Adsorption of Hydrolyzable Surfactants: Effect of Precipitation on Adsorption of Oleate on Hematite

L.J. MORGAN [1], P. SOMASUNDARAN[1] and S. PARTYKA[2]

[1]*Engineering and Applied Science, Columbia University, New York, NY (U.S.A.)*
[2]*Lab. de Physico-Chimie, Univ. des Sciences, Montpellier (France)*

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ABSTRACT

Adsorption of surfactant at the solid-liquid interface plays a governing role in many separation techniques including the concentration of mineral values by flotation. Good correlation has been obtained between collector adsorption and flotation recovery in a number of mineral-surfactant systems. However, several investigators have not found this to be the case in the hematite-oleate system. We have shown that precipitation and complexation reactions in solution contribute significantly to oleate abstraction. When these are taken into account, pH-dependent adsorption density (under flotation conditions) does show the same trend as flotation recovery. Equilibrium abstraction and adsorption are examined and evidence for specific contribution from dissolved mineral species to surfactant depletion is found. Unexpectedly, a strong effect of S/L ratio on adsorption density has been identified indicating that measured precipitation is underestimated. A method of data handling is suggested to extract adsorption density from total depletion, eliminating the effect of the presence of the mineral bed. Adsorption density is found to be quite low, less than 1% surface coverage. To explain the high hydrophobicity at such low adsorption, a mechanism involving two-point attachment is proposed.

INTRODUCTION

The adsorption of surface-active agents on a mineral surface changes many mineral–aqueous solution interfacial properties. These include both charge and potential characteristics of the interfacial region as well as interaction with the solvent, i.e. wettability by the solvent and, if the particles are colloidal, the stability (or instability) of the suspension. These changes affect subsequent processes significantly. Adsorption at the solid–liquid interface is of major scientific and commercial significance in a wide variety of systems. For mineral beneficiation by flotation, mineral processors have capitalized on this phenomenon, using surfactants as collectors for the concentration of mineral values from gangue materials. It is essential to understand adsorption mechanisms to ensure both the viability and economics of desired processes.

In many systems the adsorption has been correlated with changes in inter-

facial properties and subsequent system behavior. However, this is not always the case. A typical example is hematite flotation using oleate. Previous investigators [1-4] have reported that, although flotation recovery is maximum in the neutral pH region, the oleate adsorption density decreases across the pH range 3-10. This merits further consideration.

Typically adsorption is measured by surfactant depletion from bulk solution; thus if depletion occurs which is not due to adsorption, correlation will fail. Of particular interest in this regard is the adsorption of hydrolyzable surfactants which are very sensitive to solution conditions. Depending upon solution pH, the surfactant forms various species including monomers, dimers, ionomolecular complexes, and precipitated oleic acid. These make different contributions to adsorption and to changes in interfacial properties such as wettability. More recent work on the hematite–oleate system [5-10] has identified a close correspondence between the formation of the ionomolecular complex and maximum surface activity and minimum mineral wettability. Based on size and charge considerations, surface activity of this ionomolecular complex has been predicted to be five orders of magnitude higher than that of the neutral molecule and seven orders of magnitude higher than that of the oleate monomer [9]. Thus in seeking to understand adsorption, account must be taken of the complicated solution chemistry and the possible precipitates and colloidal complexes which may form with dissolved mineral species resulting in high apparent adsorption, that is, abstraction.

The current work recapitulates early findings [11] which identify adsorption under the non-equilibrium conditions of the flotation process. Experimental problems encountered in attempting to study this recalcitrant system are discussed. Equilibrium adsorption at neutral pH (the pH of maximum flotation) is investigated by determining isotherms which distinguish adsorption from abstraction. Calorimetric experiments attempt to measure the enthalpy of the adsorption interaction. These results also reflect the difficulty in studying oleate adsorption, making evident that other phenomena such as precipitation mask the event of interest.

