

An NMR Study on the Dynamic Behavior of Triethylamine Included in AFI Crystals — Influence of Acid Sites on the Motional State of Triethylamine Molecules —

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The ^{1}H NMR spin-lattice relaxation times (T_1) of triethylamine (TEA) molecules included in five kinds of AFI crystals with different concentrations of Si atoms in the wall were measured. The temperature and Larmor frequency dependences of T_1 were well explained by introducing a distributed motional correlation time (τ) for the pseudo-C_3 TEA reorientation. An obtained linear decrease in the τ distribution width with an increase of the Si concentration, i.e., the number of Brønsted acid sites, was shown to be related to the orientations of TEA molecules in channels.

Aluminophosphate molecular sieves constructed by AlO_4 and PO_4 tetrahedra located alternately have neutral frameworks because of no acid site on the inner wall, unlike in zeolite. This structure of the host materials enables us to investigate the properties of adsorbates in the homogeneous environment without an acid site. $AlPO_4$-5, a typical example, has one-dimensional homogeneous channels with an effective pore diameter of 0.73 nm in the framework,[1–3] and its structure type is coded as AFI by IZA (International Zeolite Association).[4] SAPO-5 is formed by replacing a part of P and Al atoms in $AlPO_4$-5 by Si, and hence Brønsted acid sites are created on the pore surface in case P atoms are substituted. We can expect that the effects from acid sites on properties of adsorbates can be estimated by comparing data on these two materials. We have already reported differences in the dynamics of triethylamine (TEA),[5] water and acetonitrile molecules[6,7] included in $AlPO_4$-5 and SAPO-5, and showed the effect of the acid site on the adsorbates.

In the preparation of $AlPO_4$-5 and SAPO-5, TEA was used as a structure-directing agent (SDA : template). We showed that TEA molecules reorient isotropically at room temperature in micropores.[5] It is noted that the motion in SAPO-5 was shown to be restricted more than in $AlPO_4$-5 due to the effect of Brønsted acid sites. In a temperature range of 90–300 K, the ^{1}H NMR spectra and T_1 of TEA molecules included in $AlPO_4$-5 and SAPO-5 could be explained by the same motional modes of molecular C_3 and isotropic reorientations, but they showed different temperature dependences in the former mode. We tentatively attributed this difference to the distribution in the motional correlation time (τ)[8] for the molecular C_3 reorientation, and the τ distribution of TEA in SAPO-5 was shown to be smaller than that in $AlPO_4$-5. TEA pseudo-C_3 axes in $AlPO_4$-5 can take random orientations in the pore compared with those in SAPO-5, and hence a wide variety of τ values were expected in $AlPO_4$-5. This result was explained by the difference in the inner-wall structure of capillaries, i.e., the existence of Brønsted acid sites in SAPO-5, but no such site in $AlPO_4$-5. The interaction between lone-pair electrons in TEA molecules and acid site protons seems to be favorable to the orientation of TEA pseudo-C_3 axes to nearly perpendicular to the pore axis.

If the above explanation is acceptable, the τ distribution in the motional correlation time of TEA molecules in AFI is influenced by the amount of Brønsted acid sites. With increasing acid sites, we can expect that the number of TEA molecules adsorbed to acid sites increases, and then the τ distribution decreases.

In order to prove our assumption concerning the origin of the τ distribution and to investigate the structure and dynamics of TEA in $AlPO_4$-5 and SAPO-5 in detail, we intend to prepare SAPO-5 crystals with different concentrations of Brønsted acid sites, and to measure ^{1}H NMR spin-lattice relaxation times (T_1) and second moments of line (M_2) of TEA in these SAPO-5 together with $AlPO_4$-5 crystals. At the same time, this study can also show the adequacy of our previous interpretation[5] of the τ distribution in terms of the fixation of molecular rotational axes by acid sites.

