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INCREASED EFFECTIVENESS OF CHROMATOGRAPHIC COLUMNS PACKED WITH ZEOLITES IN THE SEPARATION OF MIXTURES OF SOME ORGANIC COMPOUNDS

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SUMMARY

By use of model mixtures, consisting of hydrocarbons, alcohols, ethers and ketones, the effect of the nature of the zeolite cation and of the carrier gas as well as the method of column packing (volumetric or surfasce layer) on the chromatographic process has been studied. It is found that the use of a carrier gas such as carbon dioxide (as compared with helium or nitrogen), zeolites with lower cation density and also the surface layer method of packing increases the effectiveness of the chromatographic column, decreases the analysis time, makes the peaks more symmetric, allows separations at lower column temperatures and broadens the range of utilization of zeolites in gas chromatography.

INTRODUCTION

All reports on the use of zeolites as adsorbents for separation of mixtures by gas chromatography (GC) can be divided into the following eight groups, depending upon the composition of the mixtures to be separated: (1) hydrogen isotope mixture; (2) inert gas mixtures; (3) binary mixtures of oxygen and nitrogen; (4) mixtures of oxygen and argon; (5) mixtures of hydrogen, oxygen, nitrogen, methane and carbon monoxide; (6) the above mixtures, but also containing carbon dioxide or other compounds, strongly sorbed on zeolites; (7) mixtures of hydrocarbon gases; (8) liquid hydrocarbon mixtures having a wide range of boiling points[1,2]. It is noteworthy that the separation and chromatographic analysis of mixtures of liquid organic substances is sometimes difficult, due to strong adsorption of individual components[3,4], or their catalytic transformations on zeolites[5].

In order to avoid these complications and increase the effectiveness of the chromatographic columns, a combination of three methods has been suggested: packing chromatographic columns with zeolites in the surface layer mode[6]; instead of

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traditional inert carrier gases (helium, nitrogen and hydrogen), the use of so-called active carrier gases (carbon dioxide), which at the same time play the rôle of the displacer[7,8]; the use of zeolites with lower cation density[9].

In this paper we report a chromatographic investigation of the effectiveness of zeolites for the separation of model mixtures, consisting of C_5–C_{10} hydrocarbons, C_2–C_8 monobasic alcohols and certain ethers and ketones.

EXPERIMENTAL

An LHM-72 chromatograph equipped with a flame ionization detector was employed. The columns (50 cm × 4 mm I.D.) were packed with zeolites of type Y which, compared with type X generally used in GC, are characterized by a lower cation density. The hydrogen form (HY) with a decationization degree of about 78%[9] was prepared from the sodium form (NaY) of the zeolite by means of ion exchange. Zeolite samples enriched with cadmium cations (CdY), exhibiting specific interactions with molecules of compounds characterized by the presence of π-bonds, were prepared from the sodium form by ion exchange[10]. The zeolites were used both in the volumetric and surface layer modes. In the first case the granulation was 0.5–1.0 mm. In the second case the dusty zeolite, particle dimensions ca. 25–65 μm, was coated onto the solid support (Chromosorb W) to give a granulation of 0.25–0.35 mm. The amount of the zeolite coated onto the solid support was 30%. The sorbents were activated by heating at 400°C for 4 h. The columns were heated (isothermal) over the range 200–350°C. Nitrogen, helium (inert) and carbon dioxide (active) were used as carrier gases with a constant velocity of 30 ml/min.

To estimate the effect of the method of packing of the column with zeolites, the nature of the carrier gas and the cation density of the zeolites on the chromatographic separation of model mixtures, the specific retention volumes, V_g, and asymmetry coefficients, $\bar{v}$, of the peaks of certain compounds were determined. The effectiveness of the chromatographic column was defined by the number of theoretical plates per m of its length.

RESULTS AND DISCUSSION

It is seen from Tables I and II that under the experimental conditions part of the hydrocarbons is strongly sorbed on the zeolites and not eluted from the chromatographic column; this is most obvious in the cases of volumetric packing with adsorbent (Table I). The difference in column temperature employed for the columns with volumetric and surface layer packings is connected with the selection of the optimum conditions for separation of the model mixtures. In the case of volumetric packing, the analysed mixtures are separated only at 300°C, whereas with surface layer packing, at the same temperature, the analysed mixture is eluted as a single peak, *i.e.*, there is no separation of its components. Therefore, with surface layer packing a column temperature of 250°C was used.

