Investigation of normal hexane and nitrogen adsorption onto soil constituents and constituent mixtures

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Abstract

Vapor-phase adsorption of normal hexane onto some common soil constituents and simple mixtures of these constituents at 27 °C was studied. Experiments were conducted at zero relative humidity. The constituents can be classified as clays, organic matter and sand. Only the clays were significant adsorbents in both the pure constituent and mixture experiments. In all cases the adsorption isotherms had the Type II sigmoid shape. Adsorbent surface areas were estimated from the two-parameter BET adsorption model. Adsorption capacity, reflected by surface area, of the mixtures could be characterized almost completely by clay content alone. The clays, although possessing much different capacities to adsorb hexane when expressed on a mass basis, exhibited approximately equal adsorption capacities relative to their N_2/BET surface areas. Accordingly, the various dry-clay adsorption isotherms when plotted as relative capacity (amount of hexane adsorbed divided by N_2/BET surface area) versus normalized concentration were seen to collapse roughly upon one another for a large part of the concentration range. Furthermore, clay BET surface areas estimated from hexane adsorption at 27 °C were consistently seen to be approximately 0.73 times that of the value from N_2 adsorption.

1. Introduction

Leakage of solvents and fuels from underground storage tanks and other sources to soil and groundwater has become a widespread problem. One promising method of removing the volatile constituents from such spills is soil vapor extraction (SVE). The engineering of vapor extraction systems has prompted the intensive study of vapor-phase adsorption of volatile organic chemicals (VOCs) to soils and soil constituents (clays, sand, silt and organic matter) under various conditions.

Frequently, chemical spills occur in areas where the soil contains a significant amount of moisture. In these situations the competitive adsorption between VOCs

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and water, and partitioning of adsorbates between the clay minerals and organic matter of the soil must be considered, complicating site characterization. In the presence of water which preferentially adsorbs onto the polar mineral surfaces, nonpolar and slightly polar molecules like VOCs find relatively little surface area to be adsorbed to. On the other hand, VOCs are strongly adsorbed onto dry soils at very low relative humidity. This situation requires a simpler adsorption model, but is realistically limited to very arid areas.

A number of studies have been conducted for single-component VOC adsorption onto dry soils. In reviewing the literature on the subject, Valsaraj and Thibodeaux [1] have reported that under dry conditions (soil moisture content less than 2%), VOC adsorption usually displays the characteristic Types II and IV BET isotherms. Under these conditions the single-component BET model adequately describes sorption behavior. Jurinak and Volman [2] examined ethylene dibromide (EDB) adsorption onto montmorillonitic, kaolinitic and illitic soils. From a comparison of their EDB/BET surface-area estimates to the total surface areas as determined by ethylene glycol retention, they concluded that EDB adsorption by soils was essentially an external surface phenomenon limited to clay mineral surfaces and only the larger capillaries of the organic matter. The differences in the adsorptive potential of their soils were primarily a manifestation of differences in external surface areas. Similarly, Chiou and Shoup [3] concluded from their VOC adsorption experiments at zero relative humidity on dry Woodburn soil that under these conditions mineral adsorption was dominant. They also noted that adsorption of VOCs increased with increasing adsorbate polarity. Rhue et al. [4], in studying the vapor-phase adsorption of three alkylbenzenes (toluene, p-xylene and ethylbenzene) onto two soils (and also two clays, an aquifer material and silica gel), found that BET surface areas estimated from the alkylbenzene adsorption were approximately those of N_2 adsorption, except in the case of the silica gel where the surface areas from organic-vapor adsorption were much lower. They concluded that equal surface-area estimates indicate that the smectite interlamellar surfaces were inaccessible to the alkylbenzene vapors, an inference made earlier by Jurinak and Volman [2] for EDB vapors. Poe et al. [5] experimented with five VOCs and four soils of different clay mineral content. They noted, similar to Chiou and Shoup [3], that for VOC adsorption on dry soils the role of clay minerals predominates over organic matter for neutral molecules and adsorption increases with adsorbate polarity.

Single-component VOC adsorption on dry constituents of soil has also received some attention. Jurinak [6] studied the adsorption and desorption of EDB on clays (kaolinite, illite and montmorillonite) possessing different exchangeable cations. Clay mineral and exchangeable cation had a marked effect on adsorption. A comparison of EDB/BET surface areas with the surface area determined by ethylene glycol retention showed the adsorption process to be limited to external surface area, a conclusion reached by Jurinak and Volman [2] for natural soils. Rhue et al. [4], as mentioned above, included bentonite and kaolin in their experiments. Similar to their soils, the clay surface areas from VOC/BET and N_2/BET were roughly the same, with some variation. Chiou et al. [7] have studied the vapor-phase adsorption of eight VOCs on soil humic acid. They found adsorption capacity increased with adsorbate

polarity; normal hexane had the lowest limiting sorption capacity. Ong and Lion [8] performed vapor-sorption experiments for trichloroethylene (TCE) on dry soil constituents which included clays (montmorillonite and kaolinite), oxides of Fe and Al, silica, humic acid and humic-coated Al. They found that BET surface areas computed from TCE adsorption were for all solids less than that estimated by the N_2/BET method. Assuming that the N_2/BET values were correct, they computed what the molecular cross-sectional areas of TCE should be to make up those surface areas, an approach taken by Van Voorhis et al. [9]. The computed areas were 1.5 to 2 times that of the theoretical values obtained from the close hexagonal packing model (Eq. (3)).

In the presentation and comparison of sorption data, results are sometimes expressed as a relative isotherm (adsorption capacity divided by monolayer capacity). This has the effect of eliminating the surface area bias and making sorbent-specific interactions more apparent [6,8]. The concept has also been used by Jurinak and Volman [2], Rhue et al. [4] and Pennell et al. [10]. Pennell and Rao [11] have expressed isotherms relative to N_2/BET surface area.

