

Distribution Features of Triton-X100, a Nonionic Surfactant, in the Quartz–Water–Cyclohexane System during Preferential Wetting

Yu. G. Bogdanova, G. A. Badun, N. I. Ivanova, V. I. Korobkov,
Z. A. Tyasto, and M. G. Chernysheva

Colloidal Chemistry and Radiochemistry Departments
e-mail: bogd@colloid.chem.msu.ru

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Abstract—The distribution of TX-100, a nonionic surfactant, over solid surfaces in cyclohexane (CH), with quartz being preferentially wetted by aqueous solutions of TX-100, is studied using radioactive labels and wetting. From low-concentration solutions, the surfactant is adsorbed from the aqueous phase on the quartz surface preferentially near the three-phase contact line. At higher TX-100 concentrations, adsorption on the solid surface occurs from both liquid phases. The TX-100 distribution on quartz influences the kinetics of acquisition of the contact angle of preferential wetting.

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The distribution of surfactants in solid–polar liquid(1)–nonpolar liquid(2) systems is of fundamental importance for understanding the kinetics and mechanisms of preferential wetting, which is of paramount significance for solving many applied problems.

The adsorption of a surfactant at liquid(1)–liquid(2), solid–liquid(1), and solid–liquid(2) interfaces plays the key role in establishing the equilibrium contact angle under preferential wetting conditions. The adsorption of a surfactant at the solid–liquid(1) and solid–liquid(2) interfaces is much influenced by the distribution of the surfactant between the two liquid phases, because the surfactant can be adsorbed both from the bulk of the drop and the surrounding liquid(2). The influence of the adsorbate surfactant layers on the contact angle of preferential wetting can be different [1].

Thus, for analyzing preferential wetting data, it is important to know the distribution of a surfactant between two liquid phases and the structure of adsorbate surfactant layers on the solid.

The distribution of surfactants in a water–organic solvent system under preferential wetting conditions is of particular importance. The specifics of such experiments are associated with the different volumes of the two liquid phases and the monitoring of the redistribution of small surfactant amounts between these liquids. The radioactive label technique is very efficient for such studies [2, 3]. This technique detects extremely low concentrations of surfactants in liquids using liquid scintillation (LS) spectrometry. The sampling of very small aliquots makes it possible to study the kinetics of surfactant transfer during the redistribution in water–organic liquid systems for long periods of time [3].

Autoradiography (ARG) is a very informative method for studying the structure of adsorbate surfactant layers. Autoradiography involves the photographic recording of the ionizing radiation of a radioactive label aspirated to the test sample. The darkening intensity of autoradiograms bears information not only about the substance amount adsorbed on the solid surface but also on the distribution of the surfactant over this surface [4].

This work studies the distribution of Triton X-100 (TX-100), a nonionic surfactant, in the quartz–water–cyclohexane system as a function of the surfactant concentration in the aqueous phase and the contact time between the aqueous drop and the quartz surface immersed in cyclohexane (CH). Tritium was used as the radioactive label [2]. The radiochemical purity of tritium-labeled TX-100 (pure for analysis grade, from Merck) was 96%. The amount of TX-100 transferred from an aqueous drop to cyclohexane was monitored by liquid scintillation counting (the scintillating phase method [2]). The TX-100 concentration in cyclohexane was calculated from

$$c_0 = a/(VA_{sp}), \quad (1)$$

where a and V are, respectively, the radioactivity (dpm) and volume of the sample; and $A_{sp} = 2.8$ Ci/mol is the specific radioactivity of TX-100. The error in concentrations was no more than 10%.