EXPERIMENTAL

Materials

Small vials, each containing 10 mg oleic acid (> 99%) and sealed under N_2 have been obtained from NBCo Biochemicals (a subsidiary of ICN Radiochemicals). As-received vials are stored in a freezer. Reports from several investigators [11-14] indicate that handling oleate solutions requires special precautions to assure reproducibility. Exposure to oxygen must be avoided as much as possible and the age of solutions carefully controlled. In a glove bag with nitrogen atmosphere, using clean, disposable glass pipettes to effect

transfer, stock solutions are made by repeated rinsing of the vial with water at pH 11; the solutions are also stored in the glove bag. As needed, the stock solution is transferred into a flask, removed from the glove bag and diluted to obtain the required concentrations. The stock solution is kept only a few days to avoid possible effects of oleate degradation.

Radioactive oleic acid (>99%, manufacturer's chromatographic analysis) with ^{14}C in the 1-carbon position and having a specific activity of 50 mCi mmol^{-1} was purchased from ICN Radiochemicals in small ampules sealed under argon atmosphere. Ampules of as-received oleic acid, each containing 0.1 mCi in benzene, are stored in a freezer. As indicated above, oleic acid and stock solutions are only opened inside the nitrogen atmosphere glove bag. To prepare radioactive stock solution, an ampule is placed in a desiccator inside the glove bag. The desiccator is then brought out of the glove bag and the benzene evacuated. Under the N_2 atmosphere, the oleic acid is transferred to a flask using clean, disposable glass pipettes by repeated rinsing with water at pH 11. The oleate stock solution is kept in the glove bag.

Synthetic hematite (>99.9% iron oxide) of relatively high surface area ($SA \approx 7.2$ m^2 g^{-1} by N_2 adsorption method) was purchased from Alfa Chemicals, Thiokol Division. It would have been preferable to use ore, however, iron ore samples are generally of low surface area and hence not very suitable for studies to elucidate adsorption mechanisms*. The ore sample used in the earlier work [11] was also >99% pure. At the same S/L ratio, adsorption density on the two samples compared reasonably well.

Ultrapure grade potassium nitrate and potassium hydroxide were also obtained from Alfa Chemicals. Reagent grade nitric acid was obtained from Amend Drug and Chemical Corp. KNO_3 is used to control the ionic strength and KOH and HNO_3 are used to adjust the pH. Ferric nitrate is of certified A.C.S. grade and purchased from Fisher Scientific.

Procedures

Adsorption

Experiments are conducted in glass test tubes (total volume 15 cm^3) covered by Teflon tape and screw-on caps. Agitation is by tumbling in an insulated, constant temperature, wooden incubator; all tests are conducted at 24 °C. Oleate analysis is performed by the radiotracer technique using a Beckman Scintillation Counter (LSC-100). The final pH is measured after each experiment. To isolate the various contributions to depletion and to calculate adsorption, three types of depletion experiments are carried out: abstraction, precipitation

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*Even a tungstgen carbide shatter box produced only 1.6 m^2 g^{-1} specific surface area of the ore sample after 2.5 min comminution. After such an intense process, even at short duration, extreme heat is generated and agglomeration observed.

and control. In each case, conditioning is for 10 h and centrifugation (IEC clinical centrifuge set at 4) is for 10 min.

Abstraction. In the abstraction experiment, 1 gram of solid is pre-equilibrated for 2 h in 5 cm^3 of 2×10^{-3} M KNO_3 at pH 8.0. Then, 5 cm^3 of oleate solution (pH 8.0) is added at known concentration (and radioactivity). After conditioning and centrifugation, the supernatant is analyzed for residual oleate.

Precipitation. For the precipitation experiment, mineral supernatant is prepared by conditioning 2 grams of hematite in 10 cm^3 of 2×10^{-3} M KNO_3 at pH 8.0. After centrifugation, 5 cm^3 of supernatant are taken and conditioned with 5 cm^3 of oleate solution (pH 8.0). After centrifugation, the solution is analyzed for residual oleate.

