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ADSORPTION OF PARAQUAT ON MINERALS
A thermodynamic study

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Abstract

The adsorption of the paraquat molecule on silica, kaolinite, illite and montmorillonite was studied with regard to both the determination of adsorption isotherms and the microcalorimetric measurement of adsorption enthalpies. Surface concentration at saturation can be related to the neutralization of the surface charge. Part of the observed variation in adsorption enthalpies from one mineral to another can be attributed to the degree of fitting of the adsorptive molecule to the spatial repartition of surface charges. A particularly interesting system is that involving montmorillonite, where there is evidence of the possibility of neutralization, by the same paraquat molecule, of two sites relating to different platelets.

Keywords: calorimertry, clays, flocculation, silica, surface charge

Introduction

During recent decades, pesticides have been used more and more widely. They are needed to protect cultivations, but their extensive use has undesirable effects on the environment. The interactions of these compounds with the soil are among the main drawbacks to their biological activity, but also influence their retention, mobility and degradation. As a consequence, this field has been the subject of numerous studies [1–9]. Retention by adsorption at a solid/liquid interface depends on the structures of both pesticides and soil [10 11] and on the medium conditions (pH, temperature, solid/liquid ratio, etc.) [4, 7]. Clays are the main components of the mineral fraction of soils. They are efficient natural adsorbents in consequence of both their particle size lower than 2 μm [12] and their lamellar structure, which gives them a very large reactive surface area [13, 14]. Their surface is negatively charged under most conditions, which makes them good cation adsorbents. The cationic exchange capacity and the nature of the compensating cation play major roles in the interactions of organics with the solid surface of clays [6, 15].

The aim of the present work is to study the adsorption of paraquat (1,1-dimethyl-4,4’-bipyridinium dichloride) on some typical minerals. It is a frequently used com-

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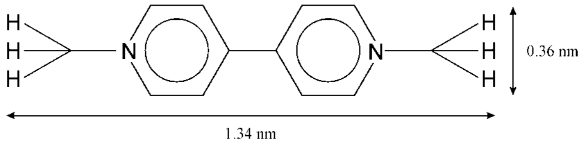
pound of the pyridinium group. It is a non-selective herbicide which is inactivated by irreversible adsorption on clays [3, 16]. Due to the complexity of natural systems, the characterization of the interactions of such a molecule with soil minerals needs to be modelled by using well-defined solids. A synthetic silica and purified kaolinite, illite and montmorillonite were selected. The thermodynamics of adsorption are evaluated through the determination of adsorption isotherms and the microcalorimetric measurement of adsorption enthalpies. The influence of ionic strength and pH is also analysed.

Experimental

All solid samples were characterized by XRD (Seifert XRD 3000TT) and nitrogen adsorption at 77 K (Omnisorb 100 from Coultronics). In the case of illite, the immersion enthalpy of the dry solid and the adsorption enthalpy of argon at 77 K were determined by previously described methods [17, 18].

The synthetic silica (XOBO30, provided by IBF) was a mesoporous sample having a mean pore size of around 30 nm, determined by the BJH method [19, 20]. Its BET surface area was 45 $m^2 g^{-1}$. The surface area of the kaolinite (provided by Sigma) was 18 $m^2 g^{-1}$. Illite and montmorillonite were provided by Clays Minerals. Their nitrogen surface areas were 19 and 30 $m^2 g^{-1}$, respectively. In aqueous solution, the montmorillonite reached a surface area of 800 $m^2 g^{-1}$ provided its concentration was below 2 $g l^{-1}$ [21]. This sample was exchanged with sodium by following standard procedures [22]. The paraquat was a Sigma product which was used as received. Its formula and molecular dimensions are given in the following diagram [3]:



Adsorption isotherms were determined by the solution depletion method. Solution concentrations were measured by UV spectrometry (absorbance peak at 260 nm). Adsorption enthalpies (or more rigorously displacement enthalpies of the solvent by the solute) were determined with a Tian-Calvet microcalorimeter by previously described procedures [17]. A stock solution was added step by step to the calorimetric cell, where the solid was maintained in suspension in the solvent by means of a propeller. For each step, a pseudo-differential enthalpy of displacement was calculated by dividing the heat effect (itself corrected for the dilution contribution) by the adsorbed amount derived from the adsorption isotherm. All experiments were performed at 25°C.

