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MACROPOROUS POLYMERIC SORBENTS INVOLVING NITRO AND AMINO FUNCTIONAL GROUPS

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SUMMARY

The gas chromatographic properties of sorbents with nitro and amino functional groups bonded directly to the carbon atoms of the benzene rings in a polymeric matrix were studied. The selectivity of the sorbents was determined and practical recommendations for the application of sorbents in gas chromatography are made.

INTRODUCTION

Chemical modification of polymeric sorbents allows one to alter the chemical characteristics of the polymer surface in order to obtain sorbents with greater selectivity. Modified sorbents with C_6H_5 , CH_3COO , OCH_3 , OCO_2CH_3 , Br and NO_2 functional groups have become available, with chromatographic properties differing from those of the original sorbents¹⁻³. However, their specificity is insufficient to provide desired elution sequences. Attachment of active functional groups, capable of donor-acceptor intermolecular interactions, to the carbon atoms of the benzene ring in polymeric matrix will enable one to obtain specific sorbents of higher selectivity with respect to sorbates that are either donors or acceptors of electrons.

EXPERIMENTAL

Sorbents with NO_2 functional groups were obtained by nitration of macroporous styrene-divinylbenzene (80:20) copolymer with potassium nitrate-concentrated sulphuric acid and subsequent reduction of the NO_2 groups with tin(II) chloride-concentrated hydrochloric acid⁴ gave sorbents with NH_2 functional groups.

Elemental analysis showed that the sorbents with NO_2 and NH_2 functional groups contained 7.3 and 9.1% of nitrogen, respectively. The completeness of the reduction process for the sample with NO_2 groups was established by IR spectroscopy.

Gas chromatographic studies were carried out on a chromatograph with katharometer using $1\text{ m} \times 3\text{ mm}$ I.D. columns at 150°C with helium as the carrier gas (flow-rate $30\text{ cm}^3/\text{min}$).

RESULTS AND DISCUSSION

The sorbents with NO₂ functional groups, according to the classification of Kiselev and Yashin⁵, are Type III sorbents with negative charge concentrated on the periphery, whereas the sorbents with NH₂ functional groups are Type II sorbents with protonated nitrogen atoms.

The sorbents studied were found to possess a high specificity of intermolecular interaction. The retention indices for polar compounds on these sorbents are higher than those on Porapack T and Chromosorb 104 (Table I). The sorbent with NH₂ groups on the benzene ring of the polymeric matrix had a higher specificity than those with NH₂ groups on the benzene ring of the polymeric matrix through the carbon chain, *e.g.*, anionite AN-221 (with ethylenediamine groups) and AN-211 (with hexamethylenediamine groups)⁶. This effect seems to result from the direct influence of the benzene ring on the electron density distribution of the sorbent studied.

TABLE I

RETENTION INDICES OF COMPOUNDS ON POLYMERIC SORBENTS

<i>Sorbate</i>	<i>Porapack T</i>	<i>Chromosorb 104</i>	<i>Sorbent with NO₂ groups</i>	<i>Sorbent with NH₂ groups</i>	<i>AN-221</i>
Ethanol	570	690	955	1180	567
Methyl ethyl ketone	700	680	1235	1195	—*
Benzene	755	835	1140	1250	668
Nitromethane	715	935	1325	1300	600
Pyridine	845	1025	1460	1485	766

* Methyl ethyl ketone is not eluted.

The dependence of the logarithm of the corrected retention volume on the number of carbon atoms in the sorbate's molecules for the sorbents studied was also investigated. A high specificity of the sorbents was observed, and also a high selectivity with respect to molecules capable of donor-acceptor interactions.

The increments of the sorption free energies were determined for a series of polar molecules (relative to *n*-hexane) on sorbents with NO₂ and NH₂ functional groups (Table II). These values are larger for the sorbent with NH₂ functional groups, which indicate its higher specificity.

TABLE II

INCREMENTS OF FREE ENERGIES FOR COMPOUNDS OF DIFFERENT CLASSES RELATIVE TO *n*-HEXANE AT 150°C

<i>Sorbate</i>	$-\Delta(\Delta G)$ (cal/mol)	
	<i>Sorbent with NO₂ groups</i>	<i>Sorbent with NH₂ groups</i>
1-Hexene	773	1697
Benzene	1692	2583
Hexanone	2764	2828
Hexanol	2975	3644
Capronitrile	3441	4431
Caproic acid	3692	5125

Some features of the gas chromatographic behaviour of the sorbents studied, which are connected with the nature of the NO_2 and NH_2 functional groups, should be emphasized. In particular, the selectivity of the sorbent with NO_2 groups with respect to ketones is close to that with respect to alcohols, whereas the selectivity of the sorbent with NH_2 groups with respect to alcohols is higher than that for ketones; in addition, the selectivity of the latter with respect to aromatic hydrocarbons approaches that for ketones. Both sorbents possess high selectivity for organic acids and nitriles.

