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

PART. I. ZEOLITES WITH MONOVALENT COUNTERIONS

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ABSTRACT

Complex DSC curves of water desorption from LiA, NaA and KA zeolites were resolved into the most probable elementary curves. The activation energies and transition temperatures of corresponding elementary processes were determined. On the basis of the results obtained a model is proposed for water binding to M^+A^- zeolites with three different phases.

INTRODUCTION

The mechanism of water sorption on natural zeolites has been the subject of numerous differential thermal analysis (DTA) and differential scanning calorimetry (DSC) investigations. However, because of the very wide energy distribution of water bound to synthetic zeolites the thermal analysis encounters serious experimental difficulties, so that the water–zeolite system has relatively little been studied.

One of the first complete DTA and thermogravimetry (TG) analysis was made by Toth[1]. He assumed that there is a correlation between the binding energy and the corresponding counterion. In the case of MgNa zeolite he assumes the possibility of existence of two endothermic peaks. In our previous works[2,3] it has been shown that the thermograms of DSC and evolved gas analysis (EGA) of various ion-exchanged zeolites are complex. In all the cases three peaks were obtained, except for Ca zeolite where also a fourth peak appears. The maximum of peaks II and III is independent of the nature of cation and always appears at 430 K and 600 K, respectively. On the basis of combined DSC and effluent gas analysis (EGA), it has also been demonstrated quantitatively that the integral sorption heat remains unchanged for ions of the same valency. The sorption heats of zeolites with monovalent cations are higher by 20% than those of zeolites with bivalent cations. On the basis of all the results the following has been assumed:

(1) peak I originates from polylayer, in which the water–cation interaction may take place;

(2) peak II is due to water (in α-cages) bound by hydrogen bonds to the oxygen of the aluminosilicate framework;

(3) peaks III arises from sorption in β-cages.

A significant progress in the study has recently been made by Dyer[4,5]. He has shown that the exchange of monovalent by bivalent cations always leads to the appearance of a new peak similar to the already discovered fourth peak in CaA zeolite. Unfortunately, in these investigations the dependence on the degree of coverage with water was not followed, so that at coverage degrees lower than $\theta = 0.8$ these results could not be reproduced. In the present work the results of the authors[2-5] have been reconsidered with a better resolution, special attention being paid to the amount of water bound to zeolites.

EXPERIMENTAL

A Perkin-Elmer DSC-1B calorimeter was used for the same analysis. The conditions for preparation and the material used are the same as those described in previous papers[2,3]. The Li NMR spectra were recorded on a Bruker SXP-100 pulse spectrometer.

The algorithm for resolving complex DSC and EGA thermograms into elementary curves is described in Ref. 6. The algorithm is based on the experimentally confirmed assumption that elementary desorption curves are of Gaussian type. Since the solution is single-valued the number of Gaussian curves is predeterminated by as many different curves as can be stated to exist in the experimental DSC thermogram. The mathematical analysis was carried out directly on a DP-8 computer with accessory equipment.

RESULTS

The results of DSC and EGA of completely exchanged LiA, NaA and KA zeolites are presented in Figs. 1–3 and in Table 1. They are in excellent agreement with those obtained previously[2]. The use of the algorithm with the assumption of the existence of three peaks resulted in elementary DSC and EGA curves from which the corresponding sorption heats were calculated. The results obtained for all the three peaks are presented in Table 1.

The first peak is characterized by a wide energy distribution. The integral sorption heat is strongly dependent on the amount of water present. For the zeolite with the highest water content, LiA (30% of H_2O per gram of zeolite), it is very close to the value for free water. The second peak is the narrowest and is characterized by a sorption heat of 15 kcal mol^{-1}, independent of the nature of counterion.

The third peak exhibits the widest energy distribution and is characterized by very high sorption heats. The maximum temperatures are within the limits of error the same as those reported in a previous work[2]. Figure 4 shows the FFT (Fast Fourier Transform) spectra of the Li nucleus from a LiA zeolite at degrees of coverage with water of about $\theta = 0$, $\theta = 0.7$ and $\theta = 1.5$. It is evident that a considerable in-

