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CHARACTERIZATION OF ADSORPTION AT KAOLINITE SURFACES BY HETEROGENEOUS GAS–SOLID CHROMATOGRAPHY

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SUMMARY

Chromatographic techniques have been utilized to determine energy distribution functions for the adsorption of butane and 1-butene on dry and hydrated kaolinite. The energy distributions indicate that the primary adsorption sites occur on the opposing faces of the kaolinite cleavage plane, with little, if any, involvement of broken-bond surfaces. Differences in the butane and butene distributions can be attributed to repulsive interactions between π-electrons of butene and negatively charged surfaces of the kaolinite cleavage plane. Studies of kaolinite hydrated with small amounts of water demonstrate that water does not form a conventional monolayer, but rather "clusters" around the high energy adsorption sites of the kaolinite surface. Furthermore, the addition of small amounts of water to kaolinite result in a surface significantly different than that of the underlying mineral.

INTRODUCTION

The study of heterogeneous surfaces by gas–liquid chromatography has received considerable attention in the past ten years. This interest is due in part to the successful development and application of model isotherms which allow calculation of the complete distribution of adsorption energies directly from chromatographic measurements. Surfaces which have been characterized by these techniques include various chromatographic supports[1,2], silica gel[3,4], glass beads[5,6] and mixed catalysts[7].

While these studies have yielded insight into the physical heterogeneity of surfaces of pure materials, no applications of gas–solid chromatography to the surfaces of pure materials, no applications of gas–solid chromatography to the surface characterization of chemically heterogeneous materials have appeared. Leboda *et al.*[7] did demonstrate, however, the utility of these methods for the study of such materials in their investigations of mechanical mixtures of silica-supported, cobalt oxide catalysts.

We report here an application of these techniques, which we refer to as "het-

erogeneous gas–solid chromatography", to the study of adsorption processes on a mineral adsorbent. Heterogeneous chromatography should have unique applicability in the study of minerals because of the inherent chemical complexity of their surfaces and also because, as was pointed out by Dormant and Adamson[8], the more heterogeneous the surface the more insensitive the resulting energy distribution will be to the model chosen.

     These initial studies have focused on the surface heterogeneity of kaolinite, a well-characterized member of the phyllosilicate group of silicate layered clays. In addition to studies of its dry surface, kaolinite was hydrated with small amounts of water in order to demonstrate another unique application of heterogeneous chromatography; the monitoring of a surface as it is altered. While an energy distribution is relatively exact for a heterogeneous surface such as a mineral, it is especially valuable for analyzing changes in an adsorbent following some form of treatment[9]. This approach has been used to study titanium dioxide–carbon black[10] and silica–alumina catalysts[11]. Since in nature all minerals are coated to some degree by water molecules, it seemed appropriate within the present context to monitor the extent to which surface-bound water alters the adsorptive properties of kaolinite.

     The adsorbates chosen for these studies were those suggested by Kiselev[12,13]: n-butane and 1-butene. Butane, with no peripheral localization of electrons, falls into the group of adsorbates capable of interacting only via universal dispersion forces, not via specific interactions associated with particular bonds. Butene, on the other hand, is capable of specific interactions with surfaces via the electronic localization of the π-bond. Any differences in energy distributions for these two adsorbates determined on the same adsorbent can thus be attributed to specific interactions between the π-electrons of butene and charge densities on the adsorbent surface.

CALCULATION OF ENERGY DISTRIBUTIONS

     The application of chromatography to the study of surface heterogeneity can be envisioned by considering first the chromatographic equation for a homogeneous surface,

$$V_R' = V_R - V_M = V_S \kappa \tag{1}$$

where V_R is the solute retention volume, V_R' the corrected retention volume, V_M and V_S the volumes of mobile and stationary phases in the chromatographic column, respectively, and κ the equilibrium constant for the adsorption process. Eqn. 1 may be expended to include heterogeneous surfaces in the following way:

$$V_R' = \sum_{i=1}^{n} V_i k_i = \int_V k \, dV \tag{2}$$

In eqn. 2, the adjusted retention volume of a solute is treated as an additive function of contributions from all possible solute–surface interactions, each interaction being characterized by a $V_i k_i$ product analogous to the $V_S \kappa$ product of eqn. 1. That is, each

adsorption site possesses a stationary phase volume V_i and the adsorption interaction is described by a local function k_i.

Chromatographic retention volumes can be related to the energy distribution function by first assuming the well-known "patch-model" of physical adsorption, in which the whole surface is considered to consist of arbitrarily small areas within which adsorption is homogenous but between which adsorption varies[14]. The character of the energy distribution will depend upon the choice of the local function, and for chromatographic methods it is convenient to assume localized adsorption without lateral interactions. This implies a "step function," with various sites, or patches, being occupied in order of decreasing energy, each type of site filling to capacity before the next weaker one becomes involved. For a step function, the situation is similar to adsorption at 0°K, *i.e.* adsorption sites fill in strict order.

