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THE ELECTRIC AND THERMAL PROPERTIES OF SOLID ELECTROLYTES - ZEOLITES

M.Šušić,N.Petranović and S.Bojović

Institute of Physical Chemistry, Faculty of Science,
Beograd

Abstract.- The thermal and electric properties of a synthetic zeolite A modified by salt inclusion are shown. The inclusion increases the electric conductivity of the zeolite, and the relatively low values of activation energy are indicative of properties of good ionic conductors. In a two- and three-electrode system with a Pt counter electrode a high double layer capacitance has been found.

1. Introduction

In recent years solid ionic conductors have been extensively studied and a large number of conductors was made with a high conductivity, mainly based on silver salts, prevailingly AgI. However, it is still a problem to obtain a solid electrolyte stable over a wide temperature range. Zeolites, in the classification of solid electrolytes, are among solid ionic conductors and in the group of non-ideal ionic crystals, the subgroup of a structure with interstitions$^{1)}$.

On the properties of zeolites and their structure there is a vast literature in the form of monographs$^{2)}$ and collected papers from scientific conferences on zeolites$^{3)}$.

The system of channels and cages in zeolite lattice makes it possible to modify the zeolite by introducing new molecular species$^{4)}$. We have paid special attention to the modification of zeolites by inclusion of molten salts, whereby inclusion complexes of zeolites are obtained which exhibit a number of a new characteristics as regards the thermal, electric and electrochemical behaviour.

2. Experiment

The preparation of inclusion complexes with nitrates of univalent and divalent metals is desvribed elsewhere[4]. Thermal analyses were carried out on a R.L.Stone differential thermal analyzer and on a Du Pont 990 thermal analysis system.

For electric measurements the polycrystaline powder of zeolite was pressed into pellets. The measurements of conuctivity were made with a 11V ac of a frequency of 1 kHz and with Keithly 610 C electrometer. Alternating current polarography, by means of which it was possible to measure faradaic and capacitive current, was carried out by a PAR-170 electrochemical system.

3. Results and Discussion

The definition of inclusion complexes was made by IR and Rö analyses. On IR spectra we distinctly see new interactions of the included component with the alumosilicate framework: changes on the fundamental band at about 1000 cm^{-1} which originates from Si-O-Al-(O) vibrations and especially on the band of the double four-ring at 550 cm^{-1} which is more or less split, which again indicates the intensity of the interacion (Fig.1).

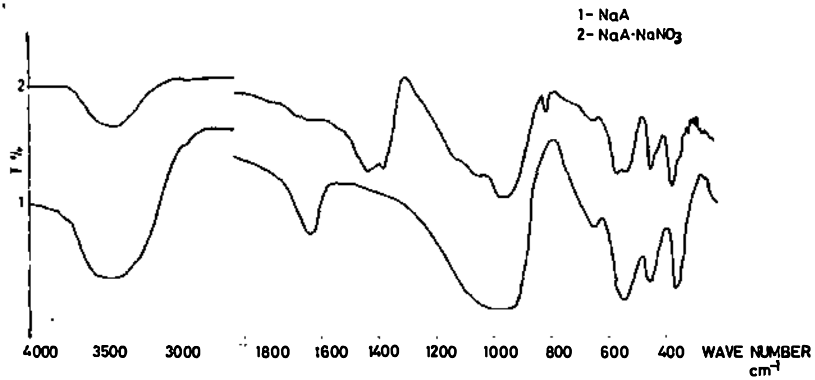

Fig.1 Infrared spectra: 1) NaA zeolite,
2) NaA·$NaNO_3$ inclusion complex

The inclusion complex itself, if a nitrate one is in question, is identified by new bands in the spectrum in the region of about 1400 cm^{-1} and at 820 cm^{-1} which are due to the vibrations of the NO_3^- group. The nitrate band at about 1400 cm^{-1} also may have a complex structure, which indicates changes undergone by the nitrate ion inside zeolite cage, as well as definite interactions and existance of ion pairs $M-ONO_2$ or complex ions of the type $M-ONO_2^+$ (M is a monovalent or divalent cation respectively, with a pronounced metal-nitrate interaction[5,6]. In IR spectra of inclusion complexes we see the decrease of the intensity of the water band at about 3400 cm^{-1}, because water molecules are replaced by salt molecules.