The purpose of this study was to investigate the vapor-phase adsorption of a single non-polar VOC, n-hexane, onto dry soil material constituents. Conventional nitrogen adsorption experiments were also performed on the same samples to determine if there was any correlation between the two adsorbates. In addition, simple mixtures were made from the constituents and subjected to the same experiments. The objective in examining the mixtures was to determine whether the surface area of a mixture can be predicted as the weighted sum of the pure-constituent surface areas. Organic matter was included in two of the mixtures to see if this in the presence of clays and sand had any additional effect on adsorption.

2. Materials and methods

The adsorbents of interest were some common clays (kaolinite, bentonite, illite and two montmorillonites, Mg and Na-rich forms), organic matter (humic acid and powdered cellulose) and sand. The suppliers, particle sizes and compositions of the adsorbents used in these experiments are given in Table 1. The clay minerals were examined by X-ray diffraction (XRD). The XRD analyses were performed on a Rigaku RU-200 (a rotating anode, Cu–K–α diffractometer) and on a Scintag PAD-V diffractometer by the Department of Chemistry, Texas A&M. The random-powder method was applied with aluminium mounts on the Rigaku and plastic mounts on the Scintag. The clay minerals were found to be medium- to well-crystallized and of high purity. In Table 1 the compositions of the clays purchased from Aldrich Chemical Co. (Milwaukee, WI) are those provided by that supplier. The XRD patterns of these adsorbents were consistent with the supplier's statement. No further impurities were found than those given in the table. The estimate of quartz content in the illite sample was made by quantitative XRD. The method uses the ratio of the intensity of a component in the mixture to an external standard, and is

Table 1
Characteristics of adsorbents used in the experiments

Adsorbent (clay mineralogy)	Supplier	Particle size (μm)	Composition
Bentonite (smectite)	Aldrich	< 44	$\approx$93% clay; < 7% oxides/salts of Fe, Ca, Na, & quartz
Illite (mica)	Clay Minerals Society, (Columbia, MO)	< 210	$\approx$90% clay; $\approx$10% quartz & other
Kaolin (kaolinite)	Aldrich	0.1–4	$\approx$98% clay; $\approx$2% oxides/salts of Ne, Fe
Na montmorillonite (smectite)	Aldrich	0.5–1	$\approx$90% clay (includes some feldspar, mica); $\approx$10% silicates of Na and Fe, quartz, nitrates and carbonates of Fe
Mg montmorillonite (smectite)	Texas A&M Dept. of Chemistry (originally from Ward's of CA)	< 4	$\approx$99% clay
Non-clay adsorbents:			
Cellulose (---)	Aldrich	$\approx$20	Powdered cellulose
Humic Acid (---)	Aldrich	< 420	Sodium salt of acid
Sand (---)	Aldrich	210–295	White quartz

described in Brindley and Brown [12]. The clays purchased from Aldrich were received in finely ground condition. Clays from other suppliers were ground by mortar and pestle. XRD was performed after the grinding. Humic acid, powdered cellulose and sand were used as is from the supplier. They are also described in Table 1.

As mentioned above, mixtures of soil constituents were also examined. The compositions of the mixtures are given in Tables 2–4. The mixtures were not separately ground.

The *n*-hexane used in the experiments was obtained from Sigma Chemical Co. (St. Louis, MO). The stated purity was 99% + . No effort was made to purify the adsorbate further.

All adsorbent samples for the hexane adsorption experiments were prepared in the same manner. This involved degassing the adsorbent under nearly complete vacuum ($< 10^{-3}$ Torr) for a period of 10–12 h at a temperature of approximately 130 °C. Degassing was performed in the adsorption measuring instrument, a Micromeritics Accusorb 2100-E (Fig. 1). Evacuation in the Accusorb 2100-E is performed by a Sargent-Welch Model 1400 vacuum pump, a combination of forepump and diffusion pump. The adsorbent resided in a flask attached to one of the open sample ports

Table 2
Mixture A surface areas: predicted and experimentally measured

Constituent	wt%	Pure constituent BET surface areas (m²/g) for adsorbate experiment	
		Hexane	N_2
Na montmorillonite	4.7	207.1	285.1
Humic acid	0.7	1.6	0.8
Sand	94.6	0.1	0.5
Predicted mixture surface area		(9.8)	(13.9)
Measured mixture surface area		(9.4)	(11.4)

Table 3
Mixture B surface areas: predicted and experimentally measured

Constituent	wt%	Pure constituent BET surface areas (m²/g) for adsorbate experiment	
		Hexane	N_2
Na montmorillonite	25.0	207.1	285.1
Cellulose	6.7	1.9	0.4
Humic acid	0.3	1.6	0.8
Sand	68.0	0.1	0.5
Predicted mixture surface area		(51.9)	(71.6)
Measured mixture surface area		(52.1)	(66.7)

Table 4
Mixture C surface areas: predicted and experimentally measured

Constituent	wt%	Pure constituent BET surface areas (m²/g) for adsorbate experiment	
		Hexane	N_2
Bentonite	25.0	23.7	31.7
Kaolin	25.0	14.8	20.2
Sand	50.0	0.1	0.5
Predicted mixture surface area		(9.7)	(13.2)
Measured mixture surface area		(9.3)	(14.2)

during this process. The mass of the adsorbent was then determined by weighing the sample in the capped flask, thereby insuring that atmospheric gases, especially water vapor, were not reintroduced to the sample.

