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ESR Study of Hydrated Synthetic Zeolites Containing Various Cations

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Hydrated cation-substituted zeolites of the Y type have been investigated by the ESR technique. The substitution of sodium ions to Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+} Cd^{2+} and Ca^{2+} ions ranged from 4 to 70%.

The paramagnetic Mn^{2+} ions permitting ESR studies were admitted into the zeolites in concentrations excluding dipole–dipole interaction.

The spectra were recorded in the X and Q bands.

A model of the state of cations in hydrated zeolites was proposed.

INTRODUCTION

The distribution of cations and water molecules in hydrated zeolites cannot be studied reliably by X-ray structural analysis, since no one has been able to find enough electron density peaks to account for all the ions and molecules. It was found that cations and water molecules can occupy both the supercage and the sodalite cage. A review on the population of cations and water molecules in hydrated zeolites has been published (*1*). Additional information on the sites of cation locations can be obtained from ESR spectra of paramagnetic ions admitted to the zeolite lattice. A bivalent manganese ion was used as the paramagnetic ion (*2–5*). This ion exhibits characteristic ESR spectra with hfs and fs structures very sensible to symmetry and to the strength of environmental local fields (*6, 7*). The present paper deals with ESR spectra of manganese ions in hydrated Y type zeolites of different cationic forms. The Mn^{2+} ions were introduced in concentrations preventing dipole–dipole interaction between these ions. Analysis and interpretation of the Mn^{2+} spectra made use of theoretical data on the relaxation mechanism of transition metal ions both in solution (*8–11*) and in solids (*12*). The results obtained show that the state of water and cations in the supercage is very near to that in concentrated electrolyte solutions (*13*).

EXPERIMENTAL METHODS

Hydrated cation-substituted zeolites of the Y type were investigated by the ESR technique. Zeolites with two- and three-valent cations were obtained from the Y type sodium zeolite by ion exchange at room temperature (*14*). The composition of the initial sodium zeolite cell was $Na_{56}Si_{135}Al_{57}O_{384}\cdot 260H_2O$. Ion exchange was conducted in 0.01 M aqueous solutions of cation chlorides by single treatment of the initial zeolite for 2 hr. Cations and the ions of sodium, aluminum and chlorine were detected both in solution and in the washings. Equivalent exchange of cations with sodium was observed in all cases. The degree of sodium ion exchange with Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+}, Cd^{2+} and Ca^{2+} cations varied from 4 to 70%. The amount of admitted cations did not exceed that of sodium ions in large cavities of the initial hydrated zeolite. Paramagnetic manganese ions were admitted to the cation zeolites also by ion exchange from an aqueous solution containing $2 \times 10^{-5}\,M$ manganese chloride. The Mn^{2+} amount was ~1 per 12.5 elementary cells, i.e., 1 per ~100 supercages. Table 1 shows the elementary compositions of the zeolites used. The tabular numbers refer to elementary cells with a manganese ion substituted for two sodium ions. As shown, the sodium ions in zeolites with exchange below 11% are those almost exclusively close to Mn^{2+} in the elementary cell and thus in the supercage. Zeolites with 40% exchange contain also another cation, along with Mn^{2+} and sodium, in every elementary cell. For zeolites with ~70% exchange the amount of sodium cations around Mn^{2+} is markedly lower.

The ESR spectra of Mn^{2+} in zeolites were recorded in the X and Q bands by USSR spectrometers described in (*2*, *3*).

The Mn^{2+} spectra were recorded in the X band, both at room temperature and over a temperature range of −40 to 100°C, and in the Q band at room temperature only.

RESULTS

ESR Spectra of the Mn^{2+} Ions in Fully Hydrated Zeolites

The Mn^{2+} spectrum parameters for fully hydrated zeolites are listed in Table 2. A broad line ($\Delta H = 500$ Oe) with an un-

