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DETERMINATION OF THE GAS CHROMATOGRAPHIC PERFORMANCE CHARACTERISTICS OF SEVERAL GRAPHITIZED CARBON BLACKS

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SUMMARY

Two graphitized carbon blacks have been evaluated as solid supports (adsorbents) for the chromatographic determination of adsorbate–adsorbent interactions.

Adsorption isotherms were chromatographically derived to provide insight into the behavior of several *n*-alkanes, aromatic hydrocarbons, and aliphatic alcohols, with four adsorbents functioning as chromatographic packings. These four adsorbents, Carbopack B, Carbopack C, Carbopack B modified with 5% (w/w) Carbowax 20M, and Carbopack C modified with 0.5% (w/w) Carbowax 20M, subsequently were utilized for the chromatographic analyses of the adsorbate groups, in the low coverage (Henry's Law) region.

INTRODUCTION

Utilization of adsorbents as solid supports for both gas–solid and gas–liquid–solid chromatography has become increasingly effective over the past two decades. The availability of adsorbents which possess homogeneous, non-porous, non-specific surfaces has allowed for linearity in the adsorption isotherms throughout a wide temperature range[1]. Graphitized carbon blacks, which possess homogeneous, non-porous, non-specific surfaces[2], provide effective chromatographic analyses of a wide range of adsorbates. For this study, choices of the surface area and/or liquid phase coated on the non-specific surface have allowed for chromatographic analyses of several *n*-alkanes (group A molecules), aromatic hydrocarbons (group B molecules), and aliphatic alcohols (group D molecules) in the equilibrium region[3]. Chromatographic determination of the BET adsorption isotherms for the adsorbates, using the peak maxima method[4,5], has provided information about the adsorbates' behavior in the chromatographic columns.

EXPERIMENTAL

Gas–solid and gas–liquid–solid chromatographic columns were utilized to obtain the adsorption isotherms and chromatographic separations for the chosen adsorbates. Carbopack B (60–80 mesh; surface area, 100 m^2/g) and Carbopack

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C (60–80 mesh; surface area, 10 m^2/g), which are commercially available graphitized carbon black adsorbents (Supelco), were utilized for the gas–solid chromatographic profiles. Two gas–liquid–solid packings, 5% Carbowax-20M on 60–80 mesh Carbopack B and 0.5% Carbowax 20M on 60–80 mesh Carbopack C (also available from Supelco), were utilized to generate comparative chromatographic profiles and to improve the behavior of the alcohols. Each adsorbent and coated adsorbent was packed in a 2 ft. × 2 mm I.D. silanized glass column. High-purity nitrogen (scrubbed to remove traces of oxygen and water) was used at a pressure-corrected[6] flow-rate of 20 ml/min. Each column was thermally conditioned at 220°C for at least 8 h prior to use.

The adsorbates were obtained from Polysciences and were not purified further. The adsorbates chosen were *n*-pentane, *n*-hexane, *n*-octane, *n*-decane, benzene, toluene, ethylbenzene, ethanol, *n*-butanol, *n*-hexanol and *n*-octanol. The injection volume ranged from 0.2 to 20.0 μl (30.0 μl for aliphatic alcohols and 40.0 μl for *n*-alkanes and aromatic hydrocarbons on Carbopack B adsorbent). Adsorbate response was determined by using a flame ionization detector with a Spectra-Physics Model 4270 integrator to obtain peak height and peak area data.

Chromatographic pictures were obtained by using a Houston Instruments strip chart recorder, and adsorption isotherm plots were generated with a Macintosh II personal computer.

Procedure

Adsorption isotherms for the eleven adsorbates were obtained at temperatures which provided similar retention volume windows for each of the adsorbent packings. The peak maxima elution method was utilized, with the adsorbate vapor pressure determined as a function of the recorder pen displacement. To obtain the isotherm plots, this pressure value was plotted against the adsorbate concentration divided by the adsorbent packing weight. The equations utilized for the X and Y axis values are:

X-Axis (pressure axis)	Y-Axis (uptake axis)
$P = \frac{mxRT}{Sf} \cdot h$	$q = \frac{m \cdot 10^5}{W}$

where m = moles of adsorbate injected, x = chart speed, R = universal gas constant, T = temperature, S = adsorbate peak area, f = corrected flow rate, h = adsorbate peak height, q = moles of sample adsorbed, W = adsorbent packing weight.