Hexane adsorption experiments were performed at 27 °C. After evacuation of the Accusorb 2100-E to less than 10^{-3} Torr, hexane vapor was introduced into the
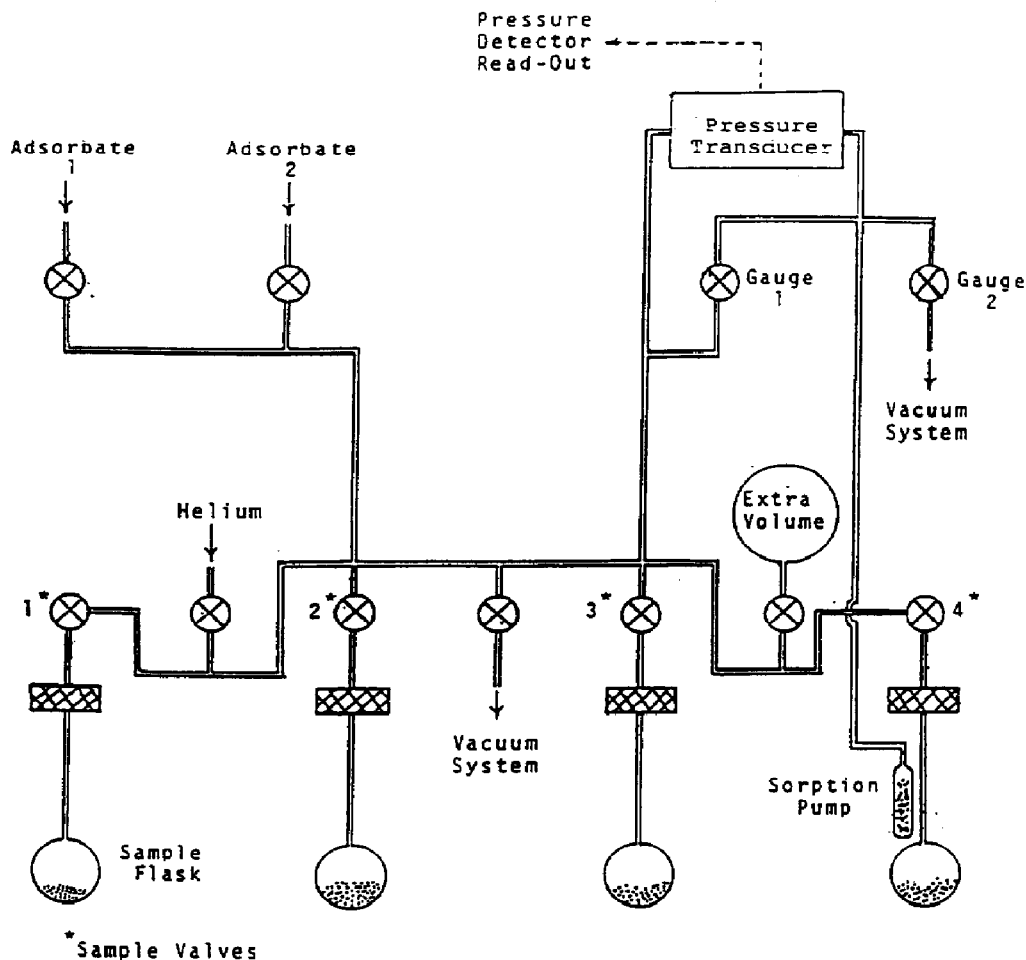
Fig. 1. Schematic diagram of the Micromeritics Accusorb 2100-E.

Accusorb manifold with the sample port valves closed. Upon equilibration, the manifold pressure was recorded. The vapor was then allowed into the sample flask containing the adsorbent by opening the sample port valve. When the system again equilibrated, the final pressure was recorded. Since the volume and temperature of the manifold, intermediate piping and flask void space were known, the number of initial and final moles of vapor were computable via the perfect gas law. The compressibility factor for *n*-hexane vapor at 27 °C is approximately 0.99 using a second-virial expression [13], indicating that the ideal gas law should be adequate for the range of P/P_0, pressure divided by adsorbate vapor pressure, from zero to unity. The quantity adsorbed was estimated from the Accusorb data by computing the difference in moles of vapor from initial to final state. The adsorption isotherm was obtained by repetition of the process at gradually higher manifold pressures.

The piping and manifold of the Accusorb are constructed from polished Monel. Wall effects on adsorption were estimated by evacuating the system after attaching an empty flask to an open sample port, then introducing hexane until the system pressure

was 149.5 mg Hg and recording the pressure response over 18 h. The final pressure after this time was 149.0 mg Hg. The leak rate of air into the evacuated system was previously determined to be approximately 10^{-4} mm Hg/min, so that the maximum wall adsorption of hexane over the time period was estimated to be approximately 0.1 mg hexane. The wall adsorption was considered to be negligible and not considered in reducing the adsorbent experimental data.

3. Data and analysis

Experimental adsorption data were reduced and plotted as mass adsorbed (mg adsorbate/g adsorbent) versus normalized concentration, P/P_0. The isotherms for the clay minerals are given in Fig. 2 and those for the mixtures in Fig. 3. The isotherms all had the characteristic Type II shape. Sand, humic acid and powdered cellulose had very little capacity for hexane adsorption. Only the surface areas for these are reported in Tables 2–4, and it should be noted that these very low values contain a large measure of error. The experiments were replicated for each adsorbent, except the kaolinite for which only one experiment was performed.

The two-parameter BET model was applied to the isotherm data of Figs. 2 and 3 to obtain the surface area for hexane adsorption. According to BET theory [4], adsorption can be represented by the following linear equation:

$$\frac{P}{X(P_0 - P)} = \left(\frac{c - 1}{X_m c}\right)\frac{P}{P_0} + \frac{1}{X_m c}, \tag{1}$$

where X and X_m are the amount adsorbed and the monolayer adsorption capacity per mass of adsorbent, and c is a parameter theoretically related to the net molar enthalpy of adsorption, ΔH_m, by the equation

$$-\ln c \simeq \frac{(\Delta H_m + \Delta H_v)}{R T}, \tag{2}$$

where R is the gas constant, T is the system absolute temperature and ΔH_v is the molar enthalpy of vaporization. For Type II isotherm data, Eq. (1) is typically applicable over the range of P/P_0 from 0.05 to 0.30. The data of Figs. 2 and 3 were fitted to Eq. (1) by least-squares linear regression. The estimates of the slope, $(c - 1)/X_m c$, and the intercept, $1/X_m c$, were solved simultaneously for the two parameters, X_m and c.

