Broad-Line and High-Resolution NMR Studies Concerning the Hydroxonium Ion in HZSM-5 Zeolites

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Brönsted sites must be able to react with adsorbed water molecules to form hydroxonium ions. This study shows by line-shape simulation of the $^1$H NMR signal measured at 4 K that for water concentrations about equal to the concentration of bridging hydroxyl groups in defect-free HZSM-5 zeolites two configurations exist: water molecules hydrogen-bonded to the bridging OH group and the hydroxonium ion. The result is confirmed by $^1$H MAS NMR investigations at room temperature. In addition, $^{27}$Al and $^{29}$Si MAS NMR were used to characterize HZSM-5 zeolites under study synthesized without template, with TPA*, with butylamine as template. All samples contain 4 bridging hydroxyl groups per unit cell. For the zeolite synthesized with butylamine and loaded with 2, 4, and 8.4 water molecules per unit cell the concentration of hydroxonium ions per unit cell is 0.28, 0.64, and 1.56, respectively.

Introduction

The hydroxonium ion is the classic Brönsted acid in aqueous solutions. Therefore, H zeolites known to be strong solid acids should also contain hydroxonium ions in the hydrated form. Jentys et al.\textsuperscript{(1)} attributed IR bands arising upon hydration of the HZSM-5 zeolite to hydroxonium ions. They excluded the possibility that the adsorbed water molecules are hydrogen-bonded to bridging hydroxyl groups, because this adsorbate structure should lead to only one band of perturbed hydroxyl groups as opposed to the various bands observed; but they did not discuss the coexistence of both the ionic and the hydrogen-bonded physisorption structure as well.\textsuperscript{(1)} Vega and Luz\textsuperscript{(2)} studied H–RHO type zeolites with $^1$H MAS NMR and found after addition of small amounts of water to activated samples a narrow peak at 5.9 ppm and a broad signal at ca. 4 ppm, while at the highest loadings the spectrum consists of two narrow peaks at 4.6 and 9.1 ppm. Only the signal at 4.6 ppm could be unambiguously identified as water physically adsorbed in the zeolite cavities. Scholle et al.\textsuperscript{(3)} studied water adsorption on HZSM-5 and assigned a broad line at 6 ppm to protons of Brönsted acid sites exchanging rapidly with protons of the water molecules adsorbed on these sites. Mastikhin et al.\textsuperscript{(4)} explained a shift of the $^1$H NMR line upon hydration of H–Y zeolite a fast proton exchange between bridging OH groups, water molecules, and hydroxonium ions. Hunger et al.\textsuperscript{(5)} studied H–Y zeolites and amorphous silica–alumina and discussed two lines in the $^1$H MAS NMR spectra: a line at ca. 6.5 ppm is caused by water adsorption

\footnotesize
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on Lewis acid sites, and a line shifting upon weak hydration from 4.3 ppm to larger values of the chemical shift was interpreted as a fast proton exchange between water molecules, bridging OH groups, and hydroxonium ions. The probability of finding a water molecule in the state of a hydroxonium ion is given as 0.20-0.30 for the H-Y zeolite hydrated with one water molecule per bridging OH group.

The solid-state line shape of the $^1$H NMR is different for hydroxonium ions and water molecules hydrogen-bonded to bridging OH groups. Doremieux-Morin et al. demonstrated that line-shape simulation of spectra measured at low temperature is a good tool to determine concentrations of species like isolated hydroxyl groups, isolated water molecules, OH groups bonded to water molecules, and hydroxonium ions in a mixture of all species.

It is the aim of this study to get quantitative information about the concentration of different hydroxyl groups, of water molecules hydrogen-bonded to bridging OH groups, of hydroxonium ions, and of physisorbed water molecules in HZSM-5 zeolite using both $^1$H MAS NMR at room temperature and $^1$H NMR line-shape simulation at 4 K. For comparison, three zeolites HZSM-5 with a common framework Si/Al ratio of 23 ± 3 were studied. One of them contains only very few defects (denoted as Bu), another one has been partially dealuminated (denoted as De), and the third contains a large number of silanol groups (denoted as TPA).

The samples were also characterized by $^{27}$Al and $^{29}$Si MAS NMR.

