

A NOTE ON THE ADSORPTION OF ORGANIC MOLECULES ON CLAYS¹

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Abstract—Results of adsorption studies of several pesticides on soils and clays show that the application of the reduced concentration concept to adsorption can either reduce the temperature effect on the isotherms, eliminate it altogether (e.g., parathion adsorption on Netanya soil), increase the temperature dependence (e.g., β -BHC adsorption on Ca-bentonite) or even reverse the temperature dependence of the isotherms (e.g., parathion adsorption on Ca-attapulgite).

Literature and experimental data for the adsorption of parathion by Ca-attapulgite and by attapulgite with organic exchangeable cations of different sizes demonstrate that for many surface interactions the terms organophilic or hydrophilic are misleading. Organic compounds which are insoluble in water and soluble in apolar solvents will not necessarily adsorb preferentially on "organophilic" surfaces. The specific interactions between adsorbate and adsorbent and steric considerations (in addition to the relative solubility of the organic molecule in water and apolar solvents and the organophilic or hydrophilic nature of the surface) will determine the partition between the adsorbed and the solution phase. An outstanding example is the order of adsorption of parathion on attapulgite: HDMA-attapulgite > Ca-attapulgite > TMA-attapulgite. This order is neither directly nor inversely related to the "organophilic" nature of the surfaces.

Key Words—Adsorption, Attapulgite, Organophilic, Parathion, Reduced Concentration.

INTRODUCTION

The general concepts of "reduced concentration" and "organophilic vs. hydrophilic interactions" have been used by Mills and Biggar (1969) and Mortland (1979), respectively, to describe the nature of the adsorption of organic molecules on clays. Although these concepts can be properly applied to explain many clay-organic molecule interactions, experimental data as well as theoretical considerations suggest that many attempts to use these concepts may lead to erroneous conclusions. On the basis of literature data and some original experimental results, this note demonstrates the limits of applicability of these two general concepts.

EXPERIMENTAL

Attapulgite (Diluex, Floridin) and bentonite (Fisher Scientific Inc.) were rendered homoionic by repeated washings with various solutions of inorganic and organic ions. Ca^{2+} , Na^+ , TMA^+ (tetramethylammonium), and HDMA^+ (hexadecyltrimethylammonium) clays were prepared. Clays were dispersed by placing 0.1 g in an ultrasonic bath with 5 ml of distilled water for 5 min and then shaking the slurries for 24 hr. Aqueous solutions of parathion (5 ml) of various concentrations were then added and the suspensions shaken for an additional 24 hr. After attainment of equilibrium, the suspensions were centrifuged and the supernatant solutions analyzed for parathion. [Ethyl- 1-C^{14}] parathion (Radiochemicals Ltd., Amersham) was used and determined in a Packard Model 3003 Tri-Carb Scintilla-

tion counter. The scintillation fluid used was as described previously (Gerstl and Yaron, 1978). Adsorption isotherms were run at 5°, 25°, and 37°C.

RESULTS AND DISCUSSION

Reduced concentration

The concept of reduced concentration (Kipling, 1965) has been used to present a unified approach to adsorbate-adsorbent interactions in different solvents in which the adsorbate has different solubilities. It was also employed (Mills and Biggar, 1969; Yaron and Saltzman, 1972) to obtain "temperature-independent" adsorption isotherms. Reduced concentration is defined as C/C_0 , where C is the equilibrium concentration and C_0 is the saturation concentration of the solute at a given temperature. Rather than the standard isotherms in which the surface concentration is plotted against C , a supposedly temperature-independent isotherm is obtained by replacing C by C/C_0 . Yet, the equilibrium adsorption and C_0 are differently dependent on the temperature; hence, they are not directly related to each other. The temperature dependence of C_0 can be described as follows:

$$\frac{d \ln C_0}{d 1/T} = - \frac{\Delta H_{\text{dis}}}{R} \quad (1)$$

where R is the gas constant and ΔH_{dis} is the enthalpy of dissolution.

$$\Delta H_{\text{dis}} = H_c - H_{\text{sol}} \quad (2)$$

where H_c is the heat of sublimation of the pure solid and H_{sol} is the heat of solvation of the solute. If the pure solute is a liquid, H_c in Eq. (2) should

