Adsorption and Self-assembly of Surfactants in Nanopores

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Adsorption phenomena of surfactants in narrow pores are of significance for a wide range of technological applications, including membrane processes for the separation of hydrophobic organics from aqueous media, and surfactant-mediated adsorption and ad-solubilization processes. To optimize such processes it is desirable to gain a better understanding of the driving forces for the adsorption of pure surfactants in nanopores. Generally, surfactant adsorption from aqueous solutions onto hydrophilic surfaces is determined by two competing interactions: Polar interactions of the surfactant head groups with the surface, and hydrophobic interactions between the tails of surfactant molecules. Different surface-aggregate structures will be favoured depending on the relative strength of these types of interaction. For atomically flat surfaces, a wealth of information about surfactant aggregate structures has been obtained by scanning force microscopy (AFM), and by neutron reflectometry and related techniques. Less is known about the nature of surfactant aggregation in narrow pores, although one expects that aggregate size and shape will be strongly affected by confinement and surface curvature effects in narrow pores.

This work is part of a systematic study to explore size effects on the aggregative adsorption of surfactants in porous solids of well-defined pore structure. Two types of mesoporous silica are used in this study: (a) Controlled-pore glass (CPG-10) materials which comprise an interconnected system of mesopores of relatively low mean surface curvature; (b) MCM-41 and SBA-15 silicas which constitute two-dimensional hexagonal packings of cylindrical mesopores of uniform width in the range 3–10 nm. Pronounced size effects on the adsorption are observed when the pore width is approaching the diameter of the surfactant micelles or bilayer aggregates. These effects can be expressed in terms of the parameters of an isotherm equation for a two-step adsorption model [1]. Nonionic surfactants of the alkyl ethoxylate (C_nE_m) type are of special interest as they exhibit a inverse temperature dependence of the adsorption which can be attributed to the gradual de-hydration of the oxyethylene head groups as the temperature is increased. This behaviour can be analyzed on the basis of a recent theory of surfactant self-assembly at surfaces [2] and an extension of this model to account for effects of confinement on the self-assembly in narrow pores.

Materials and Methods

Controlled-pore glass (CPG-10 by Electro-Nucleonics Inc.) was received from Fluka (Germany). Four materials of different nominal pore width (75, 170, 240 and 500Å) were used and characterized by nitrogen adsorption. It was found that the nominal pore width of the materials is consistent with the hydraulic pore diameter of cylinders, $d_h = 2v_p/a_s$, as derived from the specific pore volume v_p and surface area a_s of the individual samples. However, the pore diameter d_p derived from the desorption branch of the hysteresis loop by the BJH method was ca. 50% greater than this value ($d_p/d_h \approx 1.5$). MCM-41 and SBA-15 silica was synthesized in our laboratory as described elsewhere [3].

The surfactant, tetraoxyethylene-monooctyl ether (C_8E_4, Nikko Chemicals, >98%) was used as received. The critical micelle concentration (*cmc*) of C_8E_4 at the three experimental temperatures was obtained from measurements of the *cmc* and the enthalpy of micellization ($\Delta_{mic}H$ = 15.8 kJ mol^{-1}) at 25°C using titration calorimetry [4]. The following values of the *cmc* were obtained: 14.5 mM (5°C), 8.4 mM (25°C) and 6.1 mM (45°C).

Adsorption isotherms of the surfactant in the porous silica materials were determined by two complementary techniques: (a) Frontal analysis liquid chromatography (FA) was used for the initial low-affinity region of the isotherm (below the critical surface aggregation concentration of the surfactant); (b) Liquid circulation (LC) in a closed circuit was used for higher concentrations (above the critical surface aggregation concentration). Details of the two methods will be given elsewhere [6].