Results and discussion

A preliminary kinetic study demonstrated that adsorption was fast for all the studied samples. This was confirmed by the microcalorimetric peak shapes, which showed a return to the baseline within the time response of the system.

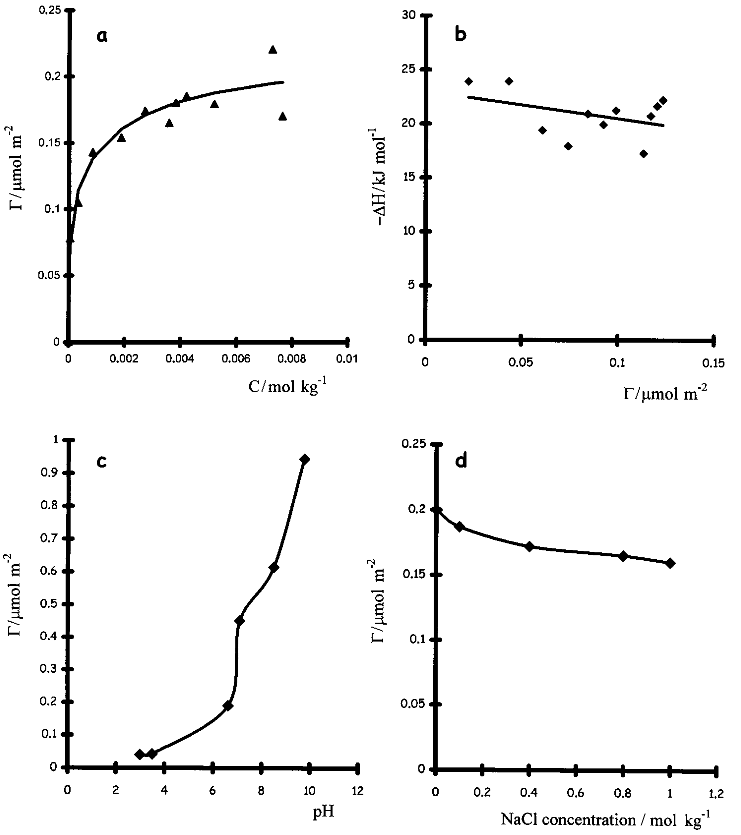


Fig. 1 Adsorption of paraquat on silica; a – adsorption isotherm; b – adsorption enthalpies as a function of surface concentration; c – influence of pH and d – influence of NaCl concentration on plateau surface concentration

Adsorption on silica

The adsorption isotherm is presented in Fig. 1a. The surface concentrations are low since the adsorption isotherm displays a plateau at around 0.18 μmol m^{-2}. The equilibrium pH was 6.5. At this pH, the silica is negatively charged (its point of zero charge is in the range pH 2–3), but the surface concentration of negative charges is low [23]. As a comparison, the surface concentration of dodecylpyridinium chloride at which the zeta potential is zero on the same silica is 0.4 μmol m^{-2} [24], which is about twice that measured for paraquat. The paraquat molecule bears two charges; this means that the main driving force for adsorption is electrostatic in nature and that adsorption is probably completed when the surface charge is neutralized. The adsorption enthalpies of paraquat on silica are reported in Fig. 1b. They range between −25 and −20 kJ mol^{-1}. These values are comparable with those obtained at low coverage for dodecylpyridinium ions [24, 25] or quaternary ammonium ions

[26], and are probably typical of the electrostatic interaction between the cationic paraquat and the SiO^- sites on the surface. The value is not doubled as compared with singly charged molecules since the distance between two charges on silica probably does not fit with the distance between the two charges of the paraquat molecule. It is well known that the surface concentration of these sites increases with increase of pH. The consequence, shown in Fig. 1c, is an increase in the plateau surface concentration of paraquat with pH. The ionic strength also has a strong influence on electrostatic interactions. A 20% decrease in surface concentration is observed (Fig. 1d) at pH 6.5 when sodium chloride is present in the medium at a concentration of 1 mol l^{-1}. This effect is due to two factors: a screening of electrostatic interactions when the ionic strength is increased, but also a direct competition between sodium and pyridinium for the adsorbing sites [26].

