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IONIC ADSORBENTS IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

To enhance the resolution of molecules having similar geometry but differing in dipole or quadrupole moments, we studied capillary columns packed with a non-porous ionic adsorbent, barium sulphate. Barium sulphate modified with sodium chloride was successfully used to separate some isomers of unsaturated, aromatic hydrocarbons, and oxygen- and nitrogen-containing heterocyclic compounds.

INTRODUCTION

Extensive use in gas chromatography of high-sensitivity detecting systems impose special requirements on the thermal stability of adsorbents used in accumulating and separating columns. These requirements are met by graphitized thermal carbon black (GTCB) and adsorbents obtained on the basis of salts. Isomeric molecules with different geometric structures were successfully separated on non-polar non-specific adsorbents, *e.g.* GTCB and MoS_2[1–6]. The specific ionic adsorbents, *e.g.* inorganic salts, are chiefly sensitive to the electron structure of the separated substances[5–16].

The use of different salts and treatment techniques makes it possible to vary widely the specificity of the intermolecular interactions with the adsorbents and, consequently, the selectivity of the adsorbents towards polar isomers[7–16].

Earlier, salts as adsorbents in gas chromatography were widely studied[5–16]. However, at high selectivity, the column efficiency was often insufficient. At present, open and packed capillary columns are used to achieve highly effective separations[12,14,17].

In this work we studied barium sulphate ionic adsorbents, of which the high selectivity towards xylene isomers has been shown earlier[8,17]. There are Ba^{2+} cations on the surface of barium sulphate crystals, whereas the negative charge is distributed over the large complex anions. Therefore, according to the classification of Kiselev and Yashin[5,6], barium sulphate is considered as a type II specific adsorbent. Due to the high specificity of the adsorption of polar organic molecules (possessing quadrupole and/or dipole moments), barium sulphate can be used for their gas chromatographic separation. In this work, we synthesized barium sulphate, modified its surface with alkaline metal halides and performed gas chromatographic studies of certain unsaturated, aromatic hydrocarbons and oxygen- and nitrogen-containing

heterocyclic compounds; to enhance the efficiency of the separation, the samples were packed into capillary columns.

EXPERIMENTAL

Barium sulphate adsorbents were prepared by the interaction of sodium sulphate and barium chloride solutions of various concentrations taken in equimolar proportions. The specific surface areas (S) determined by the thermal desorption of nitrogen varied from 2.5 to 8 m^2/g. Barium sulphate sample precipitated from 1.5 M sodium sulphate and barium chloride solutions and washed free of foreign ions (sample $BaSO_4$-1.5) was used as the main subject of investigation. Owing to the high specificity of such a sample heated at 200°C, the retention times of aromatic hydrocarbons are very large. To decrease the retention times, we modified barium sulphate with salts possessing a lower specificity of intermolecular interactions with these adsorbates. Barium sulphate was modified by keeping the samples until equilibrium in solutions of alkaline metal chlorides of various concentrations (from 1 to 20%, w/w). Then the samples were filtered and dried at 200°C.

In addition to the synthesized samples, we also examined a $BaSO_4$-2 sample described and used previously[8]. Gas chromatographic measurements were performed on Tsvet-129, LXM-80 and Varian MAT-212 gas chromatographs with a flame ionization detector. Glass capillary columns (1 mm I.D.) were packed with barium sulphate particles (0.16–0.20 mm). The column length was varied depending on the retention times of the separate components. The optimum carrier gas flow-rate from the Van Deemter curve for benzene was approximately 5 cm^3/min (with the flow-rate range from 5 to 20 cm^3/min, column efficiency changed very little).

