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THERMAL QUALITY ANALYSIS OF WATER ON SYTHETIC ZEOLITE TYPE A

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ABSTRACT

The nature of the sorbed water on zeolites type A, with mono and bivalent cations, has been studied by DSC and effluent analysis. There have been found three types of sorbed water, independent of the nature of the exchanged cation. Further, a model for hydrogen binding in α and β cavities is recommended.

INTRODUCTION

Sorbed water in zeolites has been the subject of numerous investigations. Today there are two basic viewpoints. First, that water is bound by free oxygen electrons to zeolite cations[1–5]; second, that water is bound in zeolite by hydrogen bond to the oxygen of the alumino-silicate framework[6–9].

Although the problem has not been solved yet, a direct thermal analysis has not been applied in thorough investigations. Water was studied in relation to the stability of some zeolite forms[10–13]. Detailed DTA and TG analyses made by Toth[14] showed that there was some correlation between exchanged cations and binding energy of sorbed water in zeolite, which complies with the first viewpoint. However, since the results did not relate to the same number of molecules per surface unit, such a correlation cannot be fully accepted. In the case of MgNa zeolites, there exist two thermal processes, accepted by the authors as a proof of the existence of two sorbtion centres: cationic and oxygenic.

EXPERIMENTAL

Three Carbon Air Company powder zeolites were used: 3A, K zeolite; 4A, Na zeolite; and 5A, Ca zeolite. Other zeolites were made through equilibrium exchange. MgZ, ZnZ and CdZ were also made by equilibrium exchange as described by Barrer[15]. Cationic composition of zeolites prepared this way may be represented as follows: $Li_{7.8}Na_{4.3}|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $Na_{12}|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $K_8Na_4|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $Rb_{7.8}Na_{4.2}|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $Cs_{3.2}Na_{8.0}|12AlO_2 \cdot 12SiO_2|xH_2O$; $Ag_{11.8}Na_{0.2}|12AlO_2 \cdot 12SiO_2|xH_2O$; $Mg_{2.8}Na_{6.5}|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $Ca_{4.5}Na_3|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$; $Sr_{3.0}Na_{5.9}|12AlO_2 \cdot 12SiO_2| \cdot xH_2O$;

$Ba_{4.4}Na_{3.3}|12AlO_2\cdot12SiO_2|\cdot xH_2O$; $Zn_{5.3}Na_{0.1}|12AlO_2\cdot12SiO_2|\cdot xH_2O$; $Cd_{5.3}Na_{0.7}|12AlO_2\cdot12SiO_2|\cdot xH_2O$; $Pb_{5.9}Na_{0.1}|12AlO_2\cdot12SiO_2|\cdot xH_2O$. X-ray analyses showed that all samples had retained their crystal structures except BaZ and CsZ. CsZ showed some distortion of the basic crystal latice, while BaZ apparently had a partial amorphous structure, agreeing with known results.

Thermal analysis samples were prepared by pressing the zeolites into an aluminium sample pan; further they were degased on the quartz spiral at 400 °C, in 10^{-3} Torr vacuo for a period of 3–4 hours. Then, water and alcohol vapours were sorbed directly without air, until the desired weight was obtained.

In all cases samples were examined with maximum water content. Since this quantity of water is not an exactly determined value, the degased zeolites were spontaneously cooled in a water vapour atmosphere until no weight change occurred. This was achieved in 3–4 hours.

This method has an advantage, because from the NMR spectra it is evident that a relaxation equilibrium of water molecules in zeolite cavities exists. The usual procedure of water sorbtion in a saturated solution of $Ca(NO_3)_2$ or NH_4NO_3 at room temperature does not provide a relaxation equilibrium even in some cases after six months, as shown by Pfeifer and co-workers[16].

Samples prepared as explained above, contained 27–31% water. There was no regular dependence on cation nature found, contrary to other authors[11–14].

Both for thermal and effluent analysis, a Perkin–Elmer DCS-1B calorimeter was used, together with an attachment for automatic base line interpolation, described in ref. 17. For the effluent analysis of desorbed products, dry nitrogen was used as a carrier. In cases when only thermal analysis was performed, nitrogen flow was not used, because equilibrium retention required water desorbtion.