Experimental

$AlPO_4$-5 was synthesized analogously to a method reported[9] using triethylamine (TEA) as SDA by keeping gel mixtures of Al_2O_3, P_2O_5, SiO_2, TEA and H_2O with molar ratios of 1.0:1.03:0.0:1.5:600 at 450 K in a Teflon-lined stainless-steel autoclave for 72 h. Three SAPO-5 crystals having different Si contents: (0.02, 0.05 and 0.10) were synthesized from gel mixtures of Al_2O_3:P_2O_5:SiO_2:TEA:H_2O = 1.0:1.03:0.02–0.10:1.5:600. The obtained fine crystals of 50–100 μm long were dehydrated by keeping them at 413 K in vacuo for 2 days. The samples investigated were observed under a microscope and shown to crystallize in well-shaped hexagonal prisms of roughly analogous size for all samples. These four kinds of specimens with different Si contents of 0.0–0.09 were used for measurements.

Elemental analyses for Al, Si and P on calcined crystals were conducted for determining the Al/Si ratio in the obtained samples with a JEOL JXA-8621 electron probe microanalyser(EPMA). Measurements of the spin-lattice relaxation time (T_1) and the sec-

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ond moment (M_2) of ^{1}H NMR lines were made with a Bruker SXP-100 spectrometer using the inversion recovery method in a range of 90–430 K and the solid echo pulse sequence[10] in a range of 90–295 K, respectively.

Schnabel et al. reported IR mesurements[11] in which a part of TEA molecules in $AlPO_4$-5 are hydrated and changed to triethylammonium hydroxide at 373 K, and completely dehydrated at 423 K. To investigate the existence of hydrated TEA molecules in our specimens, we measured ^{2}H NMR spectra in $AlPO_4$-5, which was synthesized using D_2O as a solvent instead of H_2O, and dried at 413 K. Since we observed no ^{2}H signal from $[(C_2H_5)_3ND]^+$ and OD^- at all, our specimens were considered to be almost dehydrated and only contain TEA molecules.

Result and Discussion

Table 1 gives the Si/Al ratios in the starting gel mixtures and the obtained crystals determined by an EPMA quantitative analysis, the amounts of SDA triethylamine molecules per unit cell calculated from the results of C, H, N elemental analysis, and the Si/TEA ratios calculated from these values for four kinds of samples, named **A** to **D**. Samples **A** and **D** were the same specimens as previously reported.[5] Since it was reported that Si substitutes only P sites in samples with not high Si contents,[12,13] the Si/Al ratios in our samples are expected to correspond to the concentration of Brønsted acid sites.

Figure 1 shows temperature dependences of the second moment (M_2) of ^{1}H NMR lines for four specimens showing similar M_2 changes to each other except for **A** ($AlPO_4$-5), although some scatter was observed in M_2 values above 220 K. Upon heating, an M_2 of $(3.8 \pm 0.4) \times 10^{-2}$ mT^2 observed in **A** at 90 K gradually decreased to $(0.5 \pm 0.1) \times 10^{-2}$ mT^2 above 210 K, while, in **B**–**D** (SAPO-5), a wide spectrum of $(10 \pm 3) \times 10^{-2}$ mT^2 observed around 100 K became (0.8–2.0) $\times 10^{-2}$ mT^2 above 220 K. Referring to the theoretical M_2 values for an isolated TEA molecule,[5,14–16] M_2 values at 90 K observed in all systems smaller than the theoretical value of 11.9×10^{-2} mT^2 calculated for the CH_3 reorientation imply the onset of this motion even at this temperature. That M_2 gradually decreased upon heating to (1–2) $\times 10^{-2}$ mT^2 is explainable by further excitations of large amplitude motions such as the C_3 reorientation of the whole molecule. The small M_2 values observed at room temperature in all samples can be explained by the onset of an isotropic molecular reorientation giving an vanishing M_2 in an isolated molecule for the following reasons: We have shown[5] the excitation of this motion by observing the narrow spectra of quadrupolar ^{14}N NMR in TEA