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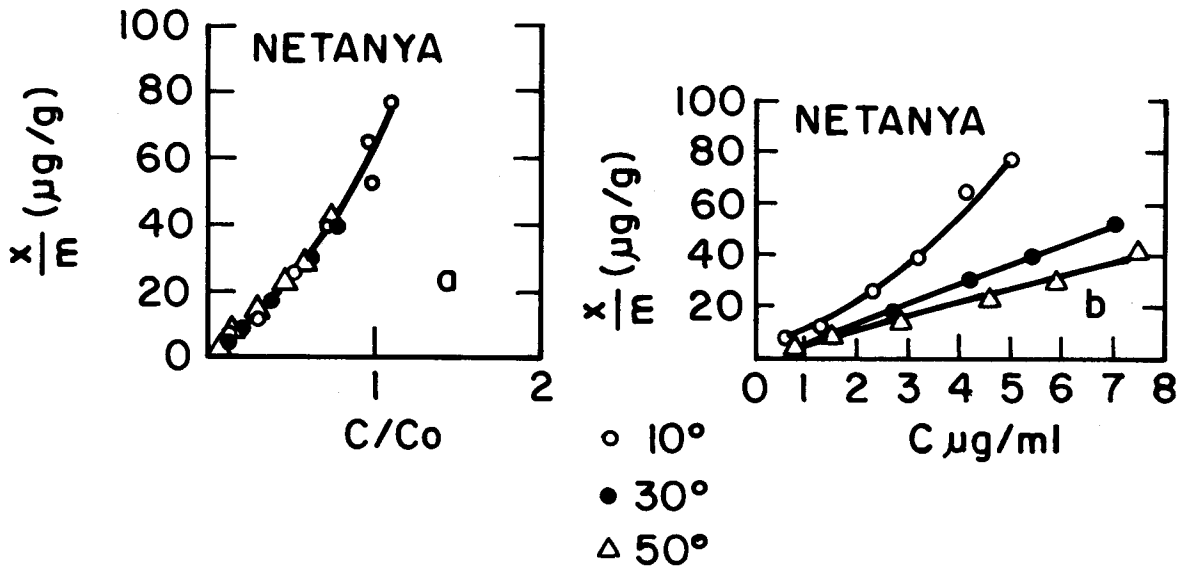


Figure 1. Reduced (a) and normal (b) adsorption isotherms of parathion from water on a Netanya soil (reproduced from Yaron and Saltzman, 1972).

be replaced by the heat of vaporization of the pure liquid.

At sufficiently low C (where the adsorption isotherm approximates a straight line):

$$\frac{d \ln K_{\text{ads}}}{d 1/T} = - \frac{\Delta H_{\text{ads}}}{R} \quad (3)$$

where K_{ads} is the ratio between the surface concentration and C , and ΔH_{ads} is the enthalpy of adsorption defined as follows:

$$\Delta H_{\text{ads}} = H_{\text{sol}} - H_s \quad (4)$$

where H_s is the heat of vaporization of the organic molecules from the adsorbed state. Frequently adsorption

is actually an exchange process between solvent and solute molecules at the surface (e.g., Mortland, 1970). H_s in Eq. (4) will then have a different definition, but ΔH_{ads} can still be written in the form of Eq. (4), bearing in mind the proper definition of H_s . H_s is independent of H_c as both arise from completely different interactions. As long as $H_s \neq H_c$, K_{ads} will vary with temperature independently of C_0 , and hence the concept of reduced concentration lacks theoretical support.

In general, C_0 increases with temperature (dissolution being endothermic) while the specific adsorption at a given C decreases with an increase in temperature (the adsorption process is usually exothermic). This means that the reduced concentration isotherm may

