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Adsorption of Nonionic Surfactant Triton X-100 on Solids from Aqueous and Nonaqueous Solutions

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Abstract—The adsorption of nonionic surfactant Triton X-100 on quartz sand and methylated quartz sand from water and toluene was investigated by means of spectrophotometry, the radiotracer technique, and wetting angle measurements.

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The adsorption of surfactants on solid–solution interfaces is an important problem. Were it solved, one would be able to govern the properties of solid surfaces and the interaction of dispersed particles and to control wetting (in air and under selective conditions), the stability of disperse systems, and other properties. Surfactant adsorption is widely used in cleansing, flotation, corrosion inhibition, lubrication, dispersion of solids, oil production, and other fields of technology. The adsorption specifics depend on the nature of the surfactant, properties of the solid surface, composition and concentration of the solution, the nature of the solvent, and other factors [1]. In this work, we consider the adsorption of a nonionic surfactant on different solid surfaces from aqueous and nonaqueous solutions.

SUBJECTS AND METHODS

The surfactant used was *tert*-octylphenyl decaethyleneglycol ester (Triton X-100 or TX-100). This surfactant is well soluble in both water and hydrocarbons (especially in aromatic hydrocarbons) owing to its structure [2]. Therefore, the nonaqueous solvent used was toluene. The concentration c of TX-100 (from Merck) in water or toluene was varied from 10^{-5} to 10^{-3} mol/l. Distilled water (with an electrical conductivity of $\chi = 1 \times 10^{-5}$ Ω/cm) and toluene (analytical grade, Russia) were used in the experiments.

The surface tension σ of aqueous TX-100 solutions was determined by the maximal air bubble pressure technique (Fig. 1). The critical micelle concentration (CMC) found from the break in the surface tension isotherm is 2×10^{-4} mol/l, which matches the related literature [2–4]. The Gibbs and Langmuir equations were used to calculate the adsorption at the solution–air interface. The maximal adsorption is 3.5×10^{-6} mol/m^2; the surface area per molecule in the saturated layer is $S_1 = 0.48$ nm^2. Various authors report a value of $S_1 = 0.52–0.55$ nm^2 [5, 6], which matches our value.

The surface tension of toluene solutions of TX-100 were determined by the capillary rise technique in glass capillaries. The value obtained for the surface tension (27.6 mN/m) coincides with the literature data (26.8–28.4 mN/m [2, 7, 8]. TX-100 practically does not effect the surface tension of toluene (Fig. 1).

The solid surfaces used were quartz sand from Aldrich with a specific surface of $S_{sp} = 0.03$ m^2/g and hydrophobic quartz sand. The sand was made hydrophobic in a chloroform solution of dimethyldichlorosilane as follows. The quartz sand was boiled in distilled water, dried in air, and then exposed to a 1% solution of dimethyldichlorosilane in chloroform for 24 h. After this, the hydrophobizing solution was removed, the sand was washed with chloroform several times and air-dried. Sand hydrophobicity was monitored by water absorption. In addition, quartz and hydrophobic glass

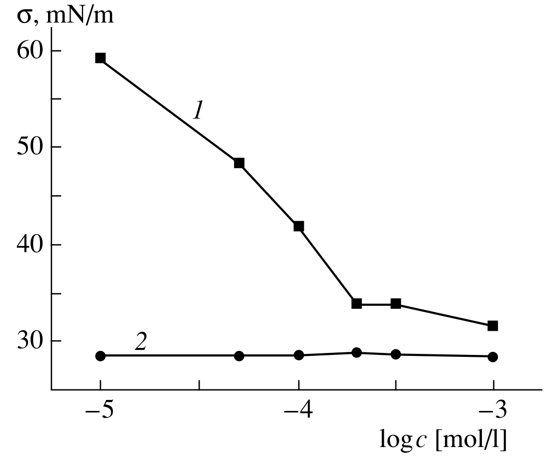

Fig. 1. Surface tension isotherms for solutions of TX-100 in (*1*) water and (*2*) toluene.

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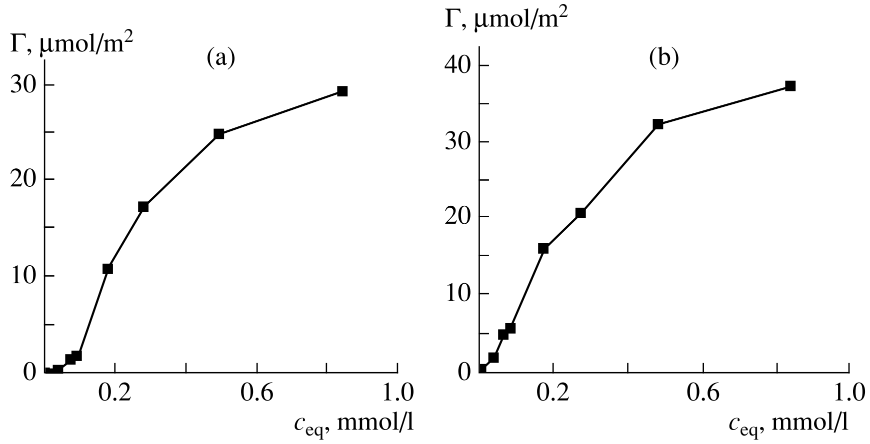

