

Adsorption Characteristics of Sodium oleate onto Calcite.

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Abstract

The adsorption of Na-oleate on the surface of calcite were investigated under various conditions of contact time, pH and temperature. The influence of pH on the adsorption of oleate onto calcite were carried out between pH 4 and pH10. The adsorption of oleate onto calcite increases at lower pH values and decreases at higher pH values studied. The effect of temperature on the adsorption of oleate onto calcite were investigated between 30 and 60 °C. The result indicates that adsorption of oleate increases at lower temperature. Rate constants, k_{ad} for different concentrations of Na-oleate were calculated to be 1.55 s^{-1} and 2.16 s^{-1} respectively. This study established that critical micelle concentration is pH dependent.

Key words: calcite, Na-oleate, adsorption, kinetics, mechanism.

3b. Introduction

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35 Calcite is a very common and widely distributed mineral in the earth's crust.

36 It is an important rock- forming mineral in sedimentary and metamorphosed

37 sedimentary rocks. Calcite is a common constituent of altered basic

38 igneous rocks, where it develops by alteration of calcium silicates (Berry

39 and Mason,1983). Calcite also is a carbonate mineral and the most stable

40 polymorph of calcium carbonate (CaCO_3). The other polymorphs are the

41 minerals aragonite and vaterite. Aragonite will change to calcite at 380 –

42 470 $^{\circ}\text{C}$. Calcite crystals are trigonal – rhombohedral, though actual calcite

43 rhombohedral are rare as natural crystals. It has a specific gravity of 2.71,

44 and its luster is vitreous in crystallized varieties. It is colourless and

45 transparent or white when pure; though shades of grey, red, orange,

46 yellow, green, blue, violet, brown, or even black can occur when the

47 mineral is charged with impurities (Berry and Mason,1983). Calcite, like

48 most carbonates, will dissolve with most forms of acid. Calcite can be either

49 dissolved by groundwater or precipitated by groundwater, depending on

50 several factors including the water temperature, pH and dissolved ion

51 concentrations.

52 Many studies have already been performed on the crystallization, kinetics

53 and processes of calcium carbonate (Abdel-Aal and Sawada, 2003;

54 Mishra,1982).

55 The adsorption of fatty acids onto apatite at various pH producing negative

56 zeta potential have been reported by Mishra(1982), the negative zeta

57 potential is due to physisorption as well as chemisorption. Marinakis and

58 Shergold (1985) studied the interaction of oleic acid with calcite and

59 found that the abstraction of oleate from aqueous solution corresponds to

the precipitation of metal soap. Na-oleate is a common surface – active agent used in industrial application of agglomeration process (Gnyran Brown,1995; Sohoni et al;1991). Alinnor and Ejike (2009) worked on thermodynamic parameters of adsorption of Na – oleate on Nigeria barite. A lot of work have been reported on the agglomeration of calcium carbonate in the presence of Na-oleate (Kawashima and Capes,1976; Kawashima et al; 1986, Sadowski,1994; Bolay Le, 2003). Ejike et al (2006) reported effect of pH and temperature on the adsorption of Na-oleate onto barite. There has been considerable interest in recent times in the separation of minerals using fatty acids. At present information on the adsorption mechanism of Na-oleate onto calcite are scanty. The aim of this study was to investigate various mechanisms for the adsorption of Na-oleate onto calcite.

2. Experimental

Calcite for this study was obtained from Akaraka Paint Industry, Imo State, Nigeria. The calcite in lump was crushed and ground in a mortar. The ground calcite was demineralized by leaching with 2M sulphuric acid, H_2SO_4 . The sample was subsequently washed with distilled water until free from acid. The sample was dried in an electric oven at 110 °C. After drying, the sample was separated into particle sizes by passing through different mesh sizes and finally collected at 300 μm using a mechanical sieve shaker. After separation, the calcite was stored in a plastic container (Alinnor and Ejike, 2009).

