

ADSORPTION OF 1,10-PHENANTHROLINE BY SOME CLAYS AND OXIDES

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Abstract—The adsorption of 1,10-phenanthroline (OP) onto some clays and oxides was studied as a function of concentration, pH, and time. The adsorption was found to be irreversible and the isotherms, except for silica gel, were hyperbolic and gave rise to plots similar to that of Langmuir. Kinetic and light scattering studies show that OP is adsorbed as a micellar unit composed on the average of 3.5 molecules/micelle. This fact explains the overestimation observed in the surface areas of some sorbents since no true monomolecular layer of OP is formed on the surfaces. The adsorption was also found to be pH dependent, attaining a maximum, independent of the sorbent, at about pH 6. This maximum was approximately at the same pH in which only the molecular form of OP began to be present. The partial desorption of OP as the pH increased beyond 6 is possibly associated with the aggregation of micelles on the surfaces.

Key Words—Adsorption, Kaolinite, Montmorillonite, Oxides, Phenanthroline.

INTRODUCTION

A variety of methods is available for the determination of the specific surface areas of clays and oxides, including gas adsorption, heats of immersion, negative adsorption, and molecular adsorption from solution (Van Olphen, 1970). In general the methods are of different reliability and accuracy; some are absolute, and others need calibration.

Among the methods used with some success is that based on orthophenanthroline adsorption from an aqueous solution. Lawrie (1961) and Bower (1963) reported that this method gives reliable results for some clays such as montmorillonite, illite, and kaolinite, but not for halloysite or vermiculite. The present study was undertaken with the purpose of examining the adsorption reaction of orthophenanthroline on some clays and oxides and its suitability for surface area determination of such materials.

MATERIALS AND METHODS

Seven substances were used as sorbents of 1,10-phenanthroline.

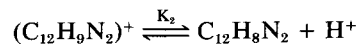
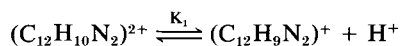
- (1) Montmorillonite from Cerro Bandera, Argentina, with a cation-exchange capacity of 0.92 meq/g and a glycerol specific surface area of 808 m²/g (Peinemann *et al.*, 1972). Particles smaller than 2 μm were saturated with Na, K, NH₄, or Ca by repeated washings with 0.5 M chloride salts followed by washing out of the excess salt with the help of a centrifuge.
- (2) Kaolin from Birch Pit, Macon, Georgia (USA), with a cation-exchange capacity of 0.06 meq/g and surface area of 7.9 m²/g as determined by paranitrophenol (PNP) adsorption from xylene (Giles and

Trivedi, 1969). Particles smaller than 2 μm were saturated with Na as described above.

- (3) Silica gel from Davison Chemicals, Baltimore, Maryland, with a N₂ surface area of 600 m²/g and an average pore diameter of 67 Å.
- (4) Synthetic amorphous silica-alumina prepared in this laboratory of composition: SiO₂ 75.6, Al₂O₃ 14.2, and H₂O 10.1% and a PNP surface area of 94.9 m²/g.
- (5) 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 m²/g.
- (6) Aluminum hydroxide that gave an X-ray powder diffraction pattern of bayerite. It has a surface area of 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.

Two samples of Merck analytical-grade orthophenanthroline (OP) were used in this study. One is a monohydrate with the composition C₁₂H₈N₂·H₂O, a water solubility of 14 mmole/dm³ giving a solution of pH 6.4 and a melting point of 117–120°C. The other is orthophenanthroline hydrochloride with the composition C₁₂H₉N₂Cl·H₂O, a melting point of 224–228°C, and a water solubility of about 2 mole/dm³ giving a pH of 3.

According to Perkampus and Kohler (1960), OP dissociates as follows:



with pK₁ = -1.4 and pK₂ = 4.85.

Orthophenanthroline was determined colorimetrically (Lawrie, 1961) from the color developed with ferrous iron in the presence of the reducing agent hydroxylamine hydrochloride and acetate buffer at pH 3.5. Usually 5-ml samples were diluted to 25 ml using a pH 3, 0.2 M sodium acetate/acetic acid solution that contained 1 ml of 0.2% (w/v) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 ml of 10% (w/v) of hydroxylamine hydrochloride per 20 ml.

