# SOME CONDITIONS AFFECTING THE ADSORPTION OF QUINOLINE BY CLAY MINERALS IN AQUEOUS SUSPENSIONS

*by*

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## ABSTRACT

The adsorption of quinoline by $Na^+$- and $Ca^{2+}$-montmorillonite, illite, and kaolinite in water suspensions was studied for varying physico-chemical conditions. The shapes of the adsorption isotherms depended upon these imposed environmental conditions, which were quinoline concentration, pH, salinity, time, and temperature.

In order to be in the range of concentrations of organic materials in natural waters, these studies covered the concentration range, from 0 to several hundred ppm. Of the variables studied, pH was critical. Throughout the pH range 8.5–6.0, adsorption increased as pH decreased. The change in adsorption as salinity increased depended on pH, clay mineral, and quinoline concentration. In our experiments, samples reached equilibrium within 2–3 hr, and moderate temperature changes made little difference in adsorption amounts.

Under the same conditions, $Na^+$-montmorillonite adsorbed the most quinoline, kaolinite the least, and $Ca^{2+}$-montmorillonite and illite intermediate amounts.

Two mechanisms seem to control this adsorption: ion exchange and molecular adsorption. This paper attempts to explain the effects of the physico-chemical environment on adsorption by these two mechanisms.

## INTRODUCTION

Many excellent articles deal with the adsorption of organic material by clay minerals. References to many of these articles, as well as general surveys of clay–organic reactions, have been given by MacEwan (1951) and Grim (1953, pp. 250–277). For the most part, however, these investigations have been concerned with adsorption of organic liquids and vapors by montmorillonite and vermiculite. The studies have been focused primarily on the swelling of the clay lattice due to organic adsorption, the bonding mechanisms operative between organic and clay, and the orientation of the organic molecules between clay layers.

More recently Brindley and Rustom (1958), Hoffmann and Brindley (1959), and Bader and Smith (1959) specifically studied organic adsorption by clays in water suspensions.

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The mere presence of water in a clay–organic reaction is important in that the water must act in competition with the organic material for sites on the clay surface. The pH of the water is a consideration since some organic types may change in their ionic-nonionic form in response to changes in hydrogen ion availability. Adsorption characteristics by clay may be quite different depending upon whether or not the organic material is ionic or nonionic. If buffer solutions are added in order to keep pH constant, the question arises as to the significance of ionic strength of the aqueous medium on adsorption. It is quickly seen that a whole series of variables are soon involved in such experiments.

This study is an attempt to show the importance of some of the physico-chemical conditions of the aqueous medium in which clay–organic reactions occur. When the term "environment" is used in this paper, the reference is to these imposed physico-chemical conditions.

## ACKNOWLEDGMENTS

## MATERIALS AND METHODS

### Clay Minerals

The clay minerals used in this investigation were $Na^+$-montmorillonite from Clay Spur, Wyoming; $Ca^{2+}$-montmorillonite from Chambers, Arizona; illite from Fithian and Morris, Illinois; and kaolinite of the Georgia type. The exact source of the kaolinite sample is not known. The effects of varying environmental conditions were our chief concern, and not maximum adsorption capacities of the clays. Consequently, the montmorillonite and kaolinite samples were used without any prior treatment; that is, small amounts of nonclay material were not separated from the clay. The illite samples, however, were dispersed in distilled water, and the $< 2\,\mu$ fraction was separated by centrifugation and used in the experiments. An imposed pH was difficult to maintain on this material. Accordingly, before using it, the clay was soaked in 0.2 N KOH for 1 hr, washed free of excess KOH with distilled water, and air-dried.

### Organic Material

Quinoline was selected as the organic material in this study because it has a favorable solubility in water, and it can be rather easily analyzed, quantitatively, by its absorption spectra in ultraviolet light (Fig. 1). Quino-

line (synthetic) from Eastman Organic Chemicals was dissolved in distilled water and used in all experiments.

## Buffers

In order to control the pH of the sample environment, it was necessary to use buffer solutions. Phosphate buffers were used for the pH range 6.0–8.0, and borate buffers for the range 8.0–10.0. Sodium phosphate or
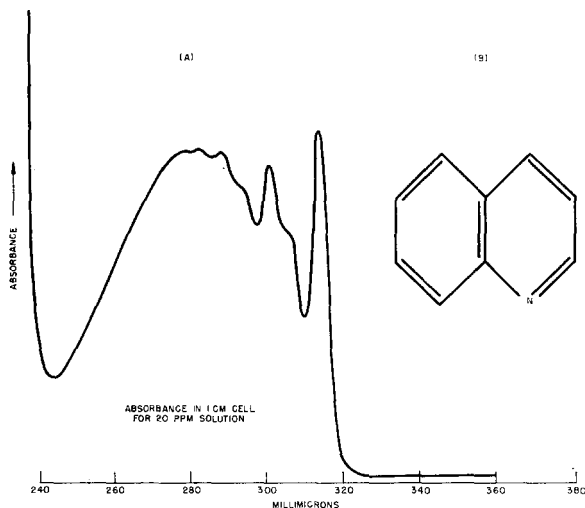


FIGURE 1.—(A) Absorption spectra of quinoline in ultraviolet light, and (B) structural formula of quinoline.

borate buffers were used with $Na^+$-montmorillonite and kaolinite, potassium buffers with illites, and ammonium buffers with $Ca^{2+}$-montmorillonite clay.

