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N.K. Khosla and G.N. Jadhav
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Adsorption of Oleic Acid on Calcium Minerals

K. Chennakesavulu, G. Bhaskar Raju* and S. Prabhakar

National Metallurgical Laboratory (Madras Centre)
CSIR Madras Complex, Taramani. Chennai-600113. India
E-mail: *gbraju55@gmail.com

ABSTRACT: Adsorption of oleic acid on fluorite and calcite was studied by adsorption isotherms and Electro kinetic measurements. The adsorption of oleic acid on calcium minerals was observed to proceed initially by monolayer formation at lower concentrations followed by the physical adsorption of hydrocarbon chains in the second layer and finally the precipitated calcium oleate at higher concentrations. Compared to calcite, oleic acid was found to adsorb on fluorite at very low equilibrium concentrations. From the zeta potential measurements. the iso electric point (iep) values of fluorite and calcite are found to be 10.5 and 8.5 respectively. In presence of oleic acid the iep values of fluorite and calcite are shifted to 3.0 and 5.8 indicating specific chemical·interaction between surface calcium and oleate ions. The Free energy of adsorption was calculated from adsorption and Zetapotential measurements. The sign and magnitude of ΔG_{sp} suggest the chemisorption of oleic acid on fluorite and calcite.

1. INTRODUCTION

Sparingly soluble calcium minerals such as fluorite, calcite, apatite and scheelite are important raw materials for chemical, cement, fertilizer and metallurgical industries. These minerals are beneficiated by flotation using oleic acid/sodium oleate as collector. The individual occurrence of these minerals in pure state is very rare and they are mostly available as a mixture of calcium minerals in different proportions. The selective separation of one calcium mineral from the other calcium minerals is a challenging task due to similar surface characteristics. Generally froth flotation is adopted using oleic acid as collector and starches and tannins as depressants for the individual separation of calcium minerals. They are separated by taking advantage of hydrophobic, hydrophilic properties of the particles created by the addition of specific flotation chemicals. The mechanism of adsorption of oleate on calcium minerals was extensively studied and a comprehensive review of the subject was published (Finkelstein, 1989; Hanumantha Rao et al., 1992). Various mechanisms viz electrostatic interaction, chemisorption, surface precipitation, chemisorption followed by surface precipitation and chemisorption followed by the formation of hydrophobic associates have been reported. The adsorption density was reported to be different when the dry mineral powder was added in to the oleate solution and oleate added in to the suspension. of mineral equilibrated with water. Also, the interpretation of adsorption isotherms of fatty acids on calcium minerals is complicated due to the fact that the fatty acids are capable of forming the precipitated phase with dissolved calcium ions. The adsorption studies of calcite, apatite and fluorite in the presence of sodium oleate suggest the two dimensional condensation of oleate on mineral surface (Hanumantha Rao et al., 1989; Hanumantha Rao et al., 1990). These studies also showed mono-layer coverage in the case of calcite, and bilayer formation in the case of apatite and fluorite. prior to the precipitation of calcium oleate which is characterized by a vertical step in the adsorption isotherms. The present study is a part of the broader project work on the selective separation of fluorite from the gangue containing calcite and apatite.

2. MATERIAL AND METHODS

2.1 Materials

The natural fluorite sample assaying 99% CaF_2 was obtained from the fluorspar mines of Kadipani. Gujarat. High grade calcite powder and oleic acid was procured from Acros organics, USA. The fluorite sample was ground to the required

particle size using an agate mortar to minimize the contamination. The average particle size and the specific surface area of the samples were determined using CILAS particle size analyzer and Micromeritics (ASAP Model) BET surface area analyzer. The average particle size and surface area of fluorite sample is 12.49μm and 0.2166 m^2/g and calcite sample is 60.42μm and 0.7196 m^2/g. All the other chemicals used in the present work are of Analar grade.

