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## CHROMATOGRAPHIC PROPERTIES OF SOME SILICA-RICH ZEOLITES\*

G. V. TSITSISHVILI, T. G. ANDRONIKASHVILI, Sh. D. SABELASHVILI and N. A. OSIPOVA  
*Institute of Physical and Organic Chemistry, Academy of Sciences of the Georgian SSR, Tbilisi (U.S.S.R.)*

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### SUMMARY

The chromatographic properties of a natural zeolite (clinoptilolite) and of synthetic specimens (zeolite of type L and erionite) have been studied, with a mixture of oxygen, nitrogen, argon, carbon monoxide, methane, ethane, ethylene, propane, propene and butane as model mixture. It is shown that modification of the zeolites by cations of lithium, sodium, potassium, caesium or silver changes the selective-separation capacity of these adsorbents to a large extent. Such changes are particularly pronounced when silver ions are introduced into a zeolite of type L.

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### INTRODUCTION

At present, different ion-exchange forms of zeolites<sup>1,2</sup> are widely used in chromatography. Mostly, these are zeolites of types A and X, which are characterised by a low ratio of silica to alumina. Relatively few papers have been published on applications of silica-rich zeolites in gas-chromatographic analysis<sup>3-8</sup>.

In silica-rich zeolites, the ratio of silica to alumina exceeds 5, and most such zeolites are characterized by the presence of free apertures of diameter similar to that of the free apertures in the framework of a type-A zeolite<sup>9</sup>.

The object of this work was to study the effects of the structure of some silica-rich zeolites on their chromatographic properties; the effects of enrichment of the zeolites by cations of certain metals on the chromatographic behaviour were also studied. The zeolites studied were clinoptilolites (tuffs containing clinoptilolite) from deposits in the Georgian SSR and synthetic zeolites L and erionite.

### MATERIALS AND METHODS

Natural clinoptilolite was modified by cation exchange with aqueous solutions of potassium nitrate. Synthetic zeolites were enriched, mostly with cations of univalent metals (type-L zeolites by cations of sodium, caesium and silver, and zeolites of the erionite type by cations of sodium, potassium and lithium). Depending on the

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number of treatments and the concentration of the solutions of the corresponding salt, specimens with different degrees of substitution of the original cations were prepared. Mixtures of argon, oxygen, nitrogen, carbon monoxide, methane, ethane, ethylene, propane, propene and butane were used as model mixtures.

Granules of size 0.5–1 mm were prepared from the zeolites (for synthetic zeolites, by compressing the powder without a binder). After thermal activation at 300° for clinoptilolite and at 500° for synthetic zeolites, the materials were loaded into chromatographic columns of length 1 m and diameter 4 mm. The zeolites were then reactivated in the column with the carrier gas (helium) flowing for 3 h at 300° or 500° as appropriate. A Tsvet 3 chromatograph was used, with a thermal-conductivity detector. The column was operated at temperatures in the range 0° to 250°, and the helium flow-rate ranged from 10 to 100 ml/min.

Tuffs containing clinoptilolites from deposits at Dzegvi, Chiatura, Khekordzula and Khekordzula (a white specimen) were studied (see Table I); they differed in the ratios of silica to alumina, in cation composition and in content of clinoptilolite. The white specimen from Khekordzula had the highest content of clinoptilolite.

Since clinoptilolites are characterized by the relatively small diameter of their free apertures ( $\approx 4 \text{ \AA}$ ), the system argon–oxygen–nitrogen (molecules of which can penetrate the channels of the above-mentioned zeolite) was chosen as a model mixture.

TABLE I  
PARAMETERS OF THE TUFFS EXAMINED

<i>Source of specimen</i>	<i>Content (%) of</i>			<i>Ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub></i>
	<i>CaO</i>	<i>Na<sub>2</sub>O</i>	<i>K<sub>2</sub>O</i>	
Dzegvi	6.30	2.00	1.18	8.03
Khekordzula	5.21	3.89	2.12	8.48
Khekordzula (white specimen)	3.92	3.34	1.68	8.60
Chiatura	3.20	1.44	3.17	10.00