RESULTS AND DISCUSSION

In the paper by Belyakova *et al.*[17], it was shown that the maximum value of separation selectivity for all xylene isomers was observed on barium sulphate samples modified with 15% sodium chloride solution. According to electron spectroscopy for chemical analysis (ESCA) measurements, these samples contained about 2% of Na^+ on the surface. To separate isomeric compounds, we prepared capillary columns packed with $BaSO_4$-1.5, washed free of foreign ions and modified with 15% sodium chloride solution (sample $BaSO_4$-1.5–15) and capillary columns packed with $BaSO_4$-2 unwashed of foreign ions[8,17]. Mechanically, the particles of $BaSO_4$-2 sample (S = 2.5 m^2/g) are less rigid than those of $BaSO_4$-1.5–15 (S = 8 m^2/g), but have a regular spherical shape (Fig. 1a and b).

Retention of hydrocarbons containing double bonds on barium sulphate
Fig. 2 shows the separation of some isomeric unsaturated hydrocarbons on modified barium sulphate. As seen, the *cis* and *trans* isomers of octene-2, all butene isomers and butadiene-1,3 are readily separated. Unlike non-specific adsorbents, *e.g.* GTGB[3,5], *trans* isomers elute earlier than *cis* isomers. This may be due to the fact that in the *cis* position, a double bond is more accessible than in the *trans* position. This increases the energy contribution of specific interaction to the total adsorption energy because of the formation of adsorption π-complexes. Due to the presence of
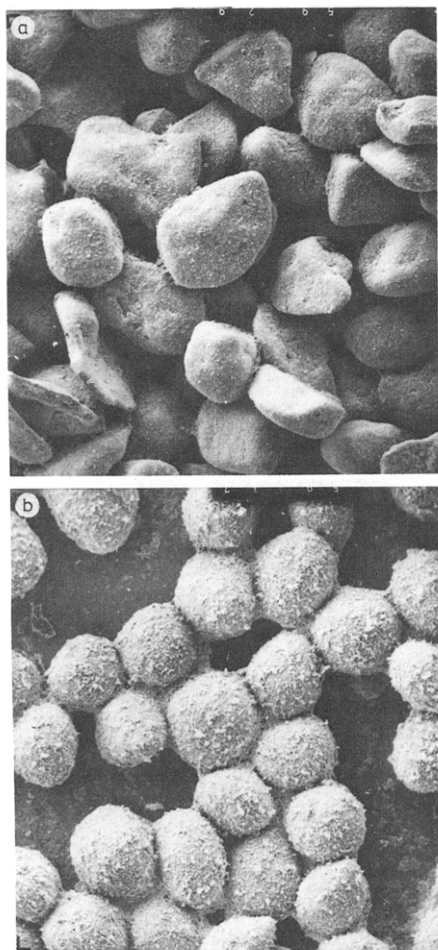
Fig. 1. Scanning electron microscopy of adsorbents: (a) $BaSO_4$-1.5–15 and (b) $BaSO_4$-2. Magnification × 56.

two double bonds in a molecule of butadiene-1,3, it is retained on barium sulphate more strongly than butene. A similar picture is observed in separating unsaturated hydrocarbons on polymers containing metal cations[13,18]. Fig. 2 also shows the chromatogram of ethane, ethylene and acetylene separation on sodium chloride-modified barium sulphate. On non-specific adsorbents (GTCB and porous carbons), acetylene elutes before ethylene[5]. On barium sulphate, like on aluminium trioxide[7], the elution order is different, namely ethane < ethylene < acetylene, acetylene being retained on the ionic adsorbent considerably longer than ethylene.

