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Adsorption Characteristics of Sodium oleate onto Calcite

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Authors' contributions

This work was carried out in collaboration between the authors. Author AIJ designed the study, performed the graphics, wrote the first protocol, wrote the first manuscript. Author ECK managed the analysis of this study and literature research. All authors read and approved the final manuscript.

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ABSTRACT

Aims: The need for separation of calcite from other minerals has been a concern. Na-oleate has been found useful as a good adsorbate for separation of calcite from other minerals. The aim of present study is to investigate the effect of various mechanisms of adsorption of Na-oleate onto calcite such as contact time, pH and temperature.

Study design: Conductivity method was used for the analysis.

Place and Duration of Study: Department of Chemistry, Federal University of Technology, Owerri, Nigeria, between February and October, 2012.

Methodology: Batch adsorption experiment were carried out by introducing oleic acid into various flasks containing sodium hydroxide, NaOH solution to form sodium oleate. 1g of purified calcite was added into flasks containing Na-oleate. The specimen flasks and content were agitated for 1hr on a mechanical shaker. Each flask content was allowed to settle for further 30min, after agitation. The content of flask was filtered with filter paper. After filtration, the conductance of each filtrate was measured. The amount of Na-oleate adsorbed onto calcite is the difference between initial and residual conductance measurement on sample.

Results: The result of this study shows that initial rate of Na-oleate adsorption onto calcite conforms to first-order reaction kinetics. This study indicates that adsorption of Na- oleate onto calcite increases at low pH values than higher pH. The amount of Na-oleate adsorbed onto calcite increases gradually as temperature increases from 30 to 35 ^{0}C. Beyond optimum temperature 40 ^{0}C, adsorption of Na-oleate on calcite decreases rapidly. The result of the analysis indicates that critical micelles concentration (cmc) changes at high pH values.

Conclusion: This study indicates optimum contact time of 80 min on adsorption process of Na-oleate onto calcite. Also this study indicates that adsorption of Na-oleate onto calcite is pH dependent. Ca-oleate formation first increases with increasing Na-oleate concentration. At low pH 4 adsorption of Na-oleate onto calcite increases, whereas adsorption decreases at high pH 9. The critical micelles concentration of Na-oleate was established at concentration 9.0 x10^{-3} M.

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1. INTRODUCTION

Calcite is a very common and widely distributed mineral in the earth's crust. It is an important rock- forming mineral in sedimentary and metamorphosed sedimentary rocks. Calcite is a common constituent of altered basic igneous rocks, where it develops by alteration of calcium silicates (Berry and Mason,1983). Calcite also is a carbonate mineral and the most stable polymorph of calcium carbonate ($CaCO_3$). The other polymorphs are the minerals aragonite and vaterite. Aragonite will change to calcite at 380 – 470 ^{0}C. Calcite crystals are trigonal – rhombohedral, though actual calcite rhombohedral are rare as natural crystals. It has a specific gravity of 2.71, and its luster is vitreous in crystallized varieties. It is colourless and transparent or white when pure; though shades of grey, red, orange, yellow, green, blue, violet, brown, or even black can occur when the mineral is charged with impurities (Berry and Mason,1983). Calcite, like most carbonates, will dissolve with most forms of acid. Calcite can be either dissolved by groundwater or precipitated by groundwater, depending on several factors including the water temperature, pH and dissolved ion concentrations.

Many studies have already been performed on the crystallization, kinetics and processes of calcium carbonate (Abdel-Aal and Sawada, 2003; Mishra,1982).

The adsorption of fatty acids onto apatite at various pH producing negative zeta potential have been reported by Mishra(1982), the negative zeta potential is due to physisorption as well as chemisorption. Marinakis and Shergold (1985) studied the interaction of oleic acid with calcite and found that the abstraction of oleate from aqueous solution corresponds to 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 adsorption mechanism of Na-oleate onto calcite are scanty. The aim of this study was to investigate various mechanisms for adsorption of Na-oleate onto calcite such as contact time, pH and temperature.

