EFFECT OF CONCENTRATION, TEMPERATURE, AND pH ON OLEATE ADSORPTION AT A NIGERIAN BARYTE - WATER INTERFACE

O. Ofor* and C. Nwoko School of Science, Federal University of Technology, Owerri, Imo State, Nigeria.

ABSTRACT

Using pure natural baryte selected from a crude Nigerian baryte, oleate adsorption densities at the baryte - water interface were determined at varying sodium oleate concentrations, mineral pulp pH, and temperatures, using electrical conductivity measurements. The specific surface area of the pure baryte powder was determined using the method of adsorption of paranitrophenol in aqueous solution. Variation of oleate adsorption density with equilibrium oleate concentration gave the critical micelle concentration of sodium oleate as 0.013 mole/litre. Maximum adsorption occurred at pH 9.5. Adsorption density increased with increasing temperature to a maximum value at 40°C and decreased above this temperature. Chemisorption is considered the dominant mode of oleate adsorption at ambient temperature (29°C) and up to 40°C, with a minor contribution of physical adsorption to the overall adsorption process. Beyond 40°C the chemisorbed species probably dissociate from the mineral surface while the primary mode of adsorption becomes physical processes.

INTRODUCTION

Several researchers have studied the adsorption of surfactants onto the mineral surface in an aqueous medium to bring about the selective flotation of the mineral. Shergold and Mellgren[1] showed that at a given pH, the percentage recovery of hematite increases with increasing adsorption density of sodium dodecylsulfate, to about 100% at a surfactant concentration corresponding to zero zeta potential. Cooke et al.[2] obtained improved flotation recovery and selectivity of an iron oxide mineral from its ore at elevated temperatures using a soap collector. By using potassium ricinoleate in a three-ingredient emulsion, Ofor[3] showed that the efficiency of separation of hematite from its high silica ore increased with increasing temperature; optimum separation occurred within the temperature range 30 - 60°C In the present investigation, the adsorption density of sodium oleate soap on a "pure" Nigerian baryte surface in an aqueous medium was determined at varying oleate concentrations, mineral pulp pH, and temperatures. The optimum values of oleate concentration, pH, and temperature that gave the maximum adsorption density were thereby determined.

Desorption studies were carried out at ambient temperature and natural pulp pH. Electrical conductivity measurements were used to monitor oleate concentration and adsorption.

EXPERIMENTAL

Materials

The baryte employed in this study was obtained from the Cretaceous sandstone in the Aloshi baryte veins in the River Benue Valley in Benue State of Nigeria, and was supplied by the Nigerian Mining Corporation. Thin sections and polished blocks of representative samples of the crude baryte were prepared and were examined under the Vickers petrological microscope. The thin sections were examined under transmitted light while the polished surfaces were examined under reflected light[4].

In thin section baryte occurred as the main mineral constituent, with quartz and goethite and limonite as the main mineral impurities.

On chemical analysis, the baryte was assayed at 85.9% $BaSO_4$; 8.41% $Si0_2$; 5.08% $Fe0$; 0.064% Na_20; 0.042% $Mg0$; 0.035% K_20; 0.020% $Ca0$; 0.008% $Pb0$ and 0.002% ZnO. The main impurities in the crude baryte are thus silica which occurs as quartz, and iron which occurs as goethite and limonite.

A representative sample of the crude baryte was crushed to 100% minus 8 mesh (2000 µm British Sieve Standard); fully liberated hematite particles were sorted out microscopically until a sizeable