In the case of aromatic hydrocarbons, ethylbenzene is retained on barium sulphate more weakly than phenylethylene (styrene) (Fig. 3). This also indicates that, in the presence of double bonds in the side-chain of the molecules, π-complexes are formed between the adsorbate molecules and Ba^{2+} cations. A similar picture is observed in separating acenaphthene and acenaphthylene; the retention of acenaphthylene, because of the double bond, is stronger than that of acenaphthene.
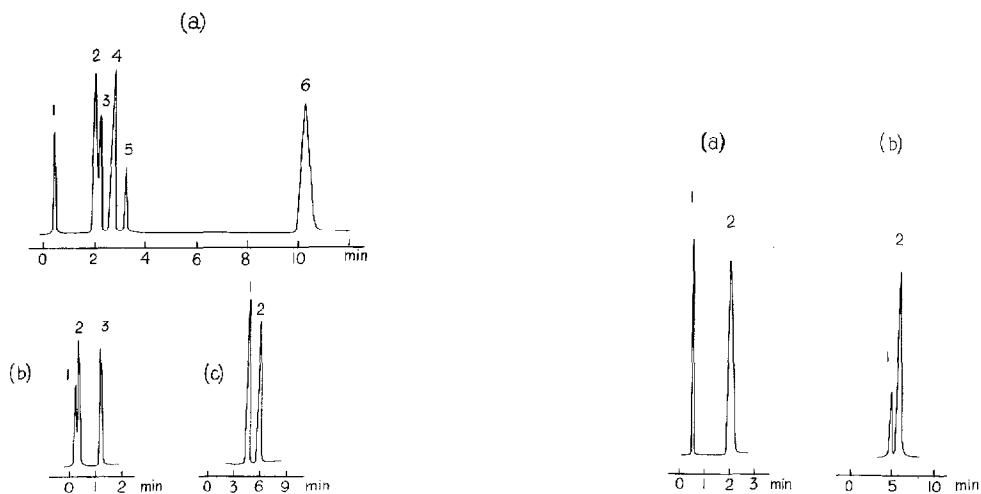
Fig. 2. Chromatograms of mixtures of saturated and unsaturated hydrocarbons on glass capillary columns packed with modified BaSO₄. (a) Column dimensions: 214 cm × 1 mm I.D.; adsorbent: BaSO₄-1.5–15; carrier gas (nitrogen) flow-rate: 9.3 cm³/min; temperature: 50°C. Peaks: 1 = *n*-butane, 2 = butene-1, 3 = *trans*-butene-2, 4 = 2-methylpropene, 5 = *cis*-butene-2, 6 = butadiene-1,3. (b) Column dimensions: 214 cm × 1 mm I.D.; adsorbent: BaSO₄-1.5–15; carrier gas (nitrogen) flow-rate: 11.3 cm³/min; temperature: 50°C. Peaks: 1 = ethane, 2 = ethylene, 3 = acetylene. (c) Column dimensions: 225 cm × 1 mm I.D.; adsorbent: BaSO₄-1.5 modified with 1% sodium chloride solution (sample BaSO₄-1.5–1); carrier gas (nitrogen) flow-rate: 6.8 cm³/min; temperature: 120°C. Peaks: 1 = *trans*-octene-2, 2 = *cis*-octene-2.

Fig. 3. Chromatograms of some aromatic hydrocarbon mixtures on glass capillary columns packed with BaSO₄-2. (a) Column dimensions: 40 cm × 2 mm I.D.; carrier gas (nitrogen) flow-rate: 25 cm³/min, temperature: 140°C. Peaks: 1 = ethylbenzene, 2 = styrene. (b) Column dimensions: 175 cm × 1 mm I.D.; carrier gas (nitrogen) flow-rate: 3.9 cm³/min, temperature: 229°C. Peaks: 1 = acenaphthene, 2 = acenaphthylene.
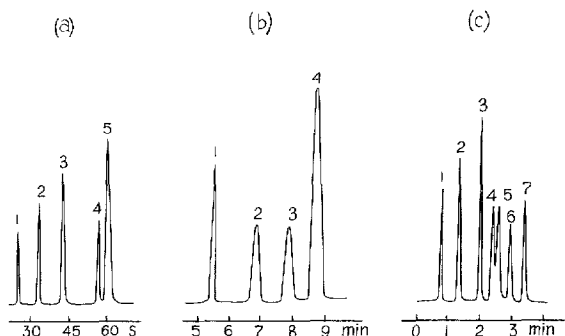