Experimental Section

Samples. The three HZSM-5 zeolites (template-free synthesized and mildly hydrothermally steamed, De; synthesized with TPA*, TPA; and with butylamine, Bu) contain 4 framework aluminum and about 4 bridging hydroxyl groups per unit cell. They were synthesized as described in ref. $^{11}$. Na$^+$/H$^+$ ion exchange was carried out at room temperature with an aqueous solution of 0.5 M HCl. Hydrothermal treatment of the template-free synthesized zeolite (Si/Al ≈ 15 before dealumination) was performed in a horizontal tubular quartz furnace of 50-mm i.d. with a maximum bed depth of 8 mm. Steaming of this sample was carried out at 810 K for 150 min at a pressure of 7 kPa, which was adjusted by the temperature of the water bath, through which the nitrogen was flowing. This zeolite contains 2 Al/uc on extraframework positions since it was not washed after steaming. The zeolites synthesized with template were calcined in air at 870 K before hydrogen exchange.

NMR Methods. $^{29}$Si MAS NMR measurements were generally carried out on rehydrated samples, which had been kept in a desiccator for 48 h over aqueous NH$_4$Cl. The same samples were used for the determination of the framework Si/Al ratio by $^{27}$Al MAS NMR. The $^1$H NMR measurements the samples were subjected to shallow-bed activation in a glass tube of 5.5- or 4.0-mm i.d. with a maximum bed depth of 8 mm. Steaming of this sample was carried out at 810 K for 150 min at a pressure of 7 kPa, which was adjusted by the temperature of the water bath, through which the nitrogen was flowing. This zeolite contains 2 Al/uc on extraframework positions since it was not washed after steaming. The zeolites synthesized with template were calcined in air at 870 K before hydrogen exchange.

$^{27}$Al MAS NMR. Aluminum spectra were run with a MAS frequency of 15 kHz to avoid the superposition of the sideband of the framework aluminum signal (54 ppm) and the signal of aluminum hexaquo complexes at ~2 ppm. Weakly hydrated samples (ca. 4 H$_2$O/uc) give badly resolved spectra, ca. 100 ppm broad, and half of the aluminum nuclei are NMR invisible. Spectra of the fully hydrated samples consist of two lines (line width 6 ppm) and show the total aluminum content of the zeolite. The spectrum of the dealuminated zeolite additionally contains a broadband at about ca. 40 ppm due to tetrahedrally coordinated extraframework aluminum. The concentrations of extraframework aluminum were determined by comparison of the line intensities with those of a reference sample. The values are given in Table II together with the concentrations of Al(H$_2$O)$_6^{3+}$ in the fully hydrated samples.

$^{29}$Si MAS NMR. Silicon spectra of the hydrated samples consist of two lines at ~111.5 and ~106.5 ppm due to Si(4Si) and Si(3Si,1Al) groupings, respectively. The concentrations of framework aluminum atoms were calculated from the convoluted spectra, using Gaussian line shapes (cf. ref 12). The results indicate a silicon-to-aluminum ratio of 23 ± 3 for all the samples.

$^1$H Broad-Line NMR. Figure 1 shows (one-half of) the derived $^1$H NMR broad-line spectrum of Bu-HZSM-5 zeolite loaded with 8.4 H$_2$O/uc; X, experimental spectrum; —, fitted spectrum; O, hydroxonium ions; O, (H$_2$O-HO); Δ, water molecules; —, free OH groups.

![Figure 1](image-url)
Figure 2. 'H NMR broad-line spectra for Bu samples loaded with 2 H₂O/uc, A; 4 H₂O/uc, B; 6 H₂O/uc, C; 8.4 H₂O/uc, D; 14.4 H₂O/uc, E, experimental (x) and fitted (—) spectra.

Finally, a signal of hydroxyl groups which do not interact with water molecules and give rise to a relatively narrow Lorentzian and Gaussian-like signal. The coefficient of the Gaussian enlargement function for the line-shape calculations takes into account dipolar interaction between groupings and with framework aluminum atoms. The second moments of the functions lie in the range (16.6-27.4) × 10^4 T². This means that water molecules adsorbed on extraframework aluminum species were included in the fitting procedure.