The tabulated data indicate the importance of the packing method, the nature of the zeolite cation and the nature of the carrier gas in the regulation of the retention ability of the zeolite. When changing from the sodium form of the zeolite to the hydrogen form, *i.e.*, with decreasing cation density, the specific retention volumes of

TABLE I

EFFECT OF THE NATURE OF THE ZEOLITE CATION AND THE CARRIER GAS ON THE SPECIFIC RETENTION VOLUMES, V_g, OF SOME HYDROCARBONS

Volumetric packing of chromatographic column. Column temperature: 300°C.

Hydrocarbon	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Octane	–	–	108.9	–	–	103.5	–	–	–
Nonane	–	–	–	–	–	163.4	–	–	–
Decane	–	–	–	–	–	–	–	–	–
Cyclohexane	42.0	33.1	13.7	19.5	15.3	11.3	53.7	38.4	36.9
1-Hexene	–	–	19.21	21.30	19.6	3.42	–	–	23.4
Benzene	–	–	125.4	66.6	60.6	41.40	–	–	–

hydrocarbons decrease, but when changing to CdY zeolite, capable of strong specific intermolecular interactions with hydrocarbon molecules, there is an increase in retention volumes.

With increasing molecular weight of the carrier gas the specific retention volumes of hydrocarbons decrease independent of the cation-exchange form of the zeolite. Obviously, in this case carbon dioxide plays the rôle not only of the carrier gas but also of a displacer, since some compounds, which are not eluted when helium or nitrogen is used as the carrier gas, are eluted by carbon dioxide. However, it is noteworthy that even such an "active" carrier gas as carbon dioxide does not suppress the specific action of Cd^{2+} and this ion-exchange form of the zeolite results in the highest values of the retention volumes of hydrocarbons, as compared with the forms NaY and HY.

The use of the surface layer mode of packing results in a better separation of the model mixtures, since unlike the volumetric method there is no irreversible adsorption of certain components (Tables I and II). Chromatograms showing the separation of model hydrocarbon mixtures are presented in Fig. 1.

Tables III and IV give the asymmetry coefficients of the peaks of hydrocarbons

TABLE II

EFFECT OF THE NATURE OF THE ZEOLITE CATION AND THE CARRIER GAS ON THE SPECIFIC RETENTION VOLUMES OF SOME HYDROCARBONS

Surface layer packing. Column temperature: 250°C.

Hydrocarbon	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Octane	378.0	441.0	257.60	245.0	155.4	105.0	–	–	616.0
Nonane	–	840.0	703.5	290.5	245.0	154.7	–	–	1187.2
Decane	–	–	147.0	319.0	298.0	200.2	–	–	–
Cyclohexane	63.0	61.6	52.50	60.50	42.0	19.60	182.0	150.5	134.4
1-Hexene	217.0	171.5	114.1	67.9	67.2	30.1	–	–	105.0
Benzene	609.0	345.5	327.6	408.0	273.0	56.0	–	–	616.0

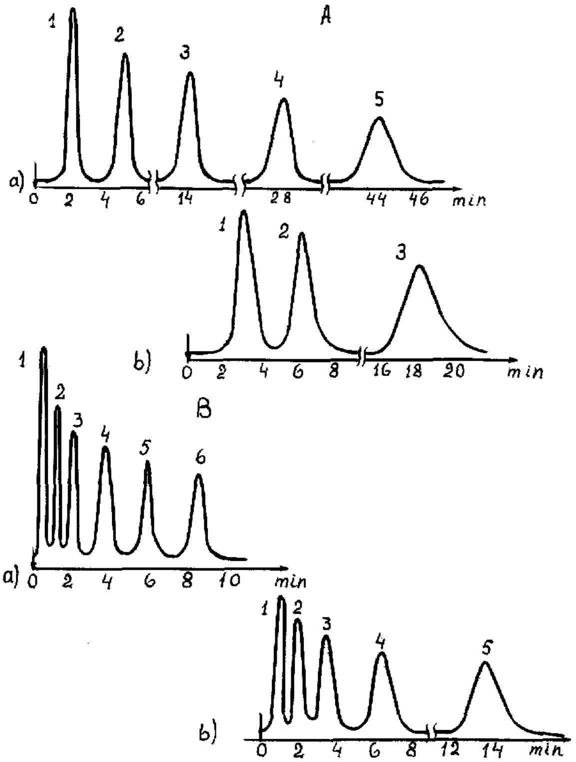

Fig. 1. Chromatograms of C_5–C_{10} hydrocarbon mixture on zeolite HY: (A) volumetric and (B) surface layer mode. Column temperatures: (A) 300°C; (B) 225°C. Column length: 0.5 m. Carrier gases: (a) carbon dioxide; (b) helium. Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane.

on zeolites packed by the volumetric and surface layer methods. The most symmetric peaks were obtained on hydrogen forms of zeolites packed with the surface layer method and by use of carbon dioxide as the carrier gas. Probably this is due to the asbsence of strong cation interactions with the adsorbate molecules, the decrease in diffusion phenomena in the thin layer of the zeolite and the displacing effect of carbon dioxide as the carrier gas.