Fig. 4. Chromatograms of some aromatic hydrocarbons mixtures on glass capillary columns packed with different adsorbents. (a) Column dimensions: 15 m × 0.25 mm I.D.; adsorbent: GTCB[2]; carrier gas (hydrogen) flow-rate: 2 cm³/min; temperature: 245°C. Peaks: 1 = benzene, 2 = toluene, 3 = ethylbenzene, 4 = *m*-xylene, 5 = *o* + *p*-xylene. (b) Column dimensions: 214 cm × 1 mm I.D.; adsorbent: BaSO₄-1.5–15; carrier gas (nitrogen) flow-rate: 7.0 cm³/ min; temperature: 170°C. Peaks: 1 = toluene, 2 = *p*-xylene; 3 = *m*-xylene, 4 = *o*-xylene. (c) Column dimensions: 175 cm × 1 mm I.D.; adsorbent: BaSO₄-2; carrier gas (nitrogen) flow-rate: 3.5 cm³/min; temperature: 140°C. Peaks: 1 = benzene, 2 = toluene, 3 = ethylbenzene, 4 = isopropylbenzene, 5 = *p*-xylene, 6 = *m*-xylene, 7 = *o*-xylene.

    Thus, the retention of unsaturated organic compounds on barium sulphate is largely determined by the contribution (to the total interaction energy) of the energy of specific interaction of barium cations with double bonds of the adsorbed molecules with the formation of π-complexes. In this case, the interaction intensifies both with an increase in multiplicity and number of double bonds (ethane, ethylene and acetylene; butenes and butadiene) and with their greater accessibility to interaction with Ba^{2+} cations.

Retention of xylene and dimethylnaphthalene isomers on barium sulphate

    Fig. 4 shows the chromatograms obtained for a mixture of aromatic hydrocarbons on GTCB[2] and on two barium sulphate samples described above. On a non-specific GTCB adsorbent, the retention is chiefly determined by dispersion interaction depending on the molecular geometry; hence the *meta* isomer elutes from the column first, and then the *para-* and *ortho*-xylenes in the same peak. The elution order on barium sulphate is different. In this case, a non-specific intermolecular interaction (dispersion and electrostatic induction) is accomponied by a strong specific intermolecular interaction between the (electrostatically oriented) dipole of the adsorbate and the ionic adsorbent. The contribution of the dipole–ion interaction energy on the $BaSO_4$-2 sample is *ca.* 12 kJ/mol for benzene (Fig. 8) and increases with growth of the molecular dipole moment μ (Fig. 5). Hence, *para*-xylene elutes first from the barium sulphate-packed column, followed by *meta*-xylene and lastly *ortho*-xylene ($\mu = 0$, 0.34 and 0.62, respectively). In this case, on the relatively short columns with $BaSO_4$-1.5–15 and $BaSO_4$-2, all three isomers are separated rapidly and fully.

    Belyakova *et al.*[17] compared the selectivity (relative retention α) of adsorbents of a different nature for the xylene isomers and showed that high α values may be attained on some adsorbents. For example, on GTCB, $\alpha = 1.32$ for the isomers of *meta-* and *para*-xylenes, and 1.05 for those of *para-* and *ortho*-xylenes[2,5,19]. On liquid crystals deposited on the support or adsorbent[20–23], and on complex organic minerals[24–26], quite high separation coefficients were obtained for all xylene isomers. Yet,
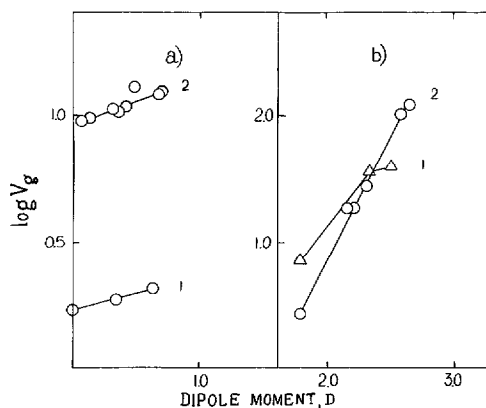

