LETTERS

Unusual Relaxation Behavior of Water Inside the Sodalite Cages of Faujasite-Type Molecular Sieves

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Broad-band dielectric spectroscopy (10^{-2} to 10^9 Hz) is applied to investigate the molecular dynamics of NaY, a zeolite of faujasite structure. A dc conductivity contribution and three relaxation processes were revealed in the dielectric spectra. The relaxation process in the high-frequency range ascribed to orientational fluctuations of water molecules inside the sodalite cages is studied in detail. As a main result it is found that its mean relaxation time has an unusual saddle-like temperature dependence, which obeys neither an Arrhenius nor a Vogel−Fulcher−Tammann law. A quantitative description was given on the basis of a model recently developed by Feldman et al. (*J. Phys. Chem. B* **2001**, *105*, 1845) to analyze the dynamics of water confined in nanoporous glasses. Reasonable values for the activation energies of orientational fluctuations and of defect formation as well as for the defect concentration were obtained.

Starting in the 60s, the dielectric properties of zeolites (or more generally, molecular sieves) have been the object of intense studies, mostly devoted to the mobility of the extraframework cations.[1] The molecular sieves exhibit no electronic conductivity, because they possess a wide band gap of ca. 7 eV. However, most of them are ionic conductors, because the charge compensating cations can undergo translational motions. Several factors, such as the nature of the cations, their size and charge, the lattice structure, and composition as well as the dehydrating degree have a strong influence on the dielectric properties of molecular sieves.

Faujasite molecular sieves of both X and Y types contain truncated octahedra (called sodalite cages) of 0.66 nm in diameter, joined by six-membered rings of 0.2 nm in diameter. These sodalite cages are arranged in a tetrahedral coordination forming a network of large cages (supercages) shaped like an hourglass. The interconnecting 12-membered rings of 0.74 nm in diameter limit the access to these large cavities (see inset of Figure 1). The sodalite cavities are accessible only for a few small molecules such as water and sodium ions.[2] A substantial number of studies, either experimental or theoretical were dedicated to the distribution of cations in faujasite cages depending on different factors. The location of the cations is only possible for some positions under well-defined conditions.[3]

The dielectric properties for dehydrated, partially hydrated, or hydrated faujasite samples were largely studied in the literature,[4−14] but mostly in the frequency range from 10^{-2} to 10^7 Hz. Dc conductivity appears along with three relaxation processes for Y zeolites. There are strong arguments that the ionic conductivity is due to the correlated motion of the cations of the supercages,[5,6,10] but no agreement concerning the interpretation of the relaxation behavior was achieved yet. The low-frequency relaxation peak was assigned either to the cations

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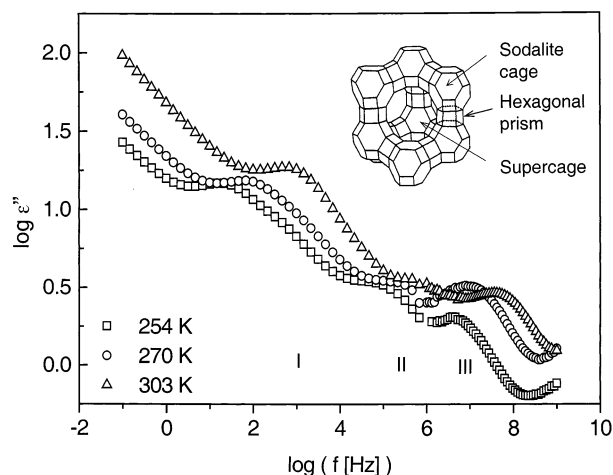
Figure 1. Dielectric loss ϵ'' vs frequency for the NaY sample at the indicated temperatures. The numerals denote different relaxation processes with increasing frequency. The inset gives a sketch of faujasite structure.

located in different sites[9,13] or to a Maxwell−Wagner-Sillars effect.[10] The processes at higher frequencies were related by Tabourier et al.[12] to correlated translational movements of Na⁺ ions in the supercages and to rotational fluctuations of water molecules inside the sodalite cages in order of increasing frequency. An Arrhenius law often analyzed the temperature dependence of the relaxation time of these processes, but a power law was also supposed[11,13,15] in some cases. NaX samples having a higher content of sodium ions than NaY show a further low-frequency relaxation process overlapping the ionic conductivity.[16]

Investigations of the dielectric properties of zeolite structure for frequencies higher than 10^7 Hz are scarce in general[17] and also for faujasite.[12,14] Therefore measurements on NaY faujasite samples are carried out between 10^{-2} and 10^9 Hz extending the known range to higher frequencies by two decades. This allows especially a detailed investigation of the temperature dependence of the high-frequency relaxation process.

