

SURFACE CONDENSATION OF ORGANOPHOSPHATE ESTERS ON SMECTITES

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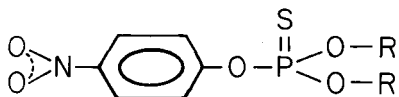
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Abstract—Parathion and methyl parathion adsorbed at high loads on clays and similar surfaces exhibited properties of a bulk phase, such as a well-defined solubility and a characteristic X-ray powder diffraction (XRD) pattern, different from those of the free substances. The aqueous solubility of parathion condensed at these surfaces was as low as 1.2 $\mu\text{g}/\text{ml}$ as compared to 14 $\mu\text{g}/\text{ml}$ for free parathion. The BET isotherm described the behavior of the investigated surface condensates even though these condensates were different from the multilayer adsorption for which the BET isotherm was originally developed. The XRD patterns of parathion and methyl parathion adsorbed on Na-bentonite exhibited reflections which were shifted towards higher angles as compared with the XRD patterns of the free compounds. This is in agreement with the lower solubility of the surface condensates. The properties of these condensates were easily controlled by the choice of adsorbent as well as by the choice of conditions under which they were prepared. The existence of such surface-condensed phases and the manipulation of their properties can be utilized for the slow-release formulation of organophosphate esters which is important, for example, in pesticides application.

Key Words—Adsorption, Organophosphate ester, Parathion, Pesticide, Smectite, Solubility, X-ray powder diffraction.

INTRODUCTION

The widely used pesticides parathion (O,O-diethyl-O-4-nitrophenyl phosphorothionate) and methyl parathion (O,O-dimethyl-O-4-nitrophenyl phosphorothionate) have the following structures:



where $\text{R} = \text{C}_2\text{H}_5$, for parathion and CH_3 for methyl parathion. A number of studies (e.g., Bowman, 1973; Bowman and Sans, 1977; Yaron and Saltzman, 1972; Gerstl and Yaron, 1978; Yaron, 1978) on the interaction of these and other organophosphate esters with various clays in aqueous and nonpolar media have shown that the adsorption of organophosphate esters on a clay surface is highly dependent on the exchangeable cation and its hydration state. Previous studies investigated the low part of the adsorption isotherms; yet, if clays are to be used as carriers for pesticides or other bioactive substances, it is important, for example, to study the interactions of organophosphate esters on clays at high surface concentrations.

In the present work the interactions of parathion and methyl parathion at high loads were studied by examining: (1) desorption isotherms of parathion into water from various homoionic bentonites; (2) X-ray powder diffraction spectra for parathion in liquid, adsorbed, and frozen phases and for methyl parathion in solid and adsorbed phases. The BET isotherm has been found to describe the type of condensation encountered

despite the differences between this condensation and the multilayer adsorption for which the BET isotherm was developed (Brunauer *et al.*, 1938).

MATERIALS AND METHODS

Materials

Na-, Ca-, Mg-, and Al-bentonites were prepared from Wyoming bentonite (Fisher B-235, Fisher Scientific Co., Fairlawn, New York) by the procedure of Shainberg and Otoh (1968). Deuterated parathion and methyl parathion synthesized in the Geoisotopes Department of Weizmann Institute of Science were used for the X-ray powder diffraction (XRD) analysis, and ^{14}C -labeled parathion (Amersham Radiochemicals Centre) was used in the desorption studies.

Procedures

Desorption isotherms. Clay samples were oven-dried at 105°C for 24 hr or equilibrated in desiccators at 15% and 32% relative humidity for three weeks. Parathion solutions in n-hexane having initial concentrations in the range 50–5000 ppm were then shaken with the homoionic bentonite at a clay to solvent ratio of 1:100. Clay portions of 0.5 g were used in each run. After the clay had been shaken for 48 hr, it was allowed to settle, and the hexane was pipeted out. The hexane traces left were determined gravimetrically, and the clay was then dried in an air-stream at room temperature. No parathion was lost during the drying as determined by the two-liquid phase extraction procedure of Saltzman *et al.* (1976) which gives a complete recovery of the adsorbed parathion.

The dried parathion-treated bentonite was suspended in water at a parathion to water ratio of 8 ppm. This fixed water to adsorbate ratio prevented large differences in the concentrations of the solute released into the solvent upon desorption. If a fixed water to adsorbent ratio had been used, both saturation of the solution at high surface concentrations and bulk concentrations below the reliably detectable limits at low surface concentration might have occurred during desorption. The aqueous bentonite suspensions were shaken for 24 hr