The local isotherm function k_i on each patch with energy Q_i may be described by the following[4,14]:

$$k_i(P,T,Q) = (P/K)\exp(Q_i/RT); \quad P < P_i \tag{3}$$

$$k_i(P,T,Q) = 1 \qquad\qquad ; P \geqslant P_i \tag{4}$$

$$P_i = K \exp[(-Q_i + Q_0)/RT] \tag{5}$$

In eqn. 3, $k_i(P,T,Q)$ is the coverage of patches with energy Q_i (calories/mole), P is the adsorbate pressure in torr, T is the absolute temperature and R the gas constant. Q_0, the interaction energy between adsorbate molecules on the surface, is zero in the present model.

The constant K of eqn. 3 is the pre-exponential or frequency factor of the Langmuir b constant (Henry's constant) and has the units of torr. Its numerical value can be obtained by balancing the fluxes to and from the surfaces. Hobson[14] derived the defining relationship of eqn. 6 using the physical constants and known monolayer densities of nitrogen,

$$K = 1.76 \cdot 10^4 \, (MT)^{1/2} \tag{6}$$

where M is the molecular weight of the adsorbate. He further checked empirically the magnitude of K against the data of Sams *et al.*[15] for the adsorption of inert gases on graphitized carbon black in the low pressure region and found the agreement to be quite good.

The energy distribution function may be determined from retention volume measurements via eqn. 7:

$$f(Q) = -\frac{\partial V_N(P)}{\partial P} \cdot \frac{(P)^2}{RT} \tag{7}$$

Several papers[1,2,4–7] have proposed a generalized expression for the retention volume function $V_N(P)$ based on the Jovanovic adsorption model:

$$V_N(P) = \exp\left(\sum_{i=0}^{m} B_i P^i\right) \tag{8}$$

which leads to

$$f(Q) = -\frac{1}{J}\left(\frac{P}{RT}\right)^2 \cdot \left(\sum_{i=1}^{m} iB_i y^{i-1}\right)\left(\exp \sum_{i=0}^{m} B_i y^i\right) \tag{9}$$

where J is the James–Martin compressibility factor and y is given by

$$y = \frac{1}{K}\exp\left(-\frac{Q}{RT}\right) \tag{10}$$

While this approach has been successful in describing the energy heterogeneity of a number of different surfaces, it does assume a particular character for the isotherm. A more general approach would be to differentiate the retention volume function $V_N(P)$ without any assumption regarding the nature of the isotherm. In this case, eqn. 7 becomes

$$N_m f(Q) = F(Q) = -\frac{1}{J}\left(\frac{P}{RT}\right)^2 \cdot \left(\frac{\partial V_N(P)}{\partial P}\right) \tag{11}$$

where N_m is the monolayer capacity. Quantitative and qualitative information can now be obtained from the function $F(Q)$ without the necessity of making *a priori* assumptions about absorption. This was demonstrated by Rudzinski et al.[3] in their studies of various silica gels.

We have chosen the more general approach for these initial studies of clay surfaces for a number of reasons. First, the nature of adsorption of organic vapors at mineral surfaces is generally unknown, and the relative merits of different adsorption models cannot be evaluated. In addition, fitting the retention volume to an analytical expression such as eqn. 8 tends to smooth small perturbations in the retention volume which might actually be due to minor heterogeneity effects. These minor heterogeneity effects can be very important in the case of naturally occurring mineral adsorbents that are generally both chemical and mechanical mixtures of pure materials which themselves possess heterogeneous surface properties.

MATERIALS AND METHODS

Chromatographic system

Chromatographic measurements were carried out using a modified Hewlett-Packard 5700A gas chromatograph (Fig. 1) capable of operation at sub-ambient temperatures ($-50°C \rightarrow 110°C$, $\pm 0.2°C$). A two-cell, 125-μl thermal conductivity (TC) detector (Model 10-952, Gow-Mac Instrument, Bridgewater, NJ, U.S.A.) was connected directly to the column outlet.