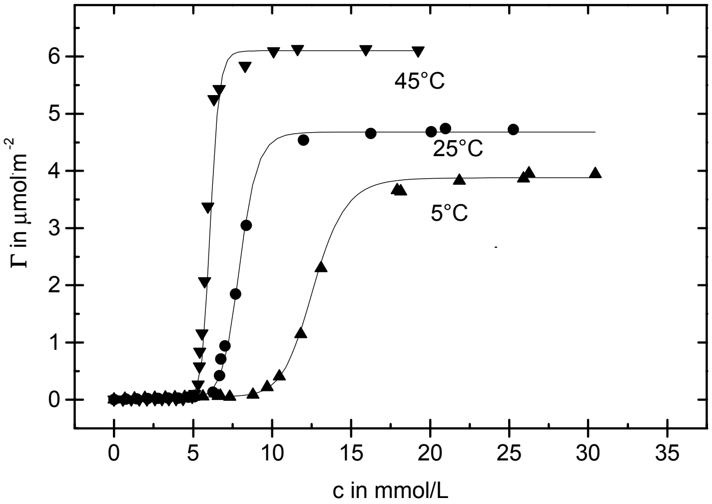

Fig. 1. Adsorption isotherms of C_8E_4 in CPG-10 (170 Å) at the temperatures 5, 25, 45°C

Results

Adsorption isotherms of C_8E_4 in the four CPG-10 materials were determined at three temperatures (5, 25 and 45°C) in a concentration range extending to ca. 1.5*cmc*. Results for C_8E_4 in CPG-10 (170 Å) are shown in Fig. 1, where the surface concentration Γ (amount of surfactant per unit surface area as determined by nitrogen adsorption) is plotted vs. the equilibrium concentration c of the surfactant in the supernatant solution. The isotherms exhibit three distinct regions: (i) An initial low-affinity region in which the surface concentration Γ is a nearly linear function of c but remains very low ($\Gamma < 0.1$ µmol m^{-2}). Adsorption in this region is attributed to hydrogen bonding of surfactant head groups to "high-energy" surface silanol groups (which involves stripping of water molecules hydrogen-bonded to the surfactant heads and surface silanol groups). (ii) An intermediate region in which Γ increases steeply with c. Adsorption in this region is attributed to surface aggregation of surfactant molecules; accordingly, the onset concentration of this region is called critical surface aggregation concentration (*csac*). (iii) A plateau region in which the surface concentration reaches a value Γ_{max} at a concentration somewhat above the *cmc* of the respective temperature. As to be seen in Fig. 1, the adsorption in regions (ii) and (iii) has a pronounced inverse temperature dependence, i.e., at any given concentration c the adsorption increases with increasing temperature. These finding are consistent with results of a calorimetric study [4] which show that the adsorption of single molecules in region (i) is exothermic but the aggregative adsorption in regions (ii) and (iii) is endothermic just like micelle formation of C_8E_4 in solution.

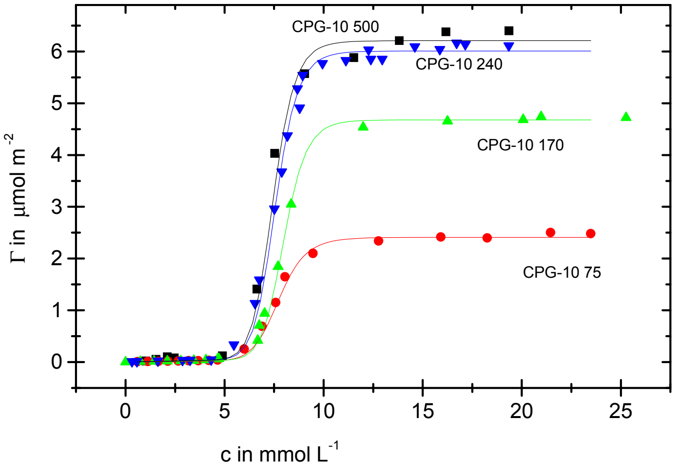

Fig. 2. Adsorption isotherms of C_8E_4 in CPG-10 materials of different pore size

The aggregative adsorption in region (ii) exhibits a pronounced dependence on the mean pore size of the matrix. This can be seen in Fig. 2 where the 25°C isotherms of C_8E_4 in the four different CPG-10 materials are again expressed by the surface concentration Γ. For the materials with nominal pore size greater 200 Å the plateau values $\Gamma_{\max}$ of the isotherms coincide within experimental accuracy, but a significant decrease of $\Gamma_{\max}$ with decreasing pore size is found for pores with nominal pore diameter below 200 Å. Results for C_8E_4 in SBA-15 (pore diameter 80 Å) and MCM-41 (40 Å) confirm this trend (not shown in Fig. 2). The results for C_8E_4 in SBA-15 and MCM-41 also indicate that the *csac* is shifted to lower concentrations for pores with diameter below 100 Å. This behaviour is not unexpected in view of the fact that micelles of C_8E_4 have a diameter of ca. 4 nm, and thus interactions of the surfactant molecules with the pore wall will be more important in these narrow pores as compared with wider pores.

