Title
The nature of the hydrated proton H(aq)$^+$ in organic solvents

Permalink
https://escholarship.org/uc/item/2jp3w86j

Journal
Journal of the American Chemical Society, 130(36)

ISSN
0002-7863

Authors
Stoyanov, ES
Stoyanova, IV
Tham, FS
et al.

Publication Date
2008-09-10

DOI
10.1021/ja803535s

Peer reviewed
The Nature of the Hydrated Proton H(aq)$^+$ in Organic Solvents

Evgenii S. Stoyanov,* Irina V. Stoyanova, Fook S. Tham, and Christopher A. Reed*

Department of Chemistry, University of California, Riverside, California 92521

Received May 16, 2008; E-mail: evgenii.stoyanov@ucr.edu; chris.reed@ucr.edu

Abstract: The nature of H(H$_2$O)$_n^+$ cations for $n = 3$–8 with weakly basic carborane counterions has been studied by IR spectroscopy in benzene and dichloroethane solution. Contrary to general expectation, neither Eigen-type H$_2$O·3H$_2$O$^+$ nor Zundel-type H$_2$O$_2^+·4$H$_2$O ions are present. Rather, the core species is the H$_2$O$_3^+$ ion.

Introduction

The current state of knowledge of the aquated proton H(aq)$^+$ is in a curious position. In water, the “excess proton” is widely believed to exist in two limiting forms, the Eigen-type H$_2$O$^+$ ion$^1$ and the Zundel-type H$_2$O$_2^+$ ion,$^2$ coexisting in a dynamic equilibrium. These ions are well characterized in crystalline salts,$^3,4$ organic solvents,$^5$–7 and the gas phase,$^8$–$^{10}$ but the extent to which they represent H(aq)$^+$ in water has not been determined experimentally. The belief that H(aq)$^+$ is an approximately 60:40 ratio of hydrated Eigen/Zundel ions is based on theory.$^{11,12}$

The problem of developing an accurate molecular description of H$^+$ in water lies in the difficulty of accurately separating its spectroscopic signature(s) from those of the background water, and in interpreting the resulting spectra. Infrared is the spectroscopic signature(s) from those of the background water, to which they represent H(aq)$^+$.

The vibrations of the excess proton extends over the much of the gas phase, but the IR spectrum of H(aq)$^+$ is notably broad. A poorly understood continuous broad absorption associated with the vibrations of the excess proton extends over the much of the useful IR range. These difficulties have shifted attention to the gas phase. The underlying assumption is that an accurate molecular description of each ion-selected hydrate H(H$_2$O)$_n^+$ via step-by-step increasing $n$ will ultimately lead to an understanding of H(aq)$^+$ in bulk water. Indeed, experiment and theory in vacuo come together very nicely to establish that the trihydrated Eigen ion (H$_2$O$_3^+$, i.e., H$_2$O$^+·3$H$_2$O) and the tetrahydrated Zundel ion (H$_3$O$_6^+$, i.e., H$_3$O$_2^+·4$H$_2$O) have extra stability in the gas phase.$^{13,14}$ Other “magic number” clusters such as H(H$_2$O)$_{21}^+$ have distinctive structural characteristics and heightened stability compared to their near $n$ neighbors.$^{15–18}$

While gas-phase studies have obvious and direct importance in atmospheric chemistry, there are reasons to doubt that such a close relationship will hold in condensed phases — where so much acid chemistry is carried out. Gas-phase ion chemistry (and theory) is carried out in the absence of counterions, whereas all condensed-phase chemistry must deal with the necessity of a conjugate base. Even strong acids that fully ionize in a solvent are subject to ion pairing. The unidirectional electric field created by the proximity of an anion will affect the structures of the H(H$_2$O)$_n^+$ cations. Structural isomers of H(H$_2$O)$_n^+$ for $n = 5$–8 are calculated in vacuo to be very close in energy,$^{10,19–22}$ so their structures should be quite sensitive to environmental influences in condensed media.

In the solid state, X-ray crystal structures of hydrated acids were studied quite extensively in the late 1970s.$^{23}$ In favorable circumstances, they can be expected to reflect the structures of ions in other phases. For example, if an H(H$_2$O)$_n^+$ ion is surrounded in a crystal by a spherically symmetric anion field, it might be expected to reflect the gas-phase structure of the cation. In anion fields of lower symmetry, an H(H$_2$O)$_n^+$ ion might be expected to reflect ion-paired structures of hydrated acids in solution.


Given these considerations, as well as the importance of the hydrated proton in acid catalysis, fuel cell electrolytes, and acid/base chemistry in general, we are focusing on the nature of the hydrated proton in organic solvents, where studies are few. Just as in the gas phase, water molecules can be controlled and sequentially attached to the proton, forming $\text{H}(_2\text{O})_n^+$ clusters. The ease of formation, structure, and composition of these cations depend strongly on the basicity of the solvent and the basicity of the anion, i.e., the strength of the conjugate acid. In weakly basic solvents like CH$_2$Cl$_2$, acids such as HCl are hydrated mainly without proton transfer to H$_2$O molecules. $^{24}$ Simple H-bonded solvates of the type HA·(H$_2$O)$_n$ prevail rather than ionized H($\text{H}_2\text{O}$)$_n^+$ clusters. With solvents of higher basicity such as tributylphosphate (TBP), whose basicity is close to that of water, proton transfer to H$_2$O becomes possible but is accompanied by waterless TBP·HA monosolvates. $^{25}$ Stronger acids such as perchloric and triflic acids certainly protonate water in weakly basic solvents, but the solubilities of the ionized acids such as perchloric and triflic acids certainly protonate water in weakly basic solvents like CH$_2$Cl$_2$, acids such as HCl are hydrated mainly without proton transfer to H$_2$O molecules. $^{24}$