Fig. 5. Dependencies of logarithm of the retention volume on dipole moment of the molecules. Adsorbent: $BaSO_4$-2. (a) 1 = Xylenes; column temperature: 200°C, 2 = dimethylnaphthalenes; column temperature: 218°C. (b) 1 = Picolines; column temperature: 219°C; 2 = lutidines; column temperature: 219°C.
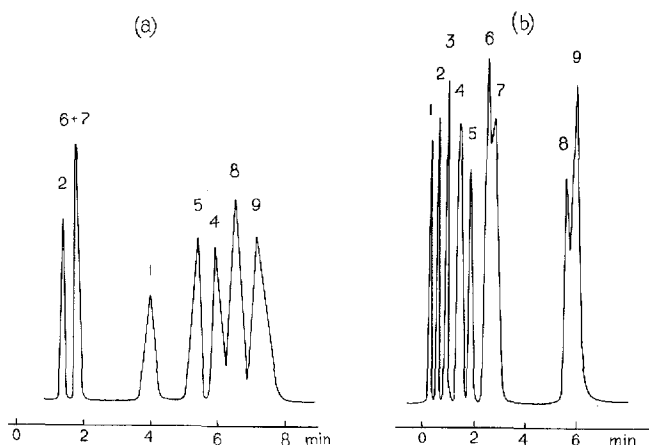
Fig. 6. Chromatograms of nitrogen-containing heterocyclic compounds on glass capillary columns packed with different adsorbents. (a) Column dimensions: 80 cm × 1 mm I.D.; adsorbent: HTGTCB[28]; carrier gas (nitrogen) flow-rate: 3 cm³/min; temperature: 150°C. (b) Column dimensions: 50 cm × 1 mm I.D.; adsorbent: BaSO$_4$-2; carrier gas (nitrogen) flow-rate: 12.7 cm³/min; temperature: initial, 200°C for 4 min, then programmed at 20°/min to end. Peaks: 1 = 2,6-lutidiene, 2 = 2-picoline, 3 = pyridine, 4 = 2,3- and 2,5-lutidine, 5 = 2,4-lutidine, 6 = 3-picoline, 7 = 4-picoline, 8 = 3,5-lutidine, 9 = 3,4-lutidine.
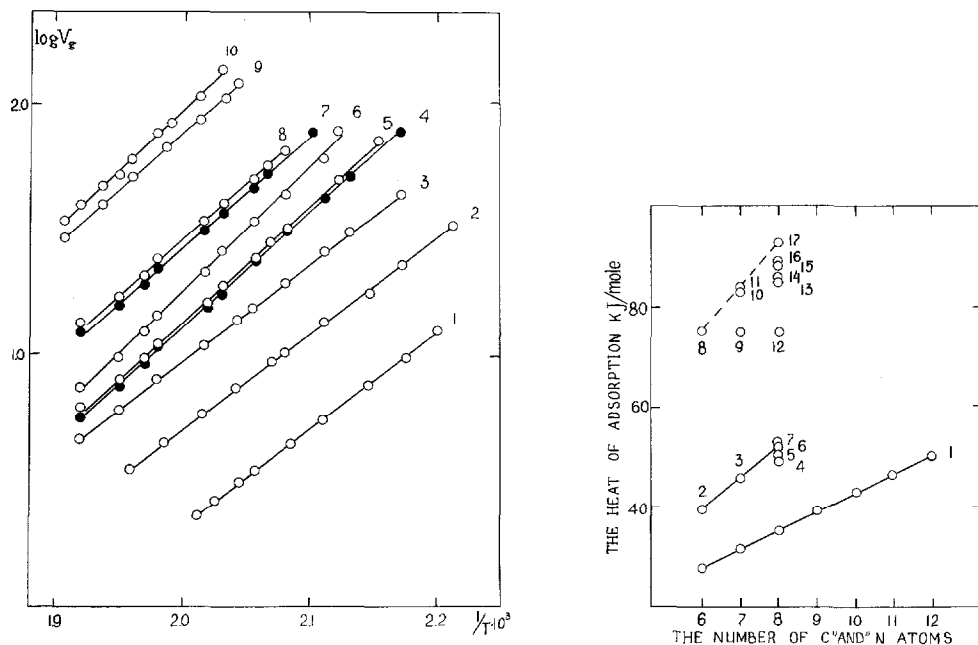

