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AND THE MOLECULAR MECHANISM OF PROTON DISSOCIATION

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THEORETICAL STRUCTURES OF TRIFLIC ACID-WATER CLUSTERS
AND THE MOLECULAR MECHANISM OF PROTON DISSOCIATION

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Structural and energetic information required for recently proposed quasi-
chemical theories of solution chemistry have been obtained for clusters of
water with triflic acid, CF₃SO₃H(H₂O)ₙ for n=1–6. Quantum mechanical
calculations on the clusters indicate that the acid proton does not dissociate
with n=1 or 2 hydrating water molecules, but does dissociate for n≥3 water
molecule partners. The computed minimum energy structures indicate that
both “Eigen” (H₃O⁺⁺) (n=3,4,6) and “Zundel” (H₃O⁺⁺⁺) (n=5) structures
are likely to play a role in the molecular mechanism of acid dissociation in
Nafion®.

INTRODUCTION

Nafion® has been extensively studied for various applications (1-5). Of
considerable current interest is the performance of this and related membrane materials in
polymer electrolyte fuel cells. Transport of protons and water in these materials is a key
factor in this application. We recently suggested (6,7) that the factors dominating transport
in such systems are closely related to the local interactions of sulfonic acid moieties and
solvating water molecules, especially the water molecules in the first solvation sphere
around the sulfonic acid. Molecular level understanding of the structural and dynamic
properties of this portion of Nafion®, which would permit optimized use of the membrane
or the design of improved membranes, is currently unavailable.

The number of water molecules per head group has been long recognized as a
significant operational parameter. The triflic (trifluoromethanesulfonic) acid molecule is a
natural model for the side-chain hydrophilic ‘head groups’ in Nafion® (6-8). The
molecular mechanism of proton dissociation from the sulfonic acid moiety is one essential
part of a molecular understanding of the membrane. Focusing attention on the sub-process
of proton dissociation, several theoretical ingredients will be required including structural,
energetic, and kinetic information encompassing the participation of hydrating water
molecules. Here we give results of large-scale electronic structure calculations on the triflic
acid molecule with one through six water molecules that illuminate the requirements for the
acid proton to dissociate from this highly acidic molecule.

Recently proposed quasi-chemical theories (9-11) provide a motivation for seeking
this particular theoretical information. These theories establish a format in which to exploit
chemical electronic structure computations to study solution chemistry. The idea is to use
electronic structure computational tools to determine the equilibrium coefficients Kₙ for the
formation of precisely defined complexes as

\[
CF₃SO₃H + nH₂O \overset{K_n}{\longrightarrow} CF₃SO₃H(H₂O)ₙ
\]  

The Kₙ are familiar forms
The \( \rho \)s are number densities for \( \alpha \)-molecules. The quasi-chemical approximations require these coefficients in the circumstances of an ideal gas, so that

\[
K_n = \frac{\rho_{CF_3SO_2H(H_2O)_n}}{\rho_{CF_3SO_2H}^n}
\]

The \( K_n \)s are partition functions (12). Standard electronic structure packages such as the Gaussian package (13) can produce these coefficients within the harmonic approximation because they can compute molecular vibrational frequencies for the structures obtained. Moreover, the interactions involved in formation of these complexes are genuinely chemical. Electronic structure methods are appropriate and classical force-field models are currently not available. The adequacy of the harmonic approximation for these purposes has yet to be directly tested and the development of these approaches is in an early stage.

The fundamental thermodynamic parameter addressed by the quasi-chemical approximations is the chemical potential of the solute, here triflic acid. The interaction part of that chemical potential, the part due to interactions of the solute with hydrating water molecules, is then given by

\[
\Delta \mu_{CF_3SO_2H} = -RT \ln \left[ p_0 \sum_{n=0}^{\infty} \bar{K}_n (\rho_{H_2O})^n \right]
\]

where the \( q_a \)s are molecule (or cluster) partition functions (12). Standard electronic structure packages such as the Gaussian package (13) can produce these coefficients within the harmonic approximation because they can compute molecular vibrational frequencies for the structures obtained. Moreover, the interactions involved in formation of these complexes are genuinely chemical. Electronic structure methods are appropriate and classical force-field models are currently not available. The adequacy of the harmonic approximation for these purposes has yet to be directly tested and the development of these approaches is in an early stage.

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\]

The \( \bar{K}_n \)s indicate that extra-cluster contributions, due to the environment more distant than the near neighbor water molecules, must be eventually considered (11,14). The notational convention is \( K_0 = 1 \). \( p_0 \) is a probability describing the free energy required to prepare for the cluster, a cavity in the medium. This contribution is associated with packing effects and is expected from an external theory addressing these features [15-20]. Again, we emphasize that the practical adequacy of the current understanding of these additional features has not been directly tested in the present context and subsequent developments will have to focus on these requirements.

