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SORPTION OF 8-HYDROXYQUINOLINE BY SOME CLAYS AND OXIDES

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Abstract—The sorption of 8-hydroxyquinoline onto some clays and oxides was studied as a function of concentration, pH, and time. The sorption reaction reached equilibrium in about 5 hr, was irreversible, and reached a maximum at pH 5. The decrease in sorption on both sides of the maximum was attributed to electrostatic interactions of charged molecules with similarly charged surfaces and/or neighbors as well as solvent and proton competition. X-ray powder diffraction of dried clays showed that a one-layer complex formed in which the molecules lay flat between the clay interlayers. The sorption onto the clays included physical and exchange sorption and was accompanied by exchangeable cation hydrolysis. At high surface coverage the silicate structure deteriorated in the direction of the Z-axis due to chemical aggressiveness of the reagent.

Key Words—Adsorption, Alumina, Charcoal, 8-Hydroxyquinoline, Kaolinite, Montmorillonite, Silica.

INTRODUCTION

In previous studies (de Bussetti *et al.,* 1980; Ferreiro *et al.,* 1983; Helmy *et al.,* 1983) the sorption reactions by clays and oxides of compounds that may have industrial and agriculture use or that could ultimately become incorporated in soils and sediments were examined. In the present work, the 8-hydroxyquinoline molecule, also known as quinolinol or oxine, was investigated. This molecule to date has received little attention despite its use in many agricultural and pharmaceutical preparations (Harris, 1979; Oladiran and Okusanya, 1980; Tinis *et al.,* 1978) and as an analytical reagent for chelation and precipitation. Furthermore, this molecule can exist as positively charged, negatively charged, and neutral species depending on the pH of the system, thereby offering aspects of sorbate-sorbent interactions of considerable interest.

In this paper, the results of a study of the sorption reaction of oxine onto clays, oxides, and charcoal are reported. Factors that affect the reaction, such as time, concentration, exchangeable cation, and pH, are also described.

MATERIALS AND METHODS

The following substances were used as sorbents of 8-hydroxyquinoline: (1) montmorillonite from Cerro Bandera, Argentina, having a cation-exchange capacity (CEC) of 0.92 meq/g and a glycerol surface area of 808 m^2/g (Peinemann *et al.,* 1972); particles <2 μm were saturated with Na or Ca by repeated washings with 0.5 M chloride salts followed by washing out of excess salt with the help of a centrifuge; (2) kaolin from Birch Pit, Macon, Georgia, having a CEC of 0.06 meq/g and a surface area of 7.9 m^2/g as determined by paranitrophenol (PNP) adsorption from xylene (Giles and Trivedi, 1969); particles <2 μm were saturated with Na or K as described above; (3) synthetic, noncrystalline silica-alumina prepared in this laboratory and having the composition: SiO_2, 75.6; Al_2O_3, 14.2; H_2O, 10.1%; and a PNP surface area of 94.9 m^2/g; (4) hydrous oxide of aluminum, chromatographic grade, from Carlo Erba, Milano, Italy; this material is amorphous to X-rays and has a PNP surface area of 48 m^2/g; (5) hematite (α-Fe_2O_3) from May and Baker Limited, Dagenham, England, having a surface area of 10.3 m^2/g as determined by water vapor adsorption; (6) active dry charcoal, from Merck, Darmstadt, Federal Republic of Germany; and (7) silica gel from Davison Chemicals, Baltimore, Maryland, having a N_2 surface area of 600 m^2/g and an average pore diameter of 67 Å.

Analytical grade 8-hydroxyquinoline (C_9H_6NOH) was obtained from Riedel de Haën, Hannover, Federal Republic of Germany. It has a molecular weight of 145.16 g, a melting point of 76°C, a boiling point of 266.6°C, and a water solubility of about 4 mmole/liter. Oxine dissociates as follows:

$$(C_9H_7NOH)^+ \underset{}{\overset{K_1}{\rightleftharpoons}} C_9H_6NOH + H^+, \qquad (1)$$

$$C_9H_6NOH \overset{K_2}{\rightleftharpoons} (C_9H_6NO)^- + H^+, \qquad (2)$$

where $pK_1 = 5.0$ and $pK_2 = 9.85$. The concentration of oxine in aqueous solutions was determined spectrophotometrically at 340 nm using a standard curve. All measurements were made in solutions adjusted to pH 12.5 with NaOH.

