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APPLICATION OF MACROPOROUS ANION-EXCHANGE RESINS AN-221 AND AN-211 AS SORBENTS FOR GAS CHROMATOGRAPHY

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SUMMARY

The structure and gas chromatographic properties of the anion-exchange resins AN-221 and AN-211, which have ethylenediamine and hexamethylenediamine groups, respectively, have been studied. It was found that these resins show specific interactions and high selectivity with respect to amines, alcohols and water. The resins can be used for the separation of aliphatic amines, nitriles, ketones and saturated and unsaturated hydrocarbons and for the determination of ammonia in water.

In addition to porous polymers, which have found wide application as sorbents for gas chromatography[1], the utilization of macroporous ion-exchange resins in different ionogenic forms for gas chromatographic separations is of interest [2–5].

For example, Hirsch *et al.*[3] used a macroporous ion-exchange resin for the separation of a mixture of hydrocarbons. The retention indices of aromatic hydrocarbons increase with increasing resin cation size. Resins in the Ag^+ form retain aromatic hydrocarbons and olefins strongly and separate the geometric isomers of olefins.

Fritz and Chang[4] used XAD-1, -2, -4, -6, -7 and -11 macroporous resins and also their ion-exchange forms (for example, Br-XAD-2, Br-XAD-4, NO_2-XAD-2 and H_2PO_3-XAD-2) for the separation of organic and inorganic gases and liquids. Burnham[5] and Junk *et al.*[6] used XAD-1, -2 and -4 macroporous resins for sorption and concentration of admixtures of organic substances from drinking water and biological liquids.

In gas chromatography and sorption procedures the macroporous anion-exchange resin AN-251 (a copolymer of 2-methyl-5-vinylpyridine and divinylbenzene) has been used and studies of its structure and gas chromatographic and adsorption characteristics have been published[7–10].

The adsorption properties of other porous anion-exchange resins, containing dimethylamine, diethylamine, ethylenediamine, hexamethylenediamine and other groups, have also been studied[11–15]. Adsorption isotherms of CO_2, SO_2 and H_2O on these resins have been studied.

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We have studied the structural and gas chromatographic properties of the anion-exchange resins AN-221 and AN-211, which contain ethylenediamine and hexamethylenediamine groups, respectively. These resins contain primary and secondary amine groups and, in accordance with Kiselev's classification[16], are sorbents of type II. The structural characteristics of the sorbents are listed in Table I. These sorbents are characterized by a homogeneous pore distribution and are transition-porous sorbents.

The gas chromatographic studies were carried out with a 1 m × 3 mm I.D. column at 150°C. The carrier gas was helium at a flow-rate of 30 ml/min.

TABLE I

STRUCTURAL CHARACTERISTICS OF AN-221 AND AN-211

Structural characteristic	*AN-221*	*AN-211*
Bulk weight (g/cm^3)	0.42	0.39
Specific surface area (m^2/g)	74.0	112.0
Pore volume (cm^3/g)	0.84	0.92
Average pore radius (Å)	150.0	170.0

It was found that in separations on AN-221 and AN-211, the local electron structure of the molecules of groups B and D[16] has a considerable influence on their capacity to undergo specific interactions. Unsaturated and aromatic compounds are retained more than the corresponding saturated compounds (Table II). Polar compounds are retained more than non-polar compounds with similar molecular masses (Table III). This can be seen particularly from the retentions of esters and ethers, nitromethane and dioxane. The molecules of group D, *i.e.*, alcohols and amines capable of forming hydrogen bonds with the surface of the sorbent, are retained most on these sorbents.

TABLE II

RELATIVE RETENTION TIMES OF SATURATED AND UNSATURATED HYDROCARBONS

Retention times relative to pentane (= 1.0).

Sorbate	*Sorbent*	
	AN-221	*AN-211*
Pentane	1.0	1.0
cis-Pentene-2	1.1	1.2
Pentadiene-1,3	1.3	1.7
Hexane	2.3	2.7
Hexene-1	2.5	3.0
Cyclohexane	2.8	3.4
Cyclohexene	3.3	4.3
Benzene	3.5	5.8
Heptane	5.4	5.5
cis-Heptene-3	5.7	5.9
Toluene	9.5	14.7

TABLE III

RELATIVE RETENTION TIMES OF SUBSTANCES WITH SIMILAR MOLECULAR MASSES

Retention times relative to pentane (= 1.0).

