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FOUNDATIONS OF THERMO-DIELECTRICAL ANALYSIS
II. Calculation of the dielectric susceptibility of dehydrated homoionic zeolites

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The dielectric susceptibility of dehydrated homoionic zeolites was calculated by using a cation hopping model consisting of classical jumps over a barrier. The calculation method was based on determination of the response function of the homoionic dehydrated zeolite under transient excitation. The dielectric susceptibility expression obtained was compared with experimental dielectric spectra at different temperatures and the activation energy for cationic diffusion in the zeolites tested was also calculated. The results were within the range of values reported for cationic migration in the solid state. Further, there is a clear difference between the activation energies of Na and Ca diffusion and this fact forms a quantitative basis for the explanation of the thermodielectric thermograms of homoionic sodium and calcium zeolites and promote the understanding of the role of cationic polarization and cationic migration in thermodielectric analysis.

The study of the role of cationic polarization in thermodielectric analysis by using the dispersion spectrum of zeolites measured with a dielectric spectrometer developed in our laboratory [1] was discussed in the first paper of the present series. The approach used was essentially qualitative and the aim of the present report is to give a quantitative discussion of the role of cationic migration in zeolite polarization phenomena. Zeolite was selected as model material because of the presence in its thermodielectric thermograms of the most important polarization effects recorded by this method [3-7].

Therefore, the object of the present paper is the calculation of the dielectric susceptibility of dehydrated homoionic zeolites based on a model of cation hopping polarization [8]. Further, we compare the experimental

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dispersion spectra with the calculated expression for the dielectric susceptibility.

Theory

The essential elements of the cation hopping polarization mechanism are contained in [6-17].

– During the cationic migration between different structural sites, a change in microscopic polarization occurs due to the disposition of the negatively charged zeolite anionic framework [18, 19] in relation to the positively charged cations situated in the zeolite pores and cavities.

– Cationic jumps change the zeolite microscopic dipolar moment, which contributes with the dielectric response.

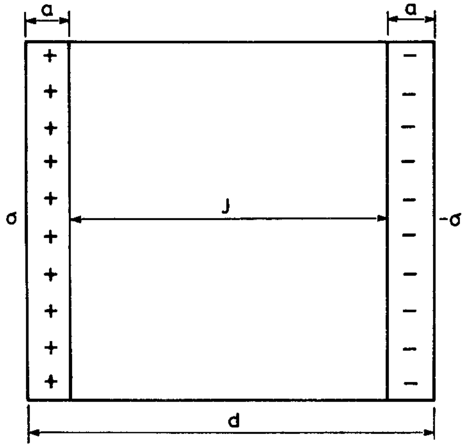

Fig. 1 Plane parallel condenser are of a and thickness d filled with a zeolite monocrystal assumed in the model

The method of calculation of the dielectric susceptibility is based on the use of the response function [20, 21] under transient excitation, particularly under a step voltage [22].

We assume a plane parallel condenser (Fig. 1) of area A and thickness D completely filled with a homoionic zeolite monocrystal, and a step voltage

$$V(t) = \begin{cases} V_0 & t < 0 \\ 0 & t > 0 \end{cases}$$

is applied; a depolarization current is then generated for $t > 0$:

$$i(t) = A\frac{dP}{dt} = C_V V f(t) \tag{1}$$

where C_V is the capacity of the empty condenser; V is the amplitude of the step voltage function; $P(t)$ is the polarization; and $f(t)$ is the response function.

It is easy to demonstrate [20, 21] that

$$\chi(w) = \chi'(w) - i\chi''(w) = \int_{0} f(t)\, e^{-iwt}\, dt \tag{2}$$

where $\chi(w)$ is the dielectric susceptibility caused by the response to depolarization. The zeolite permittivity can be expressed with the aid of $\chi(w)$ as

$$\varepsilon(w) = \varepsilon(\infty) + \chi(w) \tag{3}$$

where $\varepsilon(\infty)$ is the rapid response contribution [6-11], which includes the permittivity of the free space.

