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HEATS OF IMMERSION OF SOME ION-EXCHANGED A AND X ZEOLITES OF DIVALENT CATIONS*

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ABSTRACT

Heats of immersion in water (integral heats of hydration) of anhydrous zeolites NaA, CdA, ZnA, CoA, NaX, CdX, ZnX, CoX and NiX have been determined calorimetrically at 25°C. Sodium in NaA and NaX has been replaced by divalent cations to the extent of 70–100%. The data are correlated to the size of the cations and to the standard enthalpy changes of the corresponding ion-exchanged equilibria. The latter values are analysed in terms of three processes: hydration of ions in solution, hydration of zeolites, and electrostatic binding energy of cations to the zeolite framework.

INTRODUCTION

The heats of immersion in water (integral heats of hydration) of anhydrous zeolites are interesting at least from two viewpoints. Firstly, they reflect the dependence of the binding energy of water on the framework structure of zeolites and on the type of counter-ions which occupy characteristic sites in the crystal. Secondly, they give quantitatively the change in hydration enthalpy of a zeolite in a heterogenous ion-exchange process, when a cation of the aqueous phase replaces the original counter-ion of the zeolite.

In the present work, we measured calorimetrically at 25°C the heats of immersion in water of A and X ion-exchanged zeolites of divalent cations (Cd, Zn, Ni, Co) and of the original NaA and NaX forms. The data will be discussed primarily from the aspect of ion-exchanged thermodynamics, which has been investigated previously[1].

EXPERIMENTAL

Zeolite samples. — Divalent metal forms of A and X zeolites were prepared from 200 mesh-size 4A (B.D.H.) and 13X (Union Carbide) samples as described previously[1]. All zeolites were stored in a desiccator over a saturated NH_4Cl solution to

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*Part of the work related to the heat of immersion measurements was performed at the Danish Atomic Energy Research Establishment Risø and the Thermochemistry Laboratory of the University of Lund, Sweden.

keep the water content constant. They were analysed for M^{2+}, Na^+, SiO_2, AlO_2^- and H_2O content as described in an earlier paper[1]. The results of chemical analysis and the composition of unit cells are presented in Table I. The latter data are based on 12 Si atoms in A-zeolite and 105 Si atoms in X-zeolite per unit cell.

TABLE I

COMPOSITION OF ZEOLITES[a]

Zeolite	*wt %*						*Atoms per unit cell*			
	Na^+	M^{2+}	AlO_2^-	SiO_2	H_2O	*sum*	*Na*	*M*	*Al*	*Si*
NaA	12.15	—	32.8	33.30	22.7	100.95	11.5	—	12.0	12.0
CdA	0.02	25.60	26.5	27.45	20.6	100.17	0.0	6.0	11.8	12.0
ZnA	0.11	16.20	29.4	30.40	22.1	98.21	0.1	5.9	11.8	12.0
CoA	1.45	12.50	29.8	28.55	27.8	100.10	1.6	5.4	11.8	12.0
NaX	11.20	—	29.0	35.66	24.4	100.26	86.2	—	87.0	105.0
CdX	0.76	21.85	24.5	30.39	22.7	100.20	6.9	40.3	86.2	105.0
ZnX	2.50	11.61	27.2	33.66	26.0	100.97	20.4	33.3	86.5	105.0
CoX	3.89	8.38	27.1	33.10	28.1	100.57	32.2	27.1	87.4	105.0
NiX	2.11	9.86	25.9	32.05	28.5	98.42	18.1	33.1	86.5	105.0

[a] NiA with high nickel content is thermally unstable and is not included in the present investigation[1].

TG and DTA analyses. — These are shown for X-zeolites in Fig. 1, and for A-zeolites in Fig. 1 of ref. 1. All zeolites are assumed to be thermally stable up to the DTA peaks above 750°C, which was confirmed by X-ray powder difraction.