Fig. 2. TX-100 adsorption isotherms from aqueous solutions onto (a) quartz sand and (b) hydrophobic quartz sand.

plates were used in the experiment. Glass plates were made hydrophobic as follows: they were exposed to dimethyldichlorosilane vapor for 24 h, then washed with chloroform and air-dried. The water wetting angle at hydrophobic plates was 103°. The water wetting angle at cleansed quartz plates (which were cleansed with bichromate and then boiled three times with distilled water) was 8°.

The TX-100 adsorption uptake on quartz sand and modified quartz sand from aqueous solutions was determined spectrophotometrically as the decrease in the surfactant concentration in the solution:

$$\Gamma = \frac{(c_0 - c_{eq})V}{mS_{sp}}. \qquad (1)$$

Here, V is the volume from which adsorption was carried out, m is the adsorbent weight, and c_0 and c_{eq} are the initial and equilibrium concentrations, respectively. The TX-100 concentration was determined as the absorbance at 275 nm on an Agilent 845 spectrophotometer (Agilent Technologies). All measurements were carried out using standard quartz cells with an optical path length of 1 cm. The adsorption experiments were carried out as follows. A quartz sand aliquot was placed into a flask filled with a TX-100 solution, shaken for 10 min, and allowed to stand for a long period for adsorption equilibrium to be acquired. After adsorption, the spectra of the solution were measured, the equilibrium concentration was determined, and the uptake was calculated from Eq. (1). A constant value of the equilibrium concentration was acquired after 24 h of contact between the adsorbent and solution.

The TX-100 adsorption from toluene was studied using a radiotracer. TX-100 was labeled with tritium using the thermal activation method [9–11]. After thin-layer chromatography, the radiochemical purity of TX-100 was 98% and its specific radioactivity was 0.10 TBq/g. The adsorption experiment was carried out as follows. An aliquot (1.2 ml) of a toluene solution of unlabelled TX-100 was placed to a reaction tube, a solution of ^{3}H-TX-100 (50 μl) of a known concentration was added, and the radioactivity of the resulting solution was measured on a Rack Beta 1215 (LKB-Wallac, Finland) liquid scintillation spectrometer. Then, the adsorbent was placed into the solution; the tube was plugged and weighed (for monitoring of toluene evaporation), shaken, and allowed to stand for 24 h. After 24 h elapsed, the tube was centrifuged and an aliquot of the solution equilibrated with the adsorbent was sampled for radioactivity measurements. The uptake was calculated from

$$\Gamma = c_0(a_0 - a_{eq})V/A_{sp}vmS_{sp}, \qquad (2)$$

Here, a_0 and a_{eq} are, respectively, the radioactivities of the volume aliquots (v) before the adsorption experiment and in equilibrium with the adsorbent, Bq; and A_{sp} is the specific bulk radioactivity of the solution, Bq/l. The mean error of uptake determinations from two or three replicate measurements is strongly affected by the concentration of the starting solution: it increases with increasing concentration from 5 to 30%. The tube with the solution and adsorbent was weighed during the experiment to monitor possible toluene evaporation. The solution on the average lost 1.3% of its weight in 24 h, which was taken into account in uptake determination.

Wetting angles were measured in order to analyze the solid surface after the adsorption of the surfactant. Quartz and hydrophobic glass plates were kept in a TX-100 solution for 1 h and then air-dried. Water wetting angles at the modified surfaces were measured using a horizontal microscope equipped with a goniometer; the measurement accuracy was 1°.

RESULTS AND DISCUSSION

The uptake isotherm for TX-100 adsorption on quartz from aqueous solutions (Fig. 2) shows that as the surfactant concentration in the solution increases to

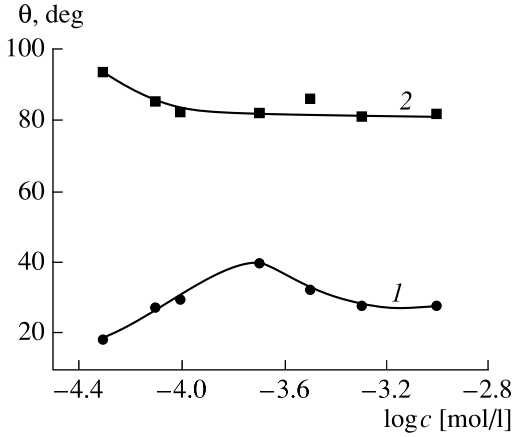

Fig. 3. Water wetting angles at (*1*) quartz and (*2*) hydrophobic glass plates modified in aqueous solutions of TX-100.

