

CHROM. 12,337

## GAS CHROMATOGRAPHIC ADSORPTION STUDIES ON SYNTHETIC IMOGOLITE

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(Received July 2nd, 1979)

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### SUMMARY

Non-equilibrium, pulse-injection chromatographic techniques have been employed to obtain the adsorption isotherms of a variety of hydrocarbons, water vapour and perfluorotributylamine on synthetic imogolite, an aluminosilicate mineral of tubular structure. With the aid of Dubinin plots, the micro-pore volume of the mineral has been computed and is seen to be dependent on the packing density of the adsorbate used as molecular probe. The isosteric heats of adsorption of a number of hydrocarbons have been determined; the values reported are in excess of those for hydroxylated silica gel.

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### INTRODUCTION

Naturally occurring imogolite is a fibrous, regular polymeric aluminium silicate mineral identified in several volcanic ash soils and other weathered pyroclastic deposits. The mineral consists of long tubes, typically greater than 1  $\mu\text{m}$  in length, with O.D. and I.D. of ca. 2.3 and 1.0 nm, respectively<sup>1</sup>. Examination of the dry material with an electron microscope shows the tubes to be partially aligned in bundles<sup>2</sup>, and the structure provides for a high specific surface. The walls of the tubes have a structure similar to that of gibbsite, with orthosilicate groups replacing the inner hydroxyl surface of the gibbsite tubes. This tubular structure has an empirical formula  $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$ , which is also the sequence of atoms encountered on passing from its outer to its inner surface. Removal of water, which activates the structure, creates a stable tubular lattice into which molecules may permeate depending on their molecular size. The material may be considered, therefore, as a molecular sieve.

The micro-porous nature of natural imogolite has been studied and characterised by Wada and Henmi<sup>3</sup> and Egashira and Aomine<sup>4</sup>. Wada and Henmi studied the retention of quaternary ammonium chlorides by the change induced in the X-ray pattern of the imogolite due to salt addition, and by the gravimetric determination of water vapour adsorbed at various relative humidities. Egashira and Aomine examined the effects of drying and heating on the surface area of imogolite, employing methods involving both nitrogen and 2-ethoxyethanol to monitor changes in surface area.

The results of these studies confirmed the micro-porous crystalline structure of natural imogolite.

Farmer *et al.*<sup>5</sup> have recently published the first synthesis of an imogolite analogue having a structure and properties similar to those of the natural mineral. The following report presents the results of a study of the adsorption characteristics of this synthetic material with a variety of non-reactive vapours as determined by pulse-injection gas chromatography at elevated temperatures. The results are consistent with synthetic imogolite having a micro-porous structure and exhibiting molecular-sieve characteristics. The isosteric heats of adsorption for a number of hydrocarbon vapours on synthetic imogolite are also recorded.

#### PHYSICO-CHEMICAL MEASUREMENTS FROM GAS CHROMATOGRAPHY

The majority of gas-solid adsorption studies are undertaken in closed static systems by volumetric or gravimetric determination of the adsorption isotherm. In recent years, however, several workers have reported on the use of gas chromatographic methods for the evaluation of physicochemical properties of adsorbents, and the subject has been reviewed by Sing<sup>6</sup> and Laub and Pecsok<sup>7</sup>.

Nelson and Eggertsen, in 1958, described a method<sup>8</sup> for the rapid determination of surface areas of adsorbents by using a continuous-flow, low-temperature chromatographic procedure. This was later modified by Roth and Ellwood<sup>9</sup> and Stock<sup>10</sup>. More recently, Ghosh *et al.*<sup>11</sup> have applied a comparative chromatographic technique using discrete sample injections. Huber and Gerritse<sup>12</sup> have reviewed and evaluated the dynamic gas chromatographic methods for the determination of adsorption isotherms. The results described here are based on the development by these workers of the non-equilibrium, pulse-injection techniques described as the peak-maxima method and the peak-profile method.

The application of the two methods may be appreciated with the aid of the diagrams shown in Fig. 1. By the peak-maxima method, Fig. 1(a), a series of chromatograms obtained by injecting differing aliquots of component *i* is recorded at constant temperature, *T*, and constant carrier-gas flow-rate. The peak-profile method, Fig. 1b, is similar to the peak-maxima method, but the distribution isotherm is obtained from a single chromatogram.

