

Dynamic gas–solid chromatographic techniques for characterizing carbon molecular sieves

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ABSTRACT

Gas–solid chromatography (GSC) was used for the evaluation of carbon molecular sieves and provided an insight into their kinetic and thermodynamic properties in both column chromatography and sample enrichment studies. GSC studies of the column chromatographic performance characteristics of these sieves allowed the derivation, from Van Deemter plots, of permeability, capacity ratio, HETP and C-term values. Both conventional (4 and 2 mm I.D.) and micropacked (0.75 mm I.D.) GSC columns were evaluated. GSC studies of the sample enrichment performance characteristics of these sieves allowed the derivation of adsorbate breakthrough volumes, adsorption isotherms and equations of state. Using probe molecules such as dichloromethane, various adsorbent surface areas were extracted from the isotherm plots. Both conventional and micro-packed GSC columns were evaluated.

INTRODUCTION

In the early 1950s, gas–solid chromatography (GSC) evolved as an analytical separation tool in addition to a method for characterizing solid supports [1,2]. The physico-chemical measurements obtained by GSC described both the kinetic and thermodynamic processes occurring at the adsorbate/adsorbent interface, and remain viable measurements for understanding these phenomena. Since then, considerable attention has been given to the development of adsorbents with physico-chemical properties [3] that facilitate the separation of complex mixtures by GSC, and with adsorption–desorption properties effective for sample enrichment purposes. Considerable attention was also given to the characterization of the kinetic and thermodynamic properties of these porous solids in chromatographic systems. These investigations provided valuable insights into the technique of GSC, which still remain useful [4]. The porous solids typically used in the fields of GSC and sample enrichment were, and remain, activated charcoals, activated silica gels, porous polymers, zeolites, carbon molecular sieves and graphitized carbon blacks.

The use of GSC for characterizing adsorbents, as described here, evolved over a 6-year period. This study began by using 4 mm I.D. GC columns designed to emulate adsorbent tubes [5], progressed to 2 mm I.D. columns [6] and ultimately led to the use of 0.75 mm I.D. micropacked columns. The use of these micropacked columns for

determining the kinetic and thermodynamic interactions occurring between the adsorbate and adsorbent surfaces is the basis for this study.

EXPERIMENTAL

Gas-solid kinetic study

Chromatographic columns were prepared using standard column packing techniques [7]. Silanized glass columns (2 m \times 0.25 in. O.D.), of both 2.0 and 0.75 mm I.D., were chosen. They were packed with the same carbon molecular sieve, Carboxen-1000 (Supelco), with 20-45, 45-60, 60-80 and 80-100 mesh particle size distributions. The columns were installed in a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector. Kinetic information was extracted from the Van Deemter plots for carbon dioxide (125°C) and ethane (225°C), using getted helium as the carrier gas. A Spectra-Physics Model 4270 integrator was used to determine adsorbate retention data, and a Macintosh II personal computer was used to generate the plots. Chromatographic profiles were obtained with a Houston Instruments strip-chart recorder.

Adsorption isotherm study

These columns were also prepared using standard column packing techniques. Silanized glass columns (1 ft. \times 0.25 in. O.D.) of 0.75 mm I.D. were packed with 10.0 mg of each of the eight chosen adsorbents (see Table II). The particle size distribution was 60-80 or 80-100 mesh, depending on the availability of the smaller fraction. The columns were installed in a Varian Model 3700 gas chromatograph equipped with a flame ionization detector. Adsorption isotherm data for the chosen adsorbate, dichloromethane, were determined at 80°C using the peak maxima elution method [8,9]. Peak-height and peak-area data were obtained using a Spectra-Physics Model 4270 integrator. Detector linearity was determined for an adsorbate concentration range chosen to obtain $p/p_0 = 1$ values. Adsorption isotherm plots were generated with a Macintosh II personal computer and chromatographic profiles were obtained with a Houston Instruments strip-chart recorder.