Batch adsorption experiment were carried out by introducing 0.0472 cm^3 of oleic acid into various 250 cm^3 flasks and 0.15 cm^3 sodium hydroxide, NaOH solution was added into the flask to form sodium oleate and the

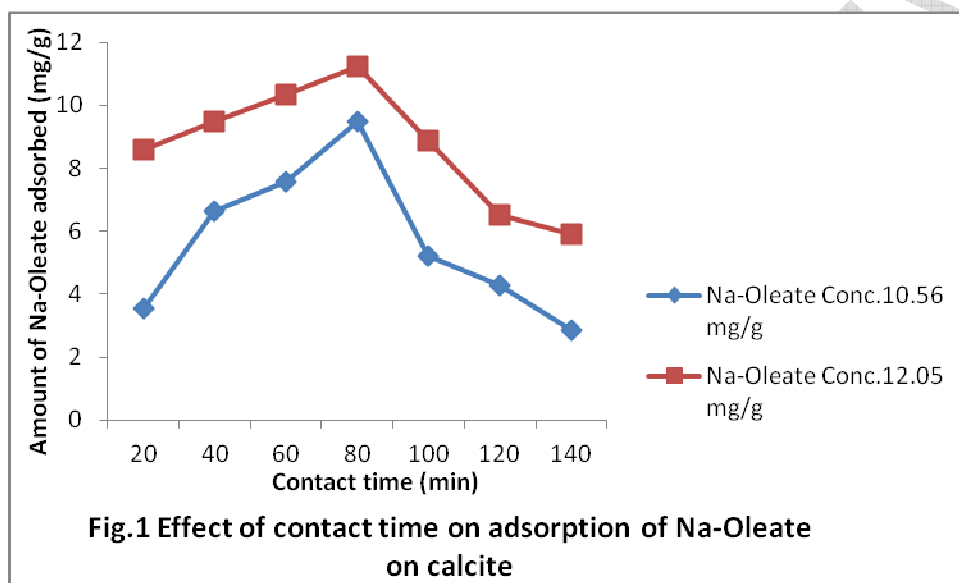
mixture was allowed to stand for 30 min. This mixture after homogenization was further diluted by addition of 150 cm³ distilled water. 1.0 g of purified calcite was added into the flask containing Na-oleate. The specimen flasks and contents were agitated for 1hr on a mechanical shaker. Each flask content was allowed to settle for further 30 min after agitation. The content of each flask was filtered through a Whatman No.4 filter paper. After filtration, the conductance of each filtrate was measured using dipping cell type conductivity meter as described by (Ejike et al; 2006). The amount of Na-oleate adsorbed onto calcite at equilibrium was determined by calibration. This process involved the difference between the initial and residual conductance measurements on sample. The contact time of adsorption of Na-oleate onto calcite were determined by performing experiment using a pH programming as reported by (Ejike et al; 2006). The influence of temperature on the adsorption process were carried out between 30 and 60 °C using thermostated water bath. At the end of agitation period, the sample was cooled to room temperature and the conductance measurement read as described above. All the chemicals used were of analytical reagent grade.

3.0 Results and Discussion

3.1 Reaction kinetics

The effect of contact time on the adsorption of 10.56 and 12.05 mg/g Na-oleate onto the surface of calcite is shown in Fig.1. The rate of adsorption of Na-oleate onto calcite increases initially with time. At initial 20 min the amount of Na-oleate adsorbed for the two concentrations studied were 3.55 and 8.57 mg/g, respectively. Fig.1 indicates that optimum adsorption was established within 80 min in both concentrations of Na-oleate. At optimum

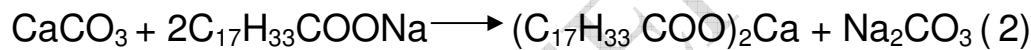
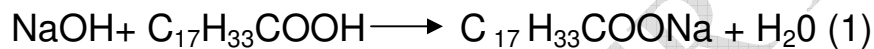
adsorption, 9.48 mg/g or 89.77% and 11.24 mg/g or 93.28% were removed from initial concentrations of oleate by calcite. After optimum time of 80 min the amount of Na-oleate adsorbed onto calcite decreases. This indicates that the surface of calcite have been saturated with Na-oleate, therefore beyond 80 min desorption of Na-oleate from calcite surface occurs.



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The effect of shaking and time of equilibration of adsorption of starch onto hematite has been reported by (Khosla et al; 1984).The result indicates that optimum adsorption was established after 7 hr of agitation.

