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^{7}Li NMR OF THE ZEOLITE INCLUSION COMPLEXES LiA·LiNO$_3$ AND LiX·LiNO$_3$.
I MOTIONAL NARROWING OF THE LINE

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Activation energies and cationic energy levels were determined, from narrowing of ^{7}Li NMR lines. In addition to this, model of energy levels earlier proposed for sorption zeolite systems was confirmed and applied to inclusion zeolite complexes.

INTRODUCTION

Zeolites are complex alumosilicates,the stable anionic structure of which forms a crystalographically well defined system of channels and cages. Foreign molecules and ions can be built in, whereupon inclusion and sorption complexes are formed/1-4/. Negative charge of an alumosilicate framework is compensated by monovalent, bivalent or trivalent cations which in the majority of cases take up well defined crystalographic positions, while a certain number of cations move freely through zeolite as a result of thermal activation. This is best illustrated by the facts that not all cations can be localised by X-ray structure analysis, a high electric conductivity of dehydrated zeolites /2,5/ and the appearance of narrow NMR lines in cationic spectra at room temperature /5/.

Inclusion complexes are formed by bringing zeolite into contact with molten salts or concentrated solutions /3,4,6/. Their basic characteristic is a high electric conductivity, which at room temperature is a few orders of magnitude higher than the conductivity of dehydrated zeolites and the corresponding salts from which the complexes are built.

In earlier ^{7}Li NMR measurements of dehydrated LiA zeolite, activation energy for the isotropic diffusion of the ^{7}Li ion 28-30 KJ/mol /7,8/ was obtained on the basis of line narrowing. In LiX zeolite, motional narrowing of the line was not observed the only thing to be established was that in addition to the bound ones there also exist a small fraction of very mobile cations /5/. There is no other data on the inclusion complexes $LiA \cdot LiNO_3$ and $LiX \cdot LiNO_3$ except the preliminary spectra of the authors /10/.

EXPERIMENTAL

Lithium forms of A and X zeolites were obtained by ionic exchange from the commercial Union Carbide zeolites NaA and NaX and a degree of exchange of over 95% was achieved. After being washed out and dried in air the samples were pressed into cyclindrical form, and degassed in a NMR cuvette at 670 K and 10^{-4} Pa (10^{-6} mmHg) for 12 hours.

Inclusion complex samples were obtained by treating LiA and LiX zeolites with molten $LiNO_3$ as described in ref. /3/. Excess $LiNO_3$ salt was removed by water rinse after which the samples were dried in air, pressed into cylindrical form and degassed in an NMR cuvette for about 6 hours at 570 K and 0.1 Pa (10^{-3} mmHg).

^7Li NMR spectra were obtained at 35 MHz on a Bruker SXP-100 pulse spectrometer in the temperature range 150 - 513 K.

RESULTS AND DISCUSSION

The basic property of all spectra, clearly evident in dehydrated zeolites, is a complex lineshape in the region of motional narrowing. At low temperatures the lines are almost of gaussian shape but at high temperatures of lorentzian, or more preciselly, of Voigt shape due to the inhomogenous broadening by the external magnetic field. In the region of motional narrowing the lines can be best described as a linear combination of lorentzian and gaussian components. It is characteristic that lines of inclusion complexes at and above room temperature are significantly narrower than the corresponding lines in dehydrated samples. This effect is obvious in Fig. 2. where line width dependence of the resulting NMR signals on temperature is shown. Shift in the region of motional narrowing of the line is noticeable, which is clear proof of the increased ionic mobility in inclusion complexes compared to corresponding zeolites.

Activation energies for ionic motion obtained by decomposing lines into components (lorentizian and gaussian) and by quantitative treatment of line narrowing, as described earlier /11/ are shown in table 1. The first column on the table shows activation energies for narrowing of the lorentzian component, the second, narrowing of the gaussian component, while column three gives values obtained on the basis of temperature dependence of the relative contribution of the lorentzian and gaussian lines to the resulting NMR spectra. Quantative confirmation and generalisation of the earlier proposed model of energetic states of cations in zeolitic systems /5/ can also be carried out on zeolitic inclusion complexes on the basis of results from table 1 and measurements of electric conductivity.

