

ADSORPTION OF QUINOLINE FROM AQUEOUS SOLUTIONS BY SOME CLAYS AND OXIDES

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Abstract—The adsorption isotherms of quinoline from aqueous solutions by some clays and oxides varied from the S type for silica to a form somewhat similar to the Langmuir type for montmorillonite and silica-alumina. The adsorption reaction reached equilibrium in about 2 hr and was irreversible. X-ray powder diffraction studies showed that a single layer of molecules is adsorbed on montmorillonite and that the molecules lie either flat or in an upright position depending on surface coverage. The adsorption showed high sensitivity towards pH, attaining a maximum at pH 6. The decrease below pH 6 was due to competition with protons as well as to problems inherent in surface packing of positively charged quinoline molecules. The decrease above pH 6 is probably due to more exchangeable metallic cations on the surface leading to a favored sorption of water over organic molecules.

Key Words—Adsorption, Montmorillonite, pH, Quinoline, Silica-alumina, X-ray powder diffraction.

INTRODUCTION


Relatively few investigations have been concerned with the study of adsorption of quinoline. Greene-Kelly (1955) showed that quinoline molecules are adsorbed in an upright position and give rise to a basal spacing of 16.9 Å. Doehler and Young (1961) investigated quinoline adsorption by kaolinite, illite, and montmorillonite in the relatively low concentration range of 0–0.2 g/liter and found that the adsorption decreased as the pH increased from 6 to 8.5, that salinity (up to 6.8 g/liter of NaCl) reduced adsorption by about 30%, and that the extent of this reduction was dependent on concentration, pH, and the nature of the clay itself.

In the present study the work of Doehler and Young was extended to provide details about the adsorption of quinoline onto clays, especially the pronounced effect of pH as reported by the above workers. Some oxides and coal were included as sorbents to understand better the adsorption reaction.

MATERIALS AND METHODS

Seven substances were used as sorbents of quinoline: (1) montmorillonite from Cerro Bandera, Argentina, with a cation-exchange capacity (CEC) of 0.92 meq/g and a glycerol surface area of 808 m²/g (Peinmann *et al.*, 1972). Particles smaller than 2 μm were saturated with Na, K, NH₄, or Ca by repeated washings with 0.5 M chloride salts followed by washing out of the excess salt with the help of a centrifuge; (2) kaolinite from Birch Pit, Macon, Georgia, with a cation-exchange capacity of 0.06 meq/g and surface area of 7.9 m²/g as determined by paranitrophenol adsorption from xylene (Giles and Trivedi, 1969) (X-ray powder diffraction data showed that the material is well crystallized and that muscovite is present as an impurity; particles smaller than 2 μm were saturated with Na or K as described above); (3)

silica gel from Davison Chemicals, Baltimore, Maryland, with a N₂ surface area of 600 m²/g and average pore diameter of 67 Å; (4) synthetic, noncrystalline silica-alumina prepared in this laboratory of composition SiO₂ 75.6, Al₂O₃ 14.2, and H₂O 10.1% and a paranitrophenol surface area of 94.9 m²/g; (5) active dry charcoal, from Merck, Darmstadt, Germany; (6) aluminum hydroxide prepared in this laboratory that gave an X-ray powder diffraction pattern of bayerite (surface area = 27.9 m²/g as determined by lauric acid adsorption from n-pentane (de Boer *et al.*, 1962)); (7) hematite (α-Fe₂O₃) from May and Baker Companies, USA, with a surface area of 10.3 m²/g as determined by water vapor adsorption.

Analytical grade quinoline  (molecular weight 129.16 g) from British Drug House Ltd., England, was used in this study. It is a liquid at room temperature and has a solubility in water of about 40 mmole/liter. The molecule acquires a proton in acid media producing a cation acid. The cation acid dissociation reaction:



has a pK_a = 4.8. The dimensions of the molecule are: 9 × 7 × 3 Å³.

The concentration of quinoline in aqueous solutions was determined spectrophotometrically at 285 nm with the help of a standard curve. All measurements were made in solutions at pH greater than 6 because the absorbance was found to decrease with the increase in the acidity of the quinoline solutions.