RESULTS

The results of water desorbtion on zeolites with monovalent cations are shown in Fig. 1. All thermograms have an identical shape, and the endothermal peaks can be noticed. The first peaks have broad distributions with weak maxima at about 363 K. With a dry nitrogen carrier or with zeolites with a small sorbed water quantity (NaZ and CaZ, below 16%), this peak does not appear, regardless of the nature of exchanged cation (see Fig. 2). The second peak is more distinct with a maximum at 431 K and, within ±7 K, does not depend on the nature of the exchanged cation. Finally, the third peak has a maximum at about 600 K. The broad maximum enables its position to be determined only to within ±20 K.

For this process, within error, no regular dependence could be established between zeolite nature and desorbtion temperature (Table 1). The only significant difference was found with AgZ, where this peak maximum falls at 700 K.

Investigations of the thermogram nature and coverage degree dependence, revealed that thermogram shape changes only in the region of the first and second

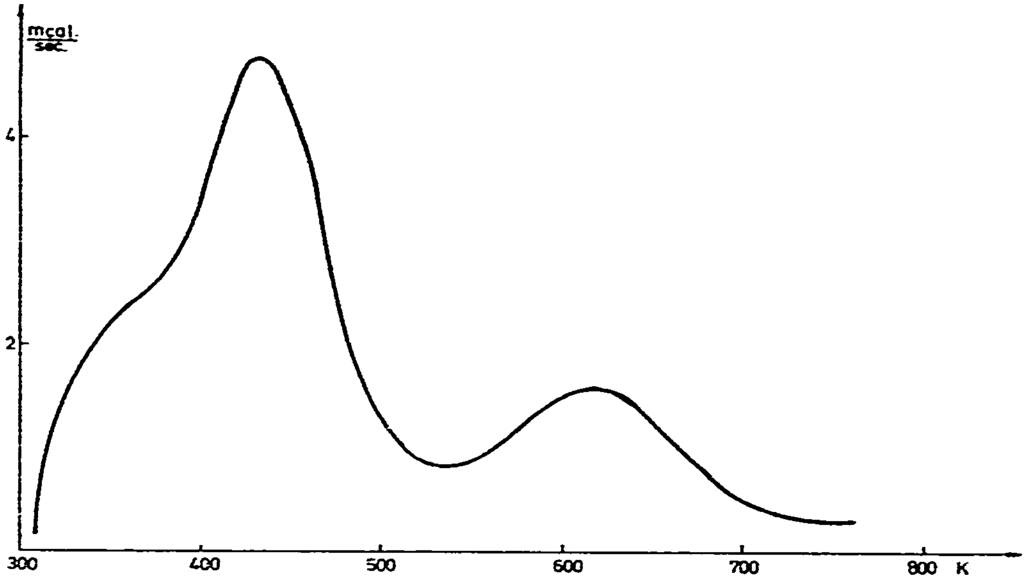

Fig. 1. DSC analysis of water sorbed on NaA zeolite ($\theta = 1.5$).