Outgassing. — Weighted samples in thin-wall ampoules were outgassed 24 hours at 200°C to a residual pressure of 1×10^{-5} mm Hg, and then sealed under reduced pressure of dry argon. The loss of water was separately controled by weight-loss determination after ignition. In all cases the water content of outgassed samples was less than 0.2 weight % (less than 1% of the initial water content). Attempts were made to dehydrate samples above 300°C, as described by Barrer and Cram[2]. Except in the case of NaA and NaX, this was not feasible owing to visible structural changes which took place in the samples. It seems that the divalent metal zeolites are appreciably less stable at low pressure than the original sodium form. For instance, the heat of immersion of some samples outgassed at 360°C were considerably lower than those obtained by outgassing at 200°C. Thus, all samples were outgassed at 200°C, which was sufficient to ensure a practically complete dehydration. This was also supported by the fact that heats of immersion of NaA and NaX have the same values when samples are outgassed at 200° and 360°C.

Calorimetry. — Heats of immersion have been measured in a LKB calorimeter, type 8721-1, at 25°C. The calorimeter was calibrated by electrical heat generation in the usual way. Heats evolved were determined using the graphical method of Dickinson[3]. Errors in heat determination, estimated from duplicate measurements, were about 1%.

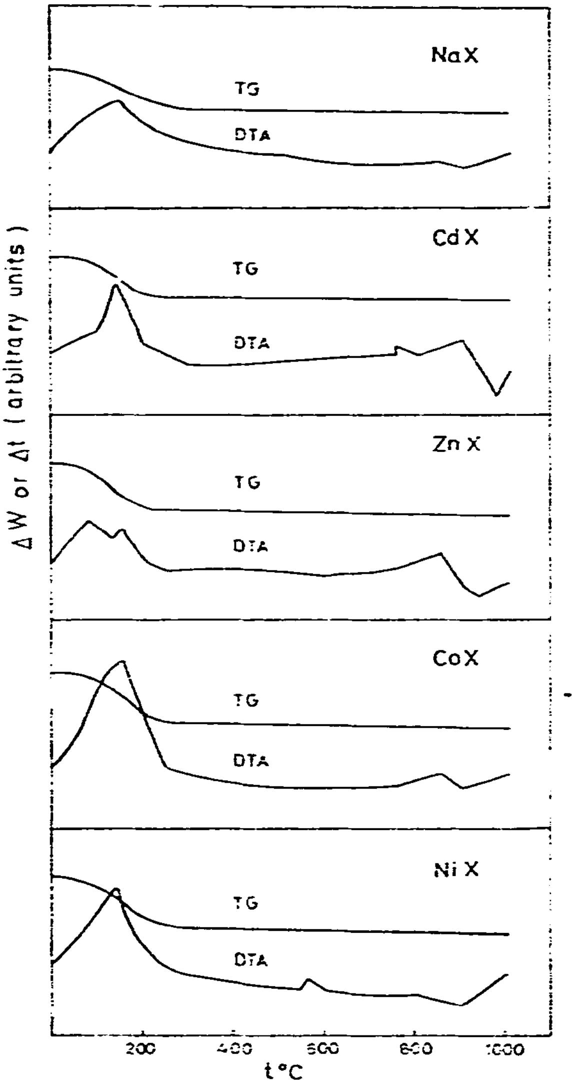

Fig. 1. TG and DTA runs of X zeolites.

RESULTS

The experimental results and other data derived from them are listed in Table II. The following notation is used: (1) q_H, J per gram of hydrated zeolite (water content is given in Table I), (2) q_D, J per gram of dehydrated zeolite, (3) Q_W, kJ per mole of water content, (4) Q_{UC}, kJ per mole of anhydrous unit cell, (5) Q_{GE}, kJ per gram equivalent of cations.

Published data are available for NaA and NaX which can be compared with our measurements. Thus, Barrer and Cram[2] found for NaA $q_H = 3.09 \times 10^2$ J/g and $Q_{GE} = 56.9$ kJ/g.-ion equivalent. However, their NaA sample was not identical with our sample, because they had a higher $NaAlO_2$ content owing to the occlusion of 0.4 $NaAlO_2$ per unit cell. Similarly, they obtained for NaX $q_H = 3.53$ J/g and $Q_{GE} = 73.6$ kJ/g.-ion equivalent with a sample which had also a slightly different Na^+ content. Taking this into account the two sets of results are in reasonablea greement.