RESULTS AND DISCUSSION

Gas-solid kinetic study

The data obtained from the kinetic study of Carboxen 1000, using columns of 2.0 and 0.75 mm I.D. packed with different particle size distributions of the same spherical carbon molecular sieve, are presented in Table I. These data, extracted from the Van Deemter plots [10], represent an improvement in chromatographic performance over sieves previously prepared and evaluated in this laboratory, hence this material was chosen as the example discussed here. The Van Deemter plots obtained for carbon dioxide and ethane are illustrated in Figs. 1 and 2, respectively (the plot for ethane with the 20-45 mesh fraction, with HETP values of 4.04-13.3 mm, was omitted from Fig. 2 so the ordinate scale could be expanded in the region of values between 0 and 4). The HETP values of 0.76 (CO₂) and 0.72 (C₂H₆) for the 80-100 mesh (0.149-0.177 mm) sieve packed in 0.75 mm I.D. columns indicate optimum efficiency for this work. This level of efficiency is accompanied by a decrease in the k'

TABLE I

PARAMETERS FOR CARBON MOLECULAR SIEVE (CARBOXEN-1000) COLUMN KINETICS-STUDY

| Parameter | Values | | | | | |
|--|--------|-------|-------|-------|--------|-------|
| Column length (m) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| d_c (mm) | 2.0 | 2.0 | 2.0 | 2.0 | 0.75 | 0.75 |
| d_p (mesh) | 80-100 | 60-80 | 45-60 | 20-45 | 80-100 | 60-80 |
| d_p/d_c | 0.08 | 0.11 | 0.15 | 0.30 | 0.22 | 0.28 |
| HETP (mm) (CO ₂) | 0.80 | 1.21 | 1.41 | 3.80 | 0.76 | 1.93 |
| HETP (mm) (C ₂ H ₆) | 0.80 | 1.23 | 1.42 | 4.04 | 0.72 | 1.77 |
| k' (CO ₂) | 22.6 | 11.6 | 11.0 | 6.0 | 20.2 | 10.7 |
| k' (C ₂ H ₆) | 23.7 | 15.2 | 13.2 | 5.9 | 21.1 | 11.7 |
| n (CO ₂) | 2500 | 1658 | 1418 | 526 | 2635 | 1036 |
| n (C ₂ H ₆) | 2500 | 1626 | 1408 | 495 | 2778 | 1130 |
| μ (cm/s) (CO ₂) | 18.9 | 11.4 | 11.4 | 3.79 | 22.7 | 18.9 |
| μ (cm/s) (C ₂ H ₆) | 18.9 | 18.9 | 15.2 | 3.79 | 18.9 | 18.9 |
| C (s $\times 10^{-4}$) (CO ₂) | 5.34 | 16.5 | 32.5 | 295 | 5.90 | 18.9 |
| C (s $\times 10^{-4}$) (C ₂ H ₆) | 7.80 | 16.0 | 23.5 | 270 | 4.80 | 15.5 |
| K (cm ² $\times 10^{-7}$) (CO ₂) | 1.42 | 3.12 | 3.72 | 25.1 | 1.53 | 4.84 |
| K (cm ² $\times 10^{-7}$) (C ₂ H ₆) | 1.46 | 3.38 | 3.28 | 29.3 | 1.36 | 4.36 |

values for both adsorbates, hence shorter analysis times without a decrease in efficiency are expected with the micropacked columns. A decrease in efficiency is seen with an increase in particle size, hence HETP values are dependent on both column diameter and sieve particle size. This trend is in good agreement with previous studies [11,12]. Fig. 3 illustrates a reduction in analysis time without a decrease in efficiency

