CHROMATOGRAPHIC PROPERTIES OF TYPE X ZEOLITES CONTAINING ALKALI METAL CATIONS

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SUMMARY

The chromatographic properties of type X zeolites containing cations of lithium, sodium, potassium, rubidium and cesium were studied for the separation of a model mixture of C_1–C_4 hydrocarbon gases and carbon monoxide. It was found that there is an inverse sequence of elution of methane and carbon monoxide in the course of the separation of this binary mixture depending on the nature of the zeolite cation. It was shown that lithium and sodium replaced forms of zeolites have a certain selectivity with respect to ethylene and propylene.

Zeolites are porous crystalline substances in which the negative charge of the aluminosilicate framework is compensated by the positive charge of cations. One of the important properties of zeolites is their pronounced capacity for cation exchange leading to a modification of these adsorbents without a practical change of the aluminosilicate framework structure.

Synthetic zeolites of the type CaA, NaX and CaX were used as adsorbents in gas chromatography in the sixties. Later, works appeared devoted to the possibility of the use of cation-exchange forms of zeolites in gas chromatography[1-8].

Studies of adsorption interactions have shown that zeolites have a definite specificity with respect to molecules of substances characterised by π-bonds, dipole and quadrupole moments[9].

It should be noted that the character of the interaction depends to an appreciable extent on the nature of the cation entering into the composition of the zeolite structure[9].

The aim of the present investigation was a study of the chromatographic properties of type X zeolites with different degrees of substitution of the sodium cations by lithium, potassium, rubidium and cesium cations; the separation of a model mixture of C_1–C_4 hydrocarbon gases, carbon monoxide and hydrogen was used as an example.

Cation-exchange forms were prepared from the sodium zeolites by means of their repeated treatment with an aqueous solution of the corresponding cation chloride or nitrate. Specimens with different contents of exchange cations were obtained depending on the number of treatments (see Table I).

Specimens 6 and 10 were obtained by the percolation technique. The stability of the zeolite crystalline structure in all synthesised specimens was controlled by the

TABLE I

DEGREE OF REPLACEMENT OF Na+ BY OTHER CATIONS FOR SPECIMENS OF TYPE X ZEOLITES

Specimen	Cation-exchange form	Degree of substitution (%)	Specimen	Cation-exchange form	Degree of substitution (%)
1	NaX	0	8	KX	47.5
2	LiX	5	9	KX	83.5
3	LiX	22	10	KX	99.5
4	LiX	43	11	RbX	30
5	LiX	87	12	RbX	54
6	LiX	91	13	CsX	28
7	KX	26.4	14	CsX	53.5

corresponding Debyegrams. Photographs were taken in RKD chambers at non-filtered copper radiation on the URS-55 installation. The analysis of the Debyegrams has shown that all the specimens studied have a zeolite crystalline lattice.

The sorbents for loading into the chromatographic column were prepared in the following way. The zeolite powder was pressed into tablets without adding any binder, then these tablets were crushed, sieved and fractions with a grain size of 0.5–1 mm (15–30 mm) were taken for the tests. All specimens had been preliminarily dehydrated by heating at 450° for 4–5 h. After loading into the chromatographic column and before the work was begun, the zeolites were activated by heating them in a flow of the carrier gas at a temperature of 300°. In the case of the lithium-containing specimens, due to their highly hydrophilic properties the activation was also carried out at a temperature of 480°.

