AN ANALYSIS OF ELEMENTARY PROCESSES OF WATER DESORPTION FROM ZEOLITES OF TYPE A

PART II. ZEOLITES WITH BIVALENT COUNTERIONS

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ABSTRACT

DSC and EGA were used to follow the process of water desorption from synthetic MgA, ZnA and CdA zeolites. Applying a semi-empirical algorithm the complex experimental curves were resolved into elementary ones. It turned out that in zeolites with bivalent cations there are four phases of sorbed water. Sorption heats were determined for each individual phase. The NMR spectra of water on a CaA zeolite were investigated. They also point out the existence of four phases. On the basis of the results obtained a possible model of water sorption on synthetic zeolites with bivalent cations is discussed.

INTRODUCTION

In Part I of this work we have studied and discussed possible elementary processes associated with water desorption from synthetic zeolites with monovalent counterions. In the present work special attention is paid to zeolites with bivalent counterions.

Previous differential thermal analysis (DTA) and differential scanning calorimetry (DSC) investigations have shown in zeolites with bivalent cations that new peaks appear relative to zeolites with monovalent cations. Thus Vučelić et al.[1,2] have observed a new peak in CaA zeolite. In recent years special attention is attracted by Dyer's[3,4] works reporting the appearance of new peaks in SrA, ZnA, CoA and NiA zeolites. Vučelić et al.[1,2], however, found no new peak in ZnA, MgA and CdA zeolites. Unfortunately, in all the works cited no special attention was paid to the dependence of DTA and DSC analysis on the degree of coverage with water, so that this question remains open.

EXPERIMENTAL

For DSC and evolved gas analysis (EGA) use was made of a Perkin-Elmer-1B calorimeter. A detailed description of obtaining zeolites by ion exchange and of

preparation for measurements has been given earlier[1,2]. A new detail is a decrease of drift in differential frequency transformer, which led to an improvement in resolution of DSC curves. NMR spectra were obtained by means of a Fast Fourier Transform (FFT) unit on a Bruker SXP-100 variable pulse spectrometer.

A mathematical analysis of complex DSC and EGA curves was carried out on PDP-8 computer. The algorithm used was worked out with boundary conditions derived from corresponding complex curves. The basic boundary conditions are: the shape of curve (usually a Gaussian or a Lorentz one), the number of possible elementary processes (otherwise the process is not mathematically unique) and the requirement of equality of the dispersions of DSC and EGA curves (in quantitative analysis). Details of the algorithm and programme are discussed in ref. 5.

RESULTS

The results of DSC and effluent gas analysis for MgA, CaA, ZnA and CdA zeolites are presented in Figs. 1–4. All the zeolites contained more than 25% of water per gram of zeolite. Solid lines represent the experimental curves. Dashed lines are the result of computer resolution of the complex curve into elementary processes. In all cases, it is evident that there is a new peak between peaks II and III, as was indicated in Part I for zeolites with monovalent counterions. The remaining peaks are similar in shape and position to corresponding peaks I, II and III in zeolites with monovalent cations.

The results of the quantitative DSC analysis are presented in Table 1. The second, third and fourth columns of the table give desorption heats corresponding to

TABLE 1

ENTHALPIES OF ELEMENTARY PROCESSES IN WATER DESORPTION FROM SYNTHETIC ZEOLITES WITH BIVALENT COUNTERIONS

zeolite	I peak ΔH (kcal mol^{-1})	II peak ΔH (kcal mol^{-1})	II' peak ΔH (kcal mol^{-1})	III peak ΔH (kcal mol^{-1})
MgA	14.0	9.9	9.8	30.3
CaA	10.4	14.3	15.2	18.6
ZnA	9.4	15.1	21.4	23.7
CdA	9.5	11.3	16.4	impossible to determinate from experimental results

peaks I, II and II', respectively. Finally, the last column gives the values of enthalpy for the process corresponding to peak III. The error in determination of these values is rather large (20%) and is mainly due to the imperfection of the mathematical solution in the algorithm.

