Electrical Conductance of Hydrogen Chloride in Oxygen-18 Water at 298.15 K[†]

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The electrical conductance of aqueous solutions of HCl has been measured at 298.15 K as a function of ^{18}O-enrichment of water and can be linearly extrapolated to isotopically pure $^1H_2{}^{18}O$. The high proton mobility in normal water ($^1H_2{}^{16}O$) is retained in $^1H_2{}^{18}O$. The conductance reduction by complete $^{18}O/^{16}O$ substitution by a factor of 1.050 approximately corresponds to the increase in solvent viscosity and is substantially lower than the reduction in the water + deuterium oxide ($^2H_2{}^{16}O + {}^1H_2{}^{16}O$) system. The nonlinear dependence of the conductance of $^2HCl/^1HCl$ upon the degree of deuteration in mixtures of normal water and deuterium oxide has no analogue in mixtures with $^1H_2{}^{18}O$.

Introduction

The proton mobility in water has been of long-standing interest. In contrast to the hydrodynamic migration of other ions, proton migration is anomalously fast,[1] as manifested by the high electrical conductance of aqueous solutions of strong acids. The high conductance is attributed to a Grotthuss-type proton transfer mechanism,[2] in which the protonic charge is shuttled through chains of water molecules. In recent years, much insight into details of proton transfer processes has come from ab initio quantum-mechanical computations such as Car–Parrinello molecular dynamics simulations.[3,4] An alternative recent approach suggests that quantum correlations between H^+ and the hydrogens of the surrounding water molecules lead to the formation of coherent dissipative structures.[5−7]

For elucidating mechanistic details, the study of isotope effects is helpful. Water offers a variety of isotopic species. The overwhelming number of studies have compared the thermophysical and solvent properties of normal water (essentially $^1H_2{}^{16}O$, for simplicity abbreviated as H_2O) with those of deuterium oxide ($^2H_2{}^{16}O$, abbreviated as D_2O). The limited availability of ^{18}O- (or ^{17}O-) labeled water ($^1H_2{}^{18}O$, abbreviated as $H_2{}^{18}O$) has prevented analogous studies based on oxygen labeling.

The substitution of normal water by deuterium oxide results in substantial changes in the transport coefficients. At 298.15 K, the shear viscosity increases by the factor[8,9]

$$\eta(D_2O)/\eta(H_2O) = 1.234$$

Essentially the same factor has been observed for the self-diffusion coefficient.[10−12] Moreover, mobilities of ions such as K^+ and Cl^- deduced from electrical conductance and transference data approximately reflect the viscosity ratio.[13] Some small, but physically significant, deviations can be rationalized by local hydration effect properties.[13] By contrast, the high proton conductance in H_2O is considerably more reduced by $^1H/^2H$ substitution than predicted from the viscosity ratio.[8,14] Moreover, in $H_2O + D_2O$ mixtures, the viscosity[8] and the self-diffusion coefficient of water[12] vary almost linearly with the deuterium fraction, whereas the proton/deuteron mobility shows a pronounced negative deviation.[8,14]

In the early 1970s, Rabinovich et al.[15] and Kudish et al.[16] measured the shear viscosity of ^{18}O-enriched water. At 298.15 K the extrapolation of their data to isotopically pure $H_2{}^{18}O$ yields[16]

$$\eta(H_2{}^{18}O)/\eta(H_2O) = 1.054$$

Later, Harris and Woolf[17] reported about the same factor for the inverse self-diffusion coefficients. Thus, $^{18}O/^{16}O$ substitution leads to substantially lower isotope effects on transport coefficients than $^1H/^2H$ substitution. It is interesting to note that the factor of 1.054 coincides with the ratio of the square-root of the molecular masses of the two molecules. Such a behavior is predicted by linear response theory for the situation where isotopic substitution does not change the moment of inertia of the molecule.[18] This is approximately the case for H_2O and $H_2{}^{18}O$ but not for H_2O and D_2O.