TABLE III

ASYMMETRY COEFFICIENTS OF SOME HYDROCARBONS

Volumetric packing. Column temperature: 300°C.

Hydrocarbon	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Octane	–	–	0.66	–	–	0.67	–	–	–
Cyclohexane	0.64	0.65	0.90	0.87	0.80	0.94	0.60	0.67	0.76
1-Hexene	–	–	0.83	0.60	0.67	0.88	–	–	0.70
Benzene	–	–	0.76	0.50	0.52	0.80	–	–	–

TABLE IV

ASYMMETRY COEFFICIENTS OF SOME HYDROCARBONS

Surface layer packing. Column temperature: 250°C.

Hydrocarbon	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Octane	0.41	0.50	0.75	0.50	0.50	0.80	–	–	0.60
Cyclohexane	0.70	0.67	0.91	0.80	0.80	0.98	0.62	0.47	0.72
1-Hexene	0.52	0.79	0.82	0.76	0.60	0.88	–	–	0.50
Benzene	0.47	0.57	0.75	0.60	0.67	0.82	–	–	0.67

In a previous study[11] only C_2–C_4 alcohol mixture could be separated on zeolites coated with Carbowax 400. The present method allows to separation of C_2–C_8 alcohol mixtures. In addition, it should be noted that each of three modifications has a specific effect on the chromatographic elution of certain alcohols (Tables V and VI).

TABLE V

EFFECT OF THE NATURE OF THE ZEOLITE CATION AND THE CARRIER GAS ON THE SPECIFIC RETENTION VOLUMES OF SOME ALCOHOLS

Volumetric packing. Column temperature: 300°C.

Alcohol	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Amyl alcohol	–	–	20.2	12.0	8.7	7.6	–	–	31.8
Hexanol	–	–	39.6	21.9	23.4	10.5	–	–	65.70
Heptanol	–	–	12.6	–	–	16.5	–	–	23.70
Octanol	–	–	18.6	–	–	*	–	–	–

* Catalytically transformed.

TABLE VI

EFFECT OF THE NATURE OF THE ZEOLITE CATION AND THE CARRIER GAS ON THE SPECIFIC RETENTION VOLUMES OF SOME ALCOHOLS

Surface layer packing. Column temperature: 250°C.

Alcohol	*NaY*			*HY*			*CdY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Amyl alcohol	99.4	–	80.5	60.5	80.50	56.0	283.5	–	147.0
Hexanol	252.0	–	161.0	80.5	105.0	73.5	–	–	–
Heptanol	479.5	–	283.5	147.0	112.5	105.0	–	–	–
Octanol	–	–	406	–	235.9	122.5	–	–	–

