# Nature of Bonding in Montmorillonite Adsorbates II: Bonding as an Ion–Dipole Interaction

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**Abstract** ☐ In connection with previous work regarding benzoic acid adsorption on montmorillonite, isotherms of diazepam in several anhydrous solvents and of various benzodiazepine derivatives in one solvent support the concepts that montmorillonite adsorbates of compounds which do not ionize in solution are surface adsorbates and that the bonding occurs *via* an ion–dipole interaction. The number of sites found from liquid adsorption fairly well matches that found by nitrogen adsorption.

**Keyphrases** ☐ Montmorillonite, adsorbates—bonding as an ion–dipole interaction, diazepam isotherms determined, equations ☐ Adsorption, organic compounds on montmorillonite—surface adsorption mediated by ion–dipole interaction, diazepam isotherms determined ☐ Diazepam—isotherms determined, nature of montmorillonite binding, surface adsorption and ion–dipole interaction suggested, equations ☐ Adsorbates, montmorillonite—nature of bonding, ion–dipole interaction hypothesized ☐ Surface adsorption—montmorillonite-diazepam bonding, ion–dipole interaction hypothesized

The problem of the sites at which organic solutes adhere to montmorillonite was discussed in an earlier publication (1); it was shown that benzoic acid adsorbs onto the surface (and does not penetrate the crystal lattice of the clay) and that the number of sites on the surface for such adsorption was of the order of $10^{19}$–$10^{20}$ per gram of montmorillonite. With this knowledge, it is possible to study further the *nature* of the interaction. Whenever isotherms adhere to Langmuir equations and give a number of sites of the quoted order, it may be assumed that adsorption is on the surface and not by intercalation. Only surface adsorption has, so far, been encountered.

Due to the biological availability of montmorillonite adsorbates, it is unlikely that the adsorbates are formed by chemisorption; on the other hand, mere physical adsorption would not account for the loss of taste associated with the formation of many montmorillonite adsorbates (2). The purpose of this study was to investigate the nature of the bonding exhibited by montmorillonite surfaces on organic solutes when adsorbates are formed.

## EXPERIMENTAL AND RESULTS

As in the previous study (1), a micronized grade of the hydrogen form of montmorillonite was used[1]; the clay was dehydrated by exposure to high vacuum ($<0.1$ $\mu$) for 1 week. Surface areas of the montmorillonite were determined by B.E.T. (Brunauer, Emmett, and Teller) measurements on a high vacuum setup with a multiple-volume gauge (McLeod). Isotherms were determined both at liquid nitrogen and at acetone–dry ice temperatures. Both adsorption and desorption branches of the isotherm were determined and showed no significant difference (*i.e.*, the porosity was negligible).

The nitrogen isotherm is shown in Fig. 1. The surface area determined in this fashion was 75 m.$^2$/g.

For a large portion of the study, diazepam was the solute; the diazepam[2] was used as received from the supplier. Solvents were all reagent grade. Adsorption isotherms of diazepam from the following solvents (all with dielectric constants of less than 20) were determined: isopropyl alcohol, *n*-propyl alcohol, isoamyl alcohol, *n*-amyl alcohol, isobutyl alcohol, *tert*-butyl alcohol, and dichloroethane. These all produced Langmuir isotherms; that is, when the reciprocal ($1/n$) of the number of molecules of diazepam adsorbed per gram of montmorillonite was plotted as the ordinate and the reciprocal ($1/C$) of the equilibrium concentration (molarity) of diazepam in solution was plotted as the abscissa, linear plots resulted. This result is in accord with Eq. 3 of *Reference 1*:

$$\frac{1}{n} = \frac{1}{N} + \frac{1}{K \cdot N} \cdot \frac{1}{C} \qquad \text{(Eq. 1)}$$

where $N$ is the number of available sites, and $K$ is the equilibrium constant for the adsorption (*i.e.*, the ratio, $k_+/k_-$, between adsorption and desorption rate constants). The number of sites per gram of montmorillonite, $N$, is obtained from the intercepts of the plots; $K$ ($M^{-1}$) is obtained from the intercept–slope ratios. Linearity should prevail (1) when $K \cdot C > 1$.