**Author for correspondence*

Table 1: Conductance and adsorption/desorption density at varying oleate concentrations at 29°C and pH 8.2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Initial Oleate concentration x 10^{-3} (mole/liter)	Initial conductance x 10^{2} (µs/cm)	Square-root of initial oleate concentration x 10^{-2}	Equilibrium conductance after oleate adsorption x 10^{2} (µs/cm)	Equilibrium oleate concentration x 10^{-3} (mole/liter)	Oleate adsorbed per gram baryte x 10^{-3} (mole/g)	Adsorption Density x 10^{2} (µmole/m^2)	Equilibrium conductance after oleate Desorption x 10^{-4} (µs/cm)	Oleate Desorbed per gram baryte x 10^{-4} (mole/g)	Desorption Density x 10^{2} (µmole/m^2)	Degree of Desorption $\frac{(10)}{(7)} \times 10^2$ (%)
1.0	1.70	3.16	0.20	0.50	0.50	1.85	0.15	-	-	-
2.0	2.50	4.47	0.50	0.83	1.17	4.32	-	-	-	-
4.0	3.30	6.32	1.75	2.50	1.50	5.54	-	-	-	-
6.0	4.10	7.75	2.40	3.90	2.10	7.73	0.90	2.25	0.83	10.74
8.0	4.65	8.94	3.00	5.30	2.74	10.12	-	-	-	-
10.0	5.15	10.00	3.55	6.81	3.19	11.79	1.40	6.25	2.31	19.60
12.0	5.65	10.95	4.10	8.56	3.44	12.71	-	-	-	-
14.0	6.00	11.83	4.65	10.25	3.75	13.83	1.55	8.01	2.95	21.30
16.0	6.45	12.65	5.13	12.21	3.80	13.98	-	-	-	-
18.0	6.80	13.45	5.45	13.39	4.34	15.90	1.80	10.56	3.90	24.50
20.0	7.15	14.14	5.95	15.70	4.34	15.90	-	-	-	-
22.0	7.42	14.83	6.40	17.70	4.35	15.90	2.00	13.30	4.92	30.90
24.0	7.80	15.49	6.80	19.54	4.47	16.50	-	-	-	-
26.0	8.15	16.12	7.18	21.19	4.81	17.76	2.15	14.80	5.47	30.80
28.0	8.45	16.73	7.45	22.78	5.22	19.25	-	-	-	-
30.0	8.70	17.32	7.60	24.30	5.70	21.03	2.25	17.00	6.27	29.80
32.0	9.10	17.89	7.90	25.80	6.20	22.88	-	-	-	-
34.0	9.30	18.44	8.25	27.40	6.60	24.35	-	-	-	-

quantity of pure baryte was obtained that was assayed at 99.6% $BaSO_4$. Adsorption tests were carried out on the pure baryte.

The oleic acid, sodium hydroxide and HCl were "Analar" grade. Conductance was measured using a conductivity meter of the dipping cell type. Temperature was maintained at a constant value ± 0.1°C using a Therm-o-watch electronic temperature controller.

Sieve analysis and microscopic counting was carried out on 100% minus 8 mesh samples of the crude Nigerian baryte; this established the size of grind at minus 80 mesh (200 μm) at which optimum liberation of the component minerals was obtained. Hence, for adsorption tests, the pure baryte was ground to 100% minus 80 mesh particle size.

The sodium oleate solutions were prepared from oleic acid and sodium hydroxide and used immediately for the adsorption tests to avoid "ageing" of the samples^5. All tests were carried out using distilled water.

Adsorption tests

The conductance of 80 cm^3 standard oleate solutions was measured at different initial concentrations, at the average ambient temperature of 29°C, and at the natural pH of 8.2 (Table 1, columns 1 and 2). From the measurements, a standard calibration graph of conductance versus the square root of oleate concentration was plotted (Fig.. 1).

1 g baryte powder was then added to each 80 cm^3 standard oleate solution; the mixture was shaken vigorously with a mechanical shaker for 1 hour to attain equilibrium adsorption and filtered until a clear filtrate was obtained.

Preliminary tests established that equilibrium was essentially complete in less than 45 minutes. The equilibrium conductance of the clear filtrate was measured (Column 4) and the equilibrium oleate concentration (Column 5) was read off the standard calibration graph. The number of moles oleate adsorbed at equilibrium at the aqueous baryte surface from the 80 cm^3 oleate solution was then determined (Column 6).