The adsorption of quinoline by the above-mentioned substances was carried out by adding 25 ml of quinoline solutions of different concentrations to 0.1–0.5 g of sor-

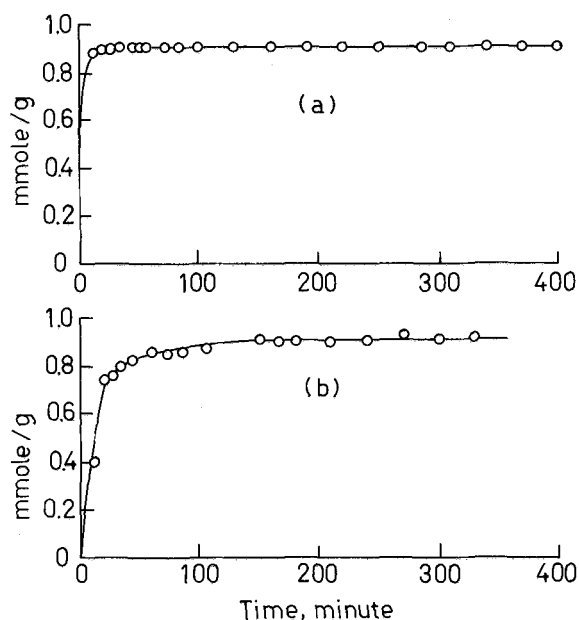


Figure 1. The adsorption of quinoline as a function of time by: (a) Na-montmorillonite from 0.04 M solutions at pH 4.2, and (b) Ca-montmorillonite from 0.05 M solutions at pH 7.5.

bent in 50-ml Pyrex bottles. The bottles were shaken for 30 min and left for 2 hr with occasional shaking. Filtration followed, and filtrates were analyzed for quinoline. The amounts adsorbed were calculated from the initial and final concentrations of quinoline. The final pH was always measured in the suspensions. The same experiment was repeated except that the quinoline solutions contained 8.5 mmole/liter phosphate buffer at pH 6.7.

The effect of pH on the adsorption of quinoline was carried out in the same way as described above except that the pH of the quinoline solutions was varied by adding HCl. The equilibrium pH range covered was 2–10, at two initial quinoline concentrations of 4 and 17 mmole/liter.

For the purpose of studying the Ca and Na released by Na- and/or Ca-montmorillonites as a function of pH, a similar experiment to that described above was carried out and a treatment in which quinoline was not added was also included. The concentration of Ca and/or Na found in the equilibrium solutions were determined by flame photometry.

The reversibility of the quinoline adsorption reaction was studied using Na-montmorillonite. To 0.16-g samples in 50-ml bottles, 40 ml of solutions containing 0–33 mmole/liter of quinoline were added. The bottles were stoppered and shaken for 30 min and left for 24 hr with occasional shaking. Twenty-milliliter samples from the supernatant liquids were withdrawn for analysis. To the bottles containing the highest concentration of quino-

line 20 ml of water was added; the bottles were then shaken and left for 24 hr at which time liquid samples were withdrawn for analysis and 20 ml of water was added. This procedure was repeated five times, producing finally a low quinoline concentration in the equilibrium solutions. The amounts of quinoline adsorbed/desorbed were then calculated after each dilution from the material balance in the systems. The initial pH of the system before dilution was 7.4.

The basal spacings of Na-montmorillonite that adsorbed quinoline were obtained by the X-ray powder diffraction (XRD) technique. The clay samples were first shaken with a 0.04 M quinoline solution at pH 5.6 where considerable adsorption takes place and/or at pH 11 where less quinoline is adsorbed. The clays were then separated and air dried.

The effect of time on the adsorption was carried out using Na- and or Ca-montmorillonites. The initial concentration of quinoline was 4 mmole/liter at pH value of 4.2 for the Na- and 5 mmole/liter at pH 7.5 for the Ca-clay.

The determination of the weight average molecular weight of dissolved quinoline was carried out by the light scattering method using a Brice Phoenix light scattering photometer (de Bussetti *et al.*, 1980). The weight average molecular weight \bar{M} is given by:

$$kc/R_{\theta} = (1/\bar{M}) + 2Bc, \quad (2)$$

where $K = 32\pi^3 n_0^2 (dn/dc)^2 / 3N\lambda^4$, R_{θ} = Raleigh's ratio, B = constant, c = concentration in g/cm³, n_0 and n = index of refraction of solvent and solution, respectively, N = Avogadro's number, and λ = wavelength of radiation. For obtaining dn/dc , a differential refractometer was used which permitted measuring the difference in refractive index between solvent and solutions of quinoline.

RESULTS AND DISCUSSION

Influence of time

The effect of time on quinoline adsorption by Na- and/or Ca-montmorillonites at pH 4.2 and/or pH 7.5 is shown in Figure 1. The adsorption reaction reached equilibrium more rapidly at the lower pH value, and about 2 hr was needed at pH 7.5 to complete the reaction. This result agrees with the data of Doehler and Young (1961) who found that above pH 6.5, the adsorption equilibrium is reached in about 200 min, though little difference in adsorption was observed between 100 and 200 min.