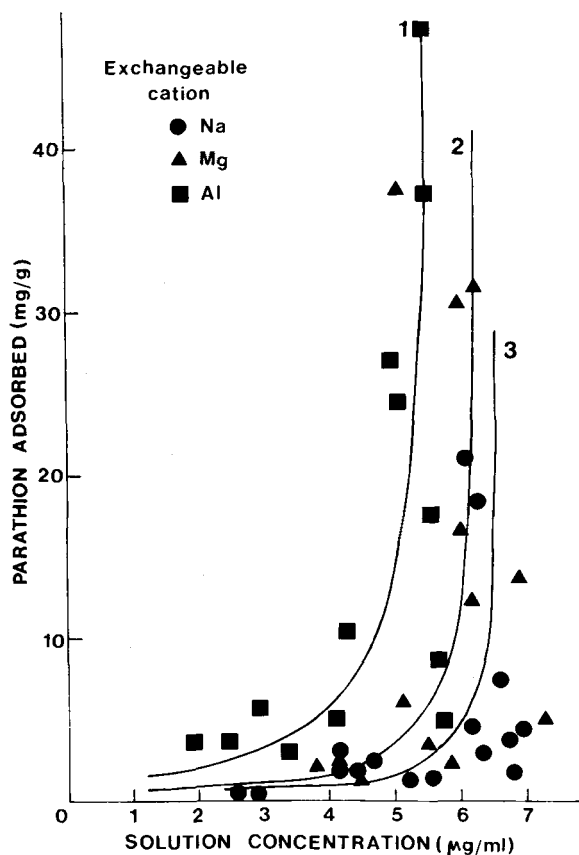


Figure 1. Desorption of parathion into water (1) from Al-, (2) Mg-, and (3) Na-bentonite on which parathion was adsorbed from hexane.

before the desorption measurements. The rate of attaining equilibrium ranged from 1 hr to nearly 24 hr; the greater the surface concentration, the slower was the attainment of equilibrium.

Preparation of samples for XRD analyses. The XRD analyses were conducted on oven-dried (105°C for 24 hr) Na-bentonite treated with parathion or methyl parathion as described below except for c-spacing determinations which were designed to study the effect of moisture content on interlayer penetration. These determinations were also conducted on air-dried Na-bentonite treated with the organophosphate esters. Parathion and methyl parathion solutions in n-hexane at initial concentrations of 5000 ppm were shaken for 24 hr with Na-bentonite at 1:26 clay to solvent ratio, and the hexane was then evaporated under a stream of air at room temperature. Clay portions of 2 g were used for each run. The resulting clay samples contained 130 mg/g of either of the phosphate esters. The adsorption capacity (240 mg/g) of oven-dried Na-bentonite for parathion was determined as follows: parathion-treated Na-bentonite samples with different parathion contents as high as 400 mg/g were prepared in the same manner as described above for the XRD analyses, but using different clay to solvent ratios. After all of the hexane had been removed, the samples were kept in the air-stream for additional 24 hr. For samples containing more than 240 mg/g parathion, the rate of evaporation of parathion decreased abruptly by

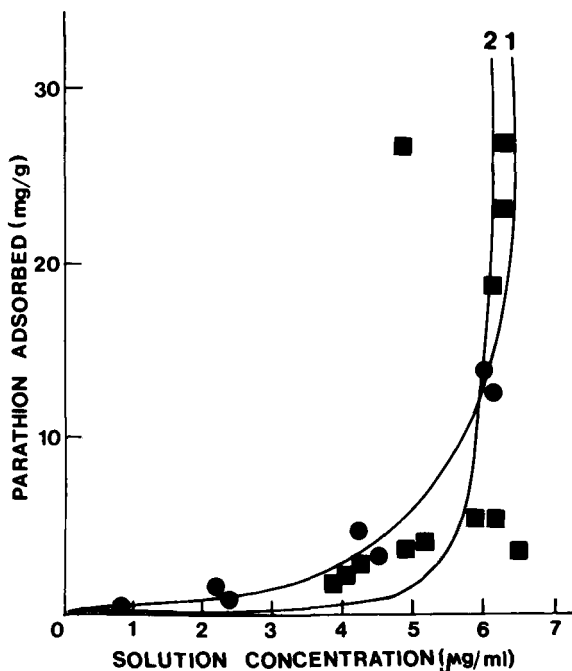


Figure 2. Calculated condensation isotherm for parathion desorbed into water: 1 = from Ca-attapulgitite (Gerstl and Yaron, 1978), and 2 = from Ca-bentonite (present study).

about tenfold. Systems whose parathion content was initially below 240 mg/g displayed the lower rate of evaporation throughout the period of exposure to the air-stream.

Apparatus and analytical methods

Gas-liquid chromatography. A Tracor 560 gas chromatograph equipped with an NP 702 detector and a glass column 90 cm long, filled with 3.4% QF-1 + 6.2% DC-200 on Gaschrom Q, was used. The operating conditions were 225°, 205°, and 225°C for the inlet, column, and detector, respectively, and the flow rate of the gas carrier (N₂) was 70 ml/min.

Liquid scintillation. Water and hexane solutions obtained in the desorption and adsorption runs were counted in the presence of a scintillation fluid containing 60 g naphthalene, 4 g PPO, 0.2 g POPOP, 100 ml methyl alcohol, and 20 ml ethylene glycol in 1 liter of dioxan. A Packard PL Tri-carb liquid scintillation spectrometer was used.

X-ray powder diffraction. A Philips X-ray diffractometer type 1030 with a Co target was used for powder samples. Liquid samples and samples requiring higher sensitivity were examined using a Debye-Scherrer microfocuss camera with Cu as a source of radiation and an exposure time of 48 hr.

