

New solid adsorbents for the separation of lower hydrocarbons and permanent gases

II. Ammonium molybdophosphate

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ABSTRACT

Ammonium molybdophosphate $[(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}]$ has been tried as a solid adsorbent in the gas chromatographic separation of lower hydrocarbons and permanent gases. It appears to be an effective adsorbent for the separation of methane, ethane, ethylene, acetylene, propane, propylene and butane. The retention characteristics of C_1 - C_4 hydrocarbons in both isothermal and temperature-programmed runs using a 20% ammonium molybdophosphate column were obtained. The retention times and peak-area percentages of lower hydrocarbons are highly reproducible in both isothermal and temperature-programmed runs. The separation of lower hydrocarbons and permanent gases obtained using ammonium molybdophosphate appears to be comparable to that obtained using either ammonium tungstophosphate or ammonium tungstosilicate.

INTRODUCTION

Analyses of lower hydrocarbons and permanent gases are generally carried out by gas-solid chromatography (GSC). With the development of capillary gas chromatography by Golay in 1960 [1] and the subsequent introduction of porous-layer open-tubular (PLOT) columns, high-resolution GSC has been gaining importance in the separation of a wide variety of organic compounds and permanent gases. Although the solid adsorbents used in GSC generally have high thermal stability and offer negligible column bleeding, they suffer from limitations such as irreversible adsorption of polar compounds and inapplicability towards the separation of higher hydrocarbons because of very long retention times. Broadening of peaks is also commonly observed in GSC. In GSC, Gaussian-shaped peaks can be produced only under ideal conditions such as high selectivity for non-specific interaction between the solid adsorbent and the adsorbate species, linear adsorption, homogeneous distribution of adsorption sites, particle size and pore size and the absence of diffusional effects [2-4]. Deviations from ideal behaviour have been observed with all the homogeneously macroporous solids, homogeneously microporous solids, inhomogeneously porous

solids and non-porous solids [5-16]. In GSC the selection of a solid adsorbent is merely based on surface area, thermal stability and pore-size distribution.

Recent studies have shown that some of the heteropoly oxometalates such as ammonium tungstophosphate and ammonium tungstosilicate are capable of separating lower hydrocarbons and permanent gases [17,18]. Another microporous heteropoly oxometalate, ammonium molybdophosphate, also appears to be a promising solid adsorbent for the separation of lower hydrocarbons and permanent gases. Like ammonium tungstophosphate and ammonium tungstosilicate, ammonium molybdophosphate has a moderately high surface area ($>150 \text{ m}^2/\text{g}$) and high thermal stability (at least up to 623 K). It is generally prepared by treating an aqueous solution of 12-molybdophosphoric acid with an aqueous solution of an ammonium salt. The structure of ammonium molybdophosphate is very similar to that of ammonium tungstophosphate except that the twelve octahedra which surround the central tetrahedron have molybdenum atoms at the centers.

TABLE I

SORPTION AND DIFFUSION OF ORGANIC COMPOUNDS IN AMMONIUM MOLYBDO-PHOSPHATE AT 293 K

Sorbate	Sorption capacity (g/g)	Diffusivity, $D \times 10^{11} \text{ (cm}^2/\text{s)}$
<i>Alcohols</i> [22]		
Methanol	0.032	4.2
Ethanol	0.035	2.7
1-Propanol	0.041	2.1
1-Butanol	0.043	1.6
2-Methyl-2-butanol	0.039	10.3
1-Hexanol	0.048	0.5
<i>Aromatics</i> [19]		
Benzene	0.036	11.0
Toluene	0.037	6.0
<i>p</i> -Xylene	0.034	3.7
<i>m</i> -Xylene	0.011	1.5
<i>o</i> -Xylene	0.009	1.8
Mesitylene	0.006	0.8
<i>m</i> -Diethylbenzene	0.035	0.5
<i>Saturates</i> [20]		
<i>n</i> -Hexane	0.028	25.0
3-Methylpentane	0.028	23.0
Cyclohexane	0.027	10.0
<i>n</i> -Heptane	0.030	18.0
<i>n</i> -Octane	0.033	12.0
Isooctane	0.031	8.8
<i>Unsaturates</i> [21]		
1-Hexene	0.030	11.0
2,3-Dimethyl-1-butene	0.029	6.6
1-Heptene	0.032	8.5
1-Octene	0.034	3.5
Cyclohexene	0.031	6.0
4-Methyl-1-cyclohexene	0.033	3.9