The quinoline units in solution

Before the quinoline adsorption results can be interpreted, it is necessary to identify the quinoline units present in solution and to know the effect of pH on the molecules. The data given in Figure 2 show that the average molecular weight, $\bar{M} = 153.8$. This value signi-

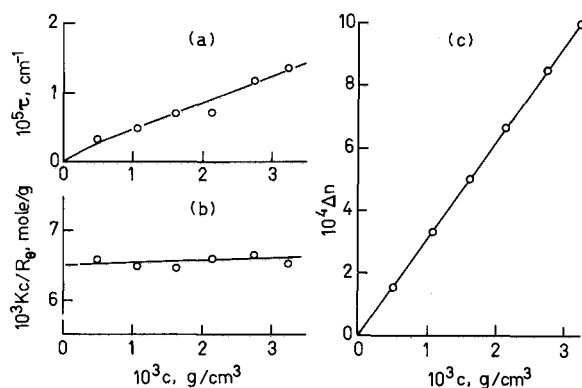


Figure 2. (a) The turbidity τ of quinoline solutions as a function of concentration; (b) the turbidity data are plotted according to Eq. (2), and (c) the increment in the refractive index of quinoline as a function of concentration.

fies that the unit in solution is composed of 1.2 molecules on the average, so that practically no association of molecules takes place.

With respect to the effect of pH on quinoline, the percentage of the neutral and/or the cation form as a function of pH is given in Figure 6 with the Na-montmorillonite curves. As may be seen from the curve, 94% of the total molecules exist in the neutral form at pH 6, and at pH 7 the cation form is practically nonexistent.

Adsorption isotherms

The adsorption isotherms of quinoline on silica and hematite (Figure 3) are of the S type (Giles *et al.*, 1974a, 1974b) indicating that the energy of adsorption is concentration dependent and that the solvent contributes negatively to it, i.e., water molecules compete with quinoline for the surface. In contrast to this situation, the adsorption isotherm on activated coal is of the high affinity type with a steep initial slope so that water offers no competition. Furthermore, the adsorption curve on coal is characterized by the presence of two plateaus with the same amount of quinoline adsorbed at each, i.e., 2.54 mmole/g. The second plateau may be attributed to a completion of a second layer or it can represent a reorientation from flatwise to end-on orientation of quinoline molecules. On montmorillonite, Na-kaolinite, and the silica-alumina the isotherms obtained are intermediate in character between those of silica and coal. They are, however, not of the Langmuir type, but possess a small plateau after which a sudden rise in the curves occurs at a concentration of about 6 mmole/liter. Rather than a deposition of a second layer, as occurs perhaps with coal, this rise represents a reorientation of adsorbed molecules in a direction of a more dense packing, because such a reorientation would permit more space for adsorption. This conclusion is in accord with the molecular dimensions of quinoline and with the XRD data obtained for the montmorillonite quinoline

