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Ionic surfactant adsorption at aqueous/organics interfaces determined by a scintillation phase method

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The results of scintillation phase experiments on the adsorption of ionic surfactants at aqueous/*p*-xylene and aqueous/octane interfaces were interpreted in respect to a radionuclide technique.

The adsorption of ionic surfactants at liquid/liquid interfaces is of industrial importance. Despite of growing interest in surfactants with saturated hydrocarbon chains, only a few methods are applicable to interfacial phenomena.[1–5] Previously, we found that the liquid scintillation spectrometry of tritium in a scintillation phase technique has a number of advantages.[6] It is irreplaceable in the investigation of compounds with a low surface activity at aqueous/organics interfaces, such as humic substances.[7] This method makes it possible to determine the adsorption of a compound from a mixture.[8]

Previously,[6] we described the behaviour of alkyltrimethylammonium bromides in the aqueous/*p*-xylene system. These compounds contribute to the formation of microemulsion phase of water in arenes at concentrations close to the critical micelle concentration (CMC). To explain the results, we conducted the experiment at low concentrations and used both aromatic and aliphatic hydrocarbons, namely, *p*-xylene and octane. Sodium dodecylsulfate (SDS, MP Biomedicals) and dodecyltrimethylammonium bromide (DTAB, Merck) were the test compounds (the CMCs are 8×10^{-3} and 14.5×10^{-3} mol dm^{-3}, respectively[9]).

Tritium-labeled surfactants were obtained by tritium thermal activation according to a published procedure[10] and purified using TLC. This purification technique provides the further radioactivity of the labeled product with tritium in CH bonds. The specific activities of the labeled products were about 160 GBq mol^{-1}, and the purity was $\geqslant 98\%$. To study the interaction of ionic surfactants with proteins, a solution of a [^{3}H]-surfactant in a phosphate buffered saline (PBS, pH 7.2±0.1; ionic strength, 0.16 M) was used as the aqueous phase. Experiments were performed with scintillation cocktails based on either *p*-xylene or octane. Naphthalene (3.8 vol%) was added to octane and 0.38 vol% 2,5-diphenyloxazole was added to both organic liquids according to a reported procedure.[11]

A 1-ml aliquot portion of a [^{3}H]-surfactant solution in PBS was placed in a polyethylene scintillation vial (Perkin–Elmer) followed by the addition of 3 ml of a scintillator. Two-phase systems were incubated at 22±1 °C for 48 h. The calculation of adsorption (Γ) and surfactant concentration in an organic phase (c_{org}) was described previously.[11] The counting rates of the system (I) and the aliquot portion of an organic phase (I_{aliq}) were measured using a RackBeta 1215 liquid scintillation spectrometer (Finland). The values of c_{org} and Γ were calculated according to the following equations:

$$c_{\mathrm{org}} = \frac{I_{\mathrm{aliq}}}{\varepsilon V_{\mathrm{aliq}} a_{\mathrm{mol}}}, \tag{1}$$

$$\Gamma = \frac{(I - I_{\mathrm{aliq}})V}{0.5\varepsilon V_{\mathrm{aliq}} a_{\mathrm{mol}} S}, \tag{2}$$

where V_{aliq} is the volume of the sampled aliquot, V is the volume of the organic phase, a_{mol} is the molar radioactivity of the surfactant, S is the surface area of the interface, and ε is the detection efficiency of tritium β-radiation in the bulk of the scintillator. According to quenching curves,[11] $\varepsilon = 43\pm2$ or $54\pm5\%$ for scintillation cocktails based on octane or *p*-xylene, respectively. Equilibrium concentrations of surfactants in an aqueous phase (c_{aq}) were estimated using equation (1).

Previously,[12] we found that such systems were equilibrated in 48 h. The process includes adsorption at the aqueous/organic liquid interface and the distribution of the surfactant in the bulk of the system. Here, we determined the adsorption kinetics of DTAB at the aqueous/*p*-xylene interface (Figure 1). Since the result is very sensitive to shaking, these experiments were carried out by continuously measuring the counting rate of systems with different organic phase volumes.[13] The DTAB concentration was 1.1×10^{-4} mol dm^{-3}.

If a diffusion-controlled adsorption model[14] is used, the diffusion coefficient of DTAB is 3.2×10^{-13} m^2 s^{-1} in the range from 5 to 50 min. However, in the first minute of the experiment, the diffusion coefficient was ~2×10^{-11} m^2 s^{-1}. The adsorption in this period corresponded to the formation of an unsaturated adsorption layer, while equilibrium adsorption corresponded to a saturated layer. Thus, the formation of a saturated monolayer by the reorientation of molecules is a rate-limiting step of the adsorption process.

Figure 2 shows the adsorption isotherms of surfactants at the liquid/liquid interface in the concentration ranges from 7.0×10^{-8} to 12×10^{-3} mol dm^{-3} for SDS and from 7.0×10^{-8} to 15×10^{-3} mol dm^{-3} for DTAB. The initial portions of the isotherms are presented in Figure 3. At concentrations < 8×10^{-5} mol dm^{-3}, the adsorption of DTAB at the aqueous/octane interface was almost the same as the adsorption of SDS at both interfaces, while DTAB superficial excess at the aqueous/*p*-xylene interface was higher by a factor

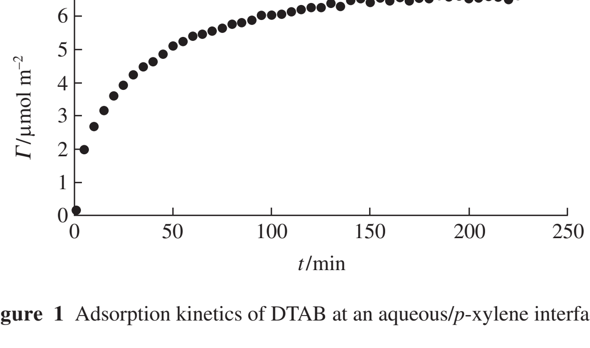

Figure 1 Adsorption kinetics of DTAB at an aqueous/*p*-xylene interface.