Faujasite powder (commercially available from Aldrich) was carefully compacted to pellets to avoid structural damage.[18] The samples were routinely characterized by XRD, nitrogen sorption, thermogravimetric (TG) measurements, and FTIR spectroscopy as described elsewhere.[19] Their structure and crystallinity were thus confirmed. To remove volatile organics, the material was heated to 573 K and kept there under a vacuum of 10^{-5} mbar for 16 h. After that the sample was stored in a desiccator up to the measurements.

The equipment to measure the complex dielectric function

$$\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f) \qquad (1)$$

(f = frequency, ϵ' = real part, ϵ'' = imaginary part) was described elsewhere.[20] Isothermal spectra were obtained in a range from 220 to 373 K using a nitrogen jet cryostat with a temperature stability better than 0.1 K. Because the dielectric measurements were not conducted in a closed cell, the effect of the dehydration degree was not taken into consideration. Also the samples can take up water during their mounting into the cryostat.

As an example, Figure 1 gives the dielectric loss ϵ'' versus frequency for different temperatures. A conductivity contribution at low frequencies followed by three relaxation processes indicated by peaks in ϵ'' are observed in agreement with literature. Due to its dielectric strength and to a recent study,
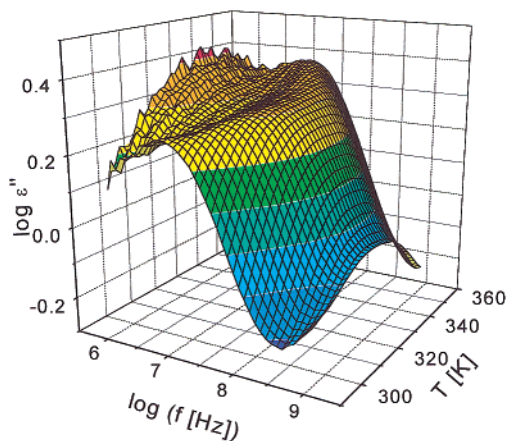
Figure 2. Dielectric loss vs frequency and temperature for process III.

which shows that, the presence of organic molecules onto the external surface of the zeolite grains (extra pores) decreases its intensity,[23] process I is ascribed in agreement with other authors[9,10,14] to a Maxwell−Wagner−Sillars polarization rather than to the correlated migration of cations in the supercages. The latter mechanism is instead related to the process II, as was already suggested.[9,10] Some further support for this assignment gives experiments[21] in which organic guests are incorporated into the supercages: This changes drastically the behavior of process II. For these two processes the loss peak shifts to higher frequency with increasing temperature as usual.

The relaxation peak at the highest frequencies (process III) is assigned to rotational fluctuations of water molecules in the sodalite cages.[10,12,14] It was reported that in faujasites water molecules are first adsorbed inside these structural units[22] and can hardly leave these cages.[23] Furthermore, the relaxation process is not affected by the presence of organic guest molecules inside the supercages.[21] Its unusual temperature dependence can been seen by plotting the raw data as a 3D plot (Figure 2). At low temperature the maximum position of the process shifts to higher frequencies with temperature, as expected. After reaching a certain value, it decreases with a further increase of temperature. Such a saddle-like variation of the relaxation process with increasing temperature is reported for molecular sieves the first time, though related systems containing water in nanoporous glasses[24,25] show a similar behavior. The maximum of the relaxation rate in the latter case was observed approximately at the same temperature as for faujasite but at a much lower frequency.

To estimate the relaxation strength $\Delta\epsilon$ and the relaxation rate at maximal loss $f_p = 1/(2\pi\tau)$ connected to the relaxation time τ for each process, the model function of Havriliak−Negami

$$\epsilon^*_{HN}(f) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (if/f_0)^\beta)^\gamma} \qquad (2)$$

(f_0 is a characteristic frequency close to f_p) has been fitted to the data. The fractional shape parameters β and γ ($0 < \beta$, $\beta\gamma \leq 1$) describe a symmetric and asymmetric broadening (for details see ref 26).