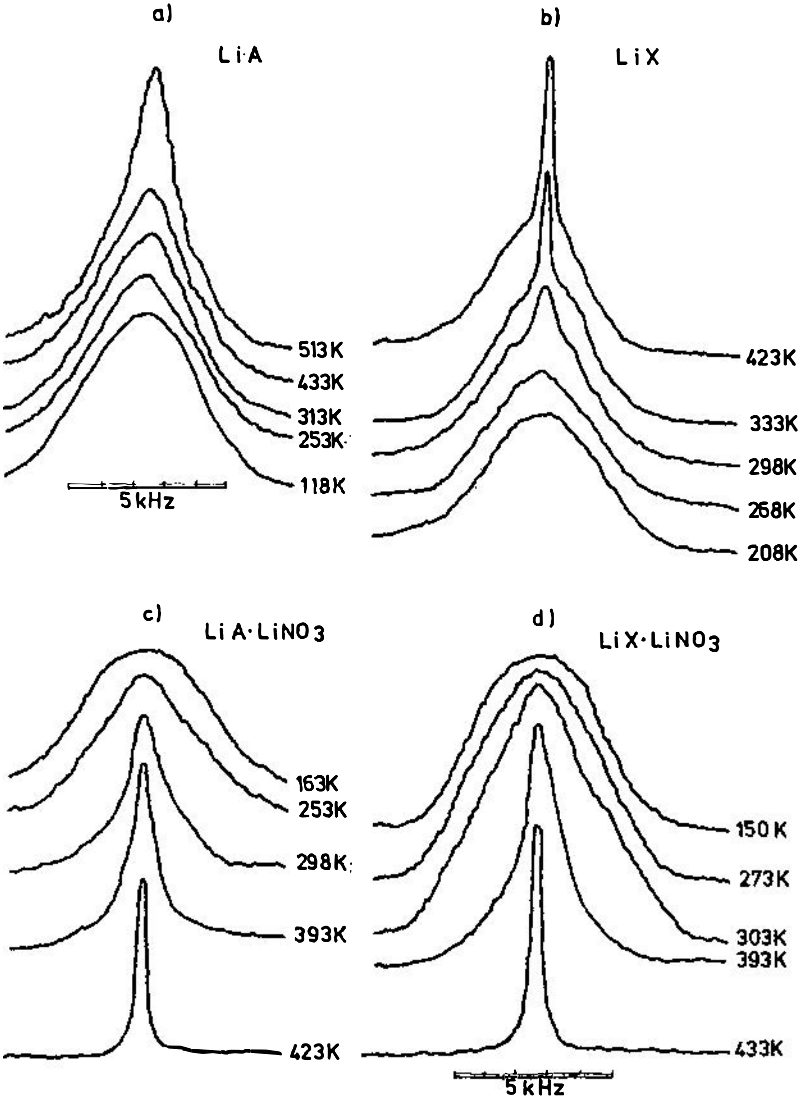
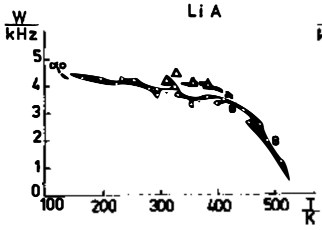


Fig.1. Characteristic ^{7}LiNMR spectra of dehydrated samples:
a) LiA; b) LiX; c) LiA·LiNO$_3$; d) LiX·LiNO$_3$

a)



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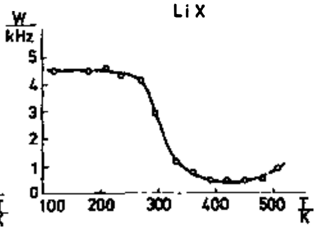