The sorption of oxine by the above-mentioned substances as a function of pH and oxine concentration was carried out by adding 25 ml of oxine solutions of different concentrations and pH to 0.1–0.2 g of sorbent in 50-ml Pyrex bottles. For charcoal, the suspensions were prepared by weighing 0.05 g of material and adding 100 ml of the oxine solutions into 150-ml Pyrex bottles. The pH of the solutions was adjusted by adding

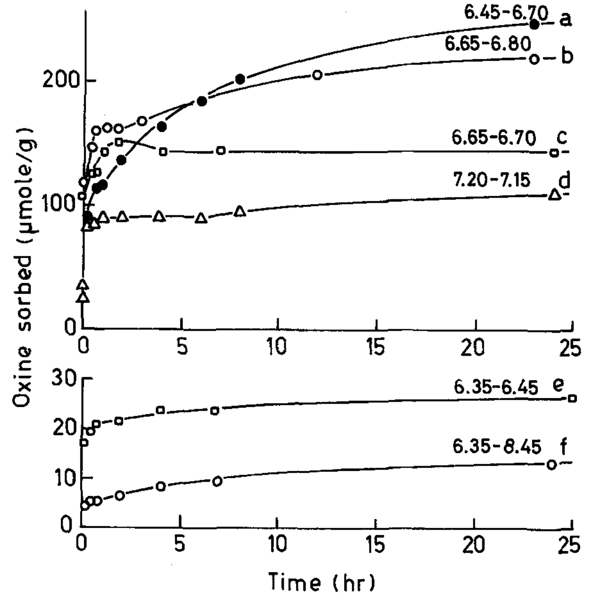


Figure 1. Sorption of oxine as function of time by: (a) aluminum oxide, (b) Ca-montmorillonite, (c) Na-montmorillonite, (d) silica-alumina, (e) K-kaolin, and (f) iron oxide. Numbers on curves represent initial and final pHs in solution.

HCl or NaOH. The equilibrium pH range covered was 2–10 at five different oxine concentrations. The bottles were shaken for 30 min and left for 48 hr with occasional shaking. The pH and oxine were determined in the filtered supernatant liquids. The amounts of oxine sorbed were calculated as the differences between final and initial concentrations. For the Na- and/or Ca-montmorillonites, the concentration of Na and/or Ca in the equilibrium solutions at each pH was determined by flame photometry.

The effect of time on the sorption reaction was investigated using separate suspensions of Al_2O_3 (1 g/liter), silica-alumina (1 g/liter), Na- and Ca-montmorillonites (2 g/liter), and K-kaolinite and hematite (8 g/liter). The initial oxine concentrations in units of mmole/liter were 0.45 (Al_2O_3), 0.33 (silica-alumina), 0.54 (Na- and Ca-montmorillonites), and 0.42 (K-kaolinite and hematite).

The reversibility of the oxine adsorption reaction was studied for Al_2O_3 and Na- and Ca-montmorillonite adsorbents only. To 0.16-g samples in 50-ml bottles, 40 ml of solutions containing 0–3.58 mmole/liter of oxine were added. The bottles were stoppered and shaken for 30 min and left for 48 hr with occasional shaking. The pH was then measured and 20-ml samples from the supernatant liquids were withdrawn for analysis. Twenty milliliters of water was added to the bottles containing the highest concentration of oxine; the bottles were then shaken and left for 48 hr, at which time liquid samples were withdrawn for analysis and 20 ml of water was added. This procedure was repeated several times and finally produced a low oxine concentration in the equilibrium solutions. The amounts of oxine sorbed or desorbed were then calculated after each dilution from the material balance in the systems. The initial pH of the systems was 6.6, 6.0, and 2.4–7.5 for Al_2O_3, Na-, and Ca-montmorillonites, respectively. Sorption-desorption reactions of oxine were also studied for Ca-montmorillonite in the presence of 0.01 M $CaCl_2$ at pH 7.5.