Adsorption on kaolinite

The adsorption isotherm of paraquat on kaolinite is presented in Fig. 2a. At the scale of the figure, this adsorption isotherm is of the high-affinity type, since a pseudo-plateau is obtained at low-concentration. The plateau surface concentration is 1.5 μmol m^{-2}. The equilibrium pH is 4.5, whereas the isoelectric point of this kaolinite without salt is pH 2.2 [27, 28]. The apparent surface charge is then negative, which allows the electrostatic attraction of paraquat molecules. The adsorption enthalpies (Fig. 2b) reveal two distinct regimes, below and above 0.6 μmol m^{-2}. In the first regime the adsorption enthalpies range between 25 and 15 kJ mol^{-1}, whereas in the second one, they decrease steeply to 2 kJ mol^{-1}. Kaolinite presents basal and lateral faces. One of the basal faces is comprised of OH groups bound to aluminium, whereas the other basal face is comprised of oxygens bound to silicon atoms. The lateral faces, more heterogeneous, consist of OH groups (bound either to silicon or to aluminium), which are responsible for the pH-dependent surface charge. Many particular properties of adsorption on kaolinite from either the gas phase or the liquid phase are clearly due to the presence of these three chemically different faces [28]. The proportion of lateral faces in the total surface area is 25%, as determined by low-temperature calorimetry [18, 29]. Figure 2c presents the plateau surface concentration plotted as a function of pH. A large increase is observed between pH 2.5 (which is close to the zero point of charge) and pH 4.5. If it is assumed that this variation corresponds to the adsorption on the lateral surface which is responsible for the surface charge variations with pH, a value of 0.57 μmol m^{-2} can be derived for the amount adsorbed on the lateral faces (taking into account only the surface area of the lateral faces, the local density of paraquat molecules on these faces would be about 2.4 μmol m^{-2}). This value is also the end of the first regime in the adsorption enthalpy curve. A possible explanation is that this first regime corresponds to adsorption on kaolinite edges; the order of magnitude of adsorption enthalpy, by comparison with silica, is in agreement with an electrostatic interaction in this range. Above 0.6 μmol m^{-2}, adsorption would occur mainly on basal faces. The basal face covered by oxygen atoms (with a high electronic density locally, even if