The sorption on and diffusion in ammonium molybdophosphate of different hydrocarbons and alcohols have already been reported [19–22]. A summary of the sorption capacity and the diffusivity of different hydrocarbons and alcohols on ammonium molybdophosphate is given in Table I. As no information on the use of ammonium molybdophosphate for the separation of lower hydrocarbons and permanent gases is available in the literature, it appeared worth exploring the possibility of using it as an adsorbent in GSC. This paper reports a study of the GSC separation of lower hydrocarbons and permanent gases using ammonium molybdophosphate as solid adsorbent.

EXPERIMENTAL

12-Molybdophosphoric acid (BDH), ammonium chloride (BDH) and all the gases (Matheson) were the highest purity available and were used as received. A stoichiometric amount of ammonium chloride solution was added slowly with constant stirring to 12-molybdophosphoric acid solution. Bright yellow ammonium molybdophosphate crystals were separated by centrifugation, washed with distilled water and dried at 110°C in an air oven for 4 h.

The chromatographic column was prepared as follows. Ammonium molybdophosphate (5 g) was added with stirring to a beaker containing about 50 ml of distilled water and 20 g of acid-washed non-porous glass beads (0.4 mm). The slurry was heated slowly with constant stirring until a dry mass was obtained. The glass bead-supported ammonium molybdophosphate crystals were dried at 100°C in an air oven for 2 h and finally transferred to a stainless-steel column (6 ft. × 1/8 in. O.D.). The separations of lower hydrocarbons and permanent gases were carried out using a Hewlett-Packard gas chromatograph equipped with flame ionization and thermal conductivity detectors. The size and shape of the ammonium molybdophosphate crystals were determined with a JEOL scanning electron microscope.

RESULTS AND DISCUSSION

Like ammonium tungstophosphate and ammonium tungstosilicate, ammonium molybdophosphate seems to be a good adsorbent for the separation of lower hydrocarbons and permanent gases. The order of retention times of lower hydrocarbons and permanent gases appears to be the same on all three adsorbents. With ammonium molybdophosphate highly reproducible retention times and peak-area percentages for different gases were obtained in both isothermal and temperature-programmed runs.

Separation of C₁–C₄ hydrocarbons

The separation of methane, ethane, ethylene, acetylene, propane, propylene and *n*-butane using the ammonium molybdophosphate column (6 ft × 1/8 in. O.D., 20% on non-porous glass beads) in a temperature-programmed run is shown in Fig. 1. The column temperature was initially held at 35°C for 4 min, increased linearly at 10°C/min to 160°C and maintained there for 30 min. Both the peak-area percentages and the retention times of the hydrocarbons showed good reproducibility.

Attempts to use a column filled with ammonium molybdophosphate only for

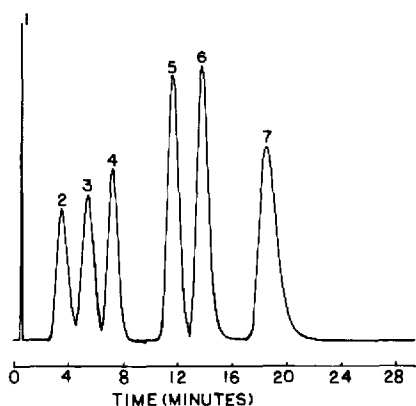


Fig. 1. Chromatogram showing the separation of (1) methane, (2) ethane, (3) ethylene, (4) acetylene, (5) propane, (6) propylene and (7) *n*-butane. Column: 20% ammonium molybdophosphate on glass beads (6 ft. \times 1/8 in. O.D.); oven temperature, 35°C for 4 min, then increased at 10°C/min to 160°C, held for 30 min; carrier gas, nitrogen; flow-rate, 8 ml/min; flame ionization detection.

the separation of lower hydrocarbons and permanent gases were unsuccessful as appropriate carrier gas flow-rates could not be maintained owing to a large pressure drop across the column. In order to reduce the pressure drop across the column, non-porous glass beads (0.4 mm) were used as a diluent. Even after loading 20% (w/w) ammonium molybdophosphate, the glass beads still appeared to be free-flowing, indicating that the Van der Waals force of attraction is strong enough to hold the glass beads and the ammonium molybdophosphate crystals together.