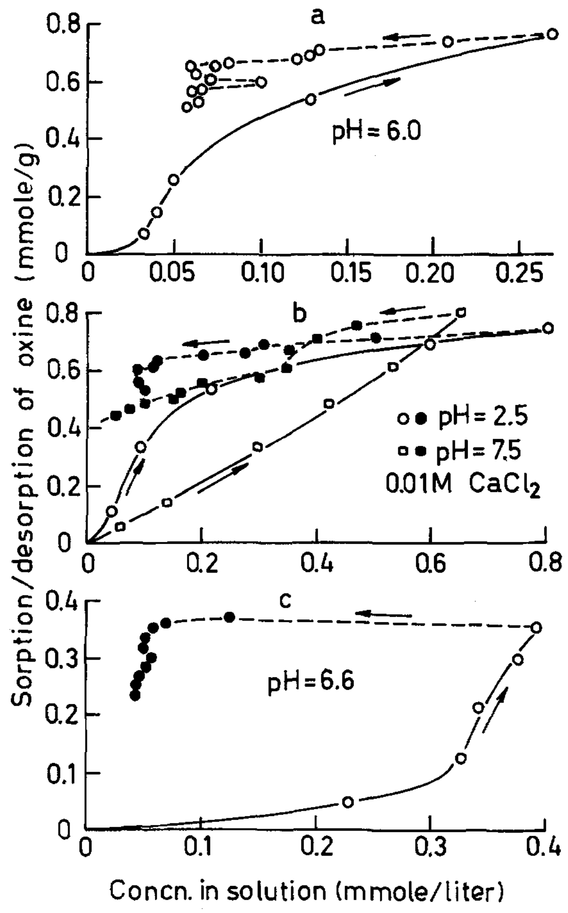


Figure 2. Sorption-desorption of oxine by: (a) Na-montmorillonite, (b) Ca-montmorillonite, and (c) aluminum oxide.

The basal spacings of air dry Na- and Ca-montmorillonites that sorbed oxine were obtained by X-ray powder diffraction (XRD) technique using CuKα radiation.

RESULTS AND DISCUSSION

Influence of time

The effect of time on oxine sorption by clays and oxides is shown in Figure 1. The initial slope of the sorption-time curves is rather steep, indicating that the reaction is rapid onto the sorbents. This initial rapid reaction was followed by a slow reaction, and the rate of the reaction became constant after about 5 hr, except