The sorbents specified provide the effective separation of compounds of different classes with similar physico-chemical properties (Table III).

TABLE III

SEPARATION COEFFICIENTS (K_p) AND RETENTION INDICES (I) OF ORGANIC COMPOUNDS WITH SIMILAR PHYSICO-CHEMICAL PROPERTIES

Sorbates	Sorbent with NO_2 groups		Sorbent with NH_2 groups	
	K_p	I	K_p	I
1-Heptene	3.2	945	8.1	1105
Heptane		700		700
Benzene	9.2	1140	32.5	1250
Cyclohexane		550		504
Propanol	1.0	1095	1.9	1245
Acetone		1100		1145
Acetic acid	6.9	1310	68.4	1540
Octane		800		800
Water	2.0	890	13.7	1180
Heptane		700		700
Acetonitrile	11.9	1210	43.0	1295
Cyclohexane		550		504
Pyridine	4.6	1460	4.9	1485
Benzene		1140		1250
Butanol	5.1	1250	3.6	1325
Diethyl ether		825		1105
1,4-Dioxan	14.1	1330	52.7	1390
Hexane		600		600

The high values of the retention indices of organic acids, alcohols, ketones, nitrated compounds and nitriles result from the formation of charge-transfer complexes with the functional groups of the sorbents. The data presented in Table III also indicate the high selectivity of the sorbents with respect to unsaturated and aromatic compounds due to the polarization interaction involving the formation of π -complexes.

The retention of chloro-substituted derivatives of methane is of interest. In particular, on the sorbent with NO₂ functional groups these compounds are eluted in the sequence carbon tetrachloride, dichloromethane, chloroform (Table IV).

TABLE IV

RELATIVE RETENTION TIMES AND RETENTION INDICES OF CHLORO-SUBSTITUTED DERIVATIVES OF METHANE

μ = Dipole moment.

Sorbate	μ (D)	t_R/t_R (<i>n</i> -hexane)		Retention index	
		Sorbent with NO ₂ groups	Sorbent with NH ₂ groups	Sorbent with NO ₂ groups	Sorbent with NH ₂ groups
Dichloromethane	1.57	3.5	4.7	975	985
Chloroform	1.01	20.6	16.4	1475	1200
Carbon tetrachloride	0.0	2.5	2.3	880	860

The presence of highly protonated hydrogen atoms in the chloroform molecule favours the formation of strong charge-transfer complexes with the active sites of the sorbent, such as hydrogen bonding⁷. This is why the retention time of chloroform is higher than that of carbon tetrachloride and dichloromethane. The sequence of elution of chloro-substituted derivatives of methane on the sorbent with NH₂ functional groups is similar to the previous case, but a larger difference in the retention times of carbon tetrachloride and dichloromethane is observed.

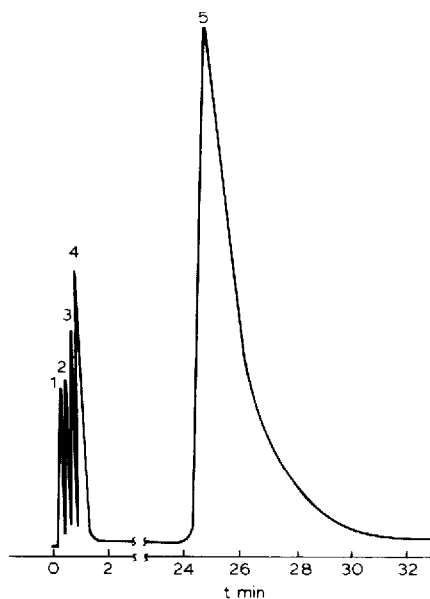


Fig. 1. Chromatogram of a mixture of the C₇-C₁₀ hydrocarbons and formic acid. Stainless-steel column (1 m × 3 mm I.D.). Sorbents with NH₂ groups (aminopolysorb); temperature, 150°C; flow-rate of carrier gas (helium), 30 cm³/min; detector, katharometer. Peaks: 1 = heptane; 2 = *n*-octane; 3 = *n*-nonane; 4 = *n*-decane; 5 = formic acid.

The application of these sorbents with increased selectivity of molecular interaction made it possible to elute C_5 – C_8 hydrocarbons (C_5 – C_{11} hydrocarbons with the sorbent with nH_2 functional groups), which are common impurities, before the polar compounds considered. This enables the detection sensitivity for hydrocarbon impurities in water, alcohols, organic acids, e.g., formic acid, to be increased (Fig. 1).

Hence these investigations of sorbents with NO_2 and NH_2 functional groups have demonstrated the selective properties of the sorbents concerned, and should allow the solution of a number of practical problems of separations of compounds with close boiling temperatures and close molecular weights, and also the problem of the determination of the content of non-polar in the polder compounds.

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