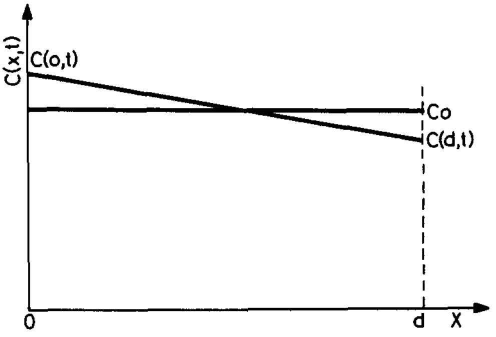

Fig. 2 Profile of the cationic concentration in the condenser after a step voltage transient

We consider (Fig. 2) that for zeolites the time dependence of the cationic concentration ($C(x, t)$) in the condenser after a step voltage transient fulfils the stationary condition [23] as follows:

$$\frac{dC(x,t)}{dx} = R(t) \tag{4}$$

with:

$$\lim_{t\to\infty} R(t) = 0$$

The volumetric charge in both plates of the condenser is then

$$\rho_o(t) = \left(C(0,t) - C_o\right)\mathrm{Ze} = \rho_o'(t)\,\mathrm{Ze}$$

$$\rho_d(t) = -\left(C(\mathrm{d},t) - C_o\right)\mathrm{Ze} = \rho_d'(t)\,\mathrm{Ze} \tag{5}$$

where Ze is the charge of the cation present in the zeolite and C_o is the anionic volumetric concentration (aluminium concentration in the zeolite) and: $\rho_o(t) = -\rho_d(t)$

The surface charge can be expressed as follows:

$$\delta = \rho_o a \tag{6}$$

where a is the width of the surface charge area of the zeolite monocrystal (Fig. 1).

The depolarization field can be calculated via the equation

$$E = \rho_o \frac{a}{\varepsilon_o}\varepsilon(0) \tag{7}$$

where ε_o is the vacuum permittivity and $\varepsilon(0)$ is the permittivity of the zeolite monocrystal for $w = 0$.

The transport equation for cations in the condenser after a step voltage transient is [23, 24]

$$J = u\,C(x,t)E - D\frac{\partial C(x,t)}{\partial x} \tag{8}$$

where $u = \mathrm{Ze}\frac{D}{kT}$ and D is the self-diffusion coefficient for cationic migration in the zeolite. It can be demonstrated that the solution for the transport equation is as follows [23, 24]:

$$J = Eu\frac{\left(C(0,t) - C(\mathrm{d},t)\right)e^{\eta}}{(1 - e^{\eta})}$$

$$\eta = uE\frac{\mathrm{d}}{D} \tag{9}$$

In the present case $\eta \cong 10^5$, and we can therefore take as an aproximate solution for Eq. (9)

$$J = uEC(\mathrm{d},t) \tag{10}$$

By using the continuity equation:

$$\frac{\partial \rho_{\mathrm{O}}'}{\partial t} = -\frac{\partial J}{\partial x} = \frac{J}{a} \tag{11}$$

and taking into consideration Eqs (7) and (10), we can obtain

$$-\frac{\partial \rho_{\mathrm{O}}}{\partial t} = \frac{u\,\mathrm{Ze}}{\varepsilon_{\mathrm{O}}\varepsilon(0)}\rho_{\mathrm{O}}'C(\mathrm{d},t) = \frac{u\,\mathrm{Ze}}{\varepsilon_{\mathrm{O}}\varepsilon(0)}\left(\rho_{\mathrm{O}}'C_{\mathrm{O}} - \rho_{\mathrm{O}}'^{2}\right) \tag{12}$$

and since ρ_{O}' is less than C_{O} it is possible to write

$$\frac{d\rho_{\mathrm{O}}'(t)}{\rho_{\mathrm{O}}'(t)} = -QDt \tag{13}$$

where $Q = (\mathrm{Ze})^2\,\frac{C_{\mathrm{O}}}{\varepsilon_{\mathrm{O}}}\varepsilon(0)kT$