The chromatographic column was a spiral tube of stainless steel, 350 cm long, with an inner diameter of 0.4 cm. The temperature range of the column was from 25 to 260°. Since the chromatograph detector was of the thermochemical type, purified
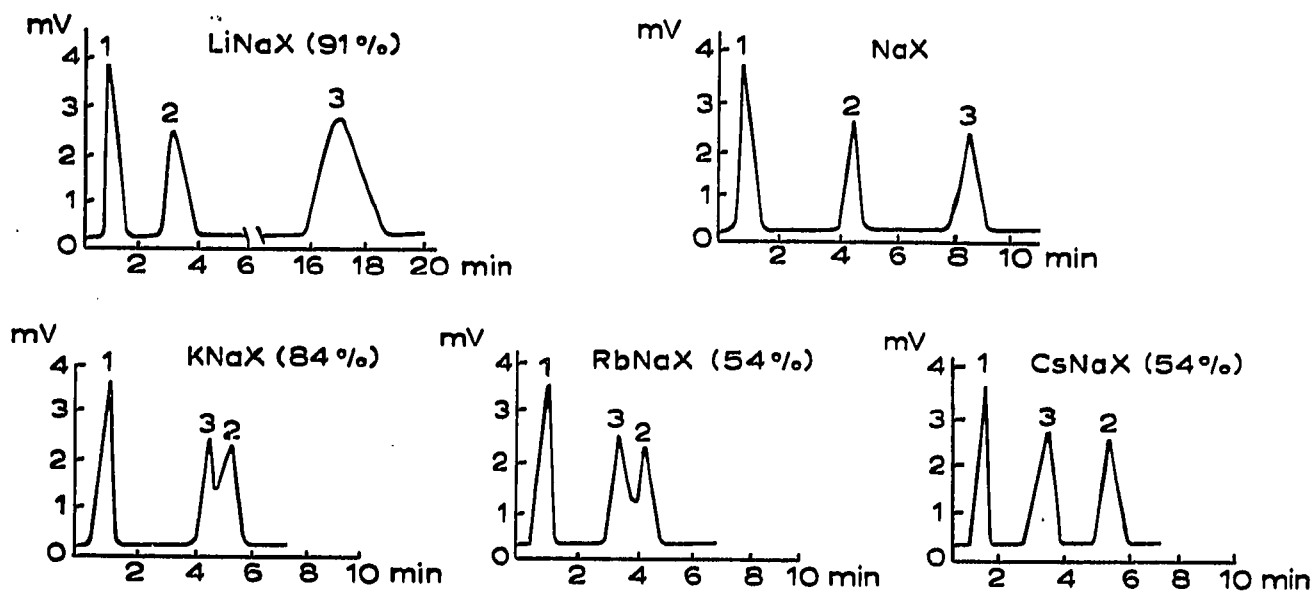

Fig. 1. Sequence of elution of methane–carbon monoxide on type X zeolites containing Li+, Na+, K+, Rb+, Cs+: 1 = hydrogen; 2 = methane; 3 = carbon monoxide. Flow rate of carrier gas (air), 100 ml/min. Column temperature, 25°.

air was used as the carrier gas. The velocity of the carrier gas during the investigation of the separation properties of the zeolites was around 100 ml/min.

As a result of the studies it was shown that the character of the chromatographic separation of the binary mixture methane–carbon monoxide depends on the cation and the degree of its substitution in the zeolite. The presence of dipole and quadrupole moments is characteristic[10] of a molecule of carbon monoxide, and differs in this way from the methane molecule. Zeolites containing Na^+ and Li^+ display a certain selectivity with respect to carbon monoxide and methane is eluted earlier than carbon monoxide; furthermore a zeolite with a higher content of Li^+ retains carbon monoxide more than the Na^+ form (Fig. 1).

In the case of specimens with a high K^+ content, it is possible to perform a partial separation on them, but with the following sequence of elution: carbon monoxide–methane (Fig. 1).

On zeolites containing rubidium and cesium separation of this mixture proceeds with the following elution order: carbon monoxide–methane, even with small degrees of sodium ion substitution. However, a more complete separation of these components is observed with the cesium form. The values of the coefficient of selectivity K_s of methane and carbon monoxide are given for zeolites containing alkali metal cations in Table II.