## Procedure

One-quarter gram portions of the air-dried clays were weighed, placed in screw-top flasks, and allowed to disaggregate by soaking in distilled water. In several instances, 0.50 g samples of kaolinite and illite were used, and these are noted in the paper. The combined volume of water, buffer, and quinoline solution in each sample was 10 ml. The quinoline was in contact with the clay for 3–4 days, after which the samples were centrifuged in order to separate the clay from the supernatant liquid. Quinoline concentration and pH measurements were made on the supernatant liquid. Quinoline concentration was determined by absorption of ultraviolet light at 314 m$\mu$ (Fig. 1A). All quinoline determinations were made in alkaline solutions, since the ultraviolet light absorption is somewhat pH sensitive. The amount of quinoline in the supernatant liquid was calculated, and then by difference the amount retained by the clay.

EXPERIMENTAL RESULTS

*Quinoline Concentration*

Fig. 2 shows adsorption isotherms for four clay minerals, at about the same pH, with quinoline concentration as the variable. The curves describe equilibrium conditions of the samples; that is, the quinoline concentrations
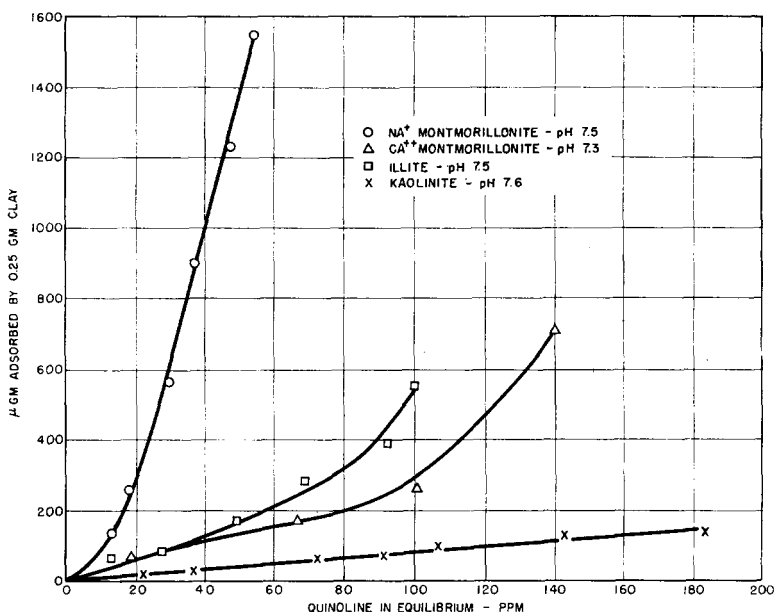


FIGURE 2.—Isotherms showing quinoline adsorption by four clay minerals in response to changing quinoline concentration.

at the end of the experiments are plotted against the amounts adsorbed by the clays. As higher concentrations of quinoline became available to the clays, more was retained. The adsorption mechanism or mechanisms, in some cases, became more efficient as the quinoline concentration increased. The data show that some of the isotherms swing upward at higher quinoline concentrations. The concentrations studied here ranged from 0 to 200 ppm, well below the value for quinoline solubility in water. For similar environmental conditions, $Na^+$-montmorillonite retained the most quinoline, kaolinite the least, and $Ca^{2+}$-montmorillonite and Fithian illite intermediate amounts. No correlations have been made for clay hydration state at room conditions.

### pH

Adsorption of quinoline by the clay increased as the pH of the environment decreased throughout the range of pH values investigated. Adsorption was more sensitive to pH changes in the case of the three-layer clays than with kaolinite. Fig. 3 and 4 show that adsorption from slightly acidic environments was always greater than from alkaline environments, regardless of the quinoline concentration or type of clay present. Particularly with Fithian illite and $Ca^{2+}$-montmorillonite, the shapes of the adsorption isotherms varied in response to pH changes.