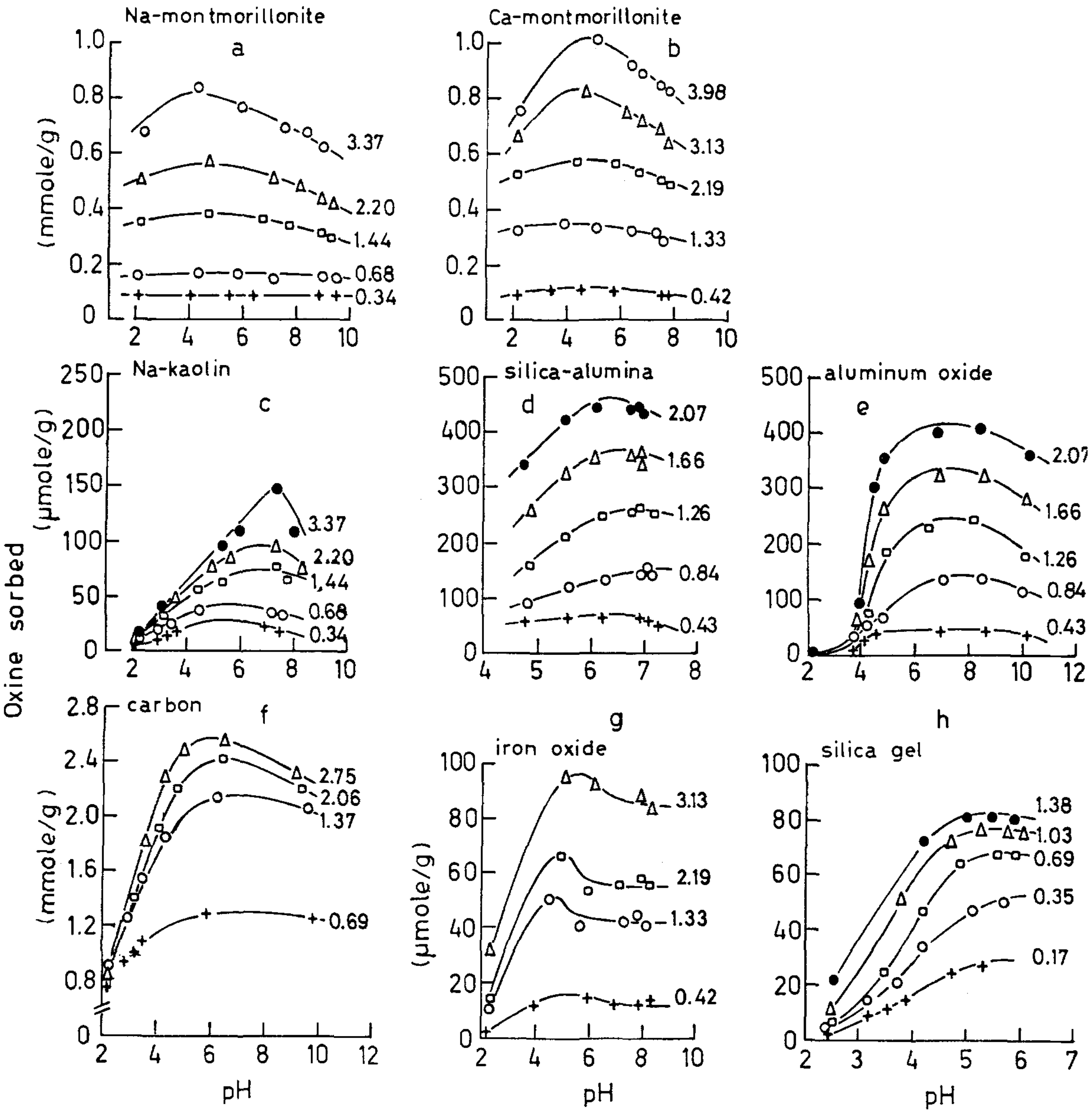


Figure 3. Effect of oxine concentration and pH on oxine sorption by: (a) Na-montmorillonite, (b) Ca-montmorillonite, (c) Na-kaolin, (d) silica-alumina, (e) aluminum oxide, (f) charcoal powder, (g) iron oxide, and (h) silica gel. Numbers on curves represent initial oxine concentration in mmole/liter.

for Ca-montmorillonite and aluminum oxide for which more time was needed for the reaction to reach equilibrium. The slow adsorption rate onto the Ca-clay may be explained by the limited expansion of the interlayers in water, which should have retarded the diffusion of the sorbate into the clay.

Reversibility of sorption reaction

The reversibility of the oxine sorption reaction was examined using Na-, Ca-montmorillonite, and aluminum oxide. For all samples the sorption reaction was found to be irreversible or very slowly reversible, as indicated by a marked difference between the sorption and desorption curves. Furthermore, the pH (2.4 or 7.5) was found to have no effect on the reversibility of the reaction on the Ca-clay (see Figure 2).

Effect of concentration and pH

Sorption onto charcoal. Charcoal was included as a reference sorbent in the study of oxine sorption because it carries almost no surface charges and no pH changes take place upon organic sorption. These properties help in the interpretation of the sorption reaction on charcoal and on the other sorbents.

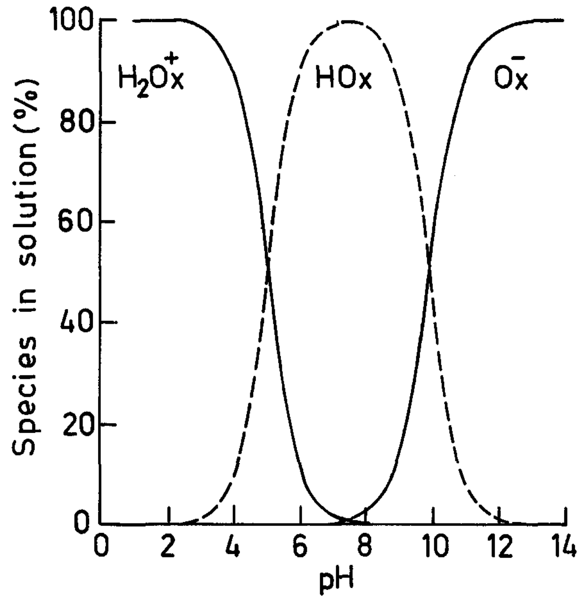


Figure 4. Percentage of cationic, neutral, and anionic state of oxine molecule as function of pH.