TABLE II

THE SELECTIVITY COEFFICIENT K_s FOR METHANE–CARBON MONOXIDE MIXTURES ON VARIOUS ZEOLITES

mp. (°)	NaX	LiX					KX			RbX		CsX	
		5%	22%	43%	87%	91%	26.4%	47.5%	83.5%	30%	54.0%	28%	53..
	0.42	0.37	0.37	0.37	0.60	0.72	0.024	−0.04	−0.08	−0.11	−0.14	−0.22	−0
	0.34	0.29	0.25	0.29	0.51	0.63	−0.023	—	−0.09	−0.12	−0.16	−0.23	−0
	0.23	0.22	0.19	0.21	0.41	0.52	−0.055	−0.07	−0.10	−0.16	−0.17		

As one can see from the data in Table II K_s of methane and carbon monoxide increases to a great extent with the transition from the specimen containing Na^+ to that with Li^+. However, in the case of forms with a low lithium content, K_s is less compared to the sodium form. This is probably due to the fact that the hydrophilic lithium cations having a small concentration occupy positions in the structure in which they are in a hydrated state and therefore their interaction with the molecules of the adsorbed substances is weakened. Regarding zeolites containing K^+, Rb^+ and Cs^+ an increase of the selectivity coefficient takes place both with the increase of the degree of their substitution and in the sequence mentioned. These cations are less hydrophilic and do not hydrate as much as Li^+.

Such behaviour may be explained as follows: electrostatic interactions caused by the existence of dipole and quadrupole moments of carbon monoxide molecules are more important for cations with small radii with a strong positive charge (Na^+, Li^+) than for larger cations K^+, Rb^+ and Cs^{+}[11].

In Table II one can also see the effect of the temperature of the chromatographic column on the degree of separation. Thus, an increase of the column temperature leads to an appreciable decrease in the values of the selectivity coefficients of the

methane–carbon monoxide mixture on zeolites containing lithium and particularly sodium. The value of the retention volume of carbon monoxide decreases more sharply than that of methane with an increase of the column temperature for all forms of cation-exchange zeolites. It is assumed that the intensity of the interactions of molecules with dipole and quadrupole moments with the zeolite is strongly disturbed with a temperature increase[12]. However in the case of sodium and lithium
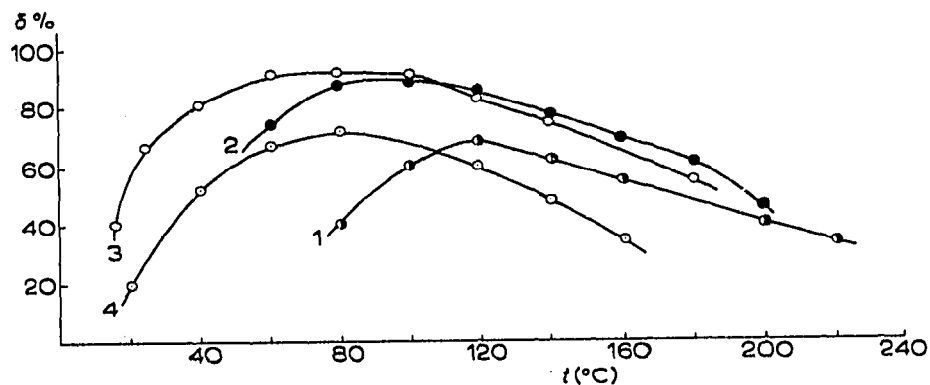

Fig. 2. Dependence of the separation extent (δ) for the mixture CH₄–CO on zeolites containing potassium on the column temperature. 1 = specimen 1; 2 = specimen 7; 3 = specimen 8; 4 = specimen 9.