2.2 Determination of Oleic Acid

Fresh solutions of sodium oleate were prepared daily. A few drops of NaOH solution were added to get a clear solution. The amount of oleate adsorbed was determined from the difference in initial and final concentrations. Adsorption tests were carried out in 250 ml Erlenmeyer flasks. The known quantity of mineral sample was suspended in water at desired pH value and equilibrated at known concentration of oleate for 30 minutes. Preliminary studies showed that the adsorption of oleate from the solution was a fast process and equilibrium is attained with in a short time. After equilibration, the suspension was centrifuged and the supernatant solution was analysed for un-adsorbed oleate by the standard procedure (Gregery, 1966).

2.3 Fluoride Ion Estimation

Fluoride in aqueous solutions was estimated using Ion Selective Electrode meter (Orion 920 A^+ model).

2.4 Zeta Potential Measurements

Zeta potential measurements were conducted by a Zeta acoustic sizer (Dispersion Technology, U.S.A) equipped with video system. Constant ionic strength of 0.1M KCl was maintained in all the experiments.

3. RESULTS AND DISCUSSION

3.1 Adsorption Isotherm

The adsorption behaviour of oleic acid on fluorite and calcite was studied at different concen-

trations and the results are shown in Figure 1. It is apparent that by increasing the oleic acid concentration, the adsorption density also increases and attains a plateau around the adsorption density of 10 μmole/m^2.
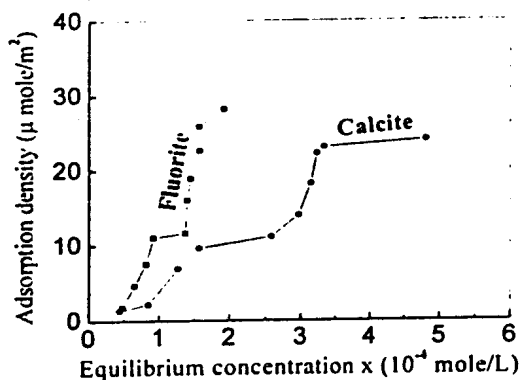

Fig.1: Adsorption isotherm of oleic acid on fluorite and calcite

Further increase in the concentration of oleic acid beyond the region of plateau leads to steep increase in adsorption density. If the adsorbed oleic acid is in the form of liquid crystal with its parking area of 33$Å^2$, the monolayer coverage is expected at 5 μmole/m^2 (Cases et al., 1985). On the other hand if the oleic acid is adsorbed in the form of hydrated oleate molecule, with a parking area of 20.5 $Å^2$, monolayer coverage is expected around 8μmole/m^2. The ionic surfactants containing more than 8 methyl groups in the alkyl chain are expected to condense two dimensionally on mineral surface because of the strong lateral bonds. Due to surface heterogeneities, the condensation initially takes place on homogeneous domain on most energetic sites at a lower concentration of oleic acid followed by successive two dimensional condensations on less energetic homogeneous domain. Hence in the monolayer range, the isotherm can take a shape of several small vertical steps or a smooth curve depending on the distribution of surface energies. But once the monolayer is covered, the bilayer formation always takes a single sub vertical step due to the homogeneity of the surface caused by the monolayer formation. In the present study, the isotherms clearly show a plateau around 10μmole/m^2. The plateau corres-

ponding to the monolayer could not be seen may be due to low surface area and high oleate concentration. Fluorite was ground to a very fine size to obtain a fine powder with high surface area. Adsorption experiments were conducted using this fluorite powder at very low oleic acid concentrations. The increment of oleic acid concentration was maintained as close as possible. The results were plotted in Fig. 2. Plateau at the adsorption density of 5.0 μmole/m^2 could be seen when the surface area was nearly increased to four fold.
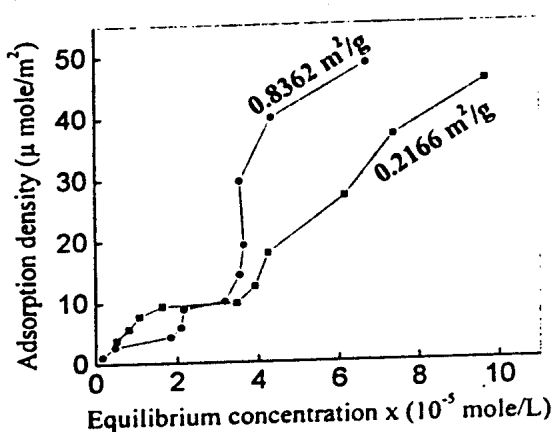