A decrease in coverage degree usually leads to disappearance of one of the peaks or to a difficult discrimination between peaks II and II'. Thus in the range from
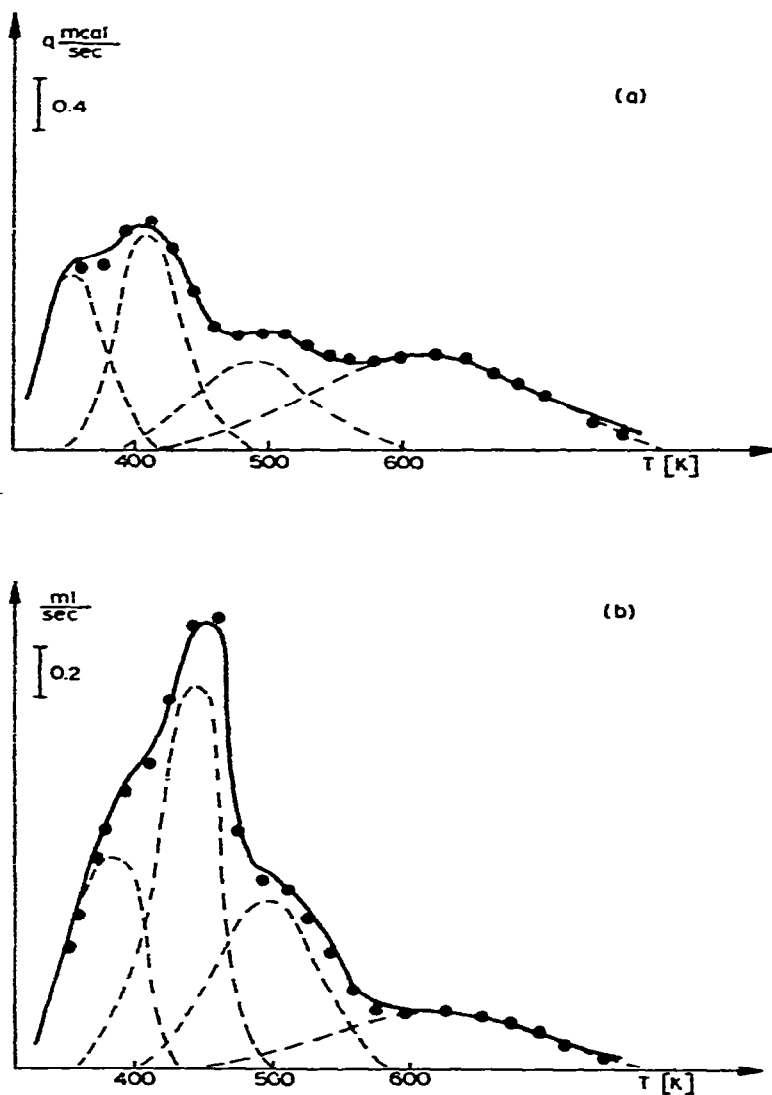
Fig. 1. Water desorption from MgA zeolite. (a) DSC curve. Solid line experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ● Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of tl.e complex curve into elementary ones. ●, Calculated EGA curve.

$\theta = 0.7$ to $\theta = 0$ usually only three peaks can be observed. A characteristic feature is that peak II, in contrast to corresponding peak II in zeolites with monovalent cations, appears at $\theta > 0.7$.