TABLE 1

ELEMENTARY COMPOSITION OF THE ZEOLITES INVESTIGATED

Cationic forms and their symbols[a]	Percentage of sodium exchange to Me^{n+} cations (without allowance for Mn^{2+})	The no. of Na^+ cations in an elementary cell	The no. of other cations in an elementary cell
Yttrium			
YY-4	4.0	51	1
YY-10	10.0	48	2
YY-70	70.0	15	13
Lanthanum			
LaY-4	4.0	51	1
LaY-11	11.0	48	2
LaY-44	44.0	29	8
LaY-72	72.0	14	13
Zinc			
ZnY-15	15.0	46	4
ZnY-36	36.0	34	10
ZnY-81	81.0	9	23
Magnesium			
MgY-14	14.0	46	4
MgY-33	33.0	36	9
MgY-60	60.0	20	17
Cadmium			
CdY-18	18.0	44	5
CdY-44	44.0	28	13
CdY-83	83.0	7	23
Calcium			
CaY-15	15.0	46	4
CaY-35	35.0	34	10
CaY-65	65.0	18	18

[a] The numbers near the symbol denote the percentage of sodium exchange in the initial zeolite.

TABLE 2

Parameters of the ESR Mn^{2+} Spectra in Fully Hydrated Zeolites

Cationic forms of zeolite	X band; (Oe)			Q band
	ΔH_1	ΔH_6	A	
Yttrium	21	22	94	All samples show no resolved hfs; the hfs component width is ~70 Oe
Lanthanum	22	24	95	
Zinc	20	21	95	
Magnesium	~22	24	95	
Sodium	~22	22	96	
Cadmium	18	18	97	
Calcium	20	23	97	

resolved hfs of six components (60–70 Oe each) is observed in the X band for all samples over the range from room temperature to −40°C (Fig. 1a). A marked change in the spectrum shape occurs within −40 to −60°C. It is accompanied by narrowing of the hfs components and appearance of a well-resolved ESR spectrum of six hfs components with weaker doublets due to transitions with $\Delta m = \pm 1$, the so-called "forbidden transitions" (*6*) (Fig. 1b). The hfs constant (A) is ≅95 Oe, and the hfs components widen monotonically towards higher fields from ≅19 Oe (the first component to ≅22 Oe (the sixth component). The spectrum shape is characteristic of Mn^{2+} in a polycrystalline solid (*6*). The same variations in the Mn^{2+} spectrum shape with temperature are observed for the type Y hydrated sodium zeolite. Similar data on the temperature dependence of the spectrum shape were obtained in (*15*).

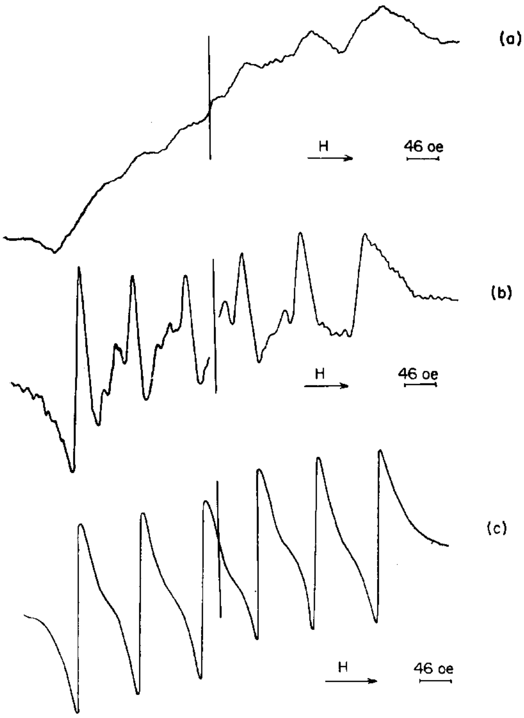

Fig. 1. ESR spectra of Mn^{2+} ions in fully hydrated zeolites (NaLaY-4): (a) $\nu = X$ band, room temperature; (b) $\nu = X$ band, −60°C; (c) $\nu = Q$ band, room temperature.

Well-defined spectra of six hfs components of a ~22 Oe width each, with splitting $A = 95 \pm 1$ Oe are observed in the Q band. The hfs component widths remain virtually unchanged (Fig. 1c).

