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Adsorption of a surfactant mixture at a water–*p*-xylene interface as studied by a scintillation phase technique

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Tetradecyltrimethylammonium bromide and pluronic P123 interference on adsorption and distribution in the water–*p*-xylene system has been studied by a scintillation phase method.

The mixtures of surfactants often give rise to enhanced performance over the individual components, and so blends are employed in a wide variety of practical applications. Thus, different types of combinations, such as anionic–cationic,[1,2] nonionic–anionic[3–5] and nonionic–cationic[6,7] surfactants are of considerable interest. Unfortunately, a few experimental techniques allow one to study the behaviour of surfactants in water–oil systems.[8,9] Scintillation phase method is included into their number.[10] Previously, we have shown that this technique can be successfully applied to the investigation of individual surfactant partitioning and adsorption at a water–nonpolar liquid interface.[11]

In this work, we applied tritium-labeled surfactants and scintillation phase method to study the behaviour of tetradecyltrimethylammonium bromide (TTAB, Merck) and a (polyethylene oxide)$_{20}$-(polypropylene oxide)$_{70}$-(polyethylene oxide)$_{20}$ block-copolymer (pluronic P123, Sigma–Aldrich) and their mixture in the water–*p*-xylene system. These approaches allow determining partition coefficient and the adsorption of ^{3}H-surfactant at liquid/liquid interfaces in the presence of other surface active components. The results were confirmed by the calculation of interaction parameter (β) and composition of adsorption layer according to the Rosen model.[12] Surface tension (σ_{OW}) in the same systems was measured by the Wilhelmy plate method.[13]

Tritium labeled substances were obtained by the tritium thermal activation method.[14]

Partition coefficients (K_{OW}) of surfactants and their adsorption (Γ) at water–*p*-xylene interface were determined by the scintillation phase method according to the procedure described elsewhere.[11] 1 ml of ^{3}H-surfactant solution in 0.1 wt% NaN$_3$ (10 mCi dm^{-3}) was placed in a scintillation vial and 3 ml of *p*-xylene with dissolved 2,5-diphenyloxazole (0.45 wt%) was added. We used both individual surfactants and their mixtures in a molar ratio of 1:1. When surfactant mixtures were tested, aqueous solution contained one tritium-labeled component.

The scintillation phase method allows us to determine the interfacial (I_S) and volumetric (I_V) constituents of the counting rate (I_Σ) as $I_S = I_\Sigma - I_V$.[10]

The partition coefficient and adsorption can be calculated according to the following equations:

$$K_{OW} = \frac{I_V/\varepsilon}{V_{aliq}A_{mol}C_W}, \qquad (1)$$

where I_V is the counting rate of organic phase bit (cps), ε is the registration efficiency of β-particles in organic phase, V_{aliq} is the volume of organic phase bit (dm^3), A_{mol} is the molar radioactivity of water phase (Bq mol^{-1}), C_W is the surfactant concentration in water phase (mol dm^{-3});

$$\Gamma = \frac{I_\Sigma - I_{aliq}V_{org}/V_{aliq}}{\varepsilon_S A_{mol} S}, \qquad (2)$$

where I_Σ is the counting rate of the whole system, V_{org} is the organic phase volume (dm^3), ε_S is the registration efficiency of β-particles at interface, which can be calculated as $\varepsilon_S = 2\varepsilon$,[15] *S* is the interface area (m^2).

Previously, it was shown that the scintillation phase method could be applied over a wide concentration range both below and above the critical micelle concentration (CMC).[11] For individual compounds in the range below CMC, K_{OW} were 0.0020±0.0002 and 0.9±0.2 for TTAB and P123, respectively. When P123 was added to TTAB aqueous solution, the partition coefficient of ionic surfactant was decreased by a factor of three. At the same time TTAB does not influence the K_{OW} of P123.

Adsorption of P123 is also higher than that of TTAB. The adsorption values were 30±5 and 100±10 μmol m^{-2} for TTAB and P123, respectively. Such huge difference between observed values of adsorption of TTAB and P123 can be explained by the formation of associates between surfactant and aromatic hydrocarbon. Indeed, aromatic compounds can be solubilized by the adsorption layer of ionic surfactants.[11] Note that the block

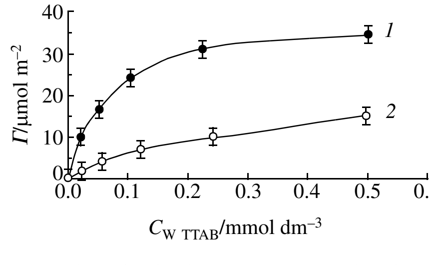

Figure 1 TTAB adsorption isotherm at water–*p*-xylene interface: (*1*) individual compound and (*2*) with P213 additive (molar ratio, 1:1).