Table 1. Si/Al Ratios in AFI Frames Determined by EPMA Quantitative Analysis, the Number of SDA Triethylamine Molecules per AFI Unit Cell, and Si/TEA Ratios Calculated from These Values for Specimens **A**–**D**

Specimen	**A**: $AlPO_4$-5	**B**: SAPO-5	**C**: SAPO-5	**D**: SAPO-5
Si/Al ratio (starting gel)*	0	0.02	0.05	0.10
Si/Al ratio (crystals)*	≈0	0.023	0.041	0.091
TEA per unit cell	—	1.10	1.13	1.18
Calculated Si/TEA ratio	≈0	0.25	0.44	0.93

∗ Obtained Si/Al ratios approximately correspond to concentrations of Brønsted acid sites in crystal micropores.

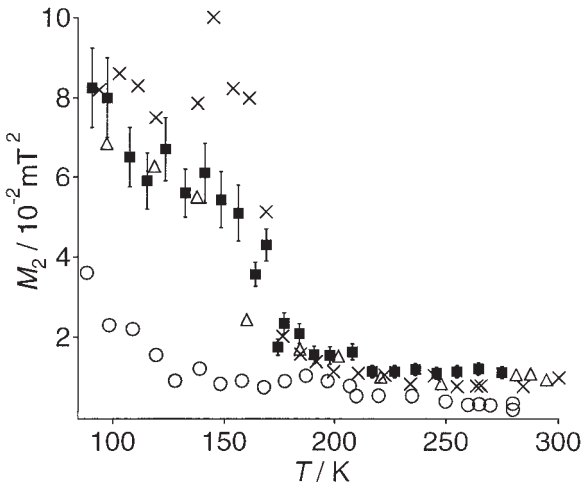

Fig. 1. Temperature dependences of second moments (M_2) of ^{1}H NMR adsorptions observed for triethylamine (TEA) included in four kinds of AFI crystals. **A**: $AlPO_4$-5 (○), **B**: SAPO-5 (△), **C**: SAPO-5 (×), **D**: SAPO-5 (■). **A** and **D** are previously reported data.[5] Error bars are shown only on data of Sample **D** and roughly the same for the other samples.

adsorbed in $AlPO_4$-5 and SAPO-5. At the same time, we reported that observed small M_2 values at room temperature can be attributed to M_2 from Brønsted acid sites, and also P and Al atoms in the wall. M_2 in **A** ($AlPO_4$-5) observed at room temperature could accordingly be explained only by the contribution from P and Al. As for **B**–**D** (SAPO-5), since the observed M_2 values at around room temperature were roughly proportional to the Si/Al ratio in SAPO-5, the M_2 contribution is attributable to protons in Brønsted acid sites on the wall. These results show that a small amount of Brønsted acid protons have a marked effect on the dynamics of the TEA molecules, although the TEA in all specimens shows an isotropic reorientation at room temperature.

Figures 2(A)–2(D) show temperature dependences of ^{1}H NMR spin-lattice relaxation times (T_1) observed in **A**–**D**, where data for **A** and **D** have already been reported.[5] For all specimens, we measured ^{1}H T_1 at two Larmor frequencies to see the frequency dependence. All four specimens showed two T_1 minima at 135–150 K and ca. 280 K, which we attributed to the pseudo-C_3 axis and the isotropic reorientation of TEA molecules, respectively, by referring to our previous report on **A** and **D**,[5] and also the foregoing M_2 values measured in this work. It is noted that similar temperature dependences in T_1 to each other were observed in all SAPO-5 specimens (**B**–**D**), but **A** behaved differently from the others, i.e., the T_1 value at the high-temperature minimum in **A** was longer than those in the other three specimens, while the low-temperature minimum value in **A** was shorter than in the others.