The average concentration of component *i* in the adsorbent stationary phase,  $C_i^s$ , and the average concentration of *i* in the mobile vapour phase,  $C_i^m$ , may be calculated from the equations

$$C_i^s = \frac{A}{sm} \text{ g g}^{-1} \quad (1)$$

$$C_i^m = \frac{nw}{vs} \text{ g cm}^{-3} \quad (2)$$

where *A* is the area ODEF on the recorder chart (after correction for diffusion), *n* is the deviation of the chart pen from the base-line, *w* is the recorder-chart speed, *v* is the average flow-rate of carrier gas in the column, *m* is the mass of adsorbent within the column and *s* is the sensitivity (defined as the peak area, before correction for diffusion, divided by the amount of component *i* injected).

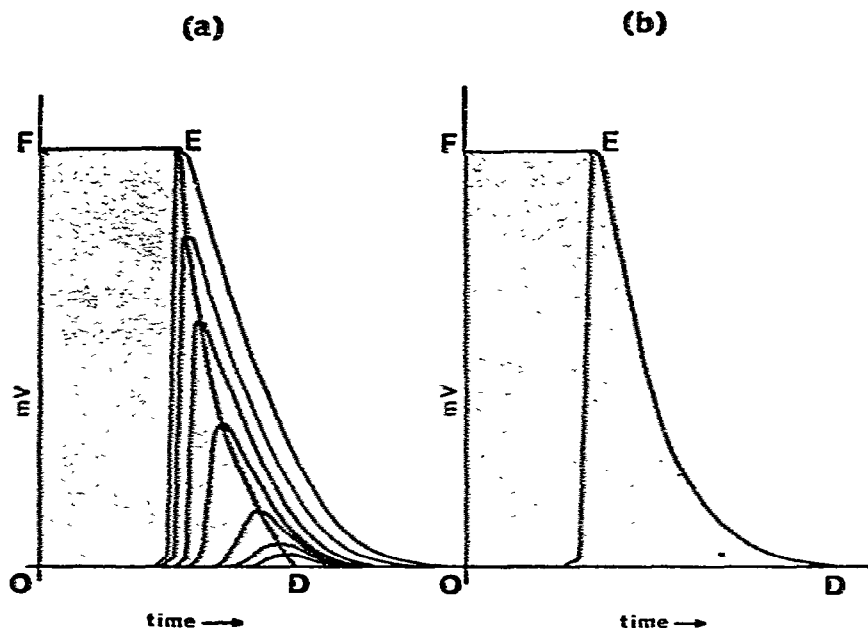


Fig. 1. Pulse-injection techniques for determination of adsorption isotherms: (a) peak-maxima method; (b) peak-profile method (following the classification by Huber and Gerritse<sup>12</sup>).

Assuming ideal-gas behaviour of the vapour, then the pressure,  $P$ , of the vapour concentration  $C_i^m$  is given by

$$P = \frac{C_i^m RT}{M} \quad (3)$$

where  $M$  is the molecular weight of component  $i$  and  $R$  is the gas constant.

## EXPERIMENTAL

The synthetic imogolite was prepared in the manner described by Farmer and Fraser<sup>13</sup>. Aluminium butoxide and silicon tetraethoxide were hydrolysed in perchloric acid, and the resulting solution was heated to 100°C. The imogolite was isolated from the acidic solution by neutralising the suspension with sodium hydroxide solution and repeatedly washing with distilled water, centrifuging the gel formed to remove salts. The gel was finally freeze-dried, and its purity and structure were confirmed by X-ray diffraction, electron microscopy and IR spectroscopy.

A sample of the air-dried imogolite powder was crushed to pass through a 150- $\mu\text{m}$ -mesh sieve, and *ca.* 1 g (accurately weighed) of that portion retained on a 106- $\mu\text{m}$ -mesh sieve was used to pack the glass chromatographic column (U-shaped; 45 cm  $\times$  2 mm I.D.). The packed column was mounted within a Pye chromatograph (model 104; Pye Unicam, Cambridge, Great Britain) and, with dry nitrogen as purge gas, was heated to *ca.* 200°C (473°K) and maintained at this temperature for at least 24 h to dry and activate the imogolite packing. After activation, the column was already for the adsorption studies.