The projected area of a single adsorbate molecule was computed by the hexagonal close-packing model:

$$\alpha = 1.091 \left(\frac{M}{N_0 \rho}\right)^{2/3}, \tag{3}$$

where α is the projected area of a single molecule, ρ is the density of the adsorbed molecule in the liquid state at the adsorption conditions, M is its molecular weight and N_0 is the Avogadro number. The projected area for hexane at 27 °C obtained
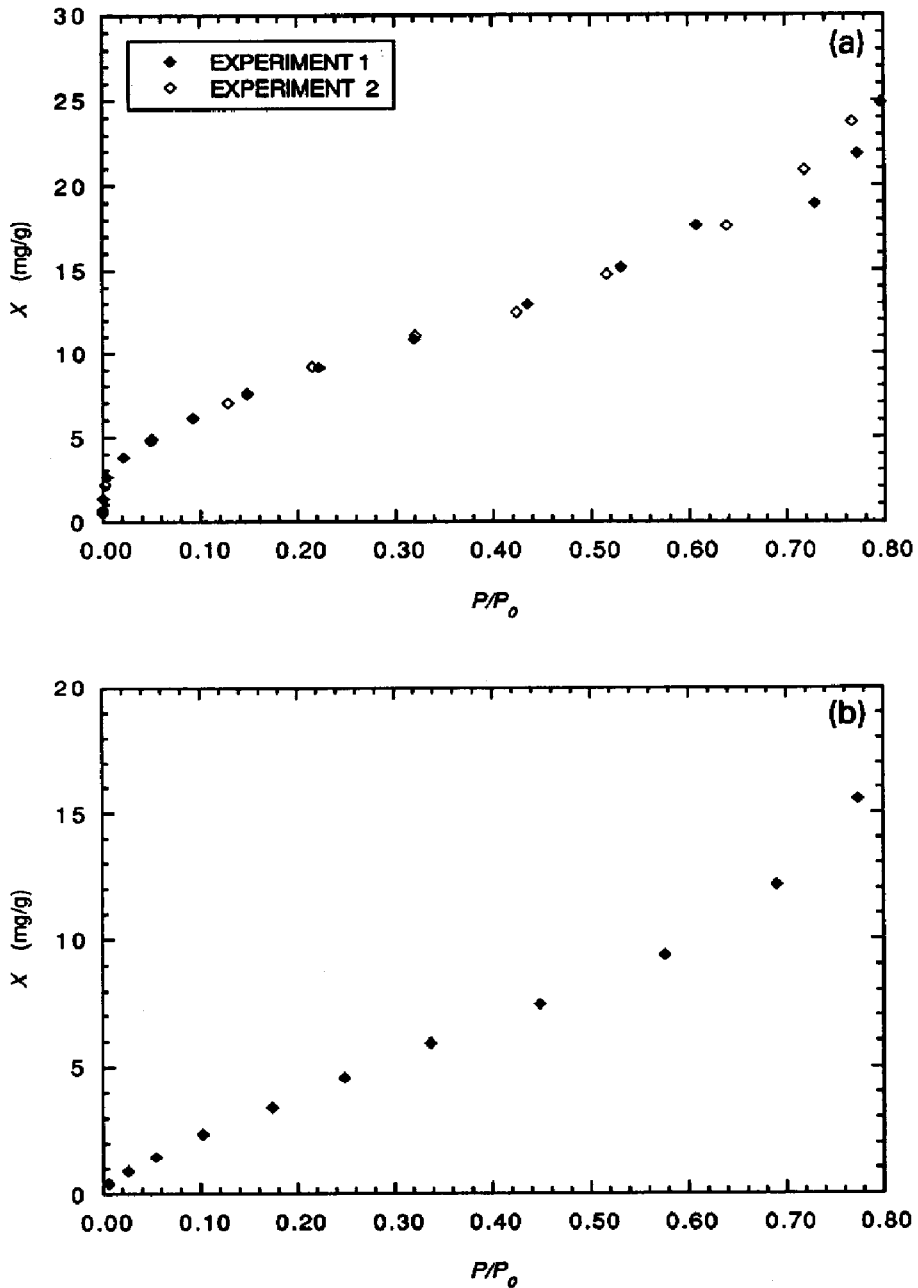
Fig. 2. Hexane vapor adsorption on clay minerals: (a) bentonite, (b) kaolinite, (c) Na-rich montmorillonite, (d) Mg-montmorillonite, (e) illite.