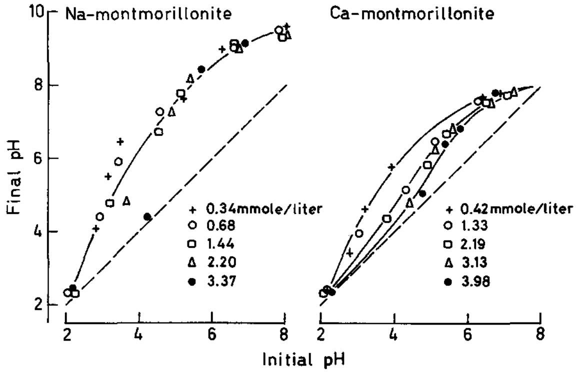


Figure 5. Final pHs as function of initial pHs of oxine solutions from which sorption took place by: Na-montmorillonite and Ca-montmorillonite. Numbers on curves represent initial concentration of sorbate.

The sorption curves for charcoal plotted as a function of pH and oxine concentration in Figure 3f have a maximum at pH 5. The reason for the existence of an adsorption maximum at pH 5 may be as follows. As shown in Figure 4 oxine exists in solution as a neutral molecule near neutral pH, as a molecular cation at low pH, and as an anion at higher pH. If these charged units were to be packed on a surface, the electric repulsion between adsorbed neighbors would be minimized. The minimization of the electric repulsion may be achieved by the maintenance of certain distances between neighbors and by the presence of neutral molecule between charged molecules. At high acidity, where a large proportion of oxine is positively charged, little sorption should take place because large distances have to be maintained between these units on the surface and because of competition with protons for exchange sites, if the sorbent has negative charges in acid media. As the pH increases and the proportion of neutral to charged units increases, a greater packing density is possible. This process continues until the adsorbed units are nearly in contact. For the units to be in contact, and for the electric repulsion between the charged units to be as small as possible, a neutral molecule must be present between two charged molecules. This configuration gives a 1:1 ratio of charged to neutral units on the surface. Because this ratio exists in solution at $pH = pK_1 = 5$, the maximum sorption takes place at this value. The above discussion assumes that the surface properties of the sorbent are not affected by pH changes; i.e., the sorption mechanism is the same for both species, and the surface has no preference for one species over the other.

If the same mechanism for the sorption at low pH is used to explain the sorption of anion and neutral oxine at high pH, a plateau of maximum sorption should occur between pH 5 and 10, where the two pK_a values of oxine are found. Such a plateau was not observed, perhaps because the anion oxine molecules must associate with highly hydrated metallic cations in order to maintain electroneutrality, thus increasing the amount of water onto the surface and provoking a decrease in organic sorption.

The sorption isotherms obtained at constant pH are shown in Figure 7c and are all of the high-affinity type. The order of the sorption curves, i.e., pH 6 > pH 9> pH 3, shows clearly that the positively and negatively charged oxine molecules are less preferred by the charcoal surface than the neutral molecule.

Sorption onto oxides. The sorption curves for aluminum oxide, silica-alumina, and kaolin, shown in Figure 3, have a maximum at pHs between 6 and 7, which are one or two units higher than the pH values for charcoal. This difference may be due to the fact that the Al–O surface is positively charged at pH 5 (Helmy and Ferreiro, 1976); the charge may well interfere with the sorption of the oxine molecules which are also charged at this pH.

Another factor which may have contributed to the displacement of the sorption maximum is the chemisorption of oxine by a ligand-exchange surface reaction in which surface OHs are released to the solution. This release explains the pH increases observed as oxine is sorbed onto oxides. This explanation for the displacement of the maximum is corroborated by the fact that the sorption maximum on silica gel is at pH 5 and no pH changes were noted upon oxine sorption. These observations can be explained by the fact that the Si–OH bond in silica gel has a high strength and low ionic character, thus obviating OH participation in ligand exchange.

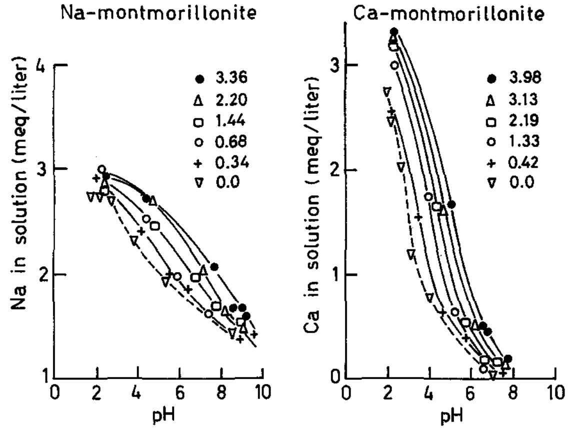


Figure 6. Exchangeable Na and/or Ca released by montmorillonite as a result of oxine sorption plotted as function of pH. Initial oxine concentrations are also given.