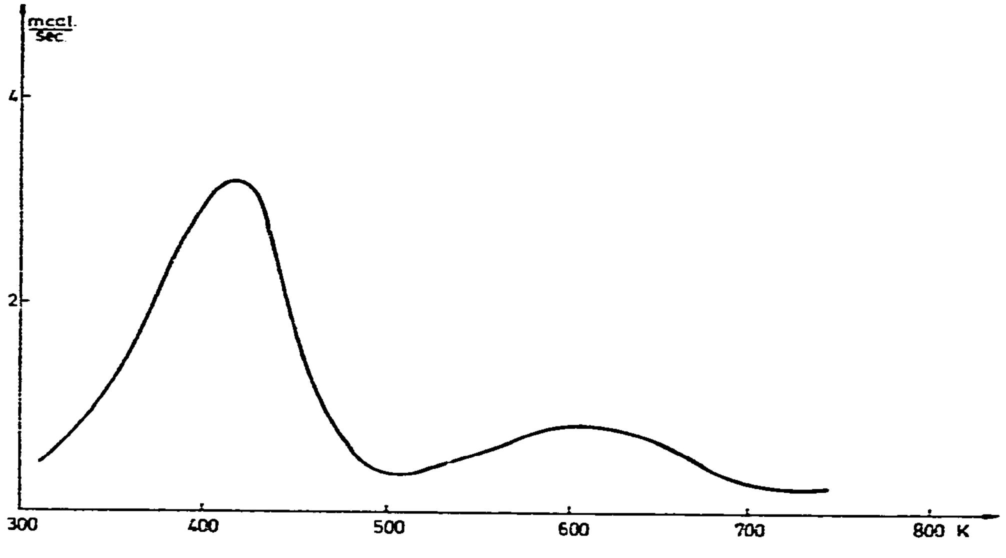

Fig. 2. DCS analysis of water sorbed on NaA zeolite. Coverage degree $\theta = 0.95$.

peaks. At low coverage degree, the first peak disappears completely while the second decreases and shifts somewhat towards higher temperatures, as shown on Fig. 3 for NaZ at $\theta \approx 0.3$ (4.36 % H_2O).

A comparison between thermal and effluent investigation results shows that all thermal effects are related to the degree of water desorption. Typical results of the effluent analysis are shown on Fig. 4. With any zeolite with monovalent cation, two

TABLE I

CHARACTERISTIC PARAMETERS OF WATER DESORBTION, OBTAINED BY DSC AND EFFLUENT ANALYSES

Zeolite	*Second peak maximum (K)*	*Third peak maximum (K)*	*Coverage degree θ (θ = 1 2A 15.3% as per ref. 18)*	*Ratio of desorbed water for second and third peaks, as per effluent analysis*
LiZ	420 ± 7	582 ± 15	1.4	5.1
NaZ	429 ± 7	605 ± 20	2.5	*6.5*
NaZ	448 ± 10	598 ± 20	0.3	0.54
KZ	430 ± 7	600 ± 20	2.0	*6.0*
RbZ	434 ± 7	600 ± 20	1.2	4.8
AgZ	422 ± 7	700 ± 20	2.0	*6.4*
MgZ	430 ± 7	582 ± 20	0.35	1.1
MgZ	438 ± 7	610 ± 20	0.65	3.4
MgZ	430 ± 7	604 ± 20	2.0	*6.1*
CaZ	428 ± 7	484 ± 7	2.0	1.5
CaZ	430 ± 7	470 ± 7	0.90	0.8
CaZ	—	478 ± 7	0.29	one peak only (III)
SrZ	434 ± 7	not clear	0.9	not clear
BaZ	438 ± 7	not clear	0.8	not clear
ZnZ	422 ± 7	590 ± 20	1.4	5.3
CdZ	444 ± 7	560 ± 20	1.3	5.0