from Eq. (3) was 0.41 nm^2. The values of X_m and α were used to compute the surface area, S_m, covered by a unimolecular layer:
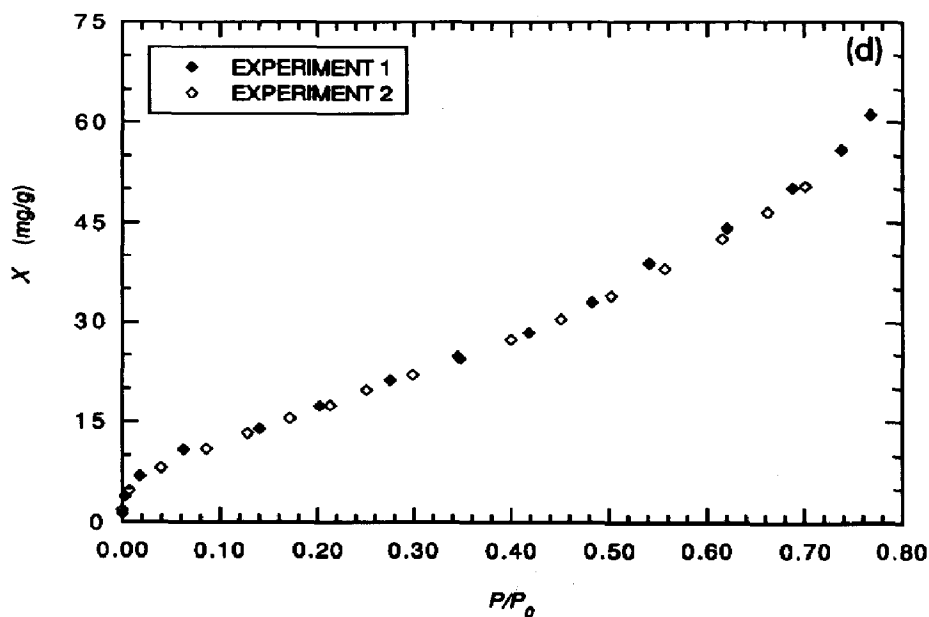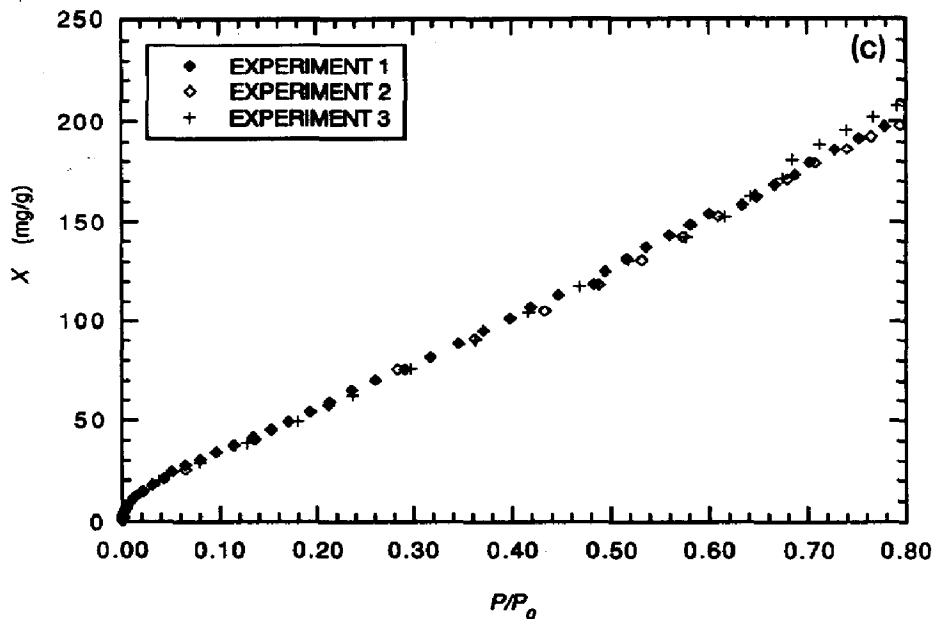
$$S_m = \left(\frac{X_m N_0}{M} \right) \alpha. \tag{4}$$

Fig. 2 (continued).

The parameters calculated from the adsorption isotherm using the BET model, the correlation coefficients of linear regression and the surface areas computed by Eq. (4) are given in Table 5. The values for each adsorbent are the average of the experiments performed.

Conventional N_2 adsorption (at the boiling point of N_2, 77.4 °K) was also performed on the soil constituents and simple mixtures using a Micromeritics Digisorb
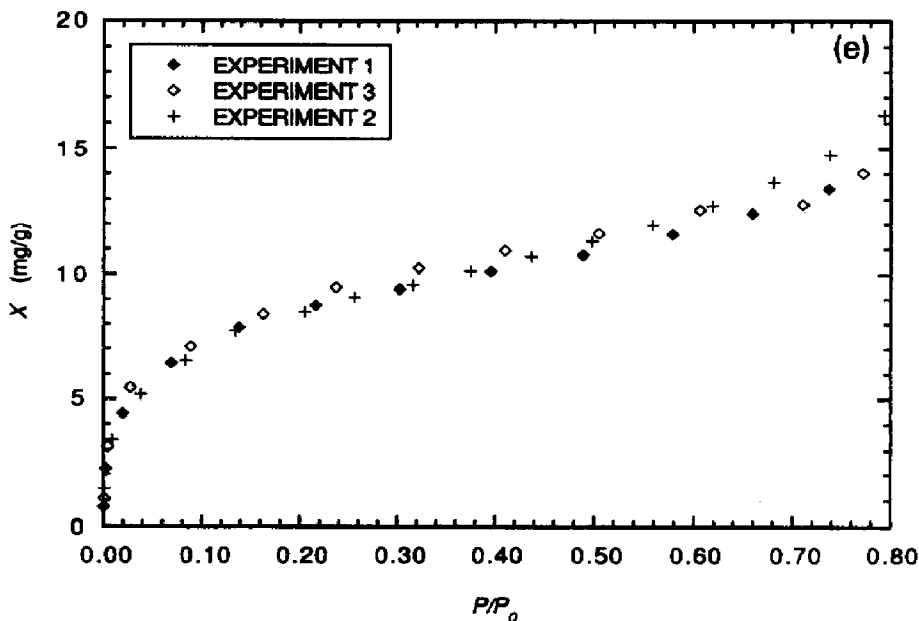
Fig. 2 (continued).

2600. The Digisorb is completely automated and possesses computation capabilities which the Accusorb 2100-E does not, but determines adsorption by the same method. The surface areas obtained from the Digisorb N_2 experiments will be referred to as "standard". The projected area of a nitrogen molecule used in the computation was $0.162 \, \text{nm}^2$. These surface areas are also reported in Table 5.

A relative hexane adsorption isotherm (Fig. 4) for each of the soil constituent samples and simple mixtures was obtained by dividing the usual ordinate unit (mg hexane adsorbed/g adsorbent) by the standard BET surface area, $A \, (\text{m}^2/\text{g}$ adsorbent). This created a new ordinate unit, X/A (mg hexane adsorbed/m^2), which effectively places the hexane adsorption for each adsorbent on a common basis of available surface area determined by the conventional N_2 method. The data points for all experiments on a particular adsorbent are given a common marker in Fig. 4.