The specific surface area of the pure baryte particles was determined at 2.71m^2 per gram using the method of adsorption of paranitrophenol in aqueous solution, following the procedure of Gilles and

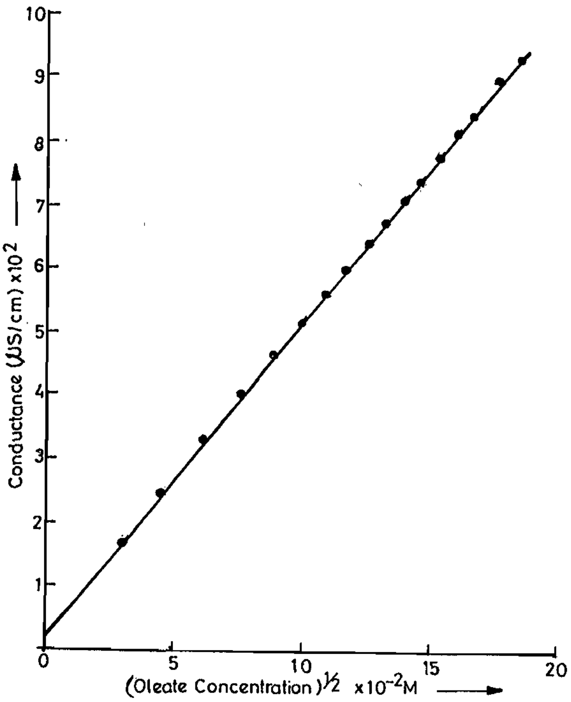

Fig.1 Conductance of standard Oleate solutions at varying concentrations.

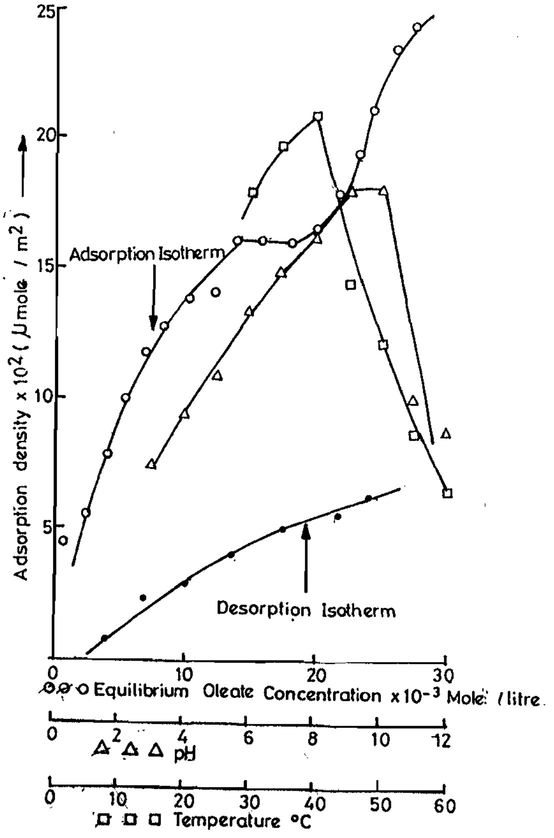

Fig.2 Adsorption density at various equilibrium Oleate Concentrations, pH, and Temperatures

Nakhwa[6]. The equilibrium adsorption density was then calculated as micromoles oleate adsorbed per m^2 of baryte surface (Column 7).

The graph of adsorption density versus equilibrium oleate concentration was plotted (Fig. 2), from which the initial oleate concentration corresponding to the optimum equilibrium oleate concentration at which maximum adsorption occurred was determined to be 0.018M.

Adsorption density was measured at different pH values, at the ambient temperature of 29°C using 80 cm^3 oleate solution at the optimum initial concentration of 0.018M. The results are presented in Table 2. From the graph of adsorption density versus pH shown in Fig. 2, the optimum pH at which maximum adsorption occurred was determined to be pH 9.5.

Finally, using the same volume (80cm^3) and initial concentration (0.018M) of oleate soap solution at the optimum pH of 9.5, adsorption density was measured at varying temperatures ranging from ambient to 80°C (Table 3). The graph of adsorption density versus temperature (Fig. 2) gave the optimum temperature at 40°C at which maximum oleate adsorption occurred.