The adsorption of OP by the above mentioned sorbents was carried out by adding 25 ml of OP solutions of different concentrations to 0.1–1 g of sorbent in 50-ml pyrex bottles. The bottles were then shaken for 30 min and left for 1.5 hr with occasional shaking. Filtration followed, and filtrates were analyzed for OP. The final pH was also measured in the suspensions. The amounts of OP adsorbed were calculated from the initial and final concentrations. The surface area of each material was calculated from the amount of OP adsorbed at the adsorption maximum, assuming that each molecule of OP occupies an area of 60 \AA^2 . This calculation assumes that each OP molecule lies flat on the surface.

The effect of pH on the adsorption of OP was carried out in the same way except that the pH of the OP solutions was adjusted by adding HCl or KOH. The equilibrium pH range covered was 3–9, at two initial OP concentrations of 5 and 1 mmole/dm³.

The reversibility of the OP sorption reaction was studied using montmorillonite and silica-alumina. To 0.16-g samples in 50-ml bottles, 40 ml of solution was added containing from 80 to 400 micromoles of OP. 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, and 20 ml of water was added. The bottles were then shaken and left for 24 hr, at which time liquid samples were withdrawn, as above. The amounts of OP adsorbed were calculated from the material balance in the systems.

The effect of time on the adsorption was carried out using montmorillonite and silica-alumina. The initial concentration of OP was 6 mmole/dm³ for montmorillonite and 1 mmole/dm³ for silica-alumina.

For the determination of the weight-average molecular weight of dissolved OP, Raleigh's ratios (ratio of scattered to incident radiation) were determined from light scattering of solutions of different concentrations at a constant pH of 6.5 using a Brice Phoenix light scattering photometer. The wavelength of the radiation was 436 nm. The weight-average molecular weight \bar{M} is related to Raleigh's ratio R_θ by the relation (Tanford, 1961):

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

where $k = 32n^3n_0^2(\text{dn/dc})^2/N\lambda^4$,
 $B = \text{constant}$,

$c = \text{concentration in g/cm}^3$,

$n_0, n = \text{index of refraction of solvent and solution respectively}$,

$N = \text{Avogadro's number}$,

$\lambda = \text{wavelength of radiation}$.

For obtaining (dn/dc) , a differential refractometer was used which permitted measurements of the difference in refractive index between a solution of OP and the solvent.

RESULTS AND DISCUSSION

The adsorption curves of OP as a function of concentration onto montmorillonite, kaolin, iron oxide, aluminum oxide, silica gel, and silica-alumina are shown in Figure 1. The data are also plotted according to the Langmuir equation in the same figure. As may be seen, straight lines are traced except for aluminum oxide. For the silica gel little adsorption took place, and the sorption is non-Langmuirian. The specific surface areas calculated from OP adsorption are much lower for Al-oxide and silica gel than for those determined by other methods, as given in the experimental section. Similar results were obtained by Lawrie (1961). For the other sorbents the following specific surface areas in