The adsorption isotherms were analysed in terms of the two-step adsorption model by Zhu and Gu [1], which assumes binding of single surfactant molecules to active surface sites as the first step, and formation of surface aggregates at these anchor molecules as the second step. The isotherm equation resulting from this model can be written as

$$\Gamma = \Gamma_\infty \frac{K_1 c_0 x + x^N}{N + N K_1 c_0 x + x^N} \qquad (1)$$

where Γ_∞ is the limiting value of the adsorption at high concentrations, K_1 the adsorption constants of the first step, $x = c/c_0$ is a reduced concentration with c_0 the critical surface aggregation concentration (*csac*), and N is the aggregation number of the surface aggregates. For concentrations $x \ll 1$ this equation reduces to the Langmuir equation for the adsorption of single surfactant molecules (limiting surface concentration Γ_∞/N), but above $x \approx 1$ the term x^N causes a steep increase of the isotherm that leads to a limiting surface concentration Γ_∞ characteristic of the surface aggregates of N molecules. Hence c_0 is defined operationally for $N \gg 1$ as the concentration in the steeply ascending region of the isotherm at which Γ reaches the value Γ_∞/N. Eq. (1) was fitted to the adsorption isotherms in order to quantify the dependence of the model parameters on the pore width.

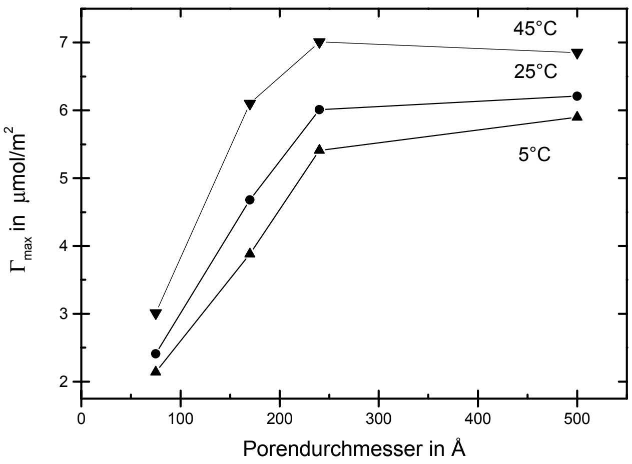

Fig. 3. Limiting adsorption Γ_∞ of C_8E_4 in CPG-10 materials as a function of their nominal pore width at 5, 25 and 45°C.

Fig. 3 shows the dependence of Γ_∞ on pore diameter for the three experimental temperatures. High values of Γ_∞ are found in the two materials with 240 Å and 500 Å pore width. The highest value, $\Gamma_\infty \approx 7$ µmol m^{-2}, observed at 45°C, corresponds to a mean area per molecule of 0.48 nm^2, assuming a surfactant bilayer. This value is similar to that reported for C_8E_4 at the air/water interface near the *cmc*, indicating that the surfactant forms a bilayer at the pore wall of these wide-pore CPG-10 materials at high temperature. The pronounced decrease of Γ_∞ for lower pore diameters is attributed to the confinement effect. The lowest value, $\Gamma_\infty \approx 2$ µmol m^{-2}, observed in the material with the smallest pore size at the lowest temperature, corresponds to a nominal area per molecule of ca. 1.6 nm^2, again assuming a bilayer. This large value implies that not the whole area of the pore walls is covered by a surfactant bilayer. This finding is in agreement with a recent NMR study of the structure and dynamics of the surfactant $C_{12}E_5$ in the CPG-10 materials with pore widths 75 Å and 240 Å [5], where it was found that the diffusion coefficient of the surfactant molecules along the pore wall is lower than in the free solution, and this reduction was much stronger in the material with 75 Å pore widths, presumably due to the confinement effect. A full account of the aggregative adsorption of C_8E_4 and other non-ionic surfactants in nanoporous silicates of well-defined pore size (CPG-10, SBA-15 and MCM-41) will be presented in a forthcoming paper [6].

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