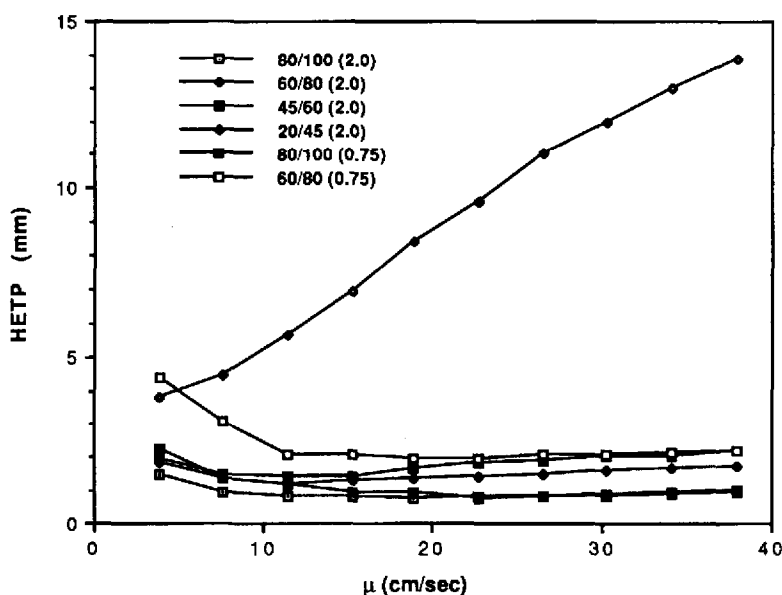


Fig. 1. Van Deemter plots for carbon dioxide with Carboxen 1000. Sieve mesh size and (in parentheses) column I.D. (mm) are given.

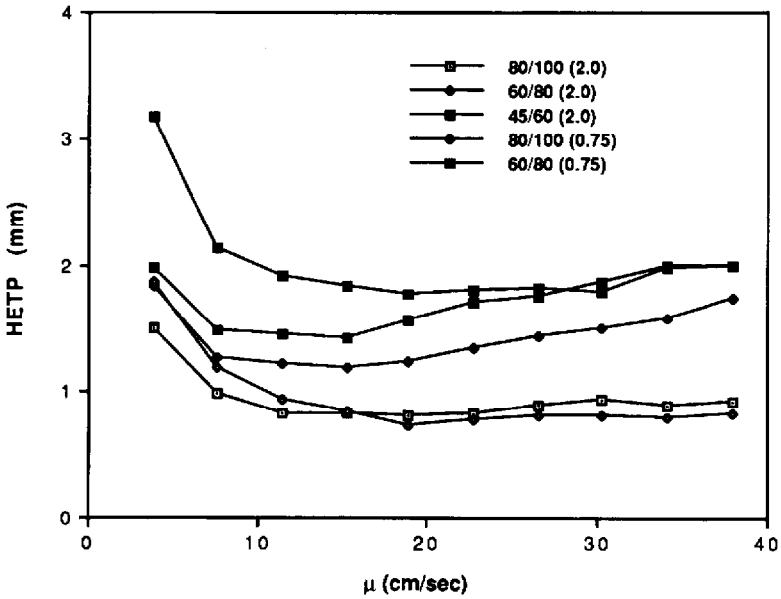


Fig. 2. Van Deemter plots for ethane with Carboxen 1000. Sieve mesh size and (in parentheses) column I.D. (mm) are given.

