Nature of Bonding in Montmorillonite Adsorbates I: Surface Adsorption

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Abstract ☐ It has been shown that organic solutes that do not have groups which are cation exchangeable adsorb on the surface of neutralized montmorillonite and do not (unlike several solvents such as alkanols and water) penetrate to the interior of the crystal. The number of available sites on the surface is of the order 10^{18}–10^{19} sites per m.^{2} of surface area. The number of interior sites available is about 600 times as high. The fact that surface adsorption is the process involved explains in part the fact that such adsorbates are physiologically available when used in pharmaceutical preparations.

Keyphrases ☐ Montmorillonite adsorbates—bonding nature ☐ Bonding nature—montmorillonite adsorbates ☐ Benzoic acid adsorption—montmorillonite ☐ Moisture isotherm—montmorillonite ☐ Particle-size determination—montmorillonite

MacEwan (1) showed by X-ray studies that some clays, including montmorillonite, have a micalike structure, being built up in layers; the interlaminar distance is large, and layers are held together by second-order forces. The interlaminar distance in montmorillonite can vary from 10 to 20 Å or even more, depending on its water content. Bradley et al. (2) showed that these water molecules form layers about 3 Å thick, whereas the thickness of the aluminum silicate framework is 9.6 Å (3). The distance in dehydrated montmorillonite can be more than 9.6 Å, due to the presence of various cations; according to Hendricks (4), these cations place themselves in the same fashion as do the water molecules. Mering (5) showed that the structure of montmorillonite (Fig. 1) is one of a repeating unit of $[Al_{2-x}Mg_x, Si_{4-y}Al_y, O_{10}(OH)_2]$ where $(x + y)$ represents the negative charge; this is compensated for by cations which position themselves on the crystal surface and, hence, are exchangable. In "neutralized" species[1], this cation is H^+.

MacEwan (1) pointed out that water can be replaced by organic molecules. He showed that the number of layers of organic solvent molecules present between silicate layers is zero for heptane; one for heptanol, ethylenediamine, and 1-propanol; two for 1,2-propanediol, ethanol, ethylene glycol, methanol, and acetone; and three for acetonitrile. This type of work has been extended and verified in many subsequent publications (6–10). Studies of this type have most frequently been conducted by exposing the montmorillonite to the organic vapor and measuring the change in crystal spacing.

MacEwan and Talib-Uddin (11), in the case of α-zinc hydroxide, showed that the sodium salt of 1-hydroxy-2,4-dinitro-7-naphthalenesulfonic acid "adsorbed" by placing itself in the interlaminar positions. Wai and Banker (12) showed that, for many organic
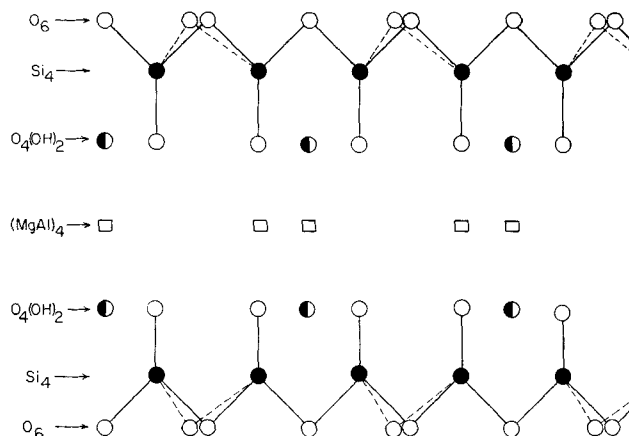

Figure 1—*Structure of montmorillonite according to Mering (5).*

compounds, adsorption on montmorillonite, which is not neutralized, is one of ion exchange. Zentner (13) showed that "neutralized" montmorillonite may be employed to make adsorbates which serve the purpose of taste-masking of bitter compounds. These adsorbates are physiologically available (14); it would, therefore, appear that they could not be too strongly adsorbed (e.g., could not be chemisorbed).

In the case of protonized substituted amines (and other protonized compounds), the adsorbates on neutralized montmorillonite are presumably of an ion-exchange nature. In the case of uncharged species, however, this cannot be the process. From the description given, the adsorbates could be either a surface adsorption or they could be brought about by an adsorption of the type described for α-zinc hydroxide, where the organic molecule actually penetrates the crystal.

An investigation of the nature of the bonding involved is presently being conducted by the authors. This preliminary publication directs itself to the question whether, in the case of neutralized montmorillonite, solutes adsorb on the surface only or whether adsorption in the interlaminar space is also taking place.

