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## CHROMATOGRAPHIC PROPERTIES OF TUFFS CONTAINING SOME ZEOLITES

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### SUMMARY

The separating properties of tuffs containing clinoptilolite and mordenite as adsorbents in gas chromatography were studied, using argon-oxygen-nitrogen-methane-carbon monoxide as a model mixture. It was shown that the treatment of tuffs containing clinoptilolite with hydrochloric acid improves the separation of the oxygen-nitrogen mixture but does not separate oxygen-argon. It was found that natural tuffs containing mordenite have better separation abilities than synthetic sodium mordenite. The enrichment of natural mordenite with calcium or strontium cations improves the separation of oxygen-nitrogen, while the introduction of strontium and barium cations into the zeolite structure improves the separation of argon-oxygen. The temperature of the thermal activation of the specimens greatly influences the separating ability of tuffs containing mordenite.

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### INTRODUCTION

At present, zeolites of Types A and X<sup>1,2</sup> are most widely used in gas chromatography, and the possibility of using some other types of zeolites as adsorbents has been studied less<sup>3-5</sup>.

Recently, interest in zeolites of natural origin has increased considerably, mainly relating to tuffs containing clinoptilolite and mordenite<sup>6</sup>. The content of a zeolite in tuffs in some instances may reach 85%. Both clinoptilolite and mordenite are high-silica zeolites: the Si:Al ratio in clinoptilolite is 4.25-5.00, while in mordenite it is 4.17-5.00 (ref. 6). The cation composition (calcium, potassium, sodium and magnesium) in these zeolites varies, depending on the conditions of their formation.

The kinetic diameters ( $\sigma$ ) of the free apertures of clinoptilolite and mordenite cavities are 3.5 and 3.9 Å, respectively. In gas chromatography, these types of zeolites are used mainly for the separation of gaseous systems in which the components, as a result of the size of their critical diameters, can penetrate the adsorbent channels<sup>8-14</sup>. Most studies have been devoted to the development of methods for the efficient separation of air into oxygen and nitrogen by using natural zeolites.

The purpose of our studies was to investigate the separating properties of

tuffs containing clinoptilolite and mordenite, both natural ones and those subjected to acidic or cationic modification, as adsorbents in gas chromatography.

#### EXPERIMENTAL

The samples were tuffs containing clinoptilolite from the Dzegvi deposit in the Georgian S.S.R. (the Khekordula region) and tuffs containing mordenite from Ratevani in the Bolnisi region of the Georgian S.S.R.

Tuffs containing 80–85% of clinoptilolite were treated at room temperature with hydrochloric acid, the concentration of which was varied in the range 0.05–5.0 *N*. The changes in the main oxide content of tuffs containing clinoptilolite on acid treatment are given in Table I. The results show that if the concentration of the acid does not exceed 0.25 *N*, mainly decationization of clinoptilolites takes place, as the content of alumina in the specimens is not changed. More concentrated acid (1–5 *N*) causes dealuminization of the specimens as well, as shown by a sharp decrease in the alumina content. The content of mordenite in tuffs varies within the range 40–50%.

TABLE I

#### CHANGES IN THE MAIN OXIDE COMPOSITION OF TUFFS CONTAINING CLINOPTILOLITE ON ACID TREATMENT

The absolute content of SiO<sub>2</sub> during the acid treatment of tuffs containing clinoptilolite remains virtually unchanged.

Concentration of HCl ( <i>N</i> )	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
—	12.85	1.65	3.92	1.50	3.34	1.68
0.05	12.80	1.56	3.00	1.30	1.68	0.80
0.10	12.80	1.56	3.20	1.34	2.08	0.70
0.25	12.14	1.50	3.00	1.30	1.98	—
1.00	10.05	1.08	2.50	0.94	—	0.60
5.00	7.60	0.60	2.35	0.68	1.50	0.09