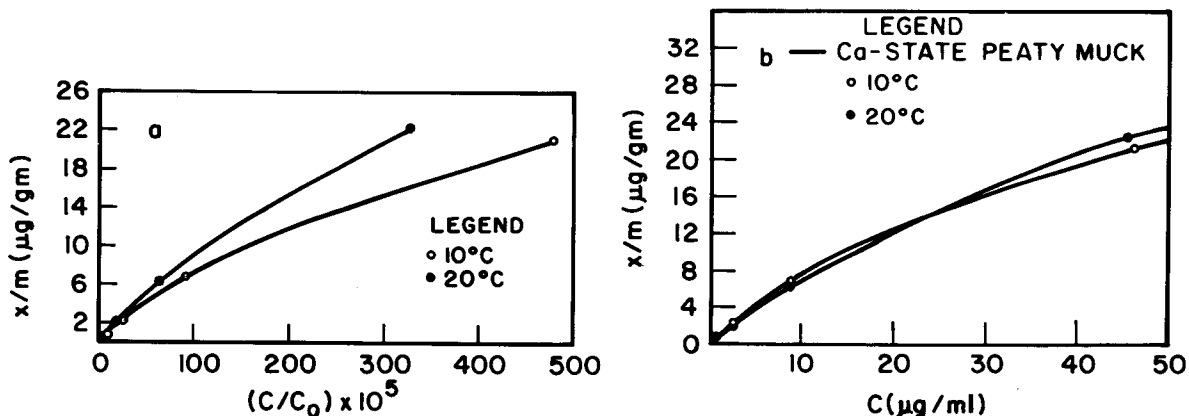


Figure 2. Reduced (a) and normal (b) adsorption isotherms of γ -BHC from hexane on Ca-staten peaty muck (reproduced from Mills and Biggar, 1969).

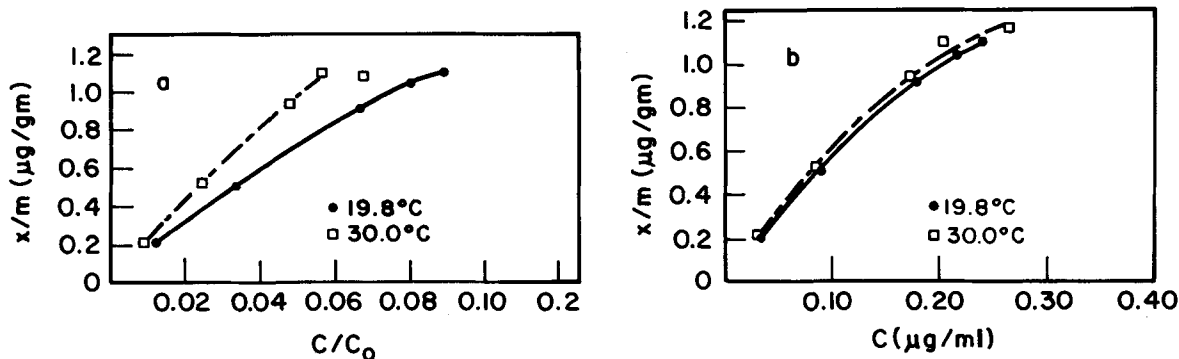


Figure 3. Reduced (a) and normal (b) adsorption isotherms of β -BHC from water on Ca-bentonite (reproduced from Mills and Biggar, 1969).

often decrease the temperature effect as compared with the conventional adsorption isotherm. This correction, however, may be of any magnitude and may even increase the dependence of the isotherm on temperature by overshooting the correction. Figures 1-5 display various specific adsorption vs. concentration and reduced concentration curves. In some cases the reduced concentration eliminates the temperature effect (Figures 1 and 5), but not in others (Figures 2-4). Where the temperature effect is eliminated either $H_s \cong H_c$ or H_c and H_s are small as compared to H_{sol} . The latter possibility does not apply to sparingly soluble compounds. The data demonstrate that the concept of reduced con-

centration lacks universal applicability and predictive ability except for those systems where it has been proven to apply.

Organophilic vs. hydrophilic interactions

Hydrophilic groups display an attraction towards water molecules, and organophilic groups display an attraction towards apolar molecules. Hydrophilic colloids, for example, will form stable suspensions in water, whereas organophilic colloids will form stable suspensions in apolar media. The terms organophilic and hydrophilic (as well as organophobic and hydro-

