

● *Short Communication***EXCHANGE DYNAMICS OF SURFACTANTS IN ADSORPTION LAYERS
INVESTIGATED BY PFG NMR DIFFUSION**

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Surfactant adsorption layers on polystyrene latex particles are investigated concerning their equilibrium exchange dynamics with surfactant molecules in solution. Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) self-diffusion measurements of the nonionic surfactant $C_{12}(EO)_5$ are performed, making use of the difference of the diffusion coefficients of adsorbed and free surfactant in solution. On variation of the gradient pulse spacing the echo decay data show a transition from fast to slow exchange, giving the possibility of a quantitative evaluation. A two-site model is applied to fit the data and obtain average residence times of the surfactant in both sites. The results are consistent with diffusion-controlled adsorption of surfactant monomers and additional micellar contributions to the exchange, whereas no evidence for kinetic barriers is found for these nonionic surfactants on the relevant timescale (10 ms). © 1998 Elsevier Science Inc.

Keywords: Exchange; Surfactant adsorption dynamics; Nuclear magnetic resonance self-diffusion; Nonionic.

INTRODUCTION

Up until now, investigations of the adsorption dynamics of surfactant layers at solid/liquid interfaces involve nonequilibrium methods such as ellipsometry or quartz balance measurements, where slow nonequilibrium adsorption/desorption dynamics can be studied. We address here the question of the measurement of the faster equilibrium exchange dynamics of surfactants at a solid/liquid interface, and show that nuclear magnetic resonance (NMR) self-diffusion, which has been successfully applied to exchange dynamics of small molecules at interfaces, can also give unique information about surfactants at solid interfaces.

MATERIALS AND METHODS

The experiments are performed on mixtures of monodisperse Polystyrene latex spheres (Polysciences Europe, Eppelheim, Germany; radius = 101 nm, 1.8 vol%) and dodecylpentaethyleneoxide ($C_{12}(EO)_5$; Nikko, Tokyo, Japan) in aqueous solution with surfactant concentrations on the order of full monolayer coverage. Surfactant self-diffusion is measured by the pulsed field gradient method

(PFG) on a Bruker DMX 200 spectrometer (Bruker, Karlsruhe, Germany) with a gradient probe providing a maximum gradient strength of 8.8 T/m. A stimulated echo sequence with three pregradient pulses is applied. Under variation of the gradient strength g the echo decay data are evaluated from the area of the ethyleneoxide ^1H line at 3.6 ppm. The echo decays for three different surfactant concentrations, determined with different gradient spacings, Δ , were measured. As an example the data for one concentration are shown in Fig. 1 in dependence on $k = \gamma^2 g^2 \delta^2 [\Delta - (\delta/3)]$ (δ : gradient pulse duration).

RESULTS AND DISCUSSION

At all surfactant concentrations, the shape of the echo decay is in the intermediate range between slow and fast exchange, with a double exponential decay for small Δ , and an almost monoexponential decay for large Δ . To quantify the information contained in these data, we describe them by a two-site model, where the surfactant is exchanging between the adsorption layer (site B) and the solution (site A). A surfactant molecule is staying in

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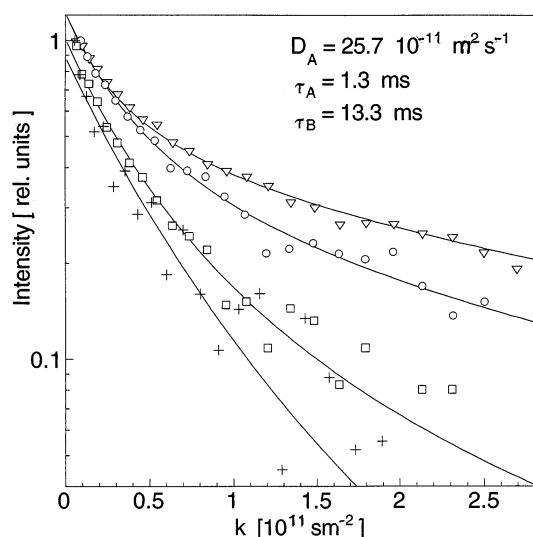


Fig. 1. Echo decay curves of the PFG-stimulated echo sequence at total surfactant concentration $c = 0.698$ mg/mL. (∇) $\Delta = 15$ ms; ($\circ$) $\Delta = 25$ ms; ($\square$) $\Delta = 50$ ms; ($+$) $\Delta = 100$ ms. The lines are the results of a global fit to all decay curves, yielding the parameters given in the figure.

either site for an average residence time τ_A or τ_B , and the difference in their diffusion coefficients D_A and D_B makes the self-diffusion experiment sensitive to the residence times and, therefore, the exchange dynamics. D_A is an averaged diffusion coefficient assuming fast exchange between monomers and micelles, and D_B is given by the translational diffusion of the particle, neglecting surfactant diffusion along the surface and particle rotational diffusion.