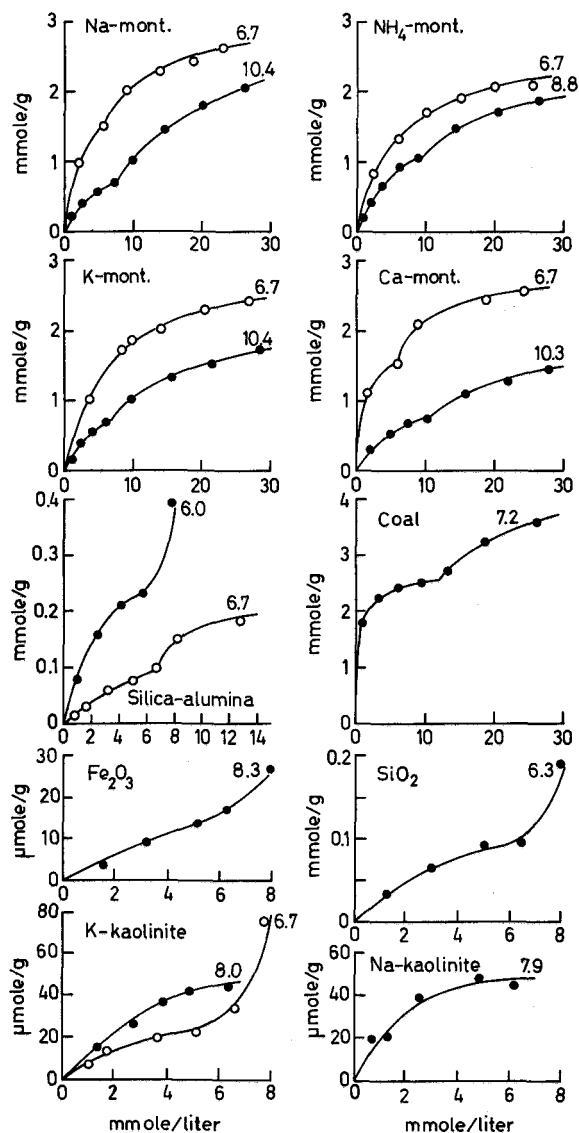


Figure 3. Adsorption isotherms of quinoline on different sorbents; open circles (O) in presence of 8.5 mmole/liter phosphate buffer and closed circles (●) in its absence. Numbers on curves are final pH values.

system which may be interpreted as that only one layer of molecules is found on the surface. At low surface occupancy the molecules lie flat on the surface and give rise to the 12.8-Å spacing, whereas at high surface occupancy they are upright, producing the 16.7-Å spacing. In the upright position there is 27 Å² of surface per molecule which is evidently much smaller than the 63 Å² required for a molecule if it lies flat on the surface and thus allows more dense packing of molecules.

In addition, adsorption of quinoline is accompanied by an average increase of 0.3 pH units, indicating that hydrolysis of adsorbed cations and/or chemisorption of

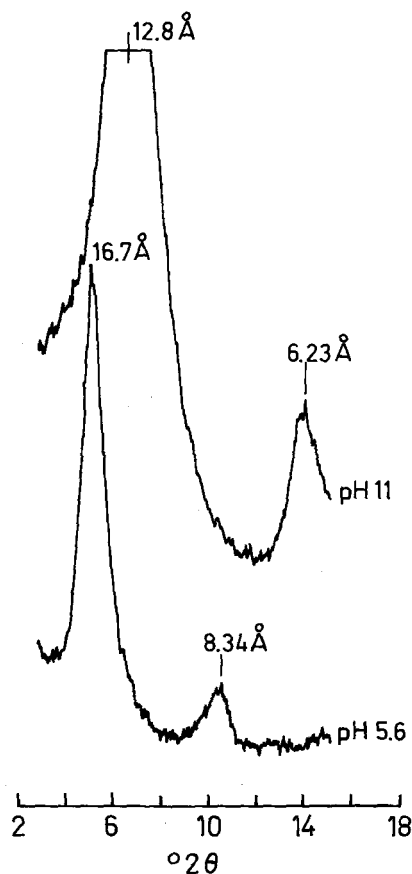
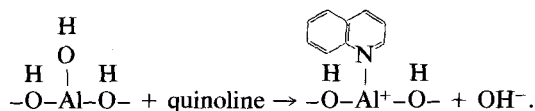


Figure 4. X-ray powder diffraction patterns of Na-montmorillonite-quinoline complexes. The complexes were prepared at pH 5.6 and/or 11.

quinoline takes place. In the latter case quinoline replaces surface hydroxyls bonded to structural atoms, such as Al and Fe (Peinemann and Helmy, 1976). The chemisorption reaction may be written as:



Also, the adsorption reaction is irreversible, as seen in Figure 5 where the desorption curve lies much above the adsorption curve.

Influence of exchangeable cations and buffer on quinoline adsorption

As may be seen from the curves in Figure 3, the exchangeable cation on the clay does not affect the general shape of the adsorption curve nor the concentration at which the second plateau in the curve is situated. The adsorption maximum, however, is slightly dependent on the exchangeable cation as already reported for

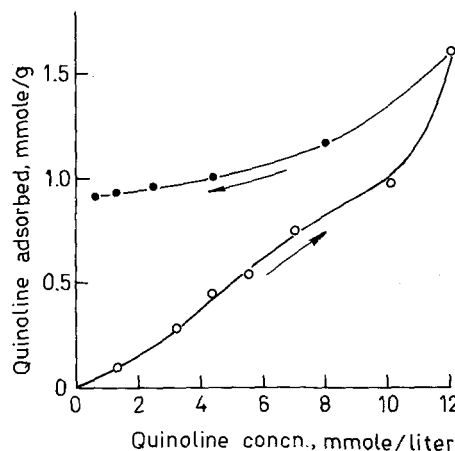


Figure 5. Adsorption/desorption isotherms of quinoline on Na-montmorillonite.

orthophenanthroline (de Bussetti *et al.*, 1980). The combined influence of pH and the exchangeable cations Na and/or Ca on quinoline adsorption is discussed below.