The possible contribution of non-porous glass beads to the separation of hydrocarbons was evaluated by injecting the C_1 - C_4 mixture into a 6 ft. \times 1/8 in. O.D. column filled with non-porous glass beads. It was found that all the constituents of the hydrocarbon mixture eluted together as one sharp peak. The retention time of this

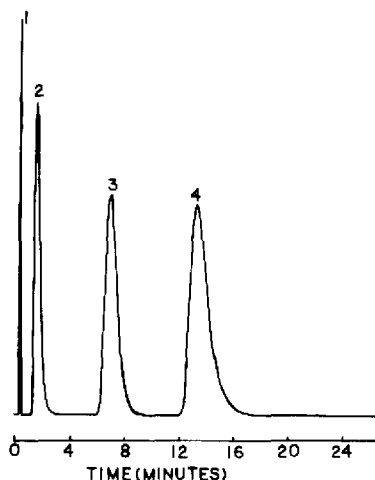


Fig. 2. Chromatogram showing the separation of C_1 - C_4 alkanes. Column as in Fig. 1; oven temperature, 50°C for 2 min, then increased at 10°C/min to 160°C, held for 15 min; carrier gas, nitrogen; flow-rate, 15 ml/min; flame ionization detection. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = *n*-butane.

TABLE II

RETENTION CHARACTERISTICS OF C_1 - C_4 ALKANES OBTAINED IN FIVE SUCCESSIVE TEMPERATURE-PROGRAMMED RUNS WITH A 20% AMMONIUM MOLYBDOPHOSPHATE COLUMN (6 ft. x 1/8 in. O.D.)

Oven temperature, 50°C for 2 min, then increased at 10°C/min to 160°C, maintained for 15 min; carrier gas, nitrogen; flow-rate, 15 ml/min; sample size, 0.05 ml.

Alkane	Mean retention time (s)	Mean peak area (%)	Relative standard deviation of retention time (%)	Relative standard deviation of peak area (%)
Methane	20.76	1.65	2.31	0.85
Ethane	91.32	18.08	1.05	0.77
Propane	417.4	32.52	0.22	0.67
<i>n</i> -Butane	804.5	47.76	0.3	0.73

unresolved peak matched that of methane obtained with the ammonium molybdophosphate column under identical conditions.

Separation of C_1 - C_4 alkanes

It appears that the separation of methane, ethane, propane and *n*-butane can be achieved rapidly by using a 20% ammonium molybdophosphate (6 ft. × 1/8 in. O.D.) column. Their baseline separation in a temperature-programmed run is shown in Fig. 2. The column temperature was initially maintained at 50°C for 2 min, then increased at 10°C/min to 160°C and maintained there for 15 min. Both the peak-area percentages and the retention times showed good reproducibility. The retention characteristics of the alkanes obtained with five successive temperature programmed runs are given in Table II.

It appears that the 20% ammonium molybdophosphate column is capable of separating C_1 - C_4 alkanes even under isothermal conditions. A representative chromatogram showing baseline separation at 120°C is shown in Fig. 3. The reproducibil-

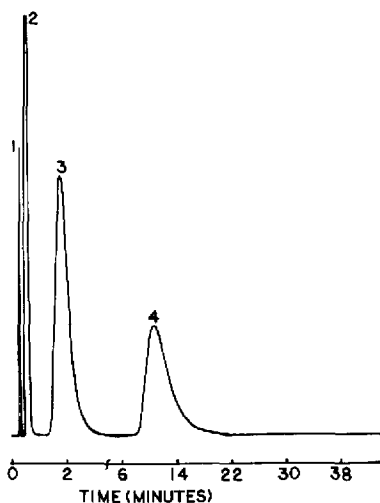


Fig. 3. Chromatogram showing the separation of C_1 - C_4 alkanes under isothermal conditions. Conditions as in Fig. 2 except oven temperature (120°C). Peaks as in Fig. 2.