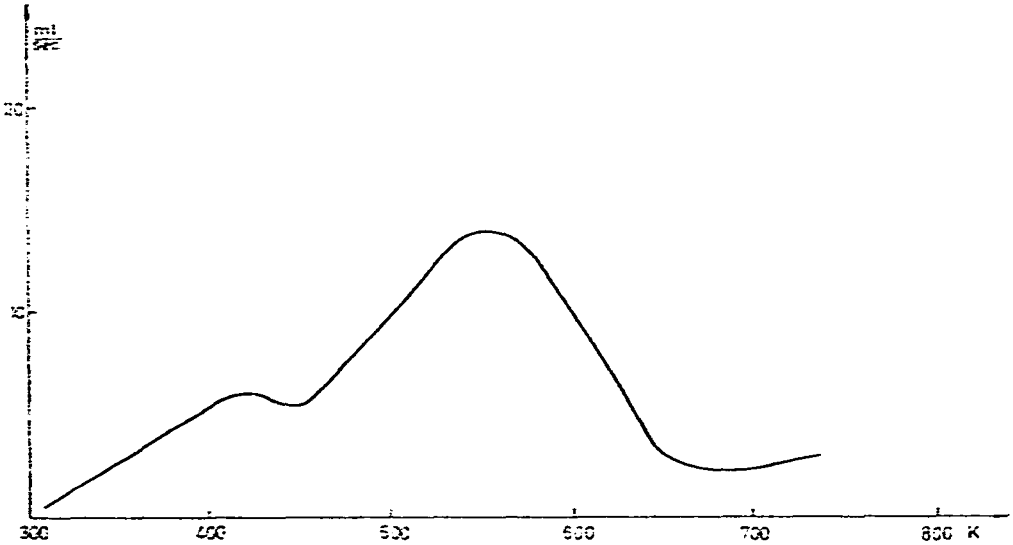

Fig. 3. DSC analysis of water sorbed on NaA zeolite. Coverage degree $\theta = 0.3$.

peaks are obtained at temperatures fully corresponding to the first and second peak temperatures of the thermogram (see Fig. 1).

It was shown that the quantity of desorbed water corresponding to the second peak is different from that of the third peak. The major amount of water is desorbed at

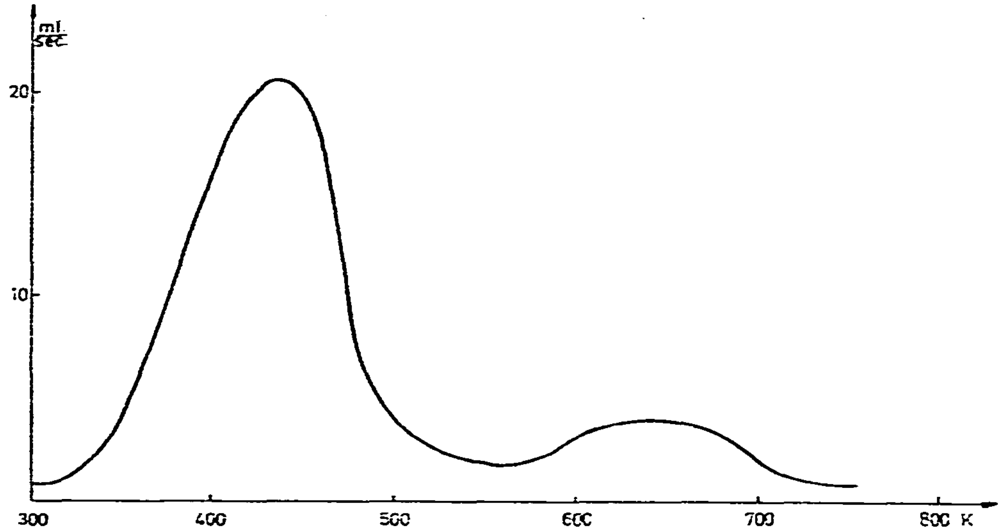

Fig. 4. Effluent analysis of water sorbed on NaA zeolite. Coverage degree $\theta = 0.95$.

lower temperatures. For fully saturated zeolite, the ratio between water quantities desorbed at 430 and 600 K is independent of the zeolite nature and is about six, as shown in column 5, Table 1. Also it is evident that this ratio decreases with coverage degree decrease which complies with the thermal analysis results where the second peak also decreases with coverage degree decrease.

Zeolites having bivalent cations, except CaZ and to some extent MgZ, behave similarily to monovalent cation zeolites. Three thermal peaks exist if no nitrogen carrier was used, otherwise two. It is characteristic that desorption temperatures and amounts of desorbed water (columns 2 and 5, Table 1) correspond to those found with zeolites with monovalent cations. It is possible that MgZ shows an exothermal reaction above 680 K, due to oxidation of magnesium.

CaZ represents a particular case. This zeolite also shows three thermal peaks, but the third peak has quite different properties than the one obtained with other zeolites. This peak is 100 K lower than the other zeolites, while the desorbed water quantity is considerably higher than the values obtained with other samples.

As evident from Fig. 5 and Table 1, at coverage degree ~ 1, the ratio between desorbed water quantities at peaks II and III is also about one.

