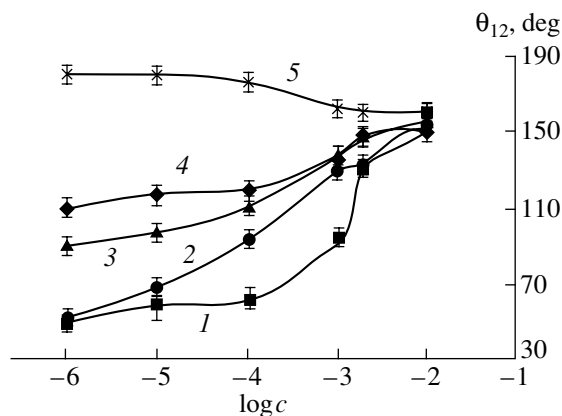
Fig. 3. Wetting of (1) glass, (5) hydrophobic glass, and (2–4) heterogeneous surfaces with the hydrophobic fraction equal to (2) 0.20, (3) 0.46, (4) 0.60 by solutions of TDTAB in p-xylene (c, mol/L).
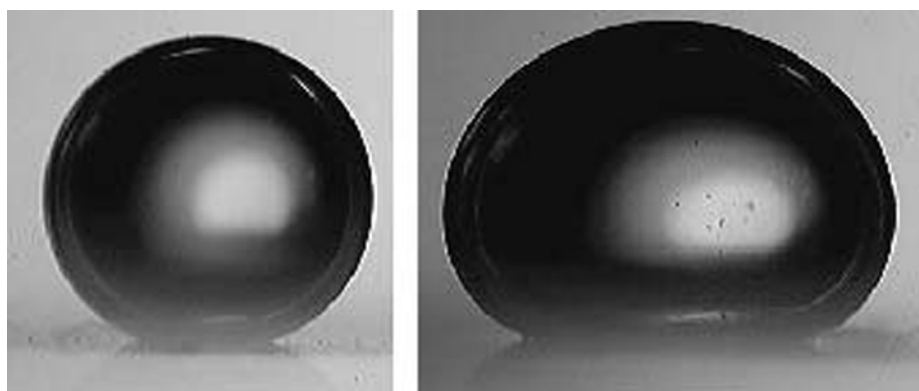
Fig. 4. Micrographs of drops of TDTAB solutions with concentrations equal to (a) 1×10^{-4} mol/L and (b) 1×10^{-2} mol/L on hydrophobic glass plates in p-xylene.
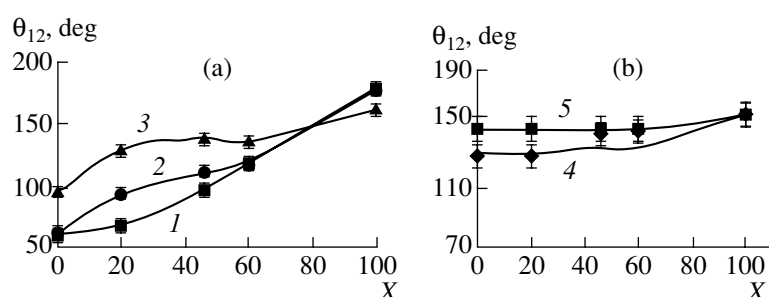

Fig. 5. Contact angles in the TDTAB solution drop–p-xylene–solid surface system vs. The hydrophobic fraction of the solid surface. TDTAB concentration c, mol/L: (1) 10^{-5}, (2) 10^{-4}, (3) 10^{-3}, (4) 5×10^{-3}, and (5) 10^{-2}.

σ_{SL2} is possible as a result of the adsorption of TDTAB on the hydrophilic regions of the heterogeneous surface. This rise occurs on glass or a heterogeneous surface when X is 0.20 or 0.46 (for the latter, the rise is insignificant). For the support with $X = 0.60$, σ_{SL2} decreases as a result of the adsorption of TDTAB on the hydrophobic regions of the solid surface. In general, these tendencies match the results obtained from the study of wetting of relevant plates in air, although there is some quantitative distinction between the forms of the wetting isotherms in Figs. 2 and 3. Although the θ angles in air decrease whereas the preferential wetting angles θ_{12} increase, the products ($\sigma_{LG}\cos\theta$) (for selective wetting, $\sigma_{L1L2}\cos\theta_{12}$) change in the same direction with rising TDTAB concentration. This is due to the fact that σ_{L1L2} decreases more abruptly (approximately

Table 3. Worksheet for the calculation of the product ($\sigma_{L1L2}\cos\theta_{12}$) for wetting of solid surfaces by TDTAB solutions

c, mol/L	($\sigma_{L1L2}\cos\theta_{12}$), mJ/m^2			
	glass	$X = 0.20$	$X = 0.46$	$X = 0.60$
10^{-5}	19	18	0	−10
5×10^{-3}	−3	−3	−3	−3

eightfold) than σ_{LG} (less than twofold) with increasing surfactant concentration. Thus, the trend of wetting isotherms for heterogeneous surfaces in the pre-CMC concentration region in air is explained by the same tendencies of TDTAB adsorption on solid surfaces as for selective wetting.

At a fixed TDTAB concentration in the solution, the contact angles of selective wetting rise with increasing hydrophobic surface fraction of the solid (Fig. 5a). However, this tendency is only observed for pre-CMC surfactant concentrations. For post-CMC concentrations, θ_{12} is virtually independent of the hydrophobic surface fraction and is roughly the same on glass, heterogeneous surfaces, and fully hydrophobic glass (Fig. 5b). This range of TDTAB concentrations corresponds to very low interfacial tensions (Fig. 1b); the drop shapes strongly differ from a sphere and close to that shown in Fig. 4b. The drop shape on a support is virtually independent of the hydrophobicity of the support. We can assume that post-CMC surfactant concentrations noticeably stabilize the p-xylene film, which keeps the drop from contact with the solid surface. The stability of the film can be due to an intermediate microemulsion phase that is formed near the aqueous solution–p-xylene interface and stabilizes the liquid–liquid interface. We considered the possibility of the

existence of such a phase earlier in analyzing data on TDTAB adsorption at water–*p*-xylene interfaces obtained using the scintillating phase method and data on aqueous TDTAB solutions in contact with *p*-xylene obtained using spectrophotometry and photon-correlation spectroscopy [13, 14].

CONCLUSIONS

Comparison of the wetting of heterogeneous surfaces in air and under selective wetting conditions elucidates the dual role of surfactants. The role of surfactants as regulators of surface tension is dominant in wetting of heterogeneous substrates in air and under selective wetting conditions for pre-CMC surfactant concentrations. In this concentration region, the trend of the wetting isotherms is due to the adsorption of surfactant at the aqueous solution–air interface (for selective wetting, the solution–*p*-xylene interface) and the aqueous solution–solid interface. The observed wetting isotherms are the result of the change in the solid–aqueous solution interfacial energy caused by the adsorption of a surfactant (the increase for glass and supports with low hydrophobic surface fractions and the decrease for hydrophobic glass and supports with high hydrophobic surface fractions). When TDTAB concentrations are higher than the CMC under selective wetting conditions, surfactants act as stabilizers of wetting films. In the post-CMC region, the contact angles are nearly independent of the nature of the support, because a stable surfactant-stabilized *p*-xylene film is retained in a drop between the solid surface and the solution.

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