RESULTS AND DISCUSSION

Desorption isotherms of parathion released from Al-, Mg-, and Na-bentonites into water are presented in Figure 1. The data for the Ca-bentonite are given in Figure 2. In the range of humidities studied the moisture content of the clays at the time of adsorption of parathion from hexane did not affect the isotherms significantly. Figure 1 shows that starting at some sur-

Table 1. Saturation concentrations (C_s or b_2^{-1}) of parathion in water.

| Solid phase | C_s ($\mu\text{g}/\text{ml}$) | Reference |
|--|--------------------------------------|----------------------------------|
| Na-bentonite ¹ (Wyoming) | 6.4 | Present study |
| Ca-bentonite ¹ (Wyoming) | 6.2 | Present study |
| Mg-bentonite ¹ (Wyoming) | 6.2 | Present study |
| Al-bentonite ¹ (Wyoming) | 5.4 | Present study |
| Oven-dried Ca-attapulgite ¹ (Georgia) | 7.5 | Gerstl and Yaron (1978) |
| Air-dried Ca-attapulgite ¹ (Georgia) | 6.6 | Gerstl and Yaron (1978) |
| Attapulgite HDMA ^{1,2} (Georgia) | 1.8 | Gerstl and Yaron (1978) |
| Clay soil (Bet Guvrin, Israel) | 1.2 | Saltzman <i>et al.</i> (1972) |
| Clay soil (Merom, Israel) | 3.5 | Saltzman <i>et al.</i> (1972) |
| Clay soil after removal of its organic matter (Merom, Israel) | 5.2 | Saltzman <i>et al.</i> (1972) |
| Sandy soil ³ (Mivtahim, Israel) | 6.5 | Yaron and Saltzman (1972) |
| Clay soil ³ (Har Barkan, Israel) | 5.0 | Yaron and Saltzman (1972) |

¹ Desorption into water after the solid phase was loaded with parathion from hexane.

² Attapulgite with hexadecyltrimethylammonium as the exchangeable cation.

³ Isotherm measured at 10°C.

face concentration of parathion, the solution approaches saturation for all the investigated bentonites. Almost no further increase in the concentration of the parathion released into the water was noted at higher initial surface concentrations. The maximum concentration in solution of desorbed parathion was 5–7 ppm (Table 1), although the solubility of parathion in water is 13–14 ppm (Bowman and Sans, 1977; Gerstl, 1979). Such saturation suggests that at a sufficiently high adsorption rate parathion at the clay surface forms a condensate having a different solubility than the free parathion. Related forms of surface condensation have been described for the adsorption of proteins (McRitchie, 1972) and surfactants (Furlong and Sasse, 1983).

Mingelgrin *et al.* (1977) suggested that at low surface concentration, parathion molecules adsorb on clay surfaces at specific sites. Subsequent condensation of parathion may occur at higher surface concentrations with the initially adsorbed molecules serving as nuclei for the condensation. Whereas the saturation concentration in solution was 5.4 ppm for the Al-bentonite, it was >6 ppm for the Ca- and Mg-bentonites and higher for the Na-bentonite. Saturation concentration is determined by the solubility of the phase forming at the adsorbing surface. Thus, solubility is dependent, to some extent, on the type of the exchangeable cations which, together with their hydration water, were suggested as the specific adsorption sites of parathion on clays (Mingelgrin *et al.*, 1977).

Structural investigations of the condensed phase formed on clay surfaces

To ascertain whether or not a phase was present at the surface, XRD spectra of liquid and frozen parathion and of parathion adsorbed on oven-dried Na-bentonite were obtained (Figure 3). A broad XRD reflection at about 5.3 Å was observed for the parathion adsorbed on bentonite (Figure 3b), but was not detected in the pattern of the untreated bentonite (Figure 3a). A weak peak at 3.4 Å was also observed in the pattern of the parathion adsorbed on bentonite. The liquid parathion pattern contained two broad peaks at 3.7 and 5.7 Å (Figure 3c), the intensity of the first being lower than that of the second. For frozen parathion, peaks at 5.0 and 3.8 Å were observed. The presence of an ordered phase at the surface is thereby suggested by the existence of an XRD pattern of adsorbed parathion. The shift of the 5.7-Å peak of the liquid parathion to 5.3 Å in the adsorbed phase and to 5.0 Å in the frozen parathion may suggest that the adsorbate-adsorbate interactions are stronger than the intermolecular interactions which occur in the free liquid parathion. These relationships are in agreement with the low solubility of the condensed phase at the surface as compared to free parathion. The same conclusion may be drawn by comparing the XRD patterns of free methyl parathion and of methyl parathion adsorbed on bentonite (Figure 4). The main peak in the powder diffraction pattern of free methyl parathion (obtained by evaporating to dryness the hexane solution of methyl parathion) was recorded at 5.12 Å. A corresponding peak was in the spectrum of the adsorbed methyl parathion at 5.06 Å. That this small difference is significant was ascertained by mixing free methyl parathion with the methyl parathion-loaded-clays (both as powders) in various proportions and observing the behavior of the resulting peaks. The difference in spacing between the adsorbed and free solid methyl parathion was smaller than the difference between the free and adsorbed liquid parathion. The other differences between the diffractograms (Figure 4) of the free and the adsorbed methyl parathion (e.g., line width and the absence of the 5.36-Å peak in the adsorbed methyl parathion) may reflect differences in crystal size as well as in the crystal structure itself.

