6266 *J. Phys. Chem. A* **2001,** *105,* 6266−6268

Variation of the Dissociation Constant of Triflic Acid with Hydration

Stephen J. Paddison,*,[†] Lawrence R. Pratt,[‡] and Thomas A. Zawodzinski, Jr.[§]

Computational Materials Group, Motorola Inc., Los Alamos Research Park, Los Alamos, New Mexico 87544, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received: February 27, 2001; In Final Form: April 25, 2001

The variation of the acid dissociation equilibrium of trifluoromethane sulfonic acid in dilute aqueous solution along the liquid−vapor dissociation curve is treated by a dielectric hydration model. The computational results indicate that the dissociation equilibrium becomes unfavorable from the point of view of the free energy change as temperature is increased above 500 K where the solvent density is less than 85% of the triple-point density. These results give additional perspective for the view that insufficient hydration can result in incomplete proton dissociation from sulfonic acid headgroups in Nafion membranes.

I. Introduction

Nafion and related materials are archetypal proton-conducting membranes used in fuel cells. Proton conduction under variable hydration conditions is significant to the performance of these materials. Extensive experimental work has been undertaken over decades to understand these processes and the various influential factors. However, a full mechanistic understanding has lagged. We have carried out extensive computational studies of substructures found in these polymeric systems,[1−4] and mesoscopic transport models were put foreword thereafter.[5−7]

The important acid activity in Nafion is appropriately represented by trifluoromethane sulfonic (triflic) acid. The level of hydration is a key parameter for satisfactory conductivity of Nafion membranes. A physical chemistry issue is the degree of dissociation of the sulfonic acid headgroups as the hydration of the membrane drops. The deprotonation chemistry of hydrated triflic acid has not been experimentally studied over the wide range of hydration and temperature that would be relevant to the function of such membrane materials. Dielectric spectroscopy has suggested that a significant amount of triflic acid is not dissociated in the ionic melt at 50% mole fraction of water.[8]

Molecular modeling can be an important adjunct to further experimental study of these systems which are chemically complicated. This report gives results of a simple theoretical molecular model of triflic acid dissociation in dilute aqueous solution along the gas−liquid saturation curve to elevated temperatures. The water liquid−vapor saturation curve serves as a simple reproducible path for reduction of the hydration of the triflic acid. These results are preparatory to molecular modeling at higher detail, to be reported subsequently, utilizing the quasi-chemical theory.[9,10] The cluster results of ref 3 will be relevant to that further work.

We also give here new analyses of the limitations of dielectric continuum hydration models which are the standard for these calculations. Those analyses provide important context for this and following work.

Data that would make this effort more conclusive are not presently available. We hope our results will encourage further experimental work along those lines.

II. Dielectric Model

The approach here will treat all solutes with a dielectric continuum model with empirical cavity radii. We will follow standard procedures in applying this dielectric model.[1,4,12−19] The specific goal below will be the treatment of the equilibrium

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+} \tag{1}$$

over an extended range of conditions. Therefore, we discuss some of those basic issues here; further information can be found in the previous studies.[9,12,13,16] The equilibrium ratio

$$K_\mathrm{a} = \frac{\rho_{\mathrm{A^-}}\,\rho_{\mathrm{H_3O^+}}}{\rho_{\mathrm{HA}}\rho_{\mathrm{H_2O}}} \tag{2}$$

can be expressed as

$$K_\mathrm{a} = K_\mathrm{a}^{(0)} \exp[-\Delta\mu^{\mathrm{ex}}/RT] \tag{3}$$

with

$$\Delta\mu^{\mathrm{ex}} \equiv \mu_{\mathrm{A^-}}{}^{\mathrm{ex}} + \mu_{\mathrm{H_3O^+}}{}^{\mathrm{ex}} - \mu_{\mathrm{HA}}{}^{\mathrm{ex}} - \mu_{\mathrm{H_2O}}{}^{\mathrm{ex}} \tag{4}$$

The factor $K_\mathrm{a}^{(0)}$ is the equilibrium ratio found from the G98[11] results for the reactions without consideration of a molecular medium; each of the interaction contributions may be estimated with the dielectric model.[12,16] We will be interested in conditions of infinite dilution of the solute but a wide range of conditions for the solvent; thus, $\rho_{\mathrm{H_2O}}$ will vary widely.

This consideration of the isodesmic eq 1, together with the model used, carries some assumptions about the chemical state of “the dissociated proton”. Here our primary interest is the triflic acid, however, so we assume here that this treatment is satisfactory as a treatment of hydration free energies without consideration of the involved issues of $\mathrm{H^+(aq)}$. If those assumptions were uncomfortable, and if the $\mathrm{OH^-(aq)}$ were viewed as chemically simpler,[20−24] then we could study the

---

* To whom correspondence should be addressed. E-mail: s.paddison@motorola.com. Fax: 505-661-8189.