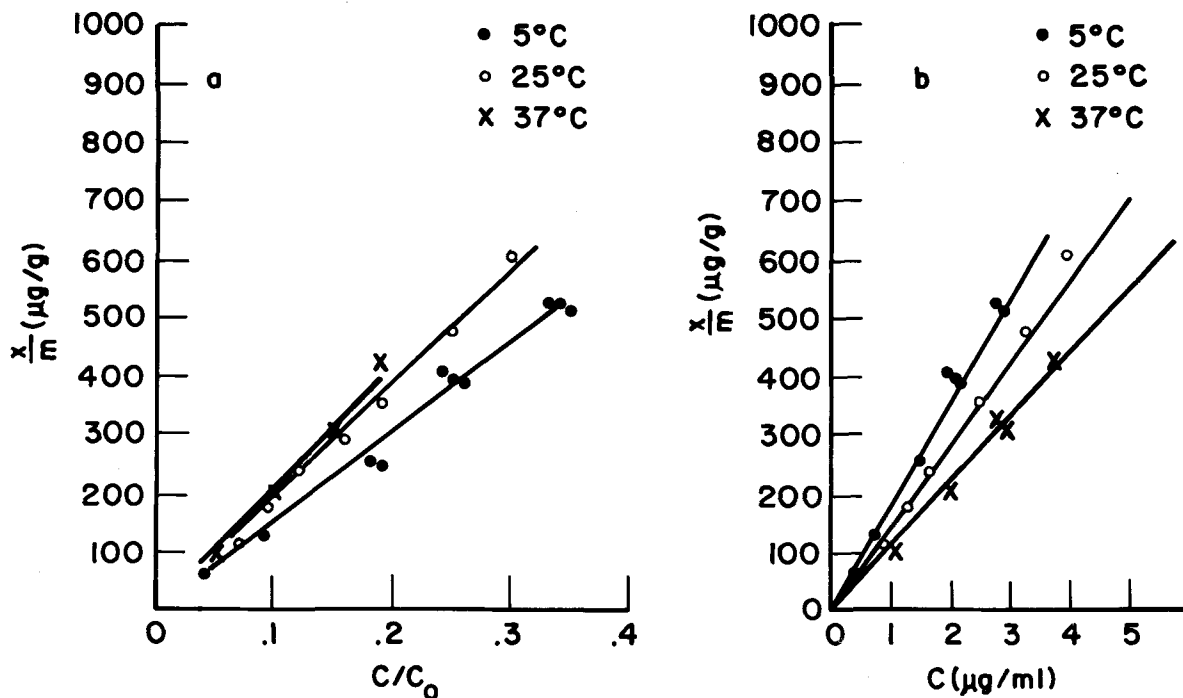


Figure 4. Reduced (a) and normal (b) adsorption isotherms of parathion on Ca-attapulgite (air-dried) from water.

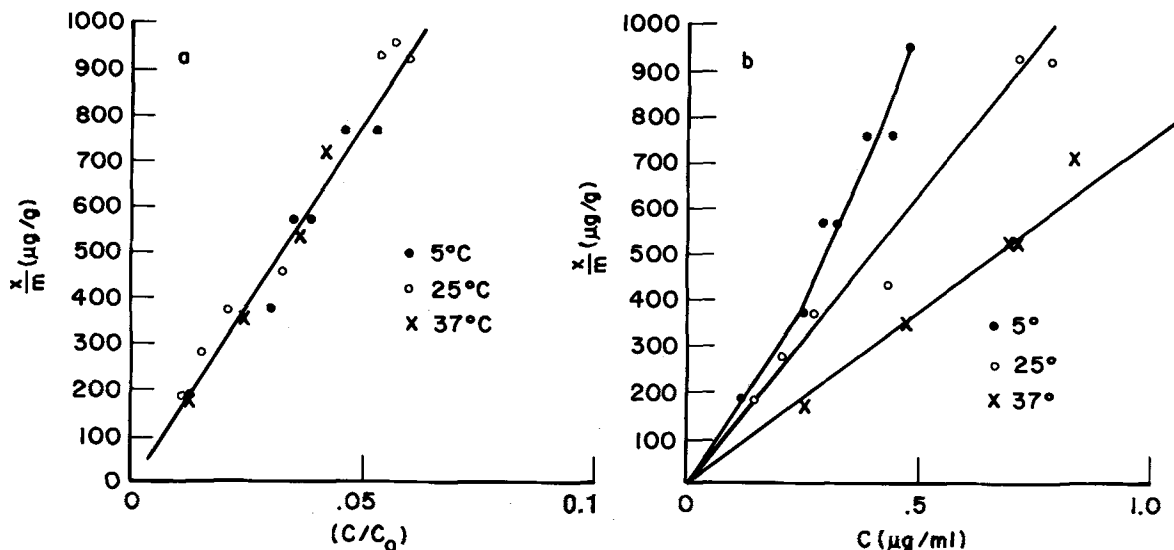


Figure 5. Reduced (a) and normal (b) adsorption isotherms of parathion on HDMA⁺-attapulgite from water.