The data concerning adsorption of diazepam on montmorillonite from the quoted solvents are exemplified in Fig. 2. Adsorption isotherms were also determined from the following solvents (with dielectric constants higher than 25): methyl alcohol, ethyl alcohol,
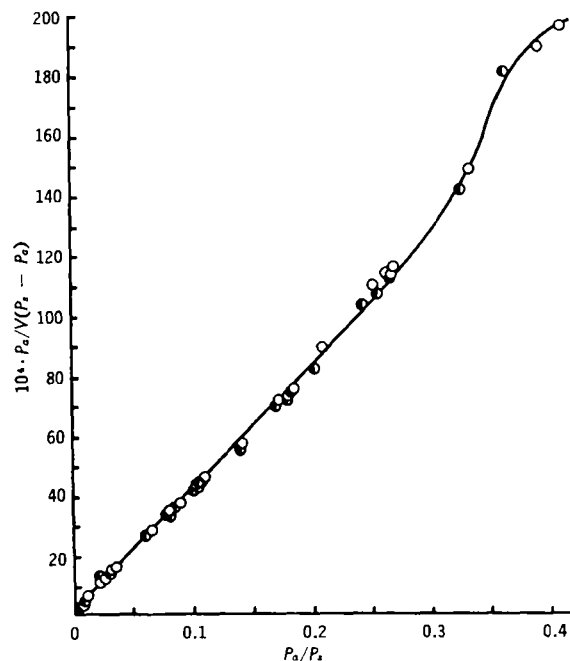


**Figure 1**—*Brunauer, Emmett, and Teller nitrogen isotherm of montmorillonite (1.436-g. sample). Key: O, adsorption points; and ●, desorption points.*
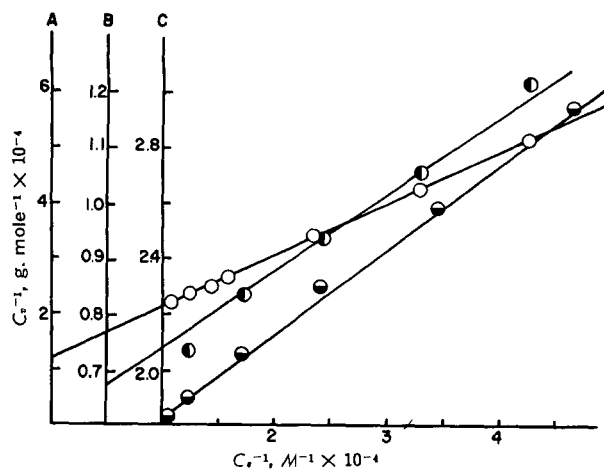
**Figure 2**—*Isotherms of diazepam from various solvents. Key: A (O), isopropyl alcohol; B (◐), dichloroethane; and C (◓), tert-butyl alcohol.*

and acetonitrile. Linear isotherms are here achieved when adjustment for solvent intercalation is made (3).

The dielectric constants of the solvents were determined by means of an oscillometer[3]. All the parameters mentioned (the dielectric constant, the adsorption equilibrium constants, and the number of sites) are listed in Table I. Adsorption isotherms were performed of a series of benzodiazepines[1,4] in isopropanol, and these all adhered to Langmuir isotherms. The compounds tested are listed in Table II.

Dipole moments were determined by the method of Guggenheim (4) and Hill *et al.* (5); in this case, dielectric constants were determined by a heterodyne-beat setup[5] and refractive indexes were determined by a refractometer[6] (6). The dipole moments are listed in Table II.

### DISCUSSION

In investigating the adsorption of various solutes on montmorillonite, it became clear at an early point in the investigation that, as a trend, the smaller the dielectric constant, the stronger was the adsorption from anhydrous solvents. The higher the dielectric constant of a solvent, the larger was the extent of *its* intercalation (7, 8). This finding, in combination with the benzoic acid studies reported earlier (1), confines considerations to adsorption to the surface of the montmorillonite.

The general trend indicates that forces of electrical nature are significant. To investigate this trend, a series of compounds of the general structure given in Table II was selected. These benzodiazepines are not ionized in solution, thus eliminating the possibility of ion exchange being a mode of adsorption. The compounds, however, possess dipole moments; and if the forces involved in the adsorption are electrical forces between surface ions and the solute dipoles, then forces can be formulated mathematically and the pertinent relations tested experimentally.

If it is assumed that the interaction is between a dipole consisting of two fundamental electrical charges, $e$, removed from one another a distance $2 \cdot d$ (*i.e.*, having a dipole moment of $2 \cdot e \cdot d$) and a surface ion with $Z$ charges (*i.e.*, $-2$ for a doubly negatively charged oxygen), then at a distance $x$ between dipole and ion, the force exerted would be:

$$f_c = -\left( \frac{Z \cdot e^2}{(x - d)^2} - \frac{Z \cdot e^2}{(x + d)^2} \right) \cdot \frac{1}{\epsilon} \qquad \text{(Eq. 2)}$$

Repulsions are counted as being negative and attractions as being positive; $\epsilon$ is here the dielectric constant of the medium between ion

[3] Sargent-Welsh oscillometer, model V, E. H. Sargent and Co., Chicago, Ill.
[4] Oxazepam was supplied by Wyeth Laboratories, Inc., Radnor, Pa.
[5] The authors are indebted to Dr. W. E. Vaughan, Department of Chemistry, University of Wisconsin, for valuable aid in this phase of the study.
[6] Abbe refractometer, W. H. Kessel and Co. Scientific Instruments, Chicago, Ill.