ESR Spectra of Mn^{2+} Ions in Zeolites Evacuated at Room Temperature

The parameters of Mn^{2+} spectra in zeolites evacuated at room temperature are shown in Table 3. Evacuating of zeolites to 10^{-4} Torr induces changes in the ESR spectrum shape for samples with a high percentage of exchange of sodium ions (40% and higher) to ions of a hydration energy higher than that of Mn^{2+}. Such are Y^{3+}, La^{3+}, Mg^{2+} and Zn^{2+} (Table 4). The most essential changes are observed in the X band: the width of hfs components decreases about 3.5-fold, resulting in the appearance of a well-resolved sextet with additional doublets due to forbidden transitions (Fig. 2a). Drop of the measurement temperature does not induce changes in the spectrum shape. A sextet is recorded in the Q band as before, but the width of individual hfs components is half that of spectra in fully hydrated zeolites (Fig. 2b). The hfs constant $A = 95 \pm 2$ Oe remains the same in all cases. It will be seen from Table 3 that presence of the ions cited above has no effect on the Mn^{2+} spectrum parameters.

When the content of calcium and cadmium ions of a hydration energy lower than that of Mn^{2+} exceeds 40%, evacuating at room temperature induces spectrum

TABLE 3
PARAMETERS OF THE ESR Mn^{2+} SPECTRA FOR SAMPLES EVACUATED AT ROOM TEMPERATURE TO ~10^{-4} TORR

Cationic forms of zeolite	Q band; (Oe)				X band; (Oe)			
	ΔH_1	ΔH_6	D^a	A	ΔH_1	ΔH_6	D^a	A
YY-70	11.2	10.7	<100	97	18.6	21.2	55	96
LaY-72	12.6	12		97	18.6	21.2		96
LaY-42	11.0	11.0		97				
ZnY-81	11.2	11.0		94	18.6	21.2		97
ZnY-36	12.7	12.7		95				
MgY-60	13.0	13.3		97	18.7	21.0		96
MgY-33	10.0	11.0		96				
NaY	~23	~24		95	Spectra with unresolved hfs			
CdY-83	~25	~27		92				
CdY-44	31	31		93				
CaY-65	~25	26		95				
CaY-35	20	26		95				

[a] Parameter D was determined from experimental spectra by the technique proposed in (*12*).

changes neither in the X nor in the Q band, compared to fully hydrated samples (Fig. 2b and d). No essential changes in the Mn^{2+} spectrum is observed for room temperature evacuated zeolites with a low content of all ions investigated.

Thus, there is a marked dependence of the ESR spectrum shape on the measurement frequency for fully hydrated zeolites, an about 3.2-fold decrease in the hfs component width being observed with higher frequencies. A dependence of the spectrum shape on measurement temperature is observed in the X band. A spectrum characteristic of ions in a polycrystalline solid is exhibited by room temperature evacuated samples containing ions of a hydration energy higher than that of Mn^{2+}. No changes induced by evacuating at room temperature are observed for zeolites with low exchange of sodium ions to all the cations investigated. The same holds for zeolites with a high content of calcium and cadmium ions.

DISCUSSION

The data obtained by various physicochemical techniques show that the cations located in supercages of hydrated zeolites are closely surrounded by water molecules and form hydrated complexes. However, the amount of water in channels and cages of the zeolites is insufficient for formation of multilayer hydrate shells similar to those in diluted aqueous electrolytes (*13*). Taking into account that an elementary cell of the type Y zeolite contains about 260 water molecules, i.e., ~30 water molecules per supercavity (*16*), it will be readily seen that the water around cations in large cavities forms hydrate shells of one or two molecular layers only. Decrease in the total number of cations in an elementary cell as a result of cation exchange to two- or three-valent cations induces only a slight increase in water molecules around each cation.

The following results must be interpreted

TABLE 4
ENERGY OF ION HYDRATION

Ion:	Y^{3+}	La^{3+}	Zn^{2+}	Mg^{2+}	Mn^{2+}	Cd^{2+}	Ca^{2+}	Na^+
kcal/g ion	853	744	479	450	433	425	373	97

