Available online at www.sciencedirect.com
ScienceDirect
*Mendeleev Commun.*, 2007, **17**, 357–358
Mendeleev Communications

# Surfactant adsorption at the water–*p*-xylene interface as studied by the scintillation phase method

**Gennadii A. Badun,* Oxana A. Soboleva and Maria G. Chernysheva**

*Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 495 939 3187; e-mail: badun@radio.chem.msu.ru*

DOI: 10.1016/j.mencom.2007.11.021

**Adsorption isotherms and partition coefficients of dodecyl-, tetradecyl- and cetyltrimethylammonium bromides in the water–*p*-xylene system were studied by the scintillation phase method.**

Surfactant adsorption at liquid–liquid interfaces plays a central role in biological, environmental and industrial processes. New methods such as nonlinear optical techniques,[1–3] light and neutron diffraction[1,4] and IR spectroscopy[5] have been developed for studying interfacial phenomena. We applied the scintillation phase method to study surfactant adsorption at an interface between two immiscible liquids. This method is based on the introduction of a tritium-labeled surfactant in an aqueous phase of the oil–water system followed by measuring the radioactivity of the whole system. Taking into account that a tritium path length in condensed media reaches a few micrometers, it is obvious that tritium-labeled compounds can be detected both in the bulk of the organic phase and at the interface. This method was successfully used to study the partition of bovine serum albumin in the water–toluene system.[6,7]

The scintillation phase method can be used over a wide concentration range both below and above the critical micelle concentration (CMC) for studying the behaviour of ionic or nonionic surfactants.[8]

We studied the adsorption of dodecyl-, tetradecyl- and cetyltrimethylammonium bromides (DTAB, TTAB and CTAB, respectively) from Merck at the water–*p*-xylene interface. The surface tension ($\sigma_{OV}$) in the test system was measured by the Wilhelmy plate method[9] (Figure 1).

The CMCs of the surfactants are $1.45\times10^{-2}$ mol dm$^{-3}$ for DTAB, $3.6\times10^{-3}$ mol dm$^{-3}$ for TTAB and $9.2\times10^{-4}$ mol dm$^{-3}$ for CTAB. Tritium-labeled surfactants were obtained by tritium thermal activation.[10] The $^3$H-surfactants were purified by extraction with toluene (radiochemical purity was ≥ 99%).

Adsorption experiments were carried out in polyethylene scintillation vials (7 ml) (Wallac Oy, Finland) according to a published procedure.[8] A 2 ml portion of an aqueous solution of a $^3$H-surfactant ($10^{-5}$–$10^{-1}$ mol dm$^{-3}$, 25 μCi ml$^{-1}$) was placed in a scintillation vial, and 3 ml of *p*-xylene with dissolved 2,5-diphenyloxazole (0.45 wt%) was added. Counting rate ($I$) was measured using a RackBeta 1215 liquid scintillation counter (Finland) until equilibrium was reached (48 h). When the system was equilibrated, the organic phase was sampled (500–1000 μl) and its counting rate ($I_V$) and residual counting rate were measured. This procedure allowed us to determine the interfacial ($I_S$) and volumetric ($I_V$) constituents of the counting rate as $I_S = I - I_V$. The surfactant concentration in the organic phase ($C_{org}$) was calculated from the equation

$$C_{org} = \frac{I_V}{\varepsilon V A_{mol}}, \quad (1)$$

where $V$ is the volume of *p*-xylene (dm$^3$), $A_{mol}$ is the specific radioactivity of the $^3$H-surfactant (Bq mol$^{-1}$), $\varepsilon$ is the registration efficiency in organic phase (0.55±0.03),[11] $I_V$ is the volumetric counting rate (counts s$^{-1}$).