2. MATERIAL AND METHODS

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 ^oC. 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 cm^3 distilled water. I.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 adsorption process were carried out between 30 and 60 ^{0}C using thermostated water bath. At end of agitation period, the sample was cooled to room temperature and conductance measurement read as described above. All chemicals used were of analytical reagent grade.

3.0 RESULTS AND DISCUSSION

3.1 Reaction kinetics

The effect of contact time on adsorption of 10.56 and 12.05 mg/g Na-oleate onto 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 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 surface of calcite have been saturated with Na-oleate, therefore beyond 80 min desorption of Na-oleate from calcite surface occurs.

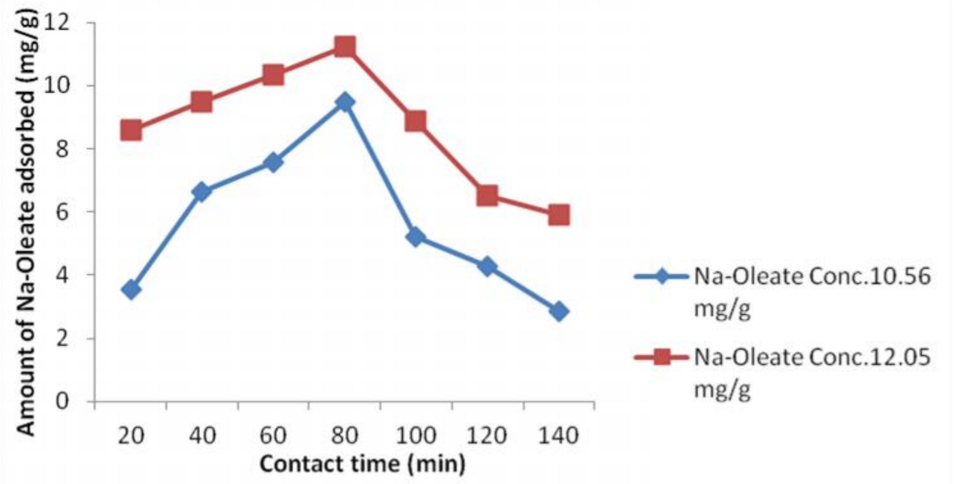

Fig.1 Effect of contact time on adsorption of Na-Oleate on calcite

The effect of shaking and time of equilibration of adsorption of starch onto hematite has been reported by (Khosla et al; 1984).They reported 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,

$$NaOH + C_{17}H_{33}COOH \longrightarrow C_{17}H_{33}COONa + H_20 \qquad (1)$$

$$CaCO_3 + 2C_{17}H_{33}COONa \longrightarrow (C_{17}H_{33}COO)_2Ca + Na_2CO_3 \qquad (2)$$

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

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

Where q_e is amount of oleate adsorbed at equilibrium (mg/l), q is amount of oleate adsorbed at time t (min) and k_{ad} is rate constant (min-^{1}). Fig. 2 shows that 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 slope the rate constants k_{ad} 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.