An eight-port gas-sampling valve (Valco, Houston, TX, U.S.A.) was used for frontal (constant pressure) injection of samples for calibration purposes. The sample loop was modified to include either a gas cylinder and flow control valve (Porter VDC 1000) in the case of compounds which are gases below room temperature or,
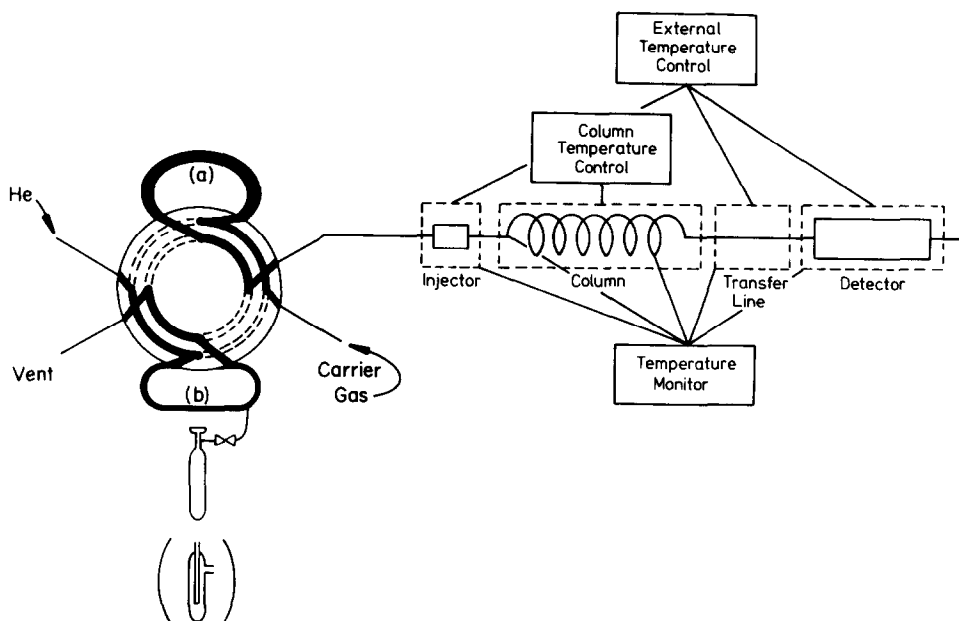
Fig. 1. Gas chromatographic system used to determine energy distributions, as modified for calibration purposes. With 8-port valve in *run* position, carrier gas flows through empty sample loop a before entering chromatographic system. In *calibrate* position, carrier gas enters the chromatographic system after flowing through sample loop b. A gas cylinder, flow control valve, and Swagelok union tee is added to sample loop b for calibration of response to gases, while a liquid bubbler is added for calibration of response to liquids.

in the case of compounds which are liquids at room temperature, a chamber in which carrier gas was sparged through the liquid.

A separate sensing and control circuit was used to maintain the temperature of the chromatographic injector and of the transfer lines. These components were maintained at temperatures great enough to insure volatilization in the injector and to prevent condensation in the transfer lines (normally *ca.* 20°C above the boiling point of the solute). The temperatures of the injector, transfer lines, detector, and column inlet and outlet were continuously monitored.

Helium (high purity, 99.995%, Matheson) was used as the carrier gas for all gas–solid studies. A molecular sieve trap was used to insure that no residual water vapor entered the chromatographic system.

Detector calibration

The frontal method was used to calibrate the TC detector. The adsorbates used in these tudies (butane and butene) are gases at room temperature and thus could be metered directly into the carrier gas stream. The partial pressure in the detector of the adsorbate, P_s, was calculated from

$$P_s = \left(\frac{F_s}{F_t}\right)P_0 \tag{12}$$

where F_s represents the adsorbate flow-rate (in ml/min) and is given by the total flow at the column outlet, denoted by F_t, minus the flow of carrier gas alone. Gas flows were measured by means of a conventional soap-film flowmeter. The pressure at the column outlet, P_o, was taken to be atmospheric (740 Torr). The detector was maintained at 70°C with a bridge current of 200 mA, the same conditions being used for determinations of retention volumes. The results of the calibrations are summarized in Table I. Note that the calibration curve is non-linear, the data being fit to a second order polynominal.

TABLE I

CALIBRATION OF MICRO-CELL THERMAL CONDUCTIVITY DETECTOR

Summary of fitting data: $P = A(mV)^2 + B(mV) + C$.

Compound	A (Torr/mV²)	δA	B (Torr/mV)	δB	C (Torr) (pressure at zero output)	δC	Reduced χ²*	Multiple correlation coefficient
n-Butane	$1.03 \cdot 10^4$	$0.78 \cdot 10^4$	0.341	0.036	−0.139	0.093	0.195	0.999
1-Butene	$2.15 \cdot 10^4$	$0.69 \cdot 10^4$	0.288	0.034	−0.861	0.089	0.677	0.997

* The sum of the squares of the deviations between individual values of detector response and those predicted from the fitting equation, divided by $n - 2$, where n is the number of data points.