TABLE II

HEATS OF IMMERSION AND OTHER DERIVED VALUES

Zeolite	q_H ($J/g \times 10^2$)	q_D ($J/g \times 10^2$)	Q_W (kJ/mol)	Q_{UC} ($kJ/mol \times 10^2$)	Q_{GE} (kJ/g.-ion eq.)
NaA	3.23	4.18	25.7	7.1	59.0
CdA	3.04	3.83	26.6	8.0	66.9
ZnA	3.46	4.45	28.2	8.1	67.8
CoA	3.48	4.82	22.5	8.7	72.0
NaX	3.36	4.45	24.8	59.8	68.6
CdX	3.05	3.95	24.2	63.2	72.8
ZnX	3.23	4.36	22.4	61.1	70.3
CoX	3.40	4.73	21.8	65.3	74.9
NiX	3.70	4.76	23.4	72.0	82.4

The data in Table II show a general trend: the heats of immersion increase in the order Cd < Zn < Co < Ni, as expected when the ionic radii of cations are considered. An apparent exception are the Q_W values, where two effects are superimposed: the binding energy of water and the total amount of water in the unit cell. Both increase with the decrease of the ionic radius of the counter-ion, but the net effect can be a decrease in Q_W values for small divalent ions. This implies that an increasing number of water molecules per unit cell is not directly attached to cations or charged sites[1].

DISCUSSION

As ion–water dipole interaction depends on the electrostatic field strength of the ion, which vary inversely as the square of the ionic radius (r_c), it is interesting to plot, say, Q_{UC} against $(r_c)^{-2}$, as in Fig. 2. These plots, which include also the data of Barrer and Cram[2], show remarkable irregularities which reflect the effect of various factors in binding water to zeolites. In the case of A-zeolites, an irregular but steady increase of Q_{UC} with $(r_c)^{-2}$ can be noted, although in CoA the exchange of sodium with cobalt is not complete. In the plot of X-zeolites, Q_{UC} first decreases from SrX to ZnX, and then rises again up to MgX. This peculiar pattern is probably caused by several effects. One is the extent of ion-exchange, which for SrX is practically complete (all Na atoms are replaced by Sr) and then decreases up to ZnX. The small divalent ions with their firmly bound hydration sphere penetrate with difficulty into the sodalite cages and hexagonal prisms of X-zeolite, and therefore they replace sodium to a lesser extent than Sr, Ca and even Cd (see Table I). As seen from Fig. 2, from ZnX up to MgX, small variations in the content of divalent ions are less