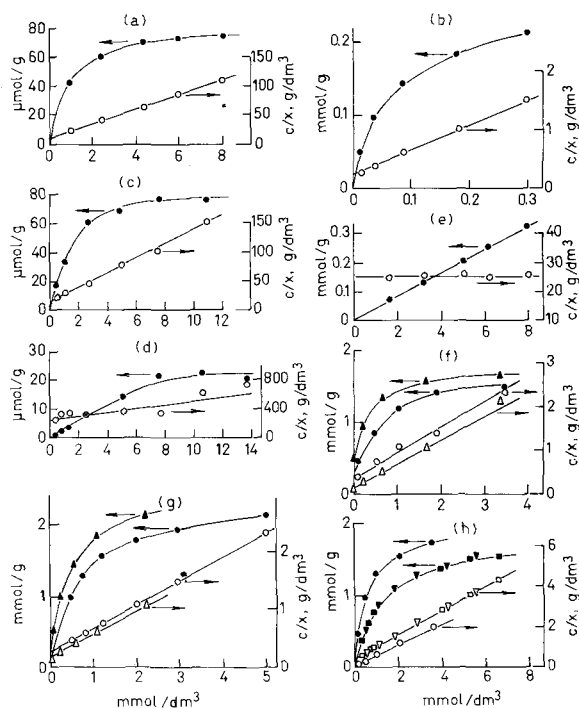


Figure 1. Adsorption isotherms and Langmuir plots of orthophenanthroline on (a) kaolin, (b) silica-alumina, (c) iron oxide, (d) aluminum oxide, (e) silica gel, (f) Ca- (▲) and NH_4 -montmorillonite (●), (g) Na-montmorillonite in presence (●) and/or absence (▲) of acetate buffer, and (h) K-montmorillonite in absence (○, ●) and/or presence of acetate (■) and phthalate (▼) buffer.

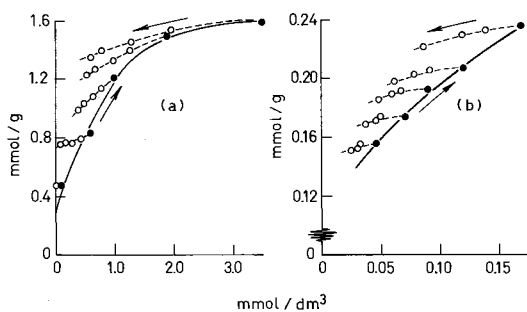


Figure 2. Adsorption/desorption isotherms of OP on: (a) montmorillonite, and (b) silica-alumina.

m^2/g were obtained: kaolin 29.5; silica-alumina 83; Na-, K-, Ca-, and NH_4 -montmorillonites 860, 708, 649, and 598, respectively.

As may be also observed in Figure 1, the presence of 0.2 M acetate buffer did not affect the calculated area for Na-montmorillonite. However, acetate and/or phthalate buffer (0.02 M) reduced the adsorption and the calculated areas for K-montmorillonite by about 14%. The use of buffers improved the experimental conditions by maintaining the pH and facilitating the filtration of the supernatant liquids.

The reduction in the OP surface areas of the montmorillonites saturated with Ca, NH_4 , and K as compared to that obtained for Na-montmorillonite is not due to a reduction in the interlamellar spacing, thus reducing penetration of OP molecules, since X-ray diffraction examination of these montmorillonites gave similar basal spacings, as may be seen from the following data in Å units: Ca-clay: 19.6 (15.3); NH_4 -clay: 18.4 (12.3); K-clay: 18.4 (12.3); and Na-clay: 18.8 (12.3). The

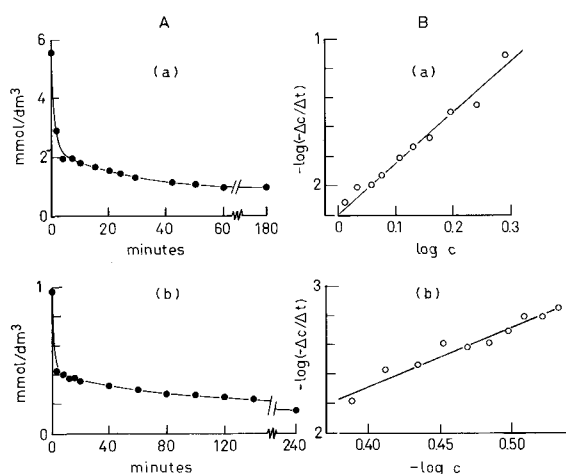


Figure 3. (A) The variation of OP concentration in solution as a function of time in: (a) Ca-montmorillonite, (b) silica-alumina. (B) The logarithm of the rate of change of OP concentration plotted against the logarithm of concentration for: (a) Ca-montmorillonite, and (b) silica-alumina.