[†] Motorola Inc.

[‡] Theoretical Division, Los Alamos National Laboratory.

[§] Materials Science and Technology Division, Los Alamos National Laboratory.

10.1021/jp010737q CCC: $20.00

isodesmic equilibrium

$$\mathrm{HA} + \mathrm{OH}^- \rightleftharpoons \mathrm{A}^- + \mathrm{H_2O} \tag{5}$$

with equilibrium ratio

$$K' = \frac{\rho_{\mathrm{A^-}}\,\rho_{\mathrm{H_2O}}}{\rho_{\mathrm{HA}}\rho_{\mathrm{OH^-}}} \tag{6}$$

Then

$$K_a = \frac{K'}{K_W \rho_{\mathrm{H_2O}}^2} \tag{7}$$

with the water ion product $K_W = \rho_{\mathrm{H^+}}\rho_{\mathrm{OH^-}}$ taken to have its empirically known value.[15]

Dielectric hydration models serve as a primitive theories against which more detailed molecular descriptions can be considered. A particular interest of more detailed theories is temperature and pressure variations of the hydration free energies, and this is specifically true of hydrated polymer electrolyte membranes. The temperature and pressure variations the free energies implied by dielectric models have been less well tested than the free energies close to standard conditions. Those temperature and pressure derivatives would give critical tests of this model.[9,15] However, we do not pursue those tests here because the straightforward evaluation of temperature and pressure derivatives should involve temperature and pressure variation of the assumed cavity radii about which we have little direct information.[9,15]

To justify this point, we give simple estimates of these derivatives assuming that the thermodynamic state dependence of the radii may be neglected. We will consider a simple ion and the Born formula, $-q^2(\epsilon - 1)/2R\epsilon$, for the hydration free energy. Here, q is the charge on the ion and R is its Born radius. We assume that these latter parameters are independent of the thermodynamic state. Considering the partial molar volume first, we have

$$v^{\mathrm{ex}} \approx -\frac{q^2}{2r\epsilon}\left(\frac{\partial \ln \epsilon}{\partial p}\right)_T = -\frac{q^2}{2r\epsilon}\left(\frac{\partial \ln \epsilon}{\partial \ln \rho}\right)_T \kappa_T \tag{8}$$

The superscript (ex) indicates that this is the contribution due to solute–solvent interactions; it is the contribution in excess of the ideal gas at the same density and temperature. $\kappa_T = (-1/V)(\partial V/\partial p)_T$ is the isothermal coefficient of bulk compressibility of the pure solvent. The required density derivative of the dielectric constant is evaluated with the fit of ref 25, yielding $(\partial \ln \epsilon/\partial \ln \rho)_T \approx 1.15$ at the standard point $T = 298.15$ K and $\rho = 997.02$ kg/m^3. We estimate the parameter $\kappa_T \approx 46 \times 10^{-6}$ atm^{-1}.[26] Finally, the leading factor $q^2/2r\epsilon$ is of the order of 1 kcal/mol or about 40 cm^3 atm/mol. The combination eq 8 thus gives as an order of magnitude 2×10^{-3} cm^3/mol. Experimental results are typically a 1000-fold larger. Thus, this dielectric model value is an unrealistically small magnitude for these properties.

TABLE 1: Results of Dielectric Model Treatment of Section II for the Deprotonation of eq 1 along the Water Liquid–Vapor Coexistence Curve[a]

T (K)	$\Delta G^{(0)b}$	$\Delta\mu^{\mathrm{ex}\ c}$	$-RT \ln K_a$
298.15	139.59	−142.62	−3.04
323.15	139.61	−142.59	−2.97
373.15	139.67	−141.84	−2.16
423.15	139.75	−141.39	−1.64
473.15	139.82	−140.42	−0.60
523.15	139.91	−139.28	0.64
553.01	139.97	−138.31	1.66
573.15	140.01	−137.70	2.31
599.75	140.06	−135.91	4.15

[a] All energies are in kcal/mol. [b] Harmonic approximation at the indicated temperature obtained from G98[11] with the B3LYP procedure and 6-31G** basis set. [c] Dielectric model result obtained as described in refs 12 and 13 with the atomic radii of ref 1.