Figure 5 presents a computed model for the packing of molecules in a methyl parathion crystal. Such packing is in line with results obtained for other organophosphate esters (Baughman and Jacobson, 1975, 1976) and is also physically feasible for the condensed phases of adsorbed parathion and methyl parathion. The proposed packing is facilitated by the interactions of the $\delta(+)$ on the P atom with the $\delta(-)$ of an O atom in the nitro group. The distance, d_1 (Figure 5), which for parathion is 5.7 Å and for methyl parathion is 5.12 Å, agrees with the van der Waals radii sums. Mingelgrin *et al.*

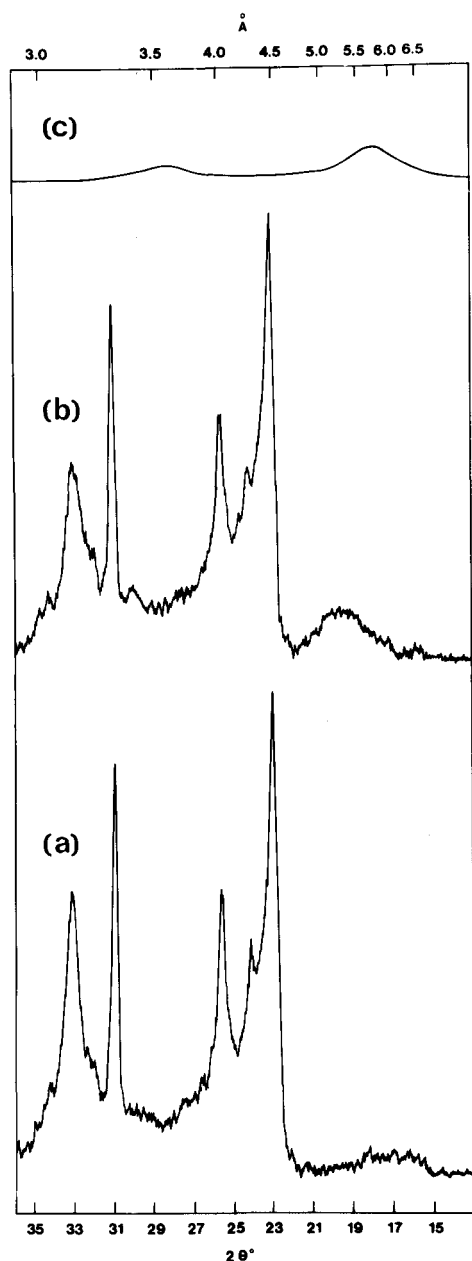


Figure 3. X-ray powder diffraction patterns of (a) Na-bentonite (powder), (b) Na-bentonite with adsorbed parathion (powder); (c) free parathion obtained by the Debye-Scherrer method. (a) and (b) = $\text{CoK}\alpha$ radiation; (c) = $\text{CuK}\alpha$ radiation. The 2θ scale applies to (a) and (b) only.

(1977) suggested that the dominant interaction between the exchangeable cation and the phosphate ester is through the thiophosphate group. This interaction may cause a shift in the electron density towards the thiophosphate group away from the nitrophenyl group. One reason for the decrease in the intermolecular dis-

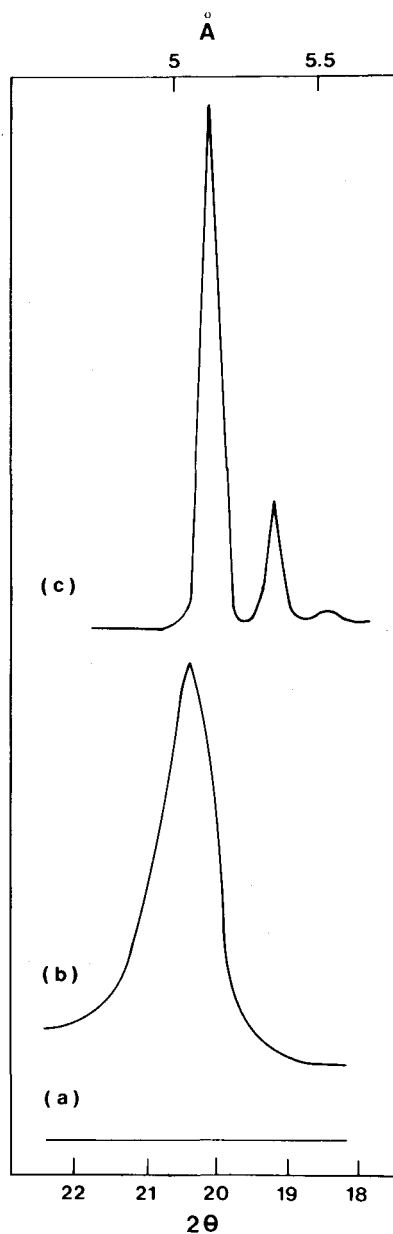


Figure 4. X-ray powder diffraction patterns of (a) Na-bentonite; (b) methyl parathion adsorbed on Na-bentonite; (c) free methyl parathion ($\text{CoK}\alpha$ radiation).