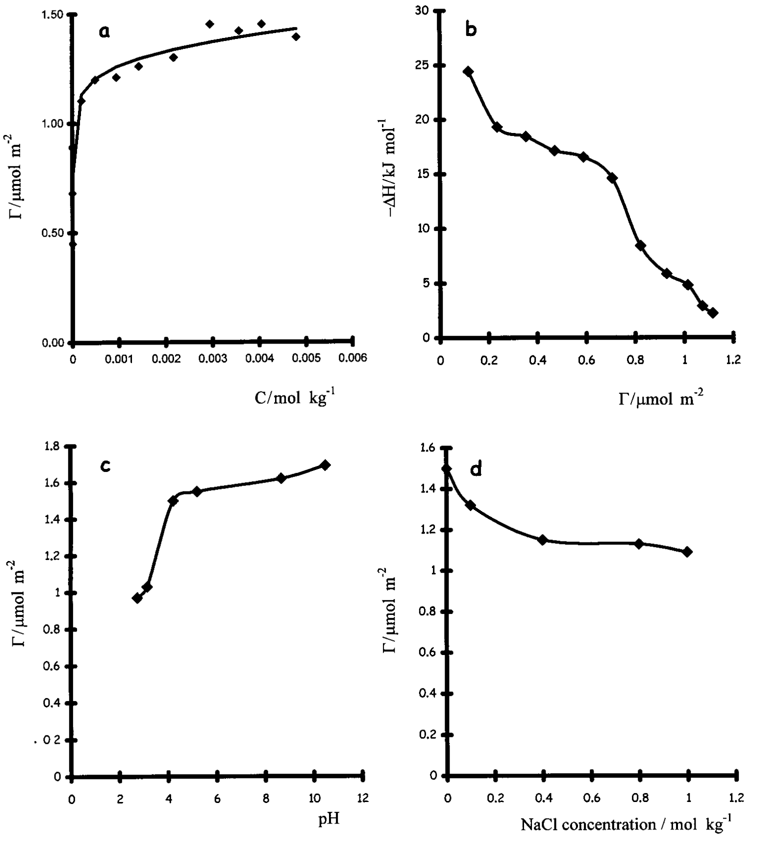


Fig. 2 Adsorption of paraquat on kaolinite; a – adsorption isotherm; b – adsorption enthalpies as a function of surface concentration; c – influence of pH and d – influence of NaCl concentration on plateau surface concentration

there is no permanent electrostatic charge) is the most likely site for this adsorption. Finally, the effect of ionic strength is of the same order as that on silica, and the decrease in surface concentration is again probably due to both screening of the electrostatic interactions and the competition between the cations for negative surface sites (Fig. 2d).

Adsorption on illite

The adsorption isotherm is reported in Fig. 3a. It is of the high-affinity type, with a pseudo-plateau at a surface concentration of 4 μmol m^{-2}. This value was calculated by using the nitrogen BET surface area. Generally, illite has only a weak swelling character: the accessibility of non-polar gas molecules or of organic molecules to the interlamellar space is limited [30, 31]. In the present case the XRD diagram reveals that surface area derived from nitrogen adsorption may be considered a reasonable value of the surface accessible to paraquat molecules.

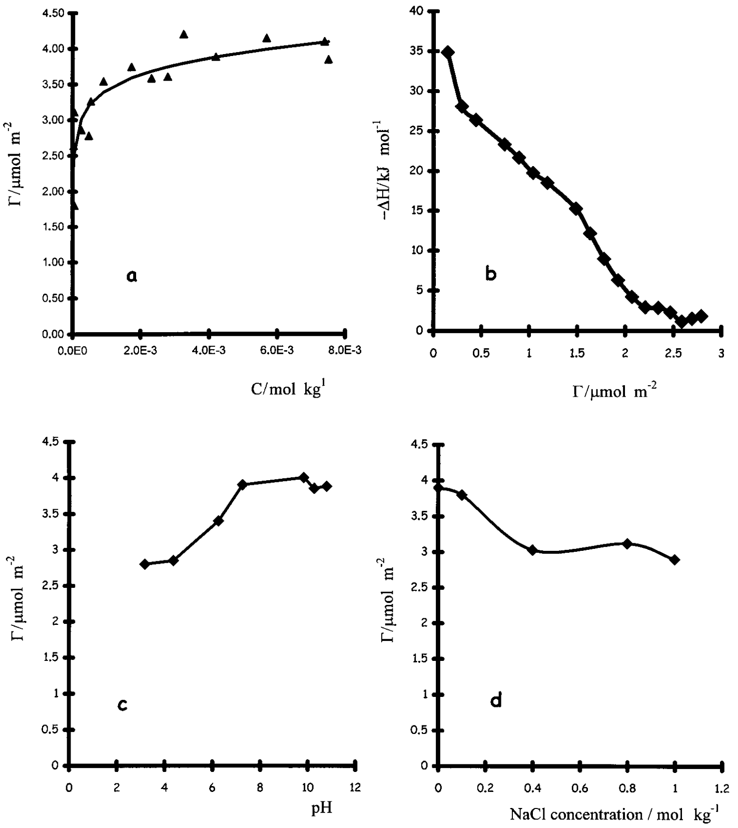


Fig. 3 Adsorption of paraquat on illite; a – adsorption isotherm; b – adsorption enthalpies as a function of surface concentration; c – influence of pH and d – influence of NaCl concentration on plateau surface concentration

The adsorption enthalpies (Fig. 3b) demonstrate a double distribution of adsorbing sites, as for kaolinite. The limit between the two regimes is around 1.3 μmol m^{-2}. In the first regime, the adsorption enthalpies range between −35 and −25 kJ mol^{-1}, i.e. slightly more exothermal than on kaolinite. If adsorption is mainly due to electrostatic interactions, the difference between the two samples depends on the respective charge densities. Indeed, the paraquat molecule (which covers a surface area of 0.84 nm^2 if it is adsorbed in a flat conformation) could interact to some extent with two negative sites of the illite surface, where the density of negative sites on the basal faces is 0.7 nm^2 per charge [31]. Since the fitting is not perfect, the adsorption enthalpies are not doubled as compared with silica or kaolinite.