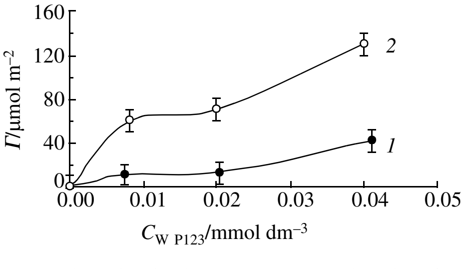

Figure 2 P123 adsorption isotherm at water/*p*-xylene interface: (*1*) individual compound and (*2*) with TTAB additive (molar ratio, 1:1).

Table 1 Mole fraction of P123 in mixed adsorption layer and interaction parameter (β) calculated according to the Rosen model.

Interfacial tension at water–*p*-xylene interface, mN m^{-1}	Mole fraction of P123 in mixed adsorption layer	Interaction parameter,[a] β
17.5	0.74	30
15.0	0.87	50
12.5	0.98	—
10.0	1.00	—

[a] $\beta = [\ln (\alpha C_{12}/X_1 C_1^0)]/(1 - X_1)^2$, where α is the molar fraction of surfactant 1 in the mixture of two surfactants, X_1 is the molar fraction of surfactant 1 in the mixed monolayer, C_1^0 and C_{12} are the molar concentrations in the bulk of surfactant 1 and in the mixture of surfactants 1 and 2, respectively.

copolymer yields a higher solubilization capacity than ionic surfactants.[16]

Figures 1 and 2 show adsorption isotherms for test mixtures. Additives of P123 reduce TTAB adsorption. At the same time, adsorption of P123 increased when TTAB added. Such observation can be explained by changes in composition of an adsorption layer. Mole fraction of P123 in mixed adsorption layers varies from 0.80 to 0.92 with the increase of total concentration from 0.07 to 0.55 mmol dm^{-3}. Thus, the surfactant with a high surface activity (P123) replaces the surfactant with a low one (TTAB) from the adsorption layer. The composition of mixed adsorption layers determined by the experiment was compared with the data calculated according to the Rosen model based on the measurement of surface tension of solutions of test surfactants and their mixtures at water–*p*-xylene interface (Figure 3, Table 1). It was shown by both experiment and calculation that adsorption layers are enriched with the nonionic surfactant. The mole fraction of P123 in mixed adsorption layer increases with surfactant total concentration growth. Addition of P123 to TTAB solution results in displacement of TTAB to water phase from both organic phase and interfacial layer. Calculations of interaction parameters between surfactant molecules in mixed adsorption layer (β) yield positive values. According to the Rosen model,[12] the value of β is related to the free energy change upon mixing of the two surfactants. The regular solution for β is

$$\beta = [W_{AB} - (W_{AA} + W_{BB})/2]RT,$$

where W_{AB}, W_{AA} and W_{BB} are the molecular interaction energies between the mixed surfactants, between the first surfactant molecules before its mixing with the second and between the second surfactant molecules before its mixing with the first, respectively; *R* is the gas constant and *T* is the absolute temperature. A negative value of β denotes either greater attraction of the two surfactants or their less repulsion upon mixing than before mixing; and a positive β value, less attraction or greater repulsion upon mixing than before mixing.[12] A value close to zero indicates little or no change in molecule interaction upon mixing. Our result indicates that in the adsorption layer, the interaction between molecules of the same type is much stronger than that between different ones. Values $\beta > 0$ were obtained only for the adsorption layer at water–*p*-xylene interface. For water–air, water–octane interfaces and for micelle formation β have negative values.[17] Such a result allows assuming that the interaction between surfactant molecules in the adsorption layer is strong influenced by the nature of the non-polar phase.

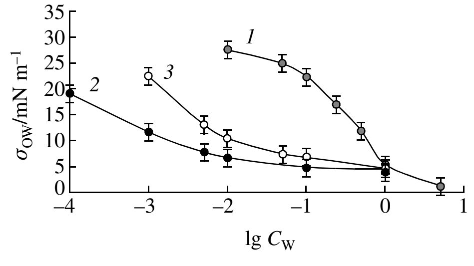

Figure 3 Isotherms of interfacial tension at water–*p*-xylene interface of (*1*) TTAB, (*2*) P123 and (*3*) their mixture.

Thus, the scintillation phase method has been successfully applied to study the behaviour of a cationic–nonionic surfactant mixture in the water–*p*-xylene system. This method allows the determination of the mutual influence of surfactants during the adsorption and distribution in liquid–liquid systems.

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