Unexpectedly Low Extent of Adsorption of Non-ionic Ethoxylated Surfactants on Alumina

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It has been shown for the first time that non-ionic ethoxylated surfactants adsorb much less extensively from aqueous solution (at temperatures below their cloud points) on alumina surfaces than on silica surfaces; this is attributed to the formation of surfactant : Al^{3+} complexes which are stable relative to the surface-adsorbed state.

The literature[1,2] does not suggest that non-ionic surfactants and polymers should show selectivity in respect of their extent of adsorption upon a unit surface area of different oxides, since the involvement of electrostatic forces is relatively small; it is therefore surprising that the extent of adsorption of non-ionic ethoxylated surfactants from aqueous solution onto a unit area of alumina is now reported to be less than 1% of that onto the same surface of silica.

Two alkyl–aryl ethoxylated surfactants [Triton N111 (100% purity) with an average poly(ethylene oxide) chain length of 11 ethylene oxide (EO) units; Triton N150 (100% purity) with an average poly(ethylene oxide) chain length of 15 EO units] were obtained from Rohm and Haas and used directly. Each contained molecules with a Poisson distribution of the number of ethylene oxide units. Silica (obtained from Shell Chemical) with particle diameters of 2.5 mm was used; its surface area was determined by N_2 Brunauer–Emmett–Teller (BET) analysis (in a Sorptomatic 1800 instrument) to be 292 $m^2 g^{-1}$ and its most frequent pore radius was estimated by Hg porosimetry (in a Carlo Erba 200 porosimeter) to be 60 nm. Boehmite alumina (obtained from Davison) was used; its surface area was determined by N_2 BET analysis to be 242 $m^2 g^{-1}$ and its most frequent pore radius was estimated by Hg porosimetry (in a Carlo Erba 2000 porosimeter) to be 15 nm. The extent of surfactant adsorption upon these oxides was determined in batch experiments by a depletion method at 318 K. This temperature was chosen since it was below the cloud point of the surfactants in distilled water. In the absence of strong electrostatic interactions, it is not surprising that equilibrium extents of adsorption were often slow to be attained; here measurements of the extent of adsorption were measured after the surfactant solution had been in contact with the oxide for 500 h, but sorption data must still be regarded as 'pseudo-equilibrium.' Nevertheless, the values are of great comparative value since the pore sizes of the oxides are both quite large and so rates of mass-transfer should not be dissimilar. Often the extent of adsorption of such non-ionic surfactants on oxides has been found[3] to increase with increasing temperature, but this is more a reflection of increasing monomer concentration in solution, owing to increased critical micelle concentration with increasing temperature, rather than as a result of increasing the kinetics of adsorption.

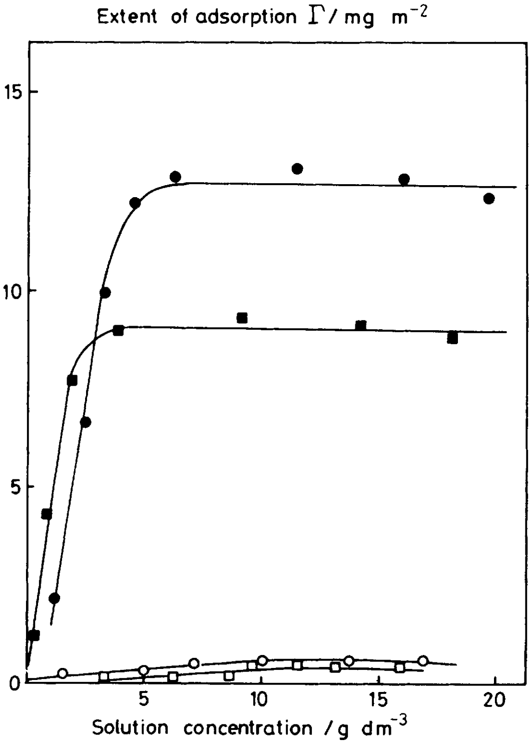

Figure 1. Extent of adsorption of non-ionic surfactants (N111: ○, ●; N150: □, ■) on oxide surfaces (●, ■: silica; ○, □: 'alumina'-coated silica) at 318 K. The method of preparation of alumina-coated silica is given in Table 1. Adsorption on the alumina sample was extremely small as shown in Table 1.