The surfactant adsorption ($\Gamma$) at the *p*-xylene–water interface was calculated according to the equation

$$\Gamma = \frac{2I_S}{\varepsilon S A_{mol}}, \quad (2)$$

where $I_S$ is the interfacial counting rate (counts s$^{-1}$), $S$ is the area of the interface (cm$^2$). Correction for registration efficiency from the bulk of organic phase was used as $0.54 C_W h$, where $C_W$ is the surfactant concentration in water (mol dm$^{-3}$), $h$ is the thickness of water where tritium registration is possible (1.6 μm[12]). A coefficient of 0.54 appears from the difference between registration efficiency from adsorption layer at the interface ($\varepsilon_S = 0.5\varepsilon$) and from the bulk of organic phase with equal distribution of beta-emitters ($\varepsilon_S = 0.27\varepsilon$).

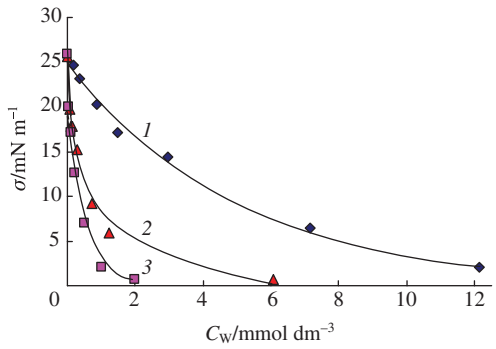


**Figure 1** Isotherms of interfacial tension at water–*p*-xylene interface for (*1*) DTAB, (*2*) TTAB and (*3*) CTAB.

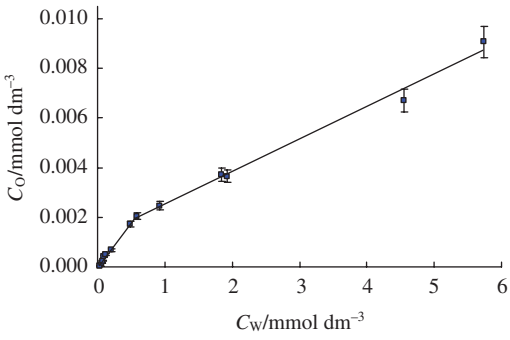


**Figure 2** Correlation between the bulk concentrations of CTAB in water and *p*-xylene.

© 2007 Mendeleev Communications. All rights reserved.

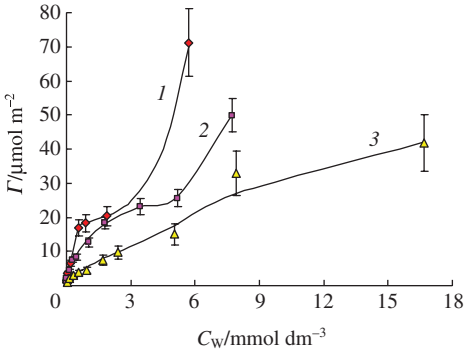


**Figure 3** Adsorption isotherms of (*1*) CTAB, (*2*) TTAB and (*3*) DTAB, obtained by the scintillation phase method.

The area of interface was changed from bossy to flat with surfactant concentration increased. Interface deformation near walls was about capillary length $a = (2\sigma_{VO}/\Delta\rho g)^{1/2}$, where $\Delta\rho$ is the difference between water and *p*-xylene densities.[13] The interfacial area was calculated as

$$S = \pi(a^2 + r^2), \quad (3)$$

where $r$ is the inner radius of the vial (0.75 cm).

Accuracy of adsorption determination was about 1% for low concentrations and around 5% for high concentrations.

The dependence of surfactant concentration in organic phase ($C_O$) on its concentration in water ($C_W$) obtained by the scintillation phase method was a linear function with a salient point at CMC. Figure 2 shows the dependence of $C_O$ on $C_W$ for CTAB. Partition coefficients in concentration range below CMC $K_{OW} = C_O/C_W$ were 0.0012, 0.0018 and 0.0042 for DTAB, TTAB and CTAB, respectively. $K_{OW}$ decreased at $C_W >$ CMC because $K_{OW}$ depends on the surfactant concentration in a molecular (non-micellar) form.