Sorbate	*Molecular mass*	*Sorbent*		
		Polysorb-1	*AN-221*	*AN-211*
Ethyl acetate	88.1	2.4	3.2	4.3
1,4-Dioxan	88.1	4.4	6.5	9.3
n-Pentanol	88.1	5.6	39.0	42.8
Cyclohexane	84.2	3.1	2.8	3.4
n-Butyric acid	88.1	5.9	Not eluted	
Diethyl ether	74.1	0.9	1.1	1.7
Pentane	72.1	1.0	1.0	1.0
Tetrahydrofuran	72.1	2.3	3.3	4.9
n-Butanol	74.1	2.8	10.5	14.3
Methyl acetate	74.1	1.1	1.6	2.1
Diethylamine	73.1	1.2	5.4	—
Pyridine	79.1	4.7	12.0	20.9
Propionitrile	55.1	1.6	3.2	6.3
Acetone	58.1	0.7	Not eluted	3 0
Nitromethane	61.0	1.0	2.8	6.0
Acetic acid	60.0	1.0	Not eluted	62.7

It can be seen from the relative retention times of compounds with similar boiling points in Table IV that the retentions on AN-221 and AN-211 differ considerably from those on Polysorb-1. The retentions of alcohols and water are 4–10 times greater on AN-221 and AN-211 than on Polysorb-1, whereas the retentions of hydrocarbons and ethers hardly change.

TABLE IV

RELATIVE RETENTION TIMES OF SUBSTANCES WITH SIMILAR BOILING POINTS

Retention times relative to pentane (= 1.0).

Sorbate	*B.p. (°C)*	*Sorbent*		
		Polysorb-1	*AN-221*	*AN-211*
Methanol	64.7	0.2	1.0	2.8
Tetrahydrofuran	64–66	2.3	3.3	4.9
Ethanol	78.37	0.4	1.5	3.3
Ethyl acetate	77.15	2.4	3.2	4.3
Carbontetrachloride	76.8	3.1	3.7	4.7
Acetonitrile	81.6	0.6	1.2	3.8
Benzene	80.1	2.9	3.5	5.8
Cyclohexane	81.4	3.1	2.8	3.4
Water	100.0	0.1	1.0	1.9
n-Propanol	97.8	0.9	4.1	10.0
1,4-Dioxane	100.8	4.4	6.5	9.3
n-Heptane	98.43	4.8	5.4	5.5

The results indicate that AN-221 and AN-211 (especially the latter) show specific interactions and high selectivity with respect to amines, alcohols and water.

In a number of instances a change in the elution sequence from the chromatographic column with is observed with AN-221 and AN-211 in comparison with Polysorb-1, particularly with acetonitrile, diethyl ether, nitromethane, water and alcohols.

Retention indices of some polar molecules on AN-221 and AN-211 are compared with corresponding values on Chromosorb 102, 104 and 107 (Table V). The retention indices are considerably higher on AN-221 and AN-211 than on the non-polar Chromosorb 102 (especially for alcohols and nitriles) and approach the values on sorbents of moderate polarity (Chromosorb 104 and 107).

TABLE V

RETENTION INDICES OF SOME COMPOUNDS ON DIFFERENT POLYMERIC SORBENTS

Sorbate	*Sorbent*				
	AN-221	*AN-211*	*Chromosorb 102*	*Chromosorb 104*	*Chromosorb 107*
Acetonitrile	548	650	460	855	550
Nitromethane	600	717	510	935	—
Ethanol	567	633	425	690	515
Benzene	668	733	650	835	660
Pyridine	766	826	705	1025	—

A characteristic feature of AN-221 is irreversible sorption of carbonyl compounds (ketones, acids and aldehydes). Probably a chemical reaction occurs between the sorbate and sorbent with isolation of water. Such a phenomenon was not observed on AN-211, with hexamethylenediamine groups. The difference in the properties of AN-221 and AN-211 can be related to the difference in the structures of their functional groups.