The results of the experiments for the sand, powdered cellulose and humic acid are not shown in Fig. 4. These proved to be such weak adsorbents that measurements contained a large amount of experimental error. Surface areas for these constituents were all approximately $0.1–2.0 \, \text{m}^2$ when estimated from either hexane or nitrogen isotherms (Tables 2–4), very much below the clay surface areas. The respective R^2 values for hexane/BET surface-area calculations were 0.95 (cellulose), 0.91 (sand) and 0.93 (humic acid).

The soil-constituent mixtures shown in Fig. 4 also exhibited Type II behavior. Since the clays alone in this study were the only constituents to show significant surface areas and therefore significant adsorption, the mixtures behaved in the same manner as the clays.
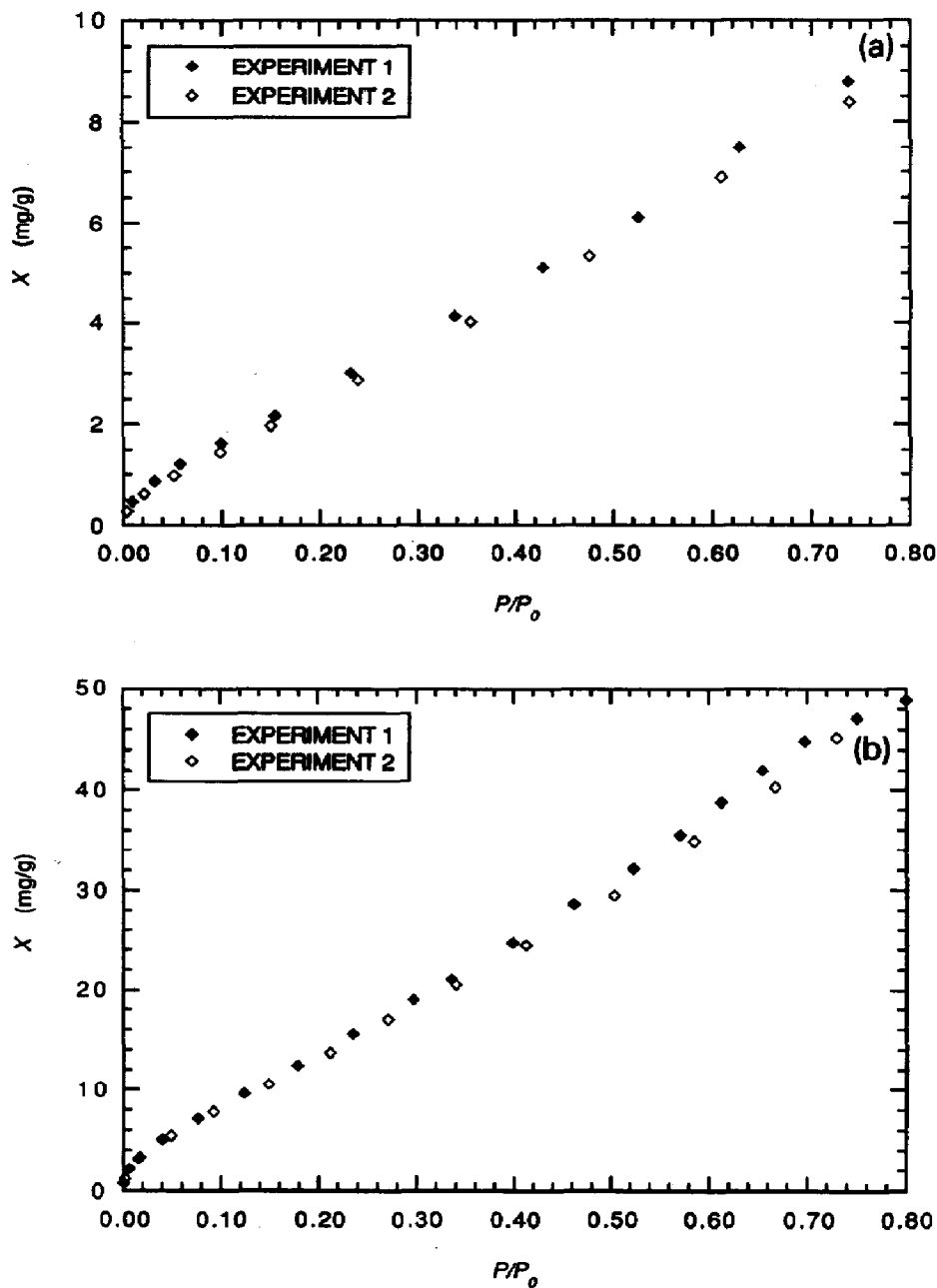
Fig. 3. Hexane vapor adsorption on mixtures: (a) mixture A, (b) mixture B, (c) mixture C.

It was noticed that the surface-area measurements for the two adsorbates showed remarkable proportionality. A comparison of the BET surface areas per clay as determined by hexane adsorption and the conventional N_2 method is shown in Fig. 5.
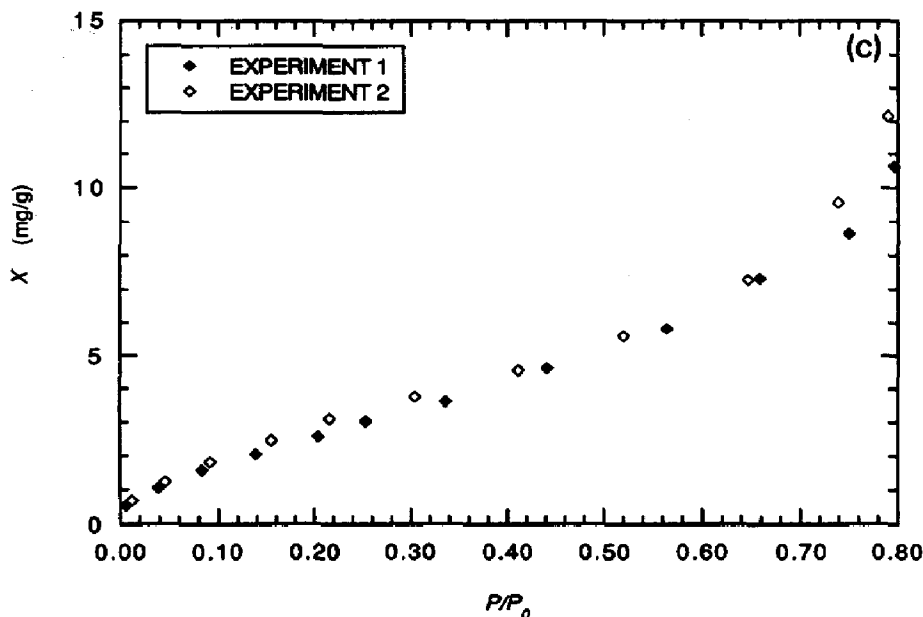
Fig. 3 (continued).