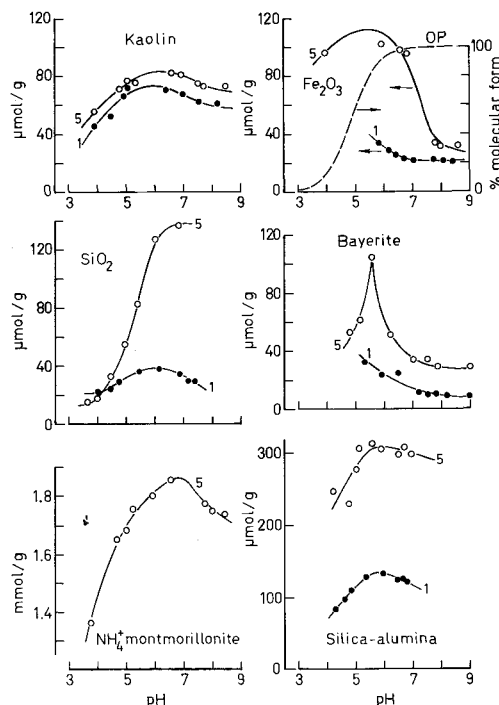


Figure 4. Effect of pH on OP adsorption at two initial concentrations of 5 and 1 mmole/dm³. The dotted line included with the iron oxide curves represents the percentage of the molecular form of OP as a function of pH.

values in parenthesis are for the air-dried, cation-saturated clays before OP adsorption. The amount of OP adsorbed, therefore, seems to be affected by the cation present on the surface of the clay.

More pronounced reduction in specific surface areas of montmorillonites saturated with Ca, NH_4 , and K (as determined from negative adsorption of chloride) was reported by Edwards *et al.* (1965a, 1965b). However, de Haan (1965) found that both Na- and Ca-montmorillonites had identical surface areas as determined by negative adsorption of chloride.

The adsorption of OP by kaolin gives rise to a Langmuir plot but leads to an overestimation of the specific area. The value calculated from OP adsorption is about 3 times that determined by parantrophenol adsorption. Similar high results were given by Lawrie (1961). Bower (1963) reported good agreement between OP and ethylene glycol specific areas for kaolin, but the value reported (18 m^2/g) is rather high.

The adsorption/desorption curves of OP on both montmorillonite and silica-alumina are shown in Figure 2. It is clear from the figure that the adsorption reaction is irreversible, since the amount present on the surface at any given equilibrium concentration is dependent on the manner by which the process took place. On both sorbents, dilution of the equilibrium solution did not result in regular desorption of molecules, and the

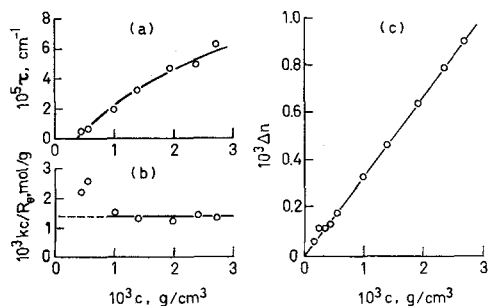


Figure 5. (a) The turbidity τ of OP solutions as a function of concentration; (b) The turbidity data are plotted according to Eq. (1), for the evaluation of the weight average molecular weight; and (c) The increment in the refractive index of OP solutions as a function of concentration.

amount desorbed depended strongly on the amount present on the surface as manifested by the occurrence of a family of desorption curves.

The effect of time on the adsorption of OP by montmorillonite and silica-alumina is shown in Figure 3. As is apparent from the figure, the adsorption reaction is complete in about 1 hr on montmorillonite and in 4 hr on silica-alumina. More information about the kinetics of OP adsorption, can be obtained by plotting $\log(-\Delta c/\Delta t)$ against $\log c$, where c is the concentration of OP in solution. As seen in Figure 3, the plots are linear for both sorbents. The slope of the lines represent the order of the adsorption reaction, which is the value of n in the kinetic equation:

$$-dc/dt = kc^n \quad (2)$$

For montmorillonite, $n = 3.50$, and for silica-alumina, $n = 3.57$. Both values are similar and indicate that OP is sorbed as a unit composed on the average of 3.5 molecules.