**Table I**—Dielectric Constants, Equilibrium Constants ($K = k_+/k_-$) of Diazepam Isotherms, and Number of Sites ($N$) on Montmorillonite for Various Solvents

| Solvent | Dielectric Constant | log $K$ | Number of Sites |
|---|---|---|---|
| Acetonitrile | 36.2 | 2.86 | $6 \cdot 10^{19}$ |
| Methyl alcohol | 30.3 | 2.46 | $4 \cdot 10^{19}$ |
| Ethyl alcohol | 28.7 | 3.18 | $1 \cdot 10^{19}$ |
| *n*-Propyl alcohol | 19.4 | 3.27 | $6 \cdot 10^{19}$ |
| Isobutyl alcohol | 17.5 | 4.01 | $7 \cdot 10^{19}$ |
| Isoamyl alcohol | 15.8 | 3.95 | $8 \cdot 10^{19}$ |
| *n*-Amyl alcohol | 15.0 | 3.97 | $8 \cdot 10^{19}$ |
| Isopropyl alcohol | 13.4 | 4.10 | $5 \cdot 10^{19}$ |
| Dichloroethane | 9.32 | 4.65 | $9 \cdot 10^{19}$ |
| *tert*-Butyl alcohol | 8.42 | 4.70 | $4 \cdot 10^{19}$ |
| | | Average | $5.8 \cdot 10^{19}$ |
| | | Standard deviation | $2.4 \cdot 10^{19}$ |

and dipole. This preliminary model assumes that only one ion and dipole interact. More realistic corrections will be introduced shortly. It should be noted that $Z$ is probably more than $-2$ (of smaller absolute value) for the montmorillonite surface oxygens since: (*a*) part of their charge is diverted by cations in the crystal interior, and (*b*) $-2$ is not the effective charge in any event, because it only represents one of the resonance forms of the silicate moiety in montmorillonite (9).

When adsorbed, the dipole is at an equilibrium distance $r$ from the surface ion, so that the energy involved is:

$$E = -\frac{Z \cdot e^2}{\epsilon} \cdot \int_\infty^r \left( \frac{1}{(x - d)^2} - \frac{1}{(x + d)^2} \right) \cdot dx = \frac{Z \cdot 2 \cdot d \cdot e^2}{\epsilon \cdot (r^2 - d^2)}$$

$$\text{(Eq. 3)}$$

When $d \ll r$, this reduces to:

$$E = \frac{Z \cdot e \cdot \mu}{\epsilon \cdot r^2} \qquad \text{(Eq. 4)}$$

where $\mu$ is the dipole moment of the dipole. Up to this point, the development partly follows the treatment by Amis (10). As mentioned, the picture is oversimplified since it accounts for only the interaction of the dipole with one surface ion (the nearest surface ion; referred to as the contact ion in the following). A further complication is the fact that the cross-sectional area of diazepam (about 25 $\text{Å}^2$) is too large to allow a 1:1 relationship between ion and dipole.

To take these factors into account, consider the geometries of Fig. 3. This model is essentially Schofield's (11); the oxygens are in a hexagonal array and 4 Å apart. Each oxygen has three nearest neighbors (denoted B) at 4 Å distance, six next-nearest neighbors (denoted C) at $4 \cdot \sqrt{3} = 7$ Å distance, and three third-nearest

**Table II**—Derivatives of Benzodiazepine Tested



| X | R | R' | R" | Dipole Moment (D) | Number of Sites[a] | log $K$ | Molecular Weight |
|---|---|---|---|---|---|---|---|
| Cl | CH$_3$ | — | C$_6$H$_5$ | 3.45 | $5 \cdot 10^{19}$ | 4.097 | 285 |
| Cl | H | O | C$_6$H$_5$ | 4.70 | $9 \cdot 10^{19}$ | 5.068 | 287 |
| Br | H | — | *o*-C$_5$H$_4$N | 3.15 | $7 \cdot 10^{19}$ | 4.233 | 316 |
| NO$_2$ | H | — | C$_6$H$_5$ | 2.02 | $9 \cdot 10^{19}$ | 3.187 | 281 |
| NO$_2$ | CH$_3$ | — | *o*-C$_6$H$_4$F | 1.26 | $8 \cdot 10^{19}$ | 3.067 | 312 |
| NO$_2$ | H | — | *o*-C$_6$H$_4$Cl | 2.57 | $8 \cdot 10^{19}$ | 3.465 | 316 |
| Cl[b] | H | — | C$_6$H$_5$ | 3.98 | $9 \cdot 10^{19}$ | 4.871 | 287 |

