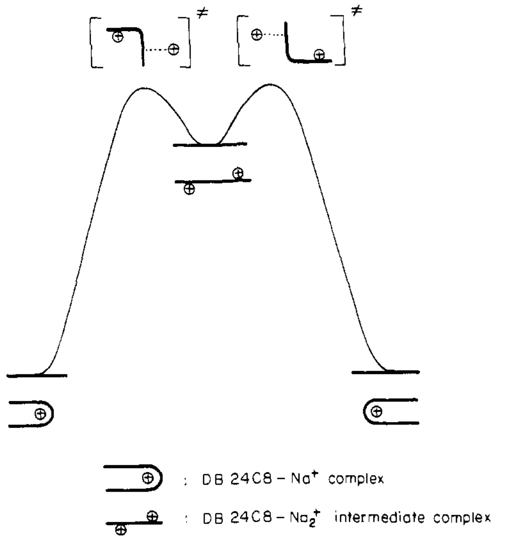
Scheme II. Scenario of the Bimolecular Cation-Exchange Mechanism of the Na^+-DB24C8 Complex[a]



[a] The opening of the wrapped crown is assisted by the approach of a second sodium cation.

Such a conformation is less probable for DB18C6. The reason a bimolecular mechanism does become competitive in nitromethane in the case of DB18C6 lies in the high free energy of activation (60 kJ mol^{-1} at 300 K) of the unimolecular decomplexation process. For nitromethane, coordinating less strongly to sodium than solvents with higher donicities, the gain of translational entropy in the desolvation step (enthalpically more favored) does not compensate for the loss of entropy accompanying the solvent cage reorganization. Consequently, even if the bimolecular process is plausibly entropically disfavored in comparison to the unimolecular process, the additional stabilization afforded by the incoming second sodium cation makes the bimolecular mechanism operative at high enough sodium concentrations.

The activation parameters of the decomplexation of $NaPF_6$–DB24C8 are $\Delta H^{\ddagger} = 30$ kJ mol^{-1} and $\Delta S^{\ddagger} = -37$ J mol^{-1} K^{-1} (see Scheme II). These values are identical with those determined previously in the case of the counteranion BPh_4^-.[12] They confirm that the extra stabilization afforded by the second cation is $\Delta G^{\ddagger}$ $\sim$20–25 kJ mol^{-1}. It is particularly interesting to point out that, in nitromethane, a poorly coordinating solvent, $\Delta G^{\ddagger}_{uni}$ is identical in the two cases studied (DB18C6 and DB24C8). In nitromethane, the unimolecular decomplexation barrier results mainly from conformational changes of the ligand. In the case of DB24C8, more oxygen ethers are available to the cation, and accordingly the bimolecular mechanism is favored both for entropy and enthalpy reasons.

In conclusion, this study has demonstrated that a bimolecular decomplexation mechanism has to be expected in poorly coordinating solvents, even in the case of crown ethers too small to wrap around the cation.

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Registry No. Na^+-DB24C8·PF_6^-, 110698-01-6; Na^+-DB18C6·PF_6^-, 39019-64-2; Na^+-DB18C6·BPh_4^-, 39152-87-9; Na^+-DB18C6·BF_4^-, 93581-87-4.

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Investigation of the Hydration of Zeolite NaA by Two-Dimensional ^{23}Na Nutation NMR

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Abstract: A two-dimensional nutation NMR experiment is used to observe the change of quadrupole parameters of sodium ions in zeolite NaA when the zeolite is loaded in steps with water. We can detect two sodium sites in the dry zeolite, at respectively 6-rings and 8-rings, and can follow the water absorption at these sites. When the amount of absorbed water is increased in steps, first the quadrupole interaction of sodium at the 6-rings decreases; with more absorbed water the quadrupole interaction of the sodium ions at the 8-rings becomes small. Relaxation effects in the rotating frame, studied by combining rotary echoes with nutation NMR, indicate a mobility of sodium ions or water molecules.