## RESULTS AND DISCUSSION

Experiments with natural and modified clinoptilolites from the different deposits showed that the separation of the model mixture was greatly affected by the contents of calcium and potassium ions in the zeolite. An increase in the potassium content of a clinoptilolite led to an increase in retention time for each component of the test mixture. In Fig. 1, the dependence of the retention times for argon, oxygen and nitrogen on the content of potassium ions (expressed as K<sub>2</sub>O) is shown for clinoptilolites from the various deposits; the temperature of the chromatographic column was 25°, and the flow-rate of carrier gas was 50 ml/min. No separation of the components of the test mixture took place on a natural specimen from Dzegvi. Replacement of calcium by potassium in this clinoptilolite caused an increase in the retention times of each component to a different extent. At a relatively low degree of substitution of calcium by potassium, the retention time for nitrogen was smaller than that for oxygen, and the elution sequence was argon, nitrogen, oxygen. Further increase

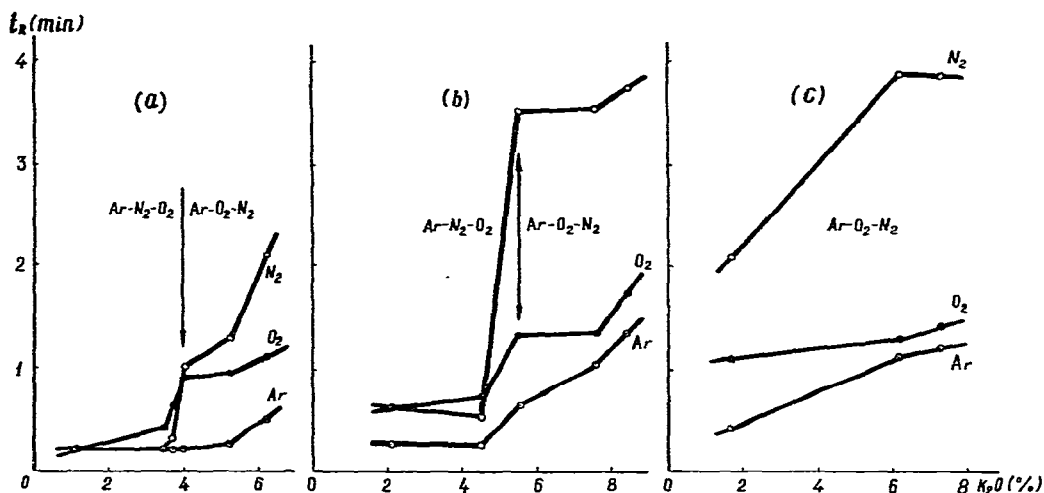


Fig. 1. Dependence of retention time ( $t_R$ ) of argon, oxygen and nitrogen on the content of  $K^+$  ions (expressed as  $K_2O$ ) in clinoptilolite tuffs: (a), Dzegvi specimens; (b), Khekordzula specimens; (c), white Khekordzula specimen. The column temperatures was  $25^\circ$  and the flow-rate of carrier gas was 50 ml/min.

in the content of potassium in clinoptilolite led to a considerable increase in the retention time for nitrogen, and the elution sequence changed to argon, oxygen, nitrogen. Such behaviour was also characteristic of clinoptilolite from the Khekordzula deposit. The white specimen from Khekordzula differed in its chromatographic properties from the above-mentioned clinoptilolites, the same elution sequence (argon, oxygen, nitrogen) being observed both on the original and the modified forms.

These results can be interpreted as follows. The activation energy (related to the diffusion of molecules in such fine-pore adsorbents as clinoptilolite) is essentially determined by the nature of the cation. Thus, Barrer<sup>10</sup>, in studying the adsorption of inert gases on cation-exchange forms of mordenite, showed that the activation energy was considerably lower for the potassium-containing adsorbent than for calcium modifications. Most probably, the same phenomenon occurs with clinoptilolite. We can also assume that, when calcium ions are substituted by potassium ions in clinoptilolite, the potassium ions occupy different positions in comparison with the initial cations and make the zeolite structure more open. In addition, it is known that the rate of adsorption of apolar gases on zeolites is decreased as a result of pre-adsorption of a small amount of polar molecules. In a clinoptilolite enriched by calcium ions (characterized by a high hydration capacity), there are evidently some water molecules arranged near calcium cations and blocking free apertures of the zeolite. Therefore, the relatively large molecules of argon and nitrogen cannot penetrate clinoptilolite and diffuse along the zeolite channels. Thermal dehydration of clinoptilolite at  $300^\circ$  does not completely remove this water, and activation at higher temperatures can destroy the clinoptilolite crystal lattice.