[a] Average of these figures is $7.8 \cdot 10^{19}$, with a standard deviation of $1.5 \cdot 10^{19}$. [b] Oxazepam, having a hydroxyl group at position 3.
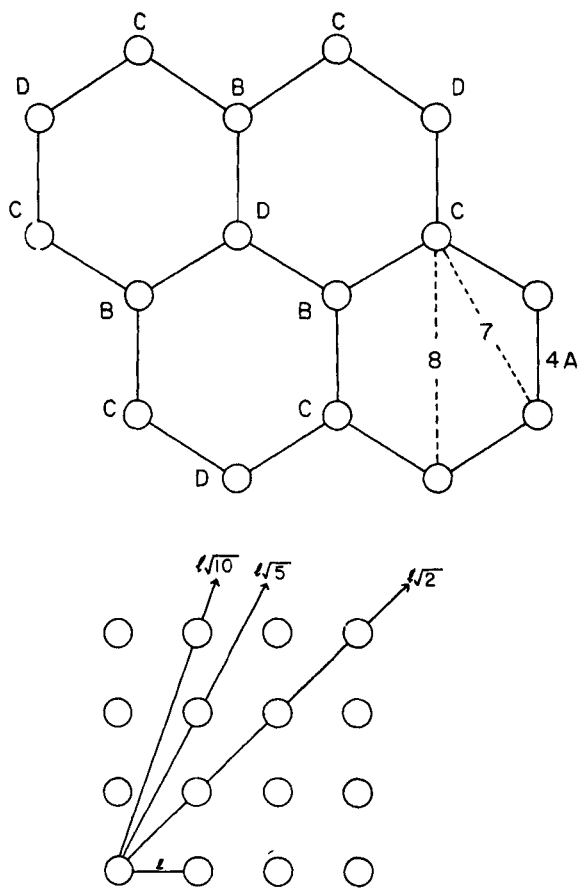
**Figure 3**—*Arrangements of surface oxygens in montmorillonite. The oxygen ions lie in almost perfect hexagonal array. By taking the midpoints of each pair (e.g., of the type DC and CB of the hexagon in the upper left corner), a quadratic array will result as shown in the lower part of the figure. This corresponds to the physical situation, since one molecule of adsorbing molecule occupies more space than one oxygen ion in the surface.*

neighbors (denoted D) at 8 Å distance. As mentioned, a 1:1 relationship between oxygen ion and organic solute dipole is not to be expected. The smallest area inscribed by four oxygens (BCCD) is 13.8 Å$^2$ and the largest (DBDC) is 27.7 Å$^2$, so that both benzoic acid (1) and diazepam could fit into this picture in spite of the disparity in cross section. Both benzoic acid (Table I of *Reference 1*) and the benzodiazepine derivatives (Tables I and II) give numbers of sites of comparable magnitude (of the order of $10^{19}$ sites/g.).

It is, hence, more rational to assume that the "sites" are in a quadratic array (e.g., located at the positions between B and D) 7–8 Å apart. In this visualization, there are arrays of the crystal surface where the distance between each surface ion is the minimum dictated by the lattice—viz., $l$ (8 Å) as shown in Fig. 3. Then there are arrays where ions are $l \cdot \sqrt{2}, l \cdot \sqrt{5}, l \cdot \sqrt{10}, \ldots, l \cdot \sqrt{m^2 + i^2}$ apart. In each array, except for $i = 0$ and $i = 1$, there are eight surface ions (N) at the same distance from the dipole. For $i = 0$ (Point A in Fig. 4), there is one and for $i = 1$, there are four surface ions (N) at a distance $b$ from A, a distance $c$ from P, and a distance $f$ from Q, where P and Q are the end-points of the dipole.

Depending on the array, $b$ will be a multiple of $l$ by $n \cdot \sqrt{m^2 + i^2}$ ($n = 1, 2, \ldots, m = 1, 2, \ldots,$ and $i = 0, 1, \ldots$). The force exerted by the four ions on the dipole has a resultant which is perpendicularly downward and of the magnitude:

$$f_b{}' = -\frac{4}{\epsilon} Z \cdot e^2 \cdot \left( \frac{(x-d)}{[b^2 + (x-d)^2]^{1.5}} - \frac{(x+d)}{[b^2 + (x+d)^2]^{1.5}} \right)$$

(Eq. 5)