Zeolites are crystalline aluminosilicates consisting of a framework of AlO_4 and SiO_4 tetrahedra which build up a network of channels and cavities.[1] In these micropores there are so-called nonframework cations which balance the negatively charged framework. Zeolites are used in the fields of catalysis, molecular sieves, ion exchange, and medicine.[2-4] For many of these applications the knowledge of the local environment, mobility, and absorptive behavior of the cations is very important; for example, molecular sieving is often controlled by the location and size of these cations.[5,6]

The investigation of these cations has involved a number of techniques,[7-11] of which nuclear magnetic resonance seems to be

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the most favorable because of its ability to directly detect the cation. A disadvantage of the NMR technique is that most of the cations, e.g., hydrogen, sodium, potassium, etc., have only a small chemical shift range, so discrimination of different environments via chemical shift becomes difficult without the use of extremely high fields.

In addition, when the nucleus under investigation has a spin quantum number $I > {}^1/_2$, only the central (${}^1/_2$, $-{}^1/_2$) transition out of all possible single quantum transitions will usually be observed and the resonance line becomes quadrupole broadened, which makes the spectral resolution even worse. These problems are overcome by the use of a so-called two-dimensional nutation experiment by which the quadrupole interaction is separated from the chemical shift.[12-14]

This experiment is divided into two time domains: in the evolution period (t_1) the system is irradiated with a radio-frequency (rf) magnetic field (H_1) and in the detection period (t_2) the free induction decay is collected. During the evolution period the spins precess around the rf field with specific nutation frequencies which depend on the magnitude of the quadrupole interaction (H_q). In the extreme cases, when $H_q \gg H_1$ or $H_q \ll H_1$, the nutation frequency amounts to $(I + {}^1/_2)\omega_{rf}$ or ω_{rf} ($\omega_{rf} = \gamma H_1$), respectively, whereas intermediate cases have to be calculated numerically.[14]

The technique works particularly well for systems in which quadrupolar interactions can be used as a monitor to follow structural changes. This is the case for many processes occurring in zeolites, as is shown by the present report of our investigation of the effect of increased water absorption of zeolite Linde 4A.

X-ray diffraction measurements[15,16] have shown that dehydrated zeolite NaA consists of α- and β-cages which are interconnected by 8-, 6-, and 4-membered rings. There are 8 sodium cations on the symmetry axis of a 6-ring but 0.2 Å displaced into the α-cage, 3 cations are located in the plane of the 8-ring but 1.23 Å away from the center, and the 12th cation is placed opposite to a 4-ring, also displaced into the α-cage.

Experimental Section

The zeolite Linde 4A was bought from Fluka A.G. and used without further purification. The zeolite was dried by heating under vacuum at 350 °C. The different water loadings were prepared by exposing the dried zeolite for 1 day to a nitrogen atmosphere with a known, variable vapor pressure of water. The goal was to prepare samples with n molecules of water per unit cell (n = 0, 1, 2, ...). The different loadings were checked afterward by absolute intensity measurements of the proton NMR signal. The potassium-exchanged zeolite was obtained by stirring the zeolite for 3 days in water containing 2 equiv of KOH.[17] All samples were measured in closed 6-mm quartz tubes which contained no sodium.

The ^{23}Na NMR experiments were performed on a Bruker CXP-300 and AM-500, working at 79.35 and 132.93 MHz, respectively. The proton measurements were done at the CXP-300, while aluminum was measured at the AM-500 working at 130.29 MHz. All experiments were performed on static samples.

To overcome the receiver dead time, the one-dimensional ^{23}Na NMR spectra were recorded with the spin-echo technique.[18] Because of this receiver dead time the two-dimensional nutation spectra are somewhat distorted in the F_2 dimension, since the free induction decays are measured directly, but this has no effect on the conclusions.

The strength of the radio-frequency field for the two-dimensional nutation experiments was 84 kHz. Each two-dimensional experiment took about an hour of spectrometer time.

The samples showed no degradations during 2 months.

Results

The measured proton content and line width of the ^{27}Al resonance as a function of the weighed water amount are shown in Figure 1. The one-dimensional ^{23}Na NMR spectrum of dried Linde 4A, recorded with a relaxation delay of 0.4 s at 11.7 T shows three lines in which the outer lines have a splitting of 31.2 kHz, while the central line shows a shoulder. This splitting increases to 53.8 kHz on recording the spectrum at 7.1 T, while the shoulder becomes more pronounced (Figure 2a,b). Integration of the spectra shows that the intensity of the outer lines is about 2 times the intensity of the central component.