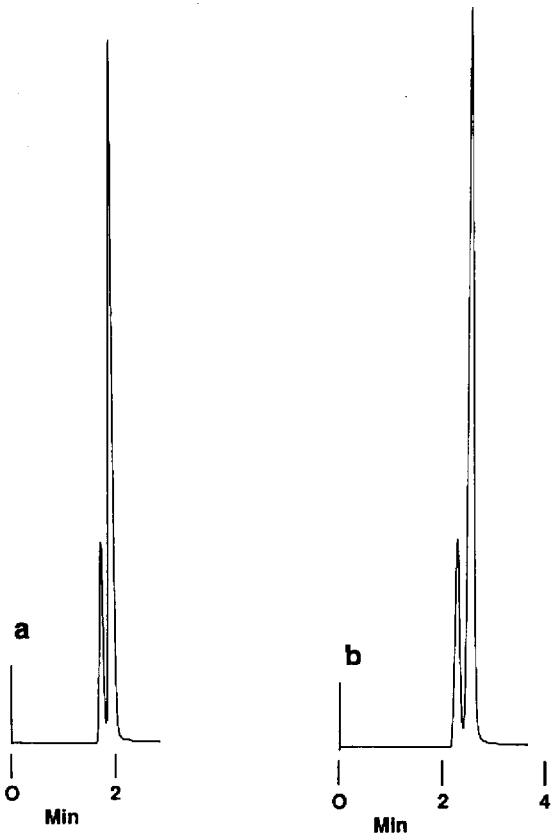


Fig. 3. Reduced analysis time without a decrease in efficiency for chromatographic analysis of oxygen and nitrogen with (a) a 0.75 mm I.D. column versus (b) a 2.0 mm I.D. column packed with 80-100 mesh Carboxen 1000. Oxygen is first peak eluted.

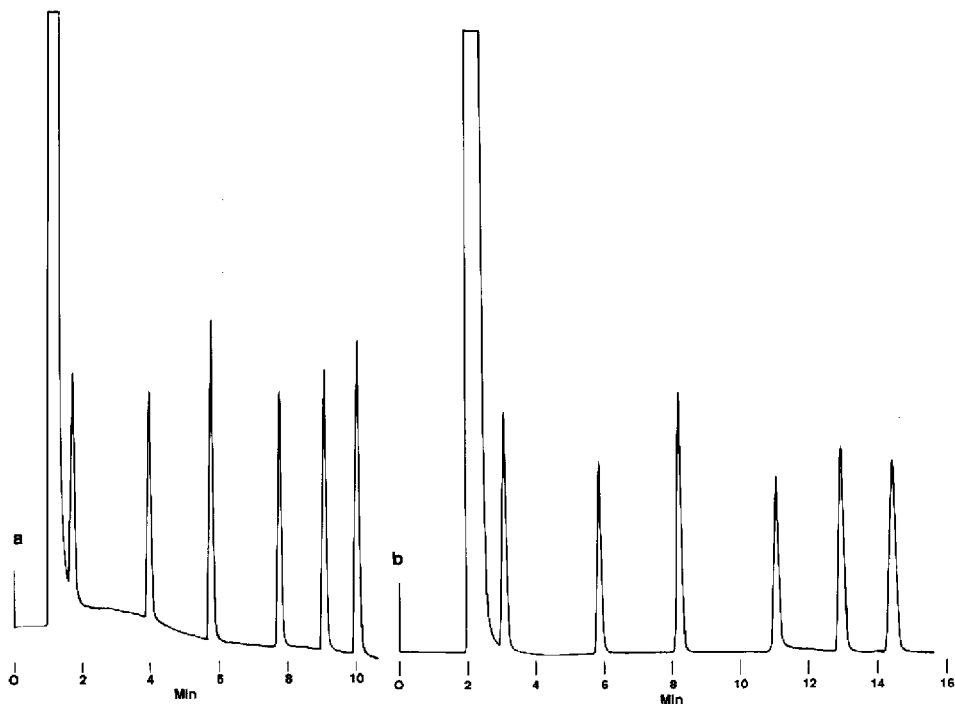


Fig. 4. Separation of permanent gases and light hydrocarbons with (a) a 0.75 mm I.D. column and (b) a 2.0 mm I.D. column. GC oven temperature: 35°C for 1 min, then increased to 225°C at 16°C/min. Peak identification (left to right): nitrogen (large), carbon monoxide, methane, carbon dioxide, acetylene, ethylene, ethane.

for the separation of oxygen and nitrogen with a 0.75 mm I.D. column at 35°C. This trend also exists for a wide temperature range, such as the 35–225°C range used to separate some permanent gases and light hydrocarbons (Fig. 4).

