Experimental determination of adsorption isotherm data for the study of the surface energy distribution of various solid surfaces by inverse gas–solid chromatography

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ABSTRACT

Fine, solid ceramic particles were coated on the inner wall of an open-tubular quartz column. The tube was filled with a slurry of the particles under investigation in an appropriate solvent, closed at one end and introduced slowly into an oven where the solvent vaporized. After thermal conditioning of the column, adsorption isotherms were determined by the classical method of elution of characteristic points, using large-size samples of organic vapors (diethyl ether, chlorobutane). These isotherms were used to calculate the distribution of adsorption energy of the probe on the ceramic surface.

INTRODUCTION

As suggested originally by Smidsrod and Guillet [1,2], gas chromatography can be used for the study of the properties of any material which can serve as a stationary phase. Chromatographic data are determined for a group of properly selected probe solutes. These data give clues regarding the interactions between these known molecules and the material under investigation. Results obtained by inverse chromatography have been reviewed by Gilbert [3]. This method is particularly suited to the analysis of solid surfaces, the only requirement being that the specific surface area of the sample exceeds about $1 \, m^2 \, g^{-1}$. Gas–solid interactions are strong and permit the use of small molecules as probe solutes, measurements being made at room or moderate temperatures. This is advantageous because, for nearly any type of interaction, it is possible to select a small molecule which embodies it almost exclusively.

Except for the determination of equilibrium isotherms, however, almost all the applications of inverse chromatography have been carried out un-der linear conditions [3]. For example, Guillet and co-workers have developed methods to measure the glass transitions of polymers [1], to study the temperature dependence of their crystallinity [4–6] and to determine the Flory interaction parameter [2, 4] and the Hildebrand–Scatchard solubility parameter [1,2]. Several studies have investigated various aspects of heterogeneous catalysis [7]. The fate of toxic solutes adsorbed on fly ash [8] and diesel particulate matter [9] has been studied. In all instances, except for the determination of isotherms, *e.g.*, with the elution by characteristic points (ECP) method, small amounts of the probe compounds are injected and the interactions at infinite dilution only are investigated. Although there have been many applications of the ECP method for the determination of single-component isotherms, the precision and accuracy of the results obtained have not been studied in great detail so far.

Gas–solid chromatography has been used for a long time to measure rapidly and conveniently the equilibrium isotherms of gases and vapors on the surface of adsorbents [10]. Several chromatographic methods have been developed. The most accurate is

probably frontal analysis [11,12], but it is not very convenient to implement in gas chromatography where ECP is preferred [13]. The detailed study of the properties of equilibrium isotherms for a group of selected probe solutes is very informative regarding the properties of the surface considered [10]. This is especially true if the surface is heterogeneous.

Although the concept of energetic heterogeneity of surfaces was introduced long ago by Langmuir [14], interest in studying this property as a means of material characterization did not develop until the past 20 years. Even in chromatography, where peak tailing is systematically blamed on the occurrence of active sites on the surface of the adsorbent or of the support used in gas–liquid chromatography [15], few experimental investigations of the energetic heterogeneity of the surface of the material used have been made [16]. The basis of these studies is the calculation of the adsorption energy distribution function of a series of probe compounds from their adsorption isotherms [16]. These functions provide valuable qualitative information regarding the energetic heterogeneity of the surface. More importantly, it has been shown that thermodynamic quantities (e.g., monolayer energies) may be calculated from the energy distributions obtained from inverse gas chromatographic experiments [17]. Thus, the surface energetics may be parameterized, and the information obtained may be much more useful for the characterization of the material than, for example, the retention times of the probe compounds, their retention indices or even their adsorption isotherm data. Considerable effort has been devoted recently to the calculation of physically meaningful energy distribution functions [16,18].

We are investigating the surface properties of ceramic powders used for the manufacturing of advanced ceramic materials. Lack of lot-to-lot reproducibility of the ceramic material properties has been blamed on differences between the chemistry of the particle surface [19]. The procedure we have developed involves the determination of the adsorption isotherm of probe solutes and the calculation of the adsorption energy distribution [18]. We have found that reproducible results can be obtained only if great care is taken to follow a carefully established procedure, minimizing the experimental errors. This paper describes the experimental procedure. A companion paper presents an analysis of the errors made

in the determination of equilibrium isotherms by the ECP method [20]. In a separate paper we present results obtained when applying the method to a series of alumina samples [21]. The same procedure could be applied to the study of stationary phases for chromatography, especially in connection with the investigation of tailing problems.