Figure 2 shows that experimental and calculated spectra of Bu zeolites with different amounts of adsorbed water are in good agreement. The values used of the H-H distance for the lineshape calculations are 162 pm in water molecules and give rise to a relatively narrow Lorentzian and Gaussian-like signal. The coefficient of the Gaussian enlargement function for the line-shape calculations takes into account dipolar interaction between groupings and with framework aluminum atoms. The second moments of the functions lie in the range (16.6-27.4) × 10^4 T². This means that water molecules adsorbed on extraframework aluminum species were included in the fitting procedure.

The line fitting gives the relative concentration of each configuration. Absolute concentrations given in Table I were calculated by using the known total number of protons determined as the sum of OH groups in the dehydrated samples (see Table II) and the number of adsorbed water molecules. Table I shows that all samples contain hydroxonium ions. Their concentration increases with increasing water loading. For relatively low hydration the water molecules are preferentially hydrogen-bonded to hydroxyl groups. Water molecules adsorbed on extraframework aluminum species cannot be observed. Up to the loading of 4 H₂O/uc the sum of hydroxonium ions and water molecules attached to hydroxyl groups is about equal to the number of loaded molecules. All spectra show the signal of isolated hydroxyl groups. Their concentration is independent of the amount of adsorbed water and agrees with the concentration of silanol groups determined on the dehydrated sample (see Table II) for De and Bu zeolites. The hydrated TPA zeolites show the concentration of isolated OH groups slightly increased in comparison with the concentrations of silanol groups in the dehydrated sample. Water molecules not attached to hydroxyl groups appear in all zeolites with increasing concentration if the number of loaded water molecules exceeds the number of bridging hydroxyl groups.

'H MAS NMR. Figures 3A, 4A, and 5A show the 'H MAS NMR spectra of the dehydrated zeolites which consist, in agreement with previous studies of HZSM-5 zeolites,¹¹,¹⁷,¹⁸ of two signals at 2.0 and 4.3 ppm due to silanol groups and bridging OH

Table I: Concentrations of Hydroxonium Ions, H₂O⁺, Hydrogen-Bonded Water Molecules, H₂O-OH, Other Water Molecules, H₂O, and Isolated Hydroxy Groups Depending on the Total Number of Protons (see Results)∗

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loaded</th>
<th>H₂O⁺</th>
<th>H₂O-OH</th>
<th>H₂O</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>De</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td>De</td>
<td>3.2</td>
<td>0.76±0.15</td>
<td>2.6±0.5</td>
<td>0</td>
<td>1.5±0.3</td>
</tr>
<tr>
<td>De</td>
<td>5.2</td>
<td>0.76±0.15</td>
<td>3.6±0.7</td>
<td>0.8±0.2</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td>De</td>
<td>7.6</td>
<td>1.00±0.20</td>
<td>2.7±0.5</td>
<td>4.0±0.8</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>TPA</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.0</td>
</tr>
<tr>
<td>TPA</td>
<td>1.85</td>
<td>0.16±0.05</td>
<td>0.9±0.2</td>
<td>0</td>
<td>6.6±1.3</td>
</tr>
<tr>
<td>TPA</td>
<td>3.35</td>
<td>0.44±0.09</td>
<td>2.6±0.5</td>
<td>0</td>
<td>3.8±0.8</td>
</tr>
<tr>
<td>TPA</td>
<td>5.2</td>
<td>0.56±0.11</td>
<td>3.7±0.7</td>
<td>0</td>
<td>3.6±0.7</td>
</tr>
<tr>
<td>TPA</td>
<td>6.0</td>
<td>0.6±0.12</td>
<td>4.2±0.8</td>
<td>0</td>
<td>3.6±0.7</td>
</tr>
<tr>
<td>Bu</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.0</td>
</tr>
<tr>
<td>Bu</td>
<td>2.0</td>
<td>0.28±0.06</td>
<td>2.3±0.5</td>
<td>0</td>
<td>0.8±0.2</td>
</tr>
<tr>
<td>Bu</td>
<td>4.0</td>
<td>0.64±0.13</td>
<td>2.5±0.5</td>
<td>1.4±0.3</td>
<td>0.5±0.2</td>
</tr>
<tr>
<td>Bu</td>
<td>6.0</td>
<td>0.84±0.17</td>
<td>2.2±0.4</td>
<td>3.4±0.7</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td>Bu</td>
<td>8.4</td>
<td>1.56±0.31</td>
<td>1.4±0.3</td>
<td>5.8±1.2</td>
<td>0.5±0.2</td>
</tr>
</tbody>
</table>

*All concentrations are given in species per unit cell.