The chromatographic analyses were performed in a defined temperature programmed range: 40°C (2 min) to 220°C at 16°C per min (250°C final temperature for the Carbopack B column).

RESULTS AND DISCUSSION

Adsorption isotherm data

Fig. 1 illustrates the adsorption isotherms obtained from the interactions between the *n*-alkanes and the surface of Carbopack B. They are representative of Type II isotherms as classified by Brunauer *et al.* and discussed by Gregg and Sing[7]. The choice of different temperatures for the adsorbates appears to minimize the trend of adsorption for a greater number of carbon atoms[3]. Fig. 2 illustrates the behavior of

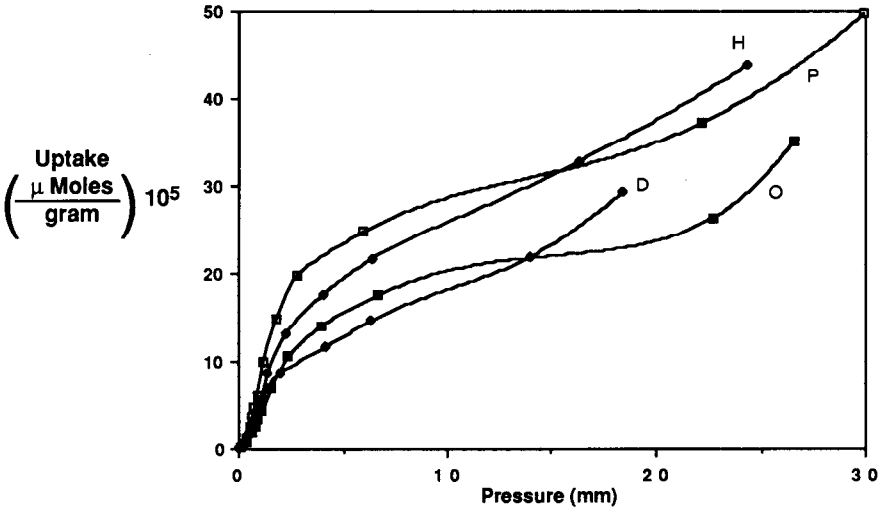

Fig. 1. Adsorption isotherms of *n*-alkanes on Carbopack B. (P) Pentane (50°C); (H) hexane (90°C); (O) octane (160°C); (D) decane (210°C).

toluene with the Carbopack B surface, and confirms the use of this elution method for isotherm determination. Fig. 3 illustrates the behavior of the aromatic hydrocarbons with the Carbopack B surface. Again, Type II isotherms appear to be well defined[1].

Fig. 4 illustrates the behavior of two aliphatic alcohols with the Carbopack B surface. The behavior is indicative of weak surface–surface interactions at low coverage (isotherms are convex to the pressure axis). Uptake becomes more significant as multiple layer coverage occurs; hence second points on inflection are present with the plots, as noted in previous documents[1].

Behavior similar to that of the *n*-alkanes and aromatic hydrocarbons and the Carbopack B surface was noted with the Carbopack C surface as well. As with the surface to surface interactions occurring with Carbopack B, Type II isotherms were