The effect of adding a salt (Fig. 3d) is the same as for silica or kaolinite and an increase in plateau surface concentration is also observed with pH. The surface concentration *vs.* pH curve presents an inflexion point which delimits two regimes: one at around 2.7 μmol m^{-2} below pH 4, and the other at around 4 μmol m^{-2} above pH 8. As for kaolinite, the pH-dependent surface charge is localized on the lateral faces, and a value for the contribution of these faces to the total surface concentration can be obtained from the difference between the two regimes, i.e. 1.3 μmol m^{-2}. Nevertheless, in contrast with kaolinite, the basal faces of illite bear a permanent charge which is initially neutralized by potassium cations, and it is therefore difficult to attribute the first regime of adsorption enthalpies (below 1.5 μmol m^{-2}) only to the interaction of paraquat molecules with edges. Indeed, the determination of argon adsorption enthalpy at 77 K (not shown here) leads to an estimation of the lateral faces as 15% at most (this value was calculated from the coverage at which the adsorption enthalpy of argon becomes constant [18]). Moreover, adsorption on montmorillonite (which occurs mainly on basal faces) indicates that a strong interaction (evidenced by highly exothermal adsorption enthalpies) is possible with basal faces (see below). The slope change at around 1.5 μmol m^{-2} in Fig. 3b may then be due to several phenomena, and it is not possible to choose between them on the basis of the present results: the end of the covering of basal or lateral faces, a change in conformation of paraquat molecules, etc.

Finally, if the surface concentration is calculated by assuming that the surface charge is simply neutralized (one paraquat molecule for two surface charges), the maximum surface concentration would be 2.4 μmol m^{-2}, which is small relative to the measured values (even at low pH). A possible reason is that the BET nitrogen surface area is not the real accessible surface area. We measured the immersion enthalpy of illite in water. The value obtained (1130 mJ m^{-2}) is higher than those reported in the literature (around 700 mJ m^{-2} [32]), indicating that the nitrogen surface area is probably smaller than the accessible surface area in aqueous solution [15].

Adsorption on montmorillonite

A high-affinity shape adsorption isotherm is obtained (Fig. 4a). The plateau surface concentration is 0.6 μmol m^{-2}. This value was calculated by using a surface area of 800 m^2 g^{-1} since the concentration of the montmorillonite suspension was lower than 2 g l^{-1}. The interlamellar space calculated from the XRD diagram was increased from 0.94 to 1.26 nm after adsorption, showing that intercalation occurs. The shift in the interlamellar space (around 0.3 nm) suggests a flat conformation of the intercalated molecules [3]. As for the two other clays studied here, the adsorption enthalpy curve (Fig. 4b) exhibits two ranges, with very different values. Below 0.3 μmol m^{-2}, the adsorption enthalpies decrease slowly from 55 to 45 kJ mol^{-1}. Above this surface concentration, they decrease in a short range towards 30 kJ mol^{-1}. The high adsorption enthalpy found at low coverage, which is about twice that observed for other samples, might be explained by the interaction of the bipyridinium molecule with two platelets of montmorillonite: this cation, which bears two charges, would neutralize two negative sites of two different platelets. The neutralization of two charges on the same particle is less favourable since the distance between two neighbouring negative surface sites does not fit that between the two positive charges on the adsorptive. Indeed, the surface density of negative sites on montmorillonite (which are initially neutralized by sodium ions) is 1.4 nm^2 per