Figure 3. 'H MAS NMR spectra of De-ZSM-5 zeolites: unloaded zeolite, A; 3.2 H₂O/uc, B; 7.6 H₂O/uc, C; 30 H₂O/uc, D. Asterisks denote spinning sidebands.

The template-free synthesized and mildly steamed zeolite (De-ZSM-5) also contains 2 Al/uc in extraframework positions.

The spectra in the hydrated sample consist of three lines: besides the above-mentioned main signal and the signal of silanol groups, a weak signal at 9.2 ppm with relatively strong sidebands can be observed and ascribed to Al(H₂O)₆³⁺ complexes. Akitt et al. found the signal of the aluminum hexaaquo cation dissolved in deuterioacetone at ca. 10 ppm. The concentrations of the

\[ \text{concentration in species per unit cell} \]

<table>
<thead>
<tr>
<th>sample</th>
<th>framework Al</th>
<th>bridging OH</th>
<th>SiOH</th>
<th>²⁷Al NMR</th>
<th>¹H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-HZSM-5</td>
<td>4.0 ± 0.4</td>
<td>4.0 ± 0.4</td>
<td>1.0</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>TPA-HZSM-5</td>
<td>4.0 ± 0.4</td>
<td>4.0 ± 0.4</td>
<td>2.0</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Bu-HZSM-5</td>
<td>4.0 ± 0.4</td>
<td>4.0 ± 0.4</td>
<td>0.5</td>
<td>0.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*The template-free synthesized and mildly steamed zeolite (De-ZSM-5) also contains 2 Al/uc in extraframework positions.

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**Figure 4.** ¹H MAS NMR spectra of TPA-ZSM-5 zeolites: unloaded zeolite, A; 4 H₂O/uc, B; 8 H₂O/uc, C; 30 H₂O/uc, D. Asterisks denote spinning sidebands.

**Figure 5.** ¹H MAS NMR spectra of Bu-ZSM-5 zeolites: unloaded zeolite, A; 4 H₂O/uc, B; 8 H₂O/uc, C; 30 H₂O/uc, D. Asterisks denote spinning sidebands.

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complexes determined from spectra of samples loaded with 8–12 water molecules per unit cell are given in Table II. Table II shows that the number of protons in species giving rise to the lines at 2.0 and 9.2 ppm can be neglected in comparison with those giving rise to the main signal at 5–7 ppm, except for the unloaded TPA zeolite. Therefore, the center of gravity of the total signal is representative of the chemical shift of the main signal. The corresponding values are given in Table III. These values, δ = 5.5–9.9 ppm, are significantly larger than values (ca. 5 ppm) that can be expected for nonionic water structures. Therefore, the existence of hydroxonium ions, which give rise to larger values of the chemical shift, must be taken into consideration.

The combined application of Hahn's echo and MAS techniques requires pulse distances that are multiples of the MAS period, but also those components of the signal which have a very large value of $T_2$ (extreme narrowing by motion) are not decreased in the signal. Figure 6 shows that spectra measured with the MAS + echo technique give a better resolution, but the proportionality between the intensity of the signal (area under the line) and the concentration of the species giving rise to the signal is lost. The spectra of the weakly hydrated De zeolite (5.2 H$_2$O/uc, Figure 6A) give a broad strong signal at 8.7 ppm and a narrow signal at 2 ppm with MAS and two narrow signals at 9.2 and 2.0 ppm for MAS + echo. For higher loading the signal in the 5–7 ppm range is not suppressed, but the signal due to the hexaaquo complex is resolved (e.g., Bu zeolite with 8.4 H$_2$O/uc, Figure 6B). The spectra of the fully hydrated TPA zeolite (Figure 6C) show that the signal of the silanol groups is not shifted by the water loading.

**Discussion**

Hydroxonium ions could be found in all HZSM-5 zeolites studied. Their relative concentration is minimum for TPA zeolite. The spectra of this zeolite show no signal of water, which is not hydrogen-bonded. The isolated OH groups are inaccessible for water molecules, because their $^1$H MAS NMR signal is not changed even upon strong hydration.