THEORY

Derivation of the adsorption isotherm by ECP

The chromatograms of the probe solutes used with alumina (diethyl ether and 1-chlorobutane) have a very sharp front and a tailing rear. These band profiles correspond to a convex upwards isotherm [10]. The isotherm is derived by integrating the rear (*i.e.*, diffuse) profile [13]. The points on the adsorption isotherm, $q(P)$ (moles of adsorbate per unit mass of adsorbent), are given by a quadrature:

$$q(P) = \frac{1}{J_3^2 \, R \, T} \int_0^P V_N(P) \, dP \qquad (1)$$

where P is the partial pressure of the probe, $V_N(P)$ is the specific retention volume corrected for the void volume, T is the column temperature, R is the universal gas constant and J_3^2 is the James and Martin correction factor [15]:

$$J_3^2 = \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \qquad (2)$$

where P_i and P_0 are the inlet and outlet pressures of the carrier gas.

The essential measurement problem is the conversion of the chromatogram, a profile of detector signal *versus* time into a profile of probe partial pressure *versus* specific retention volume. Then the application of eqn. 1 is straightforward.

Determination of the distribution of adsorption energy

If we assume that the adsorbent surface is heterogeneous and that $f(E)$ is the distribution of the adsorption energy over a certain energy range, Ω, we need to calculate $f(E)$. $f(E) \, dE$ is the amount of probe component adsorbed per unit mass of the adsorbent studied, with an adsorption energy between E and $E + dE$ [22]. We measure the adsorption isotherm, which is the total amount of material adsorbed by the surface when in equilibrium with a

gas where the probe partial pressure is P. The global adsorption isotherm is

$$q(P) = \int_\Omega \Theta(E, P) f(E) \, dE \qquad (3)$$

where $\Theta(E, P)$ is the local equilibrium isotherm of the adsorbate probe on the part of the surface which has an adsorption energy between E and $E + dE$. Only $q(E)$ is experimentally accessible, but we need to determine $f(E)$ and $\Theta(E, P)$. This problem is ill-posed and does not have a unique solution [23]. It has been extensively discussed in the literature [16,18] and it is not the purpose of this paper to discuss a new solution. The results reported here have been obtained in an attempt to implement the original solution described previously [18].

EXPERIMENTAL

The procedures have been elaborated carefully to achieve a high level of reproducibility of the data and good accuracy. For this reason, we have developed the instrumentation which permits easy detector calibration or other measurements (*e.g.*, volume flow-rates). When these measurements are easy, it is possible to repeat them often and make sure the instrument response is stable, and possible drifts can be corrected for.

Chromatograph

Chromatographic data were obtained on a Perkin-Elmer (Norwalk, CT, USA) Model 8500 gas chro-
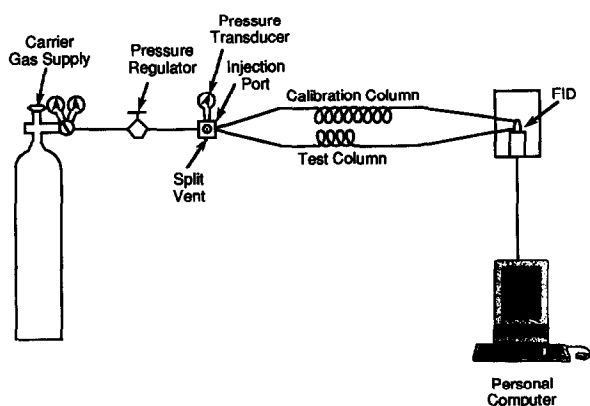

Fig. 1. Schematic diagram of the chromatographic system used to record overloaded elution band profiles.

matograph. The only instrumental modification required was to move the inlet pressure transducer to a position on the inlet carrier gas line which is closer to the injection port. The purpose of this modification was to reduce the pressure drop (to a negligible value at the flow-rates used) between the transducer and the column inlet. This gives a more accurate measure of the column inlet pressure. The analogue output from the flame ionization detector was digitized and recorded on an IBM PC. The computer was interfaced to the chromatograph by an I/O board (Data Translation, Marlborough, MA, USA) which used 12-bit A/D conversion and was controlled by in-house written software.

To permit accurate calibration of the detector and quantitative analysis, two parallel columns were used, a calibration column on which the probe is retained without experiencing irreversible adsorption and the column made with the ceramic material studied. The flow scheme of the gas chromatograph is shown in Fig. 1. Both columns are connected directly to both the injector and the detector using a two-hole ferrule. No-hole 40% graphite–60% Vespel ferrules were purchased from Alltech (Deerfield, IL, USA) and drilled in-house. The inlet pressure was 5.0 p.s.i. and the dimensions of the two columns are such that the calibration column peak elutes after the test peak has returned to the baseline.

