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5.9. Interaction of Oleate Molecules on Sillimanite and Garnet Minerals

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ABSTRACT: Adsorption of oleate on sillimanite and garnet was studied using electrokinetic measurements. Both the systems exhibit a characteristic shift in iep by increasing the concentration of oleate in solution. This shift in iep has been quantified in terms of specific interaction between the surface sites and oleate molecules. ΔG°_{sp} was estimated separately for both the systems using the equation derived on the basis of electrical double layer theory. The specific free energy of adsorption was estimated to be 7.94 kcal/mole for sillimanite-oleate system and 7.49 kcal/mole for garnet-oleate system.

Introduction

Sillimanite and garnet are obtained from beach sands and are mostly associated with other heavy minerals. Sillimanite is generally beneficiated by flotation using oleic acid as collector. Adsorption of oleate on sillimanite and garnet was examined in the present study by electrokinetic measurements. Surface properties of the minerals are generally influenced by the structure of mineral/water interface and by surface species. Wetting of mineral with water generates a surface charge and a region of electrical in-homogeneity at the solid / water interface. The charge on the mineral surface is controlled by two processes viz., a) adsorption of water molecules, H^+ and OH^- ions on the solid surface followed by a dissociation of the hydrolytic products formed and b) preferential release of certain lattice ions, ion species from the solid phase as a result of different hydration energies and re-adsorption of hydrolytic lattice products. Net positive or negative charge is generally compensated by a region of counter ions (H^+ , OH^- , lattice ions etc.,) of the opposite sign from the bulk phase. Thus an electrical double layer (EDL) results at the mineral-water interface which in many cases has an important role in the adsorption of surfactant. The EDL consists of a fixed and a mobile component. In the classical GChSG model, electrical double layer results from Gouy and Chapman's [1] conception of the diffuse layer, that is characterised by the Poisson-Boltzman equation and a layer of specifically adsorbed ions according to Stern and Grahame [2]. GChSG model assumes a firmly bound layer of adsorbed dehydrated (Grahame plane or inner Helmholtz plane) and hydrated (Stern plane or outer Helmholtz plane) ions on the electrically charged mineral surface and a layer of free mobile hydrated ions which are on the boundary towards the bulk phase in a diffused state (Gouy's layer). For the interpretation of the adsorption process, it is important to know the zeta potential (ξ) that can be calculated from the electrokinetic measurements. It may be defined as the potential difference at the shear plane between the diffuse layer outside the slipping plane and the bulk phase, when the solid and liquid phases move tangentially to each other. Hunter and Alexander [3] have located the slipping plane within a distance of 1 nm from the surface of kaolinite and Furlong et.al [4] had predicted the distance between the

shear plane and the outer Helmholtz plane with in a few tenths of nm, so that zetapotential is approximated to Stern potential ($\xi \cong \Psi_\delta$). It has been well demonstrated in the literature that except for very long chain polymers, assuming zeta potential to be identical to Ψ_δ is a reasonably accurate approximation [5-6]. Under such conditions, changes in the zeta potential will reflect changes in the surface potential [7]. One of the most powerful techniques of studying solid/liquid interface, in particular the surfactant/interface interactions is through electrokinetic measurements carried out in situ in aqueous surfactant solutions. It is possible to distinguish between physisorption (adsorption through electrostatic interaction) and chemisorption (adsorption via chemical bonding) of surfactant through electrokinetic investigations [8-10]. A method, based on the determination of iso electric point (iep) and the point of zero charge (pzc) of solids, for the interpretation of chemisorption at the mineral / water interface was proposed by Salim Akhtar and EongLip Lai [11]. Adsorption of oleate on hematite was interpreted as chemisorption based on shift in iep value.

In the present investigation, the specific free energy of adsorption (ΔG_{sp}°) was estimated using electro kinetic data.

