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INTERMOLECULAR INTERACTIONS IN GAS CHROMATOGRAPHIC SEPARATIONS ON ZEOLITES

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SUMMARY

Gas chromatography was used to determine the heats of adsorption of the hydrocarbon gases: methane, ethane, ethylene, propane, propylene, butane and also of carbon monoxide on type X zeolites containing the following cations: Na^+, Li^+, K^+, Rb^+, Cs^+, Ag^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+} and Cd^{2+}. It was found that type X zeolites containing silver and cadmium cations show specificity with respect to ethylene, propylene and carbon monoxide.

Chromatographic processes on solids are determined by intermolecular interactions taking place between the adsorbed substance and the adsorbent, as well as by the character of the diffusion of the substance caused by the specificity of the adsorption structure.

Zeolites are characterised by the presence of an orderly aluminosilicate framework leading to the formation of interconnected cavities identical in size and shape.

The possibility of modifying the zeolites by cation exchange allows their "fine structure" to be changed while maintaining a practically constant aluminosilicate framework.

Thus, the ionic forms of the same type of zeolite differ, in the main, according to the nature and position of the cations in the crystal lattice. Altogether this creates favourable conditions for the study of the character of adsorption interactions during the chromatographic separation of different substances on zeolites depending on the cation nature, assuming that the other parameters of the adsorbent remain constant.

The energy of the adsorption interaction may be approximately expressed for zeolites by the sum of the dispersion, orientation, polarisation and repulsive energies of interaction of the adsorbate molecules with the cations and atoms forming the framework[1,2].

In some cases adsorption interaction may lead to chemisorption and complex formation.

For adsorbents where concentrated positive charges are present, for example, in the case of adsorption on zeolites, when the molecules of absorbed substances are characterised by the presence of π-bonds, dipole and quadrupole moments, the role

of interactions of the type Φ_μ and Φ_0 (dipole and quadrupole interactions)[1,3] is especially important. In addition, changing from one cation form to another, interactions caused by the presence of chemically bound oxygen atoms in the zeolite framework should practically be unaffected.

We studied type X zeolites containing the following cations: Na+, Li+, K+, Rb+, Cs+, Ag+, Ca2+, Mg2+, Ba2+, Sr2+, and Cd2+.

The specimens were obtained by means of repeated treatment of the original sodium zeolite forms with the corresponding aqueous solutions of the respective salts, in some cases the method of percolation was used (LiX). Pellets were prepared from powdered zeolites, grain size 15–30 mesh (0.5–1 mm), which after the appropriate thermal treatment (dehydration) were loaded into chromatographic columns.

Thermal activation of zeolites was carried out by two methods: (1) moderate activation consisting of heating the zeolites at 450° for 5 h, before loading into the column, followed by heating in the column at 300°; (2) deeper activation reached by heating of the zeolites in the column at 480° for 5 h, first with continuous pumping out and then in a flow of the carrier gas.

A mixture of C_1–C_4 hydrocarbon gases, carbon monoxide and hydrogen was used as a model mixture. Gas chromatography[4] was used to determine the heats of adsorption of the compounds mentioned. As in the chromatographic experiment we usually deal with a low adsorption space, the adsorption heats determined in such a way correspond, mainly, to the energies of interaction between the adsorbent and adsorbate.

Adsorption heats were determined over those temperature ranges of column heating, which correspond, as far as possible, to the most symmetrical separation curves, i.e. in such regions where almost complete adsorption equilibrium is established (Table I).

The data given in brackets were obtained for the specimens exposed to deep activation. The heats of adsorption of carbon monoxide and ethylene for cadmium zeolites have an approximate character due to the asymmetry of the peaks for these compounds on the chromatogram.