In the measurements performed here, contrary to analytical applications of chromatography, it is important to know the exact amount of sample injected into the column. Therefore, syringe injection volumes must be both accurate and precise. It is necessary that the syringes used be of the type in which the injection volume is contained entirely in the needle, so that one is certain that the entire desired injection volume is vaporized in the injection port. A 0–5-μl Hamilton syringe (Model 7105NCH, obtained from Alltech), equipped with a Chaney adapter and needle spacer was calibrated by weighing injection volumes of water on a Cahn 28 automatic electrobalance (Cahn Instruments, Cerritos, CA, USA).

Chemicals

Solvents. Dimethyl sulfoxide (DMSO) was of high-performance liquid chromatographic (HPLC) grade from Aldrich (Milwaukee, WI, USA). Methanol was of HPLC grade from Baker (Phillipsburg,

NJ, USA) and was dried over 3 Å molecular sieves.

Ceramic material. A typical alumina powder used for the preparation of alumina ceramics was used. High-purity α-alumina [product identification number RHPC-DBM (w/o MgO), lot number BM-2216] was obtained from Malakoff Industries (Malakoff, TX, USA). The powder had been dry bore milled by the manufacturer to an average particle diameter of 0.5–0.8 μm. The surface area measured by the BET method was 8–10 m^2 g^{-1}.

Probe solutes. HPLC-grade diethyl ether preserved with 0.1 ppm of 2,6-di-*tert.*-butyl-4-methylphenol (BHT) was obtained from Aldrich. Chloroform (HPLC grade) was obtained from Burdick & Jackson (Muskegon, MI, USA). 1-Chlorobutane and pyridine (both of HPLC grade) were obtained from Aldrich. Each of these solutes was used as received.

Column preparation

Ceramic materials are prepared by firing cast forms made from very fine, solid particle powders. Because such fine particles filling a column of reasonable length would yield a prohibitively high back-pressure, we decided to use porous-layer open-tubular (PLOT) columns instead. The PLOT column was fabricated using a dynamic method similar to that described by Halasz and Horvath [24] for making support-coated open-tubular (SCOT) columns.

Preparation of ceramic powder sample. A 500-mg sample of the alumina powder was dried for 24 h in a vacuum oven (150°C, 381 Torr vacuum gauge pressure). It was then suspended (1%, w/v) in DMSO by placing the volumetric flask containing the mixture in an ultrasonic bath for 30 min. Heating of the suspension while in the bath was prevented by periodically measuring the bath temperature and adding ice chips to the bath as needed. The slurry was poured into a 1/8-in. O.D. stainless-steel tube, similar to those used to prepare chromatographic columns, which was fitted with 1/8-in. O.D. glass tube ports to allow Swagelok connections to the quartz column and to the helium pressure regulator.

Preparation of column tubing. The silica tubing (16 m × 530 μm I.D.) (Alltech Europe, Nazareth, Belgium) was prepared by rinsing with *ca.* five volumes of dry methanol and conditioning in a gas chromatograph at 320°C for 72 h with a helium inlet pressure of 1.0 p.s.i. The tubing, already placed on a tared low-thermal-mass column cage, was then weighed on an analytical balance which was contained in a glove-bag (I^2R, Cheltenham, PA, USA) filled with dry helium. The length of the tubing was determined by measuring it with a meter stick.

After a dry weight had been obtained for the silica tubing, it was prepared by placing a drawing hook and a drag hook on the proximal and distal ends, respectively. Each hook was constructed by attaching a loop of narrow-gauge copper wire to the respective end of the silica tubing with shrinkable PTFE tubing (Alltech). The purpose of these hooks is to provide a convenient means to attach a line to each end of the tubing.

Finally, the distal end of the column must be closed to prevent leakage of the stationary phase slurry during the coating procedure. A plug was constructed as follows. A custom-fitted seat for the plug was provided by attaching a section of 0.06-in. I.D. shrinkable PTFE tubing to the distal end of the silica tubing so that a 1.5-in. long piece of shrinkable PTFE tubing extended out past the end of the silica tube. This "hole" was then shrunk around the plug, a stainless-steel sewing needle (size 7, betweens). The plug was withdrawn as the PTFE cooled (at the point when it turned from translucent to opaque) so that the lumen of the PTFE tubing was formed into the shape of the needle.