Control. In the control experiment, 5 cm^3 of oleate solution (pH 8.0) is conditioned in the electrolyte solution at pH 8.0. Analysis for residual oleate is done after centrifugation.

Calorimetry

Two types of differential calorimeters are used in this study. A Setaram calorimeter [15] which has been modified to measure the enthalpy developed by adsorption in suspended systems, has been described elsewhere [16]. The total heat evolved includes not only the heat of the abstraction (depletion due to adsorption, precipitation and complexation), but also the dilution of the surfactant solution and desolvation of the mineral interface as solvent molecules are replaced by adsorbing surfactant molecules. An LKB Batch Microcalorimeter (2107) was used to investigate heats of solution, dilution and mixing oleate with ferric species.

RESULTS AND DISCUSSION

Adsorption

Often hematite–oleate system adsorption and flotation results in the literature show a sharp maximum in flotation at neutral pH and a decrease in adsorption with increase in pH. There have been several problems in comparing these two sets of data [11]. Primarily, all depletion of surfactant from bulk solution had been attributed to adsorption at the solid/liquid interface and also flotation and adsorption experiments were conducted under dissimilar conditions. In the first stage of work, experiments were conducted using identical conditions, same particle size and same conditioning time. Additionally, separate experiments distinguish between depletion from bulk solution (precipitation experiment) and total depletion in the presence of the mineral

(abstraction experiment) in order to identify that depletion was due to adsorption. Adsorption calculated from the difference between depletion in the abstraction experiment and depletion in mineral supernatant correlates much better with flotation [11].

While doing these studies, many experimental difficulties were encountered, most serious among them, lack of mass balance. In order to account for all of the oleate added to the tests, meticulous tracking was required. It became apparent that in spite of the numerous investigations on the hematite–oleate system, the adsorption behavior was not yet fully understood. In this part of the study, equilibrium adsorption is examined using solution conditions for which the mineral exhibits maximum hydrophobicity, that is adsorption at neutral pH.

When the decrease in oleate concentration is monitored closely so as to distinguish among the various types of depletion, interesting phenomena appear. The results for such a study at low ionic strength and initial pH 8.0 are shown in Fig. 1. The depletion isotherm in the presence of the mineral shows a smooth monotonic increase. That in the mineral supernatant shows a similar shape with lower depletion . Interestingly, when oleate is conditioned in the solvent $(2 \times 10^{-3} M$ $KNO_3)$ alone, there is also depletion and different from that in mineral supernatant. These tests are run in parallel with the same quantity of identical oleate solution added into each of the three tests. The difference in final counts is significant in each case reflecting the different depletion behavior.

The separate curves for the control and precipitation experiments suggest a specific contribution to surfactant depletion from dissolved mineral species. In the past hematite has been considered an insoluble mineral and indeed the solubility is so low that no convenient analytic technique exists for its determination. In this work, colorimetric tests using ammonium thiocyanate complexing agent essayed ferric analysis. Although quite useful above 1 ppm iron content (using $Fe(NO_3)_3$ solutions), no color developed in mineral supernatant even when extracted by amyl alcohol. Unfortunately, inductively coupled plasma spectroscopy also has a practical sensitivity limit of about 1 ppm iron. The solubility diagram of hematite [17] shows that over the pH range of interest, 4 to 10, the solubility is governed by the formation of $Fe(OH)_3$. Total iron in solution is only about $10^{-8} M$ or 0.001 ppm. However, the effect of oleate on the mineral solubility is not known. In any event, as the pK of $Fe(OH)_3$ is reportedly 34.2 [18], the solubility product is readily exceeded. For example, at $10^{-8} M$ Fe^{3+}, only $2 \times 10^{-9} M$ oleate is required. Thus it seems colloidal precipitates of oleate with dissolved mineral species could be playing a role. Oleate depletion measured in solutions of ferric nitrate corroborates this finding, however, at these concentrations, independent verification of the formation of ferric–oleate complexes is quite difficult.