Absorbates

Butane and 1-butene were obtained from Matheson Gas Products and were of instrument grade (99.5%) purity. The compounds were further purified by passing them through 10 cm × 4 mm I.D. silica gel columns before condensation at −77°C over calcium sulphate in a specially adapted test tube. The sample test tubes were modified by the addition of a threaded glass adapter to which a gas chromatography septum and plastic, single-bore stopcock were added. Samples were maintained at −77°C by immersion in a dry ice bath, and injections were made by first chilling a syringe (1-, 5-, 10- or 50-μl Hamilton microsyringes) in liquid nitrogen and then withdrawing and injecting the sample in the condensed phase. This method was found to be more reproducible than injections employing gas syringes.

Adsorbent

Kaolinite (kaolinite No. 9, Mesa Alta, NM, U.S.A.) was obtained from Ward's Scientific (Rochester, NY, U.S.A.). The kaolinite sample was gently crushed with a mortar and pestle and dry-sieved, all particles greater than 100 mesh (149 μm) being discarded. Kaolinite particles were then washed in 500 ml of an equivolume mixture of methanol–methylene chloride–benzene. The sample was elutriated extensively with deionized, double distilled water and dried in an evaporation dish at 110°C in an oven for a minimum of 24 h. The particles were then resieved to yield the 120–150 mesh (100–125 μm) fraction and drypacked under vacuum and with agitation into a glass column which had been deactivated by immersion in hexamethyldisilazane–pyridin (10:90, v/v). The column was 0.75 cm × 4 mm I.D. The pressure drop across

the column was maintained at 0.75 atm, resulting in a helium flow-rate of 15 ml/min. The surface area of the kaolinite was 26.0 m^2/g as determined by the three-point, nitrogen BET method. Porosity was 23.9% as measured by mercury porisimetry.

Mineral hydration

The kaolinite adsorbent was hydrated *in situ* by passing an inert gas (nitrogen) through a saturator chamber filled with water and held at a specific temperature, the vapor pressure of water in the gas stream being a function of this temperature. Water adsorbed to the mineral surface eventually equilibrates with the humidified gas stream, and a controlled level of hydration achieved. The water used for these studies was deionized, distilled over potassium permanganate and continually degassed during the course of the experiment.

The adsorbent column was connected to the outlet of the saturator and allowed to equilibrate with the water vapor until no further surface loading occurred, as indicated by a constant weight for the column. A 24-h period proved sufficient for equilibration. Stable hydrations were achieved at 25°C and 37°C, reflecting partial pressures of water of 24 and 47 Torr, respectively. The percent loadings (w/w) and number of monolayers which would result if water adsorbed as a series of perfect two-dimensional films are summarized in Table II. Water is assumed to have an adsorbed cross-sectional area of 12.2 Å^2 (ref. 16).

TABLE II

EXTENT OF ADSORBED WATER ON KAOLINITE

Adsorbent	Water saturator temperature (°C)	Vapor pressure of water (Torr)	Initial weight of adsorbent (g)	Final weight of adsorbent (g)	Percent* loading (w/w)	Number of ** theoretical monolayers
Kaolinite	25	24	15.582	15.722	0.90(0.90)	1.41
Kaolinite	37	47	15.582	15.753	1.11(1.09)	1.72

* Number in parentheses indicates amount of water still on surface after retention volumes were determined.
** From data of ref. 16.

Butane and butene retentive volumes were determined at −9.0°C. Even at this temperature, water has a substantial vapor pressure of 2 Torr. In order to insure that adsorbed water is not stripped from the adsorbent surface, a second saturator with water was inserted in the chromatographic system immediately upstream from the injector. The saturator was maintained at −6°C with an aniline–nitrogen slush bath in order to saturate the helium carrier gas and prevent column dehydration. The water level in the saturator was kept slightly below the gas inlet, so that the carrier gas was passed over the ice surface. Columns were weighed immediately before and after adsorption measurements, and the water loss was never greater than 1.8% of the original loading, as indicated in Table II.

Determination of retention volumes and data treatment

There are several methods for determining adsorption isotherms from chromatographic retention data, including the peak maxima[17], peak profile[18], step profile[19], minor disturbance[20], and equilibrium[21] methods. For this work, it is the first two which are of greatest interest, since these methods give directly the retention volume as a function of concentration. However, the multiple solute injections employed in the peak maxima method produce uncertainties in retention volumes, and thus the retention volume function must be smoothed by fitting the experimental results to an analytical expression such as eqn. 8. The uncertainties associated with multiple injections can be avoided by using the peak profile method, in which the retention time characteristic of various solute concentrations are obtained from a single chromatogram.

Equilibrium studies. The studies of Huber and Gerritse[22] demonstrated that the peak maxima and peak profile methods give similar adsorption results, provided that the pressure drop across the column is not so great as to affect the mass transfer of solute between adsorbed and mobile phases. In order to insure that the pressure drop of 0.4 atm used in these characterization studies was small enough that instantaneous mass-transfer equilibrium was obtained, a series of chromatograms of *n*-butyl chloride (dipole moment 2.1 D) was obtained on the kaolinite adsorbent. The criterion for equilibrium on the column was taken to be coincidence of the peak tails for different sample sizes[15].