Coating apparatus. A schematic diagram is shown in Fig. 2. It consists of a mechanical convection oven (Gallenkamp, Loughborough, UK) which was modified in-house. A 1/8 rpm high-torque electric motor (Cramer, Old Saybrook, CT, USA) was provided to turn the upper hub. The thermal gradient was constructed by passing a length of 1/4-in. O.D. stainless-steel tubing through the floor of the oven (see Fig. 3). Heated nitrogen (10 p.s.i. at the gas cylinder) flowed into this tube from a tee just below the floor of the oven. The downward flow of hot gas caused the thermal gradient tube to be heated in an approximately linear fashion, room temperature at the bottom end and the temperature of the oven at the top end. This was confirmed by drawing a thermal transducer up the tube and measuring the temperature in the tube as a function of distance traveled up the tube. The upward flow of nitrogen aided the convection motor in purging the oven of the potentially explosive DMSO–air mixture. The
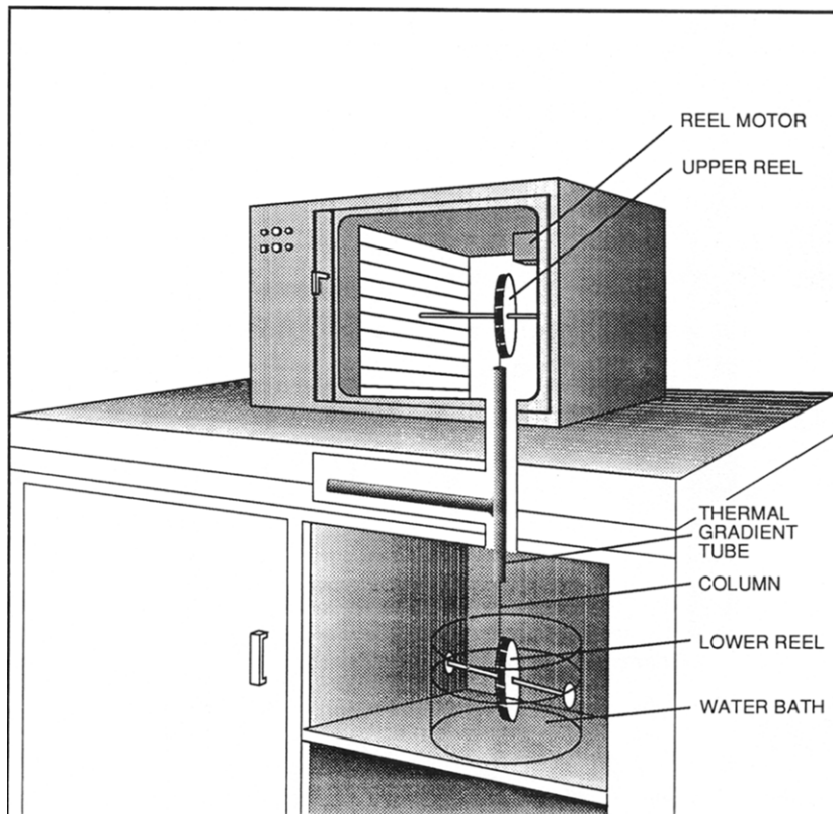
Fig. 2. Schematic diagram of the apparatus used to manufacture PLOT chromatographic columns.

oven was placed in a fume-hood and the thermal gradient tube traversed the floor of the hood.

Coating procedure. The suspension was pumped into the proximal end of the column from the chromatographic precolumn under 20 p.s.i. helium pressure. After the column had been filled and while the suspension was flowing from the distal end of the column, the hole was plugged. The integrity of the plug was insured by passing a piece of copper wire through the eye of the needle and through a pair of holes previously drilled in the wall of the PTFE tubing. This plugging method is adapted from the method suggested by Sandra and Verzele [25] but was found to be much easier experimentally.

Because of the strong tendency of fused-silica tubing to straighten, great care must be exercised in winding it around the lower hub. Also, the proper tension must be maintained on the tubing as it is drawn off the lower hub, through the thermal gradient and on to the upper hub. For that purpose, a drawing line was attached to the drawing hook at the proximal column end. This line was passed through the thermal gradient tube and attached to the upper hub so that, when the upper hub turned, the proximal end was drawn into the oven. Similarly, a drag line was attached to the distal end. This line was attached to the lower hub so that, as the column was drawn into the oven, proper tension was maintained, on the column by the resistance (to rotation) of the lower hub against the water in the bath.