Fig. 5 and 6 illustrate, a little more clearly, the dependence of adsorption values on pH throughout the range of approximately 6.0–8.0. Note that 0.50 g samples of kaolinite and illite were used for the curves in Fig. 5, but the same quinoline concentration was available to all samples plotted in both figures.
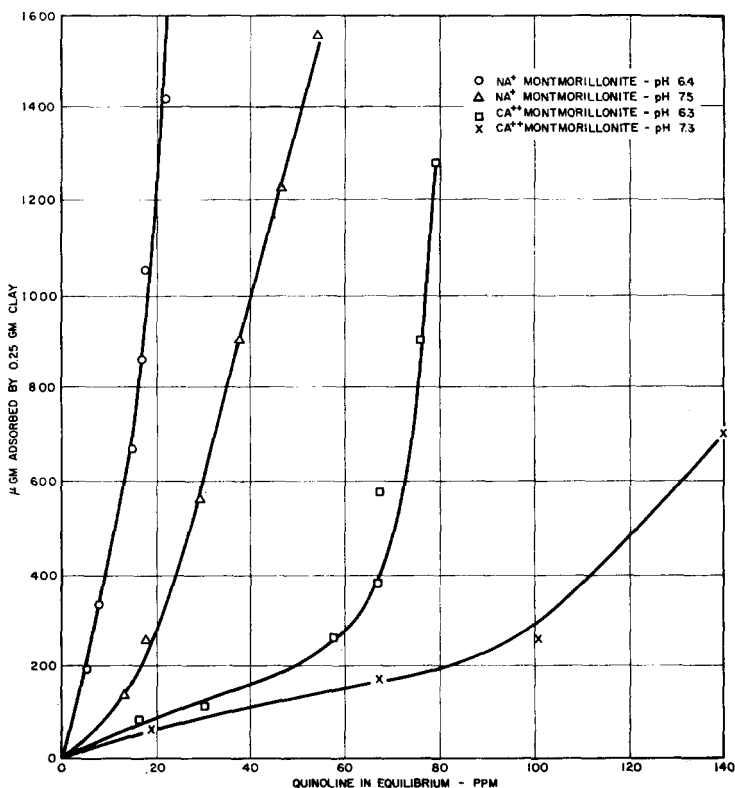


FIGURE 3.—Isotherms showing changes in quinoline adsorption by $Na^+$- and $Ca^{2+}$-montmorillonite in response to changing pH.
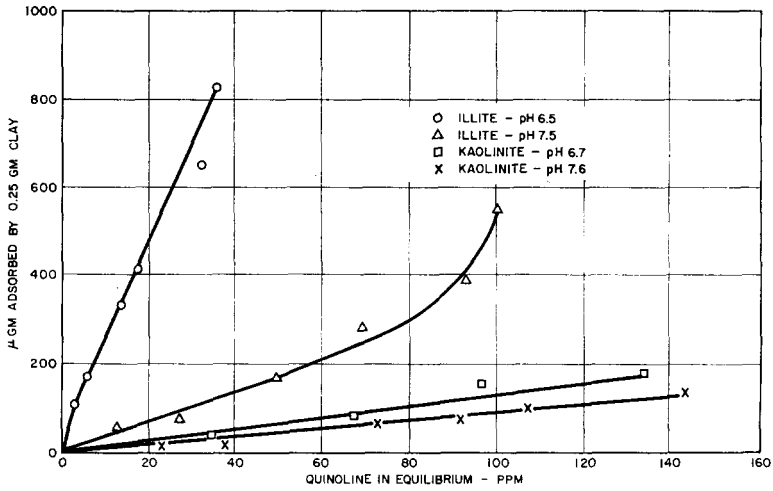
FIGURE 4.—Isotherms showing changes in quinoline adsorption by illite and kaolinite in response to changing pH.
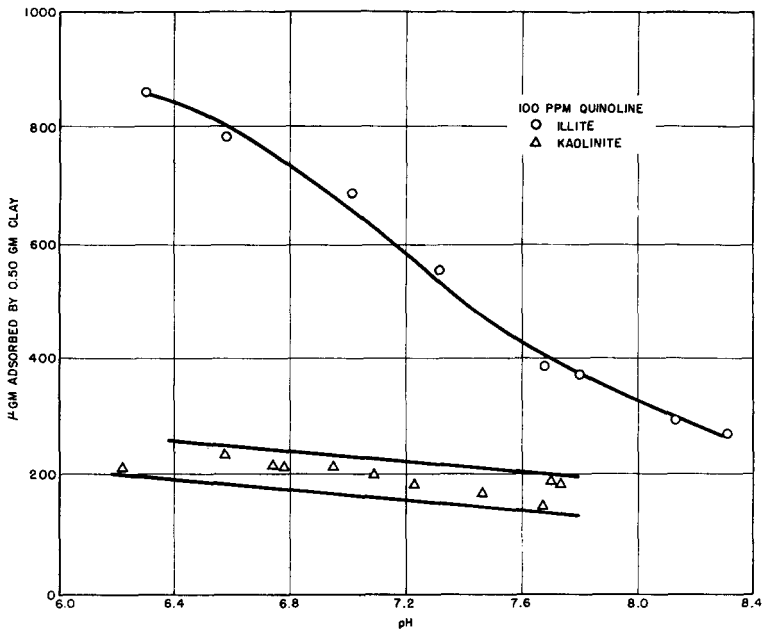


FIGURE 5.—Curves showing changes in quinoline adsorption by illite and kaolinite in response to changing pH.