EXPERIMENTAL AND RESULTS

Mering (5) pointed out that treatment of montmorillonite with mineral acids may give rise to structural changes of the surface. Micronized neutralized montmorillonite[2] was, therefore, used as received from the supplier; the entire study refers to one single lot[2], except where noted. Drying by heat also may cause structural alterations (5), so the montmorillonite was dried by exposure (on a vacuum rack with high vacuum capability) to less than 0.5-μ pressure. After exposure for 7 days, the samples had equilibrium pressures of less than 1 μ Hg. Nevertheless, the samples contained 5.6% structural water, as determined by Karl Fischer titrations.
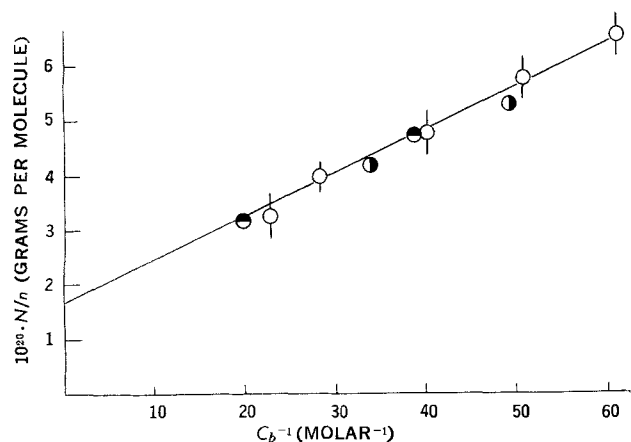
Figure 2—*Benzoic acid isotherm from anhydrous isopropanol. Ordinate represents grams of montmorillonite per molecule of benzoic acid, and abscissa is reciprocal molarity of benzoic acid. Key: O, represents the procedure described in the text; ◐, represents preextracted montmorillonite (see text); and ◑, represents a log of montmorillonite different from the lot used in the main portion of the study. The equation for the line is:* $1/n = 1.67 \cdot 10^{-20} + [8.31 \cdot 10^{-22}/C_b]$.

Benzoic acid isotherms were determined by dissolving a weighed amount of benzoic acid in the appropriate solvent. An aliquot was titrated with 0.02 N NaOH; another aliquot was exposed to a weighed amount of dried montmorillonite in a sealed conical flask and shaken mechanically at 25° for 48 hr. The sample was then centrifuged, and an aliquot of the supernatant was titrated; the amount adsorbed was determined by difference. A blank sample, containing no benzoic acid, was prepared in a similar fashion and showed zero titer.

Reciprocal plotting of the data yields straight lines, as exemplified in Fig. 2. Since anhydrous solvents (e.g., methanol) have been reported to (and were found to) extract and replace the structural water, the solvent after equilibration contains small amounts of water. One to six grams of montmorillonite was used per 100 ml. of solvent, so the moisture content of the solvent, in reality, would be 60–360 mg./100 ml. To ascertain that this small amount did not affect the results, two runs were made with montmorillonite preextracted with solvent. Results from these fall in line with the remaining results (Fig. 2); hence, the effect of the small amount of water is within experimental error. Two runs were made with a different lot of montmorillonite, also giving consistent results (Fig. 2).

Moisture isotherms were performed by exposing 5 g. of montmorillonite to 100 ml. of water–isopropanol mixtures for 3 weeks in sedimentation tubes of 4.2-cm. i.d., of the type described elsewhere (16). The water content of the solvent was determined before and after equilibration by means of Karl Fischer titrations; a plot of moisture content of the montmorillonite as a function of water content of solvent is shown in Fig. 3.

The cross-sectional area of benzoic acid was estimated by molecular model to be 7 $\mathring{A}^2$ from a lengthwise direction and 14 $\mathring{A}^2$ from the side.

Microscopic examination of the lot of montmorillonite used revealed the majority of particles to be of a 1-2-μ dimension. A few (less than 0.05% by number) were 5–10 μ. A 2-μ cube, employing a density figure obtained by displacement in hexane, results in a cal-

