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Note

Gas–solid chromatography on a cation-exchange resin loaded with quaternary ammonium ions

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As they are highly porous, macroreticular ion exchangers such as Amberlyst 15[1] generally have large specific surface areas, and they are also thermally and mechanically stable. Ion-exchange resins are similar to porous polymers which have been applied successfully in gas–solid chromatography (GSC)[2].

We earlier reported[3] the separation of carbon monoxide from carbon dioxide by means of a column packed with resin in the nickel form, which had previously been activated in a stream of hydrogen. Hirsch *et al.*[4] prepared several ionic forms of the resin and reported on their utility as column packings for GSC. The retention indices of hydrocarbons are dependent on the size and electronic structure of the cation in the resin.

This paper describes some preliminary results on the properties of several quaternary ammonium ion forms of resins as column packings. The replacement of hydrogen ion in the resin with the voluminous quaternary ammonium ion may change the adsorption activity of the resin and provide additional selectivities for the separation of gas mixtures.

EXPERIMENTAL

Apparatus and reagents

The gas chromatograph used was a Hitachi Type 063 instrument equipped with a thermal conductivity detector.

Amberlyst A-15 and XN-1004 ion-exchange resins were obtained from Rohm and Haas (Philadelphia, Pa., U.S.A.). The dry resins were crushed and separated into 60–80, 80–100 and 100–120-mesh ranges. The resins were washed successively with ethanol, 2 *M* sodium hydroxide solution, 2 *M* hydrochloric acid and deionized water and air-dried. The ion-exchange capacities of A-15 and XN-1004 were 4.60 and 4.91 mequiv. g^{-1}, respectively.

Benzyltrimethylammonium chloride (BTMA) and benzyltriethylammonium chloride (BTEA) were obtained from Tokyo Chemical Industry (Tokyo, Japan). Benzyldimethyltetradecylammonium chloride (zephiramine) and methyltrioctylammonium chloride (capriquat) were obtained from Dojindo (Kumamoto, Japan). They were used without further purification.

Preparation of resin in the quaternary ammonium form

An aqueous solution containing 0.05 M zephiramine and 5% ethanol was passed through a column packed with resin in the hydrogen form until the effluent became neutral. The column was then washed with water until no chloride ion was found in the washings, and air-dried. The other cation forms of the resins were prepared by treating the resins with an ethanolic solution of capriquat or aqueous solutions of BTMA and BTEA. The ratio of ion-exchange sites occupied by the quaternary ammonium ion to hydrogen ion (ion-exchange capacity) was determined by acid–base titration in the usual manner. The air-dried resin was pre-conditioned in a gas chromatographic column at 140° until a stable baseline was obtained.

Determination of permeability

The difference in permeability between resin columns in the hydrogen and zephiramine forms was determined on the basis of the Darcy equation:

$$v = \frac{wqF\,(p_i^2 - p_o^2)}{2l} \qquad (1)$$

where v is the carrier gas flow-rate, w the permeability coefficient, F the fraction by volume occupied by the mobile phase, p_i and p_o the inlet and outlet pressures, l the column length and q the proportionality factor. A 50-cm column was used and resins of 100–120-mesh size were dried at 110° before being packed into the column. Experiments were carried out at room temperature. The flow-rate of helium was measured as a function of the inlet pressure while the outlet pressure was kept at atmospheric, and the carrier gas flow-rate was plotted against $p_i^2 - p_o^2$.

RESULTS AND DISCUSSION

Effects of quaternary ammonium ions on the resin

The ion-exchange capacity of the resin for each quaternary ammonium ion decreased with increasing size of the ion, as shown in Table I. It is impossible to replace all of the hydrogen ions on the resin with quaternary ammonium ions because of steric hindrance of the resin matrix.