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## Time and Temperature

Time *vs.* adsorption and temperature *vs.* adsorption curves are included here primarily to show that equilibrium was being reached in the time the samples were allowed to remain mixed, and that moderate temperature
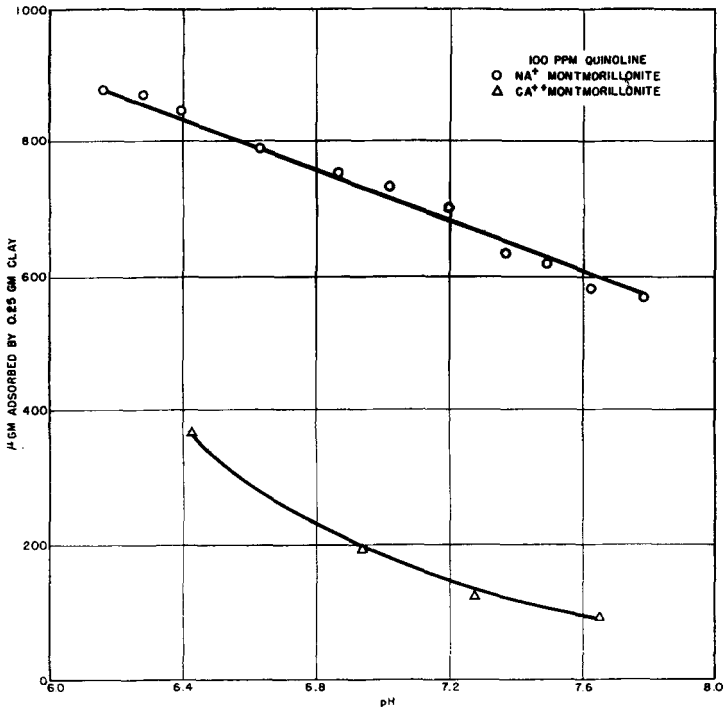


FIGURE 6.—Curves showing changes in quinoline adsorption by Na⁺- and Ca²⁺-montmorillonite in response to changing pH.

variations caused very little change in adsorption amounts. Fig. 7 shows that about 200 min after mixing, 0.25 g samples of Na⁺-montmorillonite reached equilibrium with their environments. To be sure, this time factor undoubtedly would change as sample size and organic concentration change. The samples taken 15 min after mixing were probably abnormally high in quinoline owing to the high organic concentration around the point in the suspension at which the quinoline was introduced.

There was only a slight decrease in adsorption as the temperature was raised from 4° to 60 °C (Fig. 8).

## Salinity

The overall effect of salinity in the range 0–68,000 ppm was to reduce the amount of quinoline adsorbed by the clay. Salinity, as used here, was

a combination of buffer and NaCl. The strength of the buffer solution of a median pH was about 8400 ppm.

Adsorption *vs.* salinity curves are shown in Fig. 9 for three clay minerals in comparable organic and pH environments. The isotherm for Na$^+$-mont-
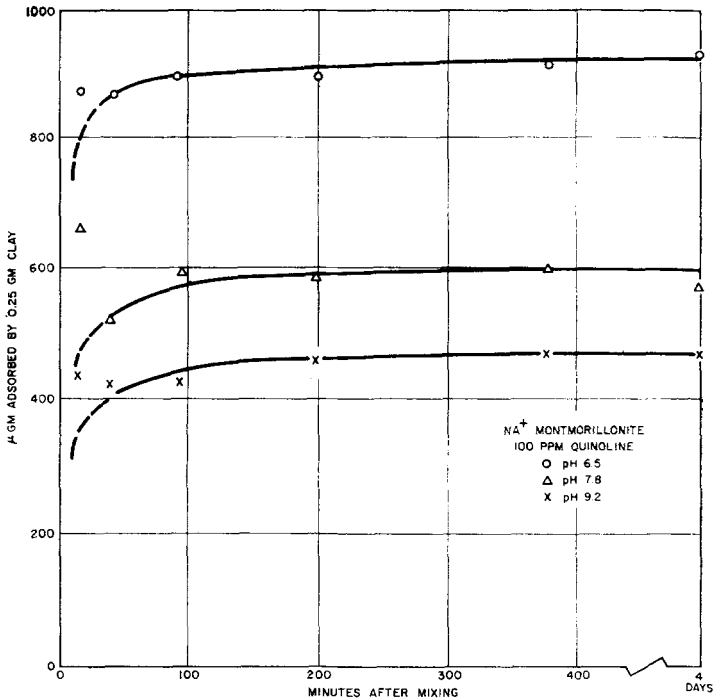


FIGURE 7.—Curves showing adsorption of quinoline by Na$^+$-montmorillonite in relation to time after mixing.

morillonite shows a minimum at about 16,000 ppm, whereas the curves for Morris illite and the kaolinite do not. The minimum on the Na$^+$-montmorillonite curve was, at least in part, related to pH. This relation is illustrated in Fig. 10 where the quinoline concentration was the same for each curve, but the pH was varied. The minimum became more pronounced and moved from lower to higher salinities as the pH changed from 6.4 to 8.3. This minimum also was related to quinoline concentration (Fig. 11). Percent adsorption was plotted *vs.* salinity because of the varying organic concentration. The curve at 300 ppm quinoline shows little effect due to salinity, while the curve at 12 ppm quinoline, at least in shape, approaches those for kaolinite and illite.