Substitution of calcium by potassium improves the dehydration capacity of the zeolite, as potassium ions are characterized by a considerably lower hydration

capacity than that of calcium ions; the conditions of our experiments (activation at  $300^\circ$ ), this permits us to attain more complete removal of water from the zeolite. Such "de-blocking" by potassium ions permits both argon and nitrogen molecules to penetrate the zeolite.

The above considerations can explain the change in elution sequence of nitrogen and oxygen with the cation composition of clinoptilolite, offering the possibility of nitrogen-molecule penetration of the zeolite structure.

Depending on the degree of enrichment of clinoptilolite by potassium ions, the character of separation of the binary mixtures argon-oxygen and oxygen-nitrogen is changed. In such a way, a ternary mixture (argon-oxygen-nitrogen) can be separated on an original clinoptilolite (the white specimen from Khekordzula). When the specimen is enriched by potassium, the separation of argon from oxygen becomes gradually worse, and eventually a point is reached at which this separation does not occur. This is apparently caused by the free penetration of the zeolite channels by argon molecules, which diffuse at a rate close to the diffusion rate of oxygen. The mixture oxygen-nitrogen is more completely separated on potassium-enriched zeolites (see Fig. 2). This also is related to the penetration, by nitrogen molecules, of the clinoptilolite cavities, but their interaction is enhanced by the presence of a quadrupole moment and they are therefore more strongly adsorbed in the zeolite channels and are eluted much less rapidly than oxygen.

Zeolites of type L were studied in the original form and when enriched by sodium or caesium ions; zeolites of this type have a structure more open than that of clinoptilolite. On the original form of such a zeolite, in which potassium ions predominate over those of sodium, methane is eluted after carbon monoxide at column temperatures of  $20-80^\circ$ ; this is a general characteristic of zeolites of type X (rich in potassium ions<sup>11,12</sup>). On an original type-L zeolite, as on a potassium-substituted type-X

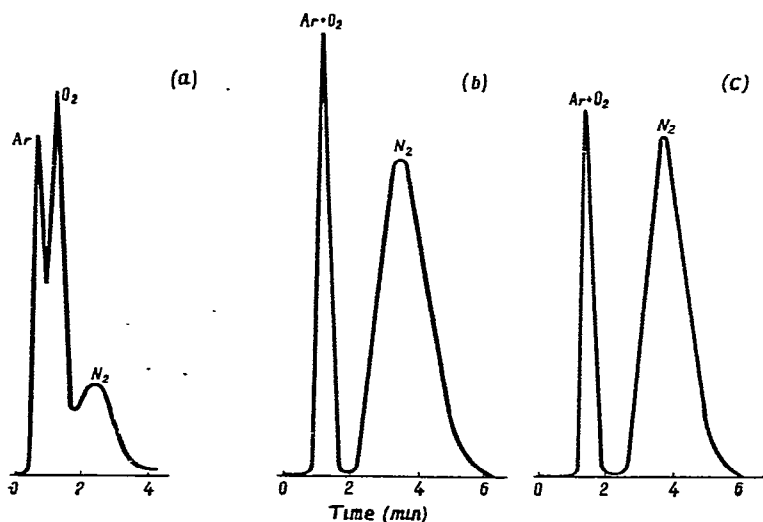


Fig. 2. Chromatograms showing separation of a mixture of argon, oxygen and nitrogen on a white specimen of clinoptilolite tuff from Khekordzula: (a), original specimen; (b), specimen with medium content of  $K^+$  ions; (c), specimen with high content of  $K^+$  ions.

zeolite<sup>12</sup>, at any temperature of the chromatographic column, each saturated hydrocarbon is eluted before unsaturated compounds with the same number of carbon atoms, *viz.*, the elution sequence is carbon monoxide plus methane, ethane, ethylene, propane, propene, butane (see Fig. 3). However, separation of such a mixture of gases takes place at lower temperatures than on a zeolite of type X; this, apparently, is attributable to the lower concentration of cations per unit cell of a zeolite of type L.

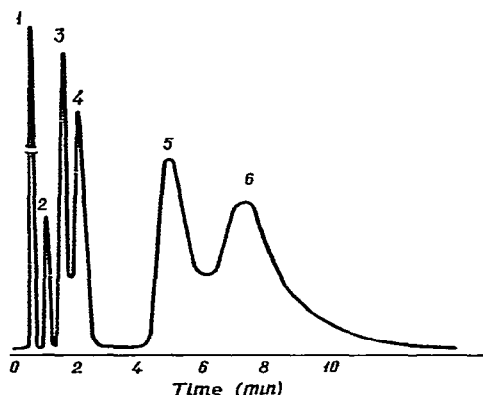


Fig. 3. Chromatogram showing separation of a mixture of carbon monoxide plus methane (1), ethane (2), ethylene (3), propane (4), propene (5) and butane (6) on the original form of a type-L zeolite. The column temperature was 140° and the flow-rate of carrier gas was 50 ml/min.