Theoretical background

When solids are brought into contact with aqueous solutions, they develop a region of electrical inhomogeneity at the solid/solution interface. An excess charge (+ve or -ve) apparently fixed at the solid surface is exactly balanced by a diffuse region of equal but opposite charge on the solution side. In order to distinguish between the adsorption mechanisms, it is appropriate to quantify the adsorption process through ΔG_{ads}° (the free energy of adsorption). ΔG_{ads}° being thermodynamic quantity, can be conveniently assumed to comprise of a number of additive terms contributed by various interactions.

$$\Delta G_{ads}^\circ = \Delta G_{elec}^\circ + \Delta G_{chem}^\circ + \Delta G_{CH_2}^\circ + \Delta G_{Hydrophobic}^\circ + \Delta G_{Solvent}^\circ + \Delta G_H^\circ \quad (1)$$

Where ΔG_{elec}° accounts for the electrostatic interaction, ΔG_{chem}° for the chemical bond formation at the surface, $\Delta G_{CH_2}^\circ$ for hydrophobic chain-chain interaction leading to hemi-micelle formation, $\Delta G_{Hydrophobic}^\circ$ for non polar chain hydrophobic surface interaction, $\Delta G_{Solvent}^\circ$ for solvation effects of ions and surfaces and the ΔG_H° contributions due to hydrogen bonding. In practice, it is not very easy to distinguish amongst all these non-electrostatic interactions and hence it is customary to combine all the specific interactions as specific free energy of adsorption [12].

$$\Delta G_{ads}^\circ = \Delta G_{elec}^\circ + \Delta G_{sp}^\circ \quad (2)$$

$$\Delta G_{ads}^\circ = ZF\Psi_\delta + \Delta G_{sp}^\circ \quad (3)$$

In the presence of surfactant, at iep $\Psi_\delta = 0$ and hence

$$\Delta G_{ads}^\circ = \Delta G_{sp}^\circ \quad (4)$$

Furthermore, when $\Psi_\delta = 0$, the electrical double layer is essentially made-up of inner layer and the potential drop is confined to Stern plane only. Thus the capacitance C is given by

$$C = C_\delta = [\sigma_0 / \Psi_0] \quad (5)$$

or $\sigma_0 = C_\delta \Psi_0$ (6)

Based on the electrical double layer theory one can write

$$\sigma_0 + \sigma_\delta + \sigma_d = 0 \quad (7)$$

Also, since $\Psi_\delta = 0, \sigma_d = 0$

Accordingly equation (7) can be written as

$$\sigma_0 = -\sigma_\delta = -ZF\Gamma_\delta \quad (8)$$

Since $\Psi_0 = \frac{RT}{Z_+F} \ln \left[\frac{a_M^{+z}}{(a_M^{+z})_{pzc}} \right] = -\frac{RT}{Z-F} \ln \left[\frac{a_M^{-Z}}{(a_M^{-Z})_{pzc}} \right]$ (9)

Equation (6) can be written as

$$C_\delta \frac{RT}{Z_+F} \ln \left[\frac{(a_{M+})_{iep}}{(a_{M+})_{pzc}} \right] = -ZF\Gamma_\delta \quad (10)$$

Since $\Gamma_\delta = \frac{\Gamma_m}{1 + \frac{55.5}{C_0} \exp(\Delta G_{ads}^\circ/RT)}$ (11)

equation (10) can further be modified as

$$\ln \left[\frac{(a_{M+})_{iep}}{(a_{M+})_{pzc}} \right] = -\frac{ZF^2}{RT C_\delta} \left[\frac{\Gamma_m}{1 + \frac{55.5}{C_0} \exp(\Delta G_{sp}^\circ/RT)} \right] \quad (12)$$

For oxides, the potential determining ions being, H^+/OH^- equation (12) can be rewritten as

$$\ln \left[\frac{(a_{H^+})_{iep}}{(a_{H^+})_{pzc}} \right] = -\frac{ZF^2}{RT C_\delta} \left[\frac{\Gamma_m}{1 + \frac{55.5}{C_0} \exp(\Delta G_{sp}^\circ/RT)} \right] \quad (13)$$

or $pH_{iep} - pH_{pzc} = \frac{ZF^2 \Gamma_m}{2.303 RTC_\delta} \left[\frac{1}{1 + \frac{55.5}{C_0} \exp(\Delta G_{sp}^\circ/RT)} \right]$ (14)

Since anionic surfactant used in the present investigation is oleate ion, $Z = -1$ and therefore

$$\Delta pH = \frac{F^2 \Gamma_m}{2.303 RTC_\delta} \left[\frac{1}{1 + \frac{55.5}{C_0} \exp(\Delta G_{sp}^\circ/RT)} \right] \quad (15)$$

Since the value of Γ_m can be calculated from the cross sectional area of the adsorbing surfactant and C_8 for oxides has been found to be around $20 \mu F/cm^2$, ΔG_{sp}° can be evaluated from ΔpH values obtained from the electrokinetic data using equation (15).