procedure. Subtraction of the dissolved water using spectra of 0.1 M water-saturated DCE or 0.2 M water-saturated benzene with a scaling factor $f$ allowed determination of the concentration of “free” water dissolved in the solutions under study: $C_{\text{H}_{2}O}^\text{free} = fC_{\text{H}_{2}O}^{\text{sat}}$, where $C_{\text{H}_{2}O}^{\text{sat}} =$ 0.1 and 0.2 M for DCE and benzene, respectively. The concentration of water involved in the $\text{H(H}_{2}\text{O)}_n^+$ cation is determined from the difference $C_{\text{H}_{2}O}^\text{H_{2}O} = C_{\text{H}_{2}O} - C_{\text{H}_{2}O}^\text{free}$, where $C_{\text{H}_{2}O}$ is the total water concentration, known from the conditions of preparation. The ratio $N = (C_{\text{H}_{2}O}^\text{H_{2}O} - C_{\text{H}_{2}O}^{\text{CaCl}_2})/C_{\text{H}_{2}O}^{\text{CaCl}_2}$ gives the average stoichiometry of $\text{H(H}_{2}\text{O)}_n^+$ cations formed in solution. This method of spectral subtraction to determine the concentration of water (or methanol) bound with $\text{H}^+$ and the average $N$ stoichiometry of the formed $\text{H}^+\text{-}{\text{L}}_y$ cations has been previously described in detail.27,28,34

The water-saturated DCE solutions of $\text{H(H}_{2}\text{O)}_n^+\{\text{I}_{11}\}_n^+$ and $\text{H(H}_{2}\text{O)}_n^+\{\text{C(D)}_1\}_n^+$ acids were prepared by extraction from water solution of their Cs$\{\text{I}_{11}\}_n$ or HNa(CCD) salts containing 2–4 M $\text{H}_2\text{SO}_4$. The separated organic phase was washed four or five times with 1–2 M $\text{H}_2\text{SO}_4$ and then with distilled water. The molar concentrations of the acids were determined from the intensity of IR absorption of the $\{\text{I}_{11}\}_n^+$ or $\{\text{C(D)}_1\}_n^+$ cations compared to standard DCE solutions of (Oct)$_3\text{NH}_n^+$ or (Oct)$_3\text{NH}_n^+\{\text{C(D)}_1\}_n^+$ ($\{\text{I}_{11}\}_n^+$ or (Oct)$_3\text{NH}_n^+$). The total water concentration was determined using $^1\text{H}$ NMR. The initial DCE solvent was made 0.2 M in chloroform as an internal standard. In the NMR spectra of water-saturated DCE solutions, the signal integrations of chloroform (at 7.26 ppm) and water (at 1.49 ppm) give the ratio 1.00:1.03, in good agreement with the known water content of 0.1 M.35 In the spectra of $\text{H(H}_{2}\text{O)}_n^+\{\text{I}_{11}\}_n^+$ and $\text{H(H}_{2}\text{O)}_n^+\{\text{C(D)}_1\}_n^+$, the ratio of these signals allowed determination of the total water concentration, $C_{\text{H}_{2}O}^\text{H_{2}O}$, and the molar ratio $N = (C_{\text{H}_{2}O}^\text{H_{2}O} - 0.1)/C_{\text{H}_{2}O}^{\text{CaCl}_2}$.

With the exception of water-saturated solvents, all solutions were prepared in a Vacuum Atmospheres Corp. glovebox under nitrogen ($\text{O}_2$, $\text{H}_2\text{O} <$ 0.5 ppm). IR spectra in the 4000–450 cm$^{-1}$ range were run on a Shimadzu-8300 FT-IR spectrometer housed inside a glovebox. A cell with Si windows having 0.036 mm separation at the beam transmission point was used. To avoid interference effects, the cell configuration was wedge-shaped. IR data were manipulated using GRAMMS software. NMR spectra were run on a Varian INOVA 400 spectrometer.

X-ray-quality crystals of [H$_5$Br$_6$]$^+\{\text{C(D)}_1\}_n^+$ were grown from o-dichlorobenzene under conditions of slow solvent evaporation at low pressure. Crystals of [H(CH$_2$OH)$_n$]$^+\{\text{C(D)}_1\}_n^+$ were grown from benzene solution with a 1:3 MeOH:H$_2$Cl mole ratio.33 Crystals of [H$_2$O]$_n^+\{\text{C(D)}_1\}_n^+$ were grown from water-saturated H[CH$_2$Cl$_2$] solution in a desiccator over CaCl$_2$. The crystallographic data for these salts are available in the Supporting Information or can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif (CCDC 687306, 687307, and 687308).

**Results and Discussion**

IR spectra of benzene and DCE solutions of carborane acids with different water/acid mole ratios $N = \text{H}_2\text{O}/\text{H(carborane)}$ change regularly with increasing $N$, indicating sequential of hydration of $\text{H}^+$. In addition, water molecules may be involved with solution of the carborane anions. In order to examine this possibility, we studied dichloroethane extracts of cesium carborane salts from water solutions. In addition to the bands from the carborane anions and dissolved water, IR spectra of these extracts developed two new narrow OH stretching bands, $\nu_s$ at 3655 and $\nu_\alpha$ at 3578 cm$^{-1}$, arising from H$_2$O molecules with free OH groups. Since these frequencies are independent of the nature of the carborane anion and are red-shifted compared to those for dissolved monomeric water molecules in DCE (3675 and 3591 cm$^{-1}$, respectively), they are assigned to H$_2$O molecules bound to the Cs$^+$ cation via the O atom. Thus, there are no water molecules involved with hydrating the carborane anions. Taking into account that the $\nu_{OH}$ frequencies of the H(H$_2$O)$_n^+$ cations discussed below are also independent of the nature of carborane anion, we can conclude that the OH groups of the cations are not H-bonded with counterion.