Table 5
Parameters computed from isotherms of hexane and nitrogen adsorption using BET theory

Adsorbent	Parameters from hexane/BET model			Hexane/BET surface area (m^2/g)	N$_2$/BET surface area (m^2/g)
	X_m (mg/g)	c	R^2		
Bentonite	8.2	22.6	0.999	23.7	31.7
Illite	7.3	71.4	0.997	21.05	29.5
Kaolinite	5.1	6.4	0.999	14.8	20.2
Na montmorillonite	71.4	7.0	0.999	207.1	285.1
Mg montmorillonite	17.6	16.6	0.993	51.1	75.8
Mixture A	3.4	6.7	0.976	9.4	11.4
Mixture B	18.0	6.3	0.992	52.1	66.7
Mixture C	3.2	10.5	0.998	9.3	14.2

4. Discussion

The adsorption isotherms for the clays varied widely when the ordinate was expressed in terms of the mass of hexane adsorbed per gram adsorbent. For example, the Na-rich montmorillonite adsorbed as much as 250 mg hexane/g adsorbent while the kaolinite adsorbed a maximum of around 30 mg/g. When, however, the quantities of adsorbed hexane are expressed per standard N$_2$ BET surface area, the isotherms can be seen from Fig. 4 roughly to collapse upon one another for a large part of the concentration range. This implies that the clays, which in some cases have dissimilar
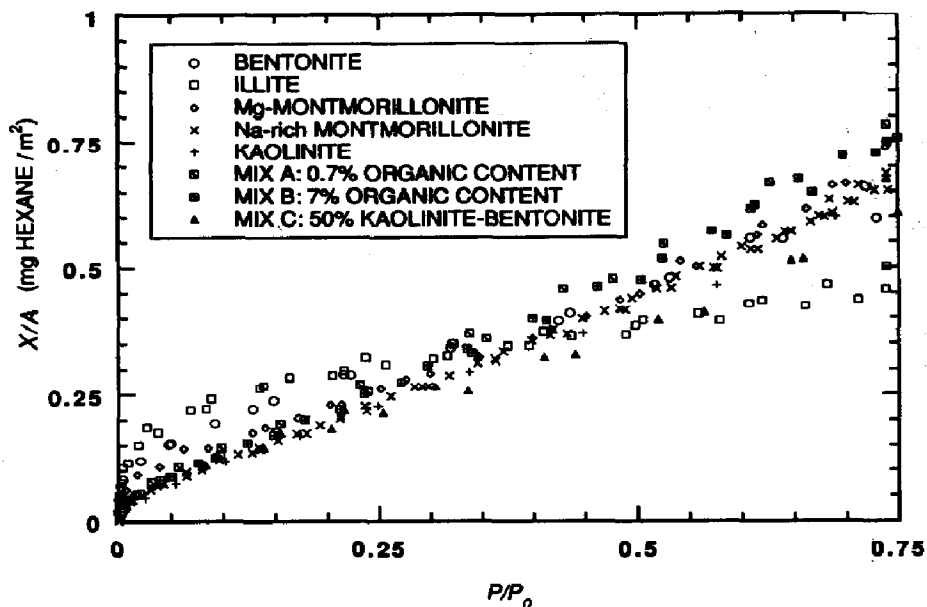
Fig. 4. Milligrams n-hexane adsorbed per square meter surface area by N_2 BET analysis versus normalized pressure.
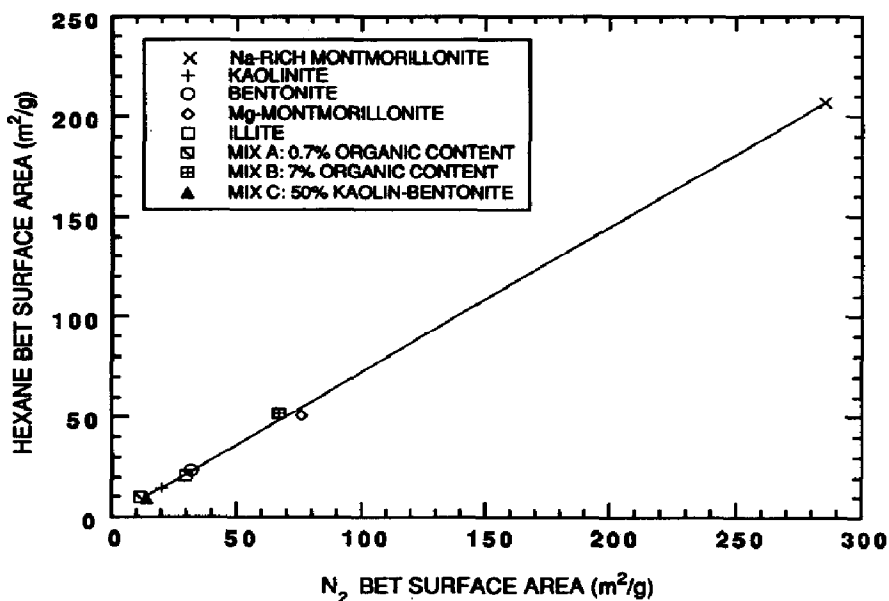

Fig. 5. Hexane/BET versus N_2/BET surface areas.

mineral structure, possess areas of mineral surface of roughly equivalent sorptive potential for hexane during the linear stage of the adsorption process. The effective amount of surface area available per gram varies, however, widely among the clays.