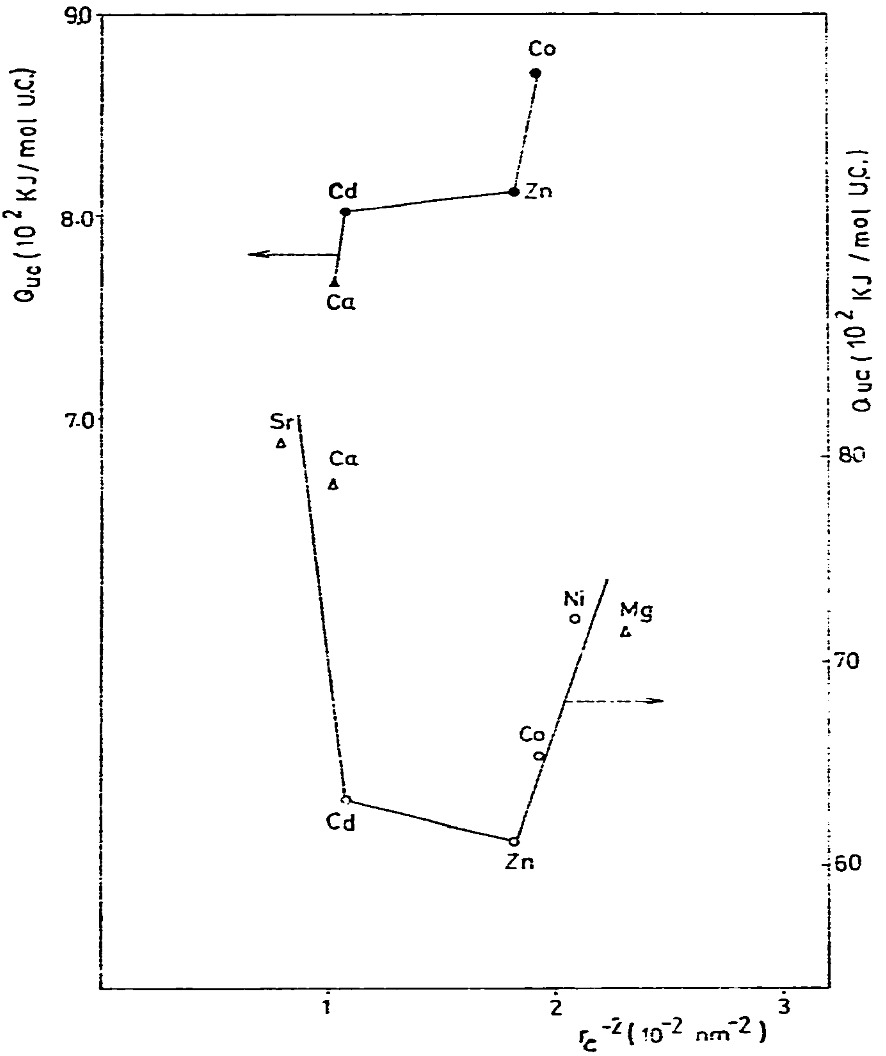

Fig. 2. Q_{UC} versus ionic radius of cation. Upper diagram A-zeolite, lower X-zeolite. Triangles are data of Barrer and Cram[2].

important, thus Q_{UC} increases as the crystalline radius of the divalent cation decreases. Probably some other effects are also important, especially the position of cations relative to the charged sites of the wet zeolite. Namely, in fully hydrated zeolites not all cations are bound to the exchange sites. A certain number of them is floating as aquated ions in the large cages, and they are probably more hydrated than cations bound to exchange sites[1].

The importance of the heats of immersion in the thermodynamics of ion-exchange can be estimated if the standard enthalpy change ($\Delta H°$) of the following heterogenous reaction is considered:

$$\tfrac{1}{2}M^{2+}_{(aq)} + NaZ_{(aq)} = M_{\frac{1}{2}}Z_{(aq)} + Na^{+}_{(aq)}\,; \qquad (\Delta H°) \qquad (1)$$

where ΔH° refers to the formation of 1 gram-ion equivalent of a divalent metal zeolite, and the notation (aq) means that the process takes place in a dilute solution. The ΔH° value of Eqn. (1) can be obtained by adding standard enthalpy changes of the following processes:

$$\tfrac{1}{2}M^{2+}_{(aq)} + Na^{+}_{(g)} = \tfrac{1}{2}M^{2+}_{(g)} + Na^{+}_{(aq)}; \qquad (\Delta H^\circ_1) \qquad (2)$$

$$NaZ_{(aq)} + M_{\frac{1}{2}}Z_{(anh)} = M_{\frac{1}{2}}Z_{(aq)} + NaZ_{(anh)}; \qquad (\Delta H^\circ_2) \qquad (3)$$

$$\tfrac{1}{2}M^{2+}_{(g)} + NaZ_{(anh)} = M_{\frac{1}{2}}Z_{(anh)} + Na^{+}_{(g)}; \qquad (\Delta H^\circ_3) \qquad (4)$$

