O. A. GLONTI, Academician of the Academy of Sciences of the Georgian SSR, G. V. TSITSISHVILI, N. A. SHISHAKOV

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Abstract

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O. A. GLONTI, Academician of the Academy of Sciences of the Georgian SSR,
G. V. TSITSISHVILI, N. A. SHISHAKOV

ON THE LOCATION OF SILVER IONS IN ZEOLITE AgX

Recently, synthetic zeolites of types A and X have been acquiring ever increasing practical importance as highly efficient adsorbents used for the separation of gas mixtures and for the deep drying and purification of gases. They are gradually replacing ordinary desiccants (silica gel, aluminum oxide, etc.) and such purification methods as freezing, distillation, and others.

Only those molecules whose dimensions do not exceed the dimensions of the entrance windows can penetrate into the primary porous structure of zeolites. In this connection, the polarity of the molecules is of great importance. For example, the large and small cavities of zeolite X are accessible to water molecules, which possess this property.

As is known, the degree of ion exchange depends on the nature of the cations. In work ([1]) the following exchange series was established: $Ag^+ > Pb^+ > Na^+ > K^+ > NH_4^+ > Li^+$. It is therefore evident that silver readily displaces sodium. It is also known that sorption properties depend strongly not only on the nature, but also on the location of the cations in the lattice. As M. M. Dubinin ([2]) showed, in zeolites of types A and X adsorption changes greatly when Na^+ ions are replaced by Ca^{2+}. Therefore, determining the position of cations in the crystal lattice of synthetic zeolites is of great importance for a better understanding of sorption processes.

The aim of the present work was to determine the position of Ag^+ ions in zeolite of type X.

The synthesis of the silver form of the zeolite was carried out by M. Adolashvili according to the method ([3,4]). This form of zeolite, unlike other forms, is characterized by a number of selective-adsorption properties ([4,5]), by the ability to change color under the influence of moisture ([6,7]), and by other qualities. All of the above indicates that the study of the structure of the silver zeolite is of considerable interest.

The object of our investigation was a synthetic zeolite NaX in which, by ionic exchange, 80% of the Na^+ ions had been replaced by Ag^+ ions. The structure of zeolite NaX was determined by Broussard and Shoemaker ([8]). The authors

Fig. 1. Projection of the electron density onto the (001) plane for zeolite AgX

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assign it to the space group $Fd3m - O_h^7$ (centrosymmetric case: the origin of coordinates coincides with the center of inversion).

Localized Na^+ ions are situated at the centers of six-membered prisms (at the origin of coordinates) and in the planes of six-membered windows. They have the following coordinates: Na_I—0.00; 0.00; 0.00; Na_{II}—0.9911; 0.7589; 0.9911. A discrepancy factor $R = 10.34$ was obtained. The photographs were taken on an ionization diffractometer. Since, with increasing angle, the distortion of intensities increases, the authors limited themselves to using interplanar spacings down to $d = 1.262$ Å, which corresponds to the sum of squares of the indices $h^2 + k^2 + l^2 = 387$.

In the present work, the principal method of investigation was the obtaining of X-ray diffraction patterns on photographic film. The method we used is, for a number of reasons, considered of little suitability for determining the structure of a substance; however, if there is a lattice of high symmetry (as in our case), the reliability of indexing the observed reflections is considerably increased, and therefore the structure can sometimes be determined rather accurately.

To increase the reliability of the results, we carried out X-ray photography with two different radiations—iron and copper. The first made it possible to study reflections at comparatively small angles, while the second made it possible to obtain more reflections of higher orders. In this way d was brought to a value of 0.988 Å, which corresponds to the sum $h^2 + k^2 + l^2 = 632$. This was important for constructing reliable projections of the electron-density distribution.

For greater accuracy in determining interplanar spacings and reliability in indexing the lines, a standard substance—metallic silicon—was sometimes added to the powder.

For analysis of the intensities of the reflections we used an MF-4 recording microphotometer. From the blackening curves S, the intensities were calculated according to the formula $I_e = \log(S_0/S)$. On the basis of the line intensities found, the experimental amplitudes F_e were calculated by the formula

$$F_e = \sqrt{\frac{I_e}{A\tau^2 LPp}}.$$

The quantity B, entering into the temperature factor τ^2, was taken equal to 1.4. In the case of overlapping lines, the total intensity was divided in proportion to the quantities pF_T^2.

Fig. 1. Projection of the electron density onto the (001) plane for zeolite AgX

We assume that the ions Ag^+ during ion exchange occupy the positions of Na^+ ions, since in size and polarizability they are close to one another, and therefore, for the calculation of F_T, the coordinates of Na^+ were assigned to the Ag^+ ion.

Table 1

Theoretical and experimental values of the structure amplitudes for AgX

$hk0$	F_T	F_e	$\|F_e\| - \|F_T\|$	$hk0$	F_T	F_e	$\|F_e\| - \|F_T\|$
220	760	507	253	1640	770	812	42
400	1334	1337	3	12120	1640	1835	195
440	560	737	177	14100	−480	493	13
620	225	332	107	1680	380	277	103
800	1200	0	1200	1820	−123	132	9
660	622	904	282	1860	−461	444	17
840	1615	1559	56	14140	5	6	1
1020	−49	53	4	2000	296	277	19
880	1490	1660	170	16120	228	217	11
1060	504	304	200	2040	207	387	180
1200	345	416	71	18100	−324	0	324
1240	770	789	19	2080	1071	1042	29
10100	−924	1125	201	2220	143	173	30
1420	−380	470	90	2260	−561	540	21
1280	868	1033	165	1840	−457	438	19
1460	−198	249	51	20120	254	286	32
1600	1210	1688	478	2400	671	646	25

Theoretical amplitudes and the projection of the electron density were calculated on the electronic computer of Moscow State University. The signs F_T obtained in this way were assigned to the experimental amplitudes, from which the map of the electron-density distribution was calculated and constructed.

onto the (001) plane. Good agreement was obtained between the quantities F_t and F_e, as is evident from the data in Table 1. From these data the discrepancy factor was found to be $R = 0.21$.

Figure 1 gives a comparison of the theoretical projection (constructed from the data of work (8)) and the experimental projection. The silver ions are denoted by bold dots, silicon by medium-sized dots, and oxygen by small dots. All these points fit well on the maxima of electron density found by us. The slight displacements of the experimental maxima compared with the theoretical ones are probably caused by the appearance of false maxima and by the superposition of projections of atoms on one another. All this makes it possible to assert that, in ion exchange, the Ag^+ ions occupy the positions of the Na^+ ions.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.