TABLE III

RETENTION CHARACTERISTICS OF C₁-C₄ ALKANES OBTAINED IN FIVE SUCCESSIVE ISOTHERMAL RUNS WITH A 20% AMMONIUM MOLYBDOPHOSPHATE COLUMN (6 ft. x 1/8 in. O.D.)

Oven temperature, 120°C. Carrier gas, nitrogen; flow-rate, 15 ml/min; sample size, 0.05 ml.

Alkane	Mean retention time (s)	Mean peak area (%)	Relative standard deviation of retention time (%)	Relative standard deviation of peak area (%)
Methane	19.32	1.70	1.24	2.54
Ethane	32.52	17.37	0.74	0.99
Propane	108.8	32.46	0.44	0.66
<i>n</i> -Butane	634.0	48.47	0.36	0.86

ity of the peak-area percentages and retention times was good. The retention characteristics obtained in five successive runs are given in Table III.

Separation of permanent gases

Like ammonium tungstophosphate [17] and ammonium tungstosilicate [18], ammonium molybdophosphate seems to be capable of separating permanent gases, with the same order of retention times. The separation of nitrogen, methane and carbon dioxide achieved by using the 20% ammonium molybdophosphate column (6 ft. × 1/8 in. O.D.) is shown in Fig. 4. The order of retention times of C₁-C₂ hydrocarbons observed with the three heteropoly oxometalates, *i.e.*, methane < ethane < ethylene < acetylene, appears to match that observed with SP-1700 or alumina PLOT columns. However with other columns, such as Carbosieve G or S series, the retention times of C₁-C₂ hydrocarbons follow the increasing order of their boiling points, *i.e.*, methane < acetylene < ethylene < ethane.

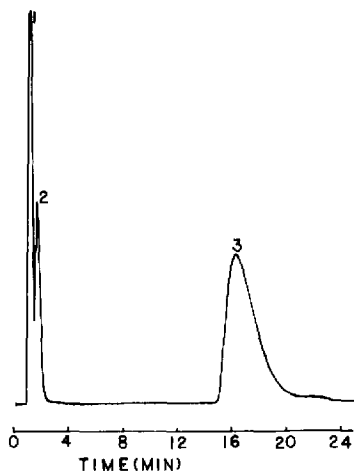


Fig. 4. Separation of permanent gases under isothermal conditions. Column as in Fig. 1. Oven temperature, 25°C; carrier gas, helium; flow-rate, 10 ml/min; thermal conductivity detection. Peaks: 1 = nitrogen; 2 = methane; 3 = carbon dioxide.