The required column temperature was selected, and the column was allowed to equilibrate overnight with a constant flow of dried nitrogen. The nitrogen flow-rate was so adjusted as to provide 15–20 cm<sup>3</sup> min<sup>-1</sup> of nitrogen, measured with the aid of a soap-bubble flowmeter at the column outlet and the column flow-rate was calculated by applying a temperature-difference correction factor as discussed by Laub and Pecsok<sup>7</sup>. Because of the short column length used and the low gas flow-rate employed, the pressure drop across the column was assumed to be negligible. The signal from the detector and associated amplifier was recorded, as a function of time, by use of a conventional potentiometric chart recorder.

For most of the studies reported, a flame ionisation system was used as detector at the outlet of the column; however, a thermal-conductivity detector was necessary to study the adsorption of water vapour.

The adsorbates examined were obtained from a variety of sources; all were sufficiently pure as to provide a single, well-defined peak at the detector.

The peak-profile and peak-maxima methods were compared by using hydrocarbon adsorbates (*n*-pentane, *n*-hexane, cyclohexane and benzene) at a column temperature of 140°C (413°K). For the peak-maxima method, known aliquots of the hydrocarbons (*ca.* 0.1–1.0 mg) were injected on to the column with the aid of a calibrated syringe; each injection of each sample was repeated at least three times. The recorder traces were examined manually and corrected for diffusion as discussed by Dollimore *et al.*<sup>14</sup> and Bechtold<sup>15</sup>, and values of  $C_i^m$  and  $C_i^s$  were determined as discussed previously; the adsorption isotherm was constructed from these values. With the peak-profile method, a single aliquot (*ca.* 1 mg) of each hydrocarbon was injected on to the column, each injection being repeated at least three times. Again, after correction for diffusion,  $C_i^m$  and  $C_i^s$  were evaluated, and the adsorption isotherm was determined. For the series of hydrocarbons examined, no differences were observed between the isotherms obtained from the two methods. Because of its greater simplicity, therefore, the peak-profile method was used exclusively for the remaining studies.

At three selected temperatures, 140°C (413°K), 147°C (420°K), and 153°C (426°K), the adsorption isotherms were determined for *n*-butane, *n*-pentane, *n*-hexane, cyclohexane and benzene on synthetic imogolite using the peak-profile method. In a similar manner, the adsorption isotherms for water vapour and perfluorotributylamine (heptacosafuorotributylamine) were determined at column temperatures of 200°C (473°K) and 207°C (480°K), respectively.

For reference purposes, the adsorption isotherms of nitrogen on synthetic and natural imogolite were determined volumetrically with the aid of a Carlo-Erba Sorptomatic 1800 apparatus, in which the isotherm was recorded automatically by measuring the equilibrium pressure in the system after the introduction of a calibrated volume of nitrogen.

## RESULTS AND DISCUSSION

Fig. 2 shows the adsorption isotherms for nitrogen adsorbed on natural and synthetic imogolite samples, measured volumetrically with the Sorptomatic system at 77°K. The adsorption-pressure curve is of the form of a Type I isotherm and is characteristic of micro-porous adsorbents, *i.e.*, those containing micro-capillaries less than a few molecular diameters wide.

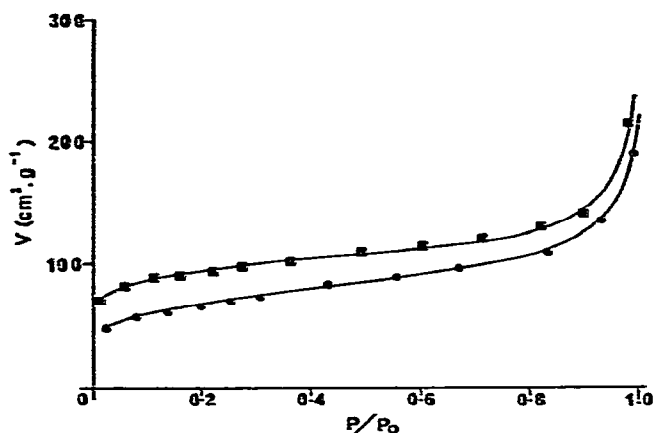


Fig. 2. Nitrogen adsorption isotherms for natural (■) and synthetic (●) imogolite; curves obtained by automatic volumetric analysis at 77 °K.

The classical interpretation of the Type I isotherm assumes the adsorbed layer to be one molecule thick and the plateau of the isotherm to correspond to the completion of this monolayer. However, this view has recently been modified, and it is now generally held that there is no monolayer point on the isotherm, but that the plateau region indicates filling of the micro-pores with adsorbate in liquid-like form, and it is common practice to determine from this the micro-pore volume. It is evident from Fig. 2 that the pore volume of the synthetic material is less than that of the natural imogolite, and Table I shows the pore volumes and surface areas, as determined from the classical Langmuir plot, for the two samples.