The column, wound on the lower hub, was then placed in the room-temperature water-bath, drawn through the thermal gradient tube and coiled on the upper hub. Approximately 4 h were required for a 16-m column to be drawn into the 250°C oven. The velocity of the column was set so that the DMSO vaporized and its meniscus stabilized somewhere in
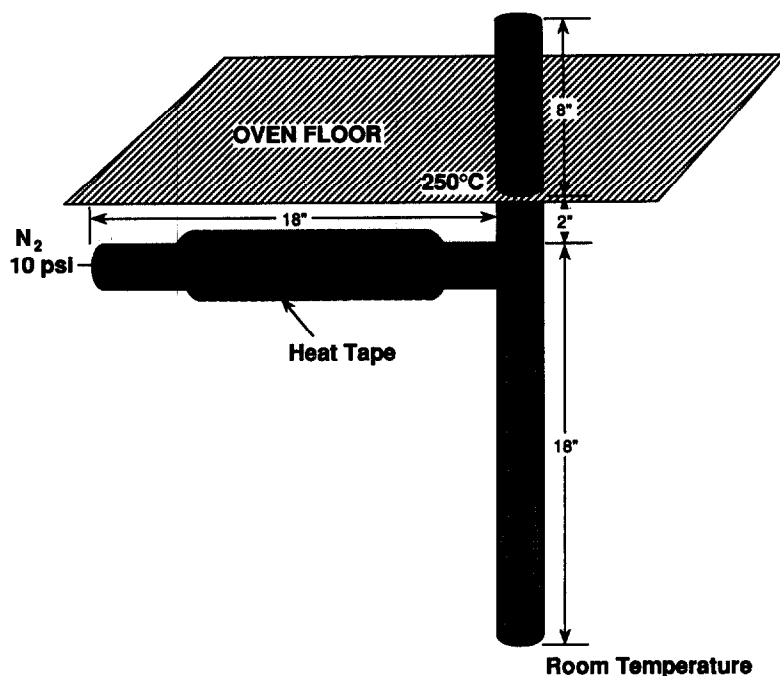
Fig. 3. Detailed schematic diagram of the thermal gradient tube.

the thermal gradient along the metal tube. When the entire length of the column was in the oven, it was cooled to room temperature. The column was placed on the column cage and 0.5 m of tubing were removed from each end. It was placed in the gas chromatograph and conditioned using 1.0 p.s.i. (inlet pressure) helium carrier gas and a slow temperature ramp followed by a 72-h period at 320°C.

Detector calibration

Detector calibration is needed to transform the profiles, which are initially recorded as detector signal *versus* retention time elution profiles, into solute partial pressure *versus* retention time elution profiles. Earlier experimental work with alumina and several other energetically microscopically heterogeneous ceramic powders (silica, nitrides and carbides), using a variety of probe solutes, revealed that, if the chromatogram is measured at a temperature where the probe is significantly retained, not all of the material injected elutes before the detector signal appears to have returned to the baseline. Because of this phenomenon of quasi-irreversible

adsorption, the amount of solute injected into the column does not correspond to the area of the elution profile. Hence there is no simple way to perform the calibration. Further, this calibration has to be repeated often to determine the amount of probe compound unaccounted for by the detector signal and to control possible drifts of the detector.

Therefore, calibration is performed using a calibration column which is parallel to the measurement column. There is no irreversible adsorption on the calibration column and the probe solute elutes from it after the end of the tail of its band on the main column.

The detector response curve is a plot of the area (V min) of the calibration-column peak (which is Gaussian) *versus* the amount injected (mol). It is determined periodically and it has always been found to be linear. The slope of this straight line is designated S_1. It is calculated from the average of a number of points. Care was taken to insure that the range of peak heights in the calibration graph included the peak height of all the test peaks. The sensitivity, S_2 (solute partial pressure in atm over detector response in V) is determined by assuming

that (i) the outlet flow-rate is not perturbed by the passage of the band and (ii) that no solute is lost through irreversible adsorption in the calibration column. S_2 is given by

$$S_2 = \frac{R\,T}{(1 + S_{P,1})(1 + S_{P,2})\,S_1\,F_0} \qquad (4)$$

where R is the universal gas constant (atm ml mol^{-1} K^{-1}), T the absolute column temperature (K), F_0 is the total outlet flow-rate of both columns and $S_{P,1}$ and $S_{P,2}$ are the splitting ratios corresponding to the inlet (injection) splitter and to the flow split between the two columns, respectively. The splitting ratios are determined by measuring the volumetric flow-rates out of the two columns and out of the inlet split vent using a soap-bubble flow meter. The measurement method is described in the next section.

Calibration column. A 60 m × 320 μm I.D. DB-5 column was obtained from J&W Scientific (Folsom, CA, USA). It was shortened to 40 m for this experiment, in order to balance properly its retention time and pneumatic resistance with that of the measurement columns.

Experimental procedure for isotherm determination

We have to measure the flow-rates and the splitting ratios, to estimate the amount of probe compound which is not eluted from the column after the signal has apparently returned to the baseline and to relate the partial pressure of the eluate to the detector response, which is done using the detector calibration (see above).

Flow-rate measurements. Because the PLOT columns are fragile, it is undesirable to disconnect them from the flame ionization detector each time data are collected in order to measure the outlet flow-rates. However, one must have an accurate knowledge of the flow-rates and the two splitting ratios in order to perform the physico-chemical calculations and these parameters change in response to changing experimental conditions. Therefore, the following procedure is used.