A comparison of the C -terms obtained for ethane indicates that no significant decrease in efficiency is expected when using increased linear velocities with the 0.75 mm I.D. column, hence a higher linear velocity was chosen for the micropacked column in Fig. 4 (25.6 cm/s, *versus* 18.9 cm/s for the 2.0 mm I.D. column). Also, the p_1 values were similar for both column I.D.s with the 80–100 mesh sieve throughout the temperature range studied (32 p.s.i.g. at 35°C and 52 p.s.i.g. at 225°C, at 18.9 cm/s). These ranges of particle size distributions and pressures allow for the use of micropacked columns possessing similar physical characteristics under normal packed column GC pressure conditions.

The permeability (K_{exp} ; Darcy equation [12]) data indicate a decrease in permeability with an increase in column diameter, and a decrease in K_{exp} with decreasing particle diameter for a fixed column diameter. These trends are in agreement with previous studies [4,12]. K_{exp} values and K values were also in good agreement when using the Kozeny–Carman [13] equation. Permeability also decreases with a decrease in the d_p/d_c ratio, and is optimum at a ratio between 0.20 and 0.25 [12]. This optimum is exemplified by an increase in the permeability values for ethane, relative to values

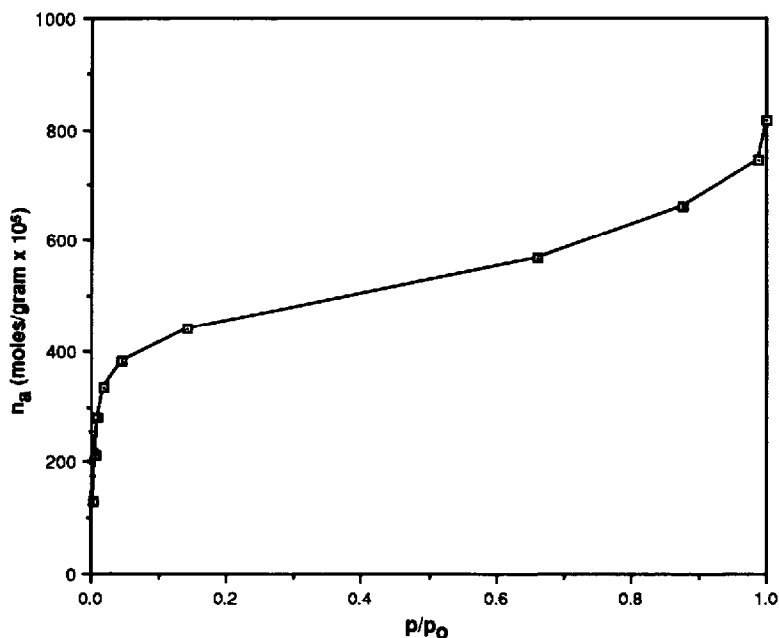


Fig. 5. Adsorption isotherm for dichloromethane with Carboxen 1000. Injection volumes: 0.1–5.0 μ l.

for carbon dioxide, when the d_p/d_c values are outside the experimental range of 0.15–0.28. Typically, a decrease would be expected as the adsorbate molecular size is increased.

Adsorption isotherm study

Previous work with 2.0 mm I.D. columns [6] provided effective characterization of non-porous solids such as graphitized carbon blacks [14]. The large internal surface areas characteristic of the carbon sieve adsorbents were more readily characterized with the 0.75 mm I.D. columns. The adsorption isotherms generated for the eight carbon adsorbents are indicative of Type IV isotherms [15] (Fig. 5). The choice of a 1 ft. (0.3 m) \times 0.75 mm I.D. column packed with 10.0 mg of the adsorbent allowed

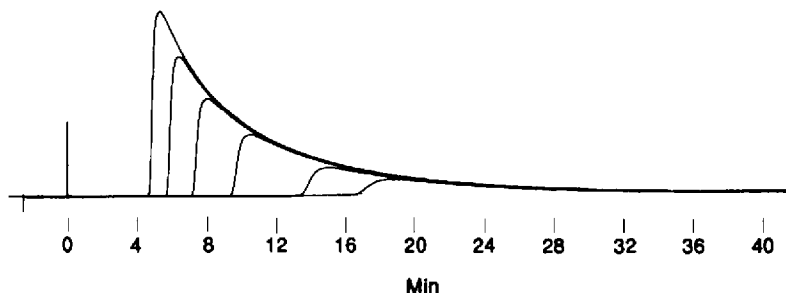


Fig. 6. Chromatographic profile for dichloromethane with Carboxen 569. Injection volumes: 0.2–1.2 μ l.