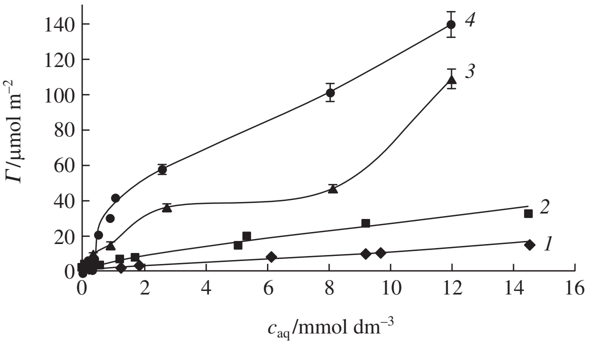

Figure 2 Adsorption isotherms of surfactants at aqueous/organic liquid interfaces in CMC region (CMC_{DTAB} = 14.5 mmol dm^{-3}, CMC_{SDS} = 8 mmol dm^{-3}): (*1*) DTAB at an aqueous/octane interface; (*2*) DTAB at an aqueous/*p*-xylene interface; (*3*) SDS at an aqueous/octane interface; (*4*) SDS at an aqueous/*p*-xylene interface.

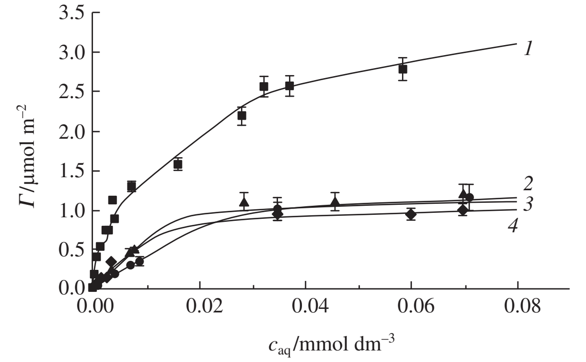

Figure 3 Initial portions of the adsorption isotherms of surfactants at aqueous/organic liquid interfaces: (*1*) DTAB at an aqueous/*p*-xylene interface; (*2*) SDS at an aqueous/*p*-xylene interface; (*3*) SDS at an aqueous/octane interface; (*4*) DTAB at an aqueous/octane interface.

of 5. Starting from 3.0×10^{-4} mol dm^{-3}, the interfacial excess of SDS dramatically increased at both of the interfaces. The adsorption of SDS was higher than that of DTAB even at the aqueous/*p*-xylene interface. DTAB adsorption at the aqueous/octane interface slowly increased with concentration. The corresponding adsorption isotherm correlates with the data obtained by measuring interfacial tension at the aqueous/*p*-xylene interface.[6]

Unfortunately, there is no data on SDS adsorption at the aqueous/organic liquid interfaces at concentrations lower than 4×10^{-4} mol dm^{-3}. However, an extrapolation supposes that SDS adsorption at low concentrations is also in good agreement with that obtained by measuring interfacial tension.[15]

The shape of the SDS adsorption isotherm at CMC was similar to that obtained for alkyltrimethylammonium bromides[6] because of the formation of a microemulsion phase. It is well known that SDS contributes to the formation of foam and stable emulsion.[16] The formation of a microemulsion phase results from the association between surfactant and organic phase molecules. The results indicate a high influence of an organic phase on surfactant adsorption at the liquid/liquid interfaces, as illustrated above by differences in the adsorption at low surfactant concentrations.

Since the adsorption calculated by the Gibbs equation from the interfacial tension obey the Langmuir adsorption law, the results presented in this study seem strange. We try to explain them. Fluctuations of interfacial tension are related to the amount of surfactant molecules at the interface, and a maximum adsorption corresponds to the formation of a dense adsorption monolayer. However, the dynamical equilibrium and concentration gradient occur between the adsorption monolayer and the surfactant bulk concentration. The diffuse layer depends on surfactant concentration and the ionic strength of solution.

Two important circumstances should be taken into account for a comparison between the results obtained using a scintillation phase technique and other methods. First, the duration of a radiochemical experiment is several days, whereas in the majority of other techniques it is a matter of several hours. Second, insignificant shaking can occur during the experiment to contribute to the formation of microemulsions in the superficial region at a low interfacial tension, which was observed in the experiments with SDS at both interfaces and with DTAB at the aqueous/*p*-xylene interface.

The scintillation phase method allowed us to determine a compound excess in the subsurface region limited by tritium β-particle path length in water (~1.6 μm). Thus, the superficial counting rate of tritium β-radiation includes the detection of labeled molecules in both the adsorption layer [a coefficient of 0.5 in equation (2)] and the subsurface aqueous phase, in which the concentration of the compound exceeds its bulk concentration. The latter can be incorporated based on the assumption that, for equal distribution of emitters in the subsurface region, the detection efficiency decreases with a coefficient of 0.27.[12,13] The contribution of the bulk component in the above experiment was 5–20%. The influence of the counting rate of labeled surfactants from the diffuse layer of organic phase is difficult to take into consideration. The detection efficiency of this component varied from 0.5ε to ε.

Since an adsorption is an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces,[17] the experimental data obtained by the scintillation phase method will contribute to an understanding of interfacial phenomena at liquid/liquid interfaces.

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