As with charcoal, oxine sorption on oxides decreased as the pH increased beyond maximum sorption. This decrease may be explained, in addition to the reason given above for charcoal, by the acquisition of negative charges by oxide surfaces as the pH became neutral or alkaline. A surface with a high negative charge density repels anion molecules and makes oxine sorption more difficult at high pHs.

Sorption reaction onto Na- and Ca-montmorillonite. The sorption curves of oxine onto montmorillonite have maxima at pH 5 (Figure 3). Furthermore, the sorption reaction of oxine onto montmorillonite was accompanied by an increase in the pH of the equilibrium solution. Figure 5 shows final pH plotted against initial pH of the oxine solutions. The increase in pH is due to the hydrolysis reaction associated with the liberation of Na and/or Ca to the solution (see Figure 6) as a result of exchange with protons and/or organic cations. Organic cations may have been produced by the protonation of neutral molecules at the surface. Hence, the overall reaction of exchange and hydrolysis may be written as: $Na^+(ads) + HOX(ads) + H_2O \rightarrow H_2OX^+(ads) + NaOH(soln)$, where HOX and H_2OX^+ represent neutral and cation oxine, respectively.

Similar pH increases on organic sorption were reported by Vansant and Uytterhoeven (1973). Such an increase, however, was not noted for charcoal, because charcoal possesses no exchangeable cations.

Furthermore, the sorption isotherms of oxine on Na- and Ca-montmorillonite are S-shaped at low concentrations (Figures 2 and 7). The isotherm on carbon plotted for comparison in Figure 7 is of the high-affinity L type, according to the classification of Giles *et al.* (1974). The S-shape of the curve is usually explained as being due to competition with the solvent. The presence of the solvent is easily understood in terms of cation hydration on the clay surface.

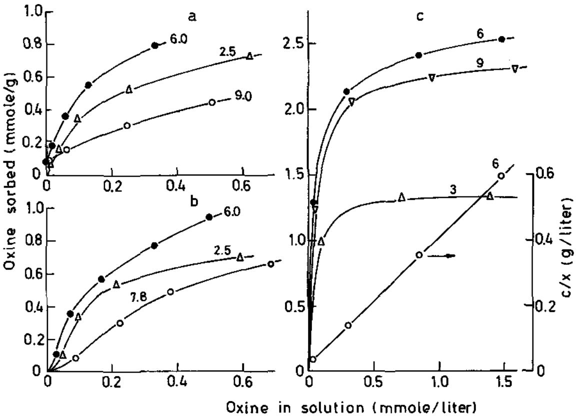


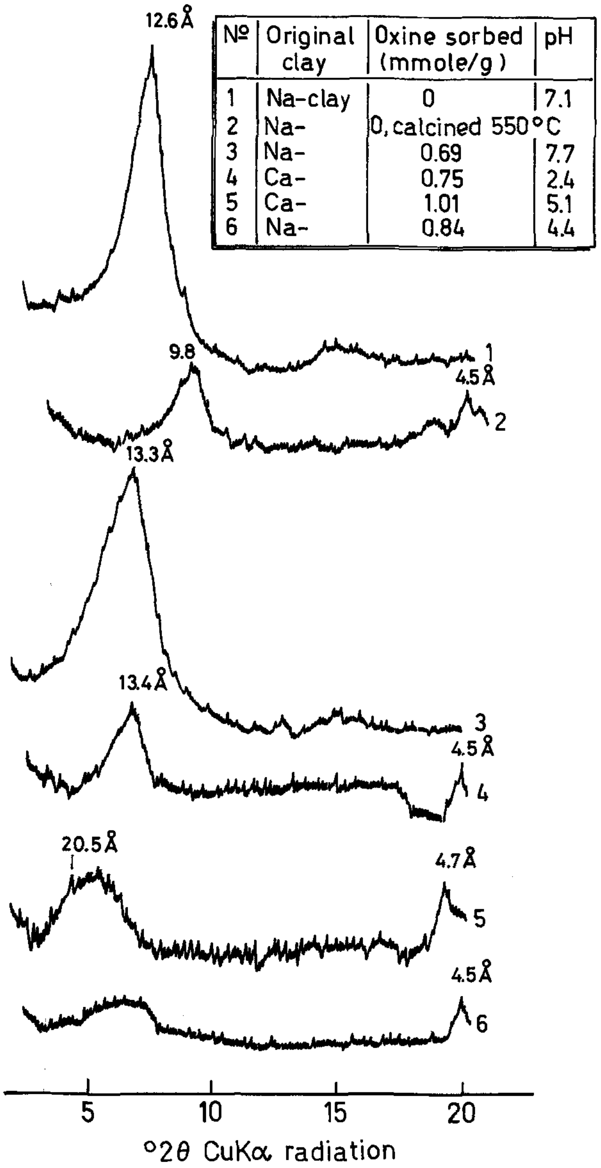
Figure 7. Sorption isotherms of oxine for: (a) Na-montmorillonite, (b) Ca-montmorillonite, and (c) charcoal powder. Straight line in (c) is a Langmuir plot of the data of the uppermost curve. Numbers on curves represent pHs at which sorption took place.