Here $_{(g)}$ and $_{(anh)}$ refer to the bare gaseous ions and to the anhydrous zeolites, respectively. Some values of ΔH° have been obtained from exchange isotherms at various temperatures[1]. ΔH°_1 is the difference in the standard enthalpy of hydration of the ions which can be calculated from tabulated data[4]. ΔH°_2 is to a good approximation equal to the difference in the heats of immersion per gram-ion equivalent of cation, $\Delta H^\circ_2 \simeq -(Q_{GE(M)} - Q_{GE(Na)})$. ΔH°_3 is equal to the difference of the electrostatic binding energy of the exchanging ions to the zeolite sites. Its value can be obtained from the equality $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$, if the three other terms are known. Some values of the standard enthalpy changes together with relevant references are listed in Table III. It should be noted however, that these data represent average values per gram equivalent of cations, neglecting inequalities of the exchange sites.

TABLE III

STANDARD ENTHALPY CHANGES (kJ/g.-ion equivalent)

Zeolite	ΔH° [1,5]	ΔH°_1 [4]	ΔH°_2	ΔH°_3
CdA	13.22	4.97×10^2	-7.95	-4.76×10^2
ZnA	15.40	6.17×10^2	-8.79	-5.92×10^2
CoA	20.07	6.09×10^2	-12.97	-5.96×10^2
CdX	17.57	4.97×10^2	-4.18	-4.76×10^2
ZnX	5.02	6.17×10^2	-1.67	-6.10×10^2
CoX	7.11	6.09×10^2	-6.28	-5.96×10^2
NiX	5.02	6.42×10^2	-13.81	-6.23×10^2

Table III shows that ΔH° is practically the difference between two large thermal effects, *i.e.*, ΔH°_1 which refers to the hydration of cations, and ΔH°_3, the difference in electrostatic binding energies of the cations to zeolite sites. ΔH°_2, the difference in hydration enthalpies of the two metal forms of zeolite is rather small.

In order to obtain an approximative value of the electrostatic term ΔH°_3, the simple model developed by Eisenman[6] could be useful. The coulomb energy of binding Na^+ to a negative O^- site of zeolite is $U_{Na} = -Ne^2(r_+ + r_-)^{-1}$, where r_+ and r_- are assumed to be the Pauling radius of the cation and the effective radius of a O^- site. Similarly, assuming a M^{2+} ion instead of two Na^+, $U_M = -2Ne^2[(r_{2+} + r_-)^{-1}$

$+(x-r_{2+}-r_-)^{-1}]$, where r_{2+} is the Pauling radius of M^{2+}, x is the shortest distance between two O^- sites (assuming O^-–M^{2+}–O^- linear), N is Avogadro's number and e the elementary charge. Thus

$$H_3^\circ \simeq \frac{1}{2}U_M - U_{Na} = -139\left(\frac{1}{r_{2+}+r_-} + \frac{1}{x-r_{2+}-r_-} - \frac{1}{r_+ + r_-}\right) \tag{5}$$

where ΔH_3° is expressed in kJ per g.-ion equivalent and r in nm. Eqn. (5) is, of course, a simplified and crude model, because O–M–O is not necessarily linear, and long-range coulomb interactions are neglected as well as Born's repulsion term, polarisability of charged species, inequality of exchange sites, etc. Nevertheless, taking for $(r_+ + r_-)$ the average Na–O distance 0.226 nm in NaA[7] and 0.292 nm in NaX[8] (from which the respective values of r_- are obtained by subtracting the Pauling radius of Na^+), the shortest site-to-site distance, x, can be calculated with the ΔH_3° values of Table III. Thus, for the A and X zeolites listed in Table III, the value of x is between 0.5–0.6 nm. This is, indeed, a reasonable value, about two times larger than the average Na–O distance. Unfortunately, no crystalographic data relevant to the exact position of divalent cations have been reported. When these data will be available, it might be possible to develop a more refined electrostatic model so that ΔH° for ion-exchange could be calculated. In that case, according to Eqns. (1–4), the only experimental data needed are the ΔH_2° values, *i.e.*, the heats of immersion. Such a procedure should be very helpful since ΔH° for many ion-exchange processes cannot be obtained calorimetrically owing to the slow attainment of equilibrium.

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