Table I—Benzoic Acid Isotherms in Various Solvents

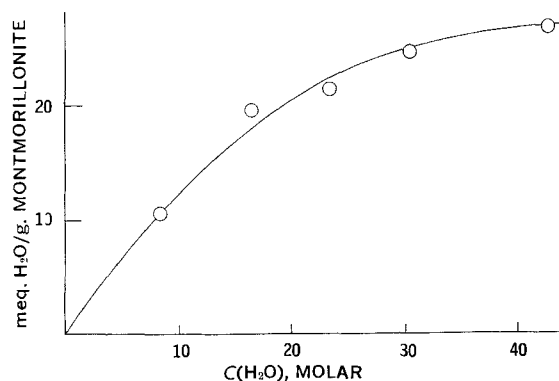| Solvent	Intercept	Sites per Gram
Isopropanol	$1.67 \cdot 10^{-20}$	$6.0 \cdot 10^{19}$
Water–isopropanol (50% w/w)	$2.07 \cdot 10^{-20}$	$4.6 \cdot 10^{19}$
Ethanol	$2.51 \cdot 10^{-20}$	$4.0 \cdot 10^{19}$
Butanol	$2.34 \cdot 10^{-20}$	$4.3 \cdot 10^{19}$
Methanol	$2.01 \cdot 10^{-20}$	$5.0 \cdot 10^{19}$
Average		$4.8 \cdot 10^{19}$
Standard deviation		$0.8 \cdot 10^{19}$

Figure 3—*Moisture isotherm of montmorillonite from aqueous solutions of isopropanol.*

culated surface area of 1 m.²/g. B.E.T. nitrogen isotherms give higher results but may involve not only external, but also internal, laminar surfaces. It is, furthermore, to be expected that the experimental figure is larger than geometrically expected, since the latter is predicated on smooth surfaces and on monodispersity.

DISCUSSION

Isotherms of benzoic acid and of water on neutral montmorillonite were determined since they give information relative to the number of adsorption sites. If the adsorption of benzoic acid is a competition between solvent (o) and benzoic acid (b), then the surface fraction covered (θ) is given in terms of the concentrations in solution (C) by (15):

$$\theta_b = \frac{K_b C_b}{1 + K_b C_b + K_o C_o} \quad \text{(Eq. 1)}$$

If $K_o C_o$ is negligible compared to unity, then (taking reciprocals) this equation becomes:

$$\frac{1}{\theta_b} = 1 + \frac{1}{K_b C_b} \quad \text{(Eq. 2)}$$

If 1 g. of montmorillonite contains N sites in total, and the number of sites occupied per gram is n (i.e., there are n molecules adsorbed per gram), then $\theta_b = n/N$ is the fractional coverage. If (as is conventionally assumed) the number of sites N equals the saturation value of n for high values of C_b, then $N = n_\infty$ and $\theta_b = n/n_\infty$ is a dimensionless quantity. Equation 2 may be written:

$$\frac{N}{n} = 1 + \frac{1}{K_b C_b} \quad \text{(Eq. 3)}$$

Since this equation is dimensionless, K_b is in reciprocal concentration units; molarity is used here so this unit is M^{-1}. Equation 3 may be written:

$$\frac{1}{n} = \frac{1}{N} + \frac{1}{K_b N} \cdot \frac{1}{C_b} \quad \text{(Eq. 4)}$$

so that a plot of the reciprocal of the number of molecules adsorbed per gram of montmorillonite *versus* reciprocal concentration yields an intercept of $1/N$ and an intercept/slope ratio of K_b. These considerations assume that $K_o C_o$ is negligible compared to unity. If $K_o C_o$ is not negligible, then Eq. 4 becomes:

$$\frac{1}{n} = \frac{1}{N} + \frac{[K_o C_o + 1]}{K_b N} \cdot \frac{1}{C_b} \quad \text{(Eq. 5)}$$

For the benzoic acid isotherms, the concentration of benzoic acid is low, so C_o is practically invariant; reciprocal plotting, therefore, still yields a straight line (Fig. 2) and the intercept still reflects the reciprocal of the number of sites (Eq. 5). However, the intercept-to-slope ratio only yields the value for K_b if the value of $K_o C_o$ is negligible compared to unity.

Figure 2 shows that in the case of isopropanol, the intercept is $1.67 \cdot 10^{-20}$; hence, $N = 6.0 \cdot 10^{19}$. Intercept and N-values for other
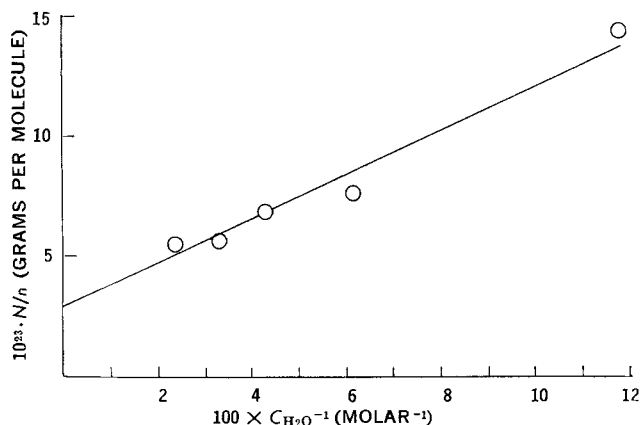
Figure 4—*Langmuir plot of data from Fig. 3. The equation of the line is:* $1/n = 2.86 \cdot 10^{-23} + [9.4 \cdot 10^{-22}/C_{H_2O}]$.