Rock containing mordenite has the following chemical composition: SiO<sub>2</sub>, 70.70; TiO<sub>2</sub>, 0.20; Al<sub>2</sub>O<sub>3</sub>, 9.25; Fe<sub>2</sub>O<sub>3</sub>, 3.85; FeO, 0.38; MnO, 0.03; Mg, 0.88; CaO, 3.36; Na<sub>2</sub>O, 1.60; K<sub>2</sub>O, 1.29; P<sub>2</sub>O<sub>5</sub>, 0.20; SO<sub>3</sub>, 0.14; H<sub>2</sub>O<sup>+</sup>, 4.41; H<sub>2</sub>O<sup>-</sup>, 4.11%. Cation-exchange modification of these tuffs was obtained in two ways: (1) replacement of the initial cations (mainly Ca<sup>2+</sup>) in mordenite with sodium cations by treatment of tuffs containing zeolites with 0.5 *N* sodium hydroxide solutions (once) and then with 25% sodium chloride solution (six times) at 85°; after these treatments, metal cations from the corresponding solutions of chlorides were introduced into the zeolite structure<sup>15</sup>; (2) by direct treatment of tuffs with the corresponding solutions of chlorides.

Specimens with high contents of exchange cations were used. All of the specimens were characterized by the conservation of the crystal lattice, except for mordenite containing barium, which was characterized by some weakening of the anion framework.

Tuffs containing zeolites were crushed and the fraction of particle size 0.5–1 mm was packed into chromatographic columns. The granules of the tuff containing clinoptilolite, after previous dehydration by heating at 300° for 5 h, were loaded into the column (1 m × 4 mm I.D.) of a Tsvet-64 chromatograph and were re-activated by heating at 300° for 2 h in a flow of the carrier gas (helium). The temperature of the column was varied in the range 25–140°, the flow-rate of the carrier gas was 20–50 ml/min and a thermal conductivity detector was used. Tuffs containing morденite were loaded into the column (50 cm × 5 mm I.D.) of a Carlo Erba Model GV chromatograph. The specimens were activated in the column in a flow of the carrier gas (helium) at two temperatures (300° and 450°) for 1 h. The column temperature was 20°, the flow-rate of the carrier gas was usually 100 ml/min and a thermal conductivity detector was used. The model system was a mixture of argon, oxygen, nitrogen, methane and carbon monoxide.

## RESULTS AND DISCUSSION

Measurement of the specific retention volumes of different components of the model system showed that those of argon and particularly of methane on the original (untreated) clinoptilolite are extremely small (Table II), presumably because molecules of argon and methane are unable to penetrate the channels of clinoptilolite owing to their geometrical sizes. The critical diameter of an argon molecule is 3.83 Å and that of methane is 4 Å, while the diameter of the free apertures of natural clinoptilolite is about 3.5 Å.

TABLE II

SPECIFIC RETENTION VOLUMES  $V_g$  (ml/g) OF ARGON, OXYGEN, NITROGEN, METHANE AND CARBON MONOXIDE ON A TUFF CONTAINING CLINOPTILOLITE AND SPECIMENS TREATED WITH ACID

Temperature of column, 25°; carrier gas flow-rate, 20 ml/min.

Concentration of <i>HCl</i> ( <i>N</i> )	Component				
	<i>Ar</i>	<i>O</i> <sub>2</sub>	<i>N</i> <sub>2</sub>	<i>CH</i> <sub>4</sub>	<i>CO</i>
—	3.20	6.1	15.6	2.0	66.6
0.05	4.6	6.1	17.1	4.3	90.5
0.10	5.6	6.9	23.1	7.8	188.1
0.25	6.3	7.0	24.0	20.0	188.1
1.00	5.7	6.1	17.0	28.0	118.3
5.00	3.6	3.6	5.9	4.8	30.0

Treatment of clinoptilolite specimens with acid caused an increase in the specific retention volumes of all of the compounds studied. However, the increases depended not only on the concentration of the acid used, but also on the size of the adsorbate molecules. The highest specific retention volumes of oxygen, nitrogen, argon and carbon monoxide were obtained on the specimens treated with 0.25 *N* hydrochloric acid, and that of methane on specimens treated with 1 *N* acid (Table II). A further increase in the acid concentration resulted in a sharp decrease in the specific retention volumes of all of the compounds studied.