Desorption test

Each solid residue after filtration was placed in 80cm^3 deionised water, shaken vigorously for 1 day and filtered. The equilibrium conductance and hence the quantity of oleate desorbed per gram of baryte were determined. The results are presented in Columns 8 and 9 respectively of Table 1. The desorption density, i.e. the amount of oleate desorbed at equilibrium from 1m^2 of the baryte surface was computed and the results are presented in Table 1, column 10. The graph of desorption density against equilibrium concentration at the ambient temperature of 29°C and natural pH 8.2 is shown also in Fig. 2.

RESULTS AND DISCUSSION

The graph of adsorption density versus equilibrium oleate concentration at the ambient temperature of 29°C and the natural pH of 8.2 (Fig. 2) shows that adsorption density increased with an increase in equilibrium oleate concentration up to the concentration value of 13.39 x 10^{-3}M. Beyond this concentration value adsorption density remained constant as oleate concentration increased. This value of 0.013 mole/litre is thus the critical micelle concentration (CMC) of sodium oleate. Beyond the equilibrium oleate concentration of 17.70 x 10^{-3}M adsorption density increased rapidly with increase in concentration.

Figure 2 shows that at ambient temperature, as pH increased, adsorption density increased rapidly to a maximum of 17.85 x 10^2 μmole/m^2 at pH 9.5, representing 26.7% oleate extraction per gram of baryte, and fell steeply. This pH of maximum adsorption is the zero point of charge (zpc) of the pure Nigerian baryte.

In the graph of adsorption density versus temperature at the optimum pH of 9.5 (Fig. 2) adsorption density increased slowly with increasing temperature to a maximum value of 20.75 x 10^2 μmole/m^2 at 40°C representing 31.2% oleate extraction per gram of baryte. Beyond this temperature, adsorption density decreased rapidly. The rise from 26.7% oleate extraction at 29°C to 31.2% oleate extraction at 40°C at the same pH emphasises the significance of increased temperature in oleate adsorption onto baryte surface in water.

Free energy of adsorption

The adsorption density vs pH isotherm (Fig. 2) shows that oleate adsorption continues appreciably several pH units beyond the zpc (pH = 9.5) of the pure Nigerian baryte. This is evidence of chemisorption[7]. Adsorption at the ambient temperature of 29°C is thus specific, in the Stern plane, involving chemical bond formation between the oleate ion and the baryte surface.

The Stern - Graham equation is applied to assess the magnitude of the standard free energy of adsorption (ΔG^{o}_{ads}):

$$\Gamma = zrc \exp. \frac{(-\Delta G^{o}_{ads})}{RT}$$

where Γ is the adsorption density in mole/cm^2, z is the valency of the adsorbed ion, r is the effective radius of the adsorbed ion (5.2 x 10^{-8}cm for the carboxylate ion), c is the equilibrium concentration in mole/cm^3, R is the gas constant and T is the

Table 2: Oleate adsorption density at varying mineral pulp pH (at ambient temperature = 29°C)

(1) pH	(2) Conductance before pH adjustment and before oleate adsorption x 10^2 (µs/cm) k_1	(3) Conductance after pH adjustment and before oleate adsorption x 10^2 (µs/cm) k_2	(4) Conductance after pH adjustment and after oleate adsorption x 10^2 (µs/cm) k_3	(5) Conductance due to pH ions x 10^2 (µs/cm) k_4 $(=k_2 - k_1)$	(6) Conductance due to oleate adsorption at equilibrium x 10^2 (µs/cm) k_5 $(= k_3 - k_4)$	(7) Equilibrium concentration x 10^{-3} (mole/g)	(8) Oleate adsorbed per gram baryte x 10^{-3} (mole/g)	(9) Adsorption density x 10^2 (µmole/m^2)
3.0	6.00	125.00	125.40	119.00	6.40	15.90	2.10	7.74
4.0	6.00	122.40	122.75	116.40	6.35	15.47	2.53	9.34
5.0	6.00	107.50	107.75	101.50	6.25	15.05	2.95	10.89
6.0	6.00	102.30	102.40	96.30	6.10	14.38	3.62	13.35
7.0	6.00	90.10	90.10	84.10	6.00	14.00	4.00	14.76
8.2	6.00	75.90	75.80	69.90	5.90	13.39	4.61	15.90
9.0	6.00	75.00	74.85	69.00	5.85	13.16	4.84	17.85
10.0	6.00	95.20	95.00	89.20	5.80	13.28	4.72	17.86
11.0	6.00	115.60	115.90	109.60	6.30	15.33	2.67	9.86
12.0	6.00	120.90	121.28	114.90	6.38	15.61	2.39	8.81