Change of coverage degree provokes changes in the results of both thermal and effluent analyses, see Fig. 6 and Table 1. Therefore, down to $\theta \sim 1$, peak I decreases and later disappears. From $\theta \sim 1$, peak II begins to disappear both in thermal and effluent analyses. At $\theta \sim 0.3$, there is only peak III, as seen on Fig. 7 (it is interesting to mention that effluent analysis probably shows the fourth peak at higher temperatures, starting at 750 K, Figs. 6 and 7, but due to the range limit to 773 K of the DSC, it is not possible to show its existence).

Besides these investigations, it was attempted to establish a relationship between degree of cation exchange and the nature of the sorbed water on KZ and LiZ, but for the zeolites no change in the thermograms was found, contrary to results obtained by Dayer[19] with BaZ and SrZ.

Figure 8 shows thermogram and effluent analysis results of methanol on CaZ, but both show only one very broad peak.

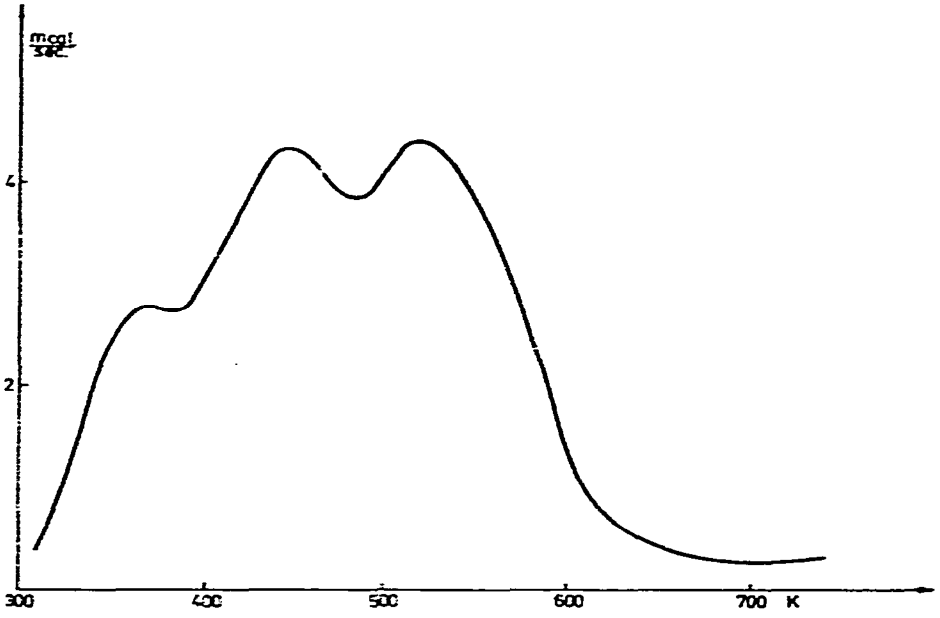

Fig. 5. DSC analysis of water sorbed on CaA zeolite. Coverage degree $\theta = 1.3$.