The forces between N and P and between N and Q, of magnitude $Z \cdot e^2/\epsilon \cdot [b^2 + (x - d)^2]$ and $Z \cdot e^2/\epsilon \cdot [b^2 + (x + d)^2]$, respectively,
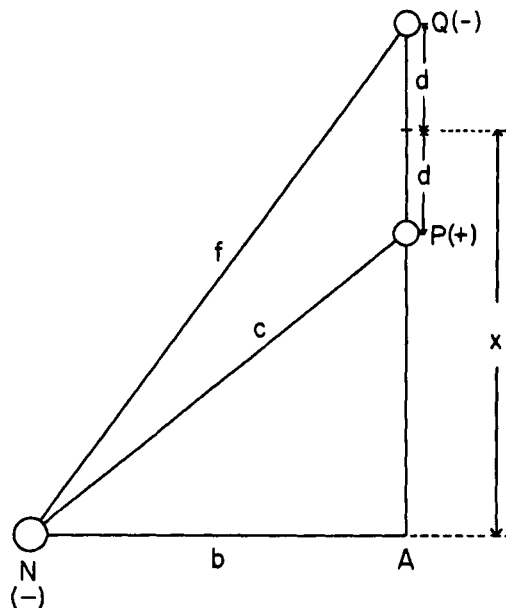


$$f^2 = b^2 + (x + d)^2$$

$$c^2 = b^2 + (x - d)^2$$

$$COS(AQN) = (x + d)/f$$

$$COS(APN) = (x - d)/c$$

**Figure 4**—*Force arrangement in an ion–dipole interaction as discussed in the text. Key: QP is the dipole, A is the closest oxygen ion, and N is another oxygen ion; A is removed from N by a distance b which is a multiple of l by a factor of $n \cdot \sqrt{m^2 + i^2}$, where n, m, and i are integers (Fig. 3).*

have been multiplied by the cosines of the angles APN and AQN {i.e., $(x - d)/[b^2 + (x - d)^2]^{0.5}$ and $(x + d)/[b^2 + (x + d)^2]^{0.5}$} to project them on the vertical axis APQ. Attractions, again, are counted as positive (i.e., Z negative) and repulsions negative. The factor 4 in Eq. 5 reflects that there are four points N for each value of $b$.

If the dipole is moved a distance $dx$, then the work done is $f_b{}' \cdot dx$, so that the energy of one dipole as a result of its interaction with the four surface ions at a distance $b$ from the contact ion is:

$$E' = -\frac{4}{\epsilon} Z \cdot e^2 \cdot \int_{\infty}^{r} \left( \frac{(x-d)}{[b^2 + (x-d)^2]^{1.5}} - \frac{(x+d)}{[b^2 + (x+d)^2]^{1.5}} \right) \cdot$$

$$dx = \frac{4}{\epsilon} Z \cdot e^2 \cdot \{[b^2 + (r - d)^2]^{-0.5} - [b^2 + (r + d)^2]^{-0.5}\} \quad \text{(Eq. 6)}$$

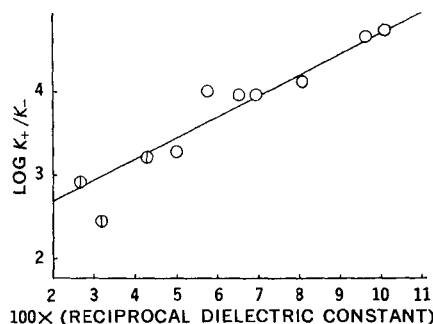If the term $b^2 + r^2 + d^2$ is denoted $a^2$ and if it is assumed that



**Figure 5**—*Plot of the logarithm of the equilibrium constant as a function of the reciprocal of the dielectric constant of the solvent. For the crosshatched circles, adjustment was made according to Carstensen and Su (3).*

**Table III—Estimation of Best $q$ Value in Eq. 17**

| log $K_\infty$ | $q$ Value from Slope | $q$ Value from Intercept | Average $q$ | Average $Z \cdot \alpha / r^2$ |
|---|---|---|---|---|
| 1.0 | −0.14 | −0.025 | −0.082 | $0.50 \cdot 10^{15}$ |
| 1.5 | −0.11 | −0.025 | −0.068 | $0.54 \cdot 10^{15}$ |
| 2.0 | +0.027 | +0.056 | +0.042 | $0.81 \cdot 10^{15}$ |
| 2.5 | +0.33 | +0.29 | +0.31 | $1.45 \cdot 10^{15}$ |
| 3.0 | +0.45 | +0.24 | +0.38 | $1.16 \cdot 10^{15}$ |

$2 \cdot r \cdot d$ is small compared to $a^2$, Eq. 6 may be simplified to:

$$E' = \frac{4 \cdot r \cdot Z \cdot \mu \cdot e}{\epsilon \cdot a^3} \qquad \text{(Eq. 7)}$$

If, furthermore, $b^2 + r^2 \gg d^2$, then Eq. 7 may be written:

$$E' = \frac{4 \cdot Z \cdot \mu \cdot e \cdot r}{\epsilon \cdot [b^2 + r^2]^{1.5}} \qquad \text{(Eq. 8)}$$