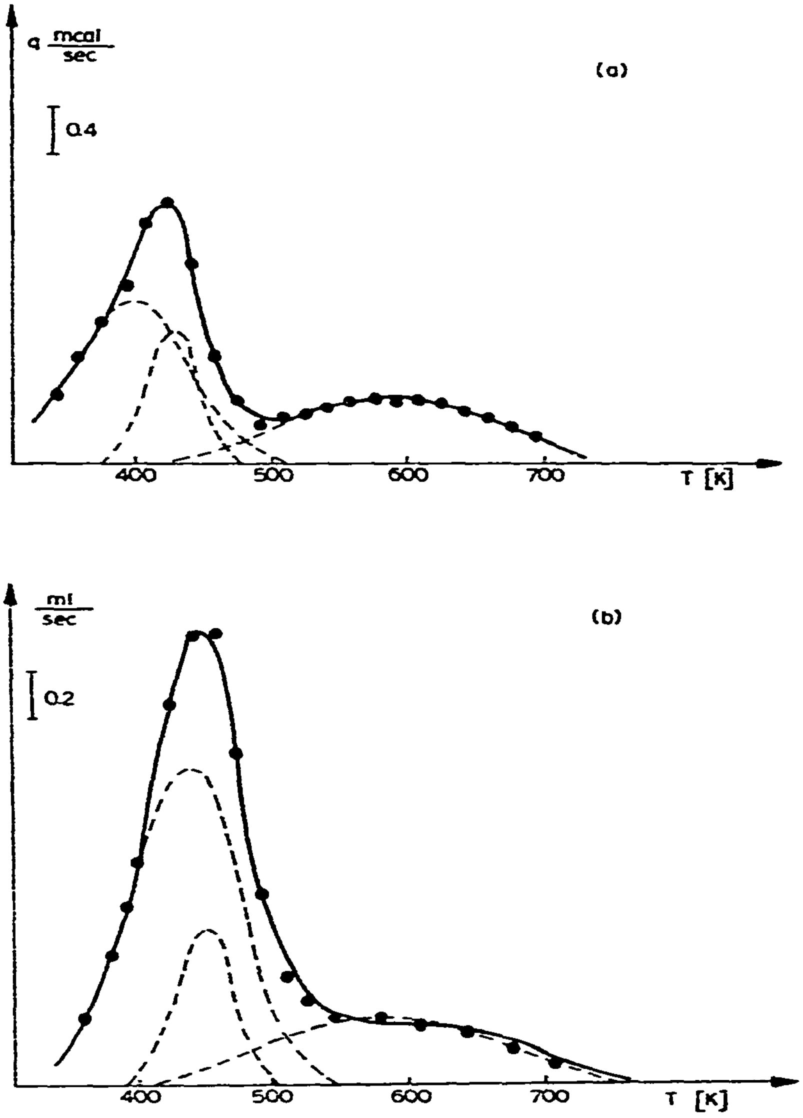

Fig. 1. Water desorption from LiA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated EGA curve.

crease in the number of highly mobile Li^+ counterions (narrow line) occurs only at high coverage degrees.

DISCUSSION

In previous papers[2,3] it has been shown that the sorption heat and the position of maximum for peaks II and III are independent of the nature of the cation. It has

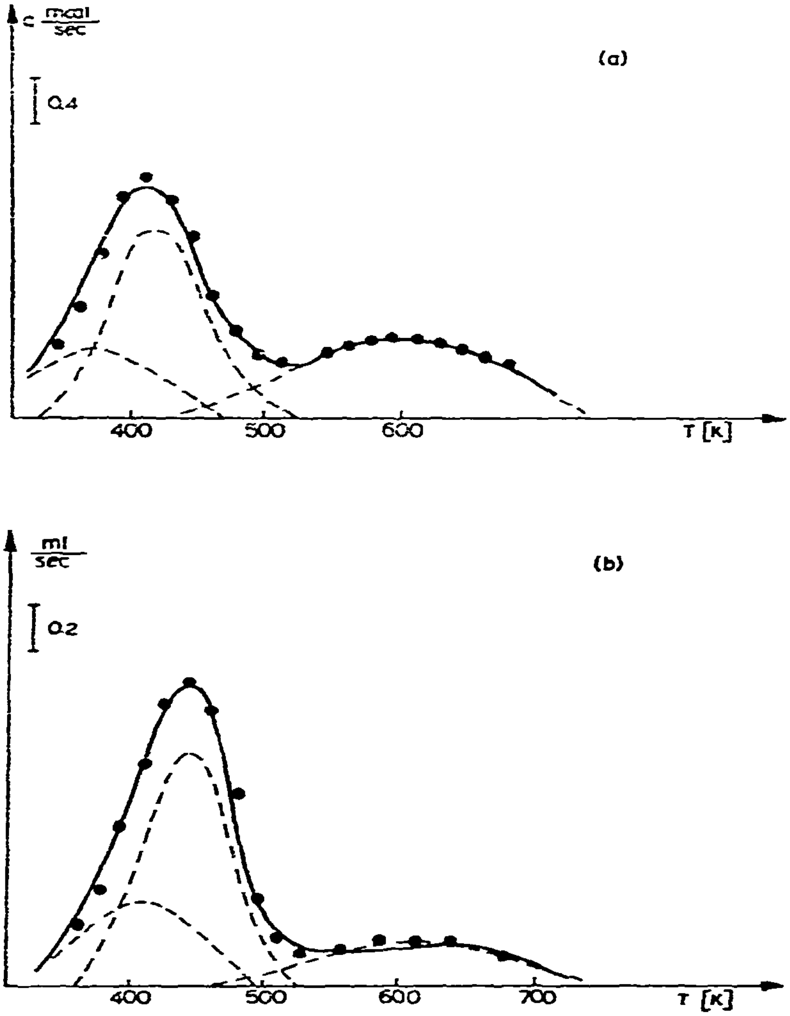

Fig. 2. Water desorption from NaA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated EGA curve.