From the difference between the depletion isotherms for the abstraction and precipitation experiments shown in Fig. 1, the adsorption of oleate on hematite
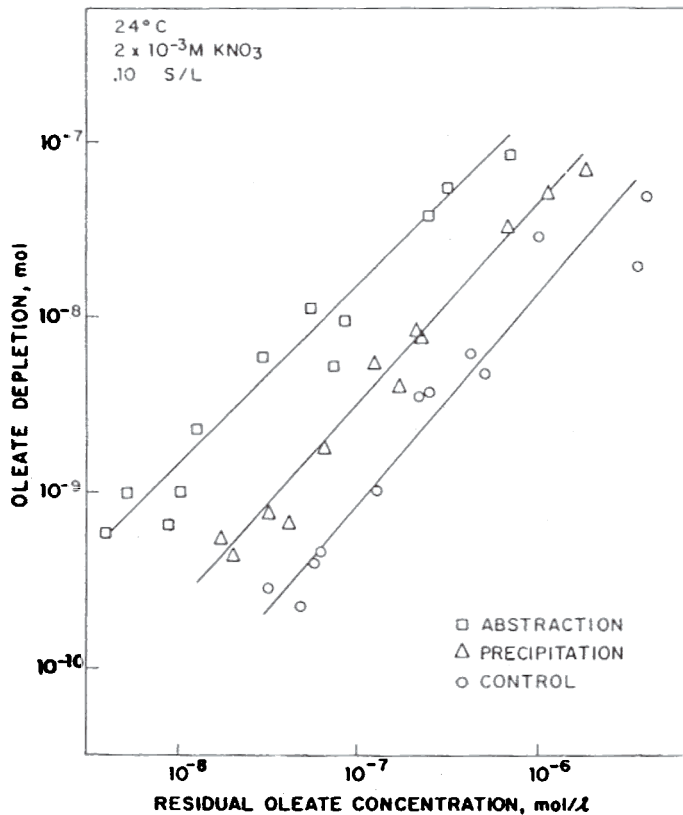
Fig. 1. Depletion isotherms for oleate on hematite for three types of tests: abstraction, precipitation and control.

can be calculated. The adsorption isotherm seen in Fig. 2 also increases monotonically and is relatively low. In this system, the maximum concentration of oleate added is restricted by the precipitation limit of oleic acid*. Once the acid precipitates, the solution becomes turbid and uncertainties arise about solution homogeneity and reproducible delivery of surfactant to the test; this narrows the range of the isotherm.

It was surprising to find the low adsorption density with no evidence of surfactant aggregation (usually indicated by a sharp increase in isotherm slope) since highly hydrated oxides such as hematite have been thought to require adsorption density of the order of hemimicellization in order to be floated [20].

Although these tests do take into account depletion in mineral supernatant, it is possible that not all of the precipitation has been accounted for. For the

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*Solubility is higher at high pH, however, there is then the problem of pH shock and possible irreversibility if oleate at e.g., pH 11 is added to the adsorption system and then the pH reduced.
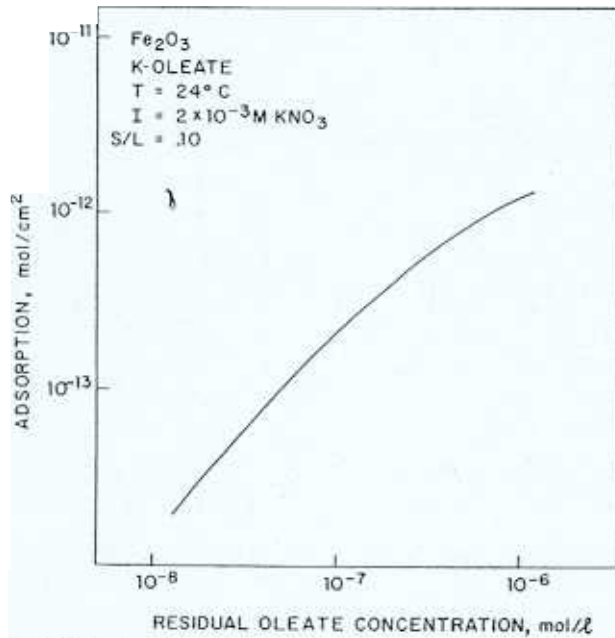
Fig. 2. Oleate adsorption isotherm calculated from difference between abstraction and precipitation tests.