The spin-lattice relaxation caused by averaging magnetic dipolar interactions due to a single molecular motion is expressed by the BPP equation:[17,18]

$$T_1^{-1} = \frac{2}{3}\gamma^2 \Delta M_2 \left(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2} \right), \qquad (1)$$

where γ, ΔM_2, τ and ω are the magnetogyric ratio of a proton,

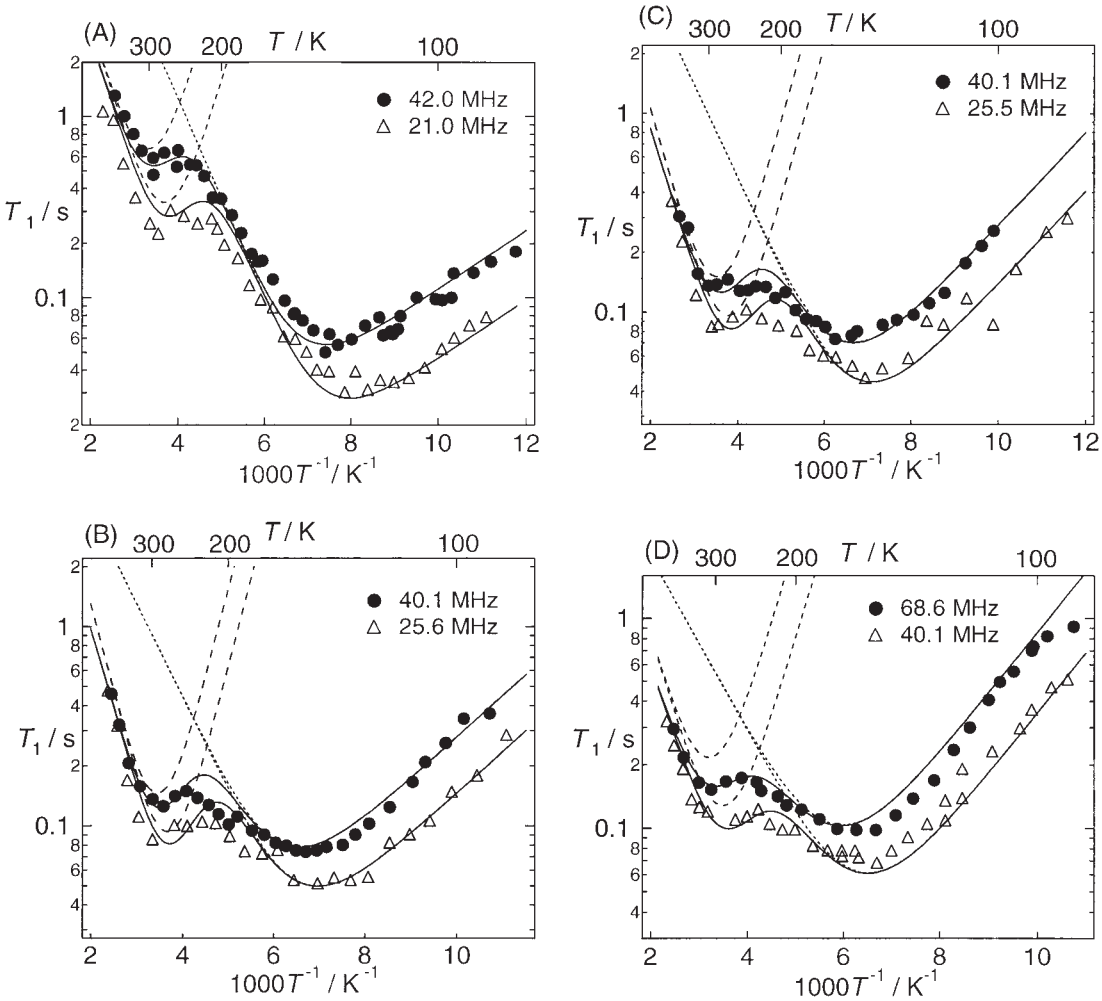

Fig. 2. Temperature dependences of ^{1}H NMR spin-lattice relaxation times (T_1) observed for triethylamine (TEA) included five kinds of AFI crystals **A**–**D** shown in (A)–(D), respectively. The best-fitted calculated curves expressed by solid lines are the sum of two T_1 components given by dotted and broken lines.

the M_2 reduction through motion, the correlation time of the motion, and the Larmor frequency, respectively. τ can be expressed by the Arrhenius equation given by

$$\tau = \tau_0 \exp \frac{E_a}{RT}. \tag{2}$$

Here, τ_0 and E_a denote the correlation time in the limit of infinite temperature and the activation energy of the motion, respectively. Eq. 1 gives a symmetric $\log T_1$ curve plotted against T^{-1} and T_1 values depending on ω^2 in the temperature range below the minimum.