The extent of adsorption of non-ionic ethoxylated surfactants on silica is readily measured and thus the system has been well-studied.[4] Figure 1 shows the adsorption isotherms observed here at 318 K; these approximate to Langmuirian forms. Table 1 shows the values of adsorption uptake observed here at 318 K on silica at an equilibrium solution concentration of 0.03 mol dm^{-3}. Interestingly, the extent of adsorption decreases as the ethoxylate chain length increases, presumably as the area occupied per molecule increases; in addition the areas occupied per molecule are small, suggesting that adsorbate is much more tightly packed than expected.

However, more surprisingly, Figure 1 and Table 1 also show that the extent of adsorption of these surfactants upon the alumina at 318 K was only about 0.8% of the extent seen on the same surface area of silica. This is unlikely to be simply due to any differences in the pore structure between these oxides making the alumina surface less accessible to the surfactants. Why then should their absorption be so low on alumina?

Table 1. Maximum extents of adsorption $\Gamma_{max.}$ of non-ionic surfactants on oxide surfaces at 318 K and 0.03 mol dm^{-3}.

	$\Gamma_{max.}$/mg m^{-2}		
Surfactant	Silica	Alumina	Alumina-coated silica[a]
N111	13.0	0.10	0.50
N150	9.0	0.07	0.40

[a] Prepared by coating the silica sample with 'alumina' by treatment with aluminium hydroperoxide in sodium acetate solution in a similar mode to that used previously for modifying alumina surfaces by alumina solution–dissolution (ref. 10).

Examination of the aqueous surfactant solutions in equilibrium with alumina surfaces by atomic absorption spectroscopy (AAS) and ^{27}Al n.m.r. spectroscopy provided some unexpected information on this point. First AAS showed that although distilled water in contact with the alumina at 318 K contained a negligible concentration of dissolved Al^{3+}, in the presence of surfactant the concentration of Al^{3+} in solution was so much higher that the molar ratio of Al^{3+} : surfactant (N150 or N111) was always in the range 1 : 2 to 1 : 4 irrespective of the initial alumina : water ratio and this ratio increased slightly as the number of ethylene oxide units increased from 11 to 15. Similar AAS of solutions above silica detected no significant Si^{4+} in solution in the presence of surfactants (*i.e.* no more than 0.1 p.p.m. Si^{4+}). ^{27}Al N.m.r. spectroscopy confirmed the formation of an Al^{3+}–surfactant complex, with a significant Al^{3+} peak in either surfactant solution in the presence of alumina (but not water alone or the surfactant solutions above silica) and importantly, this was shifted approximately 60 p.p.m. away from the position observed for $[Al(H_2O)_6]^{3+}$.[5] In addition the Al^{3+} peak in the presence of the surfactants was very much broader than that for the $[Al(H_2O)_6]^{3+}$; this is consistent with the formation of an Al^{3+}–surfactant complex with reduced mobility of the Al^{3+}.

Thus it seems that the dissolution of the alumina is increased by these mildly acidic ethoxylated non-ionic surfactants (whose pH values are in the range 5.5—6.5) even at 318 K with the ultimate formation of these complexes in solution. Conversely, the inclusion of the Al^{3+} and the formation of complexes stabilises the micellar and monomeric species in solution, thereby reducing the extent of adsorption upon a unit area of alumina, relative to that seen on silica.

At low ratios of surfactant : Al^{3+} it is likely that the surfactant chains coil round the chelated Al cation (with Al : surfactant ratios of 1 : 2), but as the surfactant concentration rises it is likely that more than one surfactant molecule chelates to the same Al ion (*i.e.* with Al : surfactant ratios approaching 1 : 4). Complexation of Al^{3+} by linear and cyclic polyethers has been reported previously,[6,7] but this is the first time that it has been associated with inducing a selectivity in adsorption from solution of surfactants.

Al_2O_3–surfactant blends are found in toothpaste formulations,[8] where it is possible that the Al^{3+}–surfactant interactions could be used to induce and possibly control liquid crystal-like properties at high concentrations. Additions of Al^{3+} ions to surfactant blends used in enhanced oil recovery might also reduce the adsorptive-consumption of non-ionic components on silica-rich reservoir rocks. The complexation process is intriguing in its effect in inducing selectivity of adsorption on oxides, but it is probable that it will also find direct application. For example, silica surfaces may be coated with alumina[9] such that the silica takes on the point of zero charge of alumina; the result shown in Figure 1 and Table 1 is that the adsorption of these ethoxylated surfactants on silica *is* reduced by coating with alumina. Therefore, oxides can be coated to produce the required adsorptive properties; equally the adsorption of ethoxylated surfactants from solution can be used to characterise the coverage of, say, silica by alumina and thus act as a surface diagnostic probe. This is potentially useful.

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