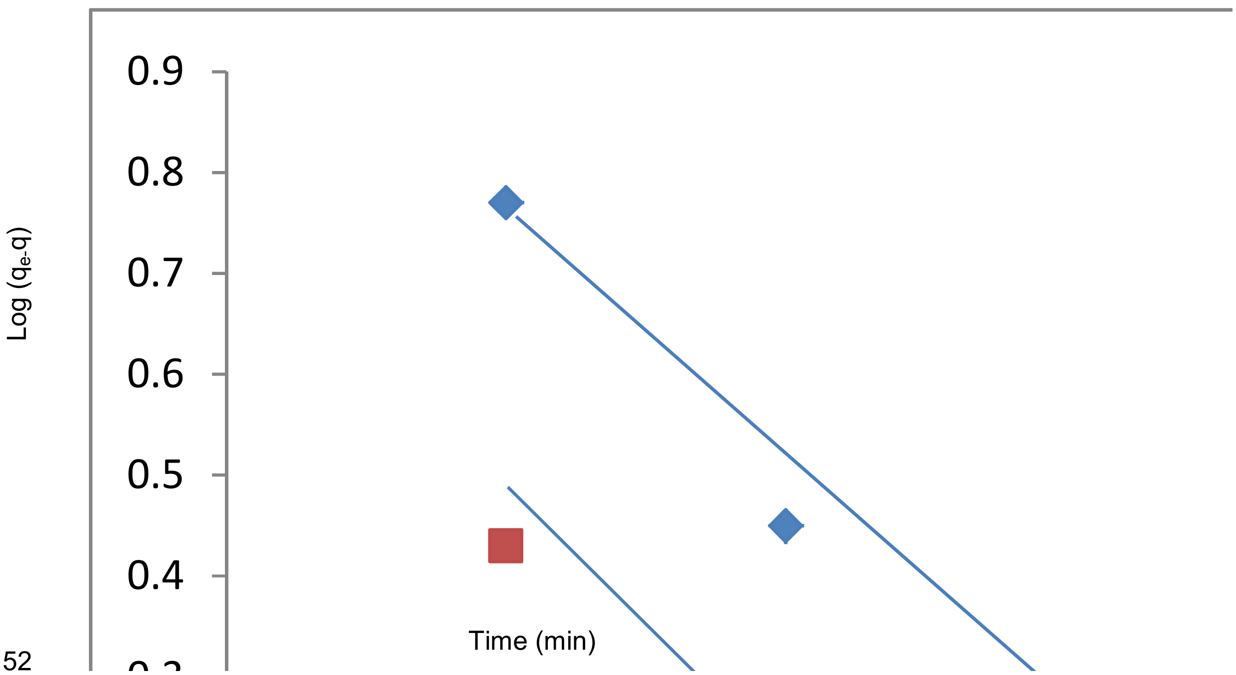

Fig.2 Lagergren plots for Na-Oleate adsorption on calcite

3.2 Effect of pH

The adsorption of Na-oleate onto calcite is pH dependent. Data presented in Fig.3 illustrates the effect of pH at various pH level. Ca-oleate formation shown in Eq.2 increased first 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 $9.0x10^{-3}$ M. Beyond this maximum adsorption concentration, adsorption decreases rapidly as Na-oleate concentration increases. At pH 6 there was also a sharp increase on adsorption of Na-oleate onto calcite, also maximum adsorption was observed at Na-oleate concentration of $9.0x10^{-3}$ M. The maximum adsorption at Na-oleate concentration of $9.0x10^{-3}$ M at pH 4 and pH 6 for formation of Ca-oleate as shown in Eq.2 may be attributed to micelle formation at Na-oleate concentration of $9.0x10^{-3}$ M. In 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 free surfactant molecules. The concentration at which micelles are formed is called the critical micelle concentration (cmc) (McBain,1942). Below cmc no micelle formation occurs.