Fig. 7. Dependencies of logarithm of the retention volume of nitrogen-containing heterocyclic compounds on the reciprocal temperature. Adsorbent: BaSO$_4$-2. 1 = 2,6-Lutidine, 2 = 2-picoline, 3 = pyridine, 4 = 2,5-lutidine, 5 = 2,3-lutidine, 6 = 2,4-lutidine, 7 = 3-picoline, 8 = 4-picoline, 9 = 3,5-lutidine, 10 = 3,4-lutidine.

Fig. 8. Dependencies of adsorption heats on BaSO$_4$-2 on the number of carbon and nitrogen atoms in molecules. 1 = n-Hydrocarbons, 2 = benzene, 3 = toluene, 4 = e'hylbenzene, 5 = p-xylene, 6 = m-xylene, 7 = o-xylene, 8 = pyridine, 9 = 2-picoline, 10 = 3-picoline, 11 = 4-picoline, 12 = 2,6-lutidine, 13 = 2,5-lutidine, 14 = 3,5-lutidine, 15 = 2,3-lutidine, 16 = 3,4-lutidine, 17 = 2,4-lutidine.

these adsorbents may operate only within a limited temperature range. Barium sulphate has no such shortcomings.

The retention values of dimethylnaphthalene isomers were measured on BaSO$_4$-2. Fig. 5 shows the dependence of the logarithm of the retention volumes of some dimethylnaphthalene isomers on their dipole moments. As seen for all isomers except 1,8-dimethylnaphthalene, this dependence is virtually linear. The reason for the stronger retention of 1,8-dimethylnaphthalene lies in its structural features[27].

Retention of nitrogen-containing heterocyclic compounds on barium sulphate

Fig. 6 shows the chromatograms of a mixture of methyl- and dimethylpyridine isomers on BaSO$_4$-2 and for comparison on hydrogen-treated graphitized thermal carbon black (HTGTCB)[28]. Upon adsorption of polar molecules on HTGTCB, the retention is determined mainly by dispersion interaction. Therefore, picolines elute earlier than lutidines and the separation of isomers depends on the number of contacts of the molecule with the adsorbent surface[28]. On the ionic surfasce of barium sulphate the elution order is chiefly determined by the value of the molecular dipole moment (Fig. 5) and by the degree of screening of the nitrogen atom (with the unshared electron pair) with the bulky methyl groups. For instance, 2,6-lutidine with two methyl groups in the α-position elutes first, then 2-picoline with one methyl group, and then pyridine. The isomeric 3,4- and 3,5-lutidines elute from the column later than the 3- and 4-picolines, mainly due to the high dipole moments of these molecules. Similar behaviour of picoline and lutidine isomers was observed in studying their retention on cobalt phthalocyanine deposited on GTCB[29]; however, the influence of the dipole moment of the adsorbed molecules is not so pronounced as in the case of barium sulphate.

The thermodynamic adsorption characteristics of picolines and lutidines were studied on barium sulphate (Figs. 7 and 8). As seen, introduction of a nitrogen atom with an unshared electron pair into the benzene ring significantly increases the energy of the specific dipole–ion interaction of the adsorbed molecules with Ba^{2+} cations; for pyridine it is ca. 45 kJ/mol, when the adsorption heat equals 75 kJ/mol.