Enrichment of a type-L zeolite by sodium ions caused an increase in the retention volume of each of the studied compounds. From such a zeolite at a column temperature of 20–80°, methane is eluted before carbon monoxide and, for such pairs of hydrocarbons as propane–ethylene and butane–propene, inversion of the elution sequence occurs with increase in temperature. Thus, at below 80°, propane is eluted before ethylene, and at a higher temperature the sequence changes. For the pair butane–propene, inversion of the elution sequence takes place at a temperature above 120°.

On caesium-substituted type-L zeolite, the retention volumes of all the compounds studied decrease, the change being more pronounced for unsaturated hydrocarbons. At all temperatures, carbon monoxide is eluted before methane. The elution sequence of the gaseous hydrocarbons is the same as on the original form of the L-type zeolite.

The coefficients of selectivity\* ( $K_s$ , which equals the ratio of the difference of the retention volumes to their sum) of the saturated hydrocarbons<sup>13</sup> are almost the same for all the three specimens.

For unsaturated and saturated hydrocarbons having the same number of carbon atoms, these values are increased in the sequence calcium, potassium, sodium, and for methane–carbon monoxide in the sequence potassium, calcium, sodium (see Table II).

The introduction of silver ions into this type of zeolite, as with a silver-containing type-X zeolite<sup>14</sup>, promotes a sharply pronounced change in selectivity with respect to compounds characterized by the presence of  $\pi$ -bonds and of dipole and

\*  $K_s$  = ratio of the difference of the retention volumes to their sum.

TABLE II

VALUES OF COEFFICIENT OF SELECTIVITY ( $K_s$ ) OF BINARY MIXTURES ON VARIOUS FORMS OF A TYPE-L ZEOLITE

Mixture	Temperature (°C)	Zeolite form		
		Original	Na-enriched	Cs-enriched
Methane-ethane	25	0.94	0.95	0.94
Ethane-propane	60	0.79	0.79	0.79
Propane-butane	120	0.73	0.75	0.68
Carbon monoxide-methane	40	0.10	0.37	0.32
Ethane-ethylene	60	0.75	0.80	0.43
Propane-propene	120	0.67	0.71	0.33

\* See ref. 13.

quadrupole moments. However, this change is much less than for zeolites of type X, obviously because of the smaller density of cations per unit cell in zeolites of type L.

One of the interesting properties of silver-enriched zeolites of type L was that, in the process of chromatography, catalytic oxidation of carbon monoxide to carbon dioxide takes place at a column temperature above 100°. This phenomenon can be explained as follows. Oxidation of carbon monoxide can be caused by the presence of lattice oxygen atoms, bound with silver cations<sup>15</sup>. It is therefore reasonable to assume that gaseous oxygen chemisorbed on silver atoms (which may be present as a result of partial reduction of the zeolite silver ions) can promote such oxidation<sup>8</sup>.

Another interesting property of silver-enriched type-L zeolites has been established. As is known, zeolites can separate oxygen from nitrogen (with this elution sequence)<sup>1</sup>, but this property disappears at column temperatures higher than 100°. However, if the vapours of the saturated hydrocarbons hexane, heptane or octane (or unsaturated hydrocarbons starting with propene) are introduced into silver-containing type-L zeolites, then, at column temperatures in the range 200–300°, separation of nitrogen from oxygen takes place in that sequence (see Fig. 4); this phenomenon is not a general characteristic of zeolites. It was also noted that, under such conditions, a mixture such as argon-oxygen, which is normally difficult to separate, was separated (Fig. 4). Such an elution sequence takes place until the hydrocarbons have been eluted from the chromatographic column. This property is not characteristic of silver-containing type-X zeolites and is only weakly pronounced for zeolites of type Y.

The same model mixtures were used to study another zeolite—erionite. Erionite, as for a zeolite of type L, is characterized by a low cation density, six or seven cations being localized per unit cell; the ratio of silica to alumina varies within the range 6.3–7.8 (see ref. 16).