For the molecular motions in inhomogeneous systems such as inclusion compounds, it has been observed that the correlation time (τ) often distributes widely, resulting in the frequency dependence of T_1 deviating from the ω^2 rule. In fact, the present samples **A**–**D** afforded ^{1}H T_1 which are unexplainable by the ω^2 rule below room temperature. In our previous report,[5] ^{1}H T_1 values observed for TEA in $AlPO_4$-5 and SAPO-5 corresponding to the present samples **A** and **D**, respectively, were well reproduced by introducing the Cole–Davidson type distribution[8] in τ. This τ distribution is given by

$$g(\tau) = \frac{\sin \beta\pi}{\pi} \left(\frac{\tau}{\tau_c - \tau} \right)^{\beta} \quad \tau \le \tau_c$$
$$= 0 \quad \tau > \tau_c \tag{3}$$

where τ_c is the cut-off time of the function $g(\tau)$, and β ($0 < \beta \le 1$) means the distribution width giving a measure of the relative weight of the correlation time shorter than τ_c. In the limit of $\beta = 1$, a single correlation time, as used in BPP theory, is obtained. The distribution width becomes wider with decreasing the value of β. Using Eq. 3, T_1 is given by[19]

$$T_1^{-1} = \frac{2}{3} \gamma^2 \Delta M_2 \left\{ \frac{\tau_c \sin(\beta \tan^{-1} \omega\tau_c)}{\omega\tau_c (1 + \omega^2 \tau_c^2)^{\beta/2}} + \frac{2\tau_c \sin(\beta \tan^{-1} 2\omega\tau_c)}{\omega\tau_c (1 + 4\omega^2 \tau_c^2)^{\beta/2}} \right\}. \tag{4}$$

Here, we fitted the T_1 data obtained in samples **B** and **C** to Eqs. 1 and 4.

The observed T_1 values consisting of two T_1 minima were fitted by superimposing two relaxation mechanisms. The high-temperature relaxation mode **1** assigned to the TEA iso-

tropic reorientation was assumed to be expressed by the usual BPP-type relaxation. This is because the T_1 frequency dependence in the low-temperature side of the minimum, which gives information about the τ distribution width, was unclear, owing to an overlap with the other T_1 minimum. T_1 of the low-temperature relaxation mode **2** due to the C_3 reorientation was explained by the Cole–Davidson type τ distribution, because it could be explained well by introducing the τ distribution, but gave a poor fit to the BPP-type frequency dependence. The best-fitted T_1 for each sample and the determined motional parameters are shown in Fig. 2(A)–2(D) and Table 2, respectively. From Table 2, we can see the following relations between the obtained values of parameters and the Si content in the samples: 1) ΔM_2 values for mode **2** decreased with increasing the Si content while those in mode **1** increased, 2) β values for mode **2** became larger with an increase of the Si content, and 3) the activation energies (E_a) for mode **1** were almost constant, while those of mode **2** decreased with increasing Si content. The 2nd relationship implies that the presence of the Brønsted acid site contributes to the formation of a homogeneous environment for the TEA C_3 reorientation.