The solution of Eq. (13) is

$$\rho_{\mathrm{O}}'(t) = \rho_{\mathrm{O}}'(0)e^{-QDt} \tag{14}$$

By using Eq. (1) for the depolarization current we can obtain

$$\mathrm{f}(t) = \kappa(0)QDe^{-QDt} \tag{15}$$

and consequently from Eq. (2):

$$\kappa(w) = \frac{\kappa(0)}{1 + i\frac{w}{QD}} \tag{16}$$

and this is the results we were looking for.

Experimental

The dependence between the apparent permittivity of powdered homoionic Na-HEU, Ca-HEU Na-MOR (homoionized natural clinoptilolite and mordenite with 75 and 85 weight per cent, respectively, of zeolite phase and the remainder quartz, calcite, montmorillonite and volcanic glass [25, 26], Na-PHI and Na-FAU (Phillipsite and faujasite synthesized in our laboratory (27)) and the frequency (0.04 to 100 kHz) was measured with a measuring device [1, 28, 29] consisting of an operational amplifier which compares the capacities of a standard and a sample capacitor. By using the relation $\varepsilon(w) = \frac{C_x}{C_e}$, where C_x is the capacity of the condenser full of sample and C_e is the capacity of the empty capacitor, and the relation $\varepsilon(w) = \varepsilon(\infty) + \chi'(w)$, it is possible to fit the experimental data with the real part of Eq. (16) by means of a non-linear regression algorithm [30, 31] implemented in a PC program. In the fitting process, we used dehydrated (20 hours at 623 K and 10^{-1} Pa) Na-HEU, Na-MOR, Na-PHI, Na-FAU and Ca-HEU, and the dielectric spectra were registered at different temperatures (303, 339, 373, 413, 453 and 500 K).

Results and discussion

At temperatures lower than 523-573 K, ohmic conduction was not detected in our samples, and at higher temperatures the process of ohmic conduction clearly starts to be dominant (this fact will be discussed thoroughly in a separate paper dedicated to cationic conduction). Our measurements were carried out at temperatures lower than 523 K, which ensures that we measured the alternating component fundamentally.

In zeolites, it is very well known that the cations occupy definite positions called cationic sites [19], more sites than cations are present per unit cell, and this ensures the free movement of this charged species. The movement of these particles can be characterized by two times, τ_s and τ_j, i.e. the time that a cation spends in a site and the time consumed in an individual jump, respectively. In the present model, $\tau_s >> \tau_j$ [6] and the hopping process consists in a classical jump over a barrier with an activation energy given by the barrier height U_0, and the diffusion coefficient can be expressed as: $D = \frac{a^2}{2} g \tau_s$ [6] (where a is the distance between adjacent sites, and g is a geometric factor) or $D = D_0 e^{-E/kT}$ (D_0 is the pre-exponential factor, and E is the activation energy). The real part of Eq. (16) is

$$\mathrm{Re}\left(\chi(w)\right) = \frac{\chi(0)}{1 - \frac{w^2}{w_0^2}} = \chi'(w) \tag{17}$$

with:

$$w_0 = QD = QD_0 e^{-E/kT} \tag{18}$$

The fitting process consists in the refinement of the parameters $\chi(0)$ and w_0 of Eq. (17) to obtain a least-square approximation of the experimental data to the theoretical expression for the real part of the dielectric susceptibility (Figs 3 and 4). Table 1 gives the values of the activation energies calculated with the help of Eq. (18), with fitting of the experimental data for different temperatures. The reported values lend quantitative support to the results of thermodielectric analysis concerning the differences in polarization between Na^+ and Ca^{2+} in zeolites [3].