Table 3: Oleate adsorption density at varying pulp temperature (at optimum pH = 9.5)

(1) Temperature °C	(2) Conductance before pH adjustment to pH 9.5 optimum x 10^2 (µs/cm) k_1	(3) Conductance after pH adjustment and before oleate adsorption x 10^2 (µs/cm) k_2	(4) Conductance after pH adjustment and after oleate adsorption x 10^2 (µs/cm) k_3	(5) Conductance due to pH ions x 10^2 (µs/cm) k_4 $(=k_2 - k_1)$	(6) Equilibrium conductance due to unadsorbed oleate in solution x 10^2 (µs/cm) k_5 $(= k_3 - k_4)$	(7) Oleate adsorbed per gram baryte x 10^{-4} (mole/g)	(8) Adsorption density x 10^2 (µmole/m^2)
29	6.00	7.50	6.80	1.50	5.30	47.75	17.85
35	6.00	7.50	6.70	1.50	5.20	53.44	19.72
40	6.00	7.50	6.65	1.50	5.15	56.23	20.75
45	6.00	7.50	7.05	1.50	5.55	38.98	14.39
50	6.00	7.50	7.20	1.50	5.70	32.98	12.17
55	6.00	7.50	7.40	1.50	5.90	23.75	8.76
60	6.00	7.50	7.60	1.50	6.10	17.44	6.43
80	6.00	7.50	7.75	1.50	6.25	7.73	2.85

absolute temperature. Under conditions involving oleate adsorption at varying pH values at the ambient temperature of 29°C (Table 2), the ΔG°_{ads} values, presented in Table 4, were obtained.

Table 4 shows that ΔG°_{ads} is negative at the pH range studied; it increases in magnitude as pH increases, to a maximum at pH 9.0 to 10.0, and falls gently at higher pH values.

The sign and magnitude of the ΔG^{0}_{ads} values show that oleate adsorption at the baryte surface in aqueous medium is feasible at both acid and alkaline pH. The feasibility increases with increasing pH, to a maximum in the region of the z.p.c. (pH 9.5) of the Nigerian baryte and decreases at higher pH values.

The observed variation of ΔG^{0}_{ads} with pH indicates that some definite change must be occurring in the nature of the adsorption process.

Table 4: ΔG°_{ads} at various baryte pulp pH values

1 pH	2 Equilibrium oleate concentration (mole/ litre) x 10^{-3}	3 Adsorption Density (μmole/m^2) x 10^2	4 ΔG°_{ads} (KJ/mole)
3.0	15.90	7.74	-29.00
4.0	15.47	9.34	-29.57
5.0	15.05	10.89	-30.00
6.0	14.38	13.35	-30.66
7.0	14.00	14.76	-30.96
8.2	13.39	15.90	-31.25
9.0	13.16	17.85	-31.63
10.0	13.28	17.86	-31.59
11.0	15.33	9.86	-29.69
12.0	15.61	8.81	-29.40

Effect of temperature

Houwing and Salomon[8] have stated that while physical adsorption decreases with an increase in temperature, chemisorption increases as temperature increases. Chemisorption would thus be the dominant mode of adsorption up to 40°C. Beyond 40°C the chemisorbed species probably dissociate from the surface while the primary mode of adsorption becomes physical processes. This would account for the fall in adsorption density at temperatures above 40°C.