tances, d_1 , in the adsorbed phases of parathion and methyl parathion may thus have been the reduced mutual repulsion of the π clouds of two parallel rings. As the valence of the exchangeable cations increased, this repulsion should have decreased, as should have d_1 . These relationships are in agreement with the observed order of solubility of the condensed phase of parathion on the homoionic bentonites: $\text{Na} > \text{Ca}(\text{Mg}) > \text{Al}$. Mingelgrin *et al.* (1977) proposed that the molecule

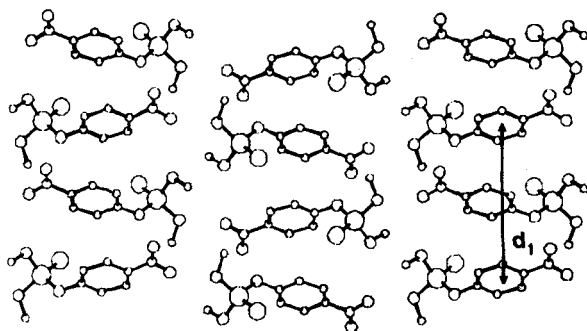


Figure 5. Structure of methyl parathion crystal computed from its single crystal X-ray diffraction pattern. d_1 represents the distance corresponding to the major reflection in the X-ray diffraction pattern.

which interacts directly with the exchangeable cation lies parallel to the clay surface. Such an orientation of the organophosphate molecule is suitable for a nucleation site of the stacking model proposed in Figure 5.

The investigated phosphate esters can adsorb either on the external surfaces of smectites or in the interlayer spaces where the condensation is, of course, hindered. Figure 6 presents the XRD patterns corresponding to the *c*-spacings of Na-bentonite which was treated with either parathion or methyl parathion, of untreated Na-bentonite, and of Na-bentonite shaken with hexane and dried in the same manner as the phosphate ester-treated samples. The analytical grade hexane may have contained traces of water, and the hydrophilic clay may have adsorbed this water causing some swelling. The organophosphate ester dissolved in hexane may have competed with water for adsorption sites in the interlayer spaces or have been adsorbed through water bridges. Even if the parathion competed for adsorption sites with water, it might have penetrated between the layers only after some swelling had occurred due to water uptake. The potentially complex effect of water on adsorption at the interlayer clay surfaces makes the elucidation of the nature and extent of such adsorption from hexane on the basis of the observed *c*-spacing rather difficult (e.g., Saltzman and Yariv, 1976 and Figure 6). At any rate, the relatively well-defined and intense reflection at about 15.3 Å of the air-dried Na-bentonite treated with methyl parathion (Figure 6) as compared to the very wide, low-intensity reflection of the parathion-treated clay centered at about 13.1 Å suggests that the methyl parathion penetrated the interlayer spaces relatively easily, whereas parathion penetration was hindered. The methyl parathion penetration was restricted, however, to some extent, when the initial *c*-spacing of the smectite was reduced due to a lower water content (Figure 6d, 6e). The above observations demonstrate that steric factors may de-

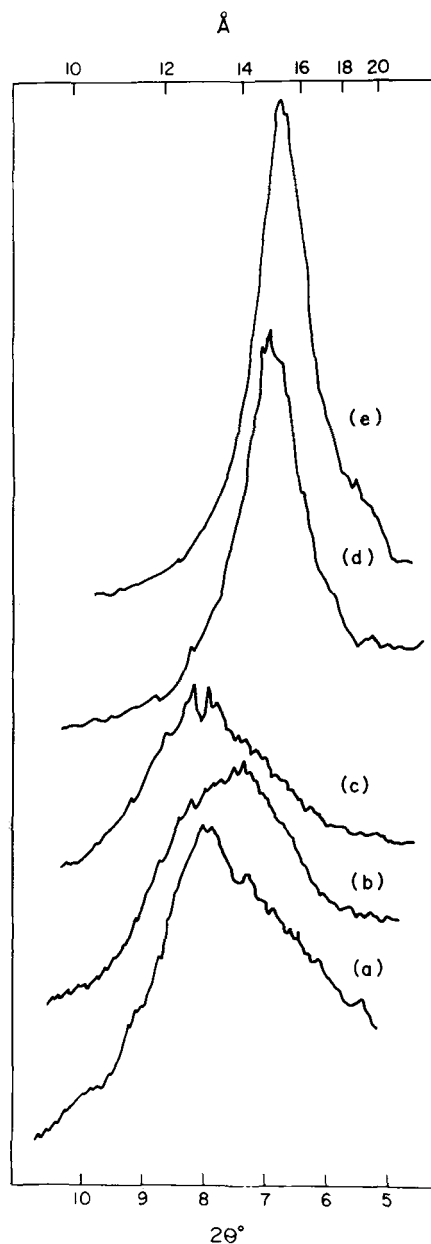


Figure 6. X-ray powder diffraction pattern corresponding to the basal spacing of (a) air-dried Na-bentonite; (b) air-dried Na-bentonite after equilibration with hexane; (c) air-dried Na-bentonite treated with ethyl parathion; (d) oven-dried Na-bentonite treated with methyl parathion; (e) air-dried Na-bentonite treated with methyl parathion ($\text{CoK}\alpha$ radiation).

termine the relative importance of condensation in the adsorption of organophosphate esters on smectites.