As indicated by Fig. 2, the coincidence was essentially perfect in the case of this relatively strong adsorbate–adsorbent interaction, and thus the pressure drop used in these studies was considered small enough that such mass-transfer equilibrium was rapidly obtained.

Data analysis. Energy distributions were calculated from retention volume data by differentiating numerically the retention volume function at each data point instead of fitting the entire function to a polynomial expression. The method of undertermined coefficients[23] was employed for this differentiation. In this method, n adjacent data points are used to fit the curve to a polynomial of order $n - 1$ which can then be differentiated. This procedure is applied at each data point and, thus, the nature of one portion of the curve does not affect other segments. Furthermore, the differentiation is exact if the curve described by n data points can be represented by an $n - 1$ order of lower polynomial. Because the retention volume is a slowly varying function of solute concentration, a five point, fourth-order differentiation was considered sufficient for the present purposes.

Once a pressure drop has been established, a concentration gradient occurs along the column. This concentration gradient is due to the compressibility of gases, and the mobile phase concentration of solute in equilibrium with the adsorbed phase at each point along the column is not the same as that at the column outlet. The mobile phase concentration of the solute was therefore averaged over the entire length of the column by means of the James-Martin compressibility factor[24].

RESULTS AND DISCUSSION

The nature of dry kaolinite surfaces

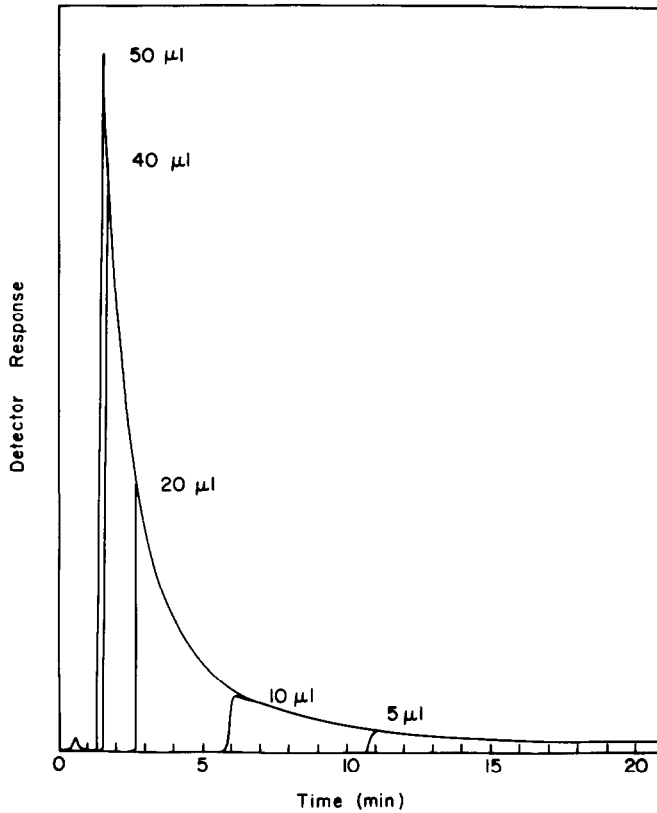While the active sites on clays have not been thoroughly characterized, the

Fig. 2. Chromatograms obtained at 88.75°C and 0.4 atm pressure drop on kaolinite column for various amounts of *n*-butyl chloride. Coincidence of peak tails is taken to indicate equilibrium is achieved under these conditions.

ion-exchange reactions of these minerals have received considerable attention. It is these reactions, and the known crystallography and morphology of clays, which can give insight into the character of their surfaces.

Kaolinite is a member of the phyllosilicate group of the silicate mineral class. The members of this group have a platey or flakey tendency and only one prominent cleavage[25]. This tendency to flake is due to the indefinitely extending sheet of SiO_4 tetrahedra, in which three of the four oxygens are shared with neighboring tetrahedra, leading to an Si:O ration of 2:5. Each sheet has six-fold symmetry, and the phyllosilicates are hydroxyl bearing with the hydroxyl group located in the center of the 6-fold rings of tetrahedra.

Cations bonded to the Si_2O_5 sheet are coordinated to two oxygen atoms and one hydroxyl group, and because the size of the triangle between the two oxygens and one hydroxyl group is approximately the same size as the triangular face of an MO_6 octahedron (M = Al or Mg), it is possible to bond the $(Si_2O_5OH)^{3-}$ sheet to a sheet of octahedra. The result is the classic "t-o" structure of kaolinite, built of one tetrahedral ("t") and one octahedral ("o") layer. These "t-o" units are bonded together by only weak van der Waals forces; hence the tendency to flake.