This is consistent with our earlier studies on the H$_2$O$_2^+$-4Solv cations where, although there is good evidence for ion pairing, H-bonding of the cation occurs only with solvent molecules. Thus, solvent-separated ion pairs of the type [H$_2$O$_2^+$H$_2$O$_n^-$mSolv]Carb$^-$ are formulated in the present work.

**DCE Solutions.** IR spectra of H$_2$O$_2^+$ solutions with water/acid mole ratios $N \geq 2$ have been studied. The spectrum of the solution with $N = 2$ belongs to the H$_2$O$_2^+$-4DCE cation.3 With gradually increasing $N$ to 3, the intensity of the H$_2$O$_2^+$ spectrum decreases and disappears. At the same time, the spectrum of the H$_2$O$_2^+$ cation appears and reaches a maximum at $N = 3$. As shown in Figure 3, there is an isosbestic point at 3494 cm$^{-1}$ up to $N = 2.9$, confirming that, in this range, only two cations, H$_2$O$_2^+$ and H$_2$O$_3^+$, are formed (i.e., $N = n$). As $N = 3$ is approached, there is a peculiar step change in the H$_2$O$_3^+$ spectrum (Figure 3). This change is consistently reproducible and indicates the existence of two forms of the H$_2$O$_3^+$ cation: the $\alpha$ isomer at $N < 3$ and the $\beta$ isomer at $N > 3$. Their individual spectra are shown in Figure 4 and, as discussed in more detail below, are ascribed to different degrees of ion pairing. With further increase of $N$ from 3 to 5.2, the spectrum of $\beta$-H$_2$O$_3^+$ is transformed into that for the more highly hydrated H(OH)$_2$O$_n^+$ cations with isosbestic points at 3542 and 3467 cm$^{-1}$ (Figure 5). This means either that H$_2$O$_3^+$ is transformed into a single H(OH)$_2$O$_n^+$ cation with constant $n$, which seems improbable, or that a set of spectroscopically indistinguishable compounds with variable $n \geq 4$ are formed, which will need a specific explanation.

Proton hydrates can be followed as a function of $N$ via the change in frequency of $\nu_s$H$_2$O from the terminal H$_2$O molecules, i.e., the “free” OH groups that are H-bonded to solvent. The $\nu_s$H$_2$O band is chosen over $\nu_\alpha$H$_2$O for this analysis because it does not overlap with bands from other types of vibrations. As
the equilibrium constant \( K_n = C_n/C_{n-1} \) includes, in addition to \( C_n \) and \( C_{n-1} \), the concentrations of \( \text{H}^+(\text{H}_2\text{O})_{n-1}^+ \) and \( \text{H}(\text{H}_2\text{O})_{n-1}^+ \) cations, respectively, the concentration of free dissolved water, \( C_{\text{H}_2\text{O}} \). However, as shown in Figure 7, the dependence of \( C_{\text{H}_2\text{O}} \) on \( n \) shows only one step at \( n = 3 \), when formation of \( \text{H}_3\text{O}^+ \) cation is complete and a detectable concentration of free dissolved water appears. With further increasing \( n \), the dependence increases steeply and linearly, indicating that the \( K_n \) constants for cations with \( n \geq 4 \) are low and do not differ significantly. Extrapolation to water-saturated DCE (\( C_{\text{H}_2\text{O}} = 0.1 \) M) results in \( n = 6 \), confirming that the highest formed proton hydrate is the \( \text{H}(\text{H}_2\text{O})_6^+ \) ion. The dependence of \( C_{\text{H}_2\text{O}} \) on \( n \) allows the determination of \( K_n \) values for cations with \( n \geq 4 \). For equal concentrations of \( \text{H}^+(\text{H}_2\text{O})_n \) and \( \text{H}^+(\text{H}_2\text{O})_{n+1} \) cations, \( K_n = 1/C_n' \), \text{H}_3\text{O}^+ \) is the free water concentration for solutions with \( C_n = C_{n-1} \). From \( C_{\text{H}_2\text{O}} = f(n) \), one can determine that \( C_n' = 0.0385, 0.0628, \) and 0.0876 M respectively for solutions with \( N = 3.5, 4.5, \) and 5.5. Then, \( K_3 = 26.0, K_4 = 15.9, \) and \( K_5 = 11.4 \). The \( K_3 \) value, for the formation of the \( \text{H}_3\text{O}^+ \) cation, cannot be determined since the \( \text{H}_3\text{O}^+ \) concentration required for calculation is below the threshold of IR detectability.

For all \( \text{H}(\text{H}_2\text{O})_n^+ \) cations with \( n \geq 3 \), the frequency of the \( \delta \text{H}_2\text{O} \) terminal water bending vibration is practically the same, 1608 cm\(^{-1}\). Its intensity \( (I_{608}) \) increases linearly with increasing \( \text{H}_3\text{O}^+ \) cation concentration in solutions as \( N \) increases from 2 to 3 and extrapolates to zero at \( N = 2 \) (Figure 8). This confirms a peculiarity established earlier, namely that, in the IR spectrum of the \( \text{H}_3\text{O}^+ \) cation, the \( \delta \text{H}_2\text{O} \) band is not observed. At \( N \approx 3 \), the \( I_{608} \) dependence on \( N \) changes slope and then continues to grow with increasing \( n \), in line with the increasing number of terminal water molecules in \( \text{H}(\text{H}_2\text{O})_n^+ \) cations. They can contain two types of terminal \( \text{H}_2\text{O} \): type (i), with both \( \text{OH} \) groups free, or type (ii), with one free and the other H-bonded.

\[
\text{H}^+(\text{H}_2\text{O})_{n-1}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+(\text{H}_2\text{O})_n^+
\]