Considering these results, we can propose the following model for the C_3 reorientation (mode **2**) of TEA molecules in AFI crystals below ca. 200 K, where no isotropic reorientation contributes to ^{1}H T_1. As shown in Fig. 3, this model is based on the assumption that lone-pair electrons on an N atom in a TEA molecule are attracted to H atoms in Brønsted acid sites in case the acid site on the micropore wall is located close to the TEA molecule, while other molecules far from acid sites can orient arbitrarily. This model can well explain the data in Table 2 showing that an increase in the number of acid site results in a decrease in the τ distribution, i.e., an increase in the β value. The large ΔM_2 for the C_3 reorientation in **A** compared with that in the others implies a large amplitude of this motion in **A**, probably because tumbling of the pseudo-C_3 rotation axis takes place together with the C_3 reorientation owing to the free orientation of TEA in micropores, whereas its axis in **B**–**D** should be fixed at the acid site. This explanation can be supported by ΔM_2 in mode **1** assigned to the isotropic reorientation, giving a much small ΔM_2 of 0.59×10^{-2} mT^2 in **A** compared with $(2.5–2.9) \times 10^{-2}$ mT^2 in the others. This implies that the TEA molecules in **A** partly obtain their motional freedom for isotropic rotation at low temperatures much more than in the others, in agreement with the large amplitude of the low-temperature motion in **A**. This is also consistent with the small M_2 values observed in **A** at high temperatures compared with those in **B**–**D** as shown in Fig. 1. A linear increase in β with the number of acid sites shown in Fig. 4 is explainable by a model where, in samples **B** and **C**, some TEA molecules are fixed on acid sites, while the others are free, as expected from the Si/TEA ratios given in Table 1. It should be noted that the activation energies for the isotropic reorientation in all specimens are close to each other. We can attribute this result to the barrier height determined by the interactions with the chan-

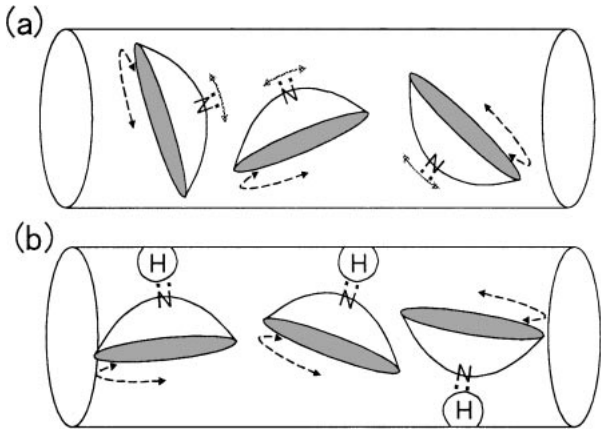

Fig. 3. Schematical two limiting models for orientations of TEA molecules in AFI pores, (a) $AlPO_4$-5, no Si content in AFI crystals where TEA molecules can orient arbitrarily. (b) In highly silicated AFI in which respective TEA molecules are attracted to nearest Brønsted acid sites.

Table 2. Motional Parameters for Two Kinds of Molecular Motions in Triethylamine (TEA) Molecules Determined from ^{1}H NMR Spin-Lattice Relaxation Times Observed in Samples **A**–**D** for (a) the High-Temperature Mode **1** and (b) the Low-Temperature Mode **2**

(a)*

Specimen	**A**: $AlPO_4$-5	**B**: SAPO-5	**C**: SAPO-5	**D**: SAPO-5
$\Delta M_2/10^{-2}$ mT^2	0.59 ± 0.2	2.5 ± 0.5	2.5 ± 0.5	2.9 ± 0.5
E_a/kJ mol^{-1}	15.0 ± 1	17.0 ± 1	15.0 ± 1	15.0 ± 1
$\tau_0/10^{-12}$ s	5.9 ± 0.5	2.5 ± 0.3	4.6 ± 0.5	5.0 ± 0.5

(b)**

Specimen	**A**: $AlPO_4$-5	**B**: SAPO-5	**C**: SAPO-5	**D**: SAPO-5
$\Delta M_2/10^{-2}$ mT^2	13.0 ± 1	8.2 ± 1	7.3 ± 1	7.2 ± 1
E_a/kJ mol^{-1}	10.5 ± 1	10.0 ± 0.7	9.0 ± 0.7	8.0 ± 0.7
$\tau_0/10^{-12}$ s	0.54 ± 0.06	2.2 ± 0.3	3.2 ± 0.4	6.2 ± 0.6
β	0.30 ± 0.05	0.40 ± 0.07	0.50 ± 0.08	0.70 ± 0.10

* Fitted by the BPP-type equation[17,18] and assigned to the TEA isotropic reorientation.