precipitation test, the mineral is removed from the supernatant and a finite amount of dissolved species is available. If the mineral in the abstraction experiment serves as a reservoir, continuously releasing dissolved species or if the solubility is enhanced by oleate, adsorption will be artificially increased. Another possible contribution to the underestimation of the precipitation is the entrapment of colloidal precipitates; if these remain in the suspension after centrifugation in the precipitation experiment but are captured by the settling particles during centrifugation in the abstraction experiment then they report as additional adsorption. One way to check for artifacts is by varying the solid–liquid ratio.

Ideally, adsorption density should not depend on the amount of solid present. The results shown in Fig. 3 are in sharp contrast to this, showing a significant dependence of the adsorption density on the amount of solid present. While the adsorption density (at constant residual oleate) versus solid present should yield the adsorption, eliminating any entrapment, in this instance the adsorption density asymptotes to infinity at zero solids. Alternatively, consider the total depletion which is due to that which adsorbs and that which precipitates [19].
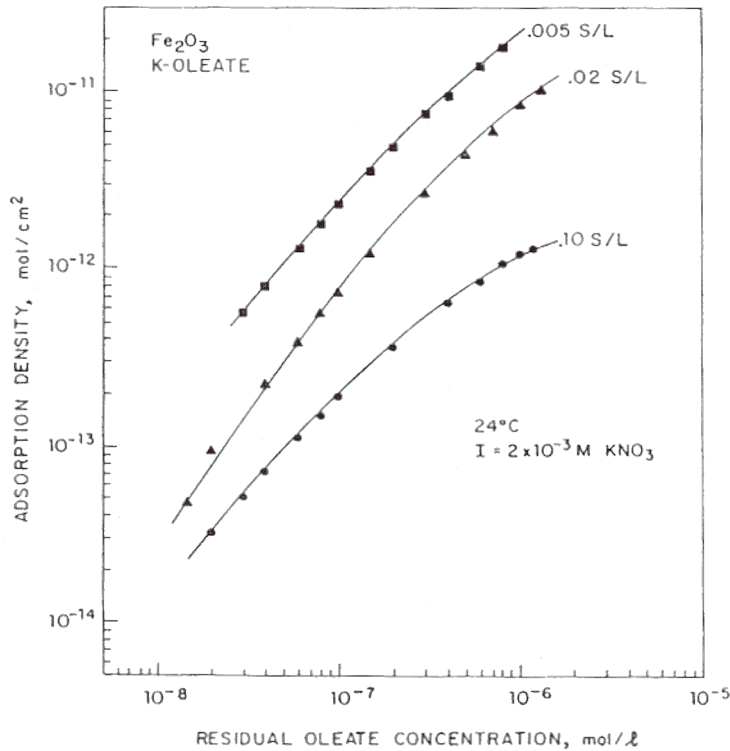
$$\Delta C = \Gamma(SA) + P$$

Fig. 3. Effect of solids loading on adsorption isotherm.

where ΔC is the depletion, Γ the adsorption density (mol cm^{-2}), SA the surface area available (cm^2), and P the precipitation (mol). As the surface area increases with additional solid, at equilibrium, the adsorption density should remain constant but the total amount adsorbed will increase. The precipitation on the other hand should remain constant. Thus a plot of depletion versus amount of solid should have a slope related to the adsorption density by a factor of the specific surface area. The depletion data are shown in Fig. 4; with a tenfold increase in surface area available for adsorption there is but slight increase in total depletion. Or, most of the depletion is entrapment and precipitation. The linear plot of depletion versus solid is shown in Fig. 5. The precipitation calculated from the intercepts is two to three times that measured in the precipitation experiments and the slopes are used to calculate the adsorption isotherm shown in Fig. 6. Again, it is noteworthy that the adsorption density is so low, less than 1% surface coverage, and yet has given rise to a sufficiently hydrophobic surface to achieve flotation.