Their \( \delta \text{H}_2\text{O} \) frequencies coincide because the addition of a single H-bond in (ii) has a minimal effect on the force constant of this vibration. On the other hand, when both \( \text{O}^\cdots\text{H} \) groups are H-bonded to additional water molecules, as in coordination type (iii), the \( \delta \text{H}_2\text{O} \) frequency is detectably higher.

\[
\begin{align*}
\text{(i)} &: \quad \text{H}^+(\text{H}_2\text{O})_{n-1}^+ + \text{H}_2\text{O} \\
\text{(ii)} &: \quad \text{H}^+(\text{H}_2\text{O})_{n-1}^+ + \text{H}_2\text{O} \\
\text{(iii)} &: \quad \text{H}^+(\text{H}_2\text{O})_{n-1}^+ + \text{H}_2\text{O}
\end{align*}
\]

In summary, IR spectra of DCE solutions show that only the \( \text{H}_2\text{O}_2^+ \) and \( \text{H}_2\text{O}_3^+ \) cations have specific identities. \( \text{H}(\text{H}_2\text{O})_n^+ \) cations with \( n = 4 \sim 6 \) develop as a single family of compounds with spectroscopic properties sufficiently similar that it is impossible to detect their successive formation. They differ only slightly in the bands arising from their terminal water molecules.

**Benzene Solutions.** The IR spectra of \( \text{H}(\text{H}_2\text{O})_6^+ \) cations in benzene solution are quite similar to those for DCE and are essentially independent of the nature of the counterion, \{Cl\}_{11}^- \) or \{MesBr\}_{6}^- \). Therefore, we will discuss the spectra of solutions of the \( \text{H}(\text{Cl}_{11}) \) acid, whose hydrates are more soluble in benzene.

The spectrum of the cation formed in solution with \( N = 2 \) belongs to \( \text{H}_2\text{O}_2^+ \). With \( N \) increasing to 3, the intensity of the

---

**Figure 4.** IR spectra of \( \text{H}_2\text{O}_3^+ \) isomers \( \alpha \) (red) and \( \beta \) (blue).

**Figure 5.** IR spectra of \( \text{H}(\text{H}_2\text{O})_{n+}^+ \) cations with \( n = 3.02 \sim 5.22 \).

**Figure 6.** Dependence of \( \nu_\text{a} \) on the stoichiometry \( n \) of \( \text{H}(\text{H}_2\text{O})_{n}^+ \).
H$_2$O$^+$ spectrum decreases as the spectrum of the H$_7$O$_3^+$ cation increases, with an isosbestic point at 3447 cm$^{-1}$ (Figure 9). However, in the range of N = 2.6–2.9, the spectrum of the H$_7$O$_3^+$ cation changes rapidly such that, at N = 3, the spectrum does not cross the isosbestic point. Just as in DCE solution, the H$_7$O$_3^+$ cation must exist in two isomeric forms in benzene solution: R (N = 2.6–2.9) and /betatwo (N = 2.9). Their spectra are given in Figure 10.

With increasing N from 3 to 4, the spectra change, with a new isosbestic point at 3544 cm$^{-1}$ indicating transformation of the H$_7$O$_3^+$ cation into H(H$_2$O)$_n^+$ (Figure 11). The spectra with N > 4 do not cross exactly at 3544 cm$^{-1}$, indicating that the H(H$_2$O)$_n^+$ cation may differ slightly more from cations with n ≥ 5 in benzene compared to DCE.

Spectra and Structures of the H(H$_2$O)$_n^+$ Cations. H$_7$O$_3^+$. IR spectra of the α and β isomers of the H$_7$O$_3^+$ cation are both in agreement with the symmetrical cation structure I.

They show two types of OH stretching vibrations from terminal OH groups: first, ν$_{H_2O}$ and ν$_{H_2O}$ from the two equivalent H$_2$O molecules and second, a lower frequency νOH band from the group labeled OH* in I. The deconvolution is shown in Figure 12, and the data are listed in Table 1. The δH$_2$O bend is at 1608 cm$^{-1}$. Vibrations from the conjugated (O···H−O−H···O)$^+$ group develop as a continuous broad absorption in the range 1400–3100 cm$^{-1}$ (Figures 4 and 10) with a particular shape (discussed below). The OH stretching frequencies of the terminal OH groups of the α isomer are somewhat red-shifted compared with those for the β isomer, and the band intensity is slightly higher (Figures 4, 10, and 12). This means that the α isomer experiences a somewhat stronger interaction with its environment. It is likely that α-H$_7$O$_3^+$ forms mixed-ion associates of the type (H$_7$O$_3^+$)$_x$(H$_5$O$_2^+$)$_y$Carb$^{x+y}$ since the α isomer exists only in the presence of H$_5$O$_2^+$ when N < 3. The destruction of these mixed associates as N approaches 3 can be understood in terms of the disappearance of the OH bands.
of the H$_2$O$_2^+$ ion, resulting in the formation of the β isomer. Related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relative associate in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl.28 They have a specific

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...

related associates were found in reverse nanomicelles formed in wet TBP solutions of HFeCl$_4$ and HCl. They have a specific relat...
that in solution (Figure 13), we should compare it to that in a more symmetrical crystalline environment.

The structure reported to have the most symmetrical H\(_7\)O\(_3\)\(^+\) cation is found in [H\(_7\)O\(_3\)]\(^+\)[H\(_2\)O\(_4\)]\(^-\)Br\(_2\)·H\(_2\)O, where the O···O distances are 2.47(1) and 2.50(1) Å (average 2.481 Å). The symmetry arises from a nearly symmetrical anion/hydrate field, while that in solution (Figure 13), we should compare it to that in a nearly symmetrical crystalline environment.