It was noted that $b = n \cdot l \cdot \sqrt{m^2 + i^2}$. Since $l$ can be expressed as some multiple of $r$, i.e., $l = \beta \cdot r$, one may write $b = n \cdot \beta \cdot r \cdot \sqrt{m^2 + i^2}$ and:

$$E' = \frac{4 \cdot Z \cdot \mu \cdot e}{\epsilon \cdot r^2} \cdot [1 + \beta^2 \cdot n^2 (m^2 + i^2)]^{-1.5} \qquad \text{(Eq. 9)}$$

The total energy then is:

$$E = \frac{Z \cdot \mu \cdot e}{\epsilon \cdot r^2} \cdot \left( 1 + 4 \cdot \sum_{n=1}^{\infty} [1 + \beta^2 n^2]^{-1.5} + \right.$$
$$\left. 8 \cdot \sum_{i=1}^{\infty} \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} [1 + \beta^2 n^2 (m^2 + i^2)]^{-1.5} \right) \qquad \text{(Eq. 10)}$$

The quantity in brackets converges; for the sake of convenience it is denoted $\alpha$ in the following, so that the energy expression becomes:

$$E = \frac{Z \cdot \mu \cdot \alpha \cdot e}{r^2} \cdot \frac{1}{\epsilon} \qquad \text{(Eq. 11)}$$

The assumptions made to this point affect only the value of $\alpha$ and not the expression in Eq. 11 as a whole. The $\alpha$ converges rapidly with $i$ and $m$ and less rapidly with $n$; the value, assuming $\beta = 1$ and truncating at $n = 10$, $m = 2$, and $i = 3$, is $\alpha = 8.0$.

When adsorption conditions are at equilibrium at one particular temperature $T$, then the equilibrium constant $K$ ($= k_+/k_-$) is related to Gibbs energy by $G = -k \cdot T \cdot \ln K$, where $k$ is Boltzmann's constant. Assuming $TS$ and $PV$ terms to be negligible and inserting in Eq. 11 give:

$$-k \cdot T \cdot \ln K = \frac{Z \cdot \mu \cdot \alpha \cdot e}{r^2} \cdot \frac{1}{\epsilon} \qquad \text{(Eq. 12)}$$

where $r$ is the equilibrium distance at temperature $T$. At small values of $\mu$, $TS$ terms cannot be expected to be small compared to the electrical terms and Eq. 12 should hold in a limited $\mu$-range only.

At any one temperature, this may be written:

$$\log K = \log K_\infty - \frac{Z \cdot \alpha \cdot \mu \cdot e}{2.3 \cdot k \cdot T \cdot r^2} \cdot \frac{1}{\epsilon} \qquad \text{(Eq. 13)}$$

i.e., with positive slope ($Z < 0$). Here, $K_\infty$ is the constant at temperature $T$ in a medium with infinitely large dielectric constant. Since the term $K_\infty$ is not temperature independent, it is not possible to test Eq. 13 by testing $K$ at various temperatures. There are, however, means by which the expression can be tested. The data in Table I can be plotted as log $K$ versus $1/\epsilon$, as in Fig. 5. It is noted that good linearity results, and via Eq. 13, the slope and intercept give the values: $Z \cdot \alpha / r^2 = -1.44 \cdot 10^{15}$ and log $K_\infty = 2.156$ at 25°.

Equation 13 may be rewritten:

$$\log K = \log K_\infty - \frac{\alpha \cdot Z \cdot e}{2.3 \cdot k \cdot T \cdot \epsilon \cdot r^2} \cdot \mu \qquad \text{(Eq. 14)}$$

so that if several substances of varying dipole moment were tested in one solvent, the plot should be linear in $\mu$. The fallacy in this
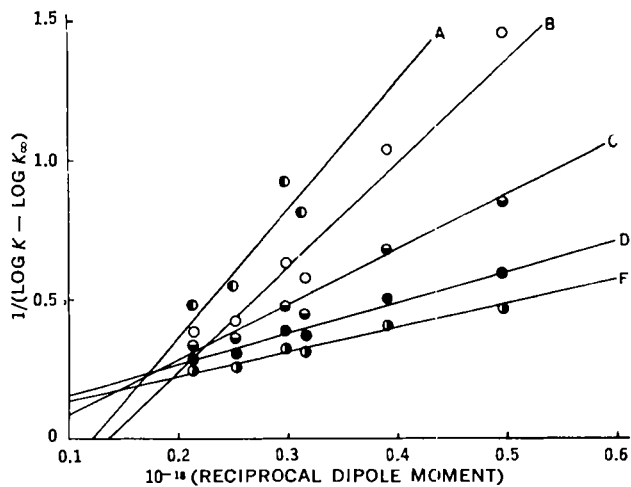