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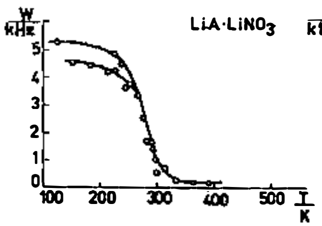

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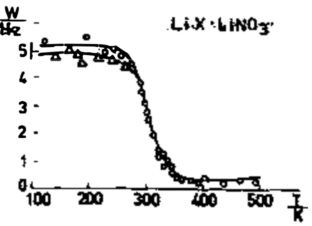

	Activation energy KJ/mol Lorentzian component	Gaussian component	Ratio of lorentzian v.s.gaussian components
LiA	27.6		41.8
LiX		27.2	15
LiA·LiNO$_3$	51.0	10.2	22.6
LiX·LiNO$_3$	44.3	11.3	48.9

The basis of the model is the fact that two lines are seen in the NMR spectra a lorentzian and gaussian, which narrow independently with a change in temperature. Narrowing of each line is a consequence of the thermal activation of ions from the basis state, A into the exited state, B. There exists a fast exchange amongst these ions in an NMR sense. However, since both a gaussian (G) and lorentzian (L) line are seen in the spectra at the same time, it is clear that between the spin phases which they represent, the exchange is slow. Accordingly there exist at least four energy levels of cations A_G, B_G, A_L and B_L with a fast ($A_G \rightleftarrows B_G$, $A_L \rightleftarrows B_L$) and a slow (A_G, $B_G \rightleftarrows A_L$, B_L) spin exchange.

A schematic representation of energy levels is given on Fig.3. In LiA zeolite, Fig.3a, regarding the fact that no change in the width of the gaussian line was observed, the situation appears sufficiently clear. Two fundamental phases of cations exist, A_G and A_L from where the corresponding components of spectra originate. Upon thermal activation the ions pass from state A_L into the "free conduction band" which is reflected both in the increase in electric conductivity and in the norrowing of the NMR line. In this zeolite two activation energy values for electric conductivity were obtained: 32,6 KJ/mol for the low temperature process and 66.0 KJ/mol for the high-temperature process /10/.

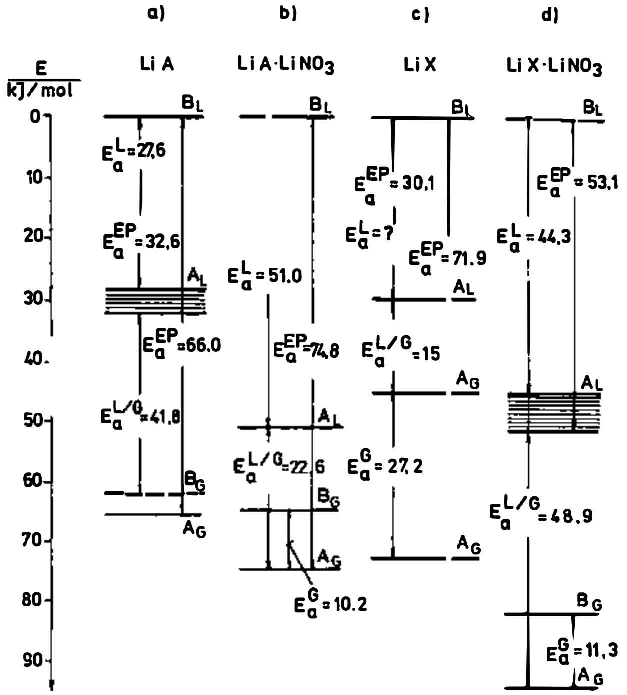

Fig. 3 Energy levels of cations
a) LiA, b) LiA·LiNO$_3$, c) LiX, d) LiX·LiNO$_3$

Accordingly at least two stable phases of cations can be identified in LiA zeolite. Of these A_G represents the firmly bound ions in the framework which is reflected both in the gaussian lineshape and in the linewidth (second moment). The second phase, A_L, originates from the ions relatively distanced from the alumosilicate framework, a consequence of which the lineshape is lorentzian, similar to the one in diluted spin systems.