The mixture oxygen-nitrogen-carbon monoxide-methane can be separated both on the original and on the modified forms of erionite at a temperature of 25° and a carrier gas flow-rate of 50 ml/min. Separation of oxygen from nitrogen occurred on all four specimens (see Fig. 5), but not to such an extent as on zeolites of type X or type A<sup>1</sup>.

Enrichment of erionite by sodium or lithium ions caused some increase in the criterion of separation of this pair, whereas enrichment by potassium led to its decrease (see Table III).

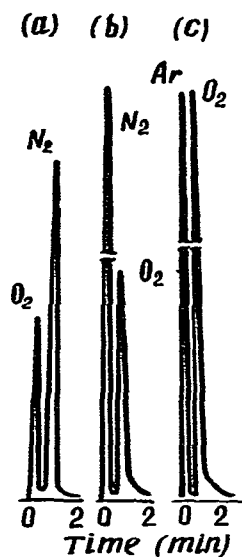


Fig. 4. Chromatograms showing separation of mixtures of nitrogen and oxygen, and argon and oxygen, on a silver-containing type-L zeolite: (a) column temperature of  $25^\circ$  and the flow-rate of carrier gas 50 ml/min; (b) and (c), column temperature of  $200^\circ$  and flow-rate 20 ml/min.

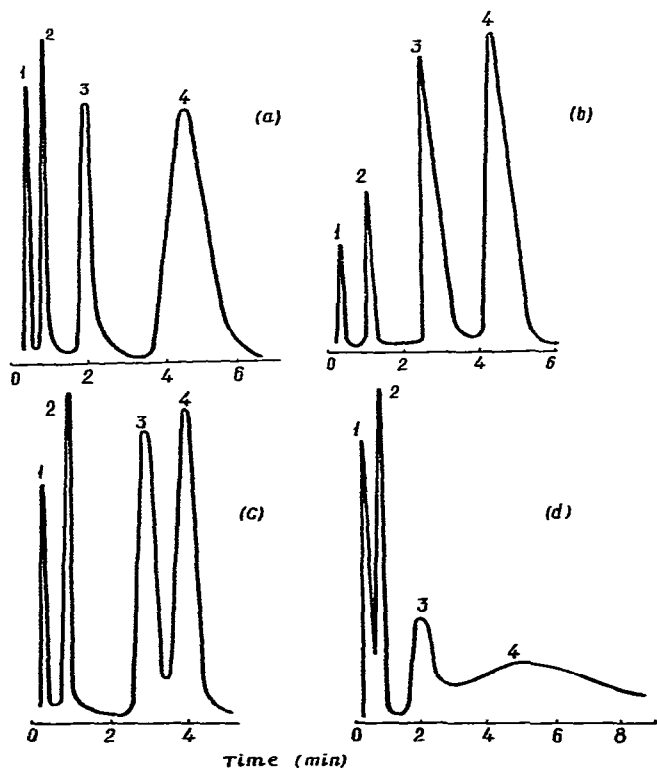


Fig. 5. Chromatograms showing separation of a mixture of oxygen (1), nitrogen (2), carbon monoxide (3) and methane (4) on (a) the original form of an erionite, and (b), (c) and (d) the Na-, Li- and K-enriched forms, respectively. The column temperature was  $25^\circ$  and the flow-rate of carrier gas was 50 ml/min.

TABLE III

VALUES OF CRITERION OF SEPARATION ( $K^*$ ) FOR OXYGEN-NITROGEN ON DIFFERENT CATION-EXCHANGE FORMS OF ERIONITE

Specimen	Temperature ( $^{\circ}\text{C}$ )		
	25	40	60
NaKE	3.3	2.5	1.0
NaE	4.7	3.7	3.1
LiE	4.3	3.2	2.9
KE	1.1	—	—

\* See ref. 17. Criterion of separation equals the ratio of the distance between the maxima of chromatographic peaks to the sum of peak widths at half height.

The mixture carbon monoxide-methane was separated (with this elution sequence) on all the cation-exchange forms of erionite studied. Transition from the original form to the sodium-enriched form causes, as might be expected, an increase in the retention volume of carbon monoxide and a slight decrease in that methane. The peaks of these compounds become closer, but the elution sequence is not inverted, so that separation becomes worse (see Table IV). Enrichment of specimens by lithium ions also promotes an increase in the retention volume of carbon monoxide and a decrease in that of methane, but not to an extent such that their inversion occurs; again, therefore, the separation of this mixture becomes worse (Table IV).