Nuclear magnetic resonance (NMR) studies are currently in progress. Preliminary results indicate that the general features of the NMR spectra of parathion adsorbed on bentonite are similar but not equivalent to

that of the free parathion. A scan at 200°–350°K showed that the D² NMR spectrum of the adsorbed deuterated parathion exhibited down to 300°K characteristics of an adsorbed liquid and at lower temperatures characteristics of a solid. This behavior suggests that the arrangement of the adsorbed parathion is in a bulky condensate capable of a transition between a liquid and a solid phase. These features of the NMR spectra are in agreement with a proposed adsorption process in which most of the adsorbate exists as a condensate similar but not identical to the free state and in which only a small fraction of the adsorbate is directly bound to adsorption sites on the clay. Parathion-parathion intermolecular interactions appear to dominate the behavior of the molecules adsorbed on the bentonites at a sufficiently high surface concentration, but the surface may determine the nature of these interactions. The desorption isotherms (Figures 1 and 2) suggest that a condensed phase may exist at the surface even at surface concentrations under 10 mg/g which is well below the level of saturation (e.g., Gerstl and Yaron, 1981) for direct adsorption (as opposed to condensation).

CONDENSATION ISOTHERM

The adsorption of the phosphate esters may consist of two steps. The first step is adsorption at specific sites; the second is condensation at sites already occupied by an adsorbed molecule which serves as a nucleus for that condensation. In the following treatment, the total number of sites per unit weight available for the specific adsorption is N , the number of such sites which are occupied is n_1 , and the number of these sites at which condensations occurred is n_2 . The treatment holds as long as the equilibrium concentration in solution is practically independent of the number of molecules condensed per site, analogous to the situation in precipitation-dissolution equilibria. The existence of an asymptote in the isotherms (Figures 1 and 2) at some solution concentration indicates that this requirement is fulfilled for the investigated range of adsorption rates. The stacking arrangement proposed in Figure 5, for example, enables a large number of molecules to condense per site before the above requirement breaks down.

The condensation observed in the present study is described well by a BET-type isotherm even though the BET isotherm was developed for a system in which a continuous monolayer of adsorbate must form before adsorption in a second layer can occur (Brunauer *et al.*, 1938). Such a multilayer adsorption is very different from the condensation studied presently and necessitates some redefinition of the parameters appearing in the BET isotherm when applied to the presently described condensation. Following Langmuir (e.g., Adamson, 1976), at equilibrium

$$C(N - n_1)A_1e^{\Delta E_1/RT} = n_1 - n_2, \quad (1)$$

and

$$Cn_1A_2e^{\Delta E_2/RT} = n_2, \quad (2)$$

where ΔE_1 and ΔE_2 are the net adsorption energies of the first and second adsorption steps, respectively, A_1 and A_2 are the corresponding constants analogous to frequency factors (e.g., Adamson, 1976), and C is the equilibrium bulk concentration. A site belonging to n_2 also belongs to n_1 , namely adsorption of the second type (condensation) can only occur on a site already occupied by an adsorbed molecule. When

$$n_1 = S_1 \leq N, \quad (3a)$$

$$n_2 \leq S_2, \quad (3b)$$

where S_1 and S_2 are the number of adsorbed molecules of the first and the second adsorption type, respectively. The amount adsorbed in the condensed phase is

$$S_2 = \sum_{m=2}^{\infty} n_m, \quad (4)$$

where n_m is the number of sites at which m molecules or more are adsorbed per site. From Eqs. (1) and (2)

$$C = \left[A_2 e^{\Delta E_2/RT} + \left(\frac{N}{n_1} - 1 \right) A_1 e^{\Delta E_1/RT} \right]^{-1}. \quad (5)$$

When $n_1 = N$, C is independent of the amount adsorbed and is then equal to the saturation concentration, namely to the solubility (C_s) of the adsorbed phase. Note that C_s is different (Figures 1 and 2) from the solubility of free parathion. Let

$$b_1 = A_1 e^{\Delta E_1/RT}. \quad (5)$$

As long as practically all of the condensate molecules form a well-defined phase, b_2 is independent of the distribution of n_m . This independence of b_2 is equivalent to the aforementioned requirement that the solution concentration at equilibrium is independent of the number of adsorbate molecules condensed per site. The mere presence of a well-defined XRD pattern of the adsorbed phase indicates the predominance of sites with a regular stacking, and hence, an apparently constant b_2 . The presence of an asymptote in the desorption isotherms indicates that b_2 is a well-defined parameter for the condensed phase because the saturation concentration, C_s , is equal to b_2^{-1} (Eq. (5)). In some systems the net condensation energy (ΔE_2) may decrease, whereas the entropy of condensation may increase as the thickness of the condensate increases. The net effect may be a very slowly varying b_2 . If b_2 varies slowly enough to be well-approximated as a constant for all surface concentrations of interest, the present development applies even though a true phase is not present.