After a stable weight is obtained for the column, it is installed in the chromatograph along with the parallel calibration column and conditioned for an additional 24 h at 320°C with an inlet pressure of 5.0 p.s.i. The outlet flow-rates of both columns are measured while the columns are held at constant

temperature. This is accomplished by connecting each column in turn to the thermal conductivity detector and attaching the flow meter to the flow output port of the detector. The two volumetric outlet flow-rates, $F_{0,T}$ and $F_{0,C}$ for the test (PLOT) column and the calibration column, respectively, are corrected for the temperature differential between the column and the flow meter and for the vapor pressure of water, using the equation given by Karger *et al.* [26]. The corrected outlet volumetric flow-rate from the test column is then

$$F_{0,T} = F_{M,T} \cdot \frac{T}{T_M} \cdot \frac{P_M - P_W}{P_M} \qquad (5)$$

where $F_{M,T}$ is the flow-rate measured at the flow meter whose pressure and temperature are P_M and T_M, respectively, P_W is the vapor pressure of water at temperature T_M and T is the column temperature.

These outlet flow-rate measurements are made only once, before the two columns are connected to the flame ionization detector. Subsequent flow-rates are calculated, based on their proportionality to the void times (measured accurately on the chromatograms) and to the outlet flow-rates initially measured.

Void volume determination. The column void volume, $V_{M,T}$, is calculated from the measured outlet flow-rate. For the test column this is given by

$$V_{M,T} = F_{0,T}\,t_{0,T}\,J_3^2 \qquad (6)$$

where J_3^2 is the James–Martin correction factor (eqn. 2) and $t_{0,T}$ is the void time for the test column measured immediately after measuring the outlet flow-rates. The void volume for the calibration column, $V_{M,C}$, is calculated similarly. The molar flow-rate is then calculated on subsequent days (or when experimental conditions change) by assuming an ideal mobile phase. For the test column, the molar flow-rate $\dot{F}_T$ is given by

$$\dot{F}_T = P_M\,V_{M,T}/R\,T\,J_3^2\,t_{0,T} \qquad (7)$$

The molar flow-rate for the calibration column, $\dot{F}_C$, is calculated similarly. The corrected molar flow-rate from the inlet splitter port is calculated from daily measurements:

$$\dot{F}_{SV} = F_{SV}(P_M - P_W)/RT_M \qquad (8)$$

where F_{SV} is the volumetric flow-rate measured at the flow meter.

Determination of splitting ratios. The splitting ratios may then be calculated by

$$S_{P,2} = \dot{F}_C/\dot{F}_T \qquad (9)$$

and

$$S_{P,1} = (\dot{F}_T + \dot{F}_C)/\dot{F}_{SV} \qquad (10)$$

The validity of the assumption that the void volumes remain constant is tested daily, by calculating the ratio of the void times of the two columns and comparing the result with the value derived on the day the columns were installed in the chromatograph. Once, after a column had been left to condition for 1 week, the deviation between the initial void time ratio and a subsequent ratio exceeded 1% (relative). The two columns were carefully disconnected from the flame ionization detector and their outlet flow-rates measured again, as described above.

Even methane is slightly retained on alumina at the column temperatures used. Measurements of the retention times of methane and nitrogen performed with a thermal conductivity detector indicate a retention factor of 0.025 for methane at 60°C. This would result in a 2.5% systematic error on the void volume at 60°C. As the correction remains small, an attempt was made to calculate the void times from the retention times of a homologous series of linear alkanes, methane, ethane and propane [27]:

$$t_{0,T} = -\frac{t_{R,2}^2 - t_{R,1}t_{R,3}}{t_{R,1} + t_{R,3} - 2t_{R,2}} \qquad (11)$$

where $t_{R,1}$, $t_{R,2}$ and $t_{R,3}$ are the retention times of methane, ethane and propane, respectively, determined by calculating the first statistical moment of each peak. The method is not accurate, however, and we chose to measure the methane retention time and to correct it for the retention of methane, using the measured figure given above ($k' = 0.025$).