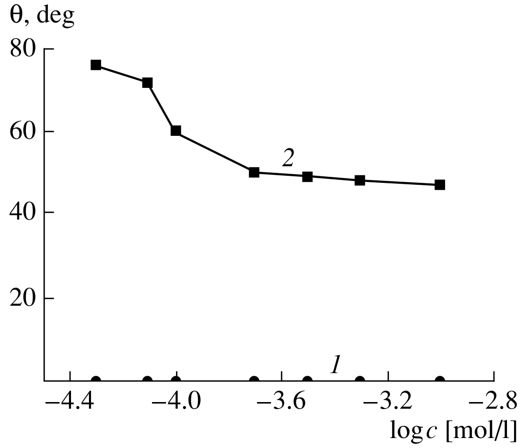

Fig. 4. Outflow wetting angles of aqueous solutions of TX-100 at (*1*) quartz and (*2*) hydrophobic glass.

reach the CMC, the uptake increases to reach a value of 2.5×10^{-6} mol/m^2 at the CMC, then it abruptly increases as a result of the adsorption of aggregates. Comparing these results with the maximal adsorption at the solution–air interface (3.5×10^{-6} mol/m^2), we see that up to the CMC, the adsorption is within the monolayer coverage. The water wetting angles at the quartz plates modified in aqueous solutions of TX-100 first increase with increasing concentration of the modifying solution to reach 40° at the CMC (Fig. 3). The use of the Cassie and Baxter equation [12] to calculate the proportion of the hydrophobic regions on the modified surface shows that for this value of the water wetting angle (40°), the proportion of the hydrophobic regions is 19%. Therefore, after the near-monolayer coverage is reached, the adsorbate layer is quite mosaic. The significant percentage of the regions (81%) corresponds to good wetting. These are either unmodified quartz regions or regions in which surfactant molecules are oriented by their polar groups toward water. The TX-100 molecules oriented by their hydrocarbon chains toward the solution constitute 19% of the regions. A further increase in the concentration of the modifying solution induces a slight decrease in the wetting angles.

On hydrophobic sand, the adsorption is higher than on unmodified sand: the value corresponding to the maximal adsorption at the solution–air interface is reached at 8×10^{-5} mol/l, a concentration far lower than the CMC (Fig. 2). Presumably, surface aggregation on the hydrophobic surface is more intense than on the hydrophilic surface: aggregates are formed on the surface at lower concentrations than in the bulk [13, 14]. At higher surfactant concentrations in the solution, the uptakes on methylated sand are also slightly higher than on unmodified sand. The higher adsorption activity of TX-100 at the interface between the solution and methylated quartz sand is due to the higher starting interfacial tension at the solid–water interface and the more favorable orientation of TX-100 molecules in the adsorbate layer.

When hydrophobic quartz plates are modified in aqueous solutions of TX-100, their surface becomes slightly hydrophilic: the water wetting angle θ changes from 103° to 80°. This decrease in the wetting angle corresponds with the appearance of 33% hydrophilic regions on the surface.

It is not always adequate to match the adsorption from solutions with the wetting of modified plates: if the adsorbate layer is weakly bound to the surface, some molecules leave the adsorbate layer when the plate is taken out of the solution. In addition, a water drop can cause surfactant molecules to desorb from the adsorbate layer to an aqueous solution in order for equilibrium between the adsorbate layer and solution to be acquired. These processes complicate data processing. A more careful effect on the adsorbate layer in the solution is caused by an air bubble brought to plates in the solution; this means that outflow wetting angles are measured (Fig. 4). For quartz, these angles are zero, indicating the formation of a strong wetting film of an aqueous solution of TX-100 on the quartz surface; this film does not break when an air bubble is brought to it. For methylated glass, the $\theta(c)$ plot is analogous to the surface tension isotherm $\sigma(c)$. In the pre-CMC region, the angles decrease because of the decrease in σ_{lg} and σ_{sl} (σ_{lg} and σ_{sl} are the surface tension at the liquid–gas and solid–liquid interface, respectively). The angles and σ_{lg} do not change after reaching the CMC; therefore, σ_{sl} also should not change. However, the uptake increases even after reaching the CMC. Therefore, we can suggest that the hydrophobicity of the adsorbate later does not change noticeably during adsorption.

To study the adsorption of TX-100 from toluene, we used compounds labeled with tritium tracer. Previously [10, 11], we employed an analogous procedure to study the adsorption of surfactant mixtures on various adsorbents from aqueous solutions.