Thermal properties.- The thermal properties of inclusion complexes depend on the nature of included component, and in nitrate inclusion complexes the stability limit is 400-450°C. Above this temperature the denitration gradually occurs, and the limit of structural stability of zeolite lattice is again defferent in defferent forms, but in the principle it lies within the range 600-700°C. It depends on whether a monovalent or divalent nitrate ion pair is present, i.e. it is associated with the presence of complex nitrate ions in the cage. Divalent cations give a stable metal-nitrate complex ion, so that nitrate bands are retained in some inclusion complexes even up to 750°C (Fig.2, curve 2).

The identification of peaks in DTA diagrams was made on the basis of the literature data for pure zeolite and pure included component and by the so-called exclusion method; peaks associated with phase changes of the nitrate component were determined by denitration, while peaks due to the present water were determined by dehydration. The peak at 130°C (Fig.2, curve 1) and the peaks at 105° and 140°C (Fig.2, curve 2) originate from water, whereas the peaks at 285° and 505° (Fig.2, curve 1) and the peaks at 466° and 750°C (Fig.2, curve 2) are associated with phase changes of the nitrate component.

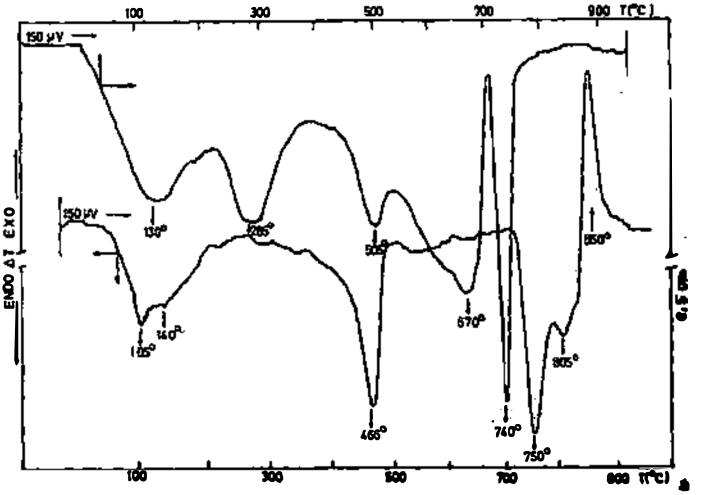

Fig.2 DTA curves for: 1) NaA·$NaNO_3$ inclusion complex, 2) $CdNO_3$,NaA·$NaNO_3$ inclusion complex.

Above these temperatures new phases occur in the structure. The identification of these phases was for the present made on tha basis of changes in the low-frequency part of the IR spectrum of inclusion complexes. There appear sodalite, nepheline and α-carnegieite, which is at room tempearture identified as β -carnegieite, because on cooling it undergoes an $\alpha \dashrightarrow \beta$ transition at 670°C. This transition is distinctly seen in the sodium-nitrate inclusion complex (Fig.2, curve 1), although the unsimmetricity of the peak indicates the presence of one more endothermal change. The common new phase of all the inclusion compleces in the structural transformation is sodalite; some complexes such as lead inclusion complex make transition to pure sodalite$^{7)}$, whereas in others e.g. cadmium inclusion complex there appears nepheline-exothermal peak at 850°C (Fig.2, curve 2). In sodium-nitrate inclusion complex there appear all the three phases and their identification was made also by X-ray structural analysis$^{8)}$.

These thermal changes are of significance, since the inclusion complexes of zeolites, as was noted in the introduction, turned out to be good ionic conductors at elevated temperatures.

Electric properties.- Zeolite in its composition and structure has a number of properties characteristic of the class of good ionic conductors: a large number of mobile ions, a rigid structural lattice through mobile ions may migrate in three dimensions, and a highly polarizable anion. By salt inclusion the number of cations is increased by a factor of about two[4)] and a new polarizable nitrate anion is introduced. However, the electric conductivity increases much more than was predicted by the relation on the basis of the increase in the number of carriers- cations[9)]. For the effect of inclusion on the increase of zeolite conductivity two factors are essential which are noticed in inclusion complexes: the interaction of included component with zeolite matrix and the metal-nitrate interaction of the included ion pair. Both the phenomena lead to an increase in mobility of cations and thereby to an increase in conductivity. The values of activation energy and diffusion coefficients (Table I), which may be calculated from conductivity by means of the Nernst-Einstein relation, indicate that inclusion complexes of zeolites are in the class of good ionic conductors,with a low energy barrier $0.1 < E_A < 1$ eV.