The concentration of Al(H$_2$O)$_6^{3+}$ species found by $^1$H MAS NMR shows no correlation with the concentration of the total extraframework aluminum (Table II). For TPA and De the same concentrations were found, but actually only the De zeolite contains a significant amount of extraframework aluminum (Table II), which is responsible for the enhanced catalytic activity of this zeolite.$^{19}$ MAS NMR experiments have shown that Bu zeolite contains very few defects, which can be neglected for the study concerning the hydroxonium ion.

Various physisorbed and ionic structures of water absorption on H zeolite have been proposed in the literature: a quantum chemical ab initio study of Sauer et al.$^{22}$ gave two structures of a complex consisting of H$_2$O and H$_2$Si-OH-Al(OH)$_2$O-SiH$_3$ model representing one water molecule adsorbed on a Brønsted
of OH-Al(OH)₃ with NH₃ for a faujasite model with a Si:Al ratio of 1:1. But the stability of the ion complex was greatly enhanced when an external field simulating an embedded cluster was added to the Hamiltonian. Jentys et al. discussed, in an IR study on HZSM-5 zeolite, three possible adsorbate structures (Figure 7, III, IV, V). The stochiometry between OH groups and adsorbed water determined by means of thermogravimetry in the range of equilibrium 10⁻³-10⁻² mbar pressure supported the attribution of the IR bands to H₃O⁺ (structure III), whereas the change in the spectrum after the increase of the equilibrium pressure (above 10⁻¹ mbar) was interpreted as growth of the ionic water clusters (structure IV). The physiosorption structure (V) was excluded because this adsorbate should lead to only one band of perturbed hydroxyl groups, in disagreement with the various bands observed.

The present low-temperature NMR supports the coexistence of the ionic and the hydrogen-bonded physiosorption structure (Figure 7, I and II, respectively). No significant amount of water without interaction with OH groups is observed up to a loading of one water molecule per bridging OH group (Table I). The reaction can be described by

\[
\text{ZOH} + H_2O \rightarrow \text{ZOH} \cdots H_2O \rightarrow \text{ZO}^- \cdots H_3O^+ 
\]

ZOH denotes the zeolitic framework with a bridging OH group. The values of Table I show that the free energy is minimum for the hydrogen-bonded physiosorption complex. The concentration of hydroxonium ions increases with the concentration of adsorbed water molecules. This cannot be quantitatively described by a simple equation for two reasons: the confinement of the species in the zeolite channel is different from the behavior in solution, and our model calculations do not include ionic water clusters. We were unable to get a good fit of the spectra of sample Bu with 22 H₂O/uc, whereas the spectrum corresponding to 14 H₂O/uc can be fitted satisfactorily (see Figure 2). Strongly hydrated samples probably contain hydroxonium hydrates. Therefore, we determined the hydroxonium concentrations from the fitted spectra only for samples containing not more than two water per bridging OH group (Table I).

The determination of the concentrations of three species (H₂O⁺, H₂O-HO, and H₂O) from the average chemical shift \(\delta_n\) measured at room temperature by \(^1\)H MAS NMR is rather problematic. The value of the chemical shift \(\delta\) of a line resulting from exchange between sites with different chemical shifts is the weighted average of the \(\delta\) values of these sites, following the equation

\[
\delta_n = \sum_i n_i \delta_i 
\]

with \(n\) as relative amounts of protons in corresponding species and \(i\) for the following species: isolated bridging hydroxyl group (1), hydroxonium ion (2), water hydrogen-bonded to a bridging hydroxyl group (3), and water without interaction with bridging hydroxyl groups (4).

A quantitative discussion of the chemical shift of protons exchanging between sites in water, bridging OH, and hydroxonium ions was performed for \(H-Y\) zeolites.6 The problem of a quantitative discussion is that in the simplest case of weak hydration of an ideal hydrogen zeolite (without silanol groups and extraneous framework aluminum) the following adsorbate structure must be taken into account: water hydrogen-bonded to bridging hydroxyl groups, hydroxonium ion doubly hydrogen-bonded to framework oxygen, as proposed by Sauer (see Figure 7, I), and water hydrogen-bonded to another water molecule or ion or to the framework oxygen. No exact reference is available in the literature for any of these sites. Only rough estimates can be given.