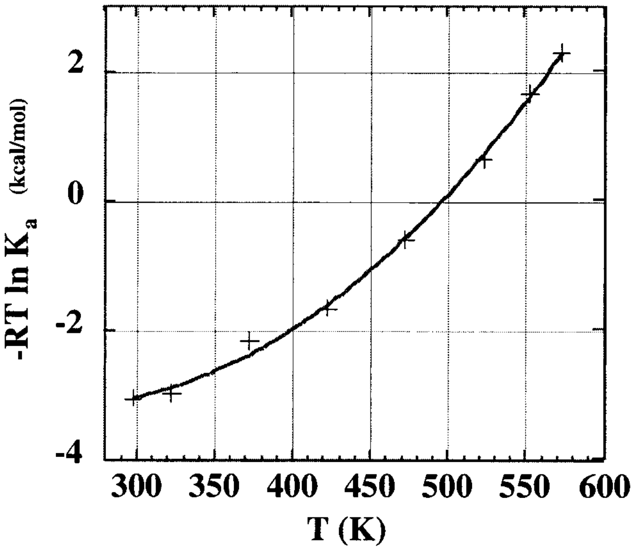

Figure 1. Variation of the dissociation coefficient eq 3 of reaction eq 1 with temperature along the water saturation curve, as described by the dielectric model of section II. In terms of the variable $\tau = -1 + T/298.15$ K, the solid curve is $-3.0 + 1.6\tau + 4.6\tau^2$, in kcal/mol. This curve crosses zero in the neighborhood of 500 K.

For the temperature dependence, we estimate

$$s^{\mathrm{ex}} \approx \frac{q^2}{2r\epsilon}\left[\left(\frac{\partial \ln \epsilon}{\partial T}\right)_\rho - \left(\frac{\partial \ln \epsilon}{\partial \ln \rho}\right)_T \alpha_p\right] \tag{9}$$

$\alpha_p = (1/V)(\partial V/\partial T)_p$ is the coefficient of thermal expansion for the pure solvent. The additional temperature derivative is $(\partial \ln \epsilon/\partial T)_\rho \approx -4.3 \times 10^{-3}$ K^{-1},[25] at this standard point, and $\alpha_p \approx 3 \times 10^{-4}$ K^{-1}.[26] This entropy contribution is negative and has a magnitude of a small multiple of 1 cal/K/mol. This magnitude is about a power of 10 smaller than typical experimental results.

The arguments suggest that the a priori confidence in the individual chemical potentials of eq 4, or in their variations with thermodynamic state, cannot be high. However, the differences required in eq 4 can be more satisfactory. In any case, this is a physical model[12−14,16,18] and sufficiently simple to be helpful.

III. Results and Discussion

Computed $\Delta G^{(0)}$ for the equilibrium of eq 1, $\Delta\mu^{\mathrm{ex}}$ according to eq 4, and corresponding $-RT \ln K_a$ over the temperature range 298.15–599.75 K are presented in Table 1. The variation of the defined dissociation constant is plotted in Figure 1. Note that the temperature variation of the net free energy $-RT \ln K_a$ is almost entirely due to the temperature variation of the hydration free energy change $\Delta\mu^{\mathrm{ex}}$ of eq 4. In the present simple model, this follows from variations in the dielectric constant. In this way, the results are indicative of changes in hydration generally rather than a specific temperature effect. The reaction eq 1 in liquid water becomes unfavorable from the perspective of the free energy upon exceeding 500 K on the saturation curve where the liquid density falls below about 85% of the triple-point density. Nevertheless, this sulfonic acid headgroup would still be considered a strong acid in bulk aqueous solution at these elevated temperature and reduced density conditions. These results give perspective for the view that insufficient hydration can result in incomplete dissociation of sulfonic acid species in membranes.[3]

The static dielectric constant of liquid water is roughly 30 in this interesting region about 500 K on the liquid−vapor coexistence curve. If a static dielectric constant were assigned to a hydrated Nafion membrane matrix, the value is unlikely to be significantly larger than 30. In this respect, the present model is not extreme. However, heterogeneity of the local environment of a sulfonic acid headgroup is probably a significant factor in both of the physical systems—liquid water and hydrated Nafion membranes—considered. The physical picture of a dielectric continuum model is more uniform than either of those systems. In this respect, this model calculation probably gives one valuable limiting possibility of the effect of hydration on the degree of dissociation of Nafion headgroups.

The dielectric properties of the aqueous components of these materials are influenced by the morphology of the polymeric system and by structural factors such as the pore dimensions, geometry, and distribution of anionic charge density. High-frequency dielectric spectroscopy studies of Nafion[27] and PEEK[28] membranes show that the real part of the relative permittivity is higher in Nafion than in PEEK at similar levels of hydration. This is consistent with the recent SAXS data[29] that suggests that typical channel radii in PEEK are smaller than those in Nafion, and thus, a larger fraction of the water is effectively immobilized in the PEEK membranes.

IV. Conclusions

The acid dissociation equilibrium of triflic acid in dilute aqueous environment was studied with a simple dielectric hydration model. The dielectric model calculation predicts that the dissociation of the acid according to reaction eq 1 becomes unfavorable from the point of view of the free energy change as temperature is increased above 500 K along the water liquid−vapor coexistence curve where the solvent density is less than 85% of the triple-point density.