The distribution of TX-100 over the quartz surface was evaluated visually as the darkening intensity of autoradiograms. The photodetector used was Retina XBM radiographic film with a sensitivity of 1300 R^{-1} . Predistilled cyclohexane (chemically pure grade) and

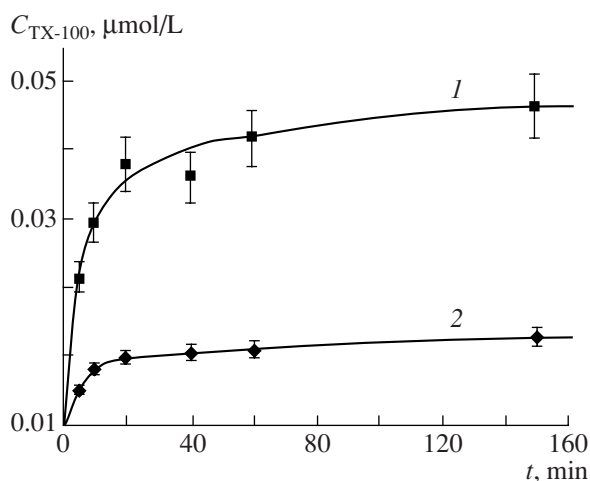


Fig. 1. TX-100 concentration in CH vs. contact time between drops of an aqueous solution of TX-100 with concentrations of equal to (1) 2.5 and (2) 10 $\mu\text{mol/L}$ and cyclohexane.

bidistilled water with the specific electrical conductivity $\chi = 5.5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ were used in the work.

Before an experiment, the liquids were mutually saturated at 20°C for 20 days, because the solubility of water in CH is $1.48 \times 10^{-2} \text{mol/kg}$ (25°C) and that of CH in water is $1.19 \times 10^{-3} \text{mol/kg}$ [6].

Quartz plates were cleaned by consecutive boiling with sulfochromic acid (10 min) and distilled water ($3 \times 20 \text{ min}$). Samples with the inflow wetting angles of water $\theta_a \leq 5^\circ$ and outflow wetting angles $\theta_r = 0^\circ$ [7] were chosen for experiments.

An experiment was carried out as follows. First, a quartz plate was exposed to CH ($V = 5 \text{ mL}$) for 30 min; then, a drop (with a volume of 10–15 μL) of an aqueous solution of TX-100 was applied to the quartz surface; CH was carefully removed from the cell; an aliquot ($V = 1 \text{ mL}$) was sampled to determine the TX-100 amount transferred from the aqueous solution drop to HC using LS spectrometry. Then, the drop was removed from the surface and the plate was taken from the cell. After drying, plates were placed into a closed chamber equipped with a photodetector for imaging. The exposure time (in contact of quartz plates with the photodetector) was 30 days. All experiments were carried out at 20°C.

The distribution of TX-100 in the quartz–water–CH system was studied at various TX-100 concentrations in water and various contact times between a drop of an aqueous TX-100 solution and the quartz surface. The TX-100 concentration in water was 2.5×10^{-6} , 10^{-5} , and $4 \times 10^{-4} \text{mol/L}$. The critical micelle concentration (CMC) for TX-100 in aqueous solutions and CH is 2.4×10^{-4} and $1 \times 10^{-5} \text{mol/L}$, respectively [8]. The contact time between an aqueous solution drop and the quartz surface was 5, 20, or 40 min or 21 h. These contact times were chosen for the following reasons:

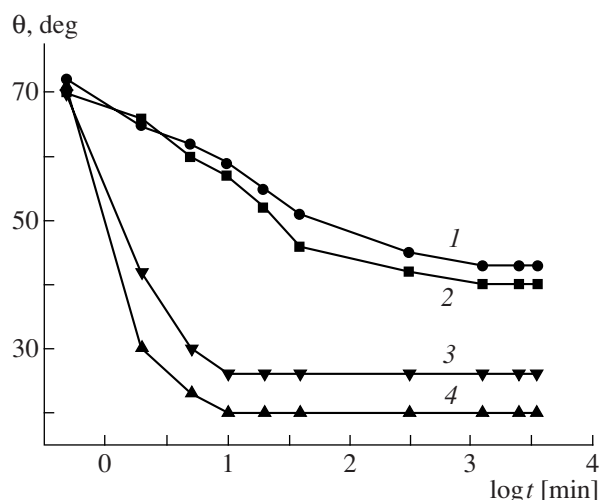


Fig. 2. Contact angle for the preferential wetting of quartz by aqueous solutions of TX-100 with concentrations (mol/L) of (1) 10^{-5} , (2) 4×10^{-4} , (3) 2.6×10^{-6} and by water (4) in cyclohexane vs. time.