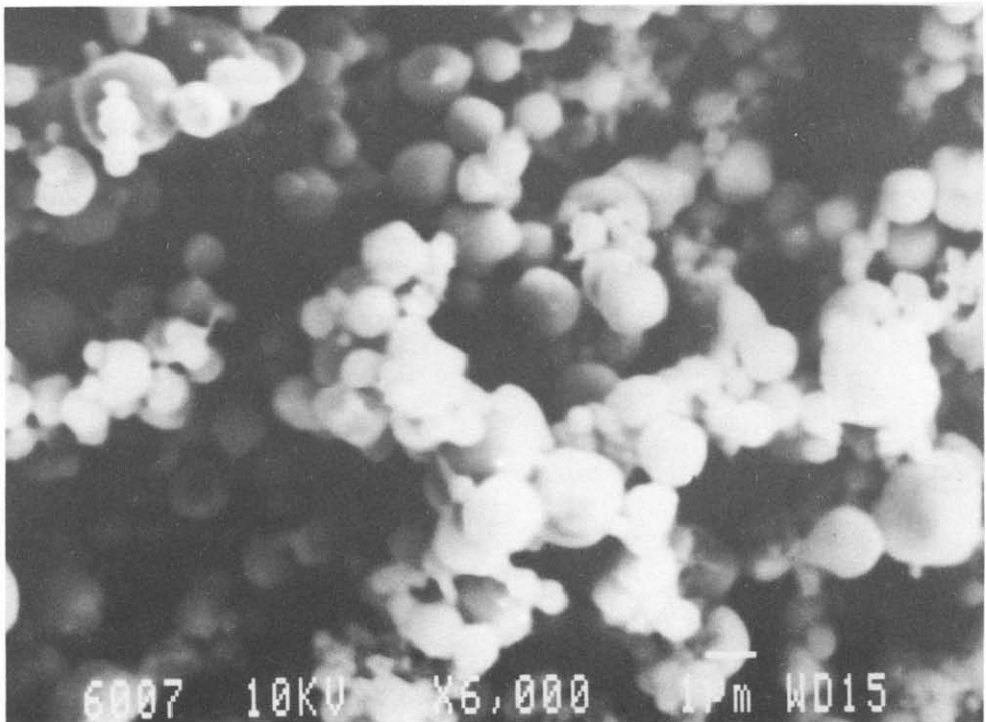
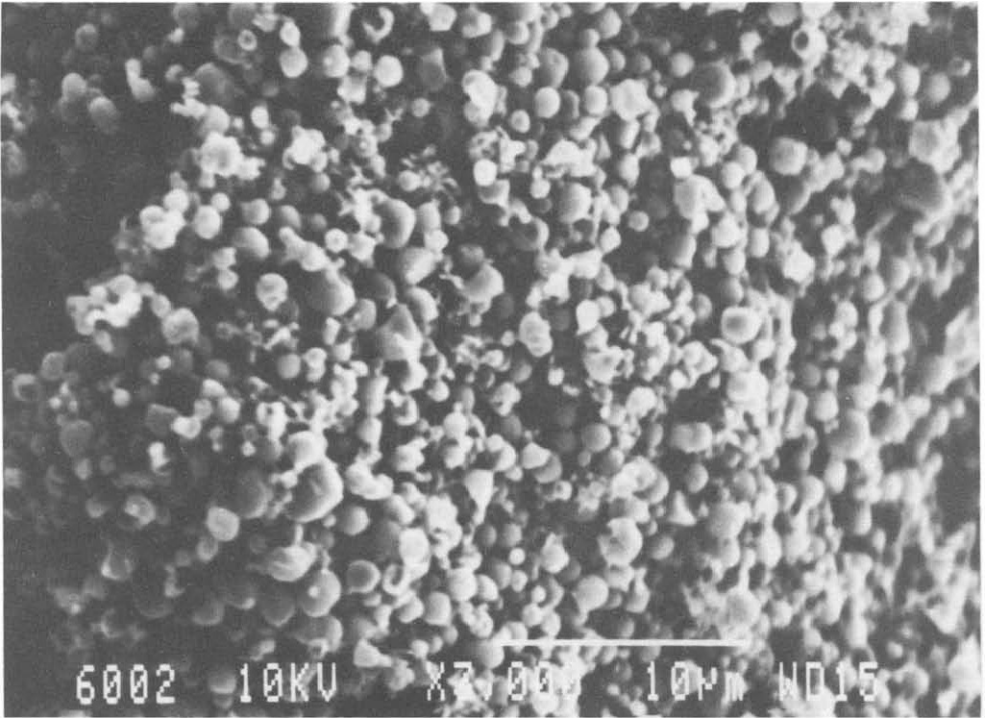


Fig. 5. Scanning electron micrographs of ammonium molybdophosphate.

From the order of retention times of C_1 – C_2 hydrocarbons it can be said that the interaction between the heteropoly oxometalates and the adsorbates is specific in nature. The elution peaks of lower hydrocarbons obtained with the 20% ammonium molybdophosphate column are fairly sharp and symmetrical and have a quasi-Gaussian shape. The elution of quasi-Gaussian-shaped peaks is an indication that the distribution of adsorption sites on ammonium molybdophosphate is homogeneous, the adsorption is linear, the interaction of ammonium molybdophosphate with the lower hydrocarbons is weak and diffusional phenomena are negligibly small. In GSC, as it is almost impossible to eliminate completely the effects of diffusional phenomena, broadening of elution peaks, at least to some extent, is expected. Like other solid adsorbents which are used in GSC, ammonium molybdophosphate appears to contain a small number of smaller and larger crystals (Fig. 5). The observed slight broadening of the elution peaks can be attributed mainly to the diffusional effects due to the particle-size distribution.

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