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New technique based on the use of tritium labeled compounds for studying the adsorption of surfactant mixtures

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Adsorption of non-ionic-cationic surfactant mixtures at SiO_2/aqueous interface using tritium labeled compounds has been investigated.

The adsorption of surfactants from single-component solutions at solid/aqueous interfaces was studied in great detail. A variety of techniques were used for adsorption investigations *in situ*: ellipsometry, fluorimetry, small angle neutron scattering, atomic forth microscopy, calorimetry, reflectometry, quartz microbalance, wettability, *etc.*[1–8] Another group of methods deals with the estimation of surfactant depletion in solutions due to adsorption on solids with a high specific surface area.[9–12] Frequently, a combination of several methods is used for the investigation of surfactant mixture adsorption.[10–17] The great practical importance of this problem (for instance, in froth flotation, detergency, solids disruption, oil recovery *etc.*) and its poor theoretical understanding require the development of new techniques for the determination of adsorption and the composition of mixed adsorption layers.

Here we propose a new technique for the determination of surfactant mixture adsorption on solid/aqueous interfaces over a wide range of concentrations. Surfactants labeled with tritium were used for adsorption measurements. In solutions with ^3H-labeled surfactants, the concentration decreases due to adsorption, which can be calculated from the decrease of radioactivity because the solution radioactivity is proportional to surfactant concentration. The surfactant adsorption Γ at a solid/aqueous interface is

$$\Gamma = (C_0 - C_{eq})V/mS^* = C_0(a_0 - a_{eq})V/A^*vmS^*, \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentration, respectively; V is the solution volume, m is the mass of the adsorbent, S^* is the specific surface area of the adsorbent, a_0 and a_{eq} are sample radioactivities before adsorption and in equilibrium with the adsorbent, respectively, A^* is the specific radioactivity of solution, and v is the sample volume. The liquid scintillation counting method was used for tritium detection.[18]

The method developed was used for studying the adsorption of a mixture of ethoxylated octyl phenol Triton X-100 (TX-100) and tetradecyltrimethylammonium bromide (TTAB) on quartz sand ($S^* = 0.5$ m^2 g^{-1}). Critical micelle concentrations (CMCs) of TX-100 and TTAB were 2.0×10^{-4} and 4.0×10^{-3} mol dm^{-3}, respectively. Total concentration C_0 varied from 10^{-5} to 10^{-3} mol dm^{-3}. Mole fractions of TX-100 in mixture solutions were $\alpha = 0.2$, 0.5 and 0.8. The CMCs of mixtures with $\alpha = 0.2$, 0.5 and 0.8 were 7.0×10^{-4}, 2.5×10^{-4} and 2.0×10^{-4} mol dm^{-3}, respectively.

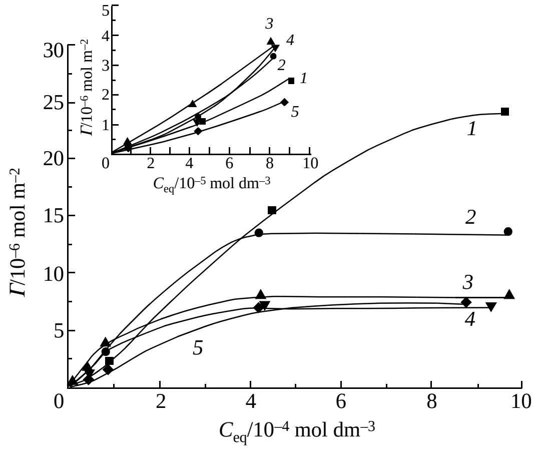

Figure 1 Adsorption of (*1*) TTAB and (*5*) TX-100 and the total adsorption of TTAB/TX-100 mixtures on quartz sand: (*2*) $\alpha = 0.2$, (*3*) $\alpha = 0.5$, (*4*) $\alpha = 0.8$.

To prepare surfactants labeled with tritium, the tritium thermal activation method was applied.[19] Under thermal activation, tritium molecules dissociate into atoms, which react with surfactant molecules. As a result, tritium replaces a part of hydrogen atoms in surfactant molecules accessible to a tritium attack. The purification of labeled compounds was performed by thin-layer chromatography and extraction. The radiochemical purity of labeled ^3H-TTAB and ^3H-TX-100 was 96%. Specific molar radioactivities of ^3H-TTAB and ^3H-TX-100 were 39 and 74 GBk mmol^{-1}, respectively. Labeled surfactants were mixed with non-labeled ones for the preparation of solutions with required concentrations and radioactivity. Specific radioactivity of initial ^3H-TTAB and ^3H-TX-100 solutions was $A^* = 44.5$ and 54.9 kBk ml^{-1}, respectively. Tritium was detected using a Rack Beta 1215 liquid scintillation spectrometer (LKB-Wallac, Finland).

For the estimation of adsorption on a SiO_2 surface for each component, in the first set of experiments, ^3H-TX-100 and non-labeled TTAB were used and in the second set, ^3H-TTAB and non-labeled TX-100 were used. The method developed is selective because adsorption data on only one component were obtained independently of the other surfactant. The error in adsorption estimations was 5%.