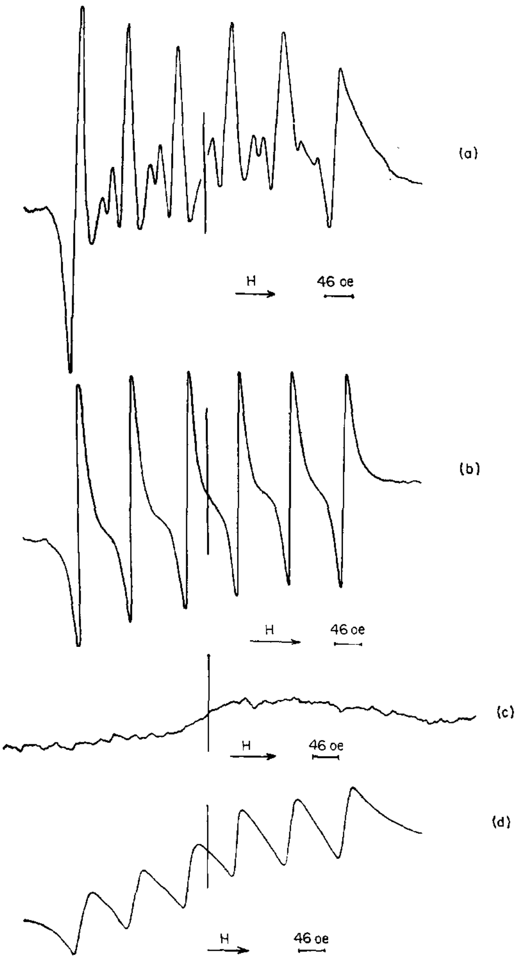

FIG. 2. ESR spectra of Mn^{2+} ions for samples evacuated at room temperature: (a) $\nu = X$ band, zeolite NaZnY-81; (b) $\nu = Q$ band, zeolite NaZnY-81; (c) $\nu = X$ band, zeolite NaCdY-83; (d) $\nu = Q$ band, zeolite NaCdY-83.

for correct description of the spectrum of hydrated Mn^{2+} ions in the water-filled cages of the crystalline lattice. First, the great width of an individual hfs component of the Mn^{2+} spectrum in a hydrated zeolite, where the spectrum components practically coalesce into the broad line with relevant decrease in the transverse relaxation time T_2. Second, increase in T_2 with higher measurement frequency (in the Q band) resulting in the appearance of a resolved ESR spectrum of the same samples (the hfs component widths decrease to ~22 Oe). Third, the marked changes in the Mn^{2+} spectrum in the X band observed at a temperature drop from −40 to −60°C, the spectrum shape becoming characteristic of a polycrystalline solid. Fourth, changes in Mn^{2+} spectra observed for zeolites evacuated at room temperature.

Let us consider first the results obtained on fully hydrated zeolites. Whatever the nature of admitted cations and the degree of exchange of sodium ions to these cations, the behavior of Mn^{2+} spectra with changes in the measurement frequency and temperature (in the X band) is similar to that of Mn^{2+} in the Y type sodium zeolites investigated before (*2*, *3*). In our earlier papers the results were interpreted under the assumption that the mechanism of spin relaxation of Mn^{2+} in hydrated zeolites is the same as for solids. However, it was reported recently (*8–10*) that the mechanism of relaxation of hydrated ions is connected with periodical distortion of the electric field symmetry around a central ion. It follows from the general theory of relaxation (*11*) that the dependence of transversional relaxation time T_2 on the correlation time τ_c of symmetry distortion and on the observation frequency ω is:

$$\left\langle \frac{1}{T_2} \right\rangle = \frac{64}{100}\left[3 + \frac{5}{1+\omega^2\tau_c^2} + \frac{2}{1+4\omega^2\tau_c^2}\right]\Delta^2\tau_c \qquad (1)$$