Probe mass balance. With each of the adsorbent–adsorbate pairs we have studied, a broadened second peak was recorded when the column was thermally conditioned between runs by heating on a 20°C min^{-1} ramp to 320°C and maintaining the column at the high temperature for 5 min. A typical example chromatogram is shown in Fig. 4. Considerable attention was paid to this phenomenon because the occurrence of irreversible or slowly reversible adsorption in studies such as ours is highly undesirable [20]. In the former instance, the solid
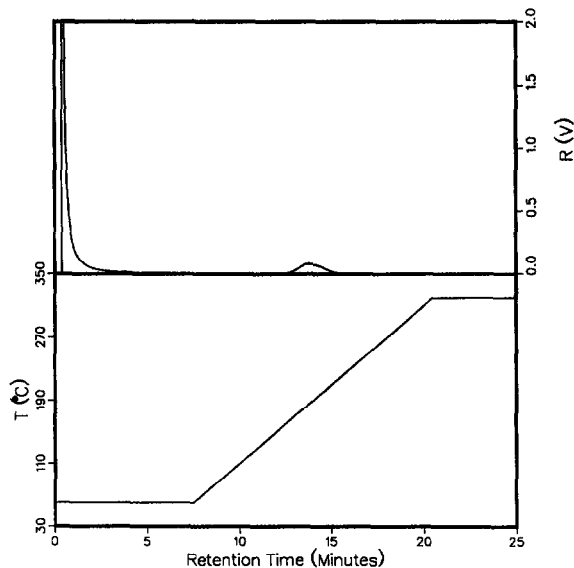

Fig. 4. Top: chromatogram obtained with an alumina column, showing the presence of a diffuse peak which elutes during column conditioning, between measurement runs. Experimental conditions: probe solute, diethyl ether; column temperature, 60°C; inlet pressure, 1.34 atm; $t_0 = 22.7$ s; outlet pressure, 1.0 atm; carrier gas, helium; column, 15 m × 0.53 mm I.D.; mass of stationary phase in the column, 44 mg. Peak areas (V min): large non-linear peak, 0.911; small diffuse peak, 0.087. Bottom: temperature program used to condition the column between runs.

surface is chemically altered and the isotherm data would be inaccurate. Material which is irreversibly adsorbed may be detected by making two successive injections of the same amount of probe compound at short intervals and thermally conditioning the column between the two runs. If the area of the second peak is greater than the first, one may suspect that irreversible adsorption is occurring. No evidence of irreversible adsorption was observed with any of the probe compounds used in this study. Calculations made on the basis of the isotherm derived from the band profile (Figs. 5 and 6) show that the second peak in the chromatogram shown in Fig. 4 is entirely accounted for by this isotherm. The initial slope is very steep, corresponding to very long retention times (*ca.* 40 min), and the apparent return to the baseline is deceptive [20].

It appears, therefore, that the material injected on to the column is physically adsorbed and either is entirely eluted before the detector signal returns to the baseline or, when it desorbs too slowly, does so

because of a very steep isotherm and not because of slow kinetics and can be desorbed entirely at a higher temperature, *e.g.*, by temperature programming [20].

Data acquisition and handling

The detector signal of the chromatograph was acquired with an IBM PC at a sampling rate of 10 Hz and stored as an ASCII file. A dedicated Fortran program written in-house and run on the PC, was used to perform several tasks on each successive file: (i) the chromatogram was baseline corrected, if the baseline was not 0 V; (ii) the peaks corresponding to both the test column (referred to later as the test peak) and the calibration column were integrated using a trapezoidal rule; (iii) the tail portion of the test peak was smoothed using five-point quadratic smoothing [28]; (iv) the test peak was written out into a separate ASCII file, recording only every fifth point, so that the final file has two data points per second of retention time.

The records for a complete experiment leading to the determination of an isotherm include (i) a set of chromatograms (usually six) used to generate a detector calibration graph [29]; (ii) a set of elution peaks, corresponding to a broad range of column loading factors; after plotting these peaks on the same graph to insure that their diffuse rear boundaries lie on the same curve as the rear boundary of the largest peak, this largest peak of the set only is used to calculate the isotherm; (iii) a duplicate elution peak corresponding to the same amount injected as the peak used for isotherm determination, to permit accuracy and precision estimation; and (iv) as ASCII file containing the following parameters: the detector sensitivity, S_2 (atm V^{-1}), determined as described earlier; the void time, $t_{0,T}$ (min); the void volume, $V_{M,T}$ (ml); the column inlet pressure, P_{IN} (atm); the column outlet pressure, P_{OUT} (atm); the mass of adsorbent in the column, M_S (g); the peak area A_P (V min); the column temperature, T (K); the vapor pressure of the probe solute at the column temperature, P_S (atm); and the heat of vaporization of the probe solute, E_V (kcal mol^{-1}); these last two parameters are obtained from the literature [30].

If the data set obtained meets the minimum quality control criteria discussed in the companion paper [20], the test peak file is transferred to the mainframe computer. Subsequent calculations, involving the determination of the adsorption isotherm and the adsorption energy distribution, are performed by a single computer program.