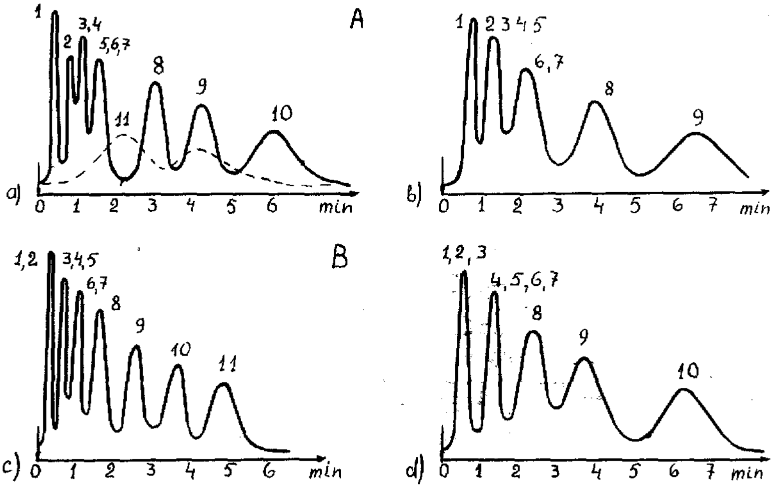

Fig. 2. Chromatograms of C_2–C_8 alcohol mixture on zeolite HY: (A) volumetric and (B) surface layer mode. Carrier gases: (a), (b) carbon dioxide; (b), (d) helium. Column temperatures: (A) 300°C; (B) 225°C. (a) Peaks: 1 = ethanol; 2 = *sec.*-butanol; 3, 4 = propanol, isopropanol; 5–7 = *tert.*-butanol, butanol, isobutanol; 8 = pentanol; 9 = hexanol; 10 = heptanol; 11 = octanol transformed catalytically. (b) Peaks: 1 = ethanol; 2–5 = propanol, isopropanol, *tert.*-butanol, *sec.*-butanol; 6, 7 = butanol, isobutanol; 8 = pentanol; 9 = hexanol. (c) Peaks: 1, 2 = ethanol, isopropanol; 3–5 = propanol, *sec.*-butanol, *tert.*-butanol; 6, 7 = butanol, isobutanol; 8 = pentanol; 9 = hexanol; 10 = heptanol; 11 = octanol. (d) Peaks: 1–3 = ethanol, isopropanol, propanol; 4–7 = *sec.*-butanol, *tert.*-butanol, isobutanol, butanol; 8 = pentanol; 9 = hexanol; 10 = heptanol.

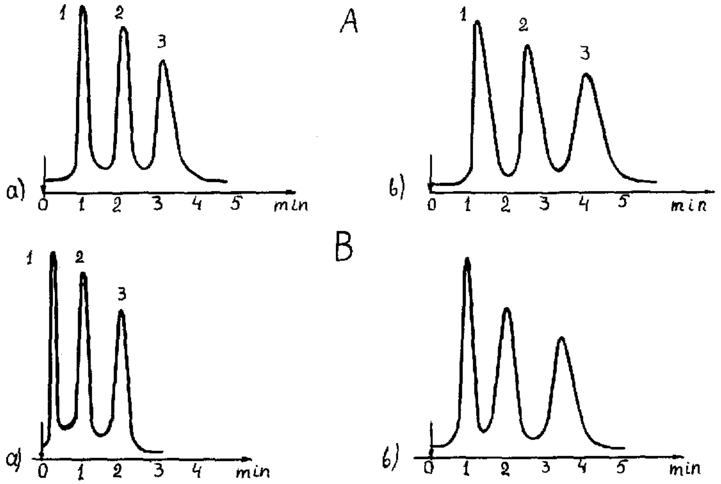

Fig. 3. Chromatograms of ether mixture on zeolite HY: (A) volumetric and (B) surface layer mode. Carrier gases: (a) carbon dioxide; (b) helium. Column temperatures: (A) 300°C; (B) 225°C. Column length: 0.5 m. Peaks: 1 = diethyl ether; 2 = diisopropyl ether; 3 = dibutyl ether.

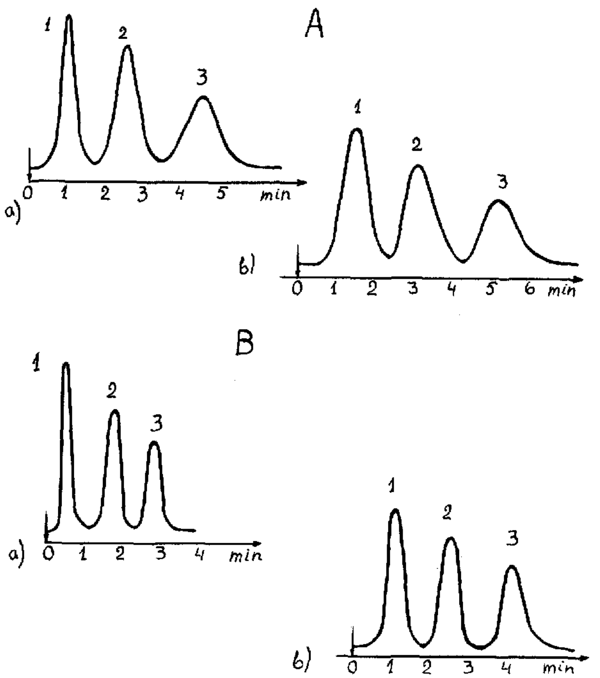

Fig. 4. Chromatogram of ether mixture on zeolite NaY. Column temperatures: (A) 300°C; (B) 250°C. Other details as in Fig. 3.