Table I

Some characteristics of zeolite inclusion complexes and other materials as solid ionic conductors.

Sample	σ_{473} $(\Omega^{-1}m^{-1})$	D_{473} (m^2sec^{-1})	E_A (eV)	remarks
NaA	$7.0x10^{-4}$	$5.3x10^{-14}$	0.49	
$NaA \cdot NaNO_3$	$1.4x10^{-2}$	$1.1x10^{-12}$	0.69	
$LiA \cdot LiNO_3$	$3.9x10^{-2}$	$2.9x10^{-12}$	0.79	
$AgA \cdot AgNO_3$	$1.2x10^{-1}$	$9.5x10^{-11}$	0.29	
$CdNO_3NaA \cdot NaNO_3$	$1.0x10^{-7}$	$7.5x10^{-16}$	1.22	
$RbAg_4I_5$	-	-	0.07*	superionic cond.
α -AgI	-	-	0.05*	" "
β -alumina	-	-	0.15*	" "
$Na_3Zr_2PSi_2O_{12}$	-	-	0.30*	good ionic cond.
ZrO_2 10% Se_2 O_3	-	-	1.0*	solid electrolyte

* from ref. (10)

One more property of these zeolites is very significant and places them in the group of solid materials with special purpose. We are dealing with the capacitance of the double lectric layer at the electrode-solid electrolyte interface. Measurement of capacitative current shows a considerable capacitance of double electric layer, the effect being especially pronouced when the counter electrode in a three-electrode system is a Pt electrode. The Pt electrode as the counter electrode exerts a blocking effect and leads to a high capacitance of the double layer. We noticed the dependence of the capacitance on the frequency and amplitude of alternating current. Calculated values of the double elctric layer capacitance are given in Fig.3. It is seen that as the frequency decreases, especially at a frequency lower than 100 Hz, the capacitance suddenly increases (Fig.3b). Also the effect of amplitude is noticed (Fig.3a).

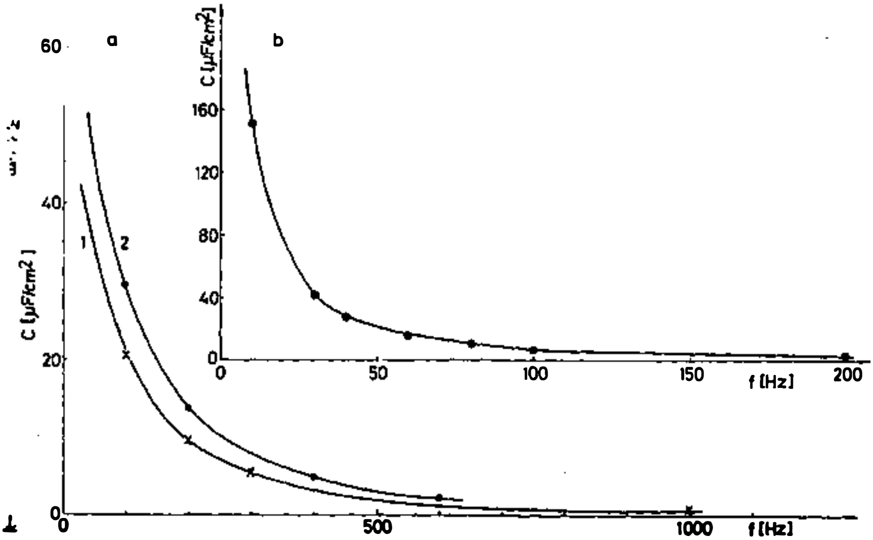

Fig.3 Electric double layer capacitance of $CdNO_3NaA\ NaNO_3$ inclusion complex at 0.0 volt d.c. as a function of frequency; 3a) at 360°C, currve 1 ΔE=10 mV, currve 2 ΔE=1 mV; 3b) at 307°C, ΔE= 5 mV (amplitude peak to peak a.c.)

The obtained values for the capacitance of the double layer in cadmium inclusion complex, at frequencies below 100 Hz, are higher than presently known values of capacitace, i.e. 0.2 Fm^{-2} in an electrochemical cell with $RbAg_4I_5$(10).

From these results one distinctly notices the electric properties of inclusion complexes and possibility of using them at elevated tempeartures. The establishment of the double electric layer capacitance promisses that capacitors of high specific capacitance for low potentials may be obtained

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