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## *Reversibility*

The reversibility of the adsorption reaction, or the ease with which the quinoline was desorbed in response to changing conditions, was studied for Na+-montmorillonite, Fithian illite, and kaolinite. The procedure in the
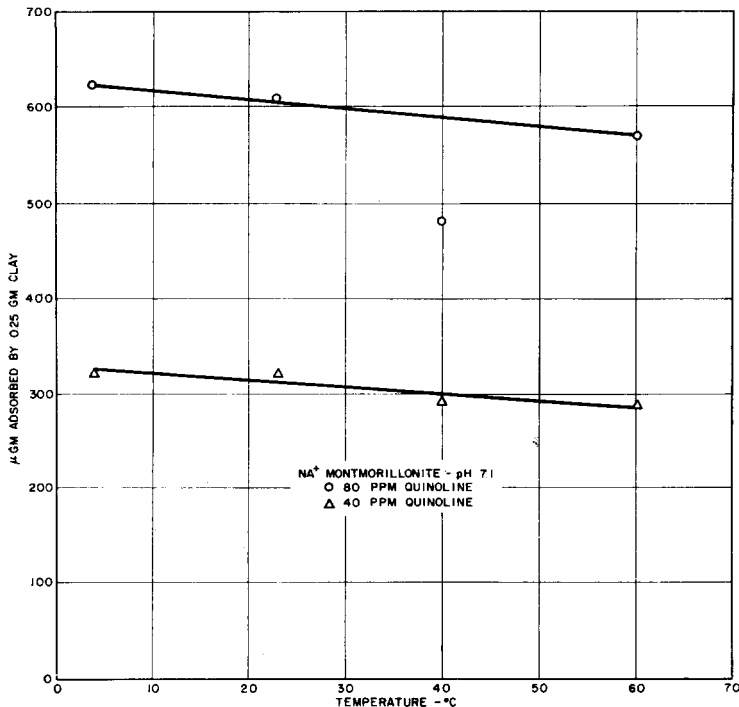


Figure 8.—Curves showing adsorption of quinoline by Na+-montmorillonite in relation to temperature.

reversibility experiments was to prepare two identical sets of samples. Each set initially covered the concentration range 400–2000 $\mu$g (40–200 ppm) quinoline per 10 ml of water. The samples in one set were analyzed 3 days after they were mixed, and at the same time the other set was diluted so that the new quinoline concentration in each sample was only 200 $\mu$g per 10 ml of water. The solution used for diluting the samples was such that the proportion of buffer to water remained constant. After 4 days at this new concentration, these samples were analyzed. With this concentration a completely reversible reaction would leave an amount of quinoline on the clay equal to that adsorbed if the concentration had always been 200 $\mu$g per 10 ml of water.
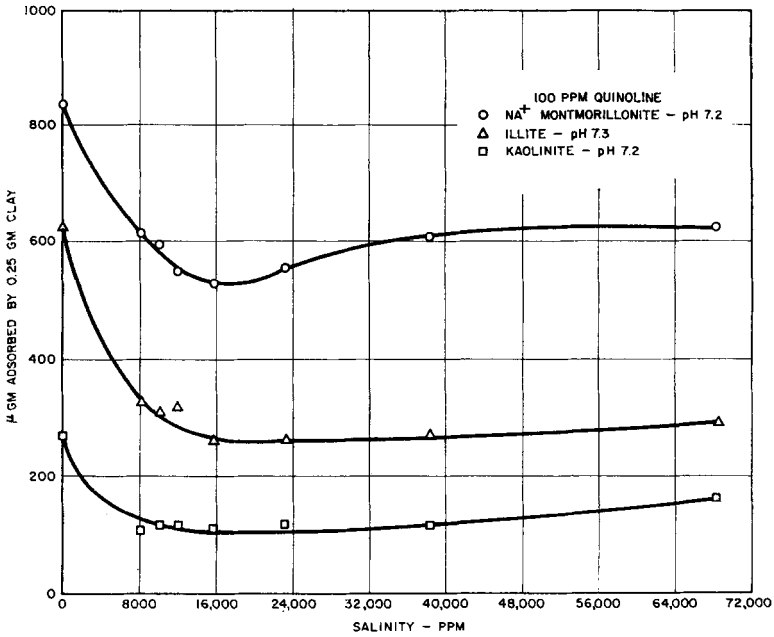
FIGURE 9.—Curves showing changes in adsorption of quinoline by three clays in response to changing salinity.
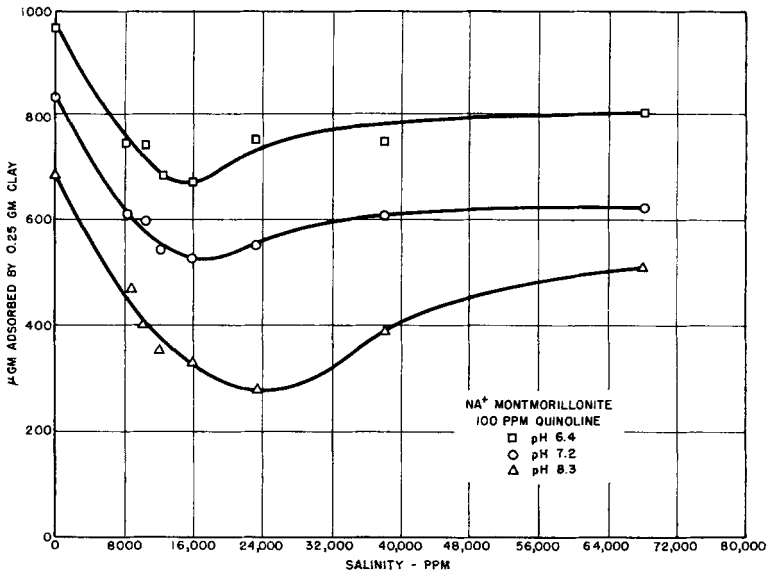