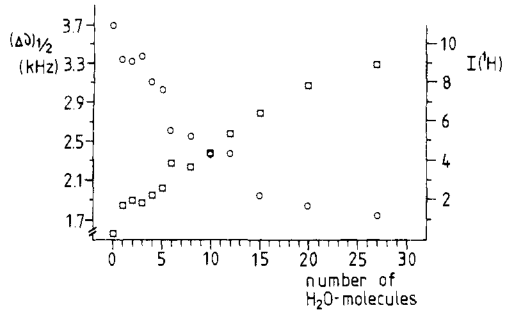

Figure 1. Values of the ^{27}Al NMR line width ($\Delta\nu_{1/2}$, circles) and the intensity of the ^{1}H resonance ($I(^1H)$, squares) in NaA as a function of water content.

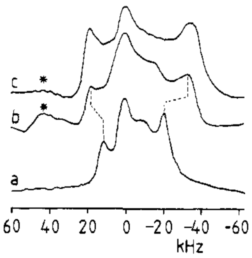

Figure 2. ^{23}Na spectra of (a) NaA at 11.7 T, (b) NaA at 7.11 T, and (c) NaA with 2 potassium ions at 7.11 T. The signal denoted with an asterisk in spectra (b) and (c) is due to a back-folded signal of copper from the probe.

The exchange of potassium for 2 sodium ions results in a decrease of the central line of the ^{23}Na spectrum (Figure 2b,c). The two-dimensional nutation spectrum of the dry zeolite shows the same three lines, but located at $2\omega_{rf}$ in the F_1 direction ($(I + {}^1/_2) = 2$ for $I = {}^3/_2$) (Figure 3).

Introducing the first amount of water causes a decrease in the splitting of the outer pairs of lines to 45.6 kHz at 7.1 T and a disappearance of the small shoulder of the central line, but in the F_1 direction no changes appear. Until 5 water molecules per unit cell there are no further changes in the spectra. The fifth water molecule induces a slight increase in the tail of the central signal in the F_1 dimension toward ω_{rf}.

The next 6 water molecules give a gradual decrease in intensity of the outer lines in the F_2 dimension. The loss of intensity of the outer lines appears as a narrow signal in the F_2 dimension but in the F_1 dimension it is found as a broad line around ω_{rf}. The remains of the outer lines are still found at $2\omega_{rf}$ in the F_1 direction. At a content of 12 water molecules per unit cell the spectrum in the F_2 dimension has collapsed to a single, relatively narrow line.

In the F_1 direction more and more intensity shifts to $F_1 = \omega_{rf}$, while the line width in this direction becomes 150 kHz.

Upon further hydration to 27 water molecules per unit cell[6] there remains a single line in the F_2 direction while the F_1 spectrum becomes located at F_1 ω_{rf} with a line width of 80 kHz.

Discussion

The proton NMR results show a gradual increase in water content, with only small deviations from the amounts of water as determined from the vapor pressure in the nitrogen atmosphere, except for the second and third samples, which both seem to have the same amount of water.

The one-dimensional ^{23}Na spectra (Figure 2a,b) taken at different field strengths show a reciprocal dependence of the splitting of the outer pair of lines with field; the inner line also shows this field dependence. This is characteristic for a dominant