X-ray powder diffraction traces for montmorillonite

Typical XRD traces for air-dry, oxine-treated montmorillonite are shown in Figure 8. Basal spacings are listed in Table 1 together with (1) the amounts of oxine sorbed and in solution, (2) the amount of the metallic cation released, and (3) the pH at which the clay-organic complex was formed. As can be seen from these data, the basal spacing of the complex is about 13.4 Å, except where small amounts of oxine were sorbed and where a small release of exchangeable cations took place; here, the spacing obtained is that of the cation-clay.

This spacing indicates that an α-complex formed, i.e., a one-layer complex in which oxine rings lie parallel to the clay layer (Aragon *et al.,* 1959). This orientation is the same as that obtained for the related compound 6-nitroquinoline (Greene-Kelly, 1955), but differs from that of quinoline which forms a β-complex in which the quinoline molecule lies at an angle to the clay layer, depending on the packing density (Helmy *et al.,* 1983). This difference in orientation between quinoline and oxine can be attributed to the OH group in the quinoline ring of oxine leading, perhaps, to H-bonding with the oxygens of the silicate layers.

At high sorption values of oxine onto the clay, the intensity of the basal reflection decreased, and the diffraction peak disappeared or changed significantly (see Figure 8). These changes were likely due to a chemical attack of the clay by the adsorbate. Interestingly, the (020, 110) reflection, having a spacing of about 4.5 Å, was not affected, indicating that the deterioration of the silicate structure was in the direction of the Z-axis and that it was not extensive enough to affect other crystal planes. The chemical attack on the clay was also evidenced by the presence of a green oxine-iron com-



Nº	Original clay	Oxine sorbed (mmole/g)	pH
1	Na-clay	0	7.1
2	Na-	0, calcined 550°C	
3	Na-	0.69	7.7
4	Ca-	0.75	2.4
5	Ca-	1.01	5.1
6	Na-	0.84	4.4

Figure 8. X-ray powder diffraction traces of montmorillonite and montmorillonite-oxine complexes.

plex in the suspensions, the green color being more intense at high concentration of oxine after long periods of contact.

Dimensions of the sorbed molecule

An estimation of the dimensions of the oxine molecule can be obtained as follows. XRD data show that a monolayer formed having a thickness of 13.4 − 9.6 = 3.8 Å. Furthermore, the adsorption maximum of oxine was 1.05 mmole/g. Based on the surface area of the montmorillonite used, 808 m²/g, the area per molecule is

Table 1. Basal spacings of Na- and Ca-montmorillonite-oxine complexes.

Material	pH	Oxine sorbed (mmole/g)	Oxine in soln. (mmole/liter)	Cations released (meq/g)	d(001) (Å)
Ca-montmorillonite	7.05	0	0	0	15.8
	2.30	0.33	0.09	0.83	13.2
	2.35	0.75	1.24	0.90	13.4
	3.45	0.11	0.03	0.43	14.9
	6.80	0.90	0.70	0.13	15.8
	7.85	0.84	0.93	0.08	15.8
Na-montmorillonite	7.10	0	0	—	12.3
	2.25	0.09	0.01	0.75	13.4
	7.70	0.69	0.71	0.54	13.4
	8.95	0.08	0.02	0.36	12.6
	9.20	0.56	1.22	0.41	13.6

The oxine sorbed, the oxine concentration, and metallic cation released as a result of oxine sorption.

$$808 \times 10^{20}/(2 \times 1.05 \times 6.023 \times 10^{20}) = 64\ \text{Å}^2.$$

Thus, the calculated area is of the same order of magnitude as that calculated for the quinoline molecule.

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