FIGURE 10.—Curves showing changes in adsorption of quinoline by Na$^+$-montmorillonite in response to changing salinity and pH.
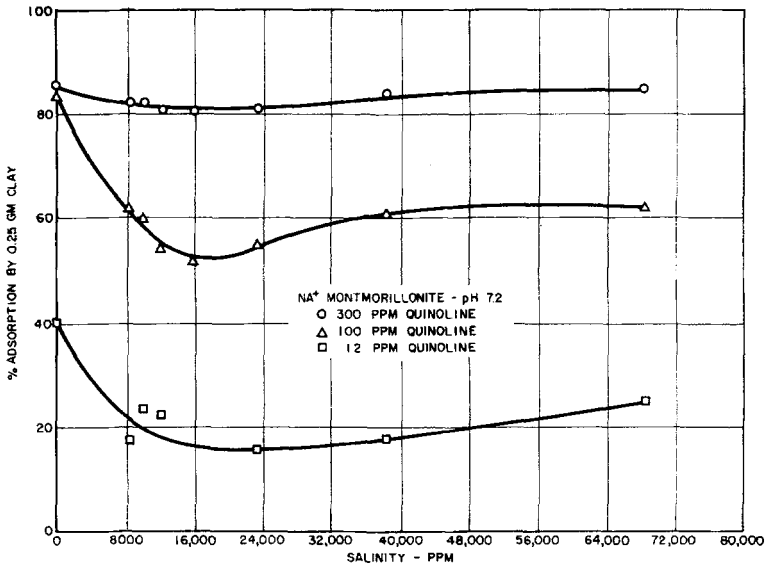
FIGURE 11.—Curves showing changes in adsorption of quinoline by Na+-montmoril-
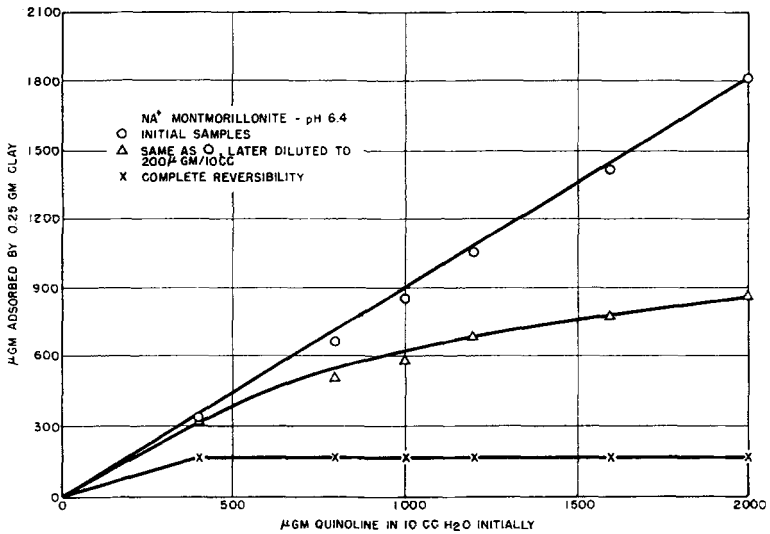lonite in response to changing salinity and quinoline concentration.



FIGURE 12.—Reversibility of quinoline adsorption by Na+-montmorillonite at
pH 6.4.

Comparison of Figs. 12 and 13 shows that quinoline adsorption was more reversible from Na$^+$-montmorillonite when the pH was 7.5 rather than 6.4. Even at pH 7.5, however, the adsorption reaction was not completely reversible.

Reversibility data for both Fithian illite and kaolinite were for 0.50 g samples. Fig. 14 and 15 show that quinoline adsorption was rather
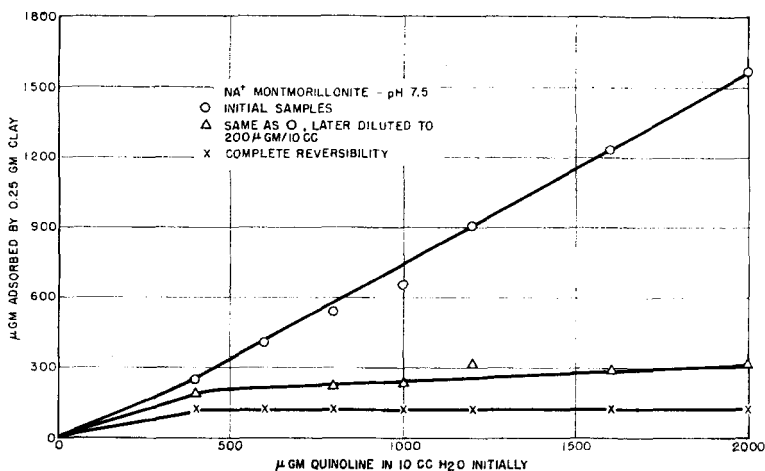