Figure 5 shows the spin–spin relaxation time of water sorbed on CaA zeolite as a function of coverage degree. As may be seen from the plot, there are four phases of sorbed water with different spin–spin relaxation times.
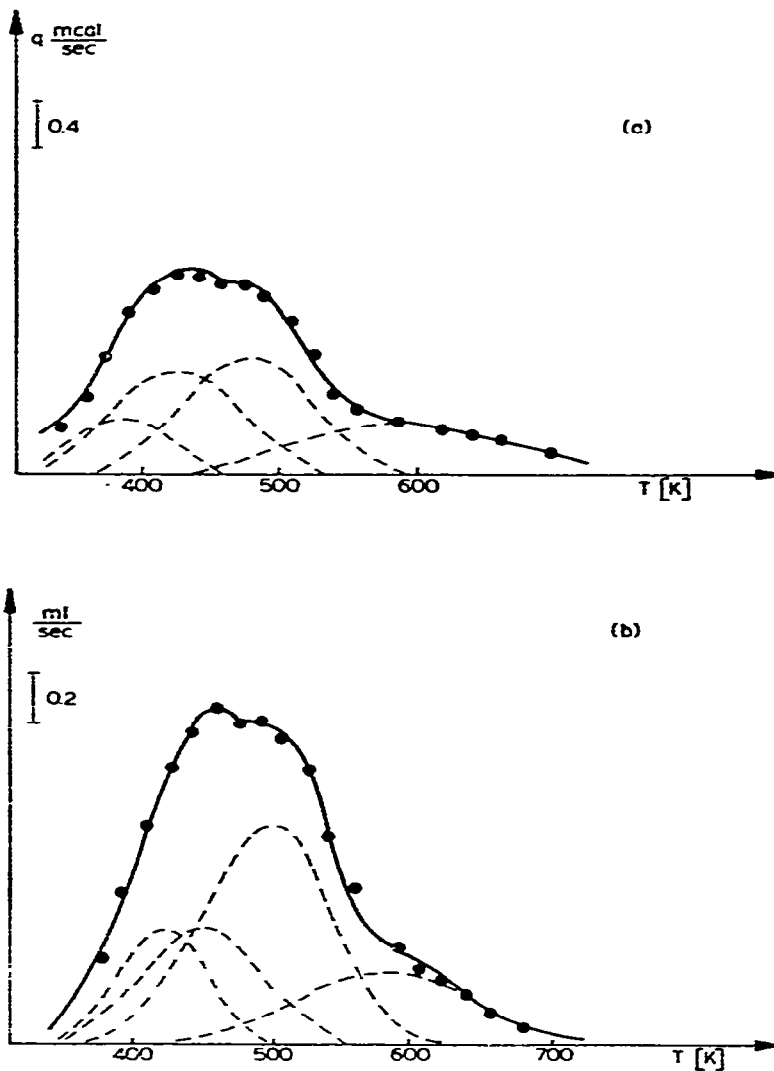
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Fig. 2. Water desorption from CaA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of the complex curve into elementary ones. ○, Calculated EGA curve.

DISCUSSION

From the results obtained it is apparent that synthetic zeolites with bivalent counterions are characterized by the appearance of a new phase of sorbed water. This cannot be due only to the formation of a new bond, because the peak would not appear in effluent analysis. Thus it can be stated that the existence of four differently bonded water phases is reliably established. Earlier results[1,2] from which this fact was not evident may be explained by either a low coverage degree, as in the case of MgA zeolite, or by poor resolution which usually appears in quantitative DSC
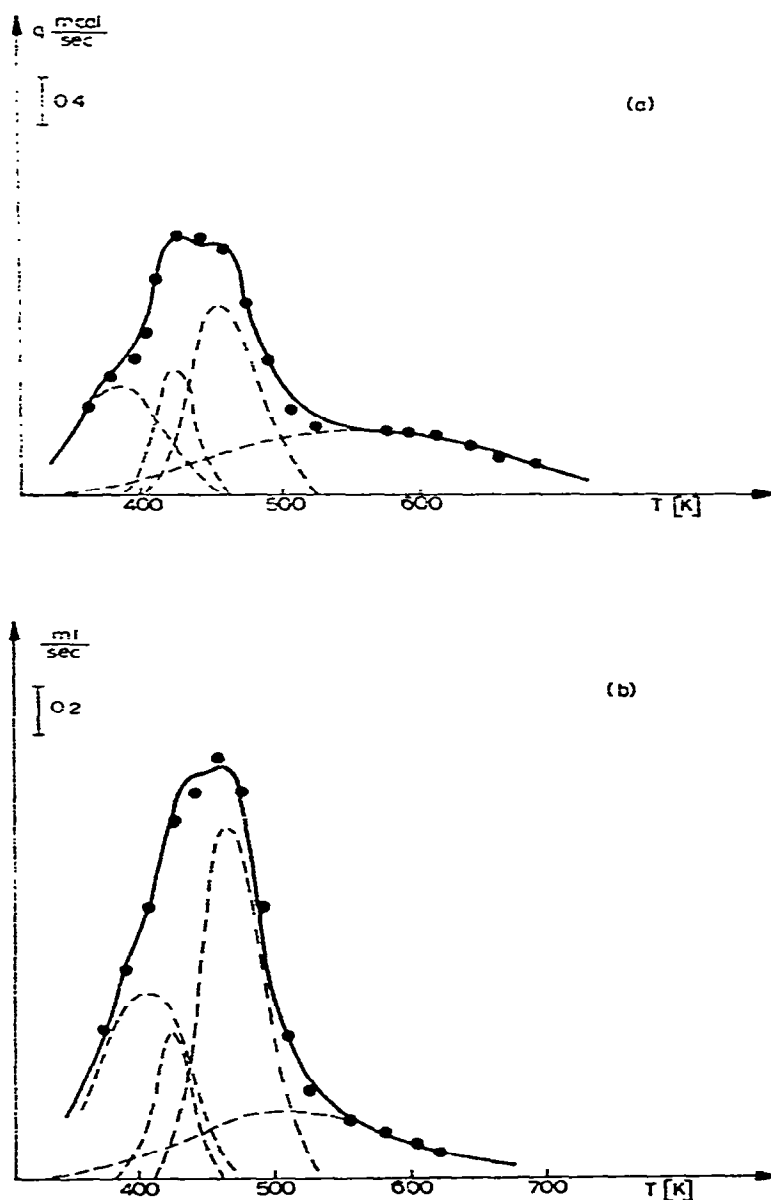
Fig. 3. Water desorption from CdA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated DSC curve; (b) EGA curve. Solid line, experimental EGA curve; dashed line. the resolution of the complex curve into elementary ones. ●, Calculated EGA curve.