These results can probably be explained as follows. Treatment of clinoptilolite with acid of concentration below 1 *N* causes partial decationization of the specimen, promoting broadening of the free apertures of the zeolite. This in turn leads to an increase in the adsorption rate, creating favourable conditions for the establishment of adsorption equilibrium in the chromatographic process. The overall result is an increase in the retention volumes of the compounds studied, and this can be seen particularly clearly with methane. On the other hand, the use of acid of higher concentration leads to dealuminization of the specimens, which causes a decrease in the number of Lewis adsorption centres and also leads to partial amorphism of the zeolite. The result in this instance is some weakening of interactions in the adsorbate-adsorbent system, leading to a decrease in the specific retention volumes of the compounds studied. On clinoptilolite in the original (untreated) form the separation of the system mixture methane-oxygen-nitrogen-carbon monoxide takes place in that order of elution, caused by methane diffusing on the "external" surface of the zeolite. Treatment of the specimen with 1 *N* acid results in a reversed order of elution, *viz.*, oxygen-nitrogen-methane-carbon monoxide. The separation of the mixture argon-oxygen-nitrogen takes place on the original clinoptilolite specimen, but the separation of oxygen-nitrogen is very poor. On other specimens of natural tuffs containing clinoptilolite, the separation of oxygen-nitrogen does not take place<sup>9,13</sup> and in some instances the components were even eluted in the order nitrogen-oxygen<sup>9</sup>. Probably a nitrogen molecule, having a larger critical diameter (3 Å) than that of oxygen (2.8 Å), cannot penetrate the zeolite free apertures and moves on the "external" surface of the adsorbent. An assumption is made that it is connected with the different ratios of calcium and potassium cations per unit cell of clinoptilolite.

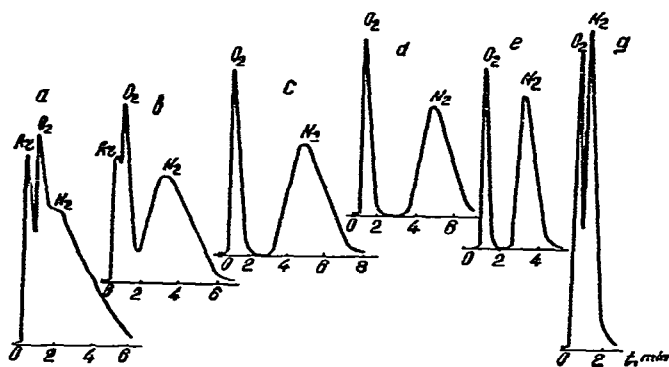


Fig. 1. Chromatograms of the separation of argon-oxygen-nitrogen on the original specimen of clinoptilolite and on specimens modified with acid. a, Original specimen; b, c, d, e, g, specimens treated with 0.05, 0.1, 0.25, 1.0 and 5.0 *N* hydrochloric acid, respectively. Column temperature, 25°; carrier gas flow-rate, 50 ml/min.

Treatment of clinoptilolite with 0.1–1 *N* hydrochloric acid considerably improves the separation of oxygen-nitrogen but gives no separation of argon-oxygen. A further increase in the hydrochloric acid concentration makes the separation of oxygen-nitrogen worse (Fig. 1). Calculations of the criteria of separation

$K_1^*$  and  $\delta^{**}$  (ref. 16) of the oxygen–nitrogen mixture clearly show that they depend to a considerable extent on the concentration of the acid used for the treatment of clinoptilolite, the temperature of heating of the chromatographic column and the carrier gas flow-rate (Table III).

TABLE III

CRITERION OF SEPARATION ( $K_1, \delta$ ) OF O<sub>2</sub>–N<sub>2</sub> ON NATURAL CLINOPTILOLITE AND ON SPECIMENS TREATED WITH HYDROCHLORIC ACID

Concentration of HCl (N)	Flow-rate of carrier gas (ml/min)	Temperature of column (°C)					
		25	40	60	80	100	120
—	20	0.63	0.69	0.75	—	—	—
	50	0.22	0.24	0.25	—	—	—
0.05	20	1.10	0.95	0.94	0.91	0.75	0.71
	50	0.78	0.76	0.76	0.71	0.65	0.50
0.10	20	2.00	1.80	1.55	1.37	0.96	0.88
	50	1.57	1.46	0.97	0.96	0.91	0.80
0.25	20	2.17	1.98	1.73	1.36	0.97	0.88
	50	1.75	1.52	0.99	0.97	0.93	0.78
1.00	20	2.20	1.87	1.88	0.97	0.88	—
	50	1.91	1.54	0.99	0.95	0.82	0.60
5.00	20	0.90	0.78	0.40	—	—	—
	50	0.63	0.38	—	—	—	—