In Figure 3 the relaxation time is plotted versus $1/T$ for all relaxation processes. $\tau(T)$ of processes I and II can be well described by the Arrhenius law[23]

$$\tau = \tau_\infty \exp\left(\frac{E_A}{k_B T}\right) \qquad (3)$$
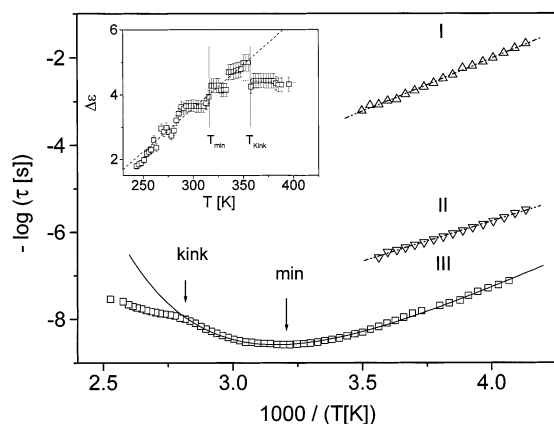
Figure 3. Relaxation time vs the inverse temperature for the different processes. Dashed lines are fits of the Arrhenius law to the data of processes I and II. The solid line is a fit of eq 6 to the data of process III up to $T = 385$ K. The inset represents the dielectric relaxation strength for process III.
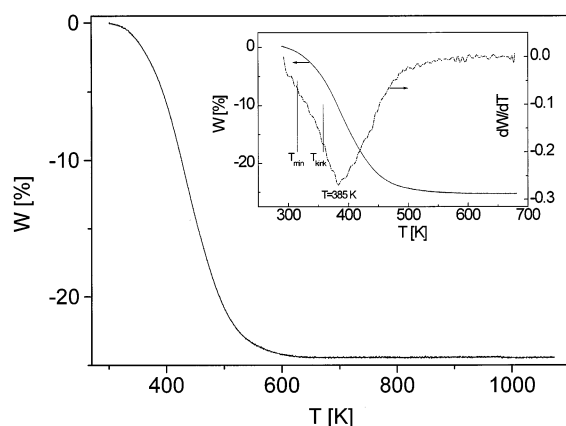
Figure 4. TG curve (heating rate of 10 K/min) for the NaY sample. The inset shows the water thermal desorption at a heating rate of 2 K/min.

(k_B = Boltzmann constant, E_A = activation energy, and τ_∞ = preexponential factor). The estimated activation energies are in agreement with the literature.[21]

As is obvious from Figure 2, the relaxation time for process III has a saddle-like dependence on temperature with a minimum at $T_{min} = 315$ K. For temperatures higher than T_{min} τ decreases with increasing temperatures with a kink-like change at $T_{kink} = 358$ K. All the data cannot be described either by an Arrhenius or by a Vogel−Fulcher−Tammann (VFT) dependence

$$\log \tau = \log \tau_\infty + \frac{A}{T - T_0} \qquad (4)$$

which is characteristic for glass-forming liquids.[27] T_0 is the so-called Vogel temperature (ideal glass transition temperature) and A is a constant.

To check if the unusual relaxation is due to a dramatic loss of water, TG measurements are carried out (see Figure 4). The data obtained up to 1073 K (where the sample is totally dehydrated) show that the pores of the faujasite samples are completely filled with water: A filling factor[14] as the ratio of the sorbed water to the weight of a dry sample was estimated to 0.32, in agreement with the value expected from the pore volume. Data measured with a heating rate of 2 K/min are represented in the inset of Figure 4. The derivative (DTG) shows that the maximum water loss takes place at $T = 385$ K. This is close to T_{kink}. Molecular water is totally removed before 523

K. Although the water is adsorbed in different states, as physically sorbed or chemisorbed water,[28] there is no significant structure in the DTG curve, especially around T_{min} where the minimum in the temperature dependence of the relaxation rates is observed. Therefore it is concluded that the minimum in the relaxation time is not directly related to the loss of water. It has to be noted that losing the physisorbed water seems to alter neither the localized adsorbed molecules nor the cation location,[29] whereas the loss/uptake of the water from/inside the sodalite cages leads to the redistribution of the cations. This is an argument that T_{kink} is related to a change in the water amount in the sodalite cages. It is worth noting that we observed the unusual dielectric behavior for a concentration corresponding to a complete first hydrating layer.[30]

These conclusions are additionally supported by the temperature dependence of the dielectric relaxation strength (see inset of Figure 3). $\Delta\epsilon$ increases with temperature approximately linearly up to T_{kink}. No change of this temperature dependence takes place at T_{min}. Because $\Delta\epsilon$ is proportional to the number density of fluctuating dipoles, it is expected that a loss of water will lead to a decrease of the dielectric relaxation strength rather than to an increase, as observed. At T_{kink} this temperature dependence changes to a constant value, which indicates a change of the water cluster structure and/or water amount in the sodalite cages.

To describe the unusual temperature dependence of the relaxation time of process III, a model developed by Ryabov et al.[25] is used. It was recently applied to the relaxation of water in nanoporous glasses. Obviously, the saddle-like behavior of this relaxation process must be due to the counterbalance of two competing events.

