

## **DIELECTRIC-DIFFERENTIAL THERMAL ANALYSIS IV THE ROLE OF WATER**

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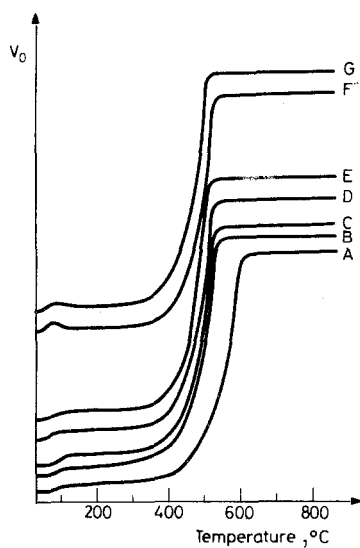
A deeper understanding of the role of water in dielectric-differential thermal analysis is presented.

In a previous paper [1] it was shown that the dielectric curves [2] of zeolites exhibit two effects; the first is related to water desorption during heating, and the second effect is ascribed to ionic conduction. In the present paper we are interested in the role of water in dielectric analysis.

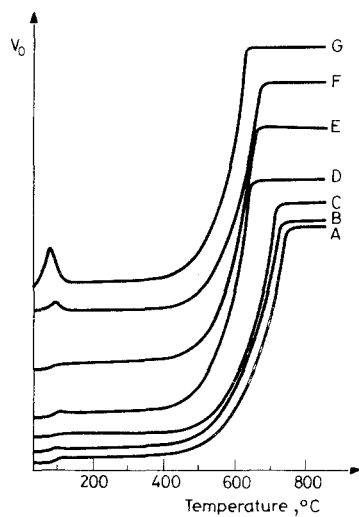
Zeolite was selected for this study, since it adsorbs water reversibly, permitting control of the water content in a wide range in the samples under test. Further, zeolite contains water in different states, relating to the formation of a hydrogen-bond between the sorbed water and a negatively charged oxygen in the zeolite framework [7] at low filling factors; a direct or indirect ion-dipole interaction with exchangeable cations [4] at low and intermediate filling factors; and finally, additional water entering the cavities then begins to form weak hydrogen-bonds with the rest of the water molecules, exhibiting the properties of liquid water [5, 6]. Thus, the dielectric curves of zeolites with different filling factors should shed light on the role of water in dielectric analysis.

Studies were made of the dielectric curves of synthetic NaX and NaA (REACHIM), NaHEU (70% clinoptilolite), NaMOR (75% mordenite) and NaERI (85% erionite) (obtained from natural samples and homoionized by ion-exchange at 373 K with a fresh 3 M solution of NaCl) at different filling fractions 0 (actual water content in the zeolite/total water content in the zeolite), where  $0.1 < 0 < 0.7$ .

The dielectric curves of NaX, NaA, NaHEU, NaMOR and NaERI are reported in Figs 1 to 5. The graphical representation shows the relation between water content and peak area, the dependence of which is shown in Figs 6 and 7. This



**Fig. 1** Dielectrical thermograms of NaX with different water content: A ( $\Theta=0$ ) B ( $\Theta=0.12$ ) C ( $\Theta=0.15$ ) D ( $\Theta=0.27$ ) E ( $\Theta=0.31$ ) F ( $\Theta=0.68$ ) G ( $\Theta=0.70$ )



**Fig. 2** Dielectrical thermograms of NaA with different water content: A ( $\Theta=0$ ) B ( $\Theta=0.12$ ) C ( $\Theta=0.20$ ) D ( $\Theta=0.31$ ) E ( $\Theta=0.42$ ) F ( $\Theta=0.64$ ) G ( $\Theta=0.68$ )

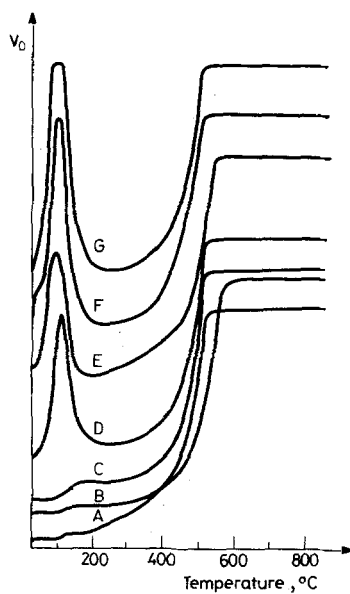


Fig. 3 Dielectrical Thermogram of NaERI with different water contents: A ( $\Theta=0$ ) B ( $\Theta=0.10$ ) C ( $\Theta=0.29$ ) D ( $\Theta=0.42$ ) E ( $\Theta=0.47$ ) F ( $\Theta=0.77$ )