TABLE I

CONVERSION OF RESIN FROM HYDROGEN FORM TO QUATERNARY AMMONIUM FORM

Quaternary ammonium ion	*Resin*	*Conversion ratio (%)*
BTMA	A-15	75.8
BTEA	A-15	52.0
Zephiramine	A-15	40.3
Zephiramine	XN-1004	40.3
Capriquat	A-15	29.3

A gas chromatogram of benzene obtained on a column packed with A-15 resin in the hydrogen form was compared with that obtained with resin in the zephiramine form. The results are shown in Fig. 1. The conversion of hydrogen ion to zephiramine ion results in a remarkably improved peak shape with a shorter retention time.

It was expected that the pressure drop along the column filled with resin in the

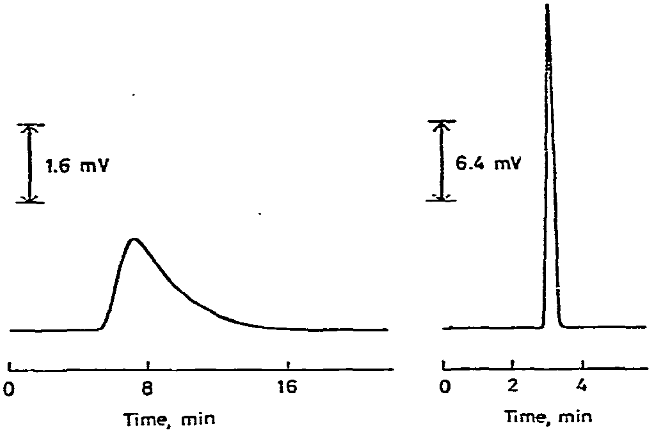


Fig. 1. Comparison of gas chromatograms. Left: hydrogen-form resin column, length 1 m, I.D. 0.3 cm, helium flow-rate 30 ml min^{-1}, volume of benzene 0.6 μl. Right: zephiramine-form resin column, length 2 m, I.D. 0.3 cm, helium flow-rate 22 ml min^{-1}, volume of benzene 0.2 μl. Resin: A-15, 100–120 mesh. Temperature: 130°.

zephiramine form would be much smaller than that with resin in the hydrogen form. The permeability of each column was estimated from eqn. 1. In duplicate experiments, the slope of each line was 24.4 and 23.7 cm^3 min^{-1} atm^{-2} for the hydrogen-form resin column and 37.0 and 37.5 cm^3 min^{-1} atm^{-2} for the zephiramine-form resin column. The increase in permeability is probably due to expansion of the resin matrix on the introduction of the voluminous quaternary ammonium ion. This effect permits the use of a longer column filled with packings of small mesh size.

The retention times of the test compounds relative to that of benzene are given in Table II. Columns packed with BTMA and BTEA forms of the resin have almost the same properties, whereas there are significant differences in the shapes of the cations and in the amounts of ions loaded on the resin. Columns of resin with a quaternary ammonium ion which has one or more long hydrocarbon chains are effective in separating *p*-xylene from *m*-xylene, if the columns have a sufficiently high efficiency.

Column efficiency

The height equivalent to a theoretical plate (HETP) depends on the compounds studied, amount injected, flow-rate and temperature, among other factors. Typical