(1) the redistribution of TX-100 in the water ($V = 10\text{--}20 \mu\text{L}$)–CH ($V = 3 \text{ mL}$) system occurred within 40 min (Fig. 1) [2];

(2) an equilibrium value of the contact angle in the quartz–water–CH system is acquired within 21 h (Fig. 2).

From [9], we know that oxyethylated surfactants are adsorbed on polar surfaces from aqueous solutions via hydrogen bonding between the solid surface and the oxyethyl groups of the surfactant:



The adsorption of TX on quartz involves three consecutive stages [10] (Fig. 3). At the first stage (for $c < c_{\text{CMC}}$), adsorption is low and increases slowly; at $c \approx 0.5 \text{ CMC}$, adsorption increases abruptly; and at $c \approx c_{\text{CMC}}$, it reaches a maximum value. Analyzing the variation of the outflow wetting angle θ_r (with an air bubble supplied to the quartz surface immersed in a TX-100 solution) as a function of TX-100 concentration (Fig. 4), we suggested that the first stage involves the adsorption of individual TX-100 molecules (which do not interact with one another). The quartz surface becomes more hydrophobic than the initial one because its hydrocarbon radicals are oriented into the bulk of the solution at a certain angle to the solid surface. As the TX-100 concentration increases further, the interactions between the hydrocarbon radicals of these adsorbate molecules and TX-100 molecules in the bulk of the solution become progressively important. The hydrophobic interactions between hydrocarbon radicals generate surfactant aggregates on the solid surface, with the polar groups of these aggregates oriented into the bulk of the solution, and make the surface hydrophilic, thus decreasing θ_r .

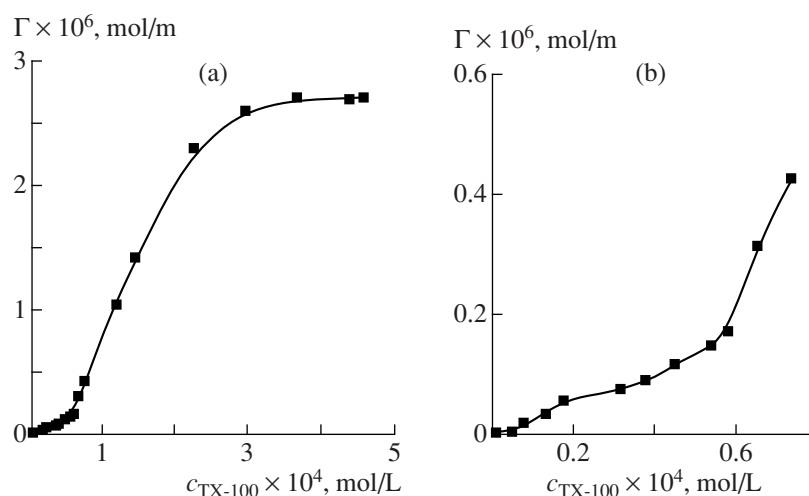


Fig. 3. Isotherms for TX-100 adsorption from aqueous solutions onto quartz.

The variations in the contact angle of wetting in the quartz–aqueous TX-100 solution–CH system is determined by the adsorption of the surfactant at various interfaces. Analyzing autoradiograms in combination with LS spectrometry data, we revealed the following features of formation of a TX-100 adsorbate layer on the quartz surface. From low-concentration solutions (containing 2.5×10^{-6} mol/L TX-100, the concentration producing a sparse surfactant monolayer on quartz; Fig. 3), TX-100 is adsorbed mainly along the wetting perimeter (Fig. 5). The surfactant concentration near the three-phase contact line (TCL) during wetting in air was earlier demonstrated by ARG [11] and observed in other systems [12].

As the contact time increases from 5 to 40 min, the amount of TX-100 adsorbed along the wetting perime-

ter remains virtually unchanged and only insignificantly increases over the entire wetted surface (Figs. 5a–5c). Importantly, TX-100 adsorption is not observed outside the drop, and the drop has clear-cut boundaries. With this pattern of surfactant distribution, the preferential wetting angle for an aqueous solution of TX-100 at quartz in CH rapidly acquires a constant value (Fig. 2).