With respect to the effect of the phosphate buffer on quinoline adsorption, the data of Figure 3 indicate that the buffer reduced the adsorption on silica-alumina and kaolinite. This reduction may be attributed to chemisorption of phosphate known to occur on these materials (Peinemann and Helmy, 1976); but further studies are needed before more about the phenomenon can be said. For montmorillonite the isotherms in the presence and/or absence of buffer were obtained at different pHs, namely 6.7 in the presence of phosphate and 10 in its absence. As shown in Figure 6, quinoline adsorption is smaller at pH 10 than at pH 6.7. Therefore the data of Figures 3 and 6 are in mutual agreement, and the phosphate buffer has probably no effect on quinoline adsorption on montmorillonite.

Influence of pH

The effect of pH on the adsorption is shown in Figure 6. Except for coal, the shape of the curves is the same for all sorbents. For coal the increase in adsorption in the range of pH 2–6 may be attributed to the increase in the concentration of the neutral molecules in solution. Above pH 6 the concentration of neutral species is almost constant, and, hence, a plateau in the curve is present at pH >6. The preference in adsorption by the coal surface of the neutral rather than the cation form of quinoline can be understood in terms of the steric difficulties associated with dense packing of charged units. Stable packing requires minimizing the electric repulsion of these units, a condition which is absent in neutral species.

For the other sorbents the adsorption curve as a function of pH is characterized by the presence of a maxi-

