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## Adsorption of surfactants onto kaolin

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**Abstract.** In support of an enhanced oil-recovery programme, surfactant adsorption by kaolin and silica from aqueous solution has been studied as a function of several parameters. The resulting isotherms show four distinct steps which are interpreted in terms of different modes of adsorption.

Aqueous surfactant solutions can be used as the basis for improved oil-recovery processes:

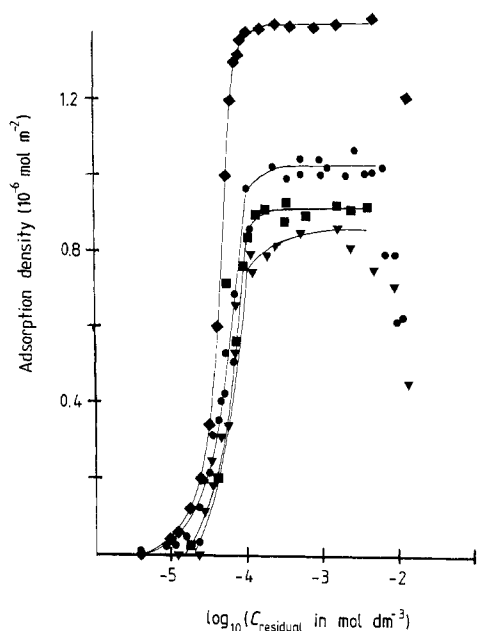
- (i) to produce foams to reduce gas mobility and overcome poor sweep efficiency resulting from fingering and gravity override; and
- (ii) to lower the oil–aqueous interfacial tension, so mobilising water-flood residual oils.

In both processes surfactant loss by adsorption may occur at the solid-liquid interface and so reduce their recovery efficiency (i.e. mass of incremental oil produced per unit mass of surfactant injected) and hence reduce the cost effectiveness of the process to an uneconomical level.

This study was initiated to measure the loss of model surfactant (sodium p-[1-propylnonyl]benzenesulphonate) from aqueous solution under conditions of varying pH, temperature, ionic strength and added alcohol (n-butanol) concentration, in order to infer the steps that might be taken to reduce the loss of a minimum. The loss of surfactant from solution, expressed as  $\mu\text{mol}$  of surfactant per  $\text{m}^2$  of surface (for kaolin and silica, having a BET,  $N_2$  surface area of 8.27 and 300  $\text{m}^2 \text{g}^{-1}$ ), has been determined by two-phase titration [1], spectroscopic absorption, surface tension measurements, and by radiochemical techniques. At identical solid/solution ratios, it was found that the surfactant adsorption by kaolin was some 1000 times greater than that shown by silica (e.g.  $1-10^{-3} \mu\text{mol m}^{-2}$ ) under the same conditions. Experiments with kaolin are therefore easier, and are felt to be more relevant, than those with silica since the clay content of the rock will dominate the adsorption.

Figure 1 shows a typical adsorption isotherm for the surfactant on kaolin at different values of pH. The isotherm shows four distinct steps which can be interpreted as:

- (i) electrostatic adsorption at the positively charged kaolin edges (lowest concentrations);
- (ii) 'hemi- and ad-micelle' formation [2, 3] at intermediate concentrations;
- (iii) the limit of surfactant monomer concentration above the critical micelle concentration; and



**Figure 1.** The effect of pH on adsorption of 4- $\varphi$ -C<sub>12</sub> ABS onto kaolin from 0.1 mol dm<sup>-3</sup> NaCl solution.  $T = 25^\circ\text{C}$ ,  $s/L = 10\%$ , pH = 4.0 (◆), 6.3 (●), 8 (■) and 12.3 (▼)

(iv) solubilisation of Al surfactant salts formed at the platelet edges at the highest surfactant concentrations, leading to reduction in the adsorption.

Additional studies show kaolin to be amphoteric, causing solution pH values to drift towards neutral under both acidic and basic conditions. Allowing for this behaviour adsorption experiments, made over 24 h, showed that at low pH the adsorption was greatest. The surfactant adsorption on kaolin was also found to increase with increased solution ionic strength, and to decrease with increasing temperature and n-butanol concentration. Calculation of the enthalpy of adsorption shows that this is mainly physical adsorption, with certain small areas of the surface (platelet edges) showing electrostatic interactions (patch adsorption: ad-micelles).

By combining the knowledge derived from the above experiments with measured values of the critical micelle concentration in the various solutions, together with the electrophoretic properties of the solids and the position for neutral (zero) surface charge from potentiometric titrations, it was possible to determine the conditions under which losses of surfactant from solution would be at a minimum.

### Acknowledgment

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