** Fitted by applying the Cole–Davidson τ distribution and assigned to the pseudo-C_3 reorientation of TEA molecules.

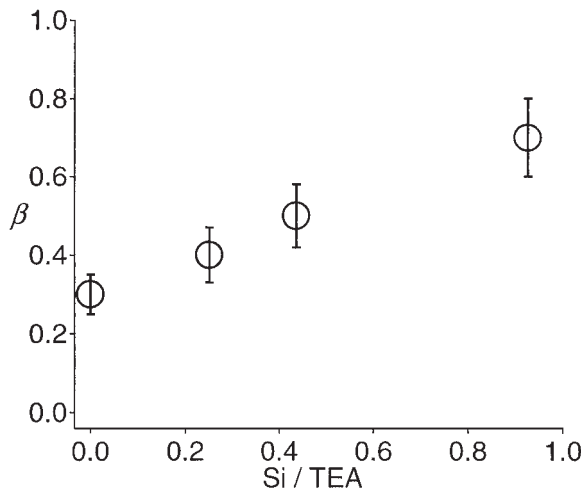

Fig. 4. A relation between the distribution parameter β of Cole–Davidson-type τ and the ratio of the number of Si atoms per TEA molecule.

nel wall. This explanation is acceptable from the pore size of 0.73 nm being close to the long diameter of 0.77 nm in a TEA molecule. On the other hand, a linear decrease was observed in the activation energies for the C_3 reorientation with the number of acid sites (Table 2(b)). This is also explainable by the same model that two states of TEA molecules, i.e., fixed on acid sites and free. $E_a = 10.5 \pm 1.0$ kJ mol^{-1} obtained in **A** is not simply the energy of the C_3 reorientation, but contains the contribution from the tumbling of the pseudo-C_3 axis as discussed above. This seems to be the reason for the high E_a in **A**, as compared with those in **B–D** where the number of TEA molecules fixed on acid sites increases.

Popescu et al. reported on the orientation of C_3 axes in TEA molecules in $AlPO_4$-5 from polarized IR spectra,[20] and showed that the C_3 axes orient perpendicular to the channel axis at 500 K. On the other hand, a head-to-tail structure along the 1-D channel was supposed from a Rietveld-analysis for neutron powder diffraction.[21] These results are consistent with the present NMR studies revealing isotropic TEA rotation at room temperature in both $AlPO_4$-5 and SAPO-5. This is because the IR and Rietveld-analysis data require the presence of the preferred orientations for which the direction molecules are most stable, and, not necessarily exclude the population of molecules with different orientations. In the NMR time scale much slower than that in vibrations, molecules are expected to take isotropic orientations although some preference of the orientations could exist in the inhomogeneous crystal field as shown in the present NMR study, giving τ distributions.

Conclusion

From measurements of the ^{1}H NMR T_1 for TEA molecules adsorbed in four kinds of AFI crystals with different concentrations of Brønsted acid sites on the wall, it was shown that the distribution width of the correlation time (τ) in the pseudo-C_3 reorientation of TEA molecules decreases linearly with an increase in the concentration of the acid sites. This result is explainable by considering two kinds of TEA molecules, i.e., one is fixed on the acid sites, and the other is free and has small interactions with them. The former molecules bonded to the acid hydrogen through the lone-pair electrons allowed to reorient about the axis roughly perpendicular to the 1-D channel direction, while the free molecules can rotate about axes with arbitrary directions with distributed potential barriers. The linear increase in β with the acid site concentration is attributable to the change in the ratio of these two kinds of TEA molecules included in AFI crystals.

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