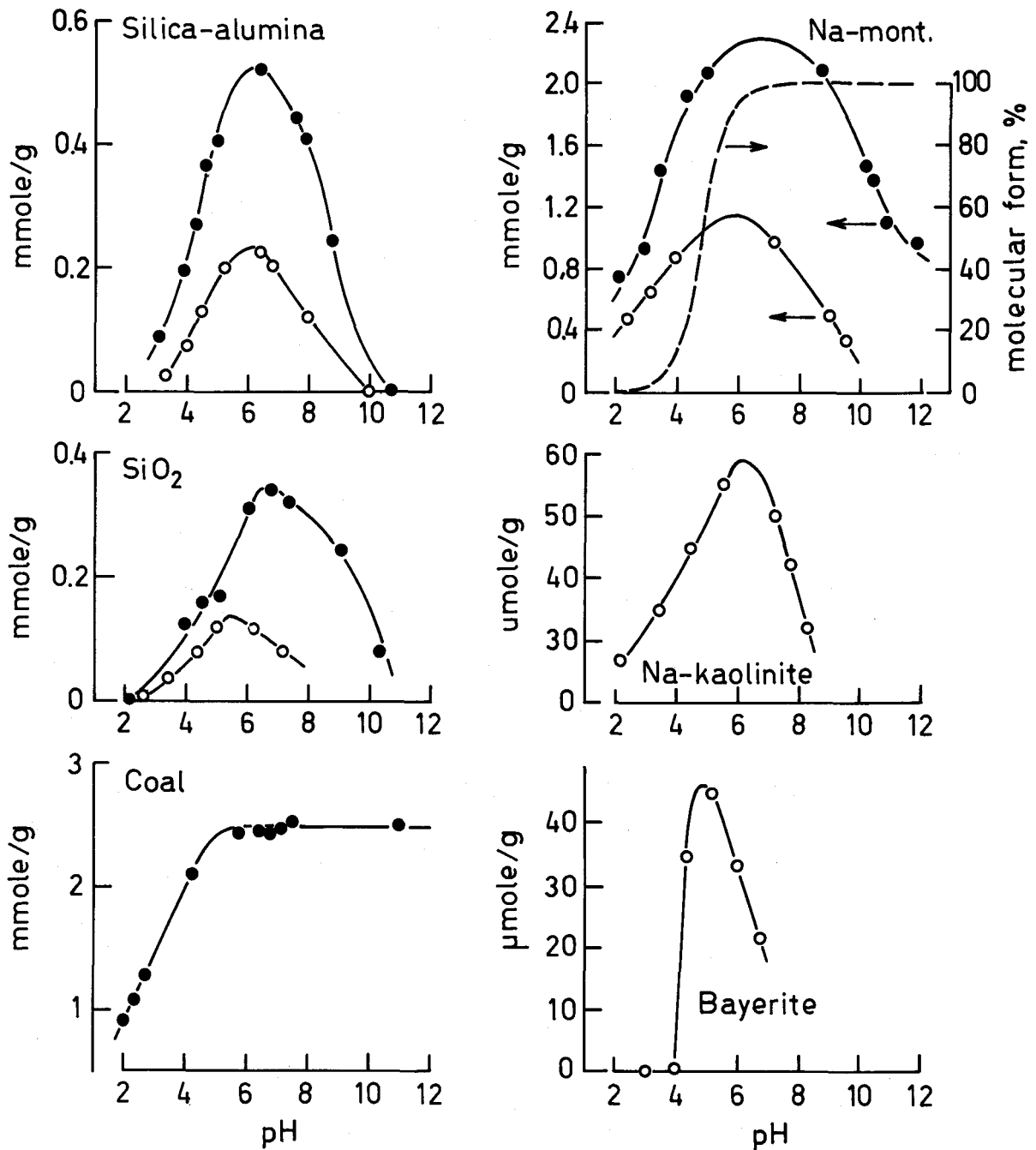


Figure 6. Effect of pH on quinoline adsorption at two concentrations: 4 mmole/liter (○), and 17 mmole/liter (●). The dotted line included with the Na-montmorillonite curves represent the percentage of the molecular form of quinoline as a function of pH.

num at pH 6 with minor differences between sorbents. On both sides of the maximum, the adsorption decreases rather steeply demonstrating a high sensitivity to pH changes. In Figures 7a and 7b the amounts of Na and Ca released from montmorillonite are given as a function of pH. In Figure 7c part of the data is plotted

as a function of the acid added in the presence and/or absence of quinoline. At pH 2 the Ca-clay loses all of its Ca in the presence of quinoline, but in the absence of quinoline, only half that amount is lost. The Na-clay loses about 70% of its Na regardless of the presence or absence of quinoline, however, 0.9 mmole/g of Ca-clay