The proton labeled H\(^\ast\) is more tightly H-bonded to bromide than those from the terminal water molecules, reflecting its closer proximity to the positive charge. The interaction with two water solvate molecules is weak. Unfortunately, because of the presence of H\(_2\)O\(_4\)\(^-\) and H\(_2\)O in these crystals, they are not suitable for IR investigation of the H\(_7\)O\(_3\)\(^+\) ion. Lacking good hydrates for structure/spectra correlation, we turn to the methanol analogue of the H\(_3\)O\(_3\)\(^+\) cation, which has a similar \(\text{cba}\) band and has been characterized by X-ray crystallography.

The proton labeled H\(^\ast\) is more tightly H-bonded to bromide than those from the terminal water molecules, reflecting its closer proximity to the positive charge. The interaction with two water solvate molecules is weak. Unfortunately, because of the presence of H\(_2\)O\(_4\)\(^-\) and H\(_2\)O in these crystals, they are not suitable for IR investigation of the H\(_7\)O\(_3\)\(^+\) ion. Lacking good hydrates for structure/spectra correlation, we turn to the methanol analogue of the H\(_3\)O\(_3\)\(^+\) cation, which has a similar \(\text{cba}\) band and has been characterized by X-ray crystallography.

The structure of the H(CH\(_3\)OH)\(_3\)\(^+\) cation in crystalline H(CH\(_3\)OH)\(_3\)\(^+\)(Cl\(_{11}\)\(^-\)) with O···O distances 2.446(2) and 2.491(2) Å is shown in Figure 14. The overall average O···O distance of 2.455 Å is close to the average of 2.481 Å in the nearly symmetrical H\(_7\)O\(_3\)\(^+\) cation in [H\(_2\)O\(_4\)][H\(_2\)O\(_4\)]Br\(_2\)·H\(_2\)O. The spectra of the H(CH\(_3\)OH)\(_3\)\(^+\) cation in benzene solution and in the crystal phase as the \(\{\text{Cl}_{11}\}\) salt are essentially the same, so the structure of the cation must be very similar in both phases.

Since the O···O distances in the H(CH\(_3\)OH)\(_3\)\(^+\) cation are shorter than those in compounds containing isolated O–H···O groups (Table 2), the νOH frequency (\(\text{cba}\) center of gravity, 1920 ± 40 cm\(^{-1}\)) is lower than, for example, that in phosphinic acid dimers (2000–2070 cm\(^{-1}\)). Comparing the spectrum of the H(CH\(_3\)OH)\(_3\)\(^+\) cation with that of the α-H\(_2\)O\(_3\)\(^+\) cation in benzene solution (Figure 13), close similarity can be seen.

The bands at ~1300 and 1732 cm\(^{-1}\) in the α-H\(_2\)O\(_3\)\(^+\) cation correspond to those at ~960 and ~1655 cm\(^{-1}\) in H(CH\(_3\)OH)\(_3\)\(^+\), and the center of gravity of the \(\text{cba}\) of α-H\(_2\)O\(_3\)\(^+\) practically coincides with that of H(CH\(_3\)OH)\(_3\)\(^+\), but for β-H\(_2\)O\(_3\)\(^+\) it is higher (Table 3). Therefore, the O···O distance of α-H\(_2\)O\(_3\)\(^+\) must be close to that of 2.455 Å in the H\(^+\)(CH\(_3\)OH)\(_3\) cation, while that in β-H\(_2\)O\(_3\)\(^+\) must be longer, approaching the value of 2.481 Å observed in the H\(_2\)O\(_4\)\(^+\) ion of [H\(_2\)O\(_4\)][H\(_2\)O\(_4\)]Br\(_2\)·H\(_2\)O. This demonstration of diminished H-bond strength in the (O···H–O···H·O···O) group of β-H\(_2\)O\(_3\)\(^+\) compared to that in H(CH\(_3\)OH)\(_3\)\(^+\) can be understood in terms of the weaker intrinsic basicity of water versus methanol. Nevertheless, the availability of five terminal OH groups in H\(_2\)O\(_3\)\(^+\) instead of two in H(CH\(_3\)OH)\(_3\)\(^+\) for H-bonding with the environment must also play an important role. The H\(_2\)O\(_3\)\(^+\) cation can more effectively transfer positive charge from the (O···H–O···H·O···O) group to the environment via a greater number of H-bonds.

![Figure 14. X-ray crystal structure of one cation of [H(MeOH)\(_3\)][CHB\(_{11}\)Cl\(_{11}\)] in the unit cell. Thermal ellipsoids are shown at the 50% probability level.](Image 238x510 to 524x750)

### Table 3. νOH of H(CH\(_3\)OH)\(_3\)\(^+\) and H(CH\(_3\)OH)\(_3\)\(^+\) Cations Determined from the \(\text{cba}\) Center of Gravity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>νOH (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-H(_2)O(<em>3)(^+)(Cl(</em>{11})(^-))</td>
<td>benzene</td>
<td>1911 ± 40</td>
</tr>
<tr>
<td>α-H(_2)O(_3)(^+)(HBr(_6)(^-))</td>
<td>DCE</td>
<td>2110 ± 40</td>
</tr>
<tr>
<td>β-H(_2)O(_3)(^+)(HBr(_6)(^-))</td>
<td>DCE</td>
<td>2285 ± 40</td>
</tr>
<tr>
<td>H(_2)O(_3)(^+)(H(_2)O(<em>4))(Cl(</em>{11})(^-))</td>
<td>crystal</td>
<td>2390 ± 40</td>
</tr>
<tr>
<td>H(_2)O(_3)(^+)·H(<em>2)O·(Cl(</em>{11})(^-))</td>
<td>benzene</td>
<td>2270 ± 40</td>
</tr>
<tr>
<td>H(CH(_3)OH)(<em>3)(^+)(Cl(</em>{11})(^-))</td>
<td>benzene</td>
<td>1920 ± 40</td>
</tr>
</tbody>
</table>
A weak blue shift of the cba center of gravity and the νOH frequencies of the terminal OH groups of the β isomer of H₂O₃⁺ compared to those for the α isomer (Tables 1 and 3) indicate a slight weakening of both the internal O⋯H−O−H⋯O core H-bonds and the external H-bonds with the environment in the β isomer. This may reflect different H₂O₃+/anion interactions. If aggregates of α-H₃O⁺[Cl₁⁻] ion pairs are associated with H₂O₃⁺[Cl₁⁻] ion pairs, α-H₂O₃⁺ may experience a more spherically symmetric anion field than the unidirectional field of the simple ion-paired structure of β-H₂O₃⁺[Cl₁⁻]. As shown schematically by II, the polarization of the β cation by the anion weakens its interaction with the environment.