Heats of adsorption, i.e. energies of interaction of saturated hydrocarbons, characterised only by the presence of σ-bonds, with zeolites containing univalent cations increase with heavier cations and have the highest value on silver-containing specimens. That is proved by the fact that polarisibility of cations increases with the increase of number of electrons in an atom, and hence the dispersion interaction with adsorbed molecules of saturated hydrocarbons increases[5].

In the case of unsaturated compounds and carbon monoxide which are characterised by the presence of π-bonds, dipole and quadrupole moments, an opposite picture is observed, viz. interaction of these compounds is most pronounced with zeolites containing cations with small radii.

The data for the cesium form of the zeolite do not fit in with the general pattern for the other cations and this may be explained in the following way. Interaction of the compounds studied with the adsorption centres of a zeolite is caused not only by the presence of π-bonds, dipole and quadrupole moments in the molecules, but also by dispersion forces which are more pronounced on cesium zeolites.

The values of the differences between the heats of adsorption of methane and carbon monoxide as well as between ethane–ethylene and propane–propylene clearly

TABLE I

HEATS OF ADSORPTION (kcal/mole)

Zeolite	Degree of substitution	25–80° CH_4	25–100° CO	60–160° C_2H_6	80–180° C_2H_4	100–180° C_3H_8	160–240° C_3H_6	160–240° C_4H_{10}	$\Delta Q(CO-CH_4)$	$\Delta Q(C_2H_4-C_2H_6)$	$\Delta Q(C_3H_6-C_3H_8)$
LiNaX	91.0	4.1	9.0	5.7	10.7	7.7	14.1	9.5	+4.9	+5.0	+6.4
NaX	100	4.5	6.9	6.2	9.0	8.0	11.1	9.9	+2.4	+2.8	+3.1
KNaX	83.5	4.5	4.8	6.4	7.0	8.2	9.1	9.9	+0.3	+0.6	+0.9
RbNaX	54.0	5.0	4.8	6.6	6.8	8.3	8.9	10.5	−0.2	+0.2	+0.6
CsNaX	53.0	5.2	5.0	7.0	7.3	8.5	9.0	10.8	−0.2	+0.3	+0.5
AgNaX	90.0	5.8	—	8.3	—	9.9					
MgNaX	65	4.2	5.9	6.1	9.1	7.8	9.9	9.1	+1.7	+3.0	+2.1
		(4.2)	(6.1)	(6.3)	(9.4)	(8.0)	(10.9)	(9.7)	(+1.9)	(+3.1)	(+2.2)
CaNaX	90	4.1	7.9	6.2	10.9	7.2	13.9	9.2	+3.8	4.7	+6.7
		(4.8)	(9.3)	(6.9)	(28)	(8.9)			(+4.5)	(+21.1)	
SrNaX	95	5.5	7.8	7.5	13.0	9.6	14.9	11.3	+2.4	+4.5	+5.3
BaNaX	73	5.2	6.9	7.9	10.0	10.3	12.2	10.6	+1.7	+3.0	+1.9
CdNaX	88	4.7	10	7.1	27	8.0		10.3	+5.7	+19.9	

show what influence the nature of the cation has on the character of the interaction with molecules of carbon monoxide, ethylene and propylene and how specifically strong this interaction is for such cations as Na+ and Li+ which are characterised by a higher density of the positive charge.

Somewhat different behaviour is observed for zeolites with bivalent cations. For zeolites containing magnesium the heats of adsorption of all the compounds studied are greatly decreased in comparison with the data obtained on NaX. This may be caused both by the strongly hydrophilic character of this cation (the conditions of thermal activation are not sufficient for the complete dehydration of this form), and by the small extent of Na+ exchange with Mg^{2+} in this specimen and by the possible destruction (partial) of the magnesium-containing zeolite[6].