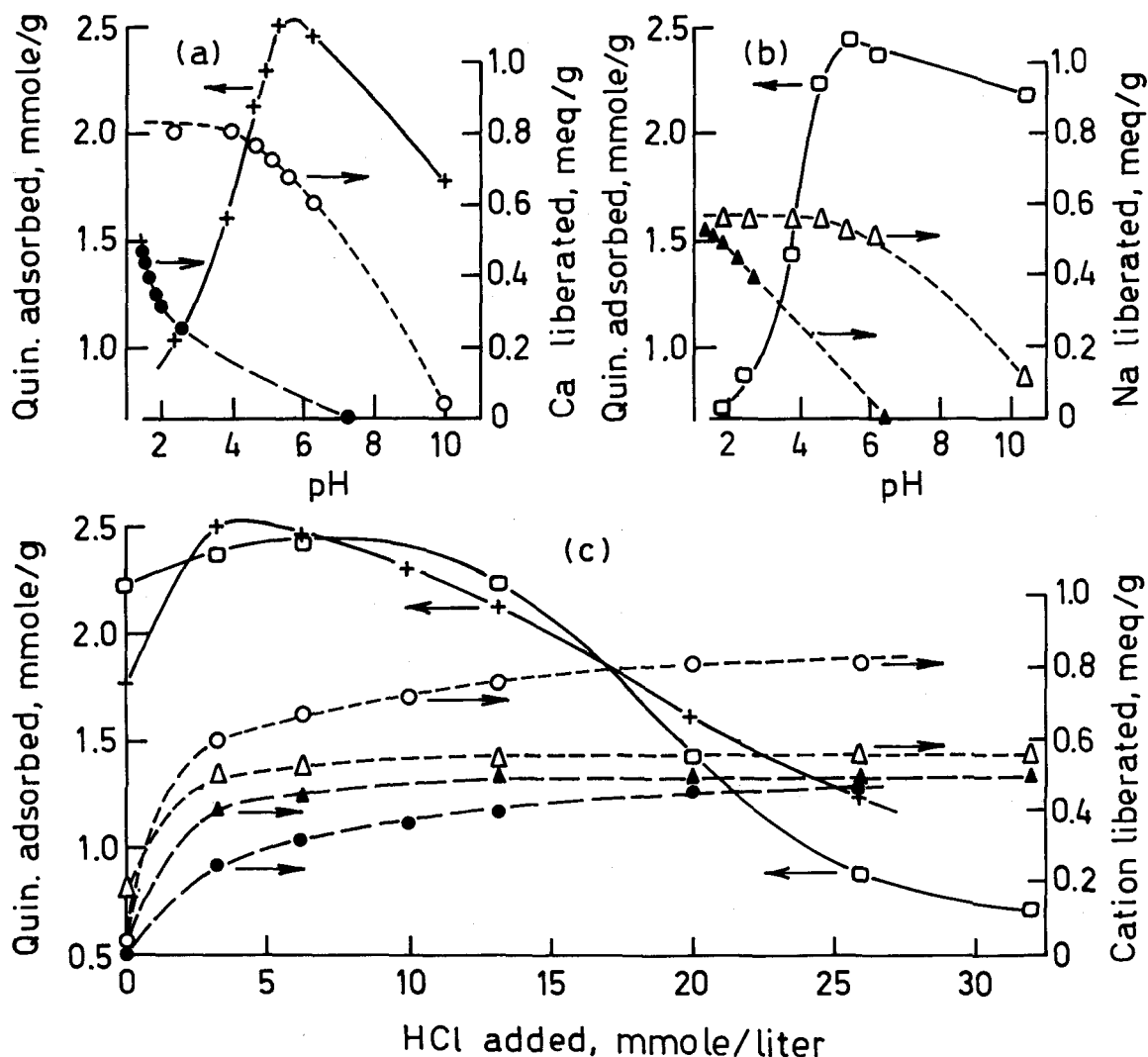


Figure 7. Quinoline adsorbed (+, \square) and (a) Ca (\circ), (b) Na (\triangle) liberated by Ca- and Na-montmorillonite as a function of pH. Closed symbols (\bullet , \blacktriangle) represent metallic cations released by the clays in absence of quinoline; open symbols, in presence of quinoline (\circ , \triangle). The same data are plotted in (c) as a function of added HCl. The concentration of quinoline was 23 mmole/liter.

and 0.7 mmole quinoline/g of Na-clay are adsorbed at this pH, indicating that both quinoline and protons balance the clay charge at low pH. At pH 6, metallic cations are more abundant in the clay as the pH increases. Thus, at pH 6 about 30% of the CEC is balanced by metallic cations, whereas at pH 10 the CEC is totally balanced by the Na and/or Ca ions. It is remarkable that a parallelism exists between the decrease in quinoline adsorption and the increase in metallic cations onto the clay.

The occurrence of maxima in sorption reactions of organic molecules from solution is a general phenomenon in systems in which the solute and the solvent could be adsorbed (Gregg and Sing, 1967). The extent of adsorption of each species depends on the forces of at-

traction between sorbent and adsorbates. Hence, the characteristics of the adsorption curve are determined by the competition between solute and solvent for association with the surface. This competition may be pH dependent, because pH can affect the properties and concentration of the adsorbate species (cation or neutral molecule) as well as the properties of the surface, i.e., the amount and sign of surface charges as occurs with oxygen-hydroxyl surfaces.

The adsorption curves on clays and oxides as a function of pH can be divided into two regions: one before and one beyond the maximum adsorption. In the first, the decrease in adsorption as the pH decreases is due to a competition between protons and cation quinoline for balancing the surface charges. This explanation has

been already given by Lailach *et al.* (1968) and Thompson and Brindley (1969) for organic cation adsorption on clays. However, this explanation does not account for the observation that between pH 6 and 2, an amount of quinoline twice the CEC of the clay is desorbed. Thus, in addition to such competition, the desorption is probably caused by quinoline molecules becoming progressively positively charged as the pH decreases and are less favored than neutral quinoline in adsorption (by a mechanism other than cation exchange) due to their steric problems in the surface zone. The increase in quinoline adsorption in the pH range 2 to 6 is due, in addition to less competition from protons for balancing the surface charges, to an increase in the concentration of the neutral species which in turn are more easily accommodated on the surface than the cation species. In this regard, taking into consideration the CEC of the clay and the total amount of adsorbed quinoline, at the maximum adsorption about 2 of every 3 adsorbed molecules are neutral.

The occurrence of the adsorption maximum at pH 6 can also be explained on the basis that the neutral species almost attains its maximum concentration at this pH. As the pH increases beyond maximum adsorption, cation quinoline and protons are progressively neutralized and only metallic cations maintain the condition of electroneutrality in the surface zone. Due to the high interaction energy (~13 kcal/mole) between cations and water, about 6–18 water molecules associate firmly with a cation (Robinson and Stokes, 1959). Small ionic radius and high valence favor cation hydration. Therefore, the cations in the clay preferentially attract water molecules, and less quinoline is adsorbed. On coal, however, the transformation of cation to neutral quinoline as a result of the increase in pH in solution and in the surface zone does not call for the presence of cations on the surface because the coal surface is not charged. Thus, coal/quinoline interactions are constant above pH 6, and no decrease in adsorption occurs. For oxides and hydrous oxides, the increase in pH usually creates extra surface charges that provoke less adsorption of organic molecules for the same reasons mentioned above for the clay (Tadros, 1978).