First, for orientational fluctuations the water molecules have to overcome energy barriers leading to an Arrhenius-like temperature dependence $\sim \exp[H_a/k_BT]$. H_a is the height of the potential barrier between the substates. Second, in the vicinity of a selected water molecule a certain amount of free volume is necessary for its reorientation, which can be provided by a defect. Ryabov et al.[25] started from the model of Macedo and Litovitz,[31] which considered the free-volume approaches of molecular transport[32] for the second event. For the relaxation time

$$\tau = \tau_\infty \exp\left[\frac{H_a}{k_BT} + \gamma\frac{v_0}{v_f}\right] \qquad (5)$$

is derived, where v_f is the free volume per molecule, v_0 is the close packed molecular volume, and γ is a numerical factor. For $H_a/k_BT \ll v_0/v_f$ and $v_f \sim (T - T_0)$ the well-known VFT equation (eq 4) is obtained, which cannot describe the temperature dependence of the relaxation time of process III.

One of the basic assumptions of Macedo and Litovitz was that the number of fluctuating units is constant. This must not be the case for molecules in confining geometries where the number of defects can be dependent on the temperature. Ryabov et al.[25] assumed for the temperature dependence of the defects $\sim C \exp[-H_d/k_BT]$, where H_d is the energy of the defect formation and C is the inverse maximum defect concentration. This means that the number of defects decreases with the temperature. For the faujasite system investigated this seems to agree with the experimental result that the dielectric relaxation strength for process III increases with temperature (see inset of Figure 3). For the relaxation time

$$\tau = \tau_\infty \exp\left[\frac{H_a}{k_BT} + C\exp\left(-\frac{H_d}{k_BT}\right)\right] \qquad (6)$$

TABLE 1: Fitting Parameters of the Relaxation Process III in NaY Faujasite-Type Molecular Sieves and of Related Systems

sample[a]	pore size (nm)	H_a (kJ/mol)	H_d (kJ/mol)	τ_∞ (s)	$1/C$	ref
NaY/III(water)	0.74; 0.2[b]	19.6	10.7	0.7×10^{-30}	0.8×10^{-2}	this work
A/2(water)[c]	50−70	55	39	3×10^{-14}	9×10^{-7}	25
C/2(water)[c]	280−400	42	30	9×10^{-13}	2×10^{-5}	25
sodalite/(ethylene glycol)	0.66	26				33

[a] Sample label includes porous material/relaxation process(dipolar molecule). [b] The size of access windows is given. [c] Authors' original notation of the corresponding process.

was derived. Equation 6 was used to fit the temperature dependence of the relaxation time of the relaxation process III in faujasite. The estimated parameters are given in the Table 1 along with the values for related systems as water in nanoporous glass or ethylene glycol in silica sodalite.[33] The high-frequency relaxation process in hydrated faujasite has a predominant Arrhenius behavior at low temperatures whereas at high temperatures the defect formation becomes important. τ_∞ for water in NaY faujasite is much smaller than for water in porous glass.[24,25] In faujasite the dynamics of the water molecules is hindered, as compared to the corresponding process for bulklike water (ice) at high frequencies,[34] reflecting the interaction of the water molecules with the inner surface of the cavities/pores. For instance, at 298 K, the water mobility in the zeolite is reduced by a factor of 2.46 compared to the bulk water (19.2 GHz).

The maximum number of defects in 1 mol of adsorbed water was estimated to be ca. 10^{19}, a number much higher than that in bulk ice and even higher than for water in nanoporous glasses.[27] This might suggest that more defects can be formed in water adsorbed in the sodalite cages of faujasite than in bulk ice. A still open question is the nature of these defects in sodalite−water systems. For water and ice, the nature of the orientation defect is complex.[35] These can involve pairs of neighboring O···O atoms not bonded by hydrogen bonds (defect L) or pairs of OH groups facing each other OH···HO (defect D) depending on the microscopic environment of the defect. A jump of a defect to a new site occurs by a 120° rotation of a molecule. In the case of water in porous systems, there are even more possibilities to form defect sites, probably due to the presence of the framework of OH groups[12] and to the particular cavity structure. At the moment, we do not have any additional data to support this unless it is a lower value for the energy of defect formation than that in nanoporous glasses.

In summary, the molecular dynamics of water in the sodalite cages of faujasite has a characteristic saddle-like temperature dependence. This is interpreted as the result of the motion of ice-like structures and additional OH defects where the concentration first depends on temperature. This is in analogy with a novel approach concerning the molecular mobility of water in porous glasses.

Because such a behavior is found for two different systems, it might be a quite fundamental phenomenon characteristic of water in confining geometries. Further studies taking into consideration other structures of molecular sieves are in progress.

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