phobic) have also been used to explain the differences in the adsorption of various organic adsorbates on clay surfaces. For example, Mortland (1979) stated that pesticides which are sparingly soluble in water will not strongly adsorb on clays in aqueous suspension, the clay being hydrophilic while the pesticide is organophilic. Similarly, Ovacharenko (1966) referred to clays saturated with organic cations as organophilic. This implies that organic molecules, specifically those of low water solubility, should adsorb more strongly on organic-cation saturated clays than on clays with an inorganic exchangeable cation. Experimental results demonstrate that this is not generally correct and hence, a classification of surfaces as hydrophilic or hydrophobic with regard to the adsorption of organic molecules may lead to erroneous conclusions.

Despite his use of the term "organophilic" for the organic cation-clay complexes, Ovacharenko (1966) pointed out that the organic cation-clay complex adsorbs some organic polymers most strongly when the clay is only partially saturated with organic cations. Parathion, which is only slightly soluble in water (about 13 ppm at 20°C; Bowman and Sans, 1977), adsorbed strongly on various clays from the apolar hexane solutions (Yaron and Saltzman, 1972; Gerstl and Yaron, 1978). The adsorption of parathion from hexane is affected by the moisture content of the clay surface. Work in this laboratory has shown that, in general, adsorption is strongest on clays at some intermediate moisture content and that parathion also adsorbs appreciably on clays from water (see also, Gerstl and Yaron, 1978; Bowman and Sans, 1977). Biggar *et al.* (1978) showed that much more parathion adsorbed on Na-bentonite and an illitic soil clay from water than did

picloram, although picloram is much more soluble in water than parathion. Bowman and Sans (1977) stated that the extent of adsorption from water at low concentrations of a group of organophosphate esters, including parathion, on Na- and Ca-montmorillonite is inversely proportional to the water solubility of the or-

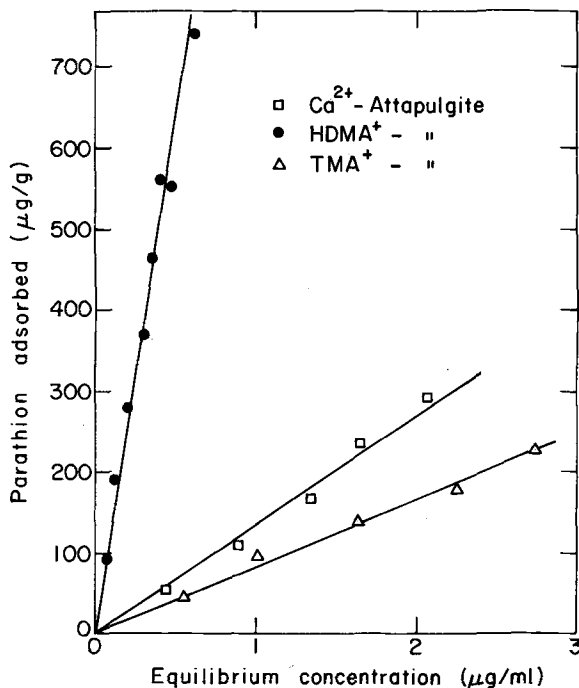


Figure 6. Adsorption isotherms of parathion on Ca²⁺-, TMA⁺-, and HDMA⁺-attapulgite from water (25°C).

ganophosphate ester. Finally, adsorption of parathion on TMA⁺-attapulgite was less than on Ca²⁺-attapulgite in an aqueous suspension (Figure 6). Here also, parathion adsorbed more on the "hydrophilic" Ca-clay than on the presumably more organophilic organic-cation TMA⁺-clay.