TABLE 1

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

Zeolite	*First peak*		*Second peak*		*Third peak*	
	T_m (*K*)	ΔH (*kcal mol*$^{-1}$)	T_m (*K*)	ΔH (*kcal mol*$^{-1}$)	T_m (*K*)	ΔH (*kcal mol*$^{-1}$)
LiA	392	9.5	425	15.2	578	17.0
NaA	370	13.5	420	14.5	590	30.0
KA			431	15.4	637	25.4

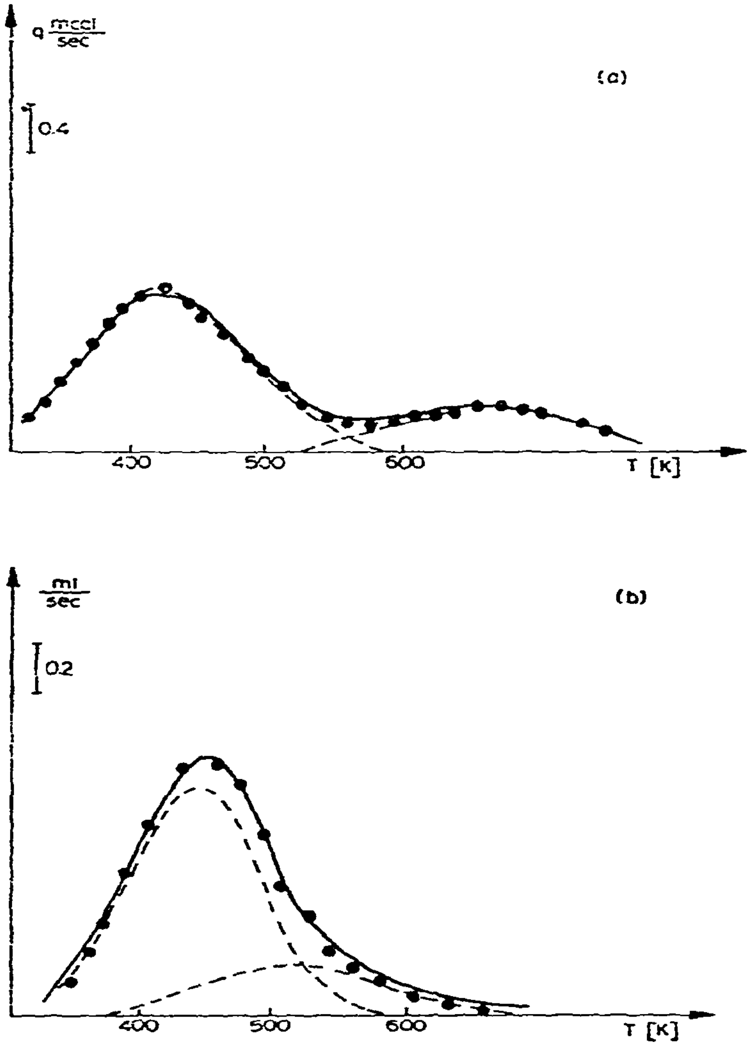

Fig. 3. Water desorption from KA zeolite. (a) DSC curve. Solid line, experimental DSC curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated DSC curve. (b) EGA curve. Solid line, experimental EGA curve; dashed line, the resolution of the complex curve into elementary ones. ●, Calculated EGA curve.

also been shown by EGA that the ratio of the amount of sorbed water corresponding to peaks (I+II) to that corresponding to peak III is 6:1. On the basis of these results a model was proposed according to which the water corresponding to peak III represents hydrogen bonded water in β-cages, while that corresponding to peak II is water bound to the oxygen of the aluminosilicate framework in α-cages. Finally, the water corresponding to peak I represents water in solvating polylayer with counterions similar to a concentrated electrolyte solution.