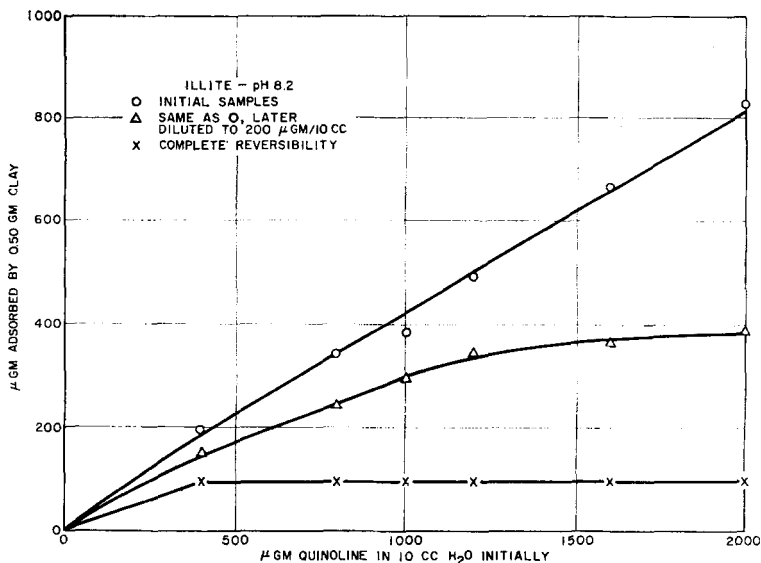FIGURE 13. — Reversibility of quinoline adsorption by Na$^+$-montmorillonite at pH 7.5.



FIGURE 14. — Reversibility of quinoline adsorption by illite at pH 8.2.

irreversible with both illite and kaolinite, even though the pH of the illite experiment was 8.2.
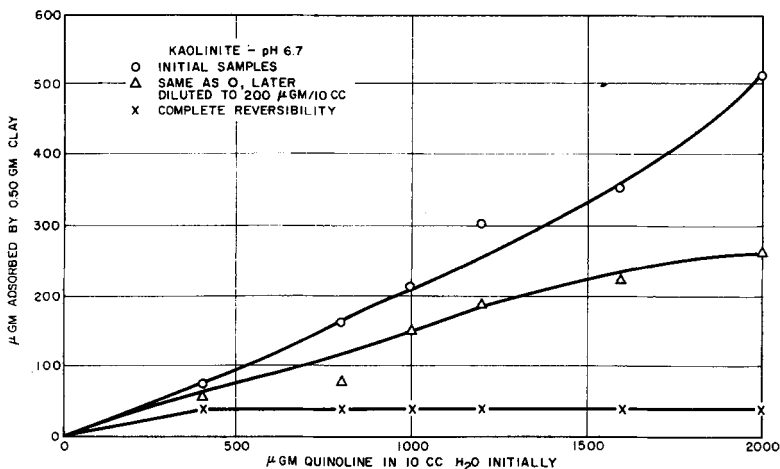


FIGURE 15.—Reversibility of quinoline adsorption by kaolinite at pH 6.7.

## DISCUSSION

Before the relations between clay and quinoline in various environments can be discussed, the effect of changing environment on quinoline alone must be understood. At pH 5, quinoline in solution exists in about equal portions of ionic and nonionic molecules. As pH increases, the percent of quinoline cations decreases, and at a pH of 7.0, only about 1 percent are cations. Accordingly, the quinoline exists in both ionic and nonionic forms in these experiments. The ratio of the two forms depends on pH.

Buffers, of the variety used in this study, and NaCl have no apparent effect on the quinoline spectra in solution for the range of concentrations in which these components were mixed.

It appears that the clay minerals adsorbed quinoline from solution by two mechanisms: cation exchange and molecular adsorption. The latter mechanism may be due to van der Waals' attractive forces or to those forces resulting from polarization of the aromatic rings as a whole, or both (Bradley, 1945).

Quinoline must compete with water for sites on the clay surfaces. The state of order or disorder of the water net, therefore, is somewhat a measure of the energy acting to keep the quinoline in solution and not adsorbed on the clay. Any condition which tends to disrupt the water net, accordingly, should promote adsorption of quinoline in relatively larger amounts.

Initially adsorbed quinoline apparently has a disruptive effect on the water nets of the three-layer clays. The data show that, as a result, the adsorbing mechanisms become more efficient at higher quinoline concentrations.

The primary effect of pH is to produce a greater number of quinoline cations at lower, rather than higher, pH values. The adsorption *vs.* pH relationship, then, apparently reflects the extent of exchange between organic and inorganic cations for sites on the clay surfaces. When large amounts of quinoline can be adsorbed through cation exchange, the upswing in the adsorption isotherm, or the increased efficiency of overall quinoline adsorption, occurs at lower organic equilibrium concentrations (Fig. 3). This suggests that quinoline cations on exchange sites exert a greater disruptive effect on the water net around clay flakes than equivalent adsorption as the free base would exert.