Previous investigators have hypothesized several mechanisms to explain the behavior of the hematite–oleate system. These usually suggest that che-
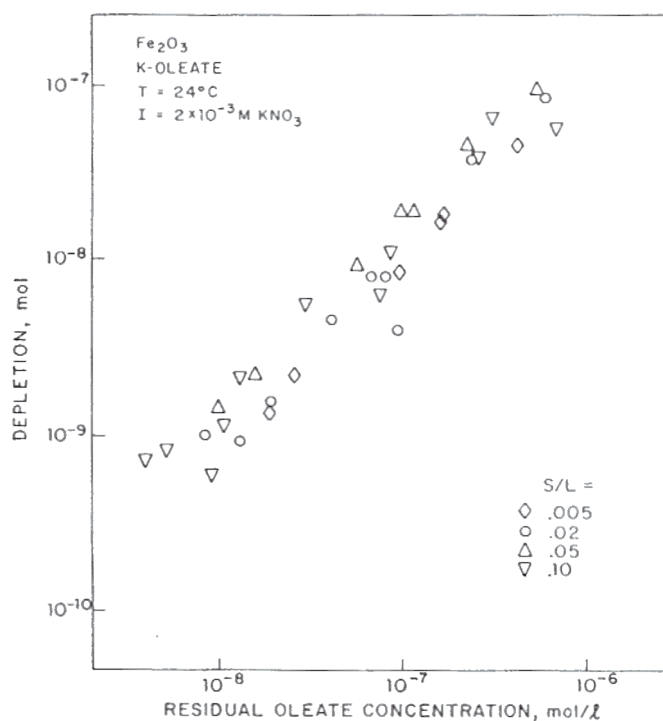
Fig. 4. Total oleate depletion at different solids loading.

misorbed oleate is responsible for the hydrophobicity reflected in flotation behavior [1–4,20]. Some say that oleate physically adsorbs from acidic media and this does not impart the requisite hydrophobicity [1–3]. In an attempt to identify the type of interaction leading to adsorption, calorimetric experiments have been carried out.

Calorimetry

Experiments aimed at measuring thermodynamic properties of the adsorbing system should help elucidate mechanisms. Calorimetry offers a good opportunity for this and has been used in the past with some success [16, 21–24]. However, in this case, very small heats were evolved and the data were widely scattered. All that can be concluded from these experiments is that the overall heat (including adsorption, surfactant dilution, desolvation, counterion replacement in the double layer, etc.) is endothermic and that the heat evolved is of the order of -10 kJ mol^{-1} of oleate abstracted.