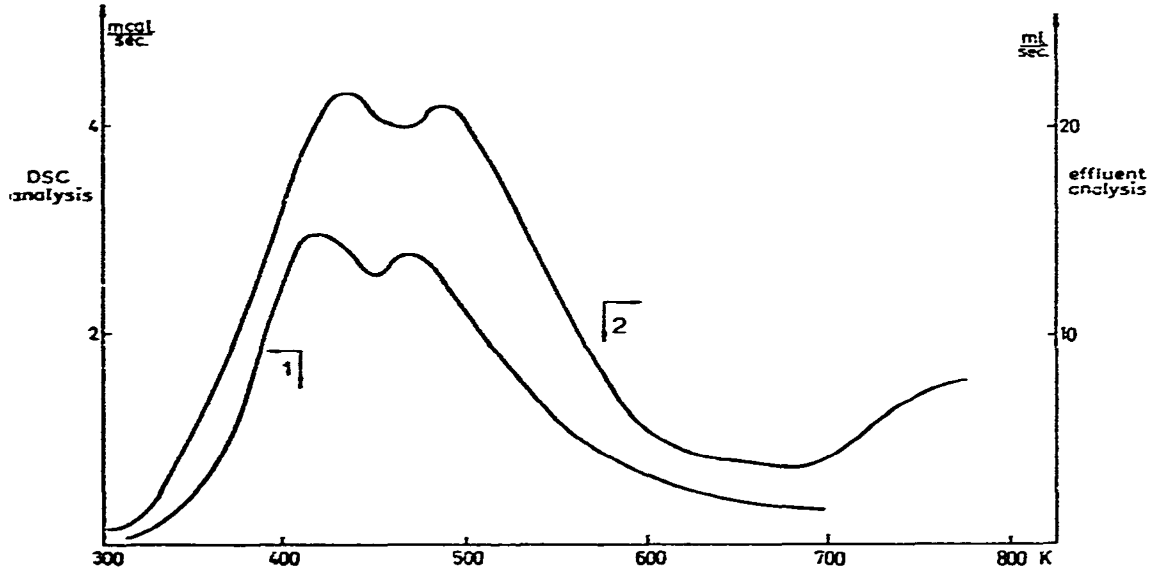

Fig. 6. DSC and effluent analyses of water sorbed on CaA zeolite for coverage degree $\theta = 0.97$. Curve 1, DSC analysis; curve 2, effluent analysis.

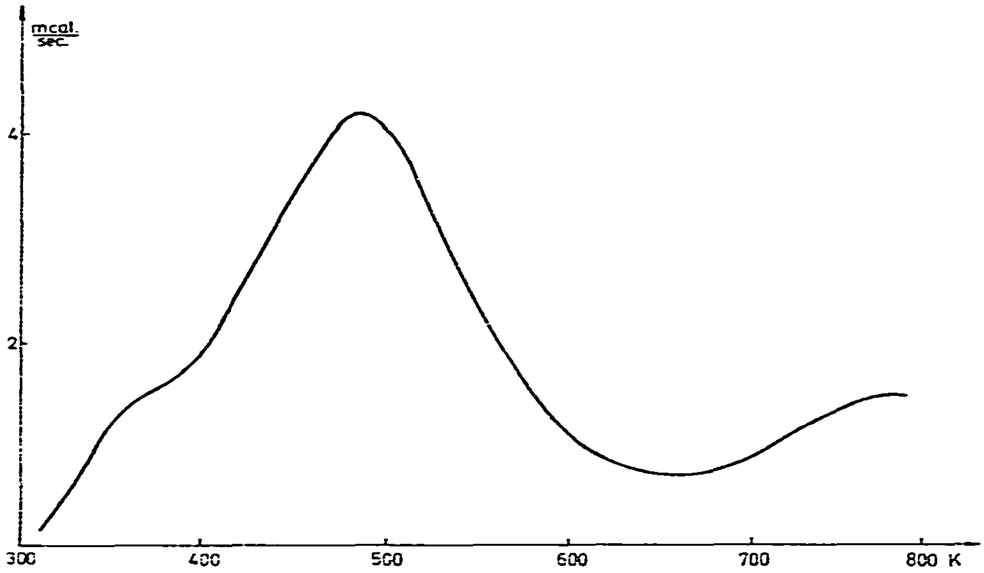

Fig. 7. DSC analysis of water sorbed on CaA zeolite for coverage degree $\theta = 0.3$.