TABLE I

COMPARATIVE DATA FOR NATURAL AND SYNTHETIC IMOGOLITE FROM THE NITROGEN ADSORPTION ISOTHERMS

Adsorbent	Micro-pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>*</sup>	Surface area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>**</sup>
Natural imogolite	0.146	402
Synthetic imogolite	0.112	313

<sup>\*</sup> As  $\text{cm}^3$  of liquid nitrogen at 77 °K per g of anhydrous adsorbent.

<sup>\*\*</sup> As determined from the Langmuir equation and expressed in terms of anhydrous adsorbent.

The adsorption isotherms for *n*-butane, *n*-pentane, *n*-hexane, cyclohexane and benzene, and those for water vapour and perfluorotributylamine, are shown in Fig. 3; these were obtained with a gas chromatographic system as described above. According to Huber and Gerritse<sup>12</sup>, the isotherms obtained by these non-equilibrium techniques at low pressures are similar to those obtained by equilibrium methods, but at higher pressures are more linear (because of kinetic effects within the column). At the low pressure of adsorbate used in these studies, the plateau region of the isotherm (corresponding to micro-pore volume filling) is not attained, and thus the pore volume is not directly given. However, the adsorption-potential theory modified and discussed

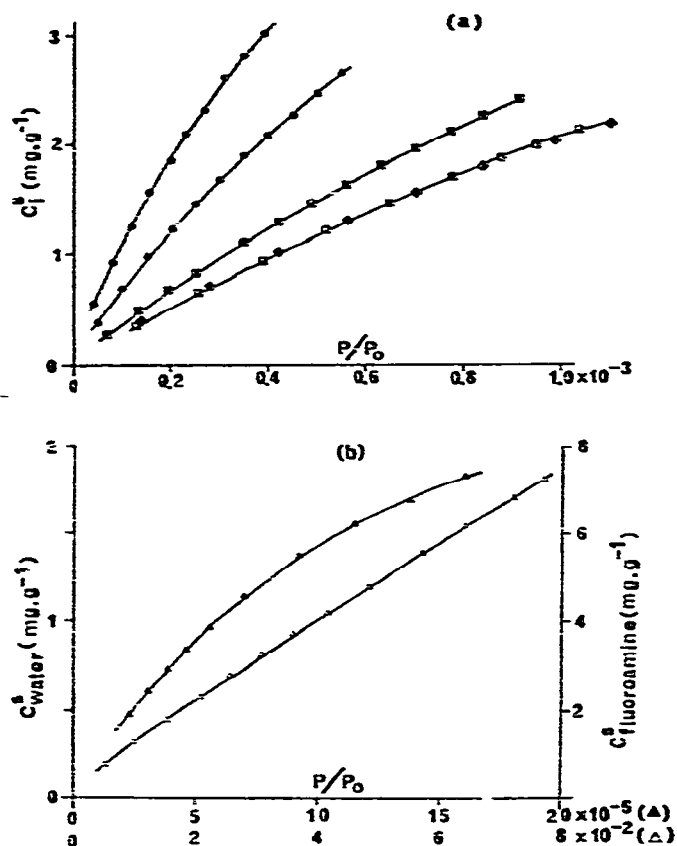


Fig. 3. Adsorption isotherms obtained by the peak-profile method with synthetic imogolite as adsorbent for: (a), benzene, (●), *n*-hexane (○), *n*-pentane (■), *n*-butane (□) and cyclohexane (◆) at 413 °K; and (b), water (▲) at 473 °K and perfluorotributylamine (△) at 480 °K.

by Dubinin<sup>16</sup> may be applied to the determination of micro-pore volumes. According to Dubinin,

$$\log_{10} C_i^s = \log_{10} (V_0 \rho) - B \left( \log_{10} \frac{P_0}{P} \right)^2 \quad (4)$$

where  $V_0$  is the total volume of micro-pores and  $\rho$  and  $P_0$  are the density of the liquid adsorbate and its saturated vapour pressure, respectively ( $B$  is a constant dependent on the affinity coefficient, the pore-size distribution and the temperature).