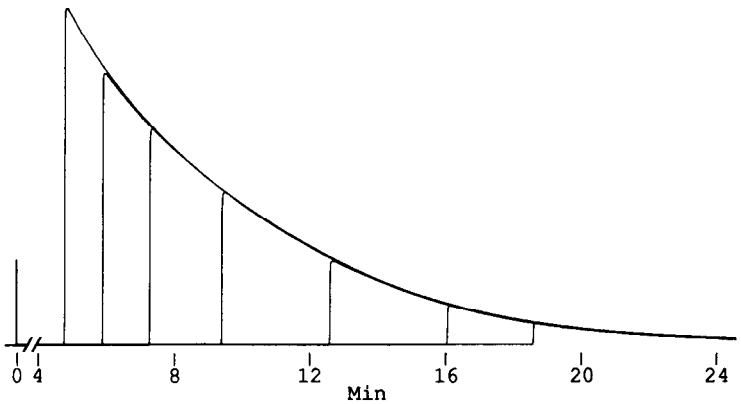

Fig. 2. Chromatographic profile of toluene using 60–80 Carbopack B, injection volumes: 0.2–5.0 μl at 110°C.

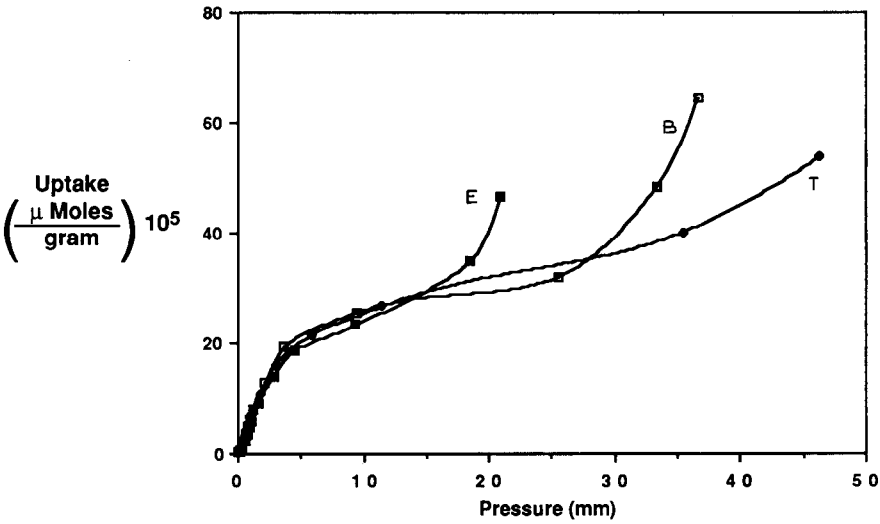

Fig. 3. Adsorption isotherms of aromatic hydrocarbons on Carbopack B. (B) Benzene (70°C); (T) toluene (110°C); (E) ethylbenzene (140°C).

represented. The homogeneous, non-porous surfaces of both of these graphitized carbon blacks allow for these similarities.

Behavior of the aliphatic alcohols with the surface of Carbopack C also was similar to that seen with the Carbopack B surface. Again, as with the Carbopack B, two points of inflection were observed.

Fig. 5 illustrates the behavior of the aromatic hydrocarbons with the modified Carbopack B surface. The isotherms for both the group A and group B molecules begin to approach those obtained for the alcohols and the unmodified graphitized

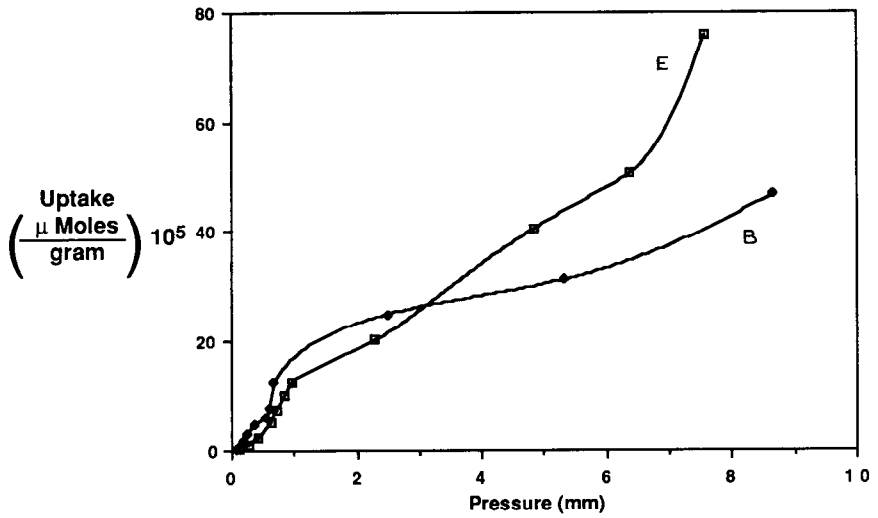

Fig. 4. Adsorption isotherms of alcohols on Carbopack B. (E) Ethanol (35°C); (B) butanol (70°C).