The surface chemistry of kaolinite is dominated by the surfaces of these layers which are exposed when the weak van der Waals forces are broken. The exposed surface of the tetrahedral sheet is a flat oxygen plane, whereas the octahedral-layer surface is a hydroxyl plane. Because electrical neutrality is maintained by atoms (Si in the "t" layer, Al or Mg in the "o" layer) which are not exposed to the surface when the t-o unit is cleaved, kaolinite exhibits a negative surface charge and considerable cation-exchange capacity, on the order of 3–15 mequiv./100 g[26].

When the t-o unit layer is disrupted and a surface not parallel to the flat unit layer exposed, a "broken-bond" or "edge" surface results, often exposing lattice cations. Since the uncompensated charges of these edge surfaces may be balanced by the sorption of anions, kaolinite shows a slight anion-exchange capacity in neutral solution (0.1 mequiv./100 g, ref. 27). However, the edges of kaolinite are, in general, neutralized at pH 5 or 6 (ref. 27).

In Fig. 3 are the energy distributions for butane and butene on kaolinite. These distributions appear to identify the two predominant sites on kaolinite, the oxygen
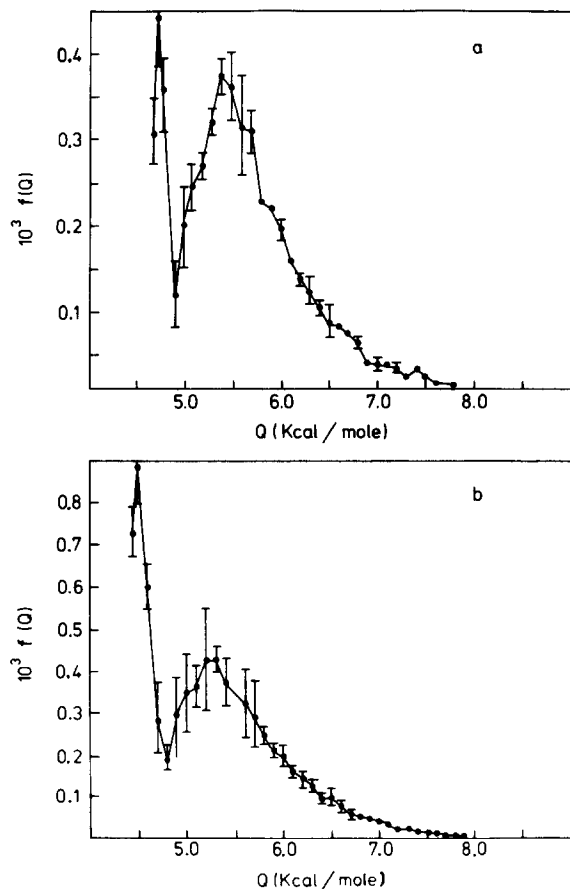

Fig. 3. Energy distributions on kaolinite determined at −9.0°C. (a) Butane and (b) 1-butene. Data points are the average of three independent values in each case, and the included ranges represent 95% confidence intervals.

(lower energy) and hydroxyl (higher energy) planes of the cleavage symmetry. It is important to note that the peaks on the distributions which reflect these two sites are both shifted to lower energies for butene (4.6 and 5.25 kcal respectively) relative to butane (4.8 and 5.4 kcal). This indicates a repulsive interaction between the π-electrons of butene and the two surfaces, and demonstrates both the constant negative charge of the flat oxygen plane[28], and the very poor hydrogen bonding characteristics of the kaolinite basal hydroxyl plane. There does not appear to be any involvement in adsorption by exposed cations at the edge surfaces.

The effect of water on surface properties

There has been considerable interest in the nature of water at or near surfaces. While spectroscopic methods are quite frequently employed, adsorption measurements have also been used in order to determine the extent to which interfacial water differs from bulk water[29-33]. A consensus has developed that water near surfaces is considerably different than bulk water, and that a dipole-ordered layer may extend for up to ten monolayers from a polar adsorbent[34]. Furthermore, it appears that water at the gas–liquid interface acts as low-energy surface for the adsorption of sparingly soluble vapors such as alkanes[35] and halogenated methanes[36].

Chromatographic measurements have been used extensively for these studies. This is a result of not only the sensitivity of chromatographic detectors, which allows the use of small sample sizes and thus low surface coverages, but also the difficulty of using conventional static methods with large surface loadings of water, since the very low pressures used remove all but the most tenaciously bound water molecules from the surfaces.