The adsorption *vs.* salinity curves show an initial decrease in adsorption values as salinity increases. This is interpreted as a cation exchange phenomenon; that is, fewer quinoline cations become adsorbed as $Na^+$ concentration increases. Since adsorption values never approached zero, even at the highest salinities, quinoline must be adsorbed, therefore, by molecular forces as well as by ionic forces.

Sodium concentration, in addition to competing with quinoline cations, disrupts the water net around clay flakes. According to Norrish (1954), the lattice expansion data for montmorillonite in NaCl solutions show an abrupt change toward smaller interplanar spacings at a concentration of about 16,000 ppm. The adsorption *vs.* salinity data for $Na^+$-montmorillonite, in general, indicate adsorption increases at salinities greater than the range 16,000–24,000 ppm, when the initial quinoline concentration is 100 ppm (Fig. 10). These data appear to be further evidence that structure of the water net and quinoline adsorption are related. The shapes of the curves, in particular the minima, may result from the interaction of both adsorption mechanisms — ion exchange and molecular adsorption.

The salinity at which the minimum occurs in each adsorption curve varies with pH. At pH 6.4, relatively large amounts of adsorbed quinoline plus the $Na^+$ concentration both act to disrupt the water net around the clay flakes. Collapse of the water net can occur, therefore, at a lower salinity when the pH is 6.4 than when the pH is 8.3, owing to the relative amounts of adsorbed quinoline at each pH. Consequently the minima trend toward higher salinities as pH increases.

The shapes of the adsorption *vs.* salinity curves for $Na^+$-montmorillonite also change with quinoline concentration. The 300-ppm quinoline concentration is evidently adequate to compete with $Na^+$ up to considerable concentrations, so that essentially no minimum is detected. Adsorption by ion

exchange and molecular forces interact so that percent adsorption is nearly constant over this salinity range. At 12 ppm, there is an initial decrease in adsorption; however, this concentration is inadequate to define a minimum in the curve.

The adsorption *vs.* salinity curves for illite and kaolinite show little increase in adsorption at the higher salinities, even though the $Na^+$-montmorillonite did adsorb more under comparable conditions. The illite and kaolinite clays possess substantially less surface area on which water nets can develop; accordingly, they can be expected to show only a small effect in relation to changes in their adsorbed water.

The reversibility of quinoline adsorption by $Na^+$-montmorillonite is more complete at pH 7.5 than at pH 6.4. Evidently these data result from a greater degree of cation exchange which occurs in the acid environment. Ion exchange, therefore, seems to bond the quinoline less reversibly to the clay than the molecular forces.

Reversibility of quinoline adsorption on illite and kaolinite appears to have a control in addition to pH. The degree of reversibility is less than expected for both clay types, even though the amount of quinoline involved is considerably less than that with $Na^+$-montmorillonite. It is suggested that the variation in surface charge and in surface composition of illite and kaolinite, as compared to $Na^+$-montmorillonite, may explain these reversibility data.

## SUMMARY AND CONCLUSIONS

Experiments were performed in which quinoline, as the organic material, was adsorbed by clay minerals in water suspensions. The clay minerals were $Na^+$- and $Ca^{2+}$-montmorillonite, illite and kaolinite. The physicochemical environments of the samples were varied in regard to quinoline concentration, pH, salinity, time, and temperature, and the adsorption data were found to vary in response to these conditions.

Both cation exchange and molecular adsorption caused quinoline to be retained by the clay. The nature of the water net around clay layers was important in that the water competes with quinoline for the clay surfaces. As the water net was disrupted, quinoline adsorption proceeded more efficiently.

The reversibility of quinoline adsorption was controlled, at least in part, by the pH of the environment and by the type of clay mineral.

From the data presented, it can be seen that the reactions between quinoline and clay minerals in water suspensions are quite sensitive to some changing environmental conditions. Different types of organic material can be expected to react differently to the same environmental changes.

## REFERENCES

Bader, R. G. and Smith, J. B. (1959) Significance of adsorption isotherms for specific organic materials on sedimentary minerals (abstr.): *Bull. Geol. Soc. Amer.*, v. 70, p. 1564.

Bradley, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Amer. Chem. Soc.*, v. 67, pp. 975–981.

Brindley, G. W. and Rustom, Mahmoud (1958) Adsorption and retention of an organic material by montmorillonite in the presence of water: *Amer. Min.*, v. 43, pp. 627–640.

Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill Book Co., Inc., New York, 384 pp.

Hoffmann, R. W. and Brindley, G. W. (1959) Adsorption of organic molecules from aqueous solutions on montmorillonite (abstr.): *Bull. Geol. Soc. Amer.*, v. 70, pp. 1618–1619.

MacEwan, D. M. C. (1951) The montmorillonite minerals (montmorillonoids): in *X-ray Identification and Crystal Structures of Clay Minerals*: Mineralogical Society, London, pp. 86–137.

Norrish, K. (1954) The swelling of montmorillonite: *Faraday Soc. Disc.*, no. 18, pp. 120–134.