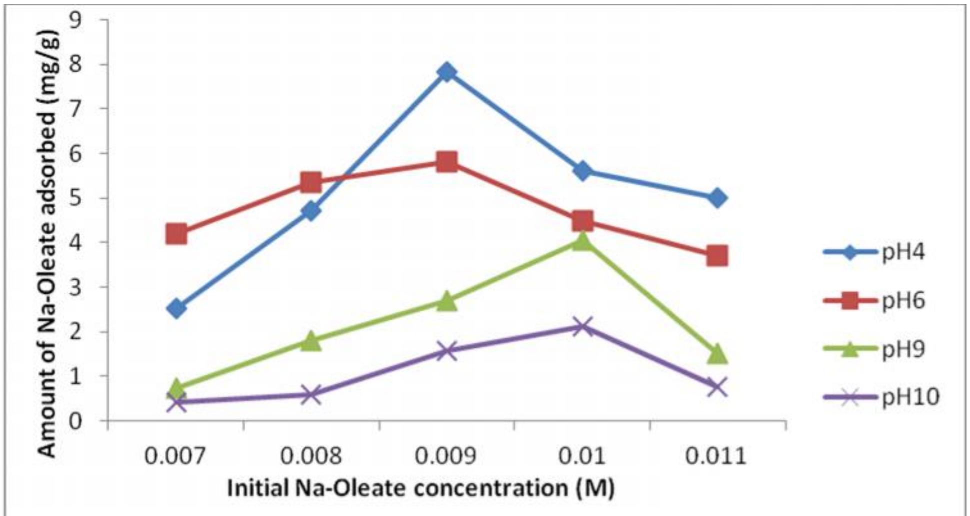

Fig.3 Effect of pH on adsorption of Na-Oleate on calcite

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 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 changes at high pH values, since a shift in cmc was observed at pH 9 and pH10 when compared to value 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:-

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$ (4)

$CO_3^{2-} + H_20 \leftrightarrow HCO_3^- + OH^-$ (5)

$Na^+ + Ol \leftrightarrow Na^+ + Ol^-$ (6)

$Ol^- + H_2O \leftrightarrow HOl + OH^-$ (7)

Where Ol^- = 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 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 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 ^{0}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 ^{0}C. Optimum temperature of adsorption of oleate onto calcite was observed at 40 ^{0}C. Beyond optimum temperature there was a rapid decrease of 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 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 ^{0}C. Beyond 35 ^{0}C there was a gradual increase from 35 to 40 ^{0}C. Optimum temperature of adsorption was observed at 45 ^{0}C. Beyond this optimum temperature Na- oleate adsorption onto calcite decreased rapidly.

The decrease in adsorption of oleate onto calcite at higher temperature as shown in Fig.4 could be associated with increase in solubility. In adsorption temperature should affect not only the adsorption process but also the solubility of adsorbate. Since solubility of a substance determines its chemical potentials, which in turn control adsorption, the solubility factor cannot be neglected in any investigation of adsorption from solutions.

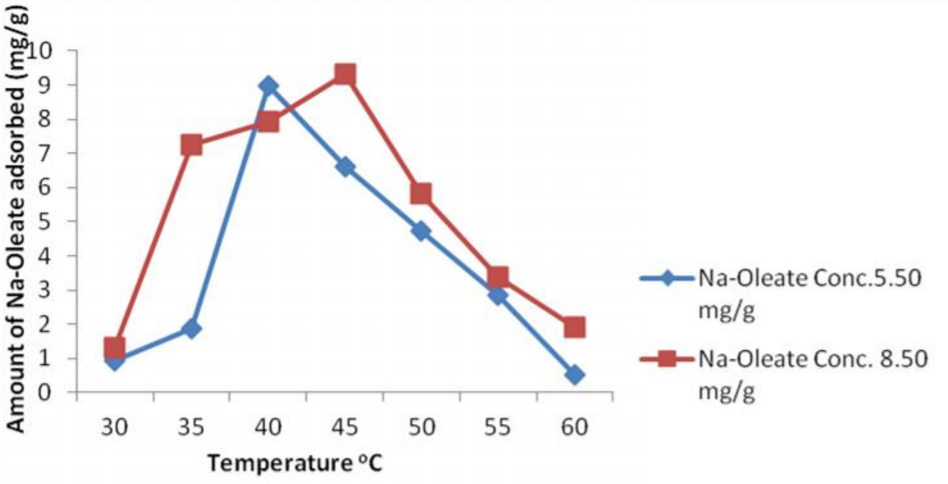

Fig.4 Effect of temperature on adsorption of Na-Oleate on calcite

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 oleate and calcite and partly due to enhancement of thermal energies of adsorbate; thus making the attractive forces between oleate and calcite insufficient to retain oleate at binding site. This could lead to desorption or cause oleate to bounce off surface of 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 changes at high pH values, since a shift in cmc was observed at pH 9 and pH10. The kinetic study indicates that Na-oleate adsorption onto calcite surface increases 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.

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COMPETING INTERESTS

Authors have declared that no competing interest exist.

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