Figure 3 shows that the adsorption of all the tested surfactants increased with concentration, achieved a plateau and then sharply increased at $C_W >$ CMC. Adsorption obtained by the scintillation phase method was compared with that calculated by the Gibbs equation

$$\Gamma = -\frac{C_W}{2RT}\frac{d\sigma_{VO}}{dC_W}, \quad (4)$$

where $R$ is the gas constant and $T$ is the absolute temperature (K).

The dependence of the Gibbs adsorption on surfactant concentration is described by the Langmuir isotherm

$$\Gamma = -\frac{\Gamma_{max} A C_W}{AC_W + 1}, \quad (5)$$

where $\Gamma_{max}$ is a maximum adsorption and $A$ is the relative adsorption activity. Maximum adsorption $\Gamma_{max}$, area per molecule $S_1$ in saturated adsorption layer $S_1 = 1/\Gamma_{max}N_A$ and adsorption activity $A$ are given in Table 1.

**Table 1** Parameters of surfactant adsorption layers at the water–*p*-xylene interface.

| Surfactant | $\Gamma_{max}$/μmol m$^{-2}$ | $A$/dm$^3$ mol$^{-1}$ | $S_1$/nm$^2$ |
|---|---|---|---|
| DTAB | 5.73 | 790 | 0.31 |
| TTAB | 4.06 | 6100 | 0.41 |
| CTAB | 4.28 | 33765 | 0.39 |

A comparison between the data of two methods (Figure 3 and Table 1) shows that the adsorption determined by the scintillation phase method is higher than that calculated by the Gibbs equation at $C_W \geq 0.1$ CMC. This fact can be explained by the formation of polylayers at the oil–water interface. When $C_W >$ CMC, the growth of the adsorption is probably due to surfactant aggregation and microemulsion phase formation.

This work was supported by the Russian Foundation for Basic Research (project nos. 06-03-33036 and 05-03-32555).

## References

1 I. Benjamin, *Ann. Rev. Phys. Chem.*, 1997, **48**, 407.
2 R. M. Corn and D. A. Higgins, *Chem. Rev.*, 1994, **94**, 107.
3 I. Benjamin, *Chem. Rev.*, 1996, **96**, 1449.
4 L. T. Lee, D. Langevin, E. K. Mann and B. Farnoux, *Physica B*, 1994, **198**, 83.
5 R. P. Sperline and H. Freiser, *Langmuir*, 1990, **6**, 344.
6 A. Yu. Alent'ev and E. S. Filatov, *Radiokhimiya*, 1991, **33**, 80 (in Russian).
7 A. Yu. Alent'ev, V. N. Izmailova and G. P. Yampolskaya, *Kolloidn. Zh.*, 1992, **54**, 14 (in Russian).
8 G. A. Badun, M. G. Chernysheva, V. Yu. Pozdnyakova and V. M. Fedoseev, *Radiokhimiya*, 2005, **47**, 536 [*Radiochem.* (*Engl. Transl.*), 2005, **47**, 584].
9 A. A. Abramson and G. M. Gaevoy, *Poverkhnostno-aktivnye veshchestva* (*Surface Active Substances*), Khimiya, Leningrad, 1979 (in Russian).
10 M. G. Chernysheva, Z. A. Tyasto, G. A. Badun and N. E. Shchepina, *Proceedings of the X All-Russian International Scientific Conference 'Physical and Chemical Processes on Selection of Atoms and Molecules'*, Zvenigorod, 2005, p. 280.
11 G. A. Badun, V. Yu. Pozdnyakova, M. G. Chernysheva, N. E. Shchepina and V. M. Fedoseev, *Proceedings of the VIII All-Russian International Scientific Conference 'Physical and Chemical Processes on Selection of Atoms and Molecules'*, Zvenigorod, 2003, p. 154.
12 L. E. Feinenegen, *Tritium Labeled Molecules in Biology and Medicine*, Academic Press, New York–London, 1967.
13 A. Adamson, *Physical Chemistry of Surfaces*, John Wiley and Sons, New York–London–Sydney–Toronto, 1976.

*Received: 27th March 2007; Com. 07/2899*