The adsorption isotherm of oleate onto calcite as shown in Fig.1 depicts monolayer adsorption. The isotherm belongs to class L, subgroup 2 of the classification of Giles et al (1960). This group of isotherms is referred to as Langmuir type isotherms. The result of this study clearly shows that Na-oleate chemically adsorbs on the calcite surface, which interact with oleate ions, giving the surface Ca-oleate product. The chemical reaction process can be written as shown in Eq.1 and 2,



The chemisorption reactions are not reversible occur only in one direction. Ca-oleate is water insoluble and remains on the calcite surface.

The rate constants for adsorption of Na-oleate onto calcite were determined using the Lagergren equation (2004):

$$\log (q_e - q) = \log q_e - k_{ad}/2.303 \times t \quad (3)$$

Where q_e is the amount of oleate adsorbed at equilibrium (mg/l), q is the amount of oleate adsorbed at time t (min) and k_{ad} is the rate constant (min⁻¹). Fig. 2 shows that the initial rate of Na-oleate adsorption conforms to first order reaction kinetics as shown in Eq. (3). A plot of $\log (q_e - q)$ versus t should yield a straight line, from the slope of which the rate constants k_{ad}

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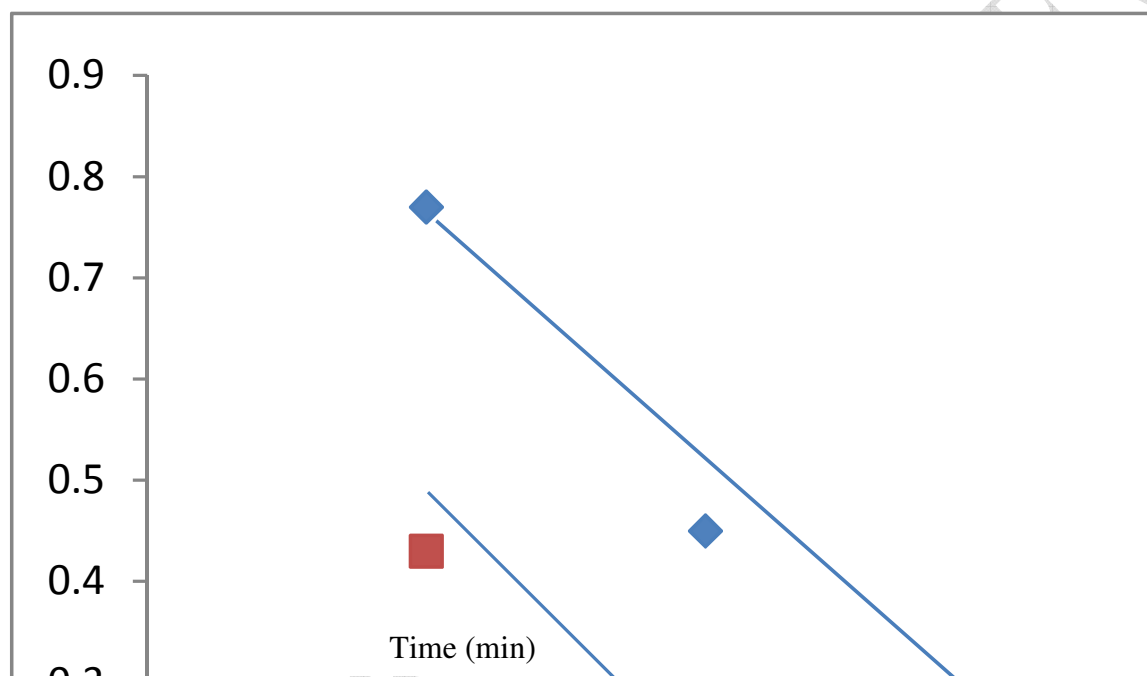


Fig.2 Lagergren plots for Na-Oleate adsorption on calcite

were calculated to be 1.55 s^{-1} and 2.16 s^{-1} for Na-oleate concentrations 12.05 mg/g and 10.56 mg/g, respectively.