The dependence of the logarithm of the retention volume on the number of carbon atoms in the sorbate molecule on AN-211 is linear for homologous series of hydrocarbons, alkylbenzenes and ketones, but a deviation from linearity is observed for alcohols.

The retention of compounds with different geometrical structures but equal numbers of carbon atoms in the molecule was studied (Table VI). Branched-chain isomers elute in the same manner as on Polysorb-1, before normal compounds, and cyclic compounds elute later in accordance with their boiling points.

Substances are eluted from AN-221 and AN-211 with symmetrical peaks, the coefficients of asymmetry for the molecules of most compounds being 1–1.6 but with higher values for amines, *e.g.*, 1.8 for diethylamine and 2.0 for triethylamine on AN-221.

On AN-221 the heights equivalent to a theoretical plate are 7–12 mm and on AN-211 9–16 mm. It would probably be possible to produce analogous anion-exchange resins with higher chromatographic efficiencies if a polymer with a more uniform geometrical structure for grafting ionogenic groups were to be used.

TABLE VI

DEPENDENCE OF RELATIVE RETENTION TIME ON THE GEOMETRICAL STRUCTURE OF MOLECULES

Retention times relative to pentane (= 1.0).

Sorbate	*Sorbent*	
	AN-221	*AN-211*
Isopropanol	2.5	6.0
n-Propanol	4.0	10.0
tert.-Butanol	3.2	5.5
sec.-Butanol	5.9	9.3
Isobutanol	7.9	10.5
n-Butanol	10.5	14.3
Isopentane	9.9	0.9
n-Pentane	1.0	1.0
Cyclopentane	1.5	2.1
Isooctane	9.3	2.7
n-Octane	14.3	10.7
n-Hexane	2.3	2.7
Methylcyclopentane	2.5	2.9
Cyclohexane	2.8	3.4

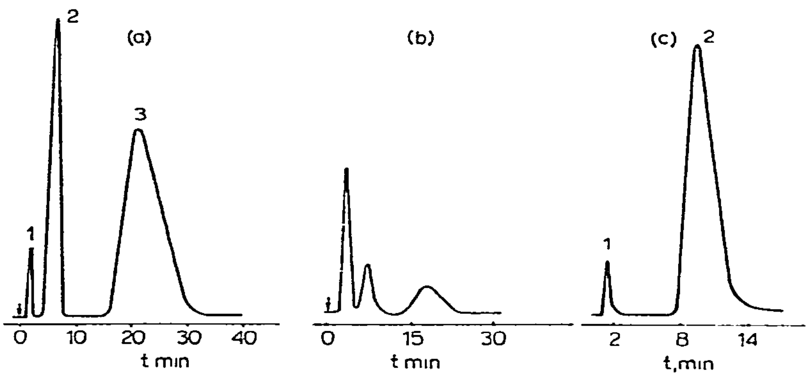

Fig. 1. Chromatograms for the separation of different mixtures on AN-221. (a) Methylamine (1), dimethylamine (2) and diethylamine (3). Column temperature, 150°C; carrier gas flow-rate, 40 ml/min. (b) Ammonia and water. Column temperature, 100°C; carrier gas flow-rate, 40 ml/min. (c) Acetonitrile, propionitrile and butyronitrile. Column temperature, 150°C; carrier gas flow-rate, 40 ml/min.

The thermal stability of AN-221 and AN-211 was determined. The thermogram showed that degradation starts at 180–200°C, *i.e.*, the upper temperature limit for the utilization of these resins is lower than that for the polymeric sorbents used previously in gas chromatography. However, owing to their high selectivity, the application of these anion-exchange resins in gas chromatography is promising. AN-221 and AN-211 have been used to separate aliphatic amines, nitriles, ketones, saturated and unsaturated hydrocarbons and to determine ammonia in water (Figs. 1 and 2).