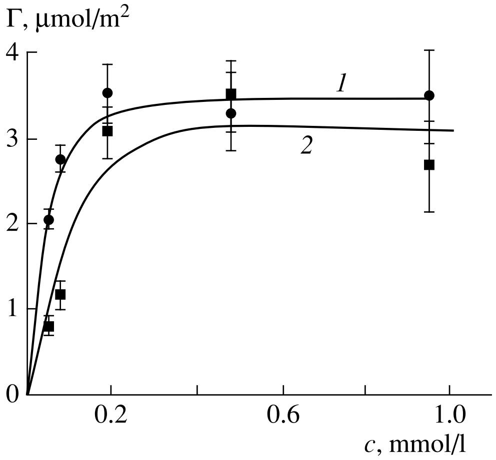

Fig. 5. Uptake isotherms for TX-100 adsorption from toluene onto (*1*) quartz sand and (*2*) hydrophobic quartz sand.

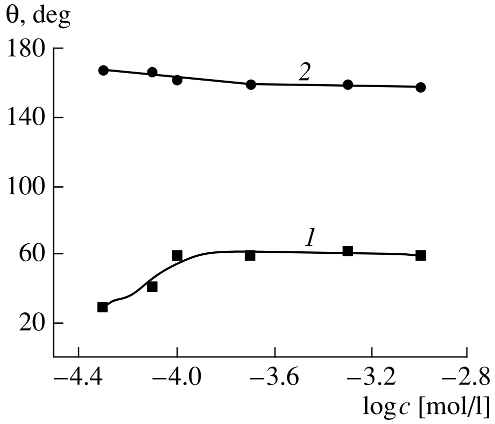

Fig. 6. Water wetting angles at (*1*) quartz and (*2*) hydrophobic glass plates modified in toluene solutions of TX-100.

For quartz sand and hydrophobic quartz sand, Langmuir isotherms are obtained: the uptake increases with increasing TX-100 concentration from 0 to 2×10^{-4} mol/l; then, a plateau occurs (Fig. 5). Fitting the isotherm by the Langmuir equation yields the following values of the maximal adsorption: 4.0×10^{-6} and 3.2×10^{-6} mol/m² for quartz sand (S_1 = 0.41 nm²) and hydrophobic quartz sand (S_1 = 0.52 nm²), respectively. Within the error, these values are close to the maximal adsorption at the solution–air interface. The relatively low uptakes from toluene solutions (compared to aqueous solutions) provide circumstantial evidence that the abrupt rise in adsorption from aqueous solutions is on account of the adsorption of surfactant aggregates. In toluene solutions, there are no aggregates (or they are very small), and individual molecules are adsorbed until the surface coverage is full.

We used the wetting method to determine the orientation of TX-100 molecules in adsorbate layers. However, the modifying of quartz and methylated plates with a toluene solution of TX-100 does not noticeably change the water wetting angles at the modified plates. Therefore, for these systems, the orientation of surfactant molecules in the adsorbate layer was determined by measuring the wetting angles of water drops at plates placed in a toluene solution of TX-100; i.e., these were selective wetting angles (the angles were measured toward the aqueous phase). The rise in the angles in this case, as in air, is due to the hydrophobicity of the solid surface, i.e., due to the adsorption of the surfactant with its polar groups directed toward the aqueous phase. The decrease in the wetting angles is due to the hydrophylicity of the solid surface, i.e., due to the adsorption with the polar groups directed toward the aqueous phase. At quartz plates, the wetting angles increase; this means the hydrophobization of the surface (Fig. 6). The TX-100 molecules in the adsorbate layer at the quartz–toluene interface are oriented so that their hydrocarbon tails are directed toward toluene, precisely as follows from the polarity leveling rule. At hydrophobic plates, the angles decrease by a very small value (from 167° to 158°); this means that there is no noticeable hydrophilization during adsorption. We can infer that when TX-100 is adsorbed on a hydrophobic surface from toluene, its molecules are oriented with their tails facing the solution. Likely, the adsorption occurs at the silanol groups of quartz sand that have not reacted with dimethyldichlorosilane.

In summary, the investigation of TX-100 adsorption from water and toluene shows that the uptake from water solution is higher on account of the adsorption of aggregates. The uptake on hydrophobic quartz sand is higher than on unmodified sand. From toluene, individual TX-100 molecules are adsorbed until a monolayer coverage is achieved, i.e., until the adsorption approaches the adsorption at the solution-air interface. The adsorptivity of TX-100 relative to the toluene–quartz interface is slightly higher than relative to the toluene–hydrophobic quartz interface. From the selective wetting angle data, we can infer that when TX-100 is absorbed from toluene, its molecules are oriented by their polar groups toward the solid surface regardless of the nature of this surface.

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