In the case of Ca^{2+}, Sr^{2+} and Ba^{2+} substituted zeolites we observe an increase in the heats of adsorption of the saturated hydrocarbons with the increase in the number of electrons in the metal cations, together with a decrease in the heats of adsorption of the unsaturated hydrocarbons and carbon monoxide, the same as in the case of zeolites with univalent cations. The strontium form of zeolite does not obey this regularity, since an increase in the heats of adsorption is observed for all the olefines. It is thought that this property of the strontium form may be caused by formation of a separate phase, enriched with strontium[7], in this zeolite and by a decrease in the hydrophilic properties of the cation with its radius increase (*i.e.* by smaller screening of the cation by water molecules).

One sees from the data given in Table I that for zeolites with bivalent cations the influence of conditions of thermal activation on the values of adsorption heats is more pronounced. This influence depends to a great extent on the value of the energy of hydration of the cation. Hence the deeper thermal activation does not cause an appreciable increase in the heats of adsorption in the case of magnesium-containing zeolites, but with zeolites containing calcium it leads to an appreciable increase in the heats of adsorption of the C_1–C_4 hydrocarbon gases and carbon monoxide.

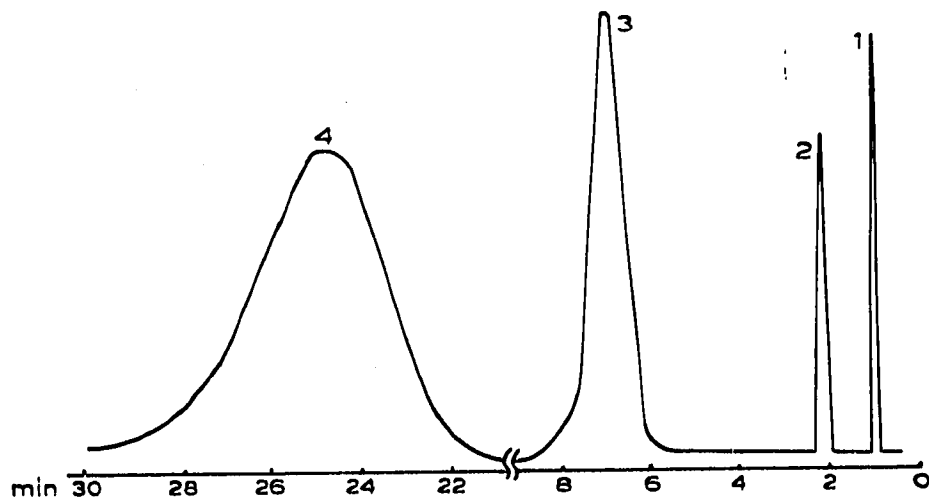One should especially note the chromatographic properties of the silver and

Fig. 1. Chromatogram of the mixture: 1 = methane; 2 = ethane, 3 = propane; 4 = butane. Adsorbent is a type X zeolite containing silver. Temperature of the column is 180°.
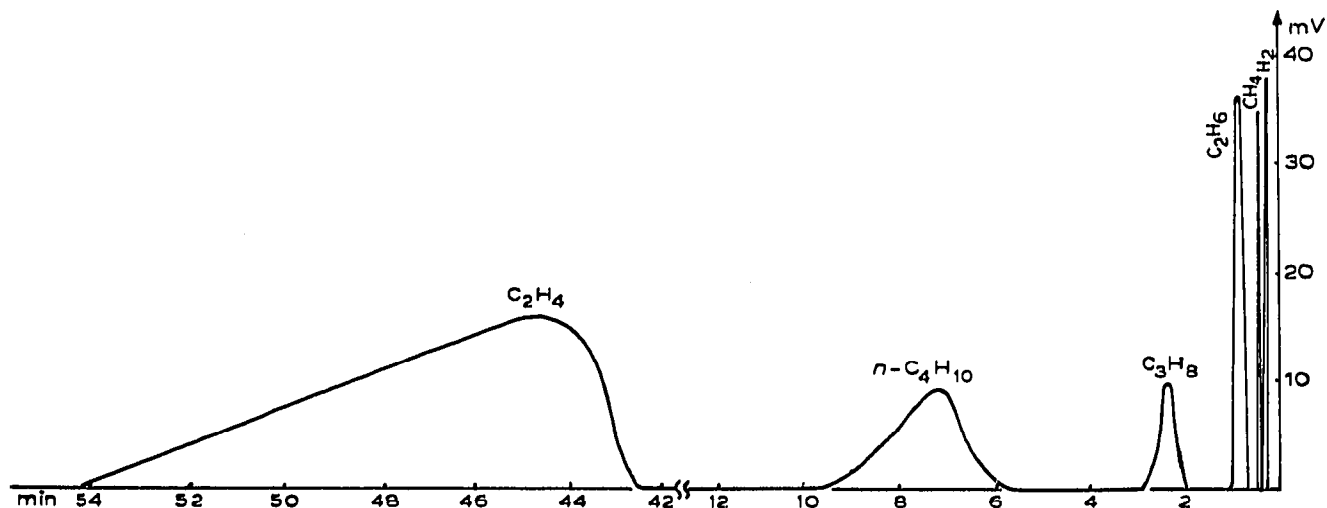
Fig. 2. Chromatogram of the mixture: hydrogen–methane–ethane–propane–butane–ethylene. Adsorbent is a cadmium-substituted zeolite. Temperature of the column is 200°.