Materials and Methods

Pure samples of Sillimanite and Garnet were obtained from Orissa Sands Complex, Indian Rare Earths Ltd., Chatrapur and subjected to grinding in an agate mortar to obtain very fine particles suitable for micro-electrophoresis measurements. The details of the materials used in this study are given below.

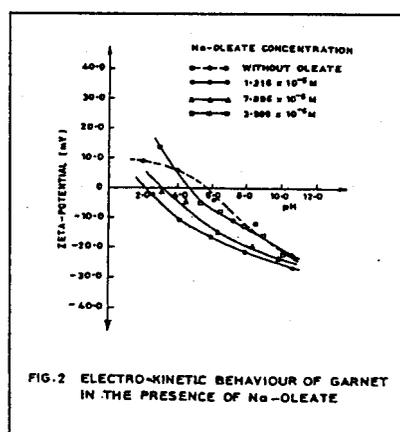
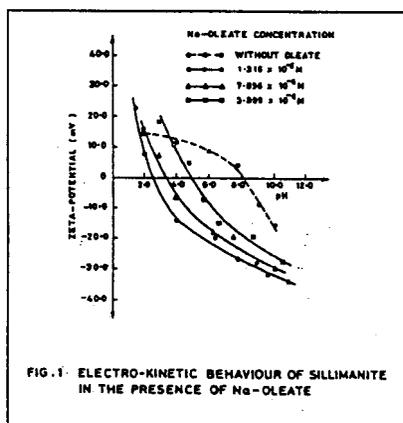
Table I : Specifications of experimental materials

Material	Chemical Formula	Purity, %	Specific Gravity
Sillimanite	Al_2SiO_4	$Al_2O_3 = 58\%$	3.25
Garnet	$Fe_3 Al_2 (SiO_4)_3$	97%	4.11
Oleic acid	$C_{17}H_{33}COOH$	65-70%, Iodine value 87 to 93	0.891
Sodium Chloride	NaCl	99.9	—

In all the experiments, double distilled water was used. 0.05 g of mineral was conditioned in 50 ml of oleate solution at desired pH for 900 seconds. The pH of the solution was adjusted using 0.1M HCl and NaOH solutions. Oleate solutions were prepared in 0.1N sodium chloride (electrolyte). After equilibrating the mineral sample with desired concentration of oleate solution, the sample was transferred into the microelectrophoresis cell and the zeta potential of the particles was measured using Zeta Meter 3+. For each measurement, minimum of 10 readings were taken and an average value with standard deviation of <2% was reported.

Results and Discussion

Initially, zeta potentials of sillimanite and garnet were measured in the absence of oleate at different pH values to determine the iso-electric-point of individual minerals. Zeta potentials of sillimanite and garnet in the presence of various concentrations of sodium oleate were also measured and the results of the same are shown in figs. 1 and 2 respectively. From the results



it may be observed that the iep of sillimanite and garnet are found to be 8.2 and 5.7 respectively.

In the presence of oleate and by increasing the concentration, the iep values were found to shift to lower pH. This characteristic shift in iep in the presence of oleate is attributed due to specific adsorption of oleate at mineral water interface. If the adsorption of oleate on sillimanite and garnet is of physisorption, shift in iep is least expected. According to IUPAC definition, iep refers to a particle showing no electrophoreses and pzc to a particle or surface carrying no fixed charge. iep characterises the charge in the diffuse layer ($\sigma_d = 0$) where as pzc refer only to the surface charge $\Psi_s = 0$. The shift in iep has been quantified in terms of specific interactions between the surface sites and the adsorbing surfactant [13-14]. Similar characteristic shift in iep was observed in the case of adsorption of hydroxamate on Fe_2O_3 [15] and oleate on rutile [16]. This shift depends on the magnitude of ΔG_{sp}° that is, on the affinity of adsorbing surfactant for the surface sites. From the above discussion, it could be concluded that the adsorption of oleate on sillimanite and garnet is due to specific interactions. Substituting the appropriate values in eq. (15), ΔG_{sp}° values were computed from zeta potential data and the same are shown in table II.