Although organophilic molecules generally are attracted to organophilic surfaces, the number of exceptions (Biggar *et al.*, 1978; Bowman and Sans, 1977; and Figure 6 of this work) indicate that a prediction of adsorption on the basis of the organophilic nature of the surface is unwarranted. Many of the exceptions encountered cannot be simply explained by steric effects. For example, no interlayer spaces are involved in attapulgite-parathion interactions which occur only on the outer surfaces of the clay. The above data demonstrate that for many surface interactions, the terms hydrophilic and hydrophobic are misleading. Many molecules of interest, such as pesticides, contain groups which may interact specifically with different sites on the clay surface. The partition between the adsorbed phase and the solution is determined, of course, by both the solute-solvent (and solute-solute at higher concentrations) interactions and the solute-adsorbent interactions. These in turn depend on such factors as the adsorption sites on the surface and the structure of the adsorbed molecule. It is not enough to know that clays interact strongly with water (hydrophilic) to predict that organic species which are sparingly soluble in water will not adsorb strongly on clays from aqueous (or any other) solutions. Where water competes for adsorption sites, the net energy difference between the adsorbed and dissolved states of the adsorbate, as compared with the net energy difference between the water-water interactions and water-surface interactions (as well as steric or entropy considerations), will determine the extent of adsorption. The complexity of the interaction of many organic molecules with the solvent and even more so with the surfaces precludes general predictions regarding the relative strength of the relevant interactions.

The myriad of surface interactions which are possible between organic substances and surfaces was reviewed by Mortland (1970). A case in point is the adsorption of parathion by the various homoionic attapulgites. The order of adsorption is HDMA⁺ > Ca²⁺ > TMA⁺, while the expected order for increasing "organophilic nature" is Ca²⁺ < TMA⁺ ≤ HDMA⁺. It is clear that there is no obvious correlation between the organophilic nature of the clay and the extent of parathion adsorption. In this particular case the greater adsorption by the Ca²⁺-clay, as compared to the TMA⁺-clay, might result from specific interactions of the phosphate moiety of parathion with the Ca²⁺. The fact that the adsorption on the Ca²⁺-clay is intermediate between the TMA⁺-clay and HDMA⁺-clay once again demonstrates

that the extent of the surface's organophilic nature is not enough to predict the extent of adsorption. Thus, the classification of surfaces as hydrophilic or organophilic is not sufficient to predict the adsorption of organic compounds (such as pesticides) on many surfaces (such as clays).

Where a true apolar or polar phase occurs at the surface, predictions can be made regarding adsorption of organic adsorbates. Such a situation occurred, for example, when parathion was adsorbed on soils equilibrated with 98% relative humidity from hexane. While drier soils strongly adsorbed parathion, this wet soil adsorbed very little (Yaron and Saltsman, 1972). The surface was coated with a water layer of sufficient thickness to form an aqueous phase with the parathion partitioning almost exclusively in the organic (hexane) phase. In addition, the adsorption of parathion from water on HDMA⁺-attapulgite (Figure 6) was much greater than with inorganic exchangeable cations (Ca²⁺ and Na⁺). In the case of HDMA, as opposed to the aforementioned TMA, the apolar tail of the organic ion is long enough to form a true apolar phase into which parathion may partition from the aqueous solution.

Several authors have already pointed out the importance of specific interactions in the systems studied (e.g., Mortland, 1970). The present work suggests that the general terms "organophilic" and "hydrophilic" are often not sufficient for predicting specific organic molecule-surface interactions.

CONCLUSIONS

The use of the reduced concentration concept, as well as the terms organophilic and hydrophilic as they have been applied to the adsorption of organic molecules, is not universally justified. In some cases, which have to be verified, the reduced concentration can be used to extrapolate (or interpolate) the temperature dependence of the adsorption isotherm. Similarly, in some systems the interface constitutes a true polar or apolar phase. In such cases the solubility of the organic molecule in water as compared to its solubility in apolar media can be used to predict its adsorption.