specimens such a decrease in the values of the retention volumes for carbon monoxide does not lead to an inversion in the order of elution of the components. However, on a zeolite with a small potassium ion content (specimen 7) an inversion of the order of elution of carbon monoxide and methane takes place. Thus, at a column temperature of 25° the retention volume of carbon monoxide is larger than that of methane. With an increase of the column temperature to 40° the retention volumes of these components are equalised. A further increase of the column temperature leads to inversion of the sequence of methane and carbon monoxide elution and their separation takes place at 80°.
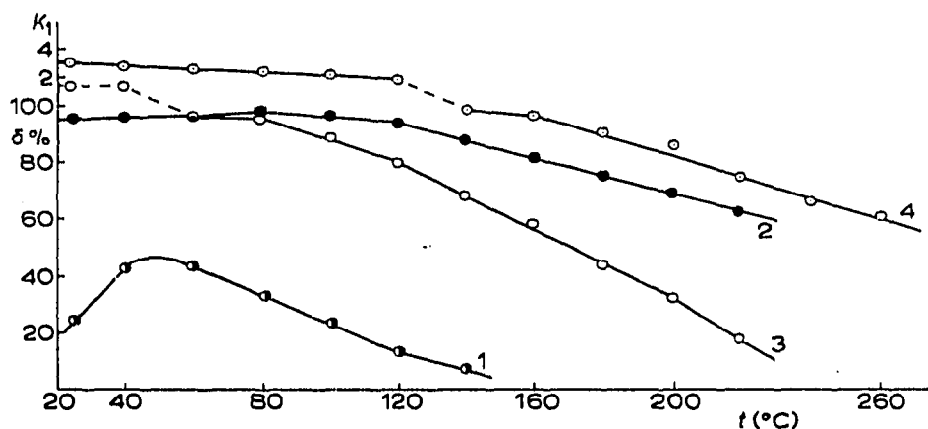
With specimens with a high potassium ion content as with Rb⁺ and Cs⁺, an

Fig. 3. Dependence of the separation extent (δ) for the mixture CH₄–CO on zeolites containing rubidium and cesium on the column temperature: 1 = specimen 11; 2 = specimen 12; 3 = specimen 13; 4 = specimen 14.

increase of column temperature leads to an increase in the values of the selectivity coefficient K_s associated with the reversibility of the methane and carbon monoxide elution order and with the weakening of direction of CO interaction with the adsorbent at increased temperatures. However, the increase in the value of the separation coefficient with the temperature increase is characterised by a certain maximum for zeolites containing K^+, Rb^+, Cs^+. Thus, curves of the separation coefficient (δ) plotted against temperature, on zeolites substituted with potassium, increase to a certain temperature limit, reach a maximum and then a decrease takes place (Fig. 2). The maximum of the curve, corresponding to the highest values of the separation coefficient, shifts on the graph from the right to the left into the lower temperature region with an increase in the potassium content in the zeolite. The same type of curve is characteristic for rubidium-substituted forms (Fig. 3), however, in the case of cesium specimens the maximum is less pronounced.

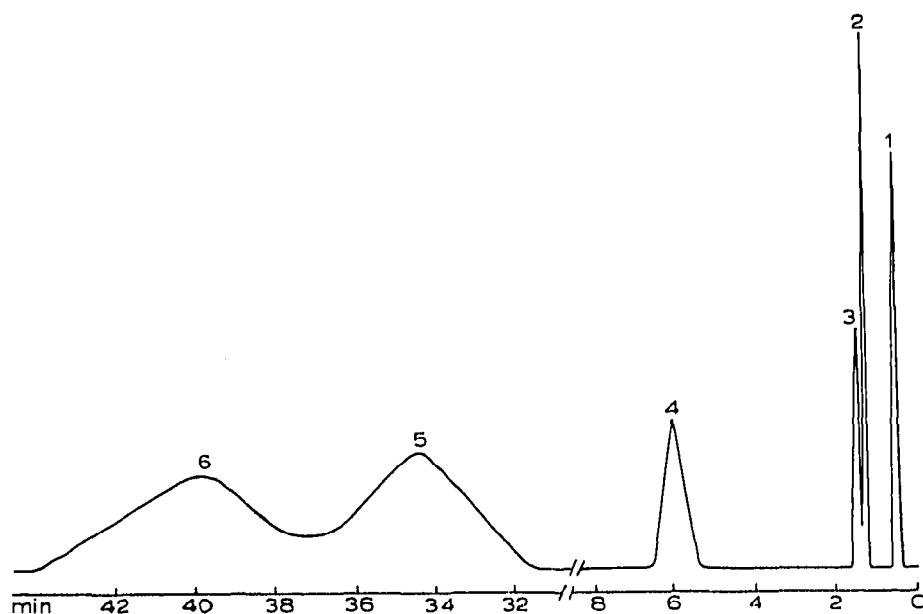A decrease of the values of the separation coefficient at high temperatures may

Fig. 4. Chromatogram of the mixture: 1 = hydrogen; 2 = methane; 3 = carbon monoxide; 4 = ethane; 5 = propane; 6 = ethylene. Adsorbent, NaX; column temperature, 100°.

be explained by a general weakening of the adsorption interaction of the chromatographed substances with the adsorbent surface.