The values of C_s ($20 \mu \text{ Farad/cm}^2$) and the effective cross sectional area of oleate molecular (20 \AA^2) reported in the literature were used in the above calculations. The cross sectional area of the oleate molecules corresponding to vertical mono layer was considered more appropriate as the adsorption is of specific nature. The value of Γ_m corresponding to vertical mono layer is $7 \times 10^{-10} \text{ mole/cm}^2$

Table II Specific free energy of adsorption computed from electro kinetic data

System	iep	Shift in iep		ΔG_{sp}°	
		iep - pzc	Oleate Conc. mole/l	RT	kcal/mole
Sillimanite/ Oleate	8.2	3.3	3.998×10^{-6}	-13.56	-8.12
		4.7	7.896×10^{-6}	-13.26	-7.97
		5.7	1.316×10^{-5}	-12.94	-7.73
Garnet/ Oleate	5.7	1.1	3.998×10^{-6}	-12.49	-7.46
		2.7	7.896×10^{-6}	-12.70	-7.59
		3.5	1.316×10^{-5}	-12.45	-7.44

The ΔG_{sp}° values thus obtained were found in good agreement with the values obtained from adsorption isotherms [15-16]. The difference of ΔG_{sp}° values between sillimanite-oleate and garnet-oleate systems was found to be meager. It is apparent that the selectivity of oleate adsorption between these minerals should be poor. Selective flotation of one from the other appears very difficult without adopting proper depressants.

By substituting the appropriate values for all the constants in equation (15), it can be written as

$$\Delta \text{pH} = \frac{57.7027}{1 + \frac{55.5}{C_0} \exp(\Delta G_{\text{sp}}^{\circ}/RT)} \quad (16)$$

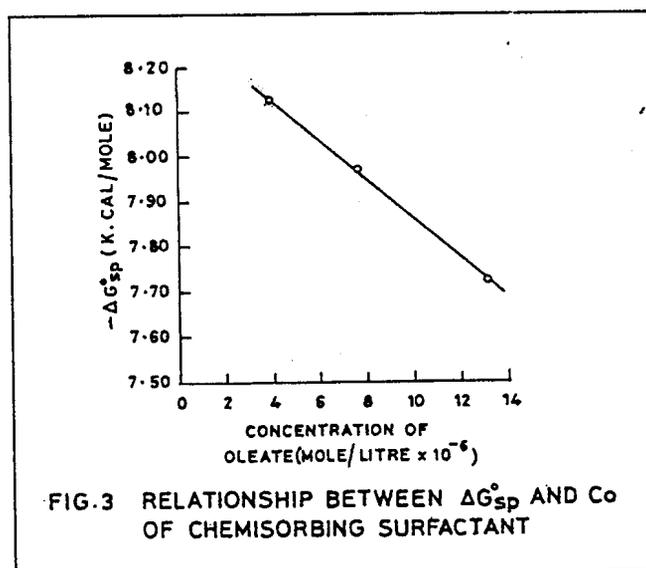
It can further be simplified as follows

$$\Delta \text{pH} = \frac{57.7027}{55.5} C_0 \exp(-\Delta G_{\text{sp}}^{\circ}/2.303 RT) \quad (17)$$

or

$$\log \Delta \text{pH} = \log 1.03 + \log C_0 - (\Delta G_{\text{sp}}^{\circ}/2.303 RT) \quad (18)$$

Thus there exists a semi-log relationship between $\Delta G_{\text{sp}}^{\circ}$ and C_0 for a fixed pH and log-log relationship between pH and C_0 for a fixed $\Delta G_{\text{sp}}^{\circ}$. The values pertaining to sillimanite-oleate system were plotted in Fig.3 to illustrate the validity of the above relationship. From Fig.3, it could be seen that the above relationship holds good for sillimanite-oleate system.



Conclusions

Adsorption of oleate molecules on sillimanite and garnet was studied by zeta potential measurements. Specific adsorption of oleate on the above minerals has been interpreted in terms of well known electrical double layer model. The characteristic shift in iep in the presence of oleate has been quantified in terms of $\Delta G_{\text{sp}}^{\circ}$, the specific free energy of adsorption with the help of electrical double layer theory. However, $\Delta G_{\text{sp}}^{\circ}$ estimated by the proposed equation using electrokinetic data is to be verified on number of systems with that of adsorption isotherms.

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