It is thus reasonable that the method of heterogenous chromatography should be applicable to studies of this type. There are certain restrictions, however, the primary one being the assumption of localized adsorption that can be described by Langmuir-type equations which relate surface interaction energies to equilibrium adsorbate pressures. For this reason, the present studies were done at column temperatures of $-9.0°C$, the assumption being that at this temperature multi-layer adsorbed water will exist on the surface in solid form. It is thus important to note that the object of this work is to monitor the extent to which small amounts of water "block" active sites on the surface of the adsorbent, and not to define in detail the properties of the surface-bound water itself.

Energy distributions for butane on dry and hydrated kaolinite are presented in Fig. 4. As in the case of distributions for dry surfaces, each data point represents the average of three measurements. The distribution of Fig. 4a is for a weight-percent loading (weight of water/weight of kaolinite) of 0.90%, while the distribution in Fig. 4b is for a loacing of 1.11%. From Fig. 4a it appears that bound water at this loading is situated preferentially on the high energy hydroxyl sites, effectively blocking these sites from participating in butane interactions. Further, it is apparent from Fig. 4a that water has not formed a complete monolayer at this loading, contrary to the calculations reported in Table II. Rather, it appears that water molecules are "clustering" around high energy sites, the strong adsorbate–adsorbate interactions resulting in multilayer formation at these sites instead of complete monolayer coverage of the entire surface. Keenan[37] observed similar variations in packing area for water molecules adsorbed onto kaolinite surfaces, and concluded that, for adsorbed water
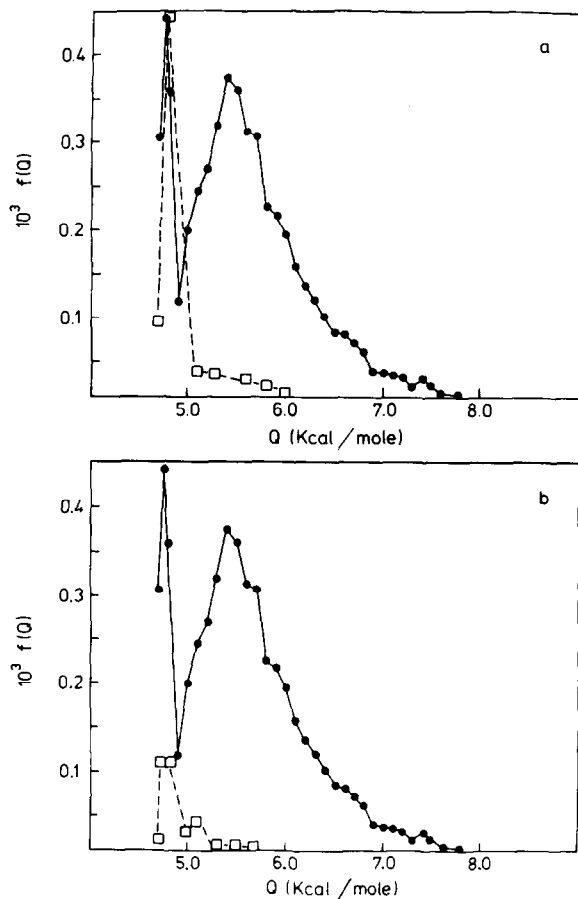
Fig. 4. Energy distributions for butane on dry and hydrated kaolinite surface. Solid line refers to dry surface, dotted line to hydrated surface. (a) Distribution for 0.90% hydrated surface, and (b) distribution for 1.11% hydrated surface.

molecules, the monolayer capacity, while still a valid parameter, does not refer to the usual concept of a monolayer.

At a loading of 1.1%, a significant number of low energy oxygen sites appear to have been affected, as indicated by the decreased magnitude of the 4.8 kcal peak. Further, at this higher loading, it also appears that a sufficient number of water molecules are located at the high energy sites so that some adsorption is occurring at these "water sites", as indicated by the appearance of the peak at 5.1 kcal. Note this agrees with previous suggestions that interfacial water is a lower-energy surface for adsorption of sparingly soluble compounds than the underlying surface[33,36].