The nature of a cation influences the character of the separation of hydrocarbon gases, in particular, the sequence of elution of separate pairs of components. Thus, on the zeolite NaX the following sequence of component elution takes place: hydrogen–methane–carbon monoxide–ethane–propane–ethylene. The column temperature was 80–100° (Fig. 4). With an increase of temperature to 120–140° there is no appreciable separation of propane and ethylene.

At temperatures of 160° and higher, the separation of this mixture is characterised by the inverse order of propane and ethylene elution (Fig. 5). As is seen from this chromatogram, butane is eluted earlier than propylene. An increase of the column heating temperature to 220° causes a considerable decrease in the propylene retention
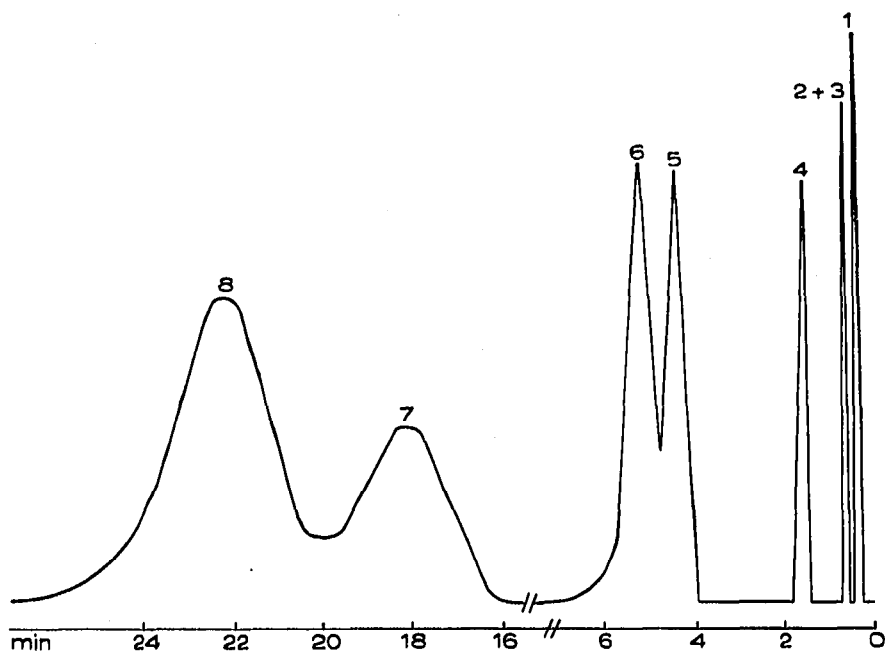
Fig. 5. Chromatogram of the mixture: 1 = hydrogen; 2 = methane; 3 = carbon monoxide; 4 = ethane; 5 = ethylene; 6 = propane; 7 = butane; 8 = propylene. Adsorbent, NaX; column temperature, 180°.