Thus, a plot of  $\log C_i^s$  vs.  $(\log P_0/P)^2$  should give a straight line of intercept  $\log (V_0 \cdot \rho)$ . Dubinin has found that eqn. 4 applies for a variety of adsorbates, within the range  $1 \cdot 10^{-5}$  to 0.2 relative pressures, on micro-porous adsorbents. The Dubinin plots calculated from the chromatographic isotherms according to eqn. 4 are shown in Fig. 4, and the data are tabulated in Table II. All gave excellent straight-line fits, with no coefficient of variation lower than 0.995 (the value for water vapour adsorption). The column temperature, within the narrow range examined, has no systematic effect on the value determined for  $V_0 \cdot \rho$ . The final column of Table II presents the

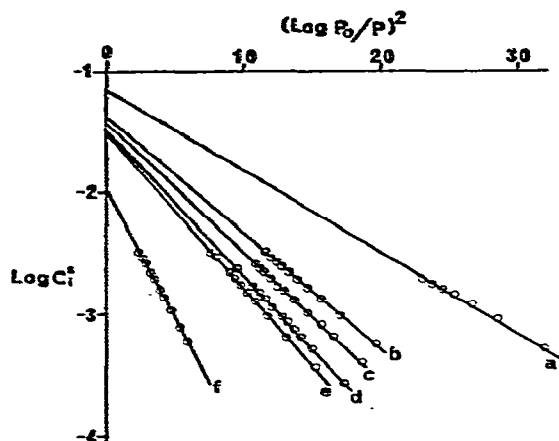


Fig. 4. Dubinin micro-pore volume plots for adsorption on synthetic imogolite: (a) water, 473 °K; (b) benzene, 413 °K; (c) *n*-hexane, 413 °K; (d) *n*-pentane, 413 °K; (e) *n*-butane/cyclohexane, 413 °K; and (f) perfluorotributylamine, 450 °K.

TABLE II

DUBININ PLOT DATA FOR SYNTHETIC IMOGOLITE

Adsorbate	$V_0$			$V_0^*$ ( $\text{cm}^3 \text{g}^{-1}$ )
	413 °K	420 °K	426 °K	
<i>n</i> -Butane	0.029	0.029	0.028	0.061
<i>n</i> -Pentane	0.030	0.030	0.028	0.057
<i>n</i> -Hexane	0.035	0.038	0.035	0.067
Cyclohexane	0.026	0.025	0.027	0.040
Benzene	0.039	0.035	0.035	0.050
Water		0.068**		0.083
Perfluorotributylamine		0.010***		0.0065

\* Assuming adsorbate densities at room temperature and anhydrous adsorbate.

\*\* Column temperature of 473.15 °K.

\*\*\* Column temperature of 450.15 °K.

values for the micro-pore volumes,  $V_0$ , calculated for the adsorbates studied assuming their liquid density in the chromatographic column to be similar to that at room temperature. Unfortunately, high-temperature liquid-density data are not readily available; as the cubic expansivity of hydrocarbons is typically  $10^{-3}$ – $10^{-4}$  °K $^{-1}$ , the values reported for  $V_0$  in Table II may be approximately 10% low because of error in the density value used. It is evident that the micro-pore volumes reported are dependent on the nature of the adsorbate and may be considered to be a function of its packing density within the imogolite structure.

The problem of adsorbate-adsorbent interactions in relation to molecular sieves has been examined by Gurfein *et al.*<sup>17</sup>. These workers computed the potential-energy curve for an adsorbate molecule within a pore as a function of the distance of the molecule from the nearest point on the pore wall. For a pore diameter of  $D$  and an adsorbate molecular diameter of  $d$ , they concluded that, if the ratio  $D/d$  is greater than 1.5, the potential energy of the molecule within the pore exhibits a ring

minima at approximately  $d/2$  from the wall. As the ratio  $D/d$  becomes smaller (by increasing the size of the probe molecule), repulsive forces play an increasing role, and, when  $D$  is less than  $2d$ , the pore can accommodate only one molecule, across its diameter. Thus, if  $2 \geq D/d \geq 1.5$ , the adsorbed molecule will move within a ring minimum inside the pore, and the packing density of the adsorbate will be lower than that of the pure liquid adsorbate.