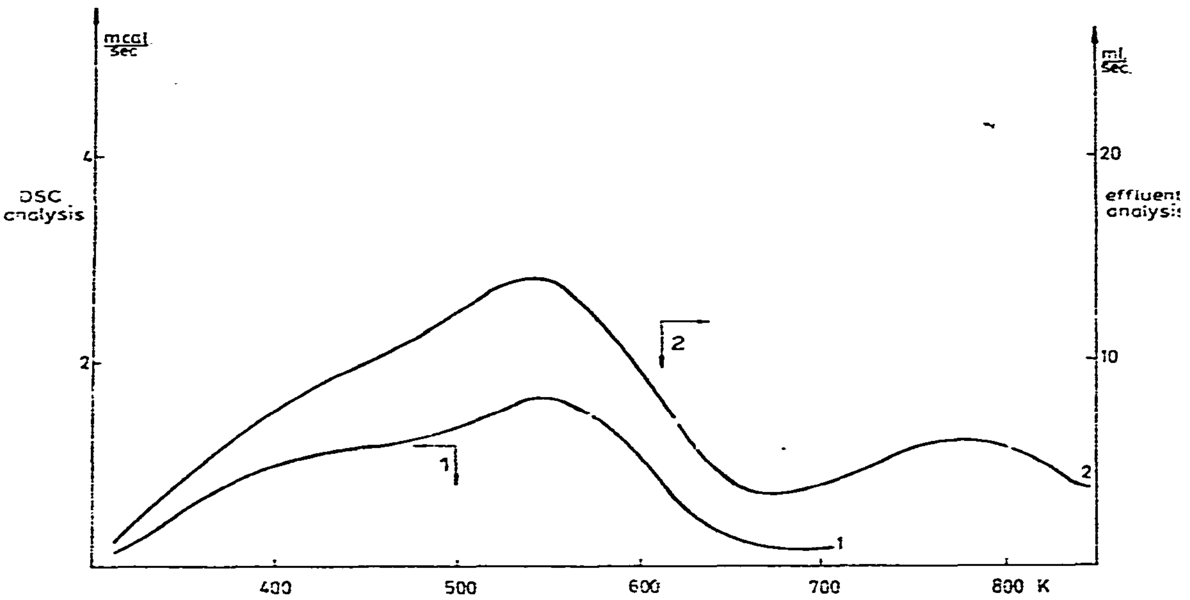

Fig. 8. DSC and effluent analyses of methanol sorbed on CaA for coverage degree $\theta = 1.0$. Curve 1, DSC analysis; curve 2, effluent analysis.

DISCUSSION AND CONCLUSIONS

At high coverage degrees, there is a clear energy distribution of the sorbed molecules at unequivalent sorbtion sites. Three sorbtion sites are evident (peaks I, II and III on experimental curves).

The weakest water bond corresponds to peak I and can be attributed to the one sorbed in polilayer. All experimental results agree with this assumption. Therefore, this peak exists only at high coverage degree. Thermodynamic equilibrium between sorbed water and gaseous phase is easily established. Desorbtion by the dry nitrogen flow leads to complete disappearance of the peak I. As a rule, immediately below boiling point of water, this peak disappears completely.

The nature of processes related to the peaks II and III is not very clear. However it is characteristic that desorbtion takes place at 430 and 600 K respectively (except for CaZ and AgZ), and it is not dependent on the nature of the cation. That means that there is an identical sorption mechanism corresponding to both peaks on all zeolites. The only explanation is that the sorption takes place by hydrogen binding with oxygen from the alumino-silicate framework, because in all cases this framework remains unchanged.

Peak II can be related to the water sorbed in large α cavities, while peak III relates to the sorption in small β cavities. Such an assumption is in good accordance with the results of effluent analysis, column 5, Table 1. The X-ray investigations[20] show that volume ratio between α and β cavities is about 6.2. Column 5, Table 1 shows this ratio between 6 and 6.4 in all cases with coverage degree exceeding 1.5.

Effluent analysis of methanol does not show the third peak, which is understandable, because large methanol molecules cannot enter small β cavities. Due to small size of the β cavities, a high potential gradient of the crystal field can be expected and this would cause considerably stronger gas–solid interaction. Consequently, sorbtion takes place firstly in β cavities, while desorption in them occurs later, as it was shown experimentally.

All experimental results completely satisfy the assumed model. The only serious disagreement exists with CaZ. Its peak II can be attributed to the hydrogen bound water, while its peak III differs considerably from those found on other zeolites. The effluent analysis shows that amounts of water corresponding to peaks II and III are very similar and this excludes the possibility of binding in small β cavities.

Also, the temperature difference of only 45 K shows that the difference between sorption energies at different sites is also lower than expected in the cases where these sites were in α and β cavities. The results obtained do not enable drawing of an acceptable conclusion on the nature of the water sorbtion in calcium zeolite.

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