We analyze the data by the equations derived by Kärger¹ for the intermediate case of two-site exchange in PFG diffusion experiments, modified only by using effective relaxation times:

$$\frac{1}{T_{A,B}} = \frac{T/\Delta}{T_{1A,B}} + \frac{2\tau/\Delta}{T_{2A,B}} \quad (1)$$

for the two sites to account for the application of a stimulated echo with τ being the time between the first

and the second 90° pulse, and T the time between the second and the third 90° pulse:

$$\varphi(g) = p_A \exp(-a_A) + p_B \exp(-a_B), \quad (2)$$

with

$$a_{A,B} = \frac{1}{2} \left\{ k(D_A + D_B) + \Delta \left(\frac{1}{T_A} + \frac{1}{T_B} + \frac{1}{\tau_A} + \frac{1}{\tau_B} \right) \right. \\ \left. \mp \sqrt{ \left[k(D_B - D_A) + \Delta \left(\frac{1}{T_B} - \frac{1}{T_A} + \frac{1}{\tau_B} - \frac{1}{\tau_A} \right) \right]^2 + \frac{4\Delta^2}{\tau_A \tau_B} } \right\}, \quad (3)$$

$p_B =$

$$\frac{1}{a_B - a_A \left\{ \frac{\tau_A}{\tau_A + \tau_B} \left(kD_A + \frac{\Delta}{T_A} \right) + \frac{\tau_B}{\tau_A + \tau_B} \left(kD_B + \frac{\Delta}{T_B} \right) - a_A \right\}}, \quad (4)$$

where $p_A = 1 - p_B$ and $k = \gamma^2 g^2 \delta^2 \Delta$.

By using a global set of input and resulting parameters, a fit of all four echo decays was made with the corresponding decay functions according to Eq. (2–4). The values of the input parameters are given in Table 1, data for the surfactant in solution were determined on micellar solutions of $C_{12}(EO)_5$,² whereas the transverse relaxation time T_{2B} was measured on concentrated samples of $C_{12}(EO)_5$ on latex particles.² The resulting parameters are given in Table 2. As the errors of the input parameters and their interdependencies influence the results, a Monte-Carlo error analysis³ was performed to obtain accurate standard deviations, which are displayed in brackets.

All residence time values are in the range of several milliseconds, which correspond to adsorption rates considerably faster than nonequilibrium rates, which are controlled by a surfactant depletion layer at the surface. In equilibrium, however, two steps are controlling the rate of adsorption and desorption: the first is the monomer flow to the surface, given by diffusion, and the second is the kinetic step of incorporating a surfactant

Table 1. Input parameters for diffusion-exchange fits

Parameter	Value	Determined from
D_A	$(2.1 \pm 0.1) \times 10^{-12} \text{ m}^2/\text{s}$	Stokes equation
$T_{1A} = T_{1B}$	$(465 \pm 20) \text{ ms}$	Measurements in micellar solution
T_{2A}	$(340 \pm 40) \text{ ms}$	Measurements in micellar solution
T_{2B}	$(5 \pm 2) \text{ ms}$	Measured in concentrated adsorption sample

Table 2. Fit results for the parameters τ_A , τ_B , and D_A with standard deviations in parentheses

c (mg/mL)	τ_A (ms)	τ_B (ms)	D_A (10^{-11} m ² s ⁻¹)	f_B	A (Å ²)
0.698	1.4 (0.54)	13.4 (0.89)	28.1 (9.8)	0.909 (0.027)	56.4 (1.7)
0.905	3.2 (1.41)	9.3 (1.07)	14.8 (4.1)	0.757 (0.060)	53.2 (4.4)
1.22	7.1 (3.0)	7.0 (0.8)	9.9 (1.6)	0.518 (0.080)	58.3 (9.1)

The fraction of adsorbed surfactant f_B and the area per molecule A are calculated from τ_A and τ_B .

into the adsorption layer, involving, e.g., chain reorientation. We calculate the residence times for the case of diffusion controlled adsorption and compare them to the experimental results. It is assumed that every monomer encountering the particle surface by diffusion with the rate coefficient $k_+ = 4\pi R_B D_1$ (R_B : particle radius; D_1 : monomer diffusion coefficient) is adsorbed without a kinetic delay. Then the desorption rate coefficient $k_- = 1/\tau_B$ is given by the rate equation:

$$k_+ c m c = k_- N. \quad (5)$$

(N : number of surfactants adsorbed per particle), which results in $\tau_B = 1/k_- = 12$ ms. The good agreement with the experimental value of $\tau_B = 13.4$ ms obtained at $c = 0.698$ mg/mL shows that monomer diffusion is indeed governing the exchange dynamics, whereas the kinetic step occurs on a timescale fast compared to τ_B . At this surfactant concentration, site A consists mainly of monomers. The decrease in τ_B with concentration shows that additional exchange contributions add, as soon as micelles are formed in the solution, probably surfactants from micelles can be exchanged on collisions between micelles and particles. The increase in τ_A is due to the increasing amount of surfactant in this site, which is also causing a decrease in D_A due to the increased contribution of micelles to D_A , which are diffusing slower than the monomer.

Furthermore, the fraction of adsorbed surfactant, $f_B = \tau_B/(\tau_A + \tau_B)$, and the resulting area per molecule A were calculated (see Table 2). Considering the fact that the latex particles carry stabilization charges, which decrease the effective hydrophobic surface available for adsorption and therefore lead to larger molecular areas, our

values correspond well to the somewhat smaller area obtained from ellipsometry data for these surfactants on silica surfaces (45 Å², from Ref. 4).

CONCLUSION

This work demonstrates the applicability of PFG NMR exchange-coupled diffusion to investigate surfactant exchange dynamics at solid interfaces. For the non-ionic surfactant C₁₂(EO)₅ we found the dynamics to be governed by diffusion-limited adsorption, and not by kinetics. For ionic surfactants, electrostatic repulsion is expected to slow the kinetics, and it will be interesting to investigate these kinetics by PFG NMR measurements.

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