Nature of adsorption

The adsorption isotherm of sodium oleate soap on the Nigeria baryte at 29°C is given in Fig. 2. The initial slope is convex to the concentration axis; it defines an increase in adsorption with increase in the external solution concentration up to 15.9 x 10^2 μmoles/m^2 adsorption density. This upper part of the curve is a plateau which indicates surface saturation in which all possible sites in the original baryte surface are filled (complete monolayer coverage). The isotherm is thus an L2 curve according to the classification of Gilles et al.[9]. This group of isotherms is generally referred to as Langmuir-type isotherms.

Since the oleate ions are adsorbed on baryte as single mono-functional units, there appears to be marked localisation of the forces of attraction over the carboxylate group leading to very strong interaction (chemisorption) with baryte at this part of the ion.

Fig. 2 further presents the desorption isotherm of oleate soap on the Nigerian baryte also at 29°C (Table 1, column 10 vs column 5). The isotherm and, in particular, the degree of desorption (column 11, Table 1) show that a small amount of the adsorbed oleate desorbed. This further confirms that at the natural pH of 8.2 at ambient temperature (29°C), oleate is chemisorbed onto the aqueous baryte surface. However, that desorption occurred at all indicates that the physical adsorption process contributed, even if in a small measure, to the overall adsorption process.

Jung et al.[10] showed that within the pH range 3-12, the stable oleate species in solution comprise 01^-, 01_2^{2-}, $H01_2^-$ and H01. These authors hold the view that H01 molecules adsorb specifically, in the stern layer, without bond formation. The present researchers consider that the ionic species would most probably chemisorb through bond formation with baryte; barium oleates are probably formed at the mineral surface.

The work of Jung et al. further shows that the concentrations of the oleate species in solution reach maximum value at about pH 8 and begin to decrease at pH 9 - 10. The latter pH is the region of the zpc of baryte. This would account for the decrease in adsorption density beyond pH 9.5.

A further reason for the decrease would come from the fact that any Ba^{2+} ions in solution arising from the solubility of baryte in water would exist in the form of precipitated $Ba01_2$ beyond the zpc of baryte, thus depleting the free oleate ions in solution capable of adsorbing at the baryte surface.

For a third reason, the preponderance of 0H ions above pH 10 would lead to $0H^-$ ions competing with oleate ions for adsorption at the mineral surface.

CONCLUSION

Sodium oleate adsorbs onto Nigerian baryte in aqueous medium at both acid and alkaline pH and at ambient and elevated temperatures. The maximum adsorption density was 15.9×10^2 μmole/m^2 at the ambient temperature of 29°C and the natural pulp pH of 8.2 and gave the critical micelle concentration value of 0.013 mole/litre for sodium oleate.

Maximum adsorption occurred at pH 9.5. This pH is the zpc of the Nigerian baryte. Adsorption density increased with increasing temperature to a maximum at 40°C beyond which temperature adsorption density decreased.

Chemisorption is considered the dominant mode of adsorption at the ambient temperature and up to 40°C with a minor contribution of physical adsorption to the overall adsorption process. Beyond 40°C the chemisorbed species probably dissociate from the surface while physical processes become the primary mode of adsorption.

Among the stable oleate species identified in solution, H01 is considered to adsorb specifically in the stern layer without bond formation; the ionic species 01^-, 01_2^{2-} and $H01_2$ would chemisorb most probably through bond formation; barium oleates are probably formed at the mineral surface.

Factors that would account for the decrease in adsorption density beyond pH 9.5 include that the concentration of the oleate species in solution begin to decrease in the pH region 9-10, any Ba^{2+} ions in solution would exist in the form of precipitated $Ba01_2$ beyond pH 9.5 thus depleting the free oleate ions available for adsorption, and that the preponderance of $0H^-$ ions above pH 9.5 would lead to $0H^-$ ions competing with oleate ions for adsorption at the mineral surface.

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