Energy distributions for butene further reveal the nature of these hydrated surfaces (Fig. 5). The distributions determined at a loading of 0.90% show a trend somewhat different than that observed for butane. While the low energy sites are again unobstructed, it appears that the sites which are speculated to be water sites are already involved at this loading, as the 5.1-kcal peak has appeared. The broadness
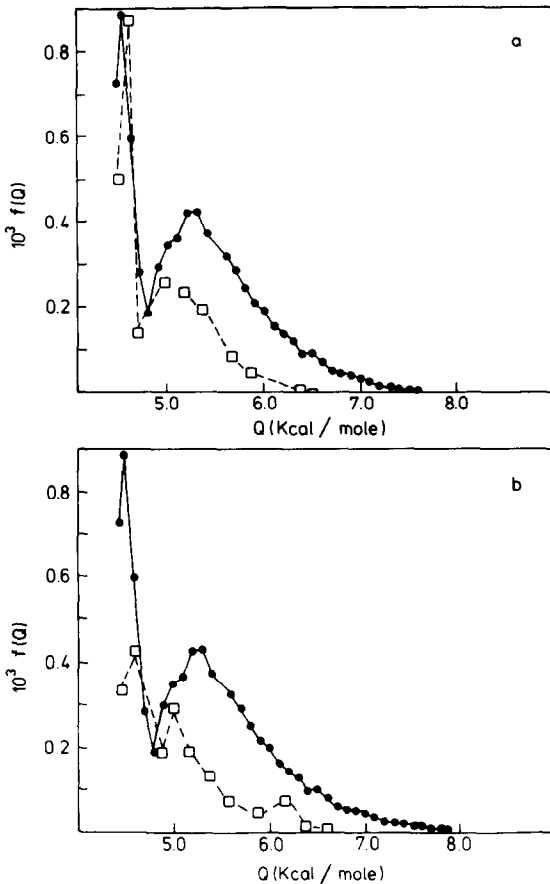
Fig. 5. Energy distributions for 1-butene on dry and hydrated kaolinite surface. Solid line refers to dry surface, dotted line to hydrated surface. (a) Distribution for 0.90% hydrated surface, and (b) distribution for 1.11% hydrated surface.

of this peak relative to both the 5.1-kcal peak for butane at 1.11% loading and the 5.1-kcal peak for butene at 1.11% loading (Fig. 5b) may be an indication that adsorption is occurring at both water sites and some immediately adjacent, unoccupied kaolinite surface sites. This is entirely plausible, in that the unsaturation of the butene molecule makes it less hydrophobic than butane. Karger *et al.*[35] observed mixed mechanisms of adsorption (adsorption at both the adsorbent surface and the surface of bound water) for slightly soluble aromatic hydrocarbons, whereas insoluble, saturated hydrocarbons were adsorbed exclusively at the bound-water surface.

The butene distribution at 1.11% loading is similar to the butane distribution at the same loading, in that the frequency of the 4.6-kcal site has been reduced, and the assumed water-site peak at 5.1 kcal is more distinctive. The decrease in the intensity of the low energy site for butene is not as pronounced as for butane, however, while the increase in the intensity of water-site peak is greater; in both instances this is assumed to result from the greater hydrophobic properties of butane relative to butene.

Finally, there appears in the butene distribution at 1.11% loading a high energy peak (6.20 kcal) not visible in the butane distribution at the same loading. This would most logically be a manifestation of a specific interaction between the π-electrons of butene and exposed hydrogen atoms in the water structure. Blank and Ottewill[33] demonstrated with adsorption studies of polar aromatic compounds that hydrogen atoms are exposed at the surface of adsorbed water layers.

CONCLUSIONS

Chromatographic retention volumes have been used to calculate energy distribution functions for the adsorption of butane and 1-butene on dry and hydrated kaolinite. The energy distributions clearly demonstrate that organic molecules are adsorbed on opposing faces of the primary cleavage plane of kaolinite, with little, if any, involvement of broken-bond, or edge, surfaces. Smaller adsorption energies for butene relative to butane indicate the presence of repulsive interactions between the π-electrons of butene and the two surfaces, demonstrating the constant negative charge of the flat oxygen pláne and the poor hydrogen-bonding characteristics of the basal hydroxyl plane.

Energy distributions for adsorption of butane and butene on hydrated kaolinite reveal that water is situated preferentially at high energy sites, and that the effectiveness with which water blocks these sites depends on the hydrophilic/hydrophobic nature of the adsorbate. Water does not appear to form a conventional monolayer on a kaolinite surface, but rather "clusters" around the high energy sites. Finally, these results confirm previous suggestions[33,35] that interfacial water is a lower energy surface for adsorption of sparingly soluble compounds than the underlying mineral surface.

These results represent only a beginning in understanding the complex nature of adsorption at mineral surfaces. It is encouraging, however, that this approach has been able to reveal subtle features of the surface adsorption characteristics of kaolinite, and further, that these features can be correlated with the known surface structure of the mineral. These results certainly do not represent the definitive statement about adsorption at clay surfaces; but they do demonstrate how heterogeneous chromatography can provide an experimental means for understanding adsorption at real mineral surfaces. Since minerals exist in nature with a variety of substances bound to their surfaces, heterogeneous chromatography should be ideally suited for studying the change in mineral surface properties due to the presence of organic substances such as humic and fulvic acids, inorganic substances such as exchangeable cations and/or anions, or even the dependency of surface properties upon the pH of associated waters.

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