In studying the molecular-sieve action of zeolites, it is normal to use molecular kinetic diameters to assess the apparent pore size of the zeolites. Breck<sup>15</sup> has discussed many examples of this, and, for the hydrocarbons used, the reported kinetic diameters range from *ca.* 0.43 nm for butane to 0.6 nm for cyclohexane. Electron microscopy and X-ray diffraction studies, as mentioned previously, show that the synthetic imogolite tube structure has an inner-tube diameter of *ca.* 1.0 nm, hence values of  $D/d$  range from *ca.* 2.3 for butane to 1.7 for cyclohexane. It is to be expected, therefore, that the packing density of these adsorbates within the imogolite pores will be lower than that in the bulk liquid, thus decreasing the apparent pore-volume measurements as shown in Table II, compared with the expected value of  $0.112 \text{ cm}^3 \text{ g}^{-1}$  determined by using nitrogen.

With perfluorotributylamine, the recorded kinetic diameter of the molecule is reported as being approximately 1.02 nm (ref. 18), *i.e.*, similar to the diameter of the pores within the imogolite adsorbent. Therefore, the diffusion of perfluorotributylamine within the micro-pores will be considerably less than that of the smaller hydrocarbon molecules; this is confirmed by the much smaller value recorded for the apparent micro-pore volume (see Table II) as determined by the Dubinin plot (Fig. 4).

The kinetic diameter of the water molecule (0.26 nm) is less than that of the nitrogen molecule (0.36 nm); thus, water may be expected to permeate totally within the imogolite structure and provide a greater value for the micro-pore volume than that obtained with the hydrocarbon probe molecules. From the Dubinin plot, the measured micro-pore volume using water vapour is  $0.083 \text{ cm}^3 \text{ g}^{-1}$  of anhydrous adsorbent, compared with the value of  $0.112 \text{ cm}^3 \text{ g}^{-1}$  when nitrogen is used. However, assuming a cubic expansivity of  $10^{-3} \text{ }^\circ\text{K}^{-1}$  at the column temperature used ( $473^\circ\text{K}$ ), then the reduced density of water provides a pore volume of  $0.091 \text{ cm}^3 \text{ g}^{-1}$ , *i.e.*, similar to that obtained with use of nitrogen.

The adsorption isotherms for the hydrocarbons examined were determined at three column temperatures ( $413$ ,  $420$  and  $426^\circ\text{K}$ ); from these isotherms, the isosteric heats of adsorption,  $q$ , were calculated. The isosteric heats of adsorption are derived from the adsorption isosteres and may be obtained from a plot of the log of the adsorbate pressure *vs.* the reciprocal of the absolute temperature at a constant adsorbate loading; the slope of such a plot is equal to  $-q/R$ . Typical plots of  $\ln P$  *vs.*  $1/T$  for the adsorption of benzene on synthetic imogolite are shown in Fig. 5 for a range of values of  $\theta$  [the adsorbate loading arc expressed as  $\text{cm}^3$  (STP) per g of adsorbent]. Similar linear relationships were obtained for the other hydrocarbons, and the isosteric heats of adsorption as a function of adsorbate loading (surface coverage) are shown in Fig. 6. Within the narrow range of adsorbate pressures examined in this work, the change in  $q$  with increasing surface coverage is very small, and the mean values are provided in Table III. Further, at the low pressures of adsorbate used, these may be considered the limiting differential heats of adsorption.



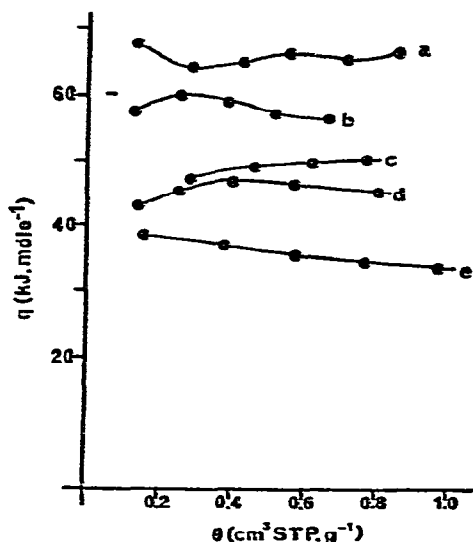
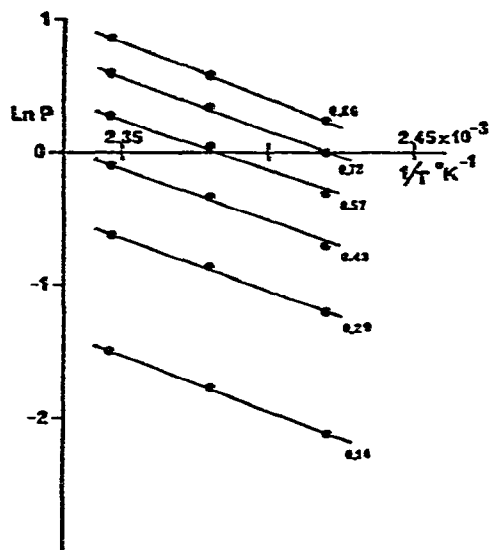