Again following Langmuir (e.g., Adamson, 1976), at equilibrium

$$n_m/n_{m-1} = b_2 C. \quad (7)$$

Eq. (2) is a special case of this general equation. From Eq. (4) and (7),

$$S_2 = S_1 \sum_{m=1}^{\infty} (b_2 C)^m, \quad (8)$$

or

$$\begin{aligned} S &= S_1 + S_2 \\ &= S_1 \sum_{m=0}^{\infty} (b_2 C)^m \\ &= S_1 (1 - b_2 C)^{-1}, \end{aligned} \quad (9)$$

where S is the number of molecules adsorbed per unit weight.

Substituting in Eq. (5) gives

$$1/C = b_2 + b_1 \left(\frac{N}{S(1 - b_2 C)} - 1 \right), \quad (10)$$

or

$$S = b_1 N C / (1 - b_2 C) [1 + (b_1 - b_2) C]. \quad (11)$$

Eq. (11) is identical in form to the BET isotherm (Brunauer *et al.*, 1938). This equation is actually more suitable for the condensation model described in the present work (stacking of adsorbate molecules at separated specific sites on the surface) than for the multilayer adsorption for which the BET isotherm was developed. In the latter adsorption a continuous monolayer is assumed to exist before a second layer can begin to form. In such a multilayer adsorption lateral interactions may be more important, and therefore the Langmuir treatment (Eqs. (1), (2) and (7)), which was used in the original derivation of the BET isotherm (Brunauer *et al.*, 1938) as well, is less applicable. Some of the difficulties encountered by Brunauer *et al.* (1938) in fitting experimental data to the BET isotherm might have resulted from these lateral interactions. Whereas in the original BET derivation, b_2 was taken as the inverse of the solubility of the free substance, this assumption is clearly not applicable to the condensate described in the present work as its solubility was significantly smaller than that of the free substance.

The condensation isotherm (Eq. (11)) has an asymptote at $C = b_2^{-1} = C_s$, in agreement with the experimental data (Figures 1 and 2). Significant deviation from the developed isotherm should have appeared when the number of molecules adsorbed in a given condensation site increased above some limit. A larger number of condensed molecules in a site means for example, a greater chance for interactions between molecules on different sites or for accumulation of irregularities in the stacking which may gradually alter the nature of the condensate at that site. Indeed, at sufficiently high S , the nature of the adsorbate began

to change as indicated by the finite adsorption capacity for parathion on Na-bentonite (240 mg/g). The observed width of the diffraction peaks of free and adsorbed methyl parathion suggest, however (James, 1965; Jones, 1938), that the condensed phase in the investigated systems was dominated by sites with a relatively small number of molecules stacked per site (≤ 10).

The initial slope of the isotherm (Eq. (11)) is equal to $b_1 N$ and is a function of the exchangeable cation (Figure 1). This slope is in the order

$$Na < Ca \approx Mg < Al,$$

in agreement with the proposal (Mingelgrin *et al.*, 1977) that the specific adsorption sites are the exchangeable cations and their hydration shell. Concave isotherms similar to those described in the present work were observed for the adsorption of parathion from water on various soils (Saltzman *et al.*, 1972; Yaron and Saltzman, 1972) and for the desorption of parathion into water after initial adsorption from hexane onto various homoionic clays (Gerstl and Yaron, 1978). The state of the directly adsorbed molecules which served as the nuclei for the condensation may have strongly affected the nature of the condensate formed on it and hence b_2 (e.g., Table 1). If adsorption is carried out from one solvent and desorption is attempted in a different medium, the nature of the surface condensation in that last medium may be determined by the direct adsorption in the first one. The rate at which the directly adsorbed molecules reequilibrate with the new solvent may be very slow because these molecules must be exposed from under all the condensed phase molecules covering them before they can equilibrate. This exposure is hindered by the fact that during equilibration adsorbate molecules join the condensed phase while others leave it. An analogous situation is the desorption of a polymer with multiple points of interaction with the surface. Accordingly, a large difference in the desorption of parathion from attapulgite into water was observed between samples in which the parathion was adsorbed from water and samples in which the parathion was adsorbed from hexane (Gerstl and Yaron, 1978).

Figure 2 presents calculated isotherms (Eq. (11)) for parathion desorbed from Ca-montmorillonite and Ca-attapulgite into water after being adsorbed from hexane. A least square fit was carried out. It is evident that Eq. (11) predicts satisfactorily the surface condensation of the type observed in the present study. The condensation of a solute at a solid surface in contact with a solution was postulated in the past (e.g., Dzhigit *et al.*, 1947). Generally, however, the condensate at the surface had the same solubility as the free solute. When C_s was different than that of the free solutes it was assigned to the effect of the surface potential on the condensed film. In condensation affected by the surface potential, however, b_2 is likely to decay monotonically

with the distance from the surface and the equilibrium concentration in solution will slowly approach the solubility of the free solute. The periodicity required for the diffraction patterns which were observed in the present study may not exist.