Previous researchers [6, 2, 4, 8, 10] have plotted adsorption data using a relative isotherm with an ordinate scaled to the monolayer adsorption capacity of the

adsorbate, X/X_m, a dimensionless quantity. One could just as conveniently plot the isotherm relative to the adsorbent surface area, X/S_m, since X_m and S_m are related to each other by constants and physical-property values which are constant for a given adsorbate and temperature (Eqs. (3) and (4)). The results from our experiments showed a nearly linear relationship between the hexane/BET surface area and the standard N_2/BET surface area for each adsorbent (Fig. 5). In Fig. 4 we plotted the amount adsorbed relative to the standard surface area, but the isotherms' relative positions would not be much different if the ordinate were X/X_m.

A review of the published literature on single-component VOC vapor-phase adsorption onto soils and clays at zero relative humidity reveals no precise relationship between BET surface areas computed from VOC isotherms and the standard nitrogen adsorption values. Jurinak and Volman [2] and Rhue et al. [4] concluded that their BET surface areas for smectite and smectite soils based upon their VOC isotherms to be equal to the standard N_2/BET values. In contrast, Ong and Lion [8] found that their surface areas computed for all adsorbents examined, using TCE as the adsorbate, to be less than the N_2/BET estimates. Thibaud et al. [15] reported data which shows the BET surface-area estimates for a standard EPA soil from chlorobenzene, toluene and the standard nitrogen method to be approximately the same. Their estimate from tetrachloroethylene adsorption for the same soil was higher than the standard surface area, while the estimate when n-hexane was the adsorbate was, however, only about 60% of the standard value. Estimates from methylene chloride and carbon tetrachloride were also significantly below the standard value. Similarly, the surface areas for all adsorbents we examined, using hexane as the adsorbate, were below the standard values (Fig. 5). It appears that BET surface-area estimates from non-polar and slightly polar VOCs will usually be not much greater than the standard N_2/BET estimates and will be frequently significantly less.

Fig. 5 displays a proportionality between the BET surface area estimated from hexane adsorption and nitrogen adsorption for each clay and mixture. The surface area derived from hexane was between 0.65 and 0.82 that of the nitrogen value for each sample with the mean being 0.73 for all samples. The data in Fig. 5 are seen to scatter around a line of slope equal to 0.73 and intercept equal to 0.09. The standard deviation of the ratio of hexane to nitrogen adsorption surface areas was 0.055, while the Pearson correlation coefficient for the line is 0.999. It should be noted that each data point contains the experimental error of both the nitrogen and hexane adsorption experiments.

If it were assumed that N_2/BET surface areas for the adsorbents in our experiments are the valid estimates, the molecular cross-sectional area of n-hexane must be approximately 1.4 times greater than the prediction of the hexagonal close-packing model, or 0.57 nm^2. This multiplier is very close to the value obtained by Ong and Lion [8], between 1.5 and 2.0, for their adsorbents and with TCE as the adsorbate. Van Voorhis et al. [9] suggested cluster formation and polymerization of molecules in the adsorbed state as possible reasons for differences in molecular cross-sectional area computed from the theory and data.

Tables 2–4 exhibit the prediction of mixture surface areas from the pure constituent values. It is clear that the predicted and experimental surface areas correspond well for

either adsorbate. Apparently, there was no interaction of constituents in the mixture which would either enhance or reduce adsorption. The organic matter (powdered cellulose and humic acid) in the mixtures had little or no effect upon adsorption. Variable organic content had no effect upon adsorption quantities and for our mixtures, adsorption was accounted for almost entirely by clay content alone. This is also demonstrated in Fig. 4 where mixtures A and B are not distinguishable although of very different organic content. It should be noted, however, the mixtures were produced from dry constituents and were never exposed to significant quantities of moisture, and so were not exposed to conditions approximating actual weathering of soils. In contrast, Call [16] after removing soil organic matter (SOM) from Whittlesey soil with hydrogen peroxide observed an increase in surface area which was attributed to the increase in mineral surface area available for adsorption, while the amount of clay present in the samples remained the same. The SOM apparently had the effect of coating or obscuring the mineral surfaces. The simple mixing of the constituents in our experiments apparently did not have the effect of coating the mineral surfaces with SOM.

Recently, Pennell and Rao [11] have discussed the large differences in dry SOM surface areas obtained from non-polar gas adsorption (often less than 1 m^2/g by BET analysis) and those obtained by ethylene glycol retention (often many hundreds of m^2/g). The adsorption of non-polar molecules occurs primarily on the external surfaces of SOM, and thus the suggestion is that the external surface area of dry SOM is quite small. However, polar adsorbates can access both internal and external surfaces, and under natural conditions more surface area in SOM may be available due to swelling so that SOM in natural soils has a larger role to play in adsorption than may be suggested by standard BET analysis.

5. Conclusions

Of the general categories of materials constituting soil, the major adsorbent under dry conditions appears to be clay minerals. All the varieties of clays used in the pure-constituent experiments demonstrated much greater capacity than either organic matter or sand. Likewise, the adsorption profiles of the simple mixtures could be accounted for almost completely by examining the clay content by weight and the adsorption isotherm for that clay type. It should be stressed that the mixtures differ from actual soils in that they were not weathered in the presence of water. For this reason, mineral surfaces were not obscured by SOM.

By composing the ordinate unit of the adsorption isotherm as mass adsorbed per standard square meter adsorbent, it was shown that the profiles approximately collapse upon one another. For all adsorbents examined, the surface area determined from hexane adsorption was less than that obtained from standard N_2/BET adsorption.

Continuing experiments with other adsorbates, both polar and non-polar, organic and inorganic, will show if the similarity in clay adsorption isotherms when put on a surface area basis as found in this study can be extended to other chemical classes, and should give insights into the mechanisms governing adsorption onto clays.

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