Acknowledgment. This work was supported by the U.S. Department of Energy under Contract W-7405-ENG-36. LA-UR-00-5135.

References and Notes

(1) Paddison, S. J.; Pratt, L. R.; Zawodzinski, T.; Reagor, D. W. *Fluid Phase Equilib.* **1998**, *151*, 235.

(2) Paddison, S. J.; Zawodzinski, T. A., Jr. *Solid State Ionics* **1998**, *115*, 333.

(3) Paddison, S. J.; Pratt, L. R.; Zawodzinski, T. A., Jr. in *Proton Conducting Membrane Fuel Cells*; Gottesfeld, S., Fuller, T. F., Eds.; Electrochemical Society Proceedings Series: Pennington, NJ, 1999; Vol. PV 98−27, pp 99−105.

(4) Paddison, S. J.; Pratt, L. R.; Zawodzinski, T. A. *J. New Mater. Electrochem. Syst.* **1999**, *2*, 183.

(5) Paddison, S. J.; Paul, R.; Zawodzinski, T. A., Jr. in *Proton Conducting Membrane Fuel Cells*; Gottesfeld., S., Fuller, T. F., Eds.; Electrochemical Society Proceedings Series: Pennington, NJ, 1999; Vol. PV 98−27, pp 106−120.

(6) Paddison, S. J.; Paul, R.; Zawodzinski, T. A., Jr. *J. Electrochem. Soc.* **2000**, *147*, 617.

(7) Paddison, S. J.; Paul, R.; Zawodzinski, T. A., Jr. *J. Chem. Phys.* **2001**, in press.

(8) Barthel, J.; Buchner, R.; Holzl, C. G.; Conway, B. E. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1953.

(9) Pratt, L. R.; Rempe, S. B. in *Simulation and Theory of Electrostatic Interactions in Solution. Computational Chemistry, Biophysics, and Aqueous Solutions*, AIP Conference Proceedings; Pratt, L. R., Hummer, G., Eds.; American Institute of Physics: Melville, NY, 1999; Vol. 492, pp 172−201.

(10) Hummer, G.; Garde, S.; García, A. E.; Pratt, L. R. *Chem. Phys.* **2000**, *258*, 349.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.2; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Corcelli, S. A.; Kress, J. D.; Pratt, L. R.; Tawa, G. J. In *Pacific Symposium on Biocomputing '96*; Hunter, L., Klein, T. E., Eds.; World Scientific: Singapore, 1995; pp 142−159.

(13) Pratt, L. R.; Tawa, G. J.; Hummer, G.; García, A. E.; Corcelli, S. A. *Int. J. Quantum Chem.* **1997**, *64*, 121.

(14) Pratt, L. R.; Hummer, G.; García, A. E. *Biophys. Chem.* **1994**, *51*, 147.

(15) Tawa, G. J.; Pratt, L. R. *ACS Symp. Series* **1994**, *568*, 60.

(16) Tawa, G. J.; Pratt, L. R. *J. Am. Chem. Soc.* **1995**, *117*, 1625.

(17) Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565.

(18) Hummer, G.; Pratt, L. R.; García, A. E. *J. Phys. Chem. A* **1998**, *102*, 7885.

(19) Rempe, S. G.; Pratt, L. R.; Hummer, G.; Kress, J. D.; Martin, R. L.; Redondo, A. *J. Am. Chem. Soc.* **2000**, *122*, 966.

(20) Andaloro, G.; Palazzo, M. A.; Migliore, M.; Fornili, S. L. *Chem. Phys. Lett.* **1988**, *149*, 201.

(21) Alicata, F.; Migliore, M.; Fornili, S. L. *J. Mol. Liq.* **1993**, *58*, 117.

(22) Grimm, A. R.; Bacskay, G. B.; Haymet, A. D. *J. Mol. Phys.* **1995**, *86*, 369.

(23) Grimm, A. R.; Bacskay, G. B.; Haymet, A. D. *J. Mol. Phys.* **1996**, *87*, 529.

(24) Turki, N.; Milet, A.; Rahmouni, A.; Ouamerali, O.; Moszynski, R.; Kochanski, E.; Wormer, P. E. S. *J. Chem. Phys.* **1998**, *109*, 7157.

(25) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Rev. Data* **1980**, *9*, 1291.

(26) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969. See Figures 4.14 and 4.15.

(27) Paddison, S. J.; Reagor, D. W.; Zawodzinski, T. A., Jr. *J. Electroanal. Chem.* **1998**, *459*, 91.

(28) Paddison, S. J.; Bender, G.; Kreuer, K. D.; Nicoloso, N.; Zawodzinski, T. A., Jr. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 291.

(29) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.