CONCLUSIONS

The XRD patterns and desorption data suggest the presence of an ordered phase of parathion and methyl parathion when adsorbed at sufficiently high loads on clay surfaces. The molecular arrangement of this phase bears a resemblance but is not identical to that of the free substances. The behavior of the condensed phase may depend on the mode of preparation of the system even at identical surfaces. The nature of that phase is affected by the nucleation sites proposed to be the exchangeable cations or their hydration shell and by the liquid medium in which the adsorption took place. The difference between the solubilities of the surface condensed phases and the free pesticides can be used to control the release of organophosphate (and possibly other) pesticides applied to media such as soil, water, or air.

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Резюме—Паратион и метилпаратион, будучи адсорбированы в больших количествах на глинах и сходных поверхностях, образуют самостоятельную фазу, характеризующуюся определенной растворимостью и рентгеноструктурными характеристиками отличными от свойств свободных паратиона и метилпаратиона. Растворимость паратиона сконденсированного на таких поверхностях может достигать 1,2 мкг/мл, в то время как растворимость свободного паратиона равна 14 мкг/мл. БЭТ-изотерма, выведенная для многослойной адсорбции, описывает поведение исследуемых конденсатов, несмотря на то, что поведение этих конденсатов отличается от многослойной адсорбции. Порошковые дифракции рентгеновских лучей адсорбированных на Na-бентоните паратиона и метилпаратиона смещены в сторону больших углов относительно аналогичных дифракций для свободных паратиона и метилпаратиона, что соответствует пониженной растворимости поверхностных конденсатов. Свойствами исследуемых конденсатов легко управлять при помощи выбора адсорбента, а также способами приготовления конденсатов. Существование описанных поверхностных конденсатов и возможность управления их свойствами могут быть использованы для осуществления подачи органофосфорных эфиров способом медленного высвобождения, что, в свою очередь, явится полезным во многих областях, в частности при применении ядохимикатов.

Resümee—Parathion und Methylparathion, die in großen Mengen an Tonen und ähnlichen Oberflächen adsorbiert waren, zeigten Eigenschaften einer Gesamphase, wie z.B. eine gut definierte Löslichkeit und ein charakteristisches Röntgenpulverdiffraktogramm (XRD), die sich von denen der einzelnen freien Substanzen unterscheiden. Die Löslichkeit im Wasser von Parathion, das an diesen Oberflächen kondensiert war, betrug nur 1,2 $\mu\text{g}/\text{ml}$ im Vergleich zu 14 $\mu\text{g}/\text{ml}$ für das freie Parathion. Das BET-Isotherm beschrieb das Verhalten der untersuchten Oberflächenkondensate, obwohl sich diese Kondensate von der Vielschichtadsorption, für die die BET-Isotherme ursprünglich entwickelt wurden, unterschieden. Die XRD-Diagramme von an Na-Bentonit adsorbiertem Parathion und Methylparathion zeigten Reflexe, die im Vergleich zu denen der freien Komponenten nach höheren Winkeln verschoben waren. Dies stimmt mit der geringeren Löslichkeit der Oberflächenkondensate überein. Die Eigenschaften dieser Kondensate konnten leicht gesteuert werden, sowohl durch die Wahl des Adsorbenten als auch durch die Wahl der Bedingungen, bei denen sie hergestellt wurden. Die Existenz solcher an die Oberfläche kondensierter Phasen und die Veränderung ihrer Eigenschaften kann bei der langsamen Abgabe von Organophosphatestern verwendet werden, was z.B. bei der Anwendung in Pestiziden von Bedeutung ist. [U.W.]

Résumé—Le parathion et le parathion méthyl adsorbés à charges élevées sur des argiles et des surfaces semblables ont exhibé les propriétés d'une phase de masse, telles qu'une solubilité bien définie et un cliché de diffraction des rayons-X caractéristique, différentes de celles des substances libres. La solubilité aqueuse du parathion condensé à ces surfaces était aussi basse que 1,2 $\mu\text{g}/\text{ml}$, comparé à 14 $\mu\text{g}/\text{ml}$ pour le parathion libre. L'isotherme BET a décrit le comportement des condensates de surface investigués, bien que ces condensates étaient différents de l'adsorption multicouche pour laquelle l'isotherme avait été développé à l'origine. Les clichés XRD du parathion et du parathion méthyl adsorbés sur la bentonite-Na ont exhibé des réflexions qui étaient déplacées vers des angles plus élevés en comparaison avec les clichés XRD des composés libres. Ceci s'accorde avec la solubilité plus basse des condensates de surface. Les propriétés de ces condensates étaient facilement contrôlables par le choix de l'adsorbant aussi bien que par le choix des conditions sous lesquelles ils étaient préparés. L'existence de telles phases condensées à la surface et la manipulation de leurs propriétés peuvent être utilisées pour la formulation d'estères organophosphates à décharge lente, ce qui est important pour, par exemple, l'application des pesticides. [D.J.]