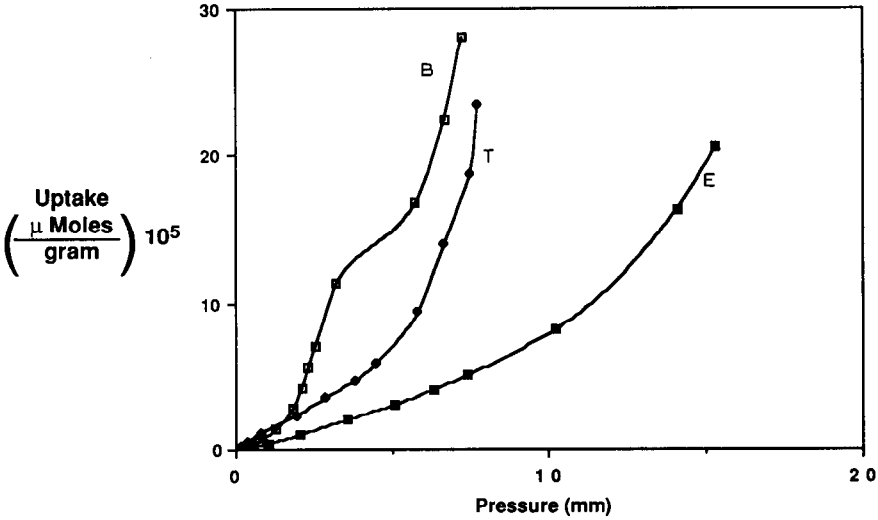

Fig. 5. Adsorption isotherms of aromatic hydrocarbons on 5% CW-20M on Carbopack B. (B) Benzene (35°C); (T) toluene (60°C); (E) ethylbenzene (100°C).

carbon black surfaces; however the inflection points are less severe and begin to approach linearity. This trend in the isotherms relates to the chromatographic analyses of the adsorbates, at low coverage, as a spreading of the hydrocarbon peaks (which retain a Gaussian shape). Similar behavior was noted with the *n*-alkanes as well. Figs. 6 and 7 illustrate this chromatographic behavioral difference between the hydrocarbons and the unmodified Carbopack B and the modified Carbopack B surface.

Fig. 8a and b illustrate the behavior of ethanol with the unmodified and modified Carbopack B surfaces. In the low coverage region, ethanol interacts weakly with the

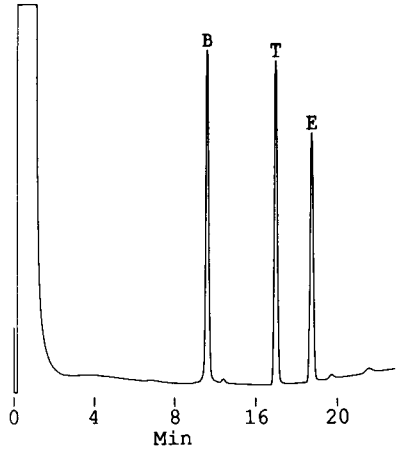

Fig. 6. Chromatographic analysis of aromatic hydrocarbons using 60–80 mesh Carbopack B. Column temperature: 40°C (2 min) to 240°C at 16°C per min; concentration: 150–200 ng on column. B = Benzene, T = toluene, E = ethylbenzene.

