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Note

Selective salt-modified adsorbents for gas-solid chromatography*

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There has been a continued interest in the area of salt-modified adsorbents as several investigators¹⁻⁵ have extended the usefulness of gas-solid chromatography (GSC) by achieving selective analytical separations with modified adsorbents. With salt modification of alumina, silica gel and porous silica beads Sawyer *et al.*¹⁻³ have demonstrated that great selectivity is noted in the separation of isomeric mixtures. In particular, the sorbate-salt-modified adsorbent interaction is a composite of non-specific and specific contributions with the latter contribution dependent upon the π -electronic nature and geometrical configuration of the sorbate.

The present GSC study focuses upon silica gel which has been coated with the chlorides of Mn(II), Co(II), and Zn(II). The cations of these salts differ in the number of available "3d" orbitals and possess electronic configurations of $3d^5$, $3d^7$, and $3d^{10}$, respectively. Since these salts are Lewis acids, electron-donating-type substances should undergo surface complexation to varying degrees with these salts.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 900 gas chromatograph equipped with dual hydrogen flame ionization detectors was employed in the investigation. The flow-rates of the carrier gas (nitrogen) and hydrogen were maintained at 40 ml/min while the air flow was held constant at 375 ml/min. A Leeds and Northrup Model W/L strip chart recorder with a chart speed of 30 in./h and a 1-mV range was used to record the chromatograms. The carrier gas was dried prior to entering the chromatograph by passage through a molecular sieve 5A and drierite gas filter. Sorbate samples were injected as vapors with a 10- μ l Hamilton syringe after a small amount of pure liquid had been placed in a 5-ml tightly sealed vial.

Column preparation

The salts used as modifiers were the Reagent Grade chlorides of Mn(II), Co(II), and Zn(II). Thermogravimetric analysis indicated that hydrated water is removed at the conditioning temperature of 250°. Davidson 62 silica gel, 80-100 mesh,

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was employed; the coating procedure has recently been reported⁶. The amount of salt added provided a 10% by weight coating of the salt in each case on the adsorbent. The coated adsorbent was then placed in a preheated oven at 250° for 3 h to ensure complete drying.

After activation the adsorbents were resieved and packed into pre-weighed 3-ft. sections of 1/8-in.-O.D. stainless-steel tubing which had been previously rinsed with hexane, acetone, and dichloromethane. After each column had been packed, the column was installed in the gas chromatograph and conditioned at 250° for 24 h with a nitrogen flow-rate of 40 ml/min.

RESULTS AND DISCUSSION

Net retention volumes were converted to specific retention volumes, V_s , at 220°, by dividing by the surface area of the adsorbent. Specific retention volumes at 220° for the sorbates under consideration appear in Table I. Examination of the data for the aromatics establishes that V_s values decrease in the sequence silica gel, 10% $MnCl_2$ /silica gel, 10% $CoCl_2$ /silica gel, 10% $ZnCl_2$ /silica gel. The same trend is exhibited for the saturated aliphatic hydrocarbons; however, this trend is not followed by the olefinic sorbates. For example, 1-pentene and 1-hexene show a greater interaction on the 10% $CoCl_2$ column while 1-heptene is not even eluted from both the $MnCl_2$ - and the $CoCl_2$ -modified silica gel. A similar sequence was observed by Grob and McGonigle⁷ in a study of olefinic interaction with only pure salts as adsorbents. It is particularly interesting to note that for aromatic sorbates the degree of surface complexation or interaction increases in the order of available half-filled "d" orbitals, $3d^{10}$, $3d^7$, $3d^5$, i.e., $ZnCl_2$, $CoCl_2$, $MnCl_2$. In addition, salt modification reduces the active surface area of silica gel, resulting in a more homogeneous sorbent surface which yields more symmetrical elution peaks with reduced retention volumes. This technique provides an additional path for achieving selective analytical separations. Typical chromatograms are presented in Fig. 1.

TABLE I
 V_s VALUES AT 220° (ml/m²)

Sorbate	Silica gel	10% $MnCl_2$	10% $CoCl_2$	10% $ZnCl_2$
Benzene	0.1335	0.0982	0.0828	0.0810
Fluorobenzene	0.1186	0.0999	0.0838	0.0810
Toluene	0.3266	0.2256	0.1934	0.1820
Chlorobenzene	0.2490	0.2173	0.1795	0.1721
Bromobenzene	0.3940	0.3468	0.2829	0.2756
Ethylbenzene	0.6468	0.4320	0.3777	0.3331
Cumene	—	0.7149	0.6239	0.5572
<i>n</i> -Pentane	0.0206	0.0201	0.0180	0.0172
1-Pentene	0.3101	0.0395	0.0441	0.0358
<i>n</i> -Hexane	0.0406	0.0376	0.0339	0.0358
1-Hexene	—	0.0675	0.0904	0.0676
<i>n</i> -Heptane	0.0767	0.0710	0.0627	0.0634
1-Heptene	—	—	—	0.1172
<i>n</i> -Octane	0.1426	0.1326	0.1156	0.1148