Fig. 2: Adsorption isotherms of oleic acid on fluorite

Thus it could be concluded that oleic acid initially forms monolayer followed by the bilayer as the concentration is increased. Bilayer formation is always feasible due to the association of hydrocarbon chains through tail-tail bonds. The steep increase in adsorption density beyond the plateau value is attributed to precipitation of calcium oleate on the surface. The oleic acid is expected to react with dissolved calcium ions and the precipitate thus formed in turn adsorb on the mineral surface. It was shown that (Anantha Padmanathan et al.,1979) the conditions of ionic concentrations at the interfacial region could satisfy the solubility product limit before it is reached in the bulk solution, which led these authors to suggest that the so called chemisorption is infact a process of surface precipitation or more probably three dimensional growth on substrate. From the present study, it could be seen that the adsorption of oleate molecules on

calcium minerals proceed by monolayer, bilayer and finally precipitation of calcium oleate. The preferential partition of oleate on to fluorite compared to calcite even at low equilibrium concentrations could be attributed due to favorable thermodynamics. Comparatively, the calcite surface is more hydrated than fluorite. Hence slightly higher equilibrium concentration of oleic acid is required to adsorb on the highly hydrated calcite surface.

The concentration of fluoride ion in aqueous solution was measured to see whether the F$^-$ ions from the mineral surface are released while oleate is adsorbed (Ion exchange mechanism). The results shown in table 1 clearly suggest that the concentration of fluoride ion almost remained same during the adsorption of oleate. Hence it could be concluded that the adsorption of oleate on mineral surface is not governed by ion exchange mechanism.

Table1: Effect of oleate adsorption on fluoride

Conc. Oleic acid (ppm)	Conc.Fluoride (ppm)
13.5	8.04
27.0	7.03
40.5	6.80
54.0	5.92
67.5	4.98
81.0	4.81
94.5	4.18

3.2 Zeta Potential Measurements

Zeta Potential is a very good tool to understand the interaction of oleic acid at mineral water interface. The zeta potential of calcite and fluorite at different pH values and in the presence of oleic acid was measured and the results are shown in Figs. 3- 4. It is apparent that the iso electric point (iep) of fluorite and calcite was observed at pH 10.5 and 8.5 respectively. In the presence of oleic acid the iep values of fluorite and calcite were shifted to 3.0 and 5.7 respectively. This characteristic shift in iep is usually attributed to specific interaction between reagent molecules and the surface sites (Pradip, 1988). Thus it is evident that the oleic acid is

adsorbed on fluorite and calcite by specific chemical interaction. The shift in iep depends on the magnitude of specific free energy of adsorption, that is, on the affinity of the adsorbing oleate for the surface sites.
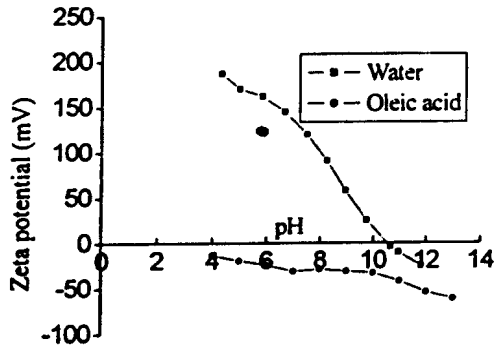