TABLE II
BREAKTHROUGH VOLUMES AND SURFACE AREAS FOR CARBON-BASED ADSORBENTS

| Adsorbent | BTV [16] (l) | Surface area (m ² /g) | |
|--------------------|-----------------|----------------------------------|----------------|
| | | CH ₂ Cl ₂ | N ₂ |
| Carbosieve S-III | 66.2 | 697 | 820 |
| Carboxen 569 | 43.2 | 466 | 485 |
| Activated charcoal | 39.2 | 526 | 1070 |
| Carbosieve S-II | 31.5 | 506 | 1060 |
| Carboxen 564 | 31.5 | 380 | 400 |
| Purasieve | 5.05 | 364 | 950 |
| Carboxen 563 | 1.56 | 291 | 510 |
| Sphero carb | 1.05 | 291 | 880 |

sufficient internal column pressures to be applied so that $p/p_0 = 1$ values could be achieved with reasonable sample sizes ($< 80 \mu\text{mol}$).

Detector linearity for a halogenated molecule such as dichloromethane also was considered when choosing the column I.D. Fig. 6 illustrates the chromatographic behavior of dichloromethane with a porous carbon sieve which possesses a large microporous region and sufficient mesoporous/macroporous regions to access the micropores. This chromatographic behaviour justifies the use of GSC for the determination of adsorption isotherms. The Type IV isotherm is similar to Type II [15] isotherms in its characteristic shape. Multiple adsorbate layers are absent in the mesoporous and macroporous regions, however, and therefore pressure unity can be readily achieved.

The lack of correlation between nitrogen surface area data and the breakthrough volume (BTV) data [16] (Table II) led to the generation of these isotherm data at 80°C. The BTV data were obtained at infinite dilution (*i.e.*, the extreme lower end of the Henry's Law region) and thus represent a migration volume rather than a saturation, or capacity, volume. This region of adsorbate coverage is applicable to sample enrichment modes, for which trace level analyses are required (*i.e.*, ambient air monitoring). Alternatively, the data obtained from static nitrogen surface area measurements represent microporous volume data rather than microporous surface area data, and may, therefore, be limited in the assistance provided when examining various adsorbent strengths. Typically, a large micropore diameter (*i.e.*, 10–20 Å) allows for effective sieve kinetics with subsequent diminished adsorption strength. These large diameters, however, provide large micropore volume values (*i.e.*, overestimates of micropore surface area) when the data are obtained via static nitrogen measurements. Correspondingly, surface area data generated by this dynamic GSC technique at the boiling points of the adsorbate probe molecules (40.7°C for dichloromethane) also provided micropore volume data which do not correlate well with the BTV values desired for trace level sample enrichment. Construction of BET plots [15] extracted from the lower end of the Henry's law region using a GSC column temperature of 80°C, however, allowed for an understanding of the sieve microporous surface area that the dichloromethane probe molecules actually encounter in this region. The surface area data obtained using this approach indicate a correlation between the BTV values and the dichloromethane surface area data.

CONCLUSION

The dynamic technique of GSC has assisted in understanding the physico-chemical characteristics of several carbon molecular sieves. The use of micropacked columns has led to an improved understanding of the kinetic and thermodynamic properties of these sieves functioning for the separation of permanent gases and light hydrocarbons. GSC has also assisted in providing an insight into the use of sieve surface area for molecules, other than nitrogen, typically encountered in sample enrichment studies.

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