The \(^1\)H shift of water in silicalite with 8 H₂O/uc (3 ppm) will be used here as a reference for water molecules bonded to each other or physiosorbed on framework oxygen atoms (group 4). The chemical shift of an isolated water molecule is 0.31 ppm,24 that for water molecules hydrogen-bonded to other water molecules in bulk water is 4.78 ppm.24 That means that the hydrogen bonds shift the resonance in this case about 4.4 ppm. Therefore, with \(\delta = 4.3\) ppm for the isolated bridging hydroxyl proton, a value of \(\delta = 8.8\) ppm results for a hydroxyl group hydrogen-bonded to a water molecule. A water molecule adsorbed on a bridging OH has one proton with and one proton without a hydrogen bond (cf. Figure 7). For protons exchanging between the three positions in a water/bridging OH complex this results in the value

\[
(1/3)0.3 + (1/3)4.8 + (1/3)8.8 = 4.6 \text{ ppm}
\]

It should be noted, however, that a change of the chemical shift, which is caused by a hydrogen bond, drastically depends on the geometry: Harris et al.26 discussed for carboxylic protons a linear change of \(\delta_{H_2O}\) shifting by 9 ppm downfield if the hydrogen bond distance \(H-O\) decreases from 1.7 to 1.24 Å.

Akiti37 gives a value of \(\delta_{\text{water}} = 19.2 \pm 0.4\) ppm for hydroxonium ions in various aqueous acids (taking into account the structure-breaking effect of all ions in the solution). In this model the three hydroxonium protons are hydrogen-bonded with three water molecules from the bulk water. Ratcliffe et al.29 measured values of \(\delta_{\text{hydrox}} = 10.7\) and 11.4 ppm for hydroxonium protons in \(H_2OCIO_4\) and on K⁺ positions in alunite, respectively. They note29 that there is little or no significant hydrogen bonding. The chemical shift of the "free" hydroxonium ion has also been determined by ab initio calculations. The most recent results lie in the range of \(\delta_{\text{hydrox}} = 7.3-9.5\) ppm.20 In conclusion, for the "free" hydroxonium ion a chemical shift of 7–12 ppm should be expected, whereas the 3-fold strongly hydrogen-bonded ion reaches a maximum value of 19 ppm. The doubly hydrogen-bonded ion could be expected at 13 ± 1 ppm.

For the weakly hydrated samples, eq 1 can be used with \(\delta_1 = 4.1\) ppm, \(\delta_2 = 13\) ppm, \(\delta_3 = 4.6\) ppm, and \(\delta_4 = 3\) ppm, respectively. Note that only for \(\delta_1\) an exact reference for the dehydrated sample exists. The other values were roughly estimated (see Results) and depend on the water loading.

We used also the concentration of the different species given in Table I (except for isolated bridging OH groups, which were calculated as 4 minus the number of hydrogen-bonded physisorbed complexes per unit cell) and calculated \(\delta_n\) for the weakly hydrated Bu zeolite. This results in 5.6, 5.7, 5.3, and 8.4 ppm for samples hydrated with 2.0, 4.0, 6.0, and 8.4 H₂O/uc, respectively. This good agreement with the experimental results given in Table II shows that the concentrations of the different species are not significantly changed on going from 4 K to room temperature.

This finding agrees with a study of hydrated antimonic acids (\(H\text{Sb}_4\text{O}_{11-n}\text{H}_2\text{O}\)).11 NMR experiments at 4 K gave for \(n = 3\) and \(n = 2\) the precise formulas \((H\text{O})_3\text{Sb}_4\text{O}_{11-n}\text{H}_2\text{O}\), \((H\text{O})_2\text{Sb}_4\text{O}_{10.5}\), and \((H\text{O})_n\text{Sb}_4\text{O}_{10-n}\), respectively.15 The \(^1\)H MAS NMR spectra of the strongly deuteriated samples at room temperature show one sharp line at 10.3 and 8.9 ppm for \(n = 3\) and \(n = 2\), respectively.24 Using the above-mentioned value of 3 ppm as reference for water molecules, which are bonded to another water or physisorbed on framework oxygen, we obtained two equations for the determination of \(\delta_{\text{hydrox}} = \delta - \delta(H\text{O}) = \delta y\), \(\delta_{\text{hydrox}} = 10.3\) ppm = (1/8)(3-1.56x + 3-0.51x + 2-1.3x), \(\delta_{\text{hydrox}} = 8.9\) ppm = (1/6)(3.08x + 3-1.2y). This gives \(\delta_{\text{hydrox}} = 15.5\) ppm and \(\delta(H\text{O}) = 4.5\) ppm, in good agreement.