New results support this model offering the possibility of obtaining better details. In the first instance the high sorption energy of 20–30 kcal mol^{-1} for peak I

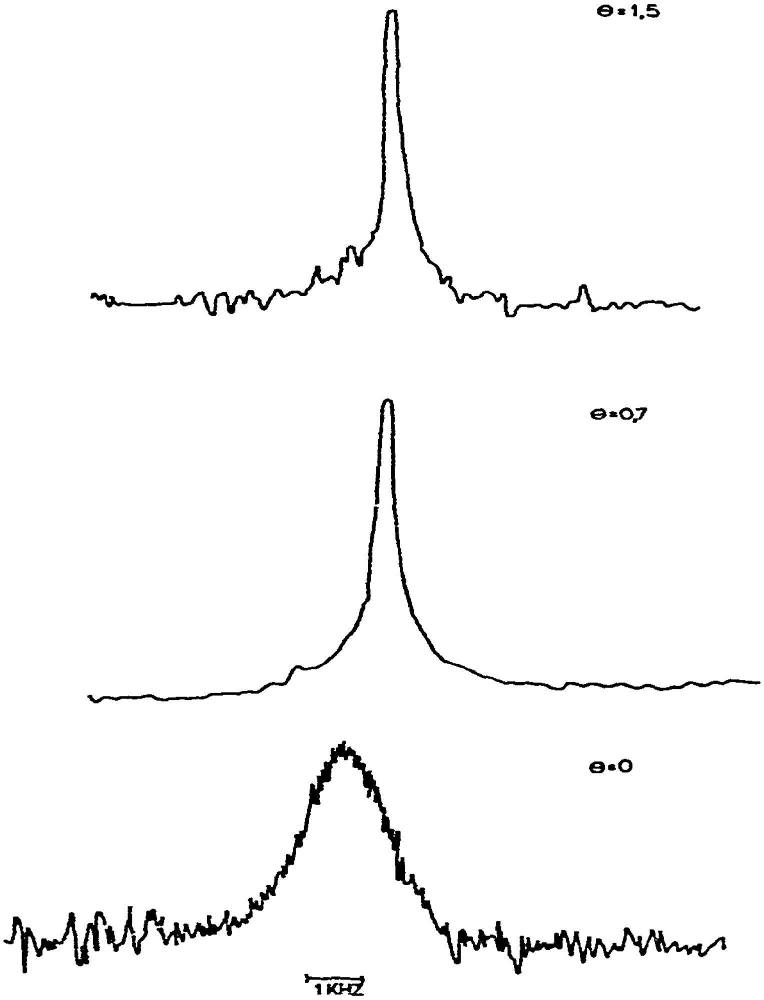

Fig. 4. The FFT spectrum of the Li^+ nucleus in LiA zeolite at coverage degree: (a) $\theta = 1.5$; (b) $\theta = 0.7$; (c) $\theta = 0$.

indicates that probably the phenomenon of chemisorption already occurs with formation of surface hydroxyl groups. As was shown by Habgood[7] the band of surface hydroxyl groups appears in infrared spectra. This band appears at low coverage degrees and no more increases, which is indicative of a limited number of sites where it may appear, which in effect points out a limited volume of β-cages. The crystal field in β-cages seems to be sufficiently strong to activate the process of chemisorption with formation of hydroxyl groups. Habgood's results confirm the proposed scheme also in other details. At moderate coverage degrees the band which may be attributed to intense hydrogen bonds to the aluminosilicate framework is very intense. According to the analysis presented in Table 1, the sorption heat is independent of cation and is of the order of 15 kcal mol^{-1}. Consequently three or at most four hydrogen bonds should be assumed. Finally, there are no new reasons for which we should henceforth attribute to peak I water of the structure of concentrated electrolytes. NMR results are in accordance with the model proposed. Namely, only at coverage degrees higher than $\theta = 0.7$ the Li^+ counterion becomes appreciably mobile. Water sorption in the range below this coverage degree does not show any considerable changes in the Li^+ spectrum, which indicates a weak counterion–water interaction. At high coverage degrees in the region of peak III, this interaction is so pronounced that the Li^+ NMR spectrum goes over from the shape corresponding to solid Li to that corresponding to aqueous solution of Li^+.

The DSC thermograms obtained for synthetic zeolites mainly correspond to those of natural zeolites[8]. The results of comparative DTA and X-ray analyses[8] are very interesting. It turned out that at temperatures corresponding to desorption to (peak I) an adaptation of crystal lattice occurs. Desorption corresponding to peak II is not accompanied by any changes in X-ray analysis. Finally, desorption corresponding to peak III is accompanied by significant changes in crystal structure which are often also irreversible. These results are also consistent with the model proposed, the desorption corresponding to peak I implies solvation of cations and their transition to new energy levels, which is accompanied by only slight changes in X-ray structure analysis. Since the second process is associated only with the cleavage of hydrogen bonds from the rigid aluminosilicate framework, it is not accompanied by any considerable changes in crystal lattice. The third process involves the cleavage of surface hydroxyl groups, which is associated with considerable energy effects (20–30 kcal mol^{-1}) sufficient to bring about phase transition in crystal structure.

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