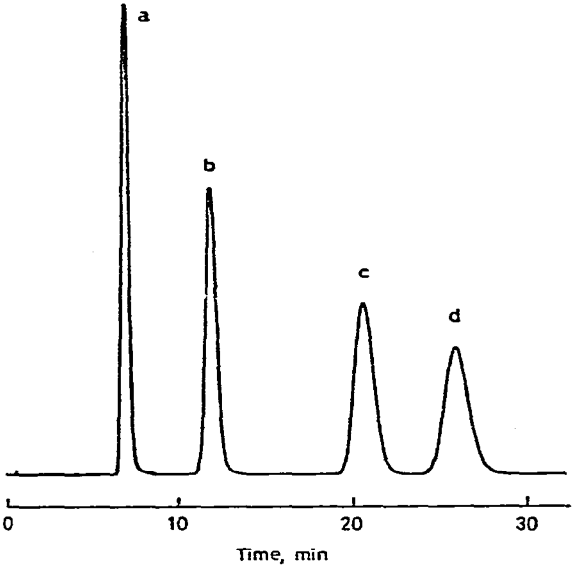
TABLE II

RELATIVE RETENTION TIMES OF AROMATIC HYDROCARBONS

Hydrocarbon	*Cation fixed on A-15*					
	BTMA, 130°	*BTEA, 120°*	*Zephiramine*			*Capriquat, 120°*
			130°	*90°*	*90°**	
Benzene	1.00	1.00	1.00	1.00	1.00	1.00
Toluene	1.65	1.67	1.58	1.55	1.74	1.55
Ethylbenzene	2.71	2.77	2.37	2.59	2.81	2.23
p-Xylene	2.79	2.84	2.48	2.75	2.97	2.38
m-Xylene	2.78	2.82	2.54	2.84	3.06	2.42
o-Xylene	3.18	3.26	3.08	3.48	3.70	2.94

* XN-1004.

chromatograms are shown in Fig. 2. The number of plates in a 2-m column for benzene, toluene, *p*- and *o*-xylene are 1391, 1413, 1397 and 1363, respectively. The HETP values are in the range 0.14–0.15 cm. The efficiency is less than that of conventional gas–liquid chromatographic columns.



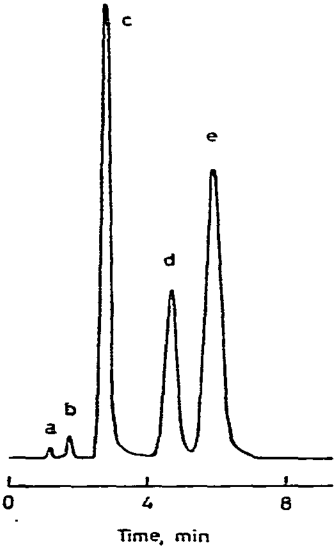


Fig. 2. Separation of aromatic hydrocarbons. Column: A-15 resin in zephiramine form, 100–120 mesh, 2 m long, 90°, helium flow-rate 22 ml min^{-1}. Compounds: (a) benzene; (b) toluene; (c) *p*-xylene; (d) *o*-xylene. A 4-μl portion of the sample containing the compounds in equal volumes was injected.

Fig. 3. Separation of aliphatic hydrocarbons. Column: A-15 resin in zephiramine form, 80–100 mesh, 5 m long, temperature 24°, helium flow-rate 28 ml min^{-1}. Compounds: (a) air and methane; (b) ethane and ethylene; (c) propane; (d) butane; (e) isobutane.

An attempt was made to separate a mixture of ethylbenzene and xylenes. The separation of *p*-xylene from *m*-xylene was incomplete even after elution for more than 1 h on a 5-m column of zephiramine-form XN-1004. A small *p*-xylene peak was found on a frontal shoulder of the *m*-xylene peak.

The quaternary ammonium columns are also applicable to the separation of hydrocarbons with low boiling points, as shown in Fig. 3.

Thermal stability of the column

The zephiramine column was kept at 130° and then the temperature was programmed to 190° at the rate of 10° min^{-1}. A column packed with silicone SE-30 was used as the reference. The shift of the baseline increased with increasing column temperature from 150 to 190°, but became almost constant at a constant temperature of 190°. It can be concluded that the resin column is thermally stable up to at least 150°.

REFERENCES

1 K. A. Kunin, E. Meitzner and N. Bortnick, *J. Amer. Chem. Soc.*, 84 (1962) 305.
2 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
3 K. Ohzeki and T. Kambara, *J. Chroma.* 55 (1971) 319.
4 R. F. Hirsch, H. C. Stober, M. Kowblansky, F. N. Huber and A. W. O'Connell, *Anal. Chem.*, 45 (1973) 2100.