**Figure 6**—*Plot of the reciprocal of* [*log* K − *log* $K_\infty$] *versus the reciprocal of the dipole moment of the solute for various estimates of* $K_\infty$. *Key: A* (⊙), *log* $K_\infty$ = 3.0; B (○), *log* $K_\infty$ = 2.5; C (◓), *log* $K_\infty$ = 2.0; D (●), *log* $K_\infty$ = 1.5; *and E* (◑), *log* $K_\infty$ = 1.0.

argument is that $r$ (and maybe also $Z$) may differ from compound to compound. If compounds of similar geometry were selected (as is the case here), $Z$ (which depends on the number of oxygen molecules "occupied" by one solute molecule) would be the same, but equilibrium distances, $r$, would still be prone to differ from compound to compound. Whether $r$ would increase or decrease with increasing dipole moment is not obvious a priori, since the increase in dipole moment from member to member in a pseudo-homologous series could be due to either an increase in charge at the dipole heads or an increase in distance between the heads. If the equilibrium distance for diazepam is used as a reference standard, then the relation:

$$r^2 = r_0^2 \cdot [1 - q \cdot (\mu - \mu_0)] \qquad \text{(Eq. 15)}$$

would qualitatively describe this change in $r$ with dipole moment. Here, $r_0$ is the equilibrium distance for diazepam. Denoting by $\mu'$ the dipole moment in debyes and inserting the value $\mu_0' = 3.45$ for diazepam allow Eq. 14 to be rewritten:

$$\log K - \log K_\infty = -\frac{Z \cdot \alpha \cdot e \cdot 10^{-18}}{2.3 \cdot k \cdot T \cdot \epsilon \cdot r_0^2} \cdot$$
$$\left( \frac{\mu'}{(1 - q' \cdot [\mu' - 3.45])} \right) \qquad \text{(Eq. 16)}$$

where $q'$ is in $D^{-1}$ (as opposed to $q$ which is in cm.$^{-1}$ e.s.u.$^{-1}$). It is easier to treat the reciprocal of Eq. 16:

$$\frac{1}{\log K - \log K_\infty} = -\frac{2.3 \cdot k \cdot T \cdot \epsilon \cdot r_0^2 \cdot 10^{18}}{Z \cdot \alpha \cdot e} \cdot$$
$$\left( \frac{1 + 3.45 \cdot q'}{\mu'} - q' \right) \qquad \text{(Eq. 17)}$$

Values of log $K_\infty$ and $Z \cdot \alpha / r_0^2$ were estimated at an earlier point from Fig. 5. If it is assumed that $Z \cdot \alpha / r_0^2 = -1.44 \cdot 10^{15}$, then the coefficient to the parentheses on the right-hand side of Eq. 17 becomes 1.784 and various values for log $K_\infty$ can be tested in this equation. Since both the slope and the intercept give a value for $q'$,

**Table IV—Values of** $r / \sqrt{(-Z)}$ **and** $l / \sqrt{(-Z)}$ **for Various Values of** $\beta^a$

| $\beta$ | $\alpha$ | $r / \sqrt{(-Z)} = [\alpha / 1.45 \cdot 10^{15}]^{0.5}$ | $l / \sqrt{(-Z)}$ $\beta \cdot [\alpha / 1.45 \cdot 10^{15}]^{0.5}$ |
|---|---|---|---|
| 0.7 | 11.9 | $9.1 \cdot 10^{-8}$ | $6.3 \cdot 10^{-8}$ |
| 0.8 | 10.3 | $8.5 \cdot 10^{-8}$ | $6.8 \cdot 10^{-8}$ |
| 1.0 | 8.0 | $7.4 \cdot 10^{-8}$ | $7.4 \cdot 10^{-8}$ |
| 1.4 | 5.8 | $6.3 \cdot 10^{-8}$ | $8.9 \cdot 10^{-8}$ |

$a$ $(-Z)$ is positive.

the value of log $K_\infty$ that gives the best consistency between the two $q'$ values yields the best fit. Plots of $1/[\log K - \log K_\infty]$ versus $1/\mu'$ are shown in Fig. 6. The corresponding $q'$ values are shown in Table III. It is noted from the table that log $K_\infty = 2.5$ inserted in Eq. 17 in the form $(Z \cdot \alpha/r^2 = -1.44 \cdot 10^{15})$:

$$\frac{1}{\log K - \log K_\infty} = 1.784 \cdot \frac{1 + 3.45 \cdot q'}{\mu'} - 1.784 \cdot q' \quad \text{(Eq. 18)}$$

gives a value of $q'$ of 0.33 from the slope and 0.29 from the intercept, so that for this value of $K_\infty$ there is good consistency. By evaluating the data by least-squares fit via Eq. 17, the slope is 3.75 when log $K_\infty = 2.5$, which, with a $q'$ value of 0.31, yields a value for $Z \cdot \alpha/r_0^2$ of $-1.45 \cdot 10^{15}$, so that this (recycled) value is in good agreement with the originally assumed value.