3.2 Effect of pH

The adsorption of Na-oleate onto calcite is pH dependent. Data presented in Fig. 3 illustrates that the amount of oleate adsorption onto calcite increases as the initial concentration of Na-oleate increases. Ca-oleate formation shown in Eq.2 first increased with increasing Na-oleate concentration, then decreased sharply with increasing Na-oleate concentration. At low pH 4 the adsorption of Na-oleate onto calcite increases and maximum adsorption was observed at Na-oleate concentration of $9.0 \times 10^{-3} \text{ M}$. Beyond this maximum adsorption concentration adsorption decreases rapidly as Na-oleate concentration increases. At pH 6 there was also a sharp increase on the adsorption of Na-oleate onto calcite, also maximum adsorption was observed at Na-oleate concentration of $9.0 \times 10^{-3} \text{ M}$. The maximum adsorption at Na-oleate concentration of $9.0 \times 10^{-3} \text{ M}$ at pH 4 and pH 6 for the formation of Ca-oleate as shown in Eq.2 may be attributed to micelle formation at Na-oleate concentration of $9.0 \times 10^{-3} \text{ M}$. In an aqueous solution, surfactant or Na-oleate is molecularly dispersed at low concentration. At higher concentration, however, when a certain critical concentration is reached the surfactant molecules form micelles. These micelles are in equilibrium with the free surfactant molecules. The concentration at which micelles are formed is called the critical micelle concentration (cmc) (McBain,1942). Below the cmc no micelle formation occurs.

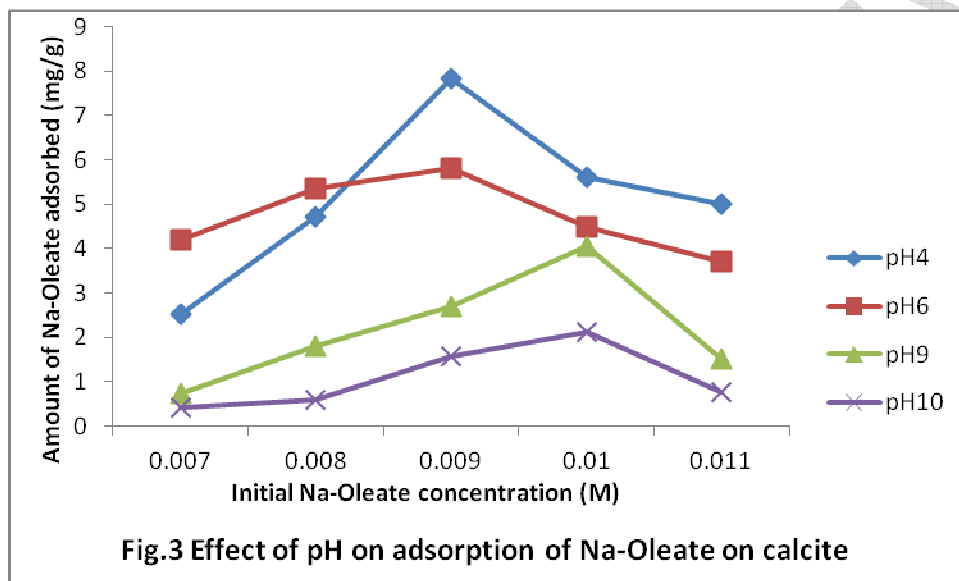
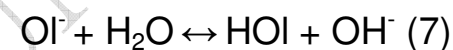
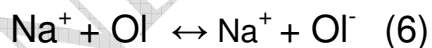


Fig. 3 shows that adsorption of Na-oleate onto calcite increases as initial Na-oleate concentration increases at both pH 9 and pH10. The maximum adsorption of Na-oleate onto calcite was observed at Na-oleate concentration of 1.0×10^{-2} M at both pH 9 and pH10. Beyond this maximum adsorption concentration, adsorption of Na-oleate onto calcite decreases rapidly. This result indicates that formation of Ca-oleate decreases at higher pH values when compared to low pH values obtained in this study, since Na-oleate adsorption determines the formation of Ca-oleate. The decrease in the formation of Ca-oleate at higher pH values may probably be due to increase in electrostatic repulsion between the increasingly negative calcite surface, due to higher pH values. Also this study shows that critical micelle concentration of Na-oleate is pH dependent, since a shift in cmc was observed at pH 9 and pH10 when compared to values obtained at pH 4 and pH 6. The sharp decrease in adsorption of Na-oleate onto calcite beyond cmc value could be explained by the following equations:-



Where OI^- = oleate ion

The reactions indicates that decrease in adsorption of Na oleate could also be explained in terms of solubility of CaCO_3 and Na-oleate in aqueous