\[ \text{H(H}_2\text{O)}_{\text{n}}^+ \text{ Cations with } n \geq 4. \text{ The formation of the H(H}_2\text{O)}_{\text{n}}^+ \text{ cation as an individual entity is detected with higher certainty in the lower permittivity solvent, benzene, rather than DCE. As shown in Figure 15, its IR spectrum is very similar to that of β-H₂O₃⁺. The two differences are that (a) the νOH* band of the “free” OH* group at 3458 cm⁻¹ is red-shifted to the region of ~3200 cm⁻¹, and (b) there is an increase in the intensity of the ν₁H₂O, ν₂H₂O, and δ₁H₂O (1610 cm⁻¹) bands from an added peripheral H₂O molecule. These changes are readily understood in terms of structure III. Compared to H₂O₃⁺, the OH* group is now H-bonded to H₂O rather than solvent, so the νOH* frequency is decreased. The fourth water molecule is not equivalent to the other two peripheral H₂O groups, and ν₂H₂O and ν₁H₂O develop as one broad, asymmetric band. The absorptions from the core (O⋯H−O−H⋯O)⁺ group are nearly unchanged, indicating that the H₂O₃⁺ ion remains the fundamental building block. The H₂O₃⁺−H₂O interaction is relatively weak, so the H(H₂O)₃⁺ cation is more correctly represented as the monohydrated H₂O₃⁺ cation, i.e., H₇O₃⁺−H₂O.

As noted earlier, the close similarity of the spectroscopic properties of H(H₂O)ₙ⁺ cations with n ≥ 4 means that these cations all belong to one family of compounds. Their spectra show isosbestic points, and the only significant differences arise from absorptions from the increasing number of peripheral water molecules (Figure 16). All the data can be rationalized by the sequential attachment of three water molecules to the H₂O₃⁺ cation in structures III, IV, and V for n = 4, 5, and 6, respectively (L = solvent). In each cation, the (O⋯H−O⋯H⋯O)⁺ structural unit of the H₂O₃⁺ ion is retained as the basic building block.

Figure 15. Spectrum of H(H₂O)₄⁺ (red) compared to that of β-H₂O₃⁺ (blue) after subtraction of solvent (benzene) and counterion \{Cl₁⁻\}.

Consistent with these structures, only the spectra for N = 5 and 6 show an increase in intensity of the broad band νOH at 3327 cm⁻¹ (Figure 16) arising from the H-bonded OH groups of semihydrated water molecules (designated earlier as type (ii) and indicated in blue in IV and V). This is accompanied by a Fermi resonance band at 3180 cm⁻¹ from the overtone of 2δH₂O. Finally, the constancy of the δH₂O frequency at 1608−1610 cm⁻¹ for all cations with n = 3−6 is in agreement with structures IV and V, since they contain closely related peripheral water molecules only of types (i) and (ii). The H(H₂O)₆⁺ cation with \{H₃Br₆⁻\} counterion is formed in DCE solution under conditions of water saturation. However, by using alternative carborane acids and extracting them from aqueous solution at varying temperatures, H(H₂O)ₙ⁺ cations with n > 6 may be obtained. Figure 17 presents the spectra of cations from aqueous H(CCD) extracts with N varying from 5.5−6.5, as well as the spectrum of an H(I₁₁) extract in which N reaches 8.2. In all spectra, the absorptions from the core (O⋯H−O⋯H⋯O)⁺ group remain unchanged, as indicated by the constancy of the cba from 3000 to 1500 cm⁻¹.

Let us now consider the interaction between the terminal water molecules and H₂O₃⁺ group in more detail. Figure 18 shows the difference spectrum of cations with n = 4 and 4.74 in order to reveal the bands associated with the fifth added water molecule. The ν₅H₂O band appears at 3650 cm⁻¹, the lower frequency ν₄H₂O band is masked by other νOH vibrations, and the νOH band from the OH group of the H₂O₃⁺ cation to which the fifth H₂O molecule is H-bonded (type (ii), marked blue in IV) appears at 3350 cm⁻¹. A small shift in the cba to higher frequency (in the range of the A band) results in a broad band at 2980 cm⁻¹. With the exception of a weak δH₂O band from the fifth H₂O molecule, there are no changes below 2500 cm⁻¹. Similar difference spectra of cations are obtained with n = 6 (counterion \{CCD⁻\}, DCE) and n = 5.2 (counterion \{H₃Br₆⁻\}, DCE), except that the relative intensity of the band at 2980 cm⁻¹ is weaker. So all changes in the spectra in accordance with structures III, IV, and V. In the difference spectra of cations with n = 6.5 and 5.5 (DCE, CCD⁻ as counterion), the intensities of the bands at 3655, 3400, and 1608 cm⁻¹ increase in accordance with additional water molecules of type (I) or (ii). The cba is not changed. However, for the first time, a δH₂O band appears at ~1630 cm⁻¹ (Figure 17 inset). This is assigned...
to water molecules of type (iii) having both OH groups H-bonded to solvating H$_2$O molecules. A similar band with higher intensity appears in the difference spectrum of cations with $n = 8$–$9$ and $n = 5.5$. Thus, attachment of the seventh and eighth water molecules to the H(H$_2$O)$_6^+$ cation leads to cation VI.