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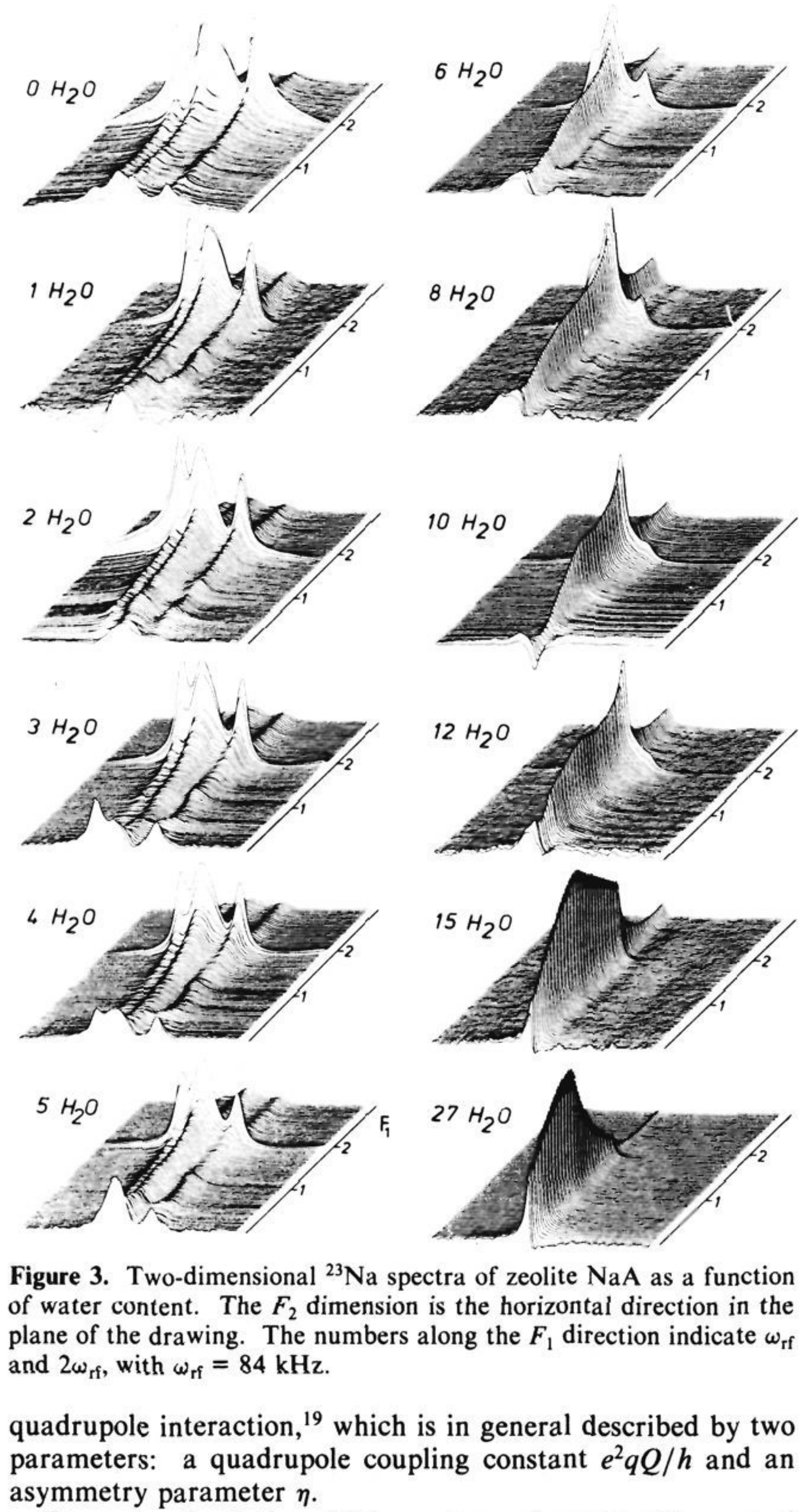

Figure 3. Two-dimensional ^{23}Na spectra of zeolite NaA as a function of water content. The F_2 dimension is the horizontal direction in the plane of the drawing. The numbers along the F_1 direction indicate ω_{rf} and $2\omega_{rf}$, with ω_{rf} = 84 kHz.

quadrupole interaction,[19] which is in general described by two parameters: a quadrupole coupling constant e^2qQ/h and an asymmetry parameter η.

Computer simulation of this spectrum shows that the central line with intensity 1 can be fitted with an asymmetry parameter of about 0.9 and a quadrupole coupling constant of 3.2 MHz, while the parameters of the outer lines with an intensity of 2 are 0 and 5.8 MHz, respectively. These values are similar to those found by Lechert et al.[10] (η = 0.7, e^2qQ/h = 3.36 MHz; η = 0, e^2qQ/h = 5.13 MHz).

The intensity ratios of both lines show that the sodium ions located near the 6-rings, which have a symmetric surrounding, give rise to the signal with the small asymmetry parameter. The other 4 sodium ions, near the 8- and 4-rings, which are in a rather asymmetric surrounding, form the central line. This assignment is also justified by the exchange experiment with potassium because of a preferential occupancy of potassium at the 8-rings,[16,20,21] resulting in a decrease of the intensity of the central line (Figure 2c). A further assignment of the 4 sodium ions to the 8-ring and 4-ring cannot be made.

Every detail of the nutation spectra obtained from the hydration experiments can be explained quite easily in terms of changing quadrupole parameters.