analysis (for ZnA and CdA zeolites). NMR spectra show that spin mobility at low coverage degrees (corresponding to peak III) is very low and close to values which are obtained for the rotation of hydroxyl groups at the surface of a solid body. The high sorption heats shown in column 5 of Table 1 are also in agreement with these results, so that we may assume with high certainty that peak III is identical with the cor-
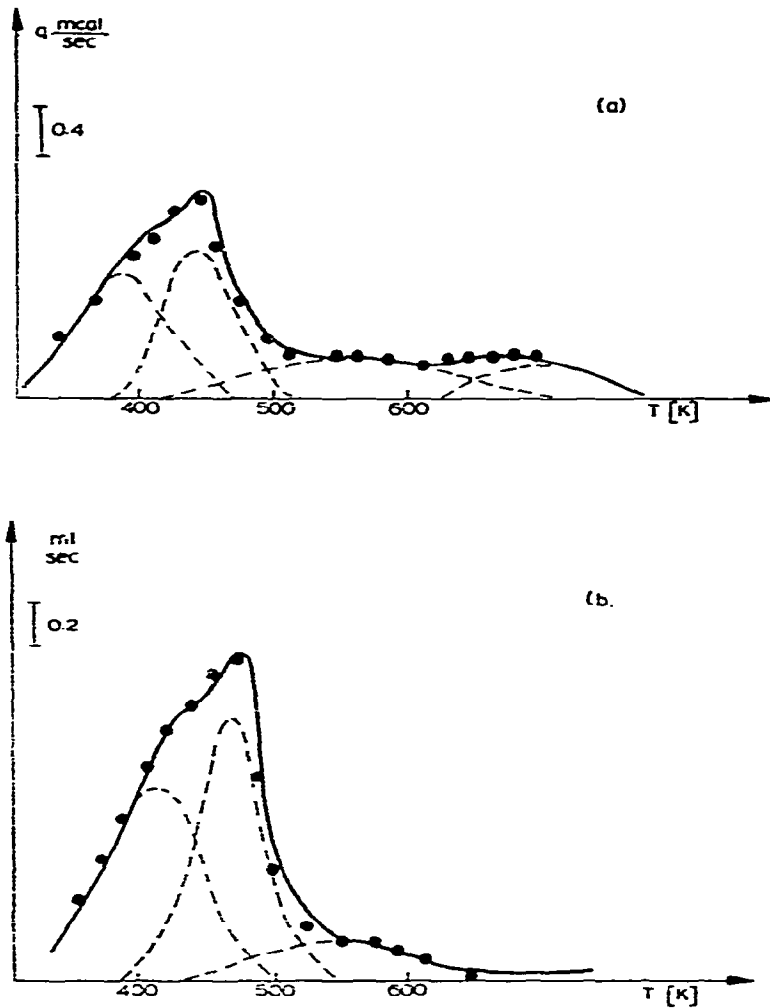
Fig. 4. Water desorption from ZnA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ● Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated EGA curve.