solvents are listed in Table I, and it is seen that these do not differ greatly from solvent to solvent; $N = 4.8 \cdot 10^{19}$ is the average value. From Fig. 2, it is seen (from intercept-to-slope ratio) that, provided $K_o C_o$ is negligible compared to unity, $K_b = 20 \, M^{-1}$.

The adherence to a Langmuir plot should preclude multiple-layer adsorption, and estimates of surface area should be possible from saturation data. The benzoic acid molecule has a cross-sectional area of about 10 Å^2, so the surface of the neutral montmorillonite in contact with solution may be estimated at 5 m.^{2}/g., *i.e.*, there are about 10^{19} sites per m.^{2} of surface.

As mentioned in the introduction, solvent (and water) molecules migrate into the crystal space in the montmorillonite. It is, *a priori*, possible that the solute molecules behave likewise (11). If so, then the total number of interstitial and surface sites should be available for adsorption, and the number of sites obtained from a water isotherm should equal that from a benzoic acid isotherm. For this reason, the amount of water removed by montmorillonite from hydroisopropanolic solutions was determined. In this case, the concentration of water in Eq. 5 is represented by C_b, and C_o is concentration of isopropanol. Since C_b in this case is not small and is varied over a large range, C_o is not invariant. If, however, $K_o C_o$ is negligible (compared to unity), Eq. 4 should be obeyed.

A plot of the data is shown in Fig. 3, and plotting according to Eq. 4 is shown in Fig. 4. The linearity of the data in Fig. 4 is good, and the number of sites calculated is $N = 3.5 \cdot 10^{22}$. This is about 600 times larger than the number of sites available for benzoic acid adsorption, and it may be concluded that the adsorption of the latter is strictly a surface phenomenon on the neutralized montmorillonite.

It is important to note that the number of sites available to benzoic acid adsorption does not change appreciably with water content, as seen from Table I; the number of sites calculated from the benzoic acid isotherm in 50% isopropanol equals those obtained in anhydrous isopropanol and other solvents.

Mering (5) showed that three to four monolayers of water are introduced per silicate layer in the intercalation process. He showed that the thickness of these is 3 Å each; the thickness of the silicate layer, as mentioned, is 9.6 Å. If four molecular layers of water exist between each layer of silicate and if there are n layers, the interior sites should amount to approximately $4 \cdot n \cdot A \cdot \gamma$, and the platelet surface sites should number $2 \cdot A \cdot \gamma$, where γ is a proportionality constant related to area, and A is the site density on the platelet. The ratio of internal to surface sites (assuming A to be

constant) should then be $2 \cdot n = 600$, *i.e.*, n should be approximately 300. The average thickness of the montmorillonite particles in contact with hydrous solvent should then be $300 \cdot [9.6 + 12] = 6500$ Å = 0.7 μ, which is not in conflict with the microscopically found dimensions. In this description the adsorption energies of the different layers cannot differ greatly, since the adsorption isotherm, otherwise, would not be of the Langmuir type.

Regarding the assumption that $K_o C_o \ll 1$, it is seen from Fig. 4 that reciprocal plotting yields a straight line; for linearity to prevail in the water isotherm, it is necessary that $K_o C_o \ll 1$ (Eq. 5). The value of $K_b = 20 \, M^{-1}$, therefore, represents a realistic figure. In the benzoic acid isotherms, C_b is in the range $0.02 \cdot 0.05 \, M$ so $K_b C_b = 0.4 \text{-} 1$; since $K_b C_b$, therefore, is of the order of unity and $K_o C_o$ is much smaller than unity, it can also be stated with acceptable credibility that $K_b C_b \gg K_o C_o$.

SUMMARY

Benzoic acid adsorbs from alkanolic solutions on the surface of neutralized montmorillonite by Langmuir isotherms.

The number of surface sites estimated from the benzoic acid isotherms is much less than that of water (which adsorbs by intercalation), showing that the benzoic acid does not penetrate the crystal.

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