When $c_{\text{TX-100}} = 10^{-5}$ mol/L, the adsorption on quartz increases abruptly (Fig. 6) and is accompanied by surfactant aggregation [9, 10]. The darkening intensity of the quartz surface in contact with the drop does not change with time (Figs. 6a–6c). This means that the formation of the surfactant adsorbate layer at the quartz–aqueous TX-100 solution interface ends within 5 min. However, TX-100 is distributed over the quartz surface and outside the drop with increasing experiment time, as proven by the uniform darkening of the quartz plate. This result is due to surfactant mass transfer from the water drop to CH and the adsorption of TX-100 from CH onto quartz. The boundaries of the wet surface area become vague, indicating the spread of TX-100 over the quartz surface in the form of a thin wetting film (Fig. 6c).

The tendency of TX-100 to transfer into CH and to subsequent adsorption on quartz is enhanced by increasing surfactant concentration in water. The surfactant is transferred to CH and adsorbs on quartz as early as 20 min after the drop of an aqueous TX-100 solution ($c = 4 \times 10^{-4}$ mol/L) was brought in contact with the quartz surface. This is proven by the noticeable darkening of the quartz surface area outside the drop. The darkening intensity rises with increasing contact time between the drop and quartz surface (Figs. 7a–7c).

After 21 h of contact between a drop of a TX-100 solution ($c = 4 \times 10^{-4}$ mol/L) with the quartz surface, the darkening intensity of autoradiograms increases (Figs. 7a–7c). The boundaries of the wetted surface

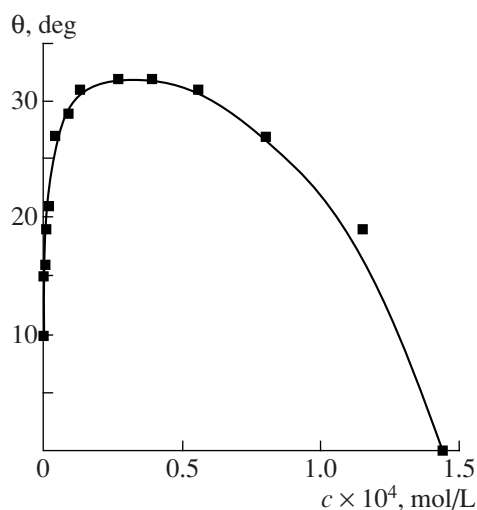


Fig. 4. Outflow wetting angles of aqueous solutions of TX-100 at quartz vs. surfactant concentration.

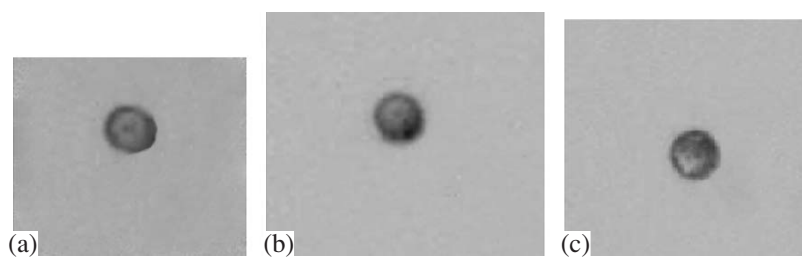


Fig. 5. Autoradiograms of quartz surfaces after contact with drops of TX-100 aqueous solutions ($c = 2.5 \times 10^{-6}$ mol/L). Contact time (min): (a) 5, (b) 20, and (c) 40. Drop volume: 10 μ L.

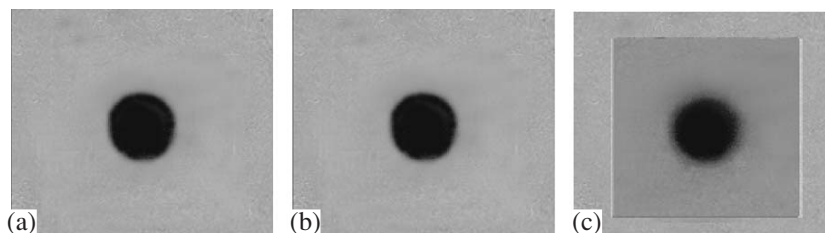


Fig. 6. Autoradiograms of quartz surfaces after contact with drops of aqueous solutions of TX-100 ($c = 1 \times 10^{-5}$ mol/L). Contact time (a) 5 min, (b) 20 min, and (c) 21 h. Drop volume: 15 μ L.