The content of the test peak file is read into the program. The response factor is derived from the calibration chromatograms and the peak voltages are converted into partial pressures. Then, the data corresponding to the tail portion of the test chromatogram are sorted into a file of increasing P. This partial pressure *versus* retention time profile is interpolated using the Akima cubic spline [31] and evaluated at 1000 values of the pressure which lie within the range of the pressures measured and which have equal logarithmic spacing [18]. The spacing is chosen to weight more heavily the low-pressure region where the isotherm curvature is greater. Retention times are converted to specific corrected retention volumes and the integration (eqn. 1) is performed using a trapezoidal rule. The actual equation calculated is

$$q(P) = \frac{V_{M,T}}{J_3^2 \, R \, T \, M_S \, t_{0,T}} \int_0^P (t_{R,T}(P) - t_{0,T}) \, dP \quad (12)$$

The adsorption isotherm is stored and printed, then the program pursues the calculation of the adsorption energy distribution [18].

RESULTS AND DISCUSSION

As an example of the experimental results which are discussed elsewhere [20,21], we show in Fig. 5 the band profile (solid line) recorded for a sample of diethyl ether on an open-tubular column prepared with the sample of RHCP alumina used for the development of our method. The band profile has a nearly vertical front and a long tailing rear, typical of convex upwards isotherms [32]. The front is eluted very early (the retention factor of the front is 0.17), indicating a high degree of column overload. The isotherm derived from the rear of the profile is given in Fig. 6. As expected, it is strongly curved in the region 0–3 mbar.

From the isotherm in Fig. 6, and using the equilibrium dispersive model [32] adapted to gas chromatography [33], it is possible to calculate numerically the elution profile of the sample considered, assuming for the column an efficiency of 8000 plates, close to that determined for the column
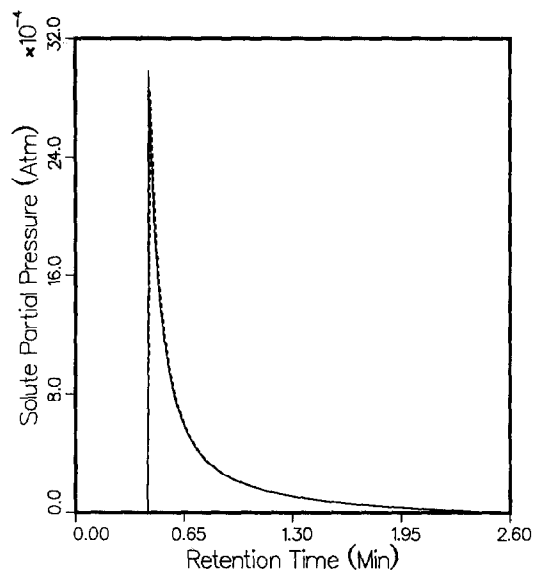
Fig. 5. Comparison between an experimental elution profile (solid line) and a calculated profile (dashed line). The calculated profile was obtained using the semi-ideal model of chromatography and the isotherm derived from the experimental profile through the ECP method. Diethyl ether on RHCP alumina at 60°C. Experimental conditions as in Fig. 4. Sample size, 0.47 μg; peak area, $4.85 \cdot 10^{-4}$ atm min; number of theoretical plates, 8000.
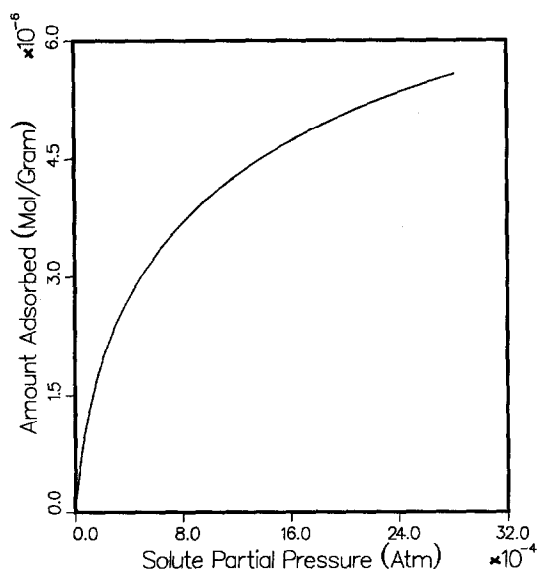

Fig. 6. Adsorption isotherm of diethyl ether on RHCP alumina at 60°C. The isotherm is derived from the elution profile shown in Fig. 5 (solid line).

under linear conditions [20]. The calculated band profile is shown in Fig. 5 (dashed line). It is very difficult to distinguish it from the experimental profile recorded. The ECP method uses the analytical solution of the ideal model of chromatography to derive the isotherm from the diffuse part of the band profile, while the equilibrium dispersive model uses the differential mass balances of the probe and of the carrier gas and calculates numerical solutions of this partial differential equation. The agreement between the two profiles in Fig. 5 shows that the calculation procedure accounts well for the influence on the band profile of the column efficiency and the gas-phase compressibility.

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