Fig. 5. Linear relationship between  $\ln P$  (adsorbate pressure) and  $1/T$  for benzene on synthetic imogolite at the indicated values of surface coverage ( $\theta$ ).

Fig. 6. Isosteric heats of adsorption ( $q$ ) as a function of surface coverage ( $\theta$ ) for (a) benzene, (b) *n*-hexane, (c) *n*-pentane, (d) cyclohexane and (e) *n*-butane on synthetic imogolite.

TABLE III

HEATS OF ADSORPTION OF HYDROCARBONS ON SYNTHETIC IMOGOLITE

Adsorbate	$q$ (kJ mole <sup>-1</sup> ) <sup>*</sup>	C.V. <sup>**</sup>	$q$ (SiOH) (kJ mole <sup>-1</sup> ) <sup>***</sup>
<i>n</i> -Butane	36.18	0.049	26.4
<i>n</i> -Pentane	49.05	0.026	30.5
<i>n</i> -Hexane	57.82	0.024	36.4
Cyclohexane	45.78	0.029	—
Benzene	66.65	0.024	43.1

\* The mean value of  $q$  from 10 results obtained with adsorbate loadings of  $\theta = 0.1$  to  $0.8$  cm<sup>3</sup> g<sup>-1</sup> of adsorbent.

\*\* Coefficient of variation (standard deviation/mean value) for the range of  $q$  values used.

\*\*\* Approximate heats of adsorption on a hydroxylated silica gel surface<sup>18</sup>.

Table III also provides the approximate heats of adsorption of the alkanes on hydroxylated silica gels, as discussed by Kiselev and Lygin<sup>19</sup>. The values for the tubular imogolite are greater by *ca.* 50% than those relating to the more macroporous structure of the silica gel. As with silica gel and zeolite molecular sieves, the heats of adsorption of the *n*-paraffins on imogolite become more exothermic with increasing number of carbon atoms within the adsorbate molecule and increasing polarizability of the hydrocarbon<sup>20</sup>.

CONCLUSION

Imogolite is a polymeric aluminosilicate mineral with a long tubular structure. The synthetic analogue of imogolite is known to exhibit a similar structure with tubes

of I.D. and O.D. ca. 1.0 and 2.0 nm, respectively. The micro-porous nature of the material, with its well-defined molecular dimensions and structure, is of interest in employing the material as a molecular-sieve adsorbent for the adsorption and separation of gas mixtures.

Dynamic, non-equilibrium gas chromatographic techniques have been used to obtain adsorption isotherms of a series of hydrocarbons (*n*-butane, *n*-pentane, *n*-hexane, cyclohexane and benzene), water vapour and perfluorotributylamine on synthetic imogolite. The results, compared with isotherms obtained volumetrically with nitrogen, indicate that the available pore volume of the material is a function of the molecular size of the probe gas used and the packing density of the liquid adsorbate within the micro-pores. Because of its large size, the fluorinated amine appears to be unable to enter the micro-pores of the mineral, thus leading to a small value for the micro-pore volume, whereas the hydrocarbons examined all provide similar pore volume results (ca. 50% of the volume calculated by using nitrogen as adsorbate). Water vapour, the smallest of the molecular probes, gave the highest recorded pore volume of the adsorbates examined by chromatography (only slightly less than that recorded for nitrogen adsorption). The results are consistent with the known internal structure of the synthetic imogolite.

The heats of adsorption of the hydrocarbons on synthetic imogolite were calculated from isotherms determined at column temperatures of 413, 420 and 426°K; the values determined for these isosteric heats of adsorption are in excess of those reported for hydroxylated silica gels.

#### ACKNOWLEDGEMENTS

I wish to acknowledge the National Research Development Corporation for the provision of a fellowship to undertake this study, and I thank V. C. Farmer and A. R. Fraser of the Macaulay Institute for the sample of synthetic imogolite.

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