TABLE IV

VALUES OF COEFFICIENT OF SELECTIVITY ( $K_s^*$ ) FOR CARBON MONOXIDE-METHANE ON DIFFERENT CATION-EXCHANGE FORMS OF ERIONITE

Specimen	Temperature ( $^{\circ}\text{C}$ )		
	25	40	60
NaKE (original form)	0.43	0.46	0.46
NaE	0.24	0.26	0.30
LiE	0.17	0.25	0.25
KE	0.39	—	0.35

\* See ref. 13.

This is evidently related to the fact that, unlike sodium zeolites of types X and L, which are characterized by a greater cation concentration, the cations in erionite (due to their low population and different distribution per unit cell) cannot exert as great an effect.

The effect of the nature of the cation on the selective-separation ability of erionite is even more pronounced in the separation of the mixture methane-ethane-ethylene-propane at a temperature of  $140^{\circ}$  and with a carrier gas flow-rate of 50 ml/min. Thus, propane and ethylene are not separated on the original form of erionite, but they are separated on the sodium-enriched form, ethylene being eluted before propane (see Fig. 6). On the lithium form of erionite, the propane peak is even broader than it is on the original form.

A sharp difference in chromatographic properties is characteristic of the



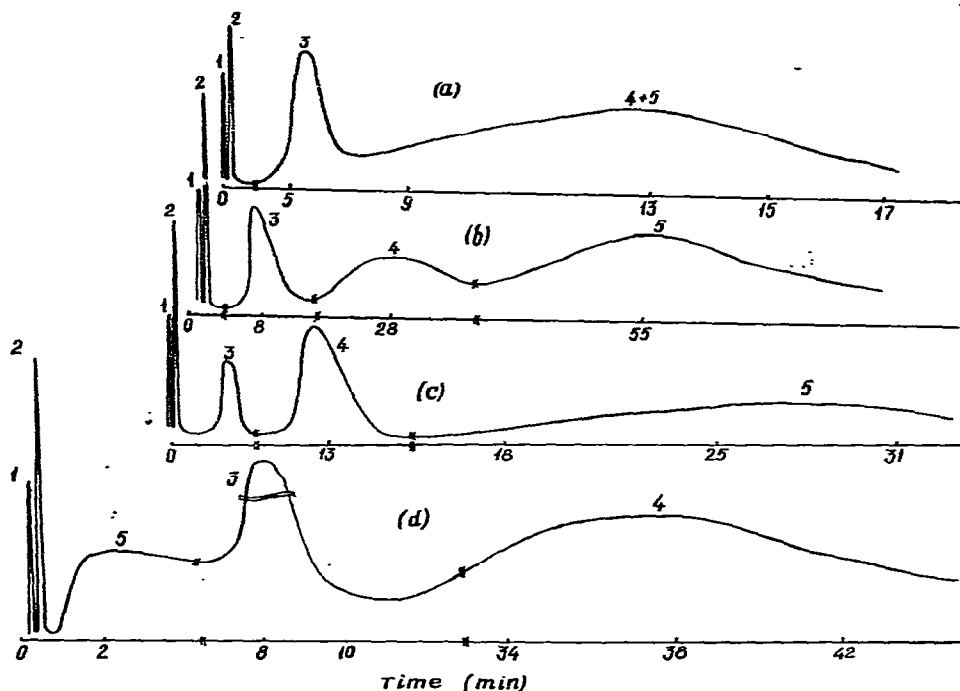


Fig. 6. Chromatograms showing separation of a mixture of air (1), methane (2), ethane (3), ethylene (4) and propane (5) on (a) the original form of an erionite, and (b), (c) and (d) the Na-, Li- and K-enriched forms, respectively. The column temperature was  $140^{\circ}$  and the flow-rate of carrier gas was 50 ml/min.

specimens enriched by potassium ions. Propane is eluted before ethane, and the elution sequence is methane, propane, ethane, ethylene; such a sequence is not characteristic of any of the cation-exchange forms of erionite. This fact can be attributed to a screening of the free apertures of erionite by the relatively large potassium ions to an extent such that propane is forced to diffuse along the "outside" surface of the erionite, since it cannot (because of the presence of potassium ions) penetrate the zeolite cavities.

These studies show that the type of zeolite, and the nature and density of the cation population per unit cell, greatly affect the selective-separation properties of zeolites.

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