The structure of the H(H$_2$O)$_7^+$ cation has been determined by X-ray in the crystalline hydrate H$_2$SiF$_6$·9.5H$_2$O.57 It comprises the H$_7$O$_3^+$ building block surrounded with five H$_2$O molecules and one F atom from a SiF$_6^{2-}$ anion as shown in (v).

This is very similar to structure VI proposed for H(H$_2$O)$_8^+$ in solution. The O···O distances in the O···H−O···O group of (v) are lengthened to 2.505(2) Å, compared with the average of 2.481 Å in [H$_2$O$_3^+${H$_5$Br$_6^-$}]H$_3$O$_7^+$·H$_2$O (iv), where the H$_2$O$_3^+$ ion is bonded with only two water molecules. It is evident that increasing the number of H-bonded water molecules solvating the H$_2$O$_3^+$ cation delocalizes the positive charge and weakens H-bonding in the core O···H−O···O unit. The 2.505 Å O···O distance is close to that in dimers of dialkylphosphinic acids (2.51–2.52 Å), which is why their $cba$'s are quite similar. Structure vi reflects the weak H-bonding between the H$_2$O$_3^+$ cation and three solvating water molecules ($R_{O\cdots O} = 2.77$–2.81 Å). They are comparable to those in neutral liquid water ($R_{O\cdots O} = 2.78$ Å).58 The OH* group forms a somewhat stronger H-bond, with $R_{O\cdots O} = 2.62$ Å, which nevertheless is insufficient to contribute to the $cba$ below 2600 cm$^{-1}$.

Comparison with Gas and Solid Phases. The structures of H(H$_2$O)$_n^+$ cations in acidified organic solutions are similar to those in the gas phase only when $n = 1$, 2, 7, 9, and 3. For $n \geq 4$, they can be quite different. In the gas phase, the Gibbs energy dependence of the addition of the $n$th molecule of H$_2$O to the H(H$_2$O)$_n^+$ cation indicates extra stability of the H(H$_2$O)$_7^+$ and H(H$_2$O)$_9^+$ cations.13 Indeed, the stability of H(H$_2$O)$_7^+$ is higher than that of H$_2$O$_3^+$. In organic solvents, the situation is different. The stability of H$_2$O$_7^+$, H$_2$O$_5^+$, and H$_2$O$_4^+$ is high, but starting with the H(H$_2$O)$_4^+$ cation, stability

Figure 19. IR spectra of H(H2O)4+{Cl11−} (N = 3.91) in benzene (red), crystalline [H3O+·3H2O][Cl11−] (blue), and [H3O+·3TBP]FeCl4− in CCl4 (black dashed). Red and blue are normalized to unit intensity of anion.

The gas-phase spectrum of VII develops two bands, νsH2O = 3644 and νasH2O = 3730 cm⁻¹, from the three equivalent H2O molecules surrounding the H3O+ ion and a broad band of νas and ν at 2665 cm⁻¹ for the central H2O⁺. In the crystalline state of [H3O+·3H2O][Cl11−], the OH stretch frequencies from H2O⁺ occur as a coalesced broad band at lower frequency, 2576 cm⁻¹ (Figure 19), because the three H-bonded water molecules are made more basic by the anion environment. A combination band appears at 2291 cm⁻¹. The frequencies of the three terminal water molecules of H2O⁺·3H2O appear at νas 3637, νs 3578, and δH2O 1605 cm⁻¹ bands. In the low-frequency region, a weak band appears ~1200 cm⁻¹, possibly νsH2O, overlapped with strong bands from counterion. The spectrum is also very similar to that of the C3v-symmetric H3O+·3TBP cation, an analogue of VII. The slightly higher basicity of TBP compared to H2O results in a small red-shift of νOH to 2530 cm⁻¹ and the combination band to 2206 cm⁻¹.

Comparing the spectrum of the symmetrical H(H2O)4+ cation in [H3O+·3H2O][Cl11−] with that in solution reveals differences ascribable to different structures: the symmetrical Eigen-type H3O+·3H2O cation in the crystal and the less symmetrical H2O⁺·H2O cation in benzene or DCE solution (Figure 19). They show some similarities in the cba region, originating from conjugated O−H···O group vibrations, but nevertheless there are important distinctions in the distribution of the cba intensity that defines the νOH frequencies. For the H2O⁺·H2O cation in benzene solution, νOH is about 120 cm⁻¹ lower than in the H2O⁺·3H2O cation (Table 3). This reflects shorter O···O distances in the O···H···OH···O core of the H2O⁺·H2O cation compared to O···H···O···H2O in H2O⁺·3H2O. In the X-ray structure of [H2O⁺]+[H2O⁺]Br₂·2H2O, where both cations appear in the same crystal, this difference is 2.48(1) versus 2.56(1) Å (averaged over equivalent bands). The average O···O distance in the H2O⁺·3H2O cation is 2.51(2) Å with [H3Br6]− as counterion and 2.53(2) Å with [Cl11]−.