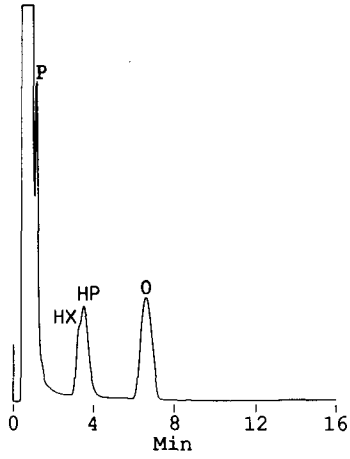

Fig. 7. Chromatographic analysis of C_5–C_8 alkanes using 5% CW-20M on 60–80 mesh Carbopack B. Column temperature: 40°C (2 min) to 210°C at 16°C per min; concentration: 250–300 ng on column. P = pentane, HX = hexane, HP = heptane; O = octane.

unmodified Carbopack B surface and chromatographically behaves poorly, while the modified Carbopack B surface allows for effective chromatographic analyses of ethanol. The utilization of a solid support (for liquid phase addition), with a large homogeneous surface, such as Carbopack B, allows for improvement of these surface–surface interactions, since adsorbate interactions are not solely dependent on the gas–liquid or gas–solid partitions and the electronic activity of the support surface is adequately modified.

Fig. 9a and b illustrates the chromatographic profiles for ethanol with the modified and unmodified Carbopack B surfaces, obtained to generate the isotherm plots. In the isotherm plots of the aliphatic alcohols with the modified Carbopack B surface, one inflection point was noted.

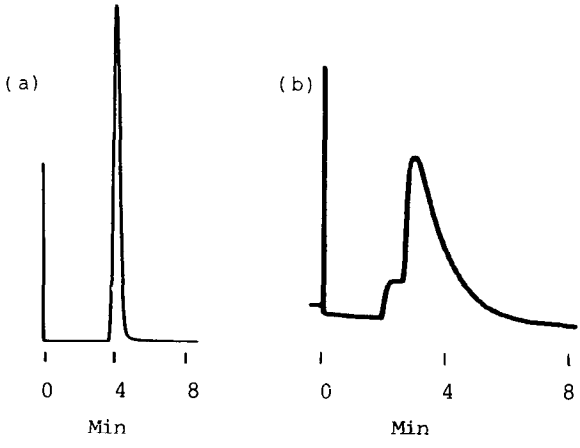

Fig. 8. Chromatographic analyses of ethanol (low coverage) using (a) 5% CW-20M on 60–80 Carbopack B, 35°C; (b) 60–80 Carbopack B, 35°C.

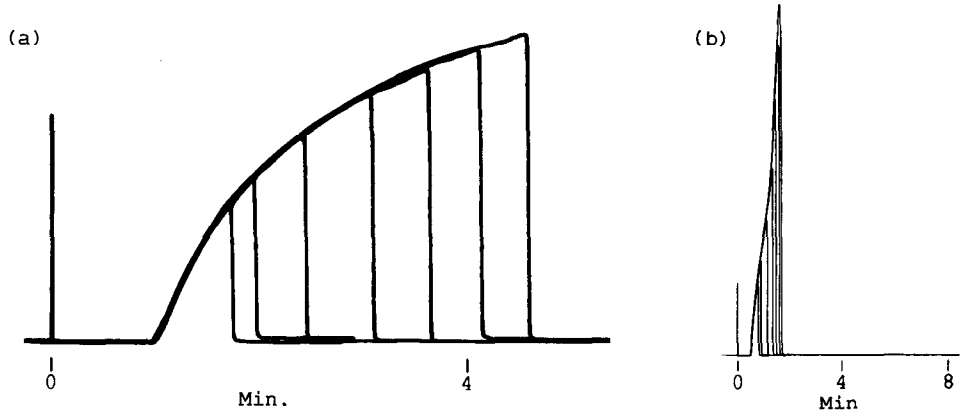

Fig. 9. Chromatographic profile of ethanol. (a) 60–80 Carbopack B (60°C); (b) 5% CW-20M on 60–80 Carbopack B (60°C). 0.2–5.0 μl.