The dependence of the adsorption heats of picoline and lutidine isomers on their dipole moments μ (Fig. 9) is linear, just as for the logarithm of the retention
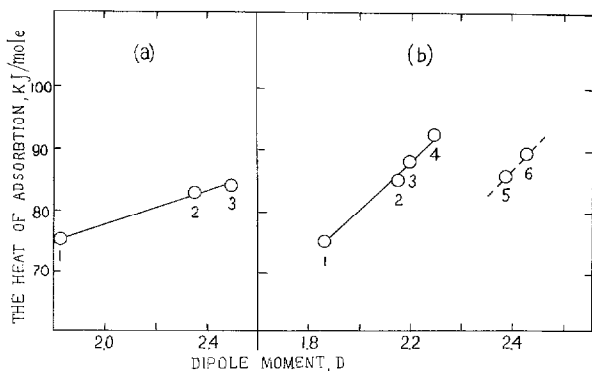

Fig. 9. Dependencies of adsorption heats on BaSO$_4$-2 on the molecular dipole moments. (a) 1 = 2-Picoline, 2 = 3-picoline, 3 = 4-picoline. (b) 1 = 2,6-Lutidine, 2 = 2,5-lutidine, 3 = 2,3-lutidine, 4 = 2,4-lutidine, 5 = 3,5-lutidine, 6 = 3,4-lutidine.
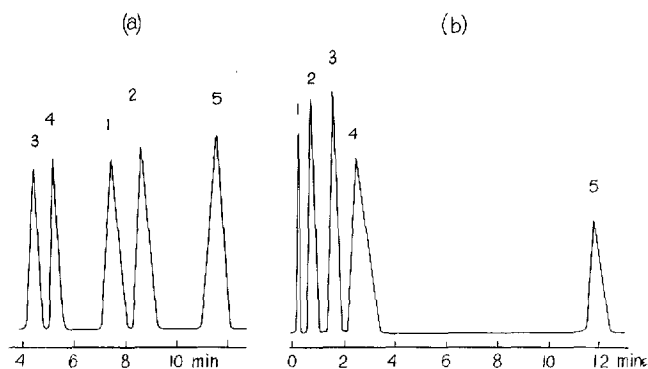
Fig. 10. Chromatograms of nitrogen-containing heterocyclic compounds on glass capillary columns packed with different adsorbents. (a) Column dimensions: 100 cm × 1 mm I.D.; adsorbent: HTGTCB[30]; carrier gas (helium) flow-rate: 8 cm³/min; temperature: 50°C. (b) Column dimensions: 30 cm × 1 mm I.D.; adsorbent: BaSO₄-2; carrier gas (helium) flow-rate: 6 cm³/min, temperature: initial, 200°C for 3 min, then programmed at 10°/min to 320°C. Peaks: 1 = benzene, 2 = pyridine, 3 = pyrazine, 4 = pyrimidine, 5 = pyridazine.
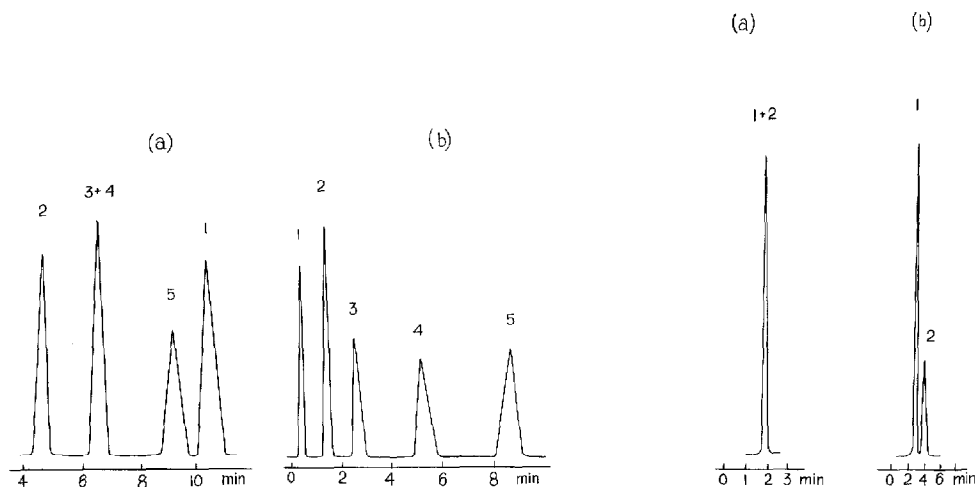