As can be seen from Table III, the best separation of oxygen–nitrogen is obtained on specimens modified with 0.1–1 N acid at a chromatographic temperature of 25° and a carrier gas flow-rate of 20 ml/min. Determination of the heats of adsorption of argon, oxygen, nitrogen, methane and carbon monoxide from chromatographic data showed that the acid modification of tuffs containing clinoptilolite considerably increases the heats of adsorption of argon and particularly of methane in comparison with the original specimens, while the heats of adsorption of nitrogen, oxygen and carbon monoxide change only slightly (Table IV). These results again confirm the above assumption that on the natural specimen, molecules of argon and methane diffuse on the “external” surface of clinoptilolite, while the acid treatment of tuffs allows molecules of these substances to be adsorbed in the zeolite cavities. Treatment of clinoptilolite with 5 N hydrochloric acid, causing partial destruction of the clinoptilolite crystal lattice, promotes a decrease in the heats of adsorption of argon, oxygen, nitrogen, methane and carbon monoxide.

Synthetic mordenites (NaM) have a better separating ability with respect to the oxygen–nitrogen mixture<sup>17,18</sup> than a well known type of zeolite such as NaX (13X).

$$* K_1 = \frac{\Delta l}{\mu_{0.5(1)} + \mu_{0.5(2)}}$$

where  $\Delta l$  is the distance between the maxima of two chromatographic peaks and  $\mu_{0.5(1)}$  and  $\mu_{0.5(2)}$  are the peak widths at half-height. The absolute value of  $K_1$  is always  $> 1$ .

$$** \delta = \frac{h_m - h_{min}}{h_m}$$

where  $h_m$  is the average height of both peaks and  $h_{min}$  is the minimum height of both peaks. The absolute value of  $\delta$  is always  $< 1$ .

TABLE IV

HEATS OF ADSORPTION (kcal/mole) OF ARGON, OXYGEN, NITROGEN, METHANE AND CARBON MONOXIDE ON NATURAL AND MODIFIED TUFFS CONTAINING CLINOPTILOLITE

Concentration of HCl (N)	Component				
	Ar	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO
0.00	1.65	3.30	4.90	1.09	6.59
0.05	2.77	3.30	4.95	1.38	7.03
0.10	3.00	3.23	5.19	1.43	8.91
0.25	3.30	3.37	4.95	4.12	8.12
1.00	3.00	3.29	5.00	5.60	7.92
5.00	2.80	2.80	3.96	2.80	6.75

On the other hand, it is known that enrichment of these zeolites with cations of alkaline earth metals and the use of thermal activation permit their separating abilities with respect to the above mixture to be almost doubled<sup>19</sup>.

Studies of the chromatographic properties of tuffs containing mordenites showed that they are characterized by good separating properties with respect to the oxygen-nitrogen mixture and they are not worse than the synthetic mordenite NaM<sup>12,19</sup>. In terms of its cation composition, tuffs containing mordenite from the deposits of the Georgian S.S.R. can be considered as a form enriched with calcium cations.

The introduction of cations of barium or strontium into the structure of natural mordenite by the first method of exchange causes a sharp decrease in the specific retention volumes of argon and methane (Table V). Probably large cations of strontium and barium, when the first method of exchange is used, occupy positions in the inner channels of mordenite, while nitrogen, oxygen and carbon monoxide penetrate these channels.

A sharp decrease in the specific retention volumes of nitrogen and oxygen takes place on barium forms of tuffs containing mordenite, obtained by the first

TABLE V

SPECIFIC RETENTION VOLUMES  $V_s$  (ml/g) OF ARGON, OXYGEN, NITROGEN, METHANE AND CARBON MONOXIDE ON TUFF CONTAINING MORDENITE AND SPECIMENS SUBJECTED TO CATION MODIFICATION

Component	Original natural specimen		MgM**	CaM*	CaM**	SrM*	SrM**	BaM*	BaM**
	Temperature of activation (°C)								
	300	450	450	450	450	450	450	450	450
Argon	1.1	2.3	2.4	1.2	2.0	0.2	2.8	0.2	1.2
Oxygen	1.3	3.4	2.8	3.2	3.7	4.9	5.5	2.3	15.5
Nitrogen	3.4	42.0	29.0	34.5	51.0	61.0	87.4	1.9	18.7
Methane	3.4	11.1	8.1	0.2	0.8	0.2	2.0	0.4	3.9
Carbon monoxide	25.6	660.0	—	553.2	783.2	579.3	826.8	49.6	273.5

\* Specimens obtained by the first method of ion exchange.