We also emphasize that this approach is constructive in style. Only a small number of terms in the series in Eq. [3] are expected to be significant; and the various contributions are well defined and physically natural. Therefore, we can take the attitude that several clear contributions need to be studied and effective descriptions of each contribution need to be secured. See also the relative work (21). Here we address an initial step of determining structures and energies of the complexes \( CF_3SO_2H(H_2O)_n \), indicated in Eq. [1].

**COMPUTATIONAL METHODS**

The electronic structure calculations were carried-out with the GAUSSIAN 94 system of programs [13] using B3LYP density functional theory and the 6-31G** basis set. No \textit{a priori} structural constraints were imposed so all structures presented below were fully optimized. However, particularly for the larger clusters, many local minima exist undoubtedly, some perhaps with similar energies. Each structure presented below is
merely the lowest energy structure found in the present work. Corrections for basis set superposition effects were not considered.

RESULTS

Minimum energy structures found for the clusters $CF_3SO_2H(H_2O)_n$ with $n=1,2,3$ and $n=4,5,6$ are shown in Figures 1 and 2, respectively. The foremost point is that the acid proton remains associated with the sulfonic acid moiety for $n=1$ and 2. Three water molecules are required before a definitely dissociated acid proton is recognized in the lowest energy structure. For the simpler case of $HCl$ (22), and for polystyrenesulfonic acid (23) also, the first water of hydration is not sufficient to stabilize an ion pair configuration. The experimental results for polystyrenesulfonic acid (23) indicate that the second water of hydration is sufficient to dissociate the acid proton.

The polystyrenesulfonic acid results also point to the importance of the $H_3O^+$ structure, the “Zundel” cation, for this proton dissociation mechanism. The present results suggest that the sufficiency of the second water molecule need not be universal. However, we emphasize that the results of Fig. 1 do not include any affects of a condensed phase environment.

In our results (Fig. 1), when the proton does separate from the acid with the third water molecule, the structure formed is highly suggestive of the “Eigen” cation, $H_9O_4^+$ (24). This could be due to the presence of the three sulfonate oxygen atoms in this particular special case.

The larger clusters (Fig. 2) show both “Eigen” ($n=4$ and 6) and “Zundel” ($n=5$) structural patterns associated with the additional proton. Thus, we anticipate that both of these structures should be involved in the fuller molecular description of acid dissociation in these materials.

Plotted in Fig. 3 are the incremental changes of the binding energies for the addition of a water molecule for the structures found. These binding energy increments do not vary monotonically with the size of the cluster; but the largest oscillations have a magnitude typical of hydrogen bonding energies, about 5 kcal/mol.

CONCLUSIONS

Structural and energetic information required for recently proposed quasi-chemical theories of solution chemistry have been obtained for clusters of water with triflic acid, $CF_3SO_2H(H_2O)_n$ for $n=1-6$. The cluster results indicate that the acid proton does not dissociate with either one or two hydrating water molecules, but does dissociate for $n\geq 3$ water molecule partners. The minimum energy structures found, indicate that both “Eigen” ($H_9O_4^+$) ($n=3,4,6$) and “Zundel” ($H_5O_2^+$) ($n=5$) structures are likely to play a role in the molecular mechanism of the acid dissociation in Nafion®.

ACKNOWLEDGEMENTS

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REFERENCES
Figure 1: Minimum energy structures found for $CF_3SO_3H(H_2O)_n$ clusters for $n=1$ (top), $n=2$ (middle), and $n=3$ (bottom). Note that the acid proton doesn't dissociate from the sulfonic acid for $n=1$ and 2 but does dissociate for $n=3$. In the latter case, the ball and labeled arrows on the right show the distances of near neighbor oxygen atoms to the oxygen atom that bears the additional proton.
Figure 2: Minimum energy structures found for $CF_3SO_2H(H_2O)_n$ clusters for $n=4$ (top), $n=5$ (middle), and $n=6$ (bottom). The ball and labeled arrows on the right show the distances between interesting oxygen atom neighbors. The $n=4$ and 6 structures are "Eigen"-like and the $n=5$ structure is "Zundel"-like.
Figure 3: Incremental binding energies for the nth water molecule to form the structures of $CF_3SO_2H(H_2O)$$_n$. The overall magnitudes are in agreement with previous results of Refs. (1-3) and the largest oscillation has a magnitude similar in size to hydrogen bonding energies, about 5 kcal/mol.