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(24) Harris, R. K., Mann, B. E., Eds. \(^1\)H NMR and the Periodic Table; Academic Press: New York, 1979; p 89.
Transfer Energetics of Tetraalkylammonium Picrates In an Aqueous Ionic Cosolvent System and the Salt Effect on Hydrophobic Hydration

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The salt effect on hydrophobic hydration has been studied by measuring the solubilities of some tetraalkylammonium picrates \((R_4NPi)\) spectrophotometrically at five different temperatures ranging from 288 to 308 K in 1.0, 2.0, and 4.0 \(m\) \(NaNO_3\) solutions. The observed free energies \(\Delta G^{\circ}\) and entropies \(\Delta S^{\circ}\) of transfer of \(R_4NPi\) salts were then dissected into individual ion contributions by using preevaluated values of picrate ion \((P^-)\), which are based on modified tetraphenylborate \((TATB)\) reference electrolyte assumption. The \(\Delta G^{\circ}\) values of the tetraalkylammonium ions \((R_4N^+)\) were analyzed in the light of cavity effect and electrostatic effect and the rest as hydrophobic hydration. The observed \(\Delta S^{\circ}\) values when corrected by subtracting the cavity and electrostatic contributions reflect the salt effect on hydrophobic hydration.

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Registry No. \(H_2O^+, 13968-08-6; H_2O, 7732-18-5\).

Introduction

As is well-known, water is highly associated through hydrogen bonding and various solutes/cosolvents can increase or decrease the distribution of hydrogen bonds. While simple hydrophilic ions with high ionic force fields attract water molecules round them and cause hydrophilic hydration\(^{1,4}\) or hydration of the first kind or positive hydration,\(^2\) hydrophobic solutes or ions with apolar residues, on the other hand, induce water molecules around them to organize in a way similar to clathrate hydrates,\(^1\) causing hydrophobic hydration\(^{18-19}\) or hydration of the second kind or negative hydration,\(^9,10\) resulting in significant increase of free energy and decrease of entropy\(^{11}\) of the system. While the phenomena of hydrophobic hydration dictate various properties of solution of hydrophilic ions, the phenomena of hydrophobic hydration and the related hydrophobic interactions\(^{10,11,12}\) among apolar sites are of great significance in the realms of micelles, mixed micelles, microemulsion, bilayer membranes, and particularly lipopolymers including proteins.\(^6,3\) Conway\(^2\) has given detailed surveys of the theories and methods involved in these hydrophobic effects that lead to different results. Recently, Grunwald\(^4\) viewed the "hydrophobic effect" induced by "hydrophobic" solutes to be composed of an "isodelphic" and "lyodelphic" term: the former term refers to solute-solvent interaction of a similar type to that observed for solution in non-associated (or molecular) solvents and the latter term refers to solute perturbation of the solvent-associated network. All these ideas correspond to the structure-promoting and structure-breaking effects of ions in water.

Although the salient features of hydrophobic hydration have been derived from various studies\(^2,3,5,12,14-19\) on thermodynamic and transport properties using tetraalkylammonium salts (as the model hydrophobic probe) either as cosolvents in water or as solutes in water and some aqueo-organic solvents, the knowledge on the salt effects on hydrophobic hydration in aqueous salt solutions is fairly scarce.

Recently Kundu and co-workers in a series of papers\(^20\) reported for the first time the transfer energetics of some hydrophilic and hydrophobic electrolytes and nonelectrolytes to an aqueo-ionic cosolvent system using 1.0, 2.0, and 4.0 \(m\) \(NaNO_3\) as the ionic cosolvent, taking infinitely dilute solutions of the solutes as the standard state exactly similar to what are being done in aquo-organic solvent systems.

In course of these studies the observed free energy behavior of ions with hydrophobic moiety, like \(Ph_4B^-/Ph_4As^+\) (Ph = phenyl), however, reflected that their behavior is largely guided by cavity\(^{20,21}\) as well as salting-out effects\(^{22,23}\) of the ionic cosolvent. Their entropic behavior shows the formation of water structure

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