With the assumption that one molecule of benzodiazepine occupies the area of two oxygens, there would be two surface oxygens involved per adsorbed benzodiazepine molecule. This means that $Z \le 4$; for $Z = 4$ and $\alpha = 8$, a value of $r = 15$ Å can be calculated, and if $Z = 2$ and $\alpha = 8.0$, then a value of $r = 10$ Å results. Since $l = 7-8$ Å, this is not compatible with the previous estimation of $\beta = 1$. The numerical calculations, of course, are based on guesses of the magnitudes of $\alpha$ and $Z$. To arrive at a reasonable and self-consistent set of values, the following may be considered: $\alpha$ is a function of $\beta$ and to gauge the effect of one on the other, calculations have been made and tabulated in the following fashion (Table IV). It follows from the previous discussion that the value of $Z \cdot \alpha/r_0^2$ should be $-1.45 \cdot 10^{15}$, i.e., $r/\sqrt{(-Z)} = [\alpha/(1.45 \cdot 10^{15})]^{1.5}$ and $l/\sqrt{(-Z)} = \beta \cdot [\alpha/(1.45 \cdot 10^{15})]^{0.5}$, where it is recalled that $(-Z)$ is a positive number. These values have been calculated for a series of $\beta$ values, truncating at $n = 10$ and $i = 3$ (leaving the last terms less than 0.1% of the leading term). The values are listed in Table IV. It will be noticed that $l/\sqrt{(-Z)}$ is fairly independent of $\beta$, and from the average value $(7.6 \cdot 10^{-8})$ and the fact that $l$ is between 7 and 8 Å $(10^{-8}$ cm.), it appears that $\sqrt{(-Z)}$ lies between $7/7.6$ and $8/7.6$, i.e., $(-Z)$ is about unity.

As mentioned earlier, the actual value of $(-Z)$ is less than 4, but how much less could not be stated a priori. The fact that $l/\sqrt{(-Z)}$ appears to be nonvariant with $\beta$ (Table IV) is a result of $\alpha$ being a function of $\beta$ and lends some measure of credence to the calculated value of $(-Z)$. The actual value of $r$ cannot be pinpointed but, as seen in Table IV, it appears to be of the right order of magnitude (i.e., in the Angstrom range).

From the Brunauer, Emmett, and Teller data, it is noted that the area is 75 m.²/g. or $75 \cdot 10^{20}$ Å²/g. of montmorillonite. The cross section of a nitrogen molecule is conventionally assumed to be 16.2 Å² (12) and, using this figure, there should be $4.6 \cdot 10^{20}$ sites per gram of montmorillonite. Since there are three sites for each sorbed benzodiazepine molecule, the number of sites available is actually $2.3 \cdot 10^{20}$. This is within an order of magnitude of the number of sites found (Tables I and II) and, with the limitations of the Brunauer, Emmett, and Teller method (13), constitutes favorable agreement. That the figure should be less for the benzodiazepine molecules is, of course, to be expected, since with the assumed model the solute molecules would only adsorb in the described fashion on the platelet surfaces, not on the edges. Since nitrogen adsorbs on the surface only and not by intercalation (14), this is a support both for the arguments presented here and for those from an earlier publication (1).

Consistent values have, therefore, been arrived at by two different procedures with respect to the type of isotherm and the equilibrium value at infinite dielectric constant (or the value of $Z \cdot \alpha/r_0^2$). A consistent relation has been found between dipole moment and equilibrium distance. The number of sites has been found to be comparable by two different approaches, and these values do not conflict with the numbers obtained from Brunauer, Emmett, and

Teller measurements. Furthermore, this latter point substantiates the concept that the solutes are adsorbed on the surface only. All these facts are based on a model whereby the solute molecule, which is not ionized but which possesses a dipole moment, is bound to the surface oxygen ions by an ion-dipole interaction; therefore, it seems reasonable to postulate that the data support such a model.

It may be worthwhile, as a last point, to examine the possible contribution of van der Waals' forces. Such forces have been shown to be the sole contributors to the adsorption of sulfonic acids onto cellulose (15). The main criterion is that $K$ is proportional to the molecular weight of the substance being adsorbed. It can be seen from Table II that this is not the case here. Van der Waals' forces, of course, contribute only negligibly in comparison with the mentioned electrical interactions.

## SUMMARY

Data were presented which support the hypothesis that adsorption of organic compounds on montmorillonite is a surface adsorption mediated via an ion-dipole interaction when the solute is a substance that is not ionized in solution.

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