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Резюме—Результаты изучения адсорбции нескольких пестицидов в почвах и глинах показывают, что уменьшение их концентрации при адсорбции может привести или к уменьшению температурного эффекта на изотермы, исключить его полностью (напр., адсорбция паратиона в почве Нетания), увеличить зависимость от температуры (напр., адсорбция β -гексахлорбензола Са-бентонитом) или даже изменить температурную зависимость изотерм на противоположную (напр., адсорбция паратиона Са-аттапуллитом). Литературные и экспериментальные данные по адсорбции паратиона Са-аттапуллитом и аттапуллитом с органическими обменными катионами различных размеров показывают, что для многих поверхностных взаимодействий термины “органофилитовый” и “гидрофилитовый” могут вводить в заблуждение. Органические соединения, нерастворимые в воде и растворимые в неполярных растворителях необязательно будут адсорбироваться преимущественно “органофилитовыми” поверхностями. Специфические взаимодействия между адсорбатом и адсорбентом и пространственные особенности (в дополнение к относительной растворимости органических молекул в воде и неполярных растворителях и в дополнение к органофилитовой или гидрофилитовой природе поверхности) определяют отделение адсорбированной и растворенной фаз. Замечательным примером является порядок адсорбции паратиона аттапуллитом: HDMA-аттапуллит > Са-аттапуллит > TMA-аттапуллит. Этот порядок ни прямым ни обратным образом не относится к органофилитовой природе поверхностей.

Resümee—Resultate von Untersuchungen der Adsorption verschiedener Pflanzenschutzmittel auf Erden und Ton zeigt, daß die Anwendung des Konzepts der reduzierten Konzentration auf Adsorption entweder den Effekt der Temperatur auf die Isothermen reduzieren kann, ihn völlig eliminieren kann (z.B., Adsorption von Parathion auf Netanya-Erden), die Abhängigkeit von der Temperatur zunehmen kann (z.B., β -BHC Adsorption auf Ca-Bentonit) oder sogar die Temperaturabhängigkeit der Isothermen umkehren kann (z.B., Parathion Adsorption auf Ca-Attapulgit).

Daten aus der Literatur und von Experimenten für die Parathionadsorption von Ca-Attapulgit und von Attapulgit mit organischen austauschbaren Kationen verschiedener Größen demonstrieren, daß für viele Wechselwirkungen an der Oberfläche, die Bezeichnungen organophil und hydrophil irreführend sind. Organische Verbindungen, welche wasserunlöslich sind und in nicht-polaren Lösungsmitteln löslich sind, werden nicht unbedingt vorzugsweise auf “organophilen” Oberflächen adsorbiert. Die spezifischen Wechselwirkungen zwischen Adsorbat und Adsorbens und sterische Erwägungen (außer der relativen Löslichkeit des organischen Moleküls in Wasser und nicht-polaren Lösungsmitteln und die organophile oder hydrophile Natur der Oberfläche) wird die Verteilung zwischen der Adsorbierten- und der Lösungsphase bestimmen. Ein ausgezeichnetes Beispiel ist die Reihenfolge von Parathionadsorption auf Attapulgit: HDMA-Attapulgit > Ca-Attapulgit > TMA-Attapulgit. Diese Reihenfolge ist weder direkt noch umgekehrt verbunden mit der organophilen Natur der Oberfläche.

Résumé—Les résultats d'études sur l'adsorption de plusieurs pesticides sur des sols et des argiles montrent que l'application de la conception de concentration réduite à l'adsorption peut soit réduire l'effet de la température sur les isothermes, soit l'éliminer complètement (adsorption de parathion sur un sol Netanya), soit accroître la dépendance de la température (adsorption β -BHC sur la bentonite-Ca), soit même renverser la dépendance de température des isothermes (adsorption de parathion sur l'attapulgit-Ca). La littérature et les données expérimentales concernant l'adsorption de parathion par l'attapulgit-Ca et par l'attapulgit ayant des cations organiques échangeables de tailles différentes démontrent que pour beaucoup d'interactions superficielles, les termes organophiles ou hydrophiles peuvent induire en erreur. Des composés organiques insolubles dans l'eau et solubles dans des solvants apolaires n'adsorberont pas nécessairement de préférence sur des surfaces “organophiles.” Les interactions spécifiques entre l'adsorbé et l'adsorbant et les considérations stériques (ajouté à la solubilité relative de la molécule organique dans l'eau et dans les solvants apolaires et la nature organophile ou hydrophile de la surface) détermineront la partition entre la phase adsorbée et la phase de solution. Un exemple excellent est l'ordre d'adsorption de parathion sur l'attapulgit: HDMA-attapulgit > Ca-attapulgit > TMA-attapulgit. Cet ordre n'est ni directement ni inversement apparenté à la nature “organophile” des surfaces.