A NOTE ON THE ADSORPTION OF ORGANIC MOLECULES ON CLAYS

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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. Ca²⁺, 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-C¹⁴] parathion (Radiochemicals Ltd., Amersham) was used and determined in a Packard Model 3003 Tri-Carb Scintillation 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 the solute concentration, the reduced concentration isotherms can be plotted against the reduced concentration, as described previously. The temperature dependence of \( C_0 \) can be described as follows:

\[
\frac{d \ln C_0}{d [1/T]} = - \frac{\Delta H_{\text{dis}}}{R}
\]

where \( R \) is the gas constant and \( \Delta H_{\text{dis}} \) is the enthalpy of dissolution.

\[
\Delta H_{\text{dis}} = H_c - H_{\text{sol}}
\]

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

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

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

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

$$\Delta H_{ads} = H_{sol} - H_{s}$$  \hspace{1cm} (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 $\Delta H_{ads}$ 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 $C_{o}$, and hence the concept of reduced concentration lacks theoretical support.

In general, $C_{o}$ 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 1. Reduced (a) and normal (b) adsorption isotherms of parathion from water on a Netanya soil (reproduced from Yaron and Saltzman, 1972).

Figure 2. Reduced (a) and normal (b) adsorption isotherms of $\gamma$-BHC from hexane on Ca-staten peaty muck (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 $H_s \equiv H_o$ or $H_c$ and $H_s$ are small as compared to $H_{ad}$. The latter possibility does not apply to sparingly soluble compounds. The data demonstrate that the concept of reduced concentration 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-
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 organo-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-
ganophosphate ester. Finally, adsorption of parathion on TMA\textsuperscript{+}-attapulgite was less than on Ca\textsuperscript{2+}-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\textsuperscript{+}-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\textsuperscript{+} > Ca\textsuperscript{2+} > TMA\textsuperscript{+}, while the expected order for increasing "organophilic nature" is Ca\textsuperscript{2+} < TMA\textsuperscript{+} < HDMA\textsuperscript{+}. 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 Ca\textsuperscript{2+}-clay, as compared to the TMA\textsuperscript{+}-clay, might result from specific interactions of the phosphate moiety of parathion with the Ca\textsuperscript{2+}. The fact that the adsorption on the Ca\textsuperscript{2+}-clay is intermediate between the TMA\textsuperscript{+}-clay and HDMA\textsuperscript{+}-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 Saltzman, 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\textsuperscript{+}-attapulgite (Figure 6) was much greater than with inorganic exchangeable cations (Ca\textsuperscript{2+} and Na\textsuperscript{+}). In the case of HDMA\textsuperscript{+}, as opposed to the aforementioned TMA\textsuperscript{+}, 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.

**REFERENCES**


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Resumé—Results of the adsorption of several pesticides on soils and clays in aqueous and hexane solutions show that the concentration of substances which adsorb or form complexes with soil components is a function of the nature of the soil-clay material, the nature of the substance adsorbed, and the temperature. The results of the adsorption of several pesticides on clays show that the nature of the clay affects the adsorption of the pesticides. The temperature at which the adsorption takes place also affects the adsorption.