The effect of pH on the adsorption of OP on kaolin, montmorillonite, bayerite, silica gel, iron oxide, and silica-alumina is given in Figure 4. The pH range covered was 3–9 at OP concentrations of 5 and 1 mmole/dm³. As is clear from the curves in Figure 4, a maximum in OP adsorption takes place at pH 6, with minor differences between the sorbents. The effect of pH on OP adsorption is probably related to the effect of pH on the OP species as it can exist as a cation or as a neutral molecule. In Figure 4, together with the data of the iron oxide, is shown the percentage of the molecular form of OP as a function of pH. At pH 6, 93% of the OP is in the molecular form, and at pH 7 the percentage rises to 99. The near coincidence of the maximum in the molecular form of OP with the maximum in OP adsorption indicates that the molecular form is preferred over the positive species by the sorbents. Hence, as the pH increases in solution, the concentration of the molecular form in solution also increases, and more adsorption takes place.

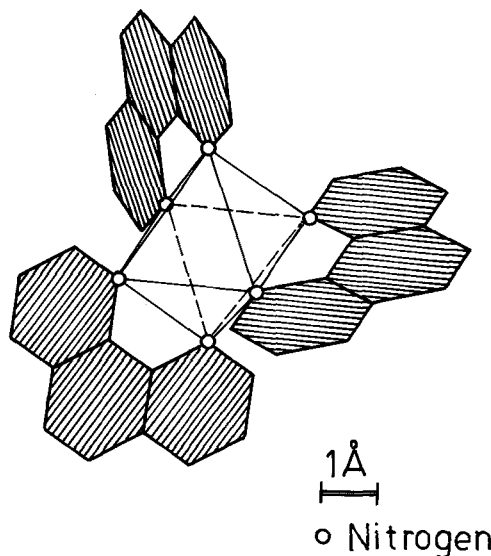


Figure 6. Schematic representation of the micelle formed of 3 molecules of OP.

The decrease in OP adsorption above pH 6 has also been reported by Herz (1978) and by Dobias (1977, 1978) for other types of molecules and may be explained as follows. Aggregation of micelles may take place on surfaces but no similar aggregation occurs in the solution phase. The chemical potential of the aggregated units is thus higher in the surface phase than in solution, causing a net movement of units from surface to solution where they disintegrate into smaller units.

To identify the units of OP present in solution, the weight average molecular weight (M) of OP in solution was determined by light scattering measurements as detailed above (see also Figure 5). The value of M obtained was 714.3 g/mole, indicating that OP forms in solution micellar units composed on the average of $(714.3/198.23) = 3.6$ molecules per micelle. This number is in excellent agreement with that obtained from the kinetic study discussed above.

The adsorption reaction of OP may thus be described as follows: OP forms micelles in solution which are composed on the average of 3.6 molecules/micelle. This is the unit adsorbed. Dispersive interactions between adjacent molecules increases with the increase in surface concentration of micelles causing their aggregation. This may cause partial desorption of units. As the pH falls below 6, more OP molecules become positively charged and the formation of micelles in the solution decreases, thus leading to little OP adsorption. The decrease in micelle formation is easily understood in terms of the electric repulsion that could take place between the positively charged OP molecules within a micelle, causing its disintegration.

That the unit adsorbed is composed of 3.6 molecules/unit causes some concern with respect to the calcula-

tion of surface areas from OP adsorption. The surface areas are calculated assuming that each OP molecule lies flat on a surface and occupies 60 \AA^2 (Lawrie, 1961). Judging by the way OP complexes ferrous iron, namely an octahedral structure formed by 3 molecules as shown in Figure 6, and taking into consideration the data obtained from light scattering, one is tempted to assume that the same unit exists in solution and on the surface albeit not as stable as the unit in the presence of ferrous iron. As may be appreciated from Figure 6, the surface area occupied by such a unit is expected to be less than 3 times the area of one molecule of OP. This explains the overestimation of specific surface area obtained for kaolin and throws doubt on the significance of the Langmuir plots in Figure 1, since the formation of a true monomolecular layer on the surface does not take place. This overestimation does not appear to take place with montmorillonite, probably because the micelle comes in contact with the two surfaces of the interlamellar spaces of the crystals. The agreement between the OP and the other methods for surface area determination of montmorillonite is perhaps due to this fact.