cadmium zeolites. For instance, if on a NaX zeolite at a column temperature of 180°, there is the possibility of separating a mixture consisting of hydrogen, carbon monoxide (methane), ethane, ethylene, propane, butane and propylene, then hydrogen, carbon monoxide and unsaturated hydrocarbon can be strongly fixed on specimens containing silver, while the saturated hydrocarbons are easily eluted (Fig. 1), separating into different components[8].

A certain amount of specificity, not so sharply pronounced, is also shown by zeolites containing cadmium[9] with respect to the above mentioned components. However, if this property is already pronounced at a small degree of substitution of silver in the zeolite, it is only pronounced at a high degree of substitution of Na^+ by Cd^{2+} (85–90%). Thus with this form of zeolite propylene is strongly fixed at a column temperature of 200°, while all the saturated hydrocarbons involving butane
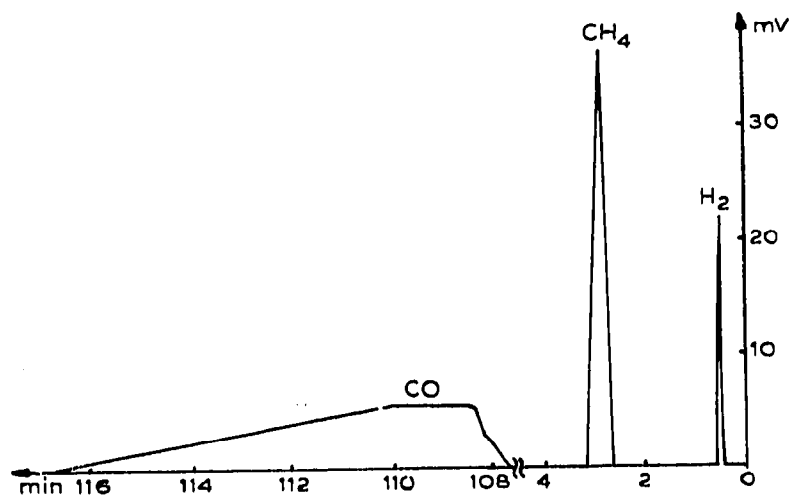

Fig. 3. Chromatogram of the mixture: hydrogen–methane–carbon monoxide on cadmium-substituted zeolite. Temperature of the column is 20°.

are eluted earlier than ethylene (Fig. 2) (it should be noted that under such circumstances, *i.e.* where the experiment is carried out with the zeolite in the silver form, ethylene is adsorbed very strongly).