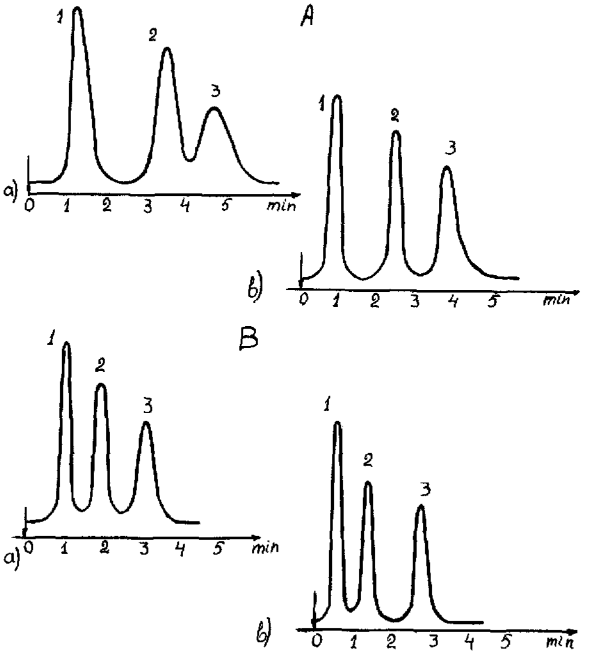

Fig. 5. Chromatogram of ketone mixture on zeolites NaY (a) and HY (b); (A) volumetric and (B) surface layer mode. Carrier gas: carbon dioxide. Column temperatures: (A) 300°C; (B) 250°C. Peaks: 1 = dimethyl ketone; 2 = methyl ethyl ketone; 3 = methyl butyl ketone.

TABLE VII

DEPENDENCE OF THE NUMBER OF THEORETICAL PLATES PER METRE OF THE CHROMATOGRAPHIC COLUMN ON THE NATURE OF THE ZEOLITE CATION, CARRIER GAS AND THE METHOD OF PACKING

Compound	*Volumetric packing, column temp. 300°C*						*Surface layer packing, column temp. 250°C*					
	NaY			*HY*			*NaY*			*HY*		
	He	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2	*He*	N_2	CO_2
Octane	–	–	1590	–	–	3131	792	755	1337	869	1866	4587
Cyclohexane	359	408	1022	517	491	1124	169	139	400	256	316	1947
Benzene	–	–	1819	1111	3025	4011	1349	879	1509	1356	1495	2936
Hexanol	–	–	1272	1600	1311	2674	399	–	696	1608	2304	3419
Dibutyl ether	676	427	1936	1024	2220	3600	631	544	676	764	1500	3000
Methyl butyl ketone	–	–	81	–	–	455	–	–	2130	750	1256	1333

As seen from Table V, when helium and nitrogen are used as the carrier gas on zeolites NaY and CdY there is a strong adsorption of alcohols, whereas with carbon dioxide as the carrier gas the alcohols are eluted. On the same packings, the heavier alcohols heptanol and octanol are eluted earlier than amyl alcohol. This may be connected with the fact that heptanol and octanol, in case of the volumetric packing of the column with zeolite, cannot penetrate the openings and are diffused over the outer surface of the adsorbent. In the case of the hydrogen form and wider entry windows, all alcohols penetrate the pores and diffuse in the inner cavities of the zeolites. Octanol is an exception, undergoing catalytic transformation on this form of the zeolite. On the surface layer packed columns all the alcohols are eluted in order of increasing molecular weight (Table VI).

The best separation of C_2–C_8 alcohol mixtures takes place on the surface layer packing of zeolite HY with carbon dioxide as the carrier gas. Basically, this concerns the higher-molecular-weight alcohols (Fig. 2) as compared with the behaviour on volumetric packings with helium as the carrier gas. The peaks are very symmetrical. On this form and on NaY, good separations of ternary mixtures of ethers (Figs. 3 and 4) and ketones (Fig. 5) are achieved. The use of the surface layer mode of packing and carbon dioxide as the carrier gas allows separation with symmetrical peaks. The separation of the ketone mixture by use of the ordinary carrier gases (helium, nitrogen) is not realized.

The effectiveness of the chromatographic column is determined by the number of theoretical plates per metre. Table VII gives the number of theoretical plates determined with some compounds and it is seen that the most effective column is the one employing carbon dioxide as the carrier gas, containing the zeolite with lower cation density and packed by the surface layer method.

We conclude that the use of zeolites in the surface layer mode and with carbon dioxide as the carrier gas for the analysis of mixtures of high boiling hydrocarbons and some other compounds results in an improvement in all basic characteristics of the chromatographic separation. Thus, the separations can be achieved at lower column temperatures, in shorter times and with greater effectiveness.

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