In the model considered, we assume the presence of the hopping charge as the only polarization mechanism, with zeolites taken as cationic conductors [6], but nevertheless zeolites are heterogeneous materials composed of

Table 1 Activation energies for cationic self diffusion for some dehydrated homoionic zeolites calculated by computer fitting of the real part of equation (17)

Zeolite	E, kJ/mol
Na-HEU	27
Na-MOR	32
Na-PHI	25
Na-FAU	24
Ca-HEU	37

microcrystals included in a matrix (scanning electron microscopy research on zeolites [32] demonstrate the above idea). The latter fact implies the presence of interfacial polarization [33], which will be the subject of a future paper.

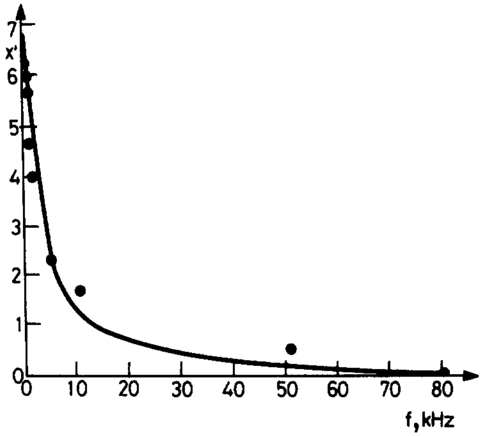

Fig. 3 Fitting of the experimental data corresponding to Na-MOR at 393 K with the real part of Eq. (16)

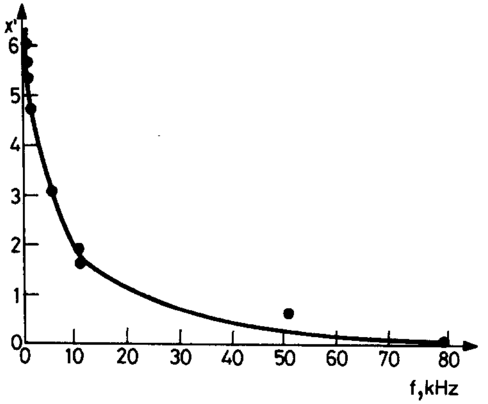

Fig. 4 Fitting of the experimental data corresponding to Na-MOR at 413 K with the real part of Eq. (16)

Finally, it is possible to state that dielectric methods could be very useful as finger-print techniques for the study of materials, e.g. the method of thermodielectric analysis that we have been trying to assess in recent years [3-5, 34-36], the method of dielectric spectrometry [5-17, 28, 29, 37] or the method of thermal stimulated current depolarization [38, 39], successfully developed recently as a poweful analytical method for polymers and inorganic glasses [40, 41].

The presence of the dielectric relaxation process as an almost universal effect in materials and the established temperature dependence of these relaxation processes makes thermal methods adequate for this research field as concerns a broad spectrum of phenomena, but a great effort is still necessary to assess the viability of those techniques from both theoretical and technical points of view.

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Zusammenfassung — Unter Anwendung eines Kationen-Hüpfmodelles, bestehend aus klassischen Hürdensprüngen, wurde die dielektrische Suszeptibilität von dehydratierten homoionischen Zeolithen berechnet. Die Berechnungsmethode basiert auf der Bestimmung der Antwortfunktion des dehydratierten homoionischen Zeolithen während einer vorübergehenden Anregung. Der ermittelte Ausdruck für die dielektrische Suszeptibilität wurde mit experimentellen dielektrischen Spektren bei verschiedenen Temperaturen verglichen, weiterhin wurde die Aktivierungsenergie für die Diffusion der Kationen in die untersuchten Zeolithe berechnet. Die Ergebnisse liegen in dem Wertebereich, der in der Literatur für die Kationenwanderung im festen Zustand beschrieben wurde. Es besteht ferner ein eindeutiger Unterschied zwischen der Aktivierungsenergie von Na- bzw. Ca- Diffusion. Dies bietet eine quantitative Grundlage zur Erläuterung thermodielektrischer Thermogramme von homoionischen Natrium- und Calciumzeolithen und hilft, die Rolle von Kationenpolarisation und -wanderung in der thermodielektrischen Analyse besser zu verstehen.