This form of zeolite also shows a certain selectivity (Fig. 3) with respect to carbon monoxide. The retention time for this component increases sharply on cadmium-containing specimens. In addition, the symmetry of the peak corresponding to carbon monoxide on the chromatogram is sharply distorted.

Another characteristic feature of the cadmium zeolite is that at high column temperatures (300°) hydrogen, ethylene and to some extent carbon monoxide are practically not eluted.

Strong fixation of hydrogen on the zeolite containing silver was explained by the formation of the hydrogen zeolite form due to silver cation reduction by hydrogen[10,11].

$$Ag_2X + H_2 \rightarrow 2HX + 2Ag^0$$
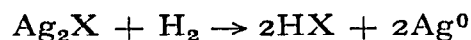
Such a reaction takes place in the case when pure helium, without any admixture of oxygen, is used as carrier gas. When air is used as carrier gas the following reactions

$$4Ag^0 \cdot HX + O_2 \rightarrow 2Ag_2O + 4HX$$
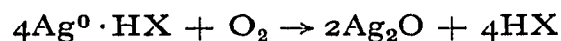
can take place and further

$$Ag_2O \cdot HX + H_2 \rightarrow 2Ag^0 \cdot HX + H_2O$$
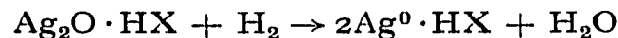
Indeed, in such cases we observe the formation of a large amount of water in the zeolite. The possibility of the existence of such reactions was also mentioned in RICKERT's paper[12].

However, the development of this reaction may be stopped, because, according to the existing opinion[13], when zeolite is heated silver atoms migrate to its outer surface, forming larger silver atom clusters, which cannot be completely oxidised and cannot be returned to their former positions.

In the case of cadmium-substituted zeolites, the development of reactions similar to those for silver is apparently characteristic, however, they take place only at high column temperatures (300°), while with the silver-substituted forms they take place readily at room temperature.

With carbon monoxide adsorption, on the basis of spectral data, one may assume a mechanism leading to complex formation[14,15] of this compound with the Ag and Cd cations. In the case of the zeolite containing silver, a more stable complex is most probably formed and the bond corresponds to a chemisorption process.

In the chromatographic separation of unsaturated hydrocarbons on these zeolites, complex formation with adsorbent cations apparently takes place. There are a number of data in the literature on the possibility of the formation of complexes between some metallic cations and olefines and acetylenes.

It is shown in our studies that these complexes are more stable for Ag^+ than for Cd^{2+}. Such a statement is confirmed by spectral studies made while investigating
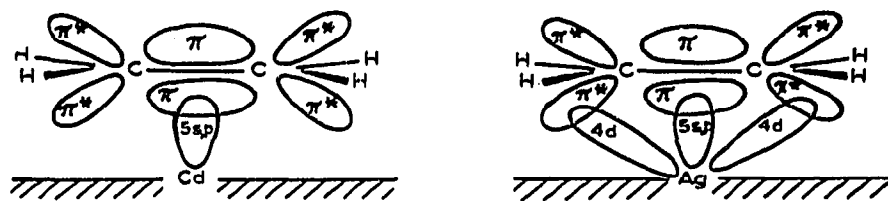
Fig. 4. Scheme of bond formation of ethylene molecules with cations Ag and Cd in a type X zeolite

ethylene adsorption on different cation-exchange forms of type Z zeolites[17].

In the case of AgX, it is possible that bond formation takes place due to over-lapping of the filled π-orbital of ethylene with the vacant 5s,p orbital of a silver ion and by overlapping of the filled 4d orbital of the silver ion with a vacant π^* orbital of ethylene.

In the case of CdX interaction only proceeds as a result of the overlapping of π and 5s,p orbitals and the molecule may rotate freely around this bond.

Thus, from the aforesaid, one sees the importance of the nature of zeolite cations when going into details concerning the separate components of the energies of interparticle interaction in chromatographic processes.

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