Adsorption of Different Surfactants on Kaolinite

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ABSTRACT: The adsorption of anionic, cationic and non-ionic surfactants on kaolinite has been investigated. Anionic surfactants are widely used in enhanced oil recovery. The lower the adsorption on the oil-bearing rock, the higher the advantage of the surfactant to be used. Whilst the adsorption of anionic and non-ionic surfactants are negligible, that of cationic surfactants is relatively high. For this reason, the use of cationic reagents in the enhanced oil recovery is not recommended. The adsorption of cationic surfactants was found to follow an ion-exchange mechanism, while that of anionic and non-ionic surfactants proceeded through electrostatic attraction and precipitation.

INTRODUCTION

Oil extraction involves three stages called primary, secondary and tertiary oil recovery (Myers 1988). In primary oil recovery the oil flows out under the influence of the internal pressure of the entrapped natural gas, while in secondary recovery water is pumped in to displace the oil. By these two means, around 40% of the potential oil is recovered. In tertiary enhanced oil recovery, additives such as polymers and surfactants are used. These help in a number of ways: (i) by lowering the oil/water interfacial tension; (ii) by the spontaneous emulsification of the oil; and (iii) by increasing the wettability of the oil-bearing rocks. Overall, these three effects lead to an increase in the efficiency of oil recovery. The modification of the wetting characteristics of oil-bearing rocks by the addition of surface-active materials is a major area of research into enhanced oil recovery.

A number of such studies have been undertaken. Thus, Kwok \textit{et al.} (1993, 1995) studied the adsorption of anionic and non-ionic surfactants on to sandstone, while Tabatabai \textit{et al.} (1993) investigated the adsorption of anionic and cationic surfactants on carbonate reservoirs. The adsorption of ionic surfactants on clay minerals was studied by Lyklema (1994) who discussed the effects of hydrophobic interaction. Hunter and James (1992) have followed the change in the charge on a kaolinite surface while Austad \textit{et al.}, in a number of studies (1991a–c, 1992a,b, 1994), have discussed different aspects of the adsorption of surfactants on to reservoir clays. Other adsorption systems have also been investigated extensively (Ananthapadmanabhan and Somasundaran 1982; Mehrian \textit{et al.} 1992; Goralczyk 1984, 1993). These studies showed that the adsorption capacity is very much influenced by the temperature, pH, salinity, type and concentration of surfactant employed.

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EXPERIMENTAL

Materials

Kaolinite, collected from the Kalabsha region, Sinai, Egypt, was supplied by the Sinai Manganese Co. Analysis of the sample showed that it consisted mainly of Al₂O₃ (35%), SiO₂ (44%), TiO₂ (4%) and Fe₂O₃ (2%) together with traces of magnesium, calcium, sodium and potassium oxides. The ignition loss was 13–14%. Dodecylbenzene sulphonate (DBS) of 80% purity, cetylpyridinium chloride (CPC) and Triton-100 (TX-100) were obtained from Sigma. The sodium chloride, sulphuric acid, phosphoric acid and nitric acid employed were all of analytical grade.

Methods

The kaolinite sample was ground and sieved, with fractions of less than 60 mesh size being used in the experiments. Treatment of the kaolinite with acids was performed by soaking 50 g of the solid in 100 ml of 20, 50 and 80 vol.% of the respective concentrated acid at room temperature. The resulting suspension was shaken occasionally for 3 d, following which the suspension was filtered and the residue washed many times with copious amounts of distilled water. It was then dried in an oven at 80°C.

The dried samples were subsequently used in the adsorption experiments. Thus, 2 g of the sample were introduced into a 100 ml round-bottomed flask containing 30 ml of the appropriate surfactant solution. The ionic strength of the resulting suspension was maintained at a constant value (1 x 10⁻³ M) by the use of sodium chloride. The contents of the flask were shaken at 25°C for 24 h at 1300 rpm after which the suspension was centrifuged for 30 min at 4000 rpm. In those cases where the resulting solution was still not clear, the above procedure was repeated for a further 30 min. The residual concentration of the supernatant liquid was determined using a Perkin-Elmer UV spectrophotometer, with measurements being undertaken at wavelengths of 224, 267 and 276 nm for DBS, CPC and TX-100, respectively.

Surface tension measurements were made using a DOGNON-ABRIBAT tensiometer (Prolabo) employing the blade technique, with each recorded point being the mean of five readings.

RESULTS AND DISCUSSION

Figure 1 depicts the change in surface tension, γ, as a function of the logarithm of the concentration of DBS, CPC and TX-100 employed. The CMC values observed for DBS, CPC and TX-100 were 2.0, 7.0 and 0.3 mM, respectively. The thermodynamic parameters for adsorption at the air/water interface were calculated using the Gibbs adsorption equation (Adamson 1982). The surface excess concentration (Γ) was calculated at the CMC values for each surfactant and found to be 3.63 x 10⁻¹⁰, 4.32 x 10⁻¹⁰ and 2.4 x 10⁻¹⁰ mol/cm² for DBS, CPC and TX-100, respectively. From these values, the area occupied per molecule at the air/water interface at the CMC region for DBS, CPC and TX-100 was calculated as 0.49, 0.38 and 0.69 nm², respectively. These values are in good agreement with those reported in the literature (Youssef et al. 1990).

Figure 2 shows the adsorption isotherms for CPC and DBS on kaolinite. Inspection of the figure reveals that while DBS shows no appreciable adsorption, CPC attains quite a high adsorption level. Other authors have investigated the adsorption of anionic and cationic surfactants on kaolinite and a variety of different mechanisms have been proposed. Thus, Mehrian et al. (1992), who studied the adsorption of dodecylpyridinium chloride on sodium kaolinite, showed that the adsorption
Figure 1. Variation in surface tension, \( \gamma \), with the logarithm of the surfactant concentration, \( C \), for the various surfactants studied.