Lorentzian and gaussian lines are immediately seen in the NMR spectrum of LiX zeolite. Taking into consideration the fact the line was inhomogenously broadened from the start, it was not possible to determine the activation energy for narrowing of the lorentzian line. Examining this system, as the previous one, a similar arrangement of energy levels is obtained, Fig.3c From measurements of electric conductivity in LiX zeolite two activation energies were also obtained: a low-temperature one of 30.1 KJ/mol and a high-temperature one of 71.9 KJ/mol /5/. In addition to this, besides the ions in the "free conduction band", B_L, which in fact represents the fraction of the most mobile ions which can move from cavity to cavity, there are also exist three phases of cations. Due to the somewhat greater dimensions of the cavities in type X zeolite it is possible to make a distinction between phases on the basis of the type of local movement. Thus besides the ions in the rigid lattice, A_G, there exists a phase of ions, B_G, which undergo surface diffusion, and a phase of ions, A_L, which move relatively freely within one cavity. Due to the large number of nonequivalent cations in type X zeolite, closercharacterisation of a phase is not possible.

In inclusion complexes,on the basis of electric conductivity measurements, only one value for activation energy was obtained in both cases: 74.8 KJ/mol for $LiA \cdot LiNO_3$/10/ and 53.1 KJ/mol for $LiX \cdot LiNO_3$ /12/. Combining these results with data from Table 1. energy level schemes shown on Figs.3b and 3d, are obtained. Basic characteristics of levels are the same as in dehydrated zeolites. There exist at least four phases of cations which differ in mobility and structure. The introduction of ionic pairs Li^+ NO_3^- into a structure of LiA zeolite leads to an increase in energy difference between ions which move within one cavity and those which move from cavity to cavity i.e. those which are inside the "free conduction band". This is a consequence of the free volume reduction for the movement of ions in the $LiA \cdot LiNO_3$ system because the cavities of the α-cages are 90% filled with built in ionic pairs. In the α cage there are 10 out of a possible 11 ionic pairs.

Another noticable effect in the $LiA \cdot LiNO_3$ complex is the reduction in energy difference between ions bound in a rigid lattice, and locally mobile ions, which is a consequence of the reduction in asymmetry of the electric field on cationic positions. Namely, built in NO_3^- ions in the vicinity of cations compensate a negative charge of the alumosilicate framework,whereupon they facilitate delocalisation of the cations, i.e. the transition from A_G into A_L level. For the same reasons it results in the narrowing of the gaussian NMR line, i.e. the appearance a mobile phase of ions, on the surface B_G. A closer characteristic of this phase and others will be discussed in connection with low-temperature spectra which are mainly guided by local spin structure and not spin motion.

In the $LiX \cdot LiNO_3$ inclusion complex two similar changes were observed in comparison with the corresponding zeolite, which cannot, however, be explained by steric factors, regarding the fact that only 2 $Li^+NO_3^-$ ionic pairs from a possible 11 are built into the zeolite structure. Here, built in $Li^+NO_3^-$ ionic pairs increase activation energy for electric conducivity in such a way that the isolated NO_3^- group captures the thermally activated Li^+ ions. For the same reasons it results in a reduction in activation energy for cation delocalisation (transition $A_G \rightarrow B_G$) although a detailed picture of the type of movement (reorientation, recombination of ions, diffusion etc.) can only be discussed after becoming better acquainted with the nature of energy levels in inclusion complexes.

Agreement of activation energies for electric conductivity and the narrowing of the NMR line points to the very important fact that high electric conductivity in the investigated systems is connected with a regular crystal structure and not with its defects or impurities.

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