volume and it cannot be readily separated from butane. At higher column temperatures propylene is eluted earlier than butane, though the separation of these components does not take place. As to specimens containing lithium with a high degree of exchange of Na+ by Li+ (90%), then at any column temperature propane is eluted earlier than ethylene, and butane before propylene, *i.e.* there is no inversion of the
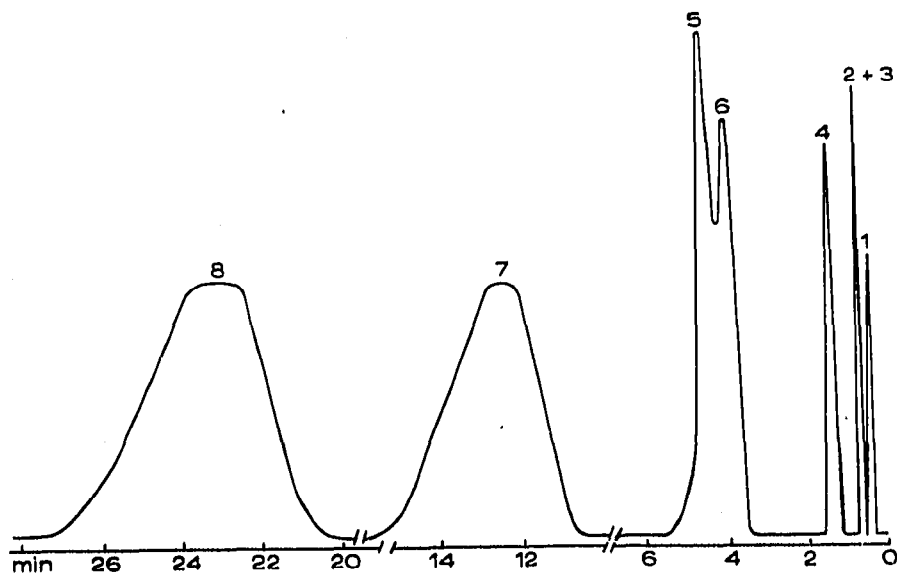
Fig. 6. Chromatogram of the mixture: 1 = hydrogen; 2 = methane; 3 = carbon monoxide; 4 = ethane; 5 = ethylene; 6 = propane; 7 = butane; 8 = propylene. Sorbent LiX (the degree of Na+ substitution by Li+ is 91 %). Column temperature, 180°.

sequence of elution of these components depending on temperature (Fig. 6). Thus, it is seen from the data obtained that zeolites with metal cations having small radii (Na^+ and especially Li^+) display a strong adsorption capacity with respect to molecules of compounds characterised by π-bonds; this is reflected in an increase of the values of their retention volumes.

As to zeolites with heavier cations, such as K^+, Rb^+ and Cs^+, an unsaturated compound is eluted on them after the corresponding saturated compound with the same number of carbon atoms in the molecule. On such cation-exchange specimens, at any column temperature, one observes the following sequence of elution: methane–ethane–ethylene–propane–propylene–butane–butylene.

Studies of the influence of the nature of the cation on the character of chromatographic properties of the zeolite and the determination of the heats of adsorption of carbon monoxide and C_1–C_4 hydrocarbon gases allowed us to construct the selectivity series for these compounds with respect to the alkali metal cation (see Table III).

TABLE III

ADSORPTION ACTIVITY OF ZEOLITES DEPENDING ON THE CATION NATURE

Selectivity rows

CH_4	
C_2H_6	$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
C_3H_8	
C_4H_{10}	
CO	$Li^+ > Na^+ > Cs^+ > K^+ > Rb^+$
C_2H_4	$Li^+ > Na^+ > Cs^+ > K^+ > Rb^+$
C_3H_6	$Li^+ > Na^+ > K^+ \sim Cs^+ > Rb^+$

As is seen from the above data for saturated hydrocarbons one observes an increase of selectivity with respect to a zeolite with the heavier cation entering its composition. This is caused by the fact that cation polarisibility increases with an increase of its radius and hence the role of dispersion forces, which mainly determine the interaction of saturated hydrocarbons, become more important.

For carbon monoxide and unsaturated hydrocarbons an opposite arrangement is characteristic. The position of cesium which does not fit this row may be explained in the following way: interaction of a molecule of these compounds with the zeolite is associated not only with the existence of π-electrons and the dipole moments in these molecules, but also with dispersion forces, which are displayed to a certain degree for the cesium form of the zeolite.

The work carried out permits some conclusions to be drawn about the important influence of the nature of the cation in type X zeolites on their separation properties.

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