Several kinds of experiments were carried out in the LKB Calorimeter in order to understand the contributions of solution mixing to the total abstraction heat and to try to obtain an independent measure of any specific inter-
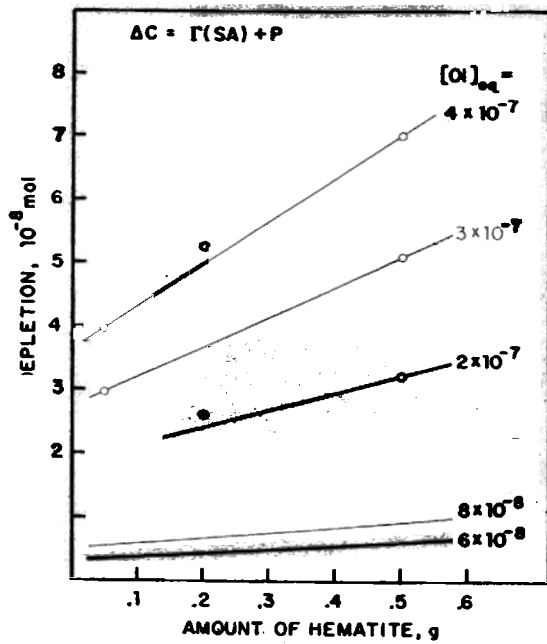
Fig. 5. Effect of solids loading on oleate depletion at constant residual oleate.
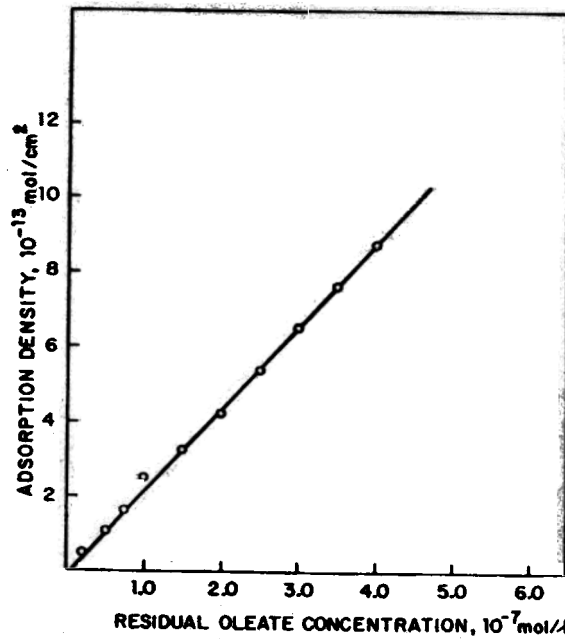

Fig. 6. Calculated oleate isotherm having eliminated the effect of the presence of the mineral bed by using the slopes from Fig. 5.

action between iron solution species and oleate species. Findings are inconclusive because total heat evolved is approximately the detection limit of the instrument; it is, however, always exothermic and of the order of $+5$ kJ mol^{-1}. Compared with the total abstraction heat, these results seem to suggest that the adsorption interaction is of the order of an endothermic 15 kJ mol^{-1}. However, since chemisorption and physisorption by either hydrogen bonding or electrostatic interaction are expected to be exothermic, it is clear that the heat from the adsorption event is masked by other phenomena.

In order to explain the hydrophobicity achieved at such low adsorption density, it is proposed that adsorption involves a chemisorption reaction between the oleate polar head forming a ferric–carboxylate species and, in addition, interaction using the pi electrons of the oleate double bond. A geometrically scaled model shows the flexibility of the molecule does permit such a two-point attachment and this affords a relatively large hydrophobic patch per adsorption event. It has already been conclusively shown that the ionomolecular complex is a major actor contributing to surface activity [5-9], thus two-point attachment of the complex may explain the high hydrophobicity at low adsorption density.

SUMMARY AND CONCLUSIONS

In the study of the adsorption of hydrolyzable surfactants whose chemistry is quite sensitive to solution pH conditions, great care must be exercised to avoid experimental artifacts and thus erroneous interpretation. In the hematite–oleate system, the surfactant is significantly depleted in the mineral supernatant and this depletion should be subtracted from that in the presence of the mineral in order to calculate the adsorption density. However, similar tests varying solid–liquid ratio suggest that even this may not account for all non-adsorptive contributions to depletion of oleate from the bulk solution. A method to handle the data has been suggested to calculate adsorption density, eliminating the effect of the presence of the mineral bed. Interestingly, the difference between depletion in solvent alone and in mineral supernatant suggests a specific interaction between dissolved mineral species and surfactant species even though the concentration of dissolved mineral species is below the detection limit of analysis. The high hydrophobicity imparted by the low adsorption density may be explained by adsorption via two-point attachment of oleate or oleate–oleic acid ionomolecular complex.

ACKNOWLEDGEMENT

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