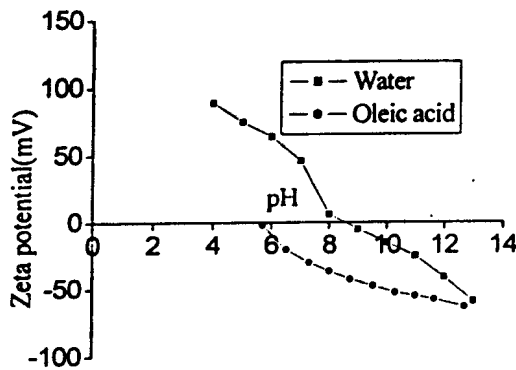**Fig.3:** Zetapotential of fluorite as function of pH

Fig.4: Zetapotential of calcite as a function of pH

3.3 Free Energy of Adsorption from Adsorption Isotherms

Free energy of adsorption was evaluated both from the adsorption results and zeta potential measurements. Adsorption densities up to mono-layer coverage were taken in the calculations.

The Stern - Graham equation is applied to assess the magnitude of the free energy of adsorption (ΔG°_{ads}).

$$\Gamma_d = z \, r \, C \, exp \, \Delta G^{\circ}_{ads} \, RT$$

Where Γ_d is adsorption density (mole/m²), r is the effective radius of the adsorbed ion, C is the equilibrium concentration mol/lit, R is the gas

constant, T is absolute temperature, and z is the valency of the adsorbed ion. The area per molecule of oleic acid is considered as 33 Å². The above equation can be rearranged as

$$\Delta G^{\circ}_{ads} = RT \, z \, r \, C \, / \, \Gamma_d$$

The free energy of adsorption was found to be 6.9 and 6.5 for fluorite and calcite respectively. The sign and magnitude of the ΔG°_{ads} values show that the oleic acid adsorption at the calcium minerals is due to chemisorption.

3.4 Free Energy of Adsorption from Electrokinetic Data

Free energy of adsorption can also be calculated from ξ potential measurements. For oxides, the potential determining ions being H^+ and OH^-, it can be related to ΔG°_{sp} (Pradip, 1988) as

$$\left[pH_{ ext{ipt}} - pH_{ ext{ipt}}\right] = \frac{-ZF^2 . \Gamma_m}{2.303 . RTC_s\left(1 + \dfrac{55.5}{C_s \exp\left[\dfrac{\Delta G^*}{RT}\right]}\right)}$$

Where F is Faraday constant, Γ_m is adsorption density, C_δ is capacitance of electrical double layer, C_0 is initial concentration of oleic acid, R is gas constant and T is temperature.

The Γ_m can be calculated from the cross sectional area of oleic acid i.e. 33 Å² and the C_δ value of 20 μF/cm² was used as reported in literature. Free energy of adsorption was calculated using the above mentioned equation and the same was found to be 8.05 kcal/ mole. Similar calculations were performed by taking in to account the shift in iep value for calcite – oleic acid system. The free energy of adsorption in this case was found to be 8.3 kcal/mole. The free energy of adsorption values obtained from two different approaches i.e. adsorption data using Stern – Graham equation and electro kinetic data are comparable. It is however to be noted that the discrepancy between the two values may be ascribed to assumption of C_δ value for oxide-water interface. By judicious choice of Γ_m and C_δ uniform values of ΔG°_{sp} can be obtained if the investigations were carried out carefully and under identical conditions. Thus the free energy of adsorption values obtained by both methods

clearly establishes the chemisorption of oleic acid on fluorite and calcite.

4. CONCLUSIONS

Adsorption of oleic acid on fluorite and calcite was studied .by adsorption isotherm and zeta potential measurements. Adsorption isotherm has exhibited two distinct plateaus. At very low equilibrium concentrations the isotherm was found to level off at the adsorption density of $5\mu m/m^2$ corresponding to mono layer formation. Second Plateau corresponding to bi layer formation was observed at $10\mu m/m^2$. The nature of adsorption during the course of monolayer formation was attributed to chemisorption. Zeta potential measurements have revealed shift in isoelectric point in the presence of oleic acid indicating chemisorption between oleic acid and calcium on the surface. Free energy of adsorption was calculated both from adsorption and zeta potentials. The sign and magnitude of free energy also suggest chemisorption of oleic acid on fluorite and calcite.

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