Fig. 11. Chromatograms of nitrogen-containing compounds on glass capillary columns packed with different adsorbents. (a) Column dimensions: 100 cm × 1 mm I.D.; adsorbent: HTGTCB[30], carrier gas (helium) flow-rate: 5 cm³/min; temperature: 210°C. (b) Column dimensions: 50 cm × 1 mm I.D.; adsorbent: BaSO₄-2; carrier gas (helium) flow-rate: 6 cm³/min; temperature: programmed 250–320°C at 10°/min. Peaks: 1 = naphthalene, 2 = quinoxaline, 3 = quinoline, 4 = isoquinoline, 5 = cinnoline.

Fig. 12. Chromatograms of oxygen-containing compounds on glass capillary columns packed with different adsorbents. (a) Column dimensions: 60 cm × 0.9 mm I.D.; adsorbent: HTGTCB; carrier gas (nitrogen) flow-rate 5 cm³/min; temperature: 42°C. (b) Column dimensions: 175 cm × 1 mm I.D.; adsorbent: BaSO₄-2; carrier gas (nitrogen) flow-rate: 12 cm³/min; temperature: 200°C. Peaks: 1 = 2,3-dihydropyran, 2 = tetrahydropyran.

volumes (Fig. 5). These dependencies may be used to estimate the approximate values of the molecular dipole moments. From the log V_R vs. μ dependence, we determined the value of μ for 3,4-lutidine, which equals approximately 2.7 D.

Fig. 10 demonstrates the separation of isomeric diazines. The elution order (pyrazine, pyrimidine and pyridazine) on barium sulphate also corresponds to an increase in the dipole moments of the molecules (0.7, 2.0 and 3.9 D). In the azonaphthalene series, quinoline and isoquinoline are not separated on HTGTCB due to the similar geometry of their molecules[30]. However, they are found to be separated very distinctly ($\mu = 2.2$ and 2.6 D, respectively) on barium sulphate (Fig. 11). On HTGTCB, cinnoline elutes earlier than naphthalene, whereas on barium sulphate it is retained very strongly because of an additional interaction of this molecule containing two nitrogen atoms with Ba^{2+} cations ($\mu = 4.1$ D).

Retention of oxygen-containing organic compounds on barium sulphate

We also studied the retention of some oxygen-containing organic compounds on barium sulphate. It is evident from Fig. 12 that on HTGTCB, di- and tetrahydropyrans elute in one peak, while on barium sulphate they are found to be distinctly separated in accord with the molecular dipole moments (1.3 D for 2,3-dihydropyran and 1.6 for tetrahydropyran).

CONCLUSION

In this work, we examined the barium sulphate ionic adsorbents. We synthesized barium sulphate and modified its surface with alkaline metal halides. Using capillary packed columns, we carried out gas chromatographic studies of certain unsaturated, aromatic hydrocarbons, and oxygen- and nitrogen-containing heterocyclic compounds.

The retention of organic compounds with double bonds on barium sulphate is determined by the contribution (to the total interaction energy) of the energy of specific interaction of barium cations with double bonds with the formation of π-complexes.

The retention of xylene and dimethylnaphthalene isomers and nitrogen- and oxygen-containing heterocyclic compounds on barium sulphate is determined by the value of the molecular dipole moments and by the degree of heteroatom screening with alkyl groups.

ACKNOWLEDGEMENT

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