where

$$\Delta^2 = \tfrac{2}{3}D^2 + 2E^2.$$

The theory is valid for the range of "fast" motion, where $\omega\tau_c \leqslant 1$; it is inapplicable in the region of "slow" motion, where $\omega\tau_c \gg 1$. In the latter case spin relaxation is controlled by the same mechanism as for solids (increase in τ_c is evidence of increasing viscosity of the system). Comparison of the hfs component width for Mn^{2+} in hydrated zeolites at room temperature in the X and Q bands permits estimating τ_c for these systems by means of a calibration curve (*8*). Its use in the estimation of τ_c by analysis of inhomogeneously broadened hfs components is possible because the main contribution to the width of the fourth hfs component in the X band is given by the width of the fs transition $-\frac{1}{2} \rightleftarrows +\frac{1}{2}$, while in the Q band the inhomogeneous broadening is considerably less (*17*). Thus the width of any hfs component can be used for analysis. The τ_c value appears to be $\sim 7 \times 10^{-12}$ sec, and the $\omega\tau_c$ value (ω in rad sec^{-1} units) for the X and Q bands is 0.405 and 1.64, respectively. In this case the theory (*8–10*) is still applicable. The τ_c value obtained is considerably higher than that for aqueous Mn^{2+} solutions (3.2×10^{-12} sec) (*10*). This accounts for the essential T_2 decrease in a hydrated zeolite, compared to the aqueous Mn^{2+} solution, and thus for the broader hfs component in fully hydrated zeolites. With an aqueous solution parameter τ_c controls the mean time between water molecule collisions with the hydrated ion shell resulting in symmetry distortion (*8*). However, zeolites contain no such free water molecules as do the diluted solutions. Thus, collisions of the hydrated complex shells with each other may appear to control the Mn^{2+} relaxation. The frequency of relevant motions will naturally be lower (approximately inversely proportional to $m^{1/2}$, m being the mass of moving particles). The effect of τ_c increase on the ESR spectrum parameters is formally the same as that of the effective viscosity increase. Indeed, similar changes of the spectrum shape depending on observation frequency were recorded by us for aqueous glycerine Mn^{2+} solutions. Better resolution of the spectrum in the Q band follows from Eq. (1). Thus, the close characteristics of Mn^{2+} spectra for very different cation forms are always accounted for by the superconcentrated ion solutions in the supercages and to the same mechanism of Mn^{2+} relaxation. Change of the Mn^{2+} spectrum with drop of temperature and coincidence of this spectrum with that of a polycrystalline solid is evidence that the hydrated complex motion terminates within the temperature range of −40 to −60°C.

In order to understand the spectrum changes induced on evacuating of the zeolites, it must be taken into account that evacuating results in gradual dehydration of the zeolite. A ZnY-81 zeolite evacuated at room temperature was found to contain about 50–60% of the water amount in a fully hydrated zeolite. Sufficiently full dehydration realized by evacuating at elevated temperatures permits reaching a state such that the Mn^{2+} spin relaxation is no more controlled by collisions between hydrated ion shells, but depends first of all on spin–lattice relaxation, as in solids. The boundary between the two relaxation mechanisms is connected with removal of the greatest part of water from the Mn^{2+} ion shell. It will be seen from general thermodynamic considerations that if Mn^{2+} and some other ion of a higher hydration energy are simultaneously present in the supercage, this boundary will appear earlier, at a time when the amount of water in the zeolite cage is still high. Thus, in the presence of Y^{3+}, La^{3+}, Mg^{2+} or Zn^{2+} showing a hydration energy higher than that of Mn^{2+} (Table 4), the latter would lose its hydrate shell in the process of evacuating even at room temperature, due to the arising water deficit. The same situation is observed for concentrated electrolytes containing different ions (*13*). For this reason the spectra of evacuated samples suffer marked changes accounted for by decreasing fs constant (parameter D) (Table 3). This parameter characterizes the cubic field distortion around the manganese ion, and its low value permits recording of the spectrum in the X band (*12*). In case of water deficit spin–lattice interaction is responsible for spin relaxation. The only site of Mn^{2+} location ensuring high symmetry of the environment is S_I, the hexagonal prism. It follows that the Mn^{2+} ion deprived of its hydrated shell will become located in the hexagonal prism.

This state of Mn^{2+} cannot be obtained by room temperature evacuating of zeolites that contain sodium, calcium, and cadmium ions in their supercage, besides Mn^{2+} (Table 4). Even with deficit in water molecules, induced by evacuating, the hydrated shell will be preserved mainly around Mn^{2+}. The latter's relaxation mechanism will be controlled, as before, by collisions between the hydrated shells.

Thus, the following conclusion can be made. Hydrated cation shells with the whole amount of water contained in supercages consist of only one or two molecular layers of water. Then shells are in immediate contact with each other. If a zeolite contains cations with different water affinity, a rearrangement of water molecules takes place at the first stages of dehydration: the hydrated shells of less hydrophylic ions become destructed and the whole amount of remaining water concentrates around the more hydrophylic ions. The ions that have lost their hydrated shells become located in the hexagonal prisms of the zeolite lattice and the system energy diminishes due to interaction of ions with negative oxygen atoms.

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