Similarly, a comparison of the H(H2O)6+ cation in solution versus the gas phase or a symmetrical crystal environment reveals considerable structural differences. For the gas phase, the measured and calculated IR spectra provide evidence that the H(H2O)6+ cation has a H2O⁺ core. However, other calculations based on different levels of theory predict that the lowest energy state in vacuo of the tetrahydrated H5O2+ ion, namely H2O⁺·4H2O cation VIII, is insignificantly lower (or even higher) than that for the H2O⁺·3H2O ion (V). For the crystal state, only one example of a type VIII cation is known. It is found in the strictly symmetric Cl− anion environment of a cage compound, [(CH3)3NH]2[HCl][Cl] complexes from HCl solution. In the solutions of the present study, the IR data on H(H2O)6+ retain the characteristics of the H2O⁺− core, indicating formulation as the H2O⁺·3H2O ion, structure V. Since the vibrations of the O···H···O···H···O core of H2O⁺·nH2O cations in solution with n ≥ 6 are very similar to those from the O···H···O group of phosphonic acid dimers, the O···O distances should be similar. They are ~2.49–2.53 Å for phosphonic acid dimers. The average O···O distance in the core of the H2O⁺·4H2O cation in the SiF6Y salt is 2.505 Å. Therefore, in H(H2O)6+ cations with n ≥ 6 in solution, the O···O distances should be ca. 2.51 Å. By comparison, the central O···O distance in H2O⁺·4H2O should be ca. 2.39(2) Å, as in crystal state. This distance is typical for L−H−L proton solvates with strong L bases, such as diethyl ether. These cations, including H5O2+, develop intense bands in the 800–1000 cm⁻¹ region from O−H···O group vibrations. In accordance with DFT/B3LYP and MP2 calculations, the H2O⁺·nH2O cations with four H2O molecules only marginally influences the frequency and strong intensity of these bands. However, they are absent in the spectra of H2O⁺·3H2O in solution.

Thus, the Eigen- and Zundel-type symmetrical cations H2O⁺·3H2O (VII) and H2O⁺·4H2O (VIII) exist in the gas phase where counterions are absent. Rare cases also exist in the solid phase where the cation happens to be nearly symmetrically surrounded by anions or other ligands. In solutions with aprotic solvents such as benzene and chlorinated hydrocarbons, the one-dimensional electrostatic influence of the anion in solvent-separated ion pairs results in higher stability of the H2O⁺·H2O cation with structure III and H2O⁺·3H2O with structure V.

(61) Bell, R. A.; Christoph, G. G.; Fronzcek, F. R.; Marsh, R. E. Science 1975, 190, 151–152.
The present results better allow us to appreciate the similarities and differences of the excess proton in water versus methanol. In benzene solution with carborane counterions, the H(H2O)n+ and H(CH3OH)3+ cations have similar spectra and structures for n = 2 and 3. At n = 4, however, different core structures become the building blocks for higher solvation. This occurs because the O−H* group in H2O3+ is replaced by an O−CH3 group in H(CH3OH)4+ and is therefore unavailable for H-bonding. Water clusters can grow in dendritic fashion, whereas methanol clusters are forced to grow as linear chains. As a result, methanol clusters grow linearly as unique cations up to n = 4, each with individual spectral properties. Solvation continues up to n = 8 chains, retaining the properties of the H(CH3OH)4+ core. On the other hand, water clusters cease to develop unique cations after n = 3, retaining the H2O3+ core.

Conclusions

Study of the stepwise bonding of water molecules to H+ in weakly basic solvents with weakly basic anions shows that the first three hydrates, namely H3O+, H2O2+, and H2O3+, behave as individual ions with unique and distinctive structures and IR spectra. Additional water molecules are H-bonded to the H2O3+ cation via stepwise replacement of organic solvent molecules from its first coordination sphere via eq 1 and Figure 20.

\[
[H_2O_3^+ (\text{Solv})_3] + mH_2O \rightarrow \quad [H_2O_3^+ (\text{Solv})_{3-m}(H_2O)_m] + m\text{Solv}
\]  

Hydration of the H2O3+·(Solv)3 ion occurs first at the strongest coordination position, site 1. The second and third H2O molecules replace solvent molecules at positions 2 and 3, forming the H+(H2O)6 cation, which is stable with all studied counterions in both benzene and DCE. Finally, with some of the studied counterions in DCE solvent, two further H2O molecules can be introduced in positions 4 and 5, to form the less stable H+(H2O)8 cluster, completing the first coordination sphere of H2O3+ cation. There are detectable changes in the spectrum of the H2O3+ ion as it is solvated by 1–3 water molecules, but the core structure is retained for all m. Comparisons of IR data and X-ray data lead to the conclusion that, in H(H2O)n+ cations with n > 4, the two O⋯O distances in the conjugated O⋯H—O⋯H⋯O group, where the excess proton resides, are ca. 2.51 Å.

Notably, neither Eigen-type structures with the H3O+ core nor Zundel-type structures with the H2O3+ core are present. This finding is contrary to popular expectation and contrary to calculation and experiment in the gas phase. It reflects the unfortunate fact that perceptions regarding the nature of the aquated proton in solution have become too biased by calculations and experiments in the gas phase, where counterions are absent. The present work suggests that the obligatory presence of a counterion in solution, no matter how weakly coordinating, exerts an anisotropic electrostatic influence on H(H2O)n+ cations that has been largely ignored. The presence of the conjugate base of the acidic H(H2O)n+ cations is the principal reason that different structures exist in the condensed phase vis à vis the gas phase. The question about where the positive charge is localized has been typically been phrased in terms of Eigen and/ or Zundel type ions, i.e., on one water molecule or shared between two. For the presently studied H(H2O)n+ clusters, the excess proton is localized between three oxygen atoms, and the positive charge influences up to six water molecules. Additional water molecules above n = 6 are essentially indistinguishable from bulk water.

The next challenge will be to determine experimentally the nature of H(H2O)n+ in liquid water. Most theory focuses on Eigen versus Zundel ions, or a continuum of structures in between, although one study favors H7O3+ as the major ion present. The present work provides an excellent experimental fingerprint for this ion.

Acknowledgment. We thank Drs. Kee-Chan Kim for experimental assistance and the National Science Foundation (CHE-039878) and the National Institutes of Health (GM 23851) for support.

Supporting Information Available: Additional characterization and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA80355S