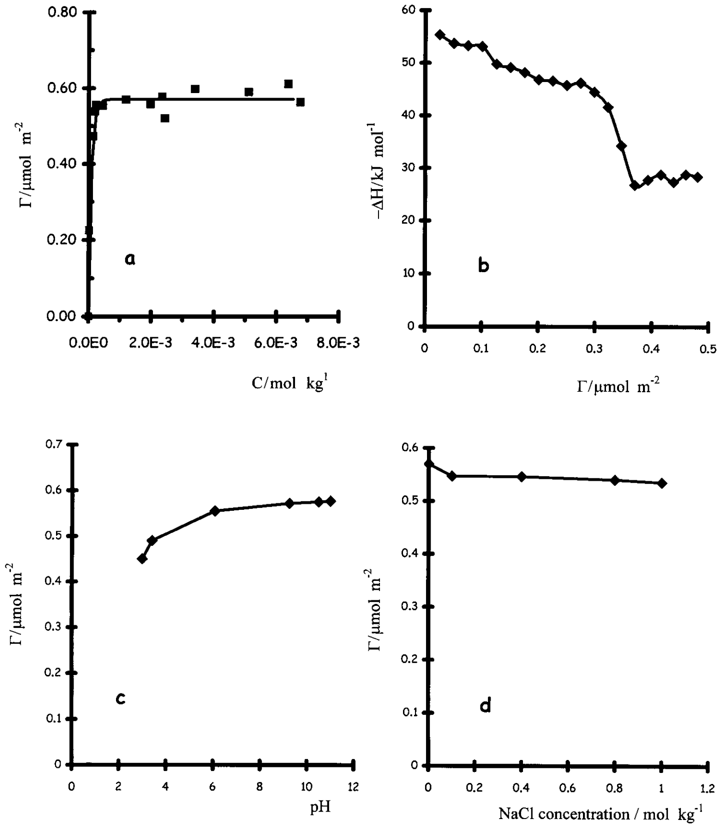


Fig. 4 Adsorption of paraquat on montmorillonite; a – adsorption isotherm; b – adsorption enthalpies as a function of surface concentration; c – influence of pH and d – influence of NaCl concentration on plateau surface concentration

charge, whereas the area covered by one paraquat molecule is 0.84 nm^2. The neutralization is confirmed by the flocculation of the montmorillonite suspension, which is not observed with illite. This is the first time to our knowledge that a calorimetric signature of flocculation has been demonstrated. Two regimes of adsorption enthalpies are nevertheless observed, since a perfect fit of adsorptive and adsorbent charges is not possible together with a more or less flat conformation without some steric hindrance leading to a repulsive contribution. If each paraquat molecule is interacting with two sites, the assumption of the exact neutralization of particles (one paraquat molecule for two sites) permits derivation of a surface concentration of adsorbed molecules from the surface charge density quoted above (1.4 nm^2 per charge). This calculation leads to 0.59 μmol m^{-2}, which is the plateau surface concentration within experimental error.

The ionic strength and pH have little effect on the surface concentration (Figs 4c and 4d), which is in agreement with the fact that the surface charge of basal faces (representing 98% of the total surface area) is not pH-dependent.

Conclusions

The adsorption of the paraquat molecule on silica, kaolinite, illite and montmorillonite is governed by electrostatic interactions. Surface concentrations at saturation can be related to the neutralization of the surface charge. The adsorption enthalpies varies between –20 and –50 kJ mol^{-1}. Part of the observed variations can be attributed to the degree of fitting of the adsorptive molecule to the spatial repartition of the surface charges. Other parts, such as the enthalpy contributions of hydration or dehydration of adsorbed or displaced molecules, are difficult to estimate. A particularly interesting system is that involving montmorillonite, where there is evidence of the possible neutralization, by the same paraquat molecule, of two sites relating to different platelets. The influence of ionic strength or pH on the surface concentrations decreases in the sequence silica, kaolinite, illite and montmorillonite. This reflects the origin of the surface charge on this set of samples. Indeed, all the surface charge on silica is due to amphoteric sites, whereas on the clays, the pH-dependent surface charge is mainly due to lateral faces, the proportion of which decreases in the sequence kaolinite, illite and montmorillonite.

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