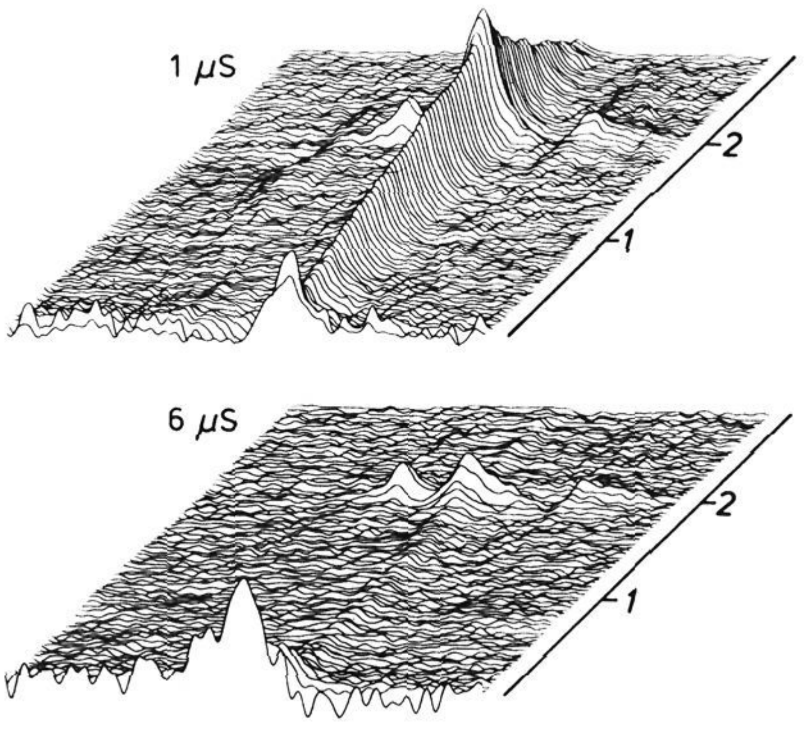

Figure 4. Two-dimensional ^{23}Na spectra of zeolite NaA loaded with 6 water molecules, with different rotary echo times. The upper spectrum is obtained when the nutation pulse is preceded by two pulses of opposite phase and lengths of 1 μs; for the lower spectrum these rotary echo pulses have a length of 6 μs.

We already observed that the first amount of water had only slight effects on the quadrupole doublet, while the shoulder of the central line vanished. This can be explained by a specific absorption of the water molecules by the 4 sodium ions in asymmetric sites, the 8- and 4-ring ions, which has been proposed before by several other authors.[7,8,22]

When a sodium ion in an 8-ring takes up 1 water molecule, the symmetry increases (lower asymmetry parameter, less pronounced shoulder), but the quadrupole interaction is not diminished, so in our two-dimensional experiment the lines remain at $2\omega_{rf}$ along the F_1 dimension. The small decrease in quadrupole splitting of the sodium spins near the 6-rings after the first water molecules have been absorbed at the 8- and/or 4-rings might be explained by a water-induced weakening of the framework strain. Because of the reduced interaction of the 8- and 4-ring sodium ions with lattice oxygen atoms,[23] these atoms tend to relax into the framework,[24] and this results in a small increase in distance between the 6-ring sodium ions and oxygen atoms. The quadrupole interaction of the sodium ions is then expected to decrease.

The effect of an increase in aluminum–sodium distance and relaxing oxygen atoms can be monitored by ^{27}Al NMR (Figure 1). A gradual decrease in line width is observed with increasing water content. Because of a dominant quadrupole interaction of the aluminum nucleus we can conclude that the symmetry of the aluminum is increased on hydration, which is found in many zeolite investigations.[19,23]

When the sodium ions near the 6-rings become hydrated, the symmetry around sodium increases from distorted trigonal to nearly tetrahedal,[25] which means a tremendous decrease of the quadrupolar interaction, as can be viewed from the narrowing in the F_2 dimension and from the increase of the signal at ω_{rf} along F_1 for 5 and more molecules of water per unit cell. At nearly 12 water molecules, the quadrupole doublet has almost disappeared, which means that all 6-ring sodium ions are occupied with 1 water molecule. When hydration continues, all sodium ions become tetrahedrally surrounded, resulting in one resonance line located at ω_{rf} for the total hydrated zeolite.

The central component in the two-dimensional spectra of the zeolite loaded with 6 or more water molecules has a Lorentzian line shape in the F_1 dimension. This indicates a relaxation effect

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