The maximum adsorption of quinoline at pH 6 and not at pH 8 where all of the molecules are in the neutral form may be understood in terms of an adsorption/desorption balance. Thus, increasing the pH above 6 produces more neutral molecules, and more adsorption should take place because their presence is favored over cation quinoline in the surface zone. However, this pH increase also produces neutral molecules out of some of the cation molecules balancing surface charges of the clay and thus provokes the presence of metallic cations and the desorption of quinoline, as shown above.

Therefore, the sorption reaction of quinoline on

charged surfaces includes in addition to a competition with the solvent, physical, chemisorption, and cation exchange. The cation to neutral transformation of quinoline molecules as a function of pH appears to be an important factor contributing to the special characteristics of quinoline adsorption on charged surfaces; namely a maximum at pH 6 and a decrease in adsorption on both sides of the maximum. For pH <6, competition with protons and the problem of dense packing on the surface of cation quinoline causes less adsorption as the pH decreases. At pH >6, quinoline can not balance the negative surface charge; the surface is populated with metallic cations, and water is attracted preferentially over organic molecules, hence less adsorption of quinoline occurs.

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Резюме—Изотермы адсорбции хинолина из водных растворов некоторыми глинами и окисями изменялись от типа S для кремнезема до некоторой формы немного положей на тип Лэнгмюра для монтмориллонита и кремнезема-глинозема. Реакция адсорбции достигала равновесия в течение 2 часов и являлась необратимой. Исследования путем рентгеновской порошковой дифракции показали, что одиночный слой молекул адсорбируется на монтмориллоните и что эти молекулы расположены либо параллельно либо перпендикулярно к поверхности, в зависимости от ее покрытия. Адсорбция является очень чувствительной к pH с максимумом при pH =6. Уменьшение адсорбции при pH <6 было результатом конкуренции с протонами, а также результатом проблем, присущих расположению положительно заряженных молекул хинолина на поверхности. Уменьшение адсорбции при pH >6 было, вероятно, результатом того, что более обменные катионы металла на поверхности благоприятствовали более адсорбции воды, чем органических молекул. [E.C.]

Resümee—Die Isotherme der Chinolinadsorption aus wässrigen Lösungen durch einige Tone und Oxide variierte vom S-Typ für Siliziumdioxid bis zu einem Typ, der in etwa dem Langmuir-Typ für Montmorillonit und Siliziumdioxid-Aluminiumoxid ähnlich ist. Die Adsorptionsreaktion erreichte in etwa 2 Stunden das Gleichgewicht und war irreversibel. Röntgenpulverdiffraktometeruntersuchungen zeigten, daß eine einzige Molekülschicht an Montmorillonit adsorbiert wird. Dabei liegen diese Moleküle entweder flach oder sie stehen senkrecht, je nach Oberflächenbedeckung. Die Adsorption ist sehr stark vom pH abhängig und erreicht bei pH 6 ein Maximum. Eine Abnahme der Adsorption bei pH-Werten unter 6 wurde durch die Konkurrenz mit Protonen bedingt sowie durch Probleme, die mit der Oberflächenbedeckung durch positiv geladene Chinolinmoleküle zusammenhängen. Die Abnahme der Adsorption bei einem pH über 6 hängt wahrscheinlich mit dem leichter austauschbaren Metallkationen auf der Oberfläche zusammen, wodurch eher Wasser als organische Moleküle adsorbiert werden. [U.W.]

Résumé—Les isothermes d'adsorption de quinoline à partir de solutions aqueuses de certains argiles et oxides ont varié du type S pour la silice à une forme quelque peu semblable au type Langmuir pour la montmorillonite et l'alumine-silice. La réaction d'adsorption a mis à peu près 2 heures pour être équilibrée, et était irréversible. Des études de diffraction poudrée aux rayons-X ont montré qu'une seule couche de molécules est adsorbée sur la montmorillonite et que les molécules sont soit allongées soit debout dependant de la couverture de surface. L'adsorption s'est montrée très sensible au pH, atteignant un maximum de pH =6. Le décroissement sous pH 6 était dû à la compétition avec des protons ainsi qu'à des problèmes impliqués dans l'empilement de surface de molécules de quinoline chargées positivement. Le décroissement au delà du pH 6 est probablement dû à des cations métalliques plus facilement échangeables à la surface, menant à une sorption favorisée d'eau par rapport aux molécules organiques. [D.J.]