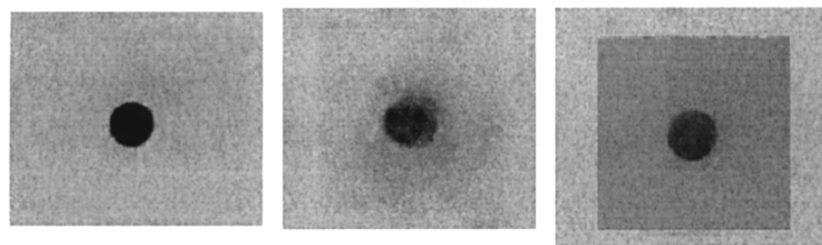


Fig. 7. Autoradiograms of quartz surfaces after contact with drops of aqueous solutions of TX-100 ($c = 4 \times 10^{-4}$ mol/L). Contact time (min): (a) 5, (b) 20, and (c) 40. Drop volume: 10 μ L.

area become more clear (Fig. 7c). Thus, the TX-100 distribution between a water drop, CH, and the solid surface changes as the contact time increases from 20 min to 21 h; TX-100 is transferred from the thin wetting film to CH and is adsorbed on quartz, being uniformly distributed over the surface.

Liquid scintillation spectrometry data verify ARG data. The table shows how the TX-100 concentration transferred from an aqueous solution drop to CH changes as a function of the contact time between the drop and the quartz surface immersed in CH. For drop volumes of 10–15 μ L, the TX-100 distribution coefficient in the water–CH system is $K_d = c_0/c_w = 0.008$ (where c_0 and c_w are TX-100 concentrations in CH and water, respectively) [3]. The TX-100 concentration in CH (with TX-100 adsorption at interfaces ignored) was calculated taking into account K_d .

The difference between the experimentally determined and calculated values of the TX-100 concentra-

tions in CH, with its initial concentration in the aqueous phase equal to 10^{-5} mol/L, drops strongly as the contact time between the phases involved in wetting increases. Analogous evolution is observed for the concentration equal to 4×10^{-4} mol/L ($c \approx 2\text{CMC}$).

The adsorption of TX-100 from CH on quartz causes the preferential wetting angle change with time. TX-100 molecules in this adsorbate layer will be oriented with their polar groups toward the quartz surface and their hydrocarbon groups toward the bulk of the nonpolar phase. As a result of surface hydrophobization outside the drop, the kinetics of acquisition of the contact angle of preferential wetting slows down (Fig. 2) and the quasi-equilibrium value ($\theta = 40\text{--}43^\circ$) becomes far higher than the initial contact angle of preferential wetting ($\theta = 20^\circ$). We should also note that the acquisition time of a constant value of the preferential wetting angle increases as the surfactant concentration c increases from 2.5×10^{-6} to 4×10^{-4} mol/L.

TX-100 concentration in cyclohexane as a function of contact time between an aqueous solution drop and the quartz surface immersed in cyclohexane (the error in concentration is 10%)

Starting TX-100 concentration in aqueous phase, mol/L	Volume of an aqueous solution drop	Contact time of drop with quartz surface, min	Measured TX-100 concentration in CH c, mol/L	TX-100 concentration in CH calculated from (1), mol/L
10^{-5}	15	5	1.2×10^{-10}	3×10^{-8}
	15	20	1.8×10^{-9}	
	15	40	9.0×10^{-9}	
	15	1440	2.0×10^{-8}	
4×10^{-4}	10	5	1.2×10^{-7}	8×10^{-7}
	10	20	2.1×10^{-7}	
	10	40	2.6×10^{-7}	
	10	1440	3.5×10^{-7}	

To summarize, our experimental results show that the acquisition of the contact angle of preferential wetting in the quartz–TX-100 aqueous solution–cyclohexane system is affected not only by the adsorption of the surfactant at various interfaces but also by the distribution of the surfactant between polar and nonpolar phases and the possibility of its adsorption from the nonpolar phase onto the solid surface.

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