responding peak III in monovalent zeolites and attribute it to chemisorbed surface hydroxyl groups. The situation with peaks II and II' is by far not so clear. NMR spectra show the existence of two spin phases with rather different mobility, both spin times being typical of sorbed molecules. The phase corresponding to peak II' in DSC and EGA appears in the coverage range $0.2 > \theta > 0.6$ and has a mobility considerably lower than that of the phase corresponding to peak II in the coverage range $0.6 > \theta > 1$.

Results given in Table 1 confirm the validity of the assumption that water in the region of peak II' is bound more tightly than that in the region of peak II. (It is interesting to note the decrease of the integral sorption heat at $\theta > 0.7$ is apparent
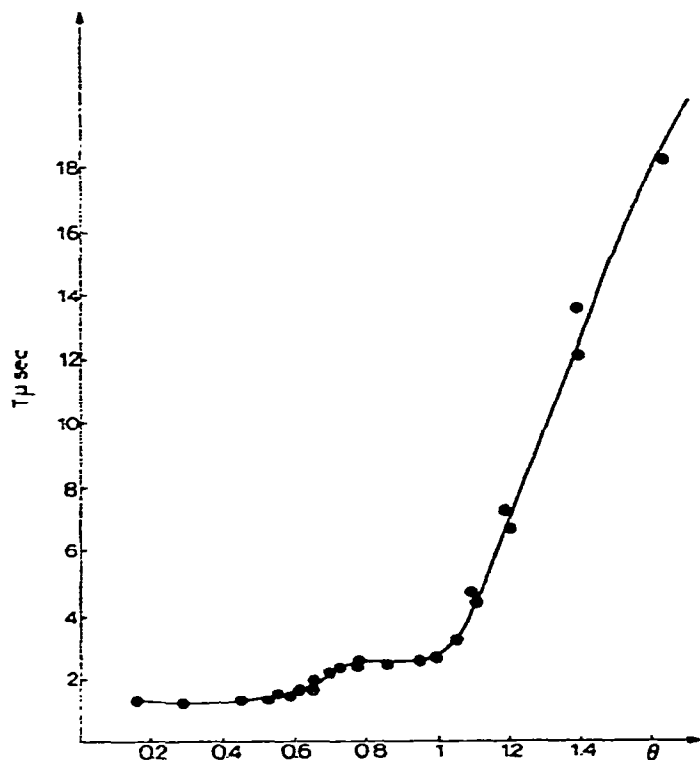
Fig. 5. Spin–spin relaxation time of water sorbed on CaA zeolite as a function of coverage degree.

already from results reported previously[2]. This fact, however, has not been noticed, and only in the light of new results it is clearly noticeable.) Since peak II' appears only in zeolites with bivalent counterions, we have to attribute it to water binding to cation. Results obtained with natural zeolites also show that this peak exists only in the presence of bivalent counterions, the desorption process related to this peak being accompanied by more or less considerable adaptations of crystal lattice.

According to DSC and NMR results, peaks I and II are quite similar to the corresponding peaks I and II of monovalent zeolites, hence they may still be assigned the same structure as before. Water related to peak II is bound by hydrogen bonds to the aluminosilicate framework, while that related to peak III corresponds to concentrated electrolyte solutions of the corresponding cation.

A new fact may be noticed. Because of the competing water binding to cation, the energy of binding of water complex to the aluminosilicate framework is lower than in the case of monovalent zeolites (see Table 1 of Part I, Table 1 of Part II and ref. 2.) This is also in accordance with the considerably higher spin mobility in the coverage range $0.7 > \theta > 1$, which points out the possibility of determining the structure of the corresponding complex in monovalent and bivalent zeolites. Unfortunately, in view of the low accuracy of the method of resolving complex DSC and EGA curves into elementary ones, definite conclusions would be as yet premature.

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