The behavior of the *n*-alkanes, aromatic hydrocarbons, and aliphatic alcohols with the modified Carbopack C surface is similar to that seen with the modified Carbopack B. Fig. 10 illustrates the chromatographic behavior of the alcohols (low coverage) with the unmodified Carbopack C surface throughout a temperature programmed profile. Fig. 11 illustrates the improved adsorbate–adsorbent surface behavior for these alcohols with the modified Carbopack C surface. Behavior for the modified Carbopack B surface is similarly improved.

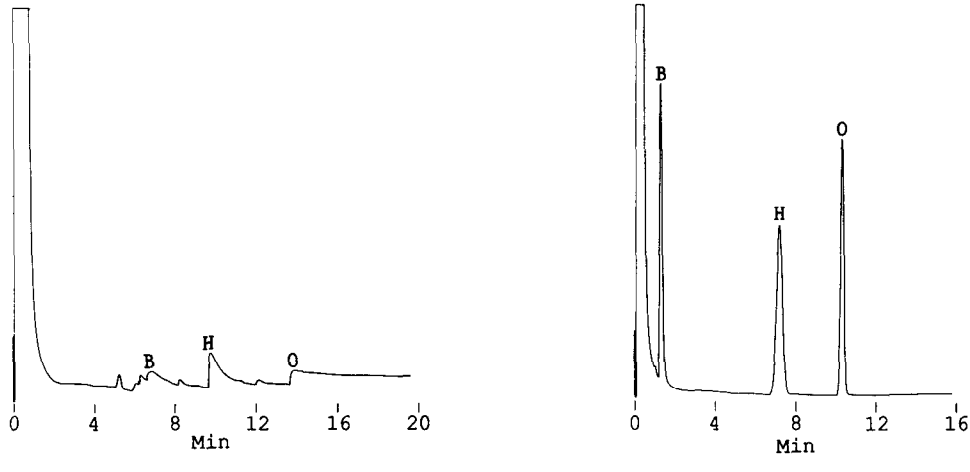

Fig. 10. Chromatographic analysis of C_4–C_8 alcohols using 60–80 Carbopack C. Column temperature: 40°C (2 min) to 210°C at 16°C per min; concentration: 250–300 ng on column. B = *n*-butanol, H = *n*-hexanol, O = *n*-octanol.

Fig. 11. Chromatographic analysis of C_4–C_8 alcohols using 0.5% CW-20M on 60–80 Carbopack C. Column temperature: 40°C (2 min) to 210°C at 16°C per min; concentration: 250–300 ng on column. B = *n*-butanol, H = *n*-hexanol, O = *n*-octanol.

CONCLUSION

Utilization of non-specific, non-porous, homogeneous graphitized carbon black adsorbents as gas–solid chromatographic packings allows for excellent chromatographic behavior of *n*-alkanes and aromatic hydrocarbons (group A and group B adsorbates). Use of appropriate surface modifiers for these adsorbents also ensures effective chromatographic behavior of aliphatic alcohols (group D adsorbates). The chromatographic behavior of these three groups of adsorbates is well represented by the defined adsorption isotherms and chromatographic analyses (in the low coverage region) presented herein. Further investigations will be conducted to evaluate the use of other surface modifiers for other group D adsorbates.

REFERENCES

1 A. V. Kiselev and Y. I. Yashin, *Gas Adsorption Chromatography*, Plenum Press, New York, 1969.
2 F. Bruner, P. Ciccioli, G. Crescentini and M. T. Pistolesi, *Anal. Chem.*, 45 (1973) 1851.
3 W. R. Supina, *The Packed Column in Gas Chromatography*, Supelco, Bellefonte, PA, 1974.
4 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 58 (1971) 137.
5 M. Domingo-Garcia, F. J. López-Garzón, R. López-Garzón and C. Moreno-Castilla, *J. Chromatogr.*, 324 (1985) 19.
6 J. R. Conder, *Chromatographia*, 7 (1974) 387.
7 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.