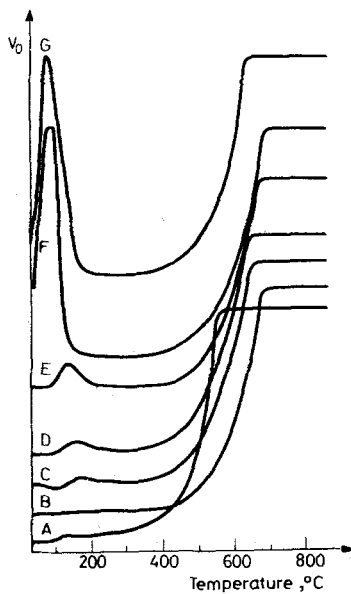


Fig. 4 Dielectrical Thermogram of NaMOR with different water content: A ( $\Theta=0$ ) B ( $\Theta=0.22$ ) C ( $\Theta=0.28$ ) D ( $\Theta=0.54$ ) E ( $\Theta=0.58$ ) F ( $\Theta=0.66$ ) G ( $\Theta=0.71$ )

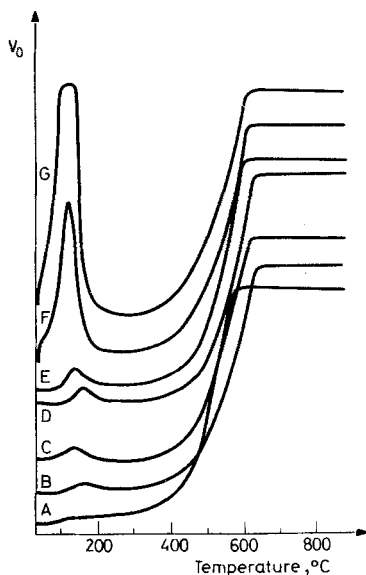


Fig. 5 Dielectrical Thermogram of NaHEU with different water content: A ( $\Theta=0$ ) B ( $\Theta=0.10$ ) C ( $\Theta=0.22$ ) D ( $\Theta=0.26$ ) F ( $\Theta=0.42$ ) G ( $\Theta=0.74$ ) E ( $\Theta=0.39$ )

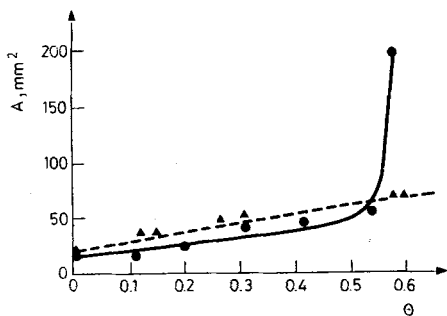


Fig. 6 Relation between the water peak area ( $A$  in  $\text{mm}^2$ ) and the filling factor ( $\Theta$ )for: NaX ( $\bullet$ ) and NaA ( $\blacktriangle$ )

relation is obtained from the circuit equation for the output voltage  $V_0$  [1, 2]:

$$V_0 = \frac{|Z_r|}{|Z_x|} V_i = \frac{\sqrt{(\omega C_x)^2 + (\sigma_x \lambda)^2}}{\sqrt{(\omega C_r)^2 + (\sigma_r \lambda)^2}}$$

where  $V_i$  is the output voltage,  $C_x$  and  $C_r$  are the capacities of the sample and reference capacitors, respectively,  $\delta_x$  and  $\delta_r$  are the conductivities, and  $\lambda$  is the form

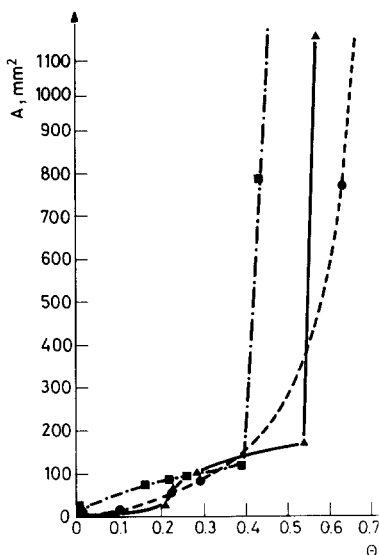


Fig. 7 Relation between the water peak area and the filling factor for: Na ERI (●), Na MOR (▲) and Na HEU (■)

factor [1]. At low temperatures, it has been shown [7] that the behaviour of the circuit is capacitive and  $\lambda\delta_x$  and  $\lambda\delta_r$  can be neglected in comparison with  $C_x = C_0E_x$  and  $C_r = C_0E_r$ , and

$$V_0 \approx \frac{E_x}{E_r} V_i$$

where  $E_x$  and  $E_r$  are the apparent dielectric constants of the powdered sample and the reference, and  $C_0$  is the capacity of the empty cylindrical capacitor.

It is possible to explain the peak form of the  $V_0$  vs.  $T$  curve by the fact that at low temperature the dielectric constant of adsorbed water is low, as the mobility of water is restricted in the zeolite cavity, and during heating an increase in the dielectric constant occurs because of the higher water mobility; this process is followed by a decrease in dielectric constant, ascribed to the chaotic motion at higher temperatures. This process is different at low filling fractions and at intermediate and high filling fractions, because of the different water mobilities in the first stage of adsorption, in which hydrogen-bonds with framework oxygen are developed, and in the last step of adsorption, in which liquid water properties are exhibited.

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