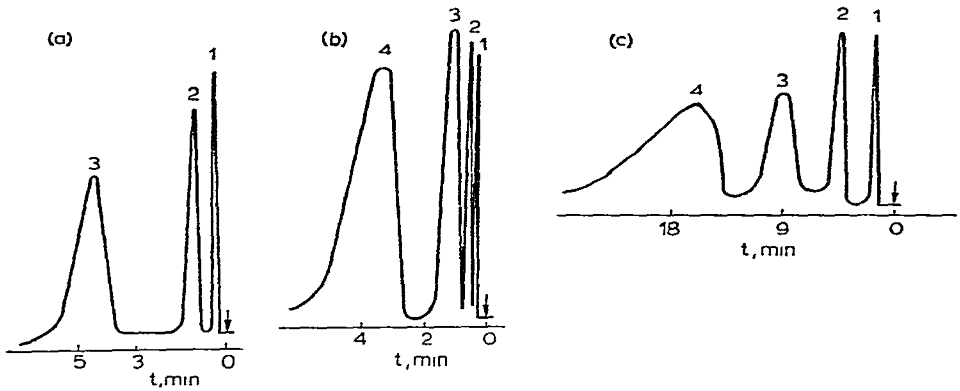

Fig. 2. Chromatograms for the separation of different mixtures on AN-211. (a) Ethylene (1), propylene (2) and butylene (3). Column temperature, 80°C; carrier gas flow-rate, 50 ml/min. (b) Methane (1), ethane (2), propane (3) and butane (4). Column temperature, 80°C; carrier gas flow-rate, 50 ml/min. (c) Acetone (1), methyl ethyl ketone (2), diethyl ketone (3) and methyl butyl ketone (4). Column temperature, 150°C; carrier gas flow-rate, 50 ml/min.

REFERENCES

1 K. I. Sakodynskii and L. I. Panina, *Polymeric Sorbents in Molecular Chromatography*, Nauka, Moscow, 1977.
2 K. Ohzeki and T. Kambara, *J. Chromatogr.*, 55 (1971) 319.
3 R. F. Hirsch, H. C. S.ober, M. Kowblansky, F. N. Hubner and A. W. O'Commell, *Anal. Chem.*, 45 (1973) 2100.
4 J. S. Fritz and R. C. Chang, *Anal. Chem.*, 46 (1974) 938.
5 A. K. Burnham, *Anal. Chem.*, 44 (1972) 139.
6 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
7 L. I. Panina, N. S. Klinskaya, L. D. Glazunova and K. I. Sakodynskii, *J. Chromatogr.*, 77 (1973) 51.
8 N. S. Klinskaya, N. B. Galitskaya, L. I. Panina, K. I. Sakodynskii and I. G. Stobeneva, in K. I. Sakodynskii (Editor), *Properties and Application of Sorbents*, L. Karpov Institute of Physical Chemistry, Moscow, 1976, p. 11.
9 L. D. Belyakova, N. B. Galitskaya, A. V. Kiselev, A. B. Pashkov, N. P. Platonova and T. I. Shevchenko, *Dokl. Akad. Nauk SSSR*, 210 (1973) 1117.
10 L. D. Belyakova, N. B. Galitskaya, A. V. Kiselev, N. P. Platonova and I. G. Stebeneva, *Kolloidn. Zh.*, 38 (1976) 1060.
11 L. D. Belyakova, A. V. Kiselev, E. I. Lyustgarten, A. B. Pashkov, N. P. Platonova and T. I. Shevchenko, *Dokl. Akad. Nauk. SSSR*, 213 (1973) 1311.
12 L. D. Belyakova, V. N. Davankova, A. V. Kiselev, T. Y. Muttik, M. P. Tsuryupa and T. I. Shevchenko, *Kolloidn. Zh.*, 40 (1978) 6.
13 V. M. Kiryutenko, A. V. Kiselev and V. I. Ligin, *Kolloidn. Zh.*, 37 (1975) 382.
14 N. N. Avgul, T. V. Bermakova, L. D. Belyakova, L. D. Vorobieva, N. T. Dadugina, A. V. Kiselev and T. Y. Muttik, *Kolloidn. Zh.*, 39 (1977) 339.
15 L. D. Belyakova, A. V. Kiselev, N. P. Platonova, T. I. Shevchenko, G. A. Artyushin and A. K. Valikova, *Kolloidn. Zh.*, 41 (1979) 4.
16 A. V. Kiselev and Ya. I. Yashin, *Gas Adsorption Chromatography*, Nauka, Moscow, 1967.