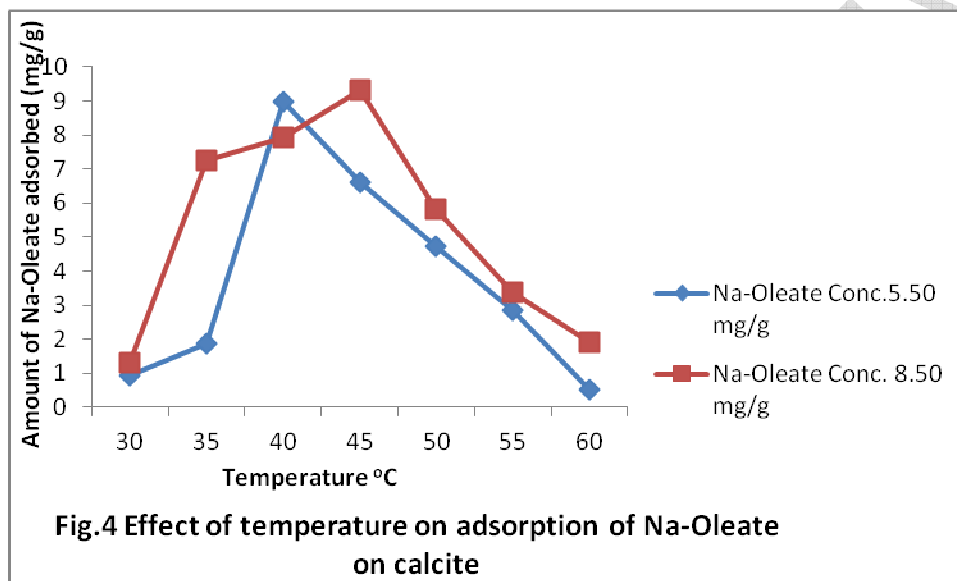
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solution. Sayan (2005) working on agglomeration of Na – oleate on calcium carbonate reported decrease in agglomeration of Na- oleate due to increase in solubility.

3.3 Effect of temperature

The adsorption of Na- oleate onto calcite is temperature dependent. Fig. 4 shows the amount of Na- oleate adsorption onto calcite in the formation of Ca- oleate. This study was carried out at Na-oleate concentrations 5.5 and 8.50 mg/g, respectively. The range of temperatures considered were between 30 and 60 °C. At Na- oleate concentration 5.50 mg/g, the amount of Na-oleate adsorbed onto calcite increases gradually as temperature increases from 30 to 35 °C. Optimum temperature for the adsorption of oleate onto calcite was observed at 40 °C. Beyond optimum temperature there was a rapid decrease on the adsorption of Na-oleate onto calcite as temperature increases. Similar trend was observed when 8.50 mg/g concentration of Na- oleate was used for the adsorption process. At 8.50 mg/g Na-oleate, the amount of Na-oleate adsorbed onto calcite increases rapidly as temperature increases from 30 to 35 °C. Beyond 35 °C there was a gradual increase from 35 to 40 °C. Optimum temperature of adsorption was observed at 45 °C. Beyond optimum temperature Na-oleate adsorption decreased rapidly.

The decrease in adsorption of oleate at higher temperature as shown in Fig.4 can be related to increase in solubility. In adsorption temperature should affect not only the adsorption process but also the solubility of the adsorbate. Since the solubility of a substance determines its chemical potentials, which in turn control the adsorption, the solubility factor cannot

be neglected in any investigation of adsorption from solutions. The temperature dependence of adsorption of solids from solution at



different temperatures have been reported by (Kumari et al; 1988) that adsorption decrease with increasing temperature. The decrease in adsorption with increase in temperature may also be attributed to weak attractive forces between the oleate and calcite and partly due to enhancement of thermal energies of the adsorbate; thus making the attractive forces between oleate and calcite insufficient to retain the oleate at the binding site. This could lead to desorption or cause the oleate to bounce off the surface of the calcite instead of colliding and combining with it.

4. Conclusion

This study revealed that adsorption of oleate onto calcite surface increases at lower pH values and decreases at higher pH values. This investigation shows that critical micelle concentration of Na- oleate is pH dependent, since a shift in cmc was observed at pH 9 and pH10. The kinetic study shows that Na-oleate was adsorbed onto the calcite surface rapidly within the first 20 min, while equilibrium was attained within 80 min for both concentrations studied. The present study revealed that adsorption of oleate onto calcite is most effective at lower temperature in view of low solubility of calcite at lower temperature.

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