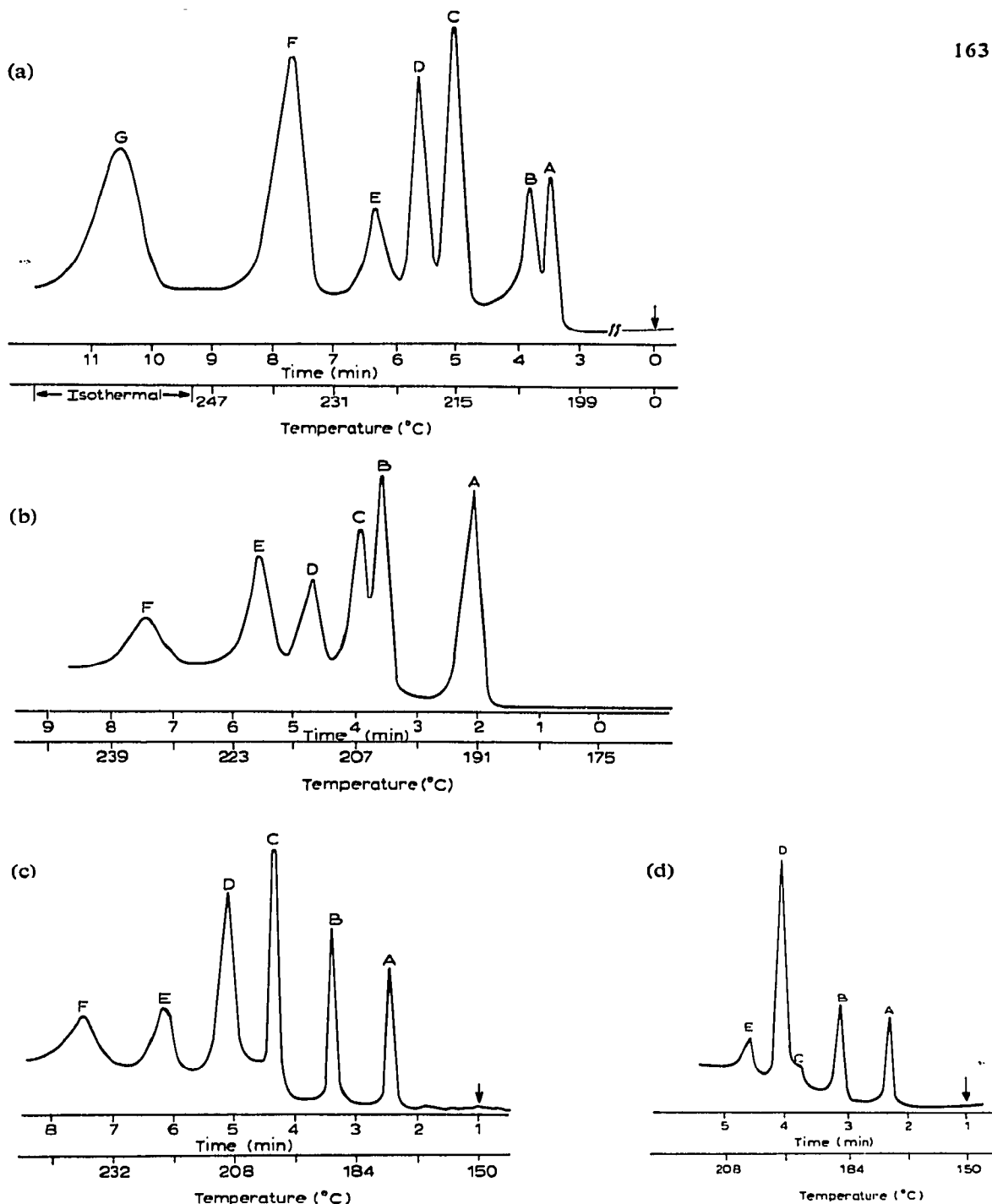


Fig. 1. Typical chromatographic profiles on silica gel and 10% CoCl_2 on silica gel. (a) Column, silica gel; temperature programmed at $8^\circ/\text{min}$. A = Benzene and fluorobenzene; B = benzene; C = chlorobenzene; D = toluene; E = bromobenzene; F = ethylbenzene; G = cumene. (b) Column, 10% CoCl_2 on silica gel; temperature programmed at $8^\circ/\text{min}$. A = Fluoronaphthalene; B = chlorobenzene; C = toluene; D = bromobenzene; E = ethylbenzene; F = cumene. (c) Column, silica gel; temperature programmed at $12^\circ/\text{min}$. A = *n*-Pentane; B = *n*-hexane; C = *n*-heptane; D = 1-pentene; E = 1-hexene; F = 1-heptene. (d) Column, 10% CoCl_2 on silica gel; temperature programmed at $12^\circ/\text{min}$. A = *n*-Pentane; B = *n*-hexane; C = 1-pentene; D = *n*-heptane; E = 1-hexene. 1-Heptene was not eluted.

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REFERENCES

- 1 D. J. Brookman and D. T. Sawyer, *Anal. Chem.*, 40 (1968) 106.
- 2 D. F. Cadogan and D. T. Sawyer, *Anal. Chem.*, 43 (1973) 941.
- 3 G. L. Hargrove and D. T. Sawyer, *Anal. Chem.*, 40 (1968) 409.
- 4 C. G. Scott, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworth, London, 1962, p. 36.
- 5 C. G. Scott and C. S. G. Phillips, in A. Goldup (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1956, p. 266.
- 6 N. H. C. Cooke and E. F. Barry, *J. Chromatogr.*, 101 (1974) 175.
- 7 R. L. Grob and E. J. McGonigle, *J. Chromatogr.*, 59 (1971) 13.