The adsorption isotherms of single TX-100 and TTAB, as well as the total adsorption isotherms of the surfactant mixtures are shown in Figure 1.

The adsorption isotherms of single-component TX-100 and TX-100/TTAB mixtures are of the Langmuir type (curves *2–5*, Figure 1). The adsorption reaches a plateau at a CMC. This suggests that the surfactant adsorption on a SiO_2 surface is determined by monomer adsorption. The TX-100 molecule cross-section area for single-component solution at a plateau concentration is 0.23 nm^2. This value is lower than the surface area per molecule in a saturated monolayer at a liquid/vapour interface (0.52 nm^2 according to ref. 9 and our data). The results obtained suggest that a polylayer adsorption of TX-100 occurs at a SiO_2/water interface at concentrations above CMC.

The adsorption of TTAB from single solution is sufficiently high because of significant interaction between the cationic surfactant and the negatively charged quartz surface (curve *1*, Figure 1). There is no plateau in the adsorption isotherm, perhaps, because the TTAB concentration is below CMC. A comparison of surface areas per molecule at SiO_2/water and water/vapour interfaces (0.33 nm^2 for a saturated monolayer at a water/vapour interface) allowed us to conclude that monolayer adsorption at a SiO_2/water interface is completed at $C_{eq} \approx 10^{-4}$ mol dm^{-3}. The sharp increase of adsorption values at $C_{eq} > 10^{-4}$ mol dm^{-3} may be attributed to the formation of big surface aggregates, admicelles. Such an increase of adsorption at the concentration region corresponding to transition from monolayer formation to surface clustering was observed.[15,16] Adsorption values of TX-100–TTAB mixtures demonstrate that, at $C_{eq} \approx 10^{-4}$ mol dm^{-3},

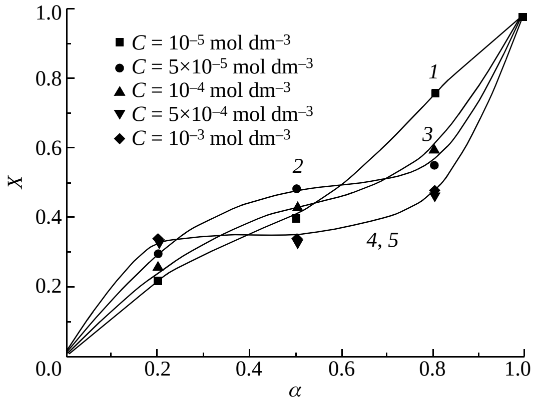

Figure 2 The relationship between the composition of mixed adsorption layers at a SiO_2/aqueous interface and the composition of solution.

the transition from monolayer formation to surface aggregation takes place.

A comparison of adsorption isotherms of single and mixed solutions indicates that TX-100 and TTAB exhibit a synergistic effect at $C_{eq} = 5\times10^{-5}$–10^{-4} mol dm^{-3} (the initial stage of adsorption isotherms is shown in the insert of Figure 1). The synergistic effect was attributed to interactions between the hydrocarbon chains of components in adsorption layers.[12,16,17] At high concentrations the synergistic effect disappears, as supposed, due to mixed micelle formation. At these concentrations, surfactant mixtures already contain micelles, but for pure TTAB it corresponds to monomer solution. The TTAB concentration in a monomer form in mixed solutions is lower (at the same C_{eq}) than that in single solution. Because the adsorption process is determined by monomer adsorption, the adsorption from mixed solutions must be lower than that calculated from additive contributions of individual components.

From adsorption data for each component individually and for total adsorption, the composition of mixed adsorption layers was determined. The dependence of TX-100 mole fraction (X) in a mixed adsorption layer at a SiO_2/water interface on TX-100 mole fraction (α) in solution is represented in Figure 2. There is no noticeable preference in adsorption of any component at $C_0 = 10^{-5}$ mol dm^{-3}, the compositions of solution and adsorption layer close to each other (curve *1*, Figure 2). We found that at low mole fraction of TX-100 in solution ($\alpha = 0.2$) the adsorption layers are enriched with TX-100. For high TX-100 mole fraction ($\alpha = 0.8$), the adsorption layers are enriched with TTAB. At $C_0 >$ CMC the adsorption layers of approximately constant composition are formed (curves *4* and *5*, Figure 2): the mole fraction of TX-100 $X = 0.36\pm0.03$. Probably, small additions of a component to the solution result in a sufficient enrichment of the adsorption layer with this component. Similar results were obtained, for example, for mixed micelle formation.[20,21]

Thus, a new technique for the investigation of mixed surfactant adsorption on solid/aqueous interfaces is presented. This technique is based on the application of tritium-labeled surfactants, total adsorption calculations and the estimation of adsorption layer composition from individual component adsorption data. This method can be used for studying the adsorption of different surfactant mixtures on various solids.

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