\*\* Specimens obtained by the second method of ion exchange.

method of exchange, in comparison with the original form. In addition, inversion of the elution order of oxygen and nitrogen occurs on this cation-exchanged form.

Calculations of the criteria of separation showed that the best separation of the oxygen-nitrogen mixture takes place on natural mordenite and also on the specimens enriched with cations of calcium and strontium by the first method of exchange (Table VI). The separation of argon-oxygen on mordenite containing strontium improves on increasing the flow-rate of the carrier gas (at 50 ml/min,  $\delta = 0.50$ , while at 200 ml/min,  $\delta = 0.75$ ). For barium-substituted tuffs containing mordenite, on the contrary, an increase in the carrier gas flow-rate results in a poorer separation of this mixture (Fig. 2).

TABLE VI

CRITERIA OF SEPARATION ( $K_1$ ,  $\delta$ ) OF  $O_2$ - $N_2$  AND  $Ar$ - $O_2$  ON TUFF CONTAINING MORDENITE AND CATION-MODIFIED SPECIMENS

Temperature of activation of the specimen, 450°; column temperature, 20°; carrier gas flow-rate, 100 ml/min.

Mixture	Tuff containing mordenite	Synthetic mordenite (NaM)	MgM**	CaM*	CaM**	SrM*	SrM**	BaM*	BaM**
Ar-O <sub>2</sub>				0.11	—	0.64	—	0.45	0.11
O <sub>2</sub> -N <sub>2</sub>	1.0	1.0	0.67	0.98	1.1	1.2	1.4	—	0.39

\* Specimens obtained by the first method of ion exchange.

\*\* Specimens obtained by the second method of ion exchange.

Evidently, large barium cations in the structure of mordenite, owing to steric effects, prevent the diffusion of argon molecules into zeolite channels, while oxygen molecules can freely penetrate them. At a low flow-rate of the carrier gas, oxygen molecules move more slowly in mordenite channels, interacting with the cations of the zeolite framework, while argon molecules diffuse on the "external" surface of mordenite and the carrier gas has less influence on the velocity of their motion.

With strontium forms of mordenites, the steric factor of strontium cations is lower than that of barium cations and therefore, at low flow-rates of the carrier gas, argon penetrates, although with difficulty, the channels of the zeolite, making the separation of the argon-oxygen mixture worse. At high flow-rates of the carrier gas,

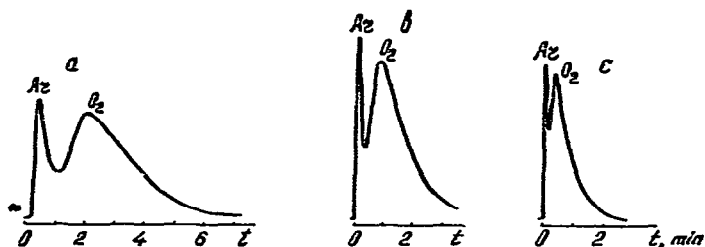


Fig. 2. Chromatograms of the separation of argon-oxygen on natural barium-modified mordenite (BaM) activated at 450°, at room temperature and different flow-rates of the carrier gas: (a) 25; (b) 50; (c) 100 ml/min.

the argon molecules have no time to penetrate the mordenite channels, which are blocked by strontium cations, and diffuse on the external surface. The difference between the retention times of argon and oxygen is increased and the separation of this mixture is improved.

The results obtained show that tuffs containing clinoptilolite treated with acid and also mordenite-containing rocks can be used successfully in adsorption processes for the separation of gaseous mixtures with the purpose of obtaining fractions enriched with some component, particularly air enriched with oxygen.

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