Figure 2. Adsorption of CPC and DBS on kaolinite surfaces not subjected to acid treatment.
proceeds both through ion-exchange and electrostatic mechanisms. The isotherm obtained by these workers could be divided into four distinct regions. Region I involves the ionic exchange of the CPC⁺ ion with Na⁺ ions located on the kaolinite surface. This region corresponds to the horizontal orientation of the monomers. A change in the orientation of the adsorbed species on the surface occurs in Region II where the adsorption increases smoothly with increasing surfactant concentration. If the surface area of the kaolinite used in this work is taken to be 12 m²/g as determined by the BET technique, this level of adsorption represents a monolayer coverage of 0.4 nm² per adsorbed CPC⁺ ion. Region III corresponds to the formation of a second layer of adsorbed CPC⁺. In this layer the polar heads are orientated outwards into the medium. The adsorption levels off in Region IV and this may be explained in two ways. Firstly, at the CMC region for CPC (7 mM) the individual species exhibit a preference for micelle formation rather than a third adsorbed layer and, secondly, the orientation of the second layer retards further adsorption of CPC⁺ ions.

In order to obtain further support for this mechanism, the adsorption of CPC was studied on a kaolinite surface which had been pretreated with acid. The results obtained are depicted in Figure 3 and exhibit the following features: (i) the adsorption level of CPC on acid-treated kaolinite is less than on non-treated samples; (ii) the adsorption density decreases as the concentration of acid used in the treatment increases; and (iii) the isotherm trends are quite similar to that obtained previously for CPC with non-treated kaolinite. These features appear to support the proposed mechanism for the adsorption of cationic surfactant on to a kaolinite surface and indicate that such adsorption is significantly affected by acid treatment of the surface. Such treatment causes the replacement of Na⁺ ion sites on the surface by H⁺ ion sites. However, as the density of the Na⁺ sites decreases, the
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Figure 4. Adsorption of DBS on kaolinite surfaces pretreated with various concentrations of sulphuric acid.

Figure 5. Adsorption of DBS on kaolinite surfaces pretreated with various concentrations of nitric acid.
extent of ionic exchange with CPC$^+$ also decreases. This indicates that whereas the CPC$^+$ ion has a high affinity towards the replacement of Na$^+$ ions, such affinity is diminished towards the replacement of H$^+$ ions. In consequence, the adsorption is limited to monolayer coverage. Thus, although acid treatment of kaolinite results in an increase in surface area, the adsorption capacity on the surface is lower than for non-treated samples as a consequence of the lower exchange of CPC$^+$ ions with H$^+$ ions than with Na$^+$ ions.

Figures 4–6 show the adsorption behaviour of DBS on kaolinite pretreated with $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, and $\text{H}_3\text{PO}_4$, respectively. However, inspection of the figures shows that such adsorption was comparatively low. The extent of adsorption appears to increase in the order $\text{H}_2\text{SO}_4 < \text{H}_3\text{PO}_4 < \text{HNO}_3$. For each individual acid, the adsorption levels appear to lie in the order 80% > 50% > 20% for the concentration of acid used in the pretreatment. With increasing sulphonate concentration, the adsorption increased up to a maximum at the CMC value for DBS (1 mM), but decreased dramatically beyond the CMC value. It is clear that the adsorption behaviour of DBS is opposite to that for CPC; whereas the adsorption of CPC is controlled by ion exchange, that of DBS proceeds through electrostatic (or specific) attraction and surface precipitation. Previous workers have shown that sulphonates interact with kaolinite through electrostatic and precipitation mechanisms (Ananthapadmanabhan and Somasundaran 1983). The decrease in adsorption after the CMC value is attributed to the precipitated sulphonate species peeling from the surface and dissolving in the micellar phase. Increasing the concentration of the acid used in the pretreatment of the surface only increased the adsorption capacity to a limited extent. This implies that such acid treatment does not change the surface charge to any great extent. The observed increase in adsorption may therefore be attributed to an increase in the surface area which leads to more surface being available for adsorption.

The adsorption of TX-100 on kaolinite is depicted in Figure 7, from which it is seen that the trend
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Figure 7. Adsorption of TX-100 on a kaolinite surface pretreated with 80% nitric acid (the DBS isotherm is included for comparative purposes).

is quite similar to that for DBS with the extent of adsorption increasing with increasing surfactant concentration up to the CMC value. Yet again, the adsorption capacity decreases beyond the CMC value. This behaviour suggests that the adsorption of non-ionic surfactants on kaolinite follows the same mechanism as that controlling the adsorption of anionic surfactants.

CONCLUSIONS

The adsorption of cationic surfactants on kaolinite was found to be higher than that of anionic or non-ionic surfactants. The adsorption mechanism is suggested to be ion-exchange in nature with Na+ ions being replaced by CPC+ ion species. Acid treatment of the kaolinite depressed the adsorption of cationic surfactants. This was interpreted by preferential exchange of CPC+ species with Na+ ion sites rather than with H+ ion sites on the kaolinite surface.

In contrast, the adsorption of DBS on kaolinite was found to proceed via electrostatic and surface precipitation mechanisms. Acid treatment of kaolinite led to an approximately threefold increase in the adsorption of surfactant species on the surface. Treatment of kaolinite with H₃PO₄ and HNO₃ was found to be more effective in increasing the extent of adsorption of DBS than treatment with H₂SO₄. The adsorption behaviour of non-ionic surfactant was closely similar to that of anionic surfactants. From the calculated area per molecule for each surfactant, it was concluded that the adsorption of anionic and non-ionic surfactants occurs at the sub-monolayer level while that of cationic surfactants leads to bilayer formation.

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