Bower (1963) observed that the OP adsorption on a bentonite is associated with an increase of 5.3–7.8 Å in the basal spacings, while Berkheiser and Mortland (1977) obtained an increase of 3.8 and 3.9 Å in the basal spacings of hectorite saturated with Fe(II) and Cu(II) phenanthroline complexes, respectively. The present XRD data and those of Bower (1963) indicate that two molecules of OP could be present within the interlamellar spaces (the OP molecular thickness is about 3 Å), though perhaps not in a totally uniform manner. This is because of the dependence of the amount adsorbed on the saturating cation and the tendency of OP to micellar formation.

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(Received 23 July 1979; accepted 25 September 1979)

Резюме—Изучалась адсорбция 1,10-Фенатролина (ОП) некоторыми глинами и окислами как функция концентрации, рН, и времени. Адсорбция оказалась необратимой и изотермы, кроме изотерм для кремневого геля, были гиперболические, которые позволили построить графики подобные графикам Лангмуира. Кинетические исследования и изучения с помощью рассеяния света показывают, что ОП адсорбируется как мицелловая единица, составленная в среднем из 3,5 молекул/мицелла. Этот факт объясняет переоценку, замеченную в поверхностных зонах некоторых сорбентов, поскольку настоящие мономолекулярные слои ОП не формируются на поверхностях. Было обнаружено также, что адсорбция зависит от рН, доходя до максимума, независимо от сорбента, при рН равном примерно 6. Этот максимум был приблизительно при том же рН для случая, когда только молекулярная форма ОП начала появляться. Частичная адсорбция ОП при увеличении рН свыше 6 возможно связана с объединением мицелля на поверхностях. [N. R.]

Resümee—Die Adsorption von 1,10-Phenanthrolin (OP) an einige Tone und Oxide wurde in Abhängigkeit von Konzentration, pH, und Zeit untersucht. Es zeigte sich, daß die Adsorption irreversibel ist, und daß die Isothermen, mit Ausnahme von Silica-Gel, hyperbolisch sind und Darstellungen ähnlich denen von Langmuir ermöglichen. Kinetische und Lichtstreuungs-Untersuchungen zeigen, daß OP in Form einer micellaren Einheit aus durchschnittlich 3,5 Molekülen/Micelle adsorbiert wird. Diese Tatsache erklärt die Überbewertung, die in den Oberflächenbereichen einiger Adsorber beobachtet wurde, da keine echten monomolekularen Schichten von OP auf den Oberflächen gebildet werden. Es zeigte sich, daß die Adsorption pH-abhängig ist, und unabhängig vom Adsorber ein Maximum bei pH ~6 erreicht. Dieses Maximum war etwa bei dem gleichen pH, bei dem nur die molekulare Form von OP aufzutreten beginnt. Die teilweise Desorption von OP, wenn der pH über 6 ansteigt, hängt möglicherweise mit der Aggregation von Micellen auf den Oberflächen zusammen. [U. W.]

Résumé—L'adsorption de 1,10-phenanthroline (OP) sur certains argiles et oxides a été étudiée en fonction de la concentration, du pH, et du temps. On a trouvé que l'adsorption était irréversible et que les isothermes, sauf pour le gel de silice, étaient hyperboliques, produisant des graphes semblables à celui de Langmuir. Des études cinétiques et de dispersion de lumière montrent que OP est adsorbé en tant qu'unité micellaire composée en moyenne de 3,5 molécules/micelle. Ce fait explique la surestimation observée dans les régions de surface de quelques sorbants puisqu'aucune vraie couche monomoléculaire de OP n'est formée sur les surfaces. On a aussi trouvé que l'adsorption était dépendante du pH, atteignant un maximum, indépendant du sorbant, à ~pH 6. Ce maximum était approximativement au même pH auquel seule la forme moléculaire de OP commençait à être présente. La désorption partielle de OP lorsque le pH croissait au-delà de 6 est possiblement associée avec l'aggrégation de micelles à la surface. [D. J.]