The present study continues our earlier work on isotope effects on the effect of the electrical conductance of HCl in $H_2O + D_2O$ mixtures.[14] The paper reports on electrical conductances of solutions of HCl in ^{18}O-enriched water, which allow us to extrapolate the limiting molar conductance of HCl in isotopically pure $H_2{}^{18}O$. The study is part of more general efforts to exploit isotopic substitution for studying mechanistic details of transport processes in liquids.[11,12,19−21]

Table 1. Isotopic Compositions of the Primary Oxygen-Enriched Samples[a]

	atom fraction		
sample	^{18}O	^{17}O	^2H
#1	0.9097	0.0349	0.00014
#2	0.5342	0.0826	0.00014

[a] Isotopic compositions quoted by the manufacturer. No uncertainties quoted.

Materials and Methods

The water referred to as H_2O or normal water was local tap water purified by vacuum distillations. Two samples of ^{18}O-enriched water were obtained from IC Chemikalien (Munich). Table 1 summarizes the isotopic compositions as quoted by the manufacturer without giving uncertainties. Because the major factor in the precision of the experiments is due to limitations

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in sample preparation caused by the limited availability of $H_2{}^{18}O$, we assume that the uncertainties in the composition of the primary samples can be neglected compared to further sources of experimental error. All experimental procedures were carefully optimized. Part of these preliminary experiments are documented by Gluth.[22] To avoid isotopic exchange with atmospheric water vapor, all samples were prepared and handled in a dry nitrogen atmosphere or in a vacuum line.

Solutions in ^{18}O-enriched water with molar concentrations C of about (0.1, 0.05, and 0.01) M, respectively, were prepared from the samples #1 and #2 by adding small amounts of concentrated (> 1 M) HCl solutions in normal water. For varying the isotopic composition at given HCl concentrations, these stock solutions were mixed with HCl solutions in normal water, which were adjusted to the same HCl concentration. This adjustment was done by weight because there were no limitations in the amount of sample to be prepared. In all calculations, the mass fractions were converted to molar concentrations by using reported molar volumes of H_2O, $H_2{}^{17}O$, and $H_2{}^{18}O$.[23] (Actually these molar volumes are practically the same.)

Electrical conductances were measured with a Wayne–Kerr bridge, model 6425, using standard procedures.[1] The conductance cell was of the design of Baker and La Mer,[8] rescaled from a sample volume of about 5 cm^3 to about 1 cm^3. The experiments were conducted in an oil bath at (298.15 ± 0.01) K. Measurements were performed at frequencies f between 400 Hz and 10 kHz. The marginal frequency dependence of the resistance was extrapolated to zero frequency assuming a $1/f$ dependence.[1] The resistance measurements are accurate to ± 0.01 %.

Experimental Results

Isotope effects upon the conductance were determined by comparative measurements of pairs of solutions in ^{18}O-enriched water and natural water which were adjusted to the same HCl concentration. Thus, the primary experimental result is the ratio of the electrical resistance, R, of the solution in ^{18}O-enriched water to that of the solution in normal water at the same HCl concentration. This ratio directly reflects the isotope effect on the specific conductivities, σ, of the two solutions. Because at the HCl concentrations of interest the conductance contribution due to the autoprotolysis of water has a negligible effect on the conductance ratio, the resistance ratio also reflects the isotope effect upon the molar conductances, $\Lambda = \sigma/C$. Denoting the resistance ratio by ξ, we have

$$\xi = \frac{R(H_2{}^{18}O)}{R(H_2O)} = \frac{\sigma(H_2O)}{\sigma(H_2{}^{18}O)} = \frac{\Lambda(H_2O)}{\Lambda(H_2{}^{18}O)} \qquad (1)$$

The absolute values of the specific and molar conductance of an ^{18}O-enriched sample can then be calculated from Stokes' conductance data for HCl in normal water.[24]

Table 1 summarizes the experimental results for the H_2O/$H_2{}^{18}O$ isotope effects upon the molar conductance of HCl solutions at (298.15 ± 0.01) K. The conductance ratios were found to vary linearly with the average molar mass, M_{av}, of water. Actually, in the ternary mixtures $H_2{}^{18}O + H_2{}^{17}O + H_2{}^{16}O$, one would have expected to find a curvature, but detailed analysis showed that only a linear dependence was justified by the accuracy of the data. Figure 1 exemplifies this behavior for solutions with $C = 0.108$ M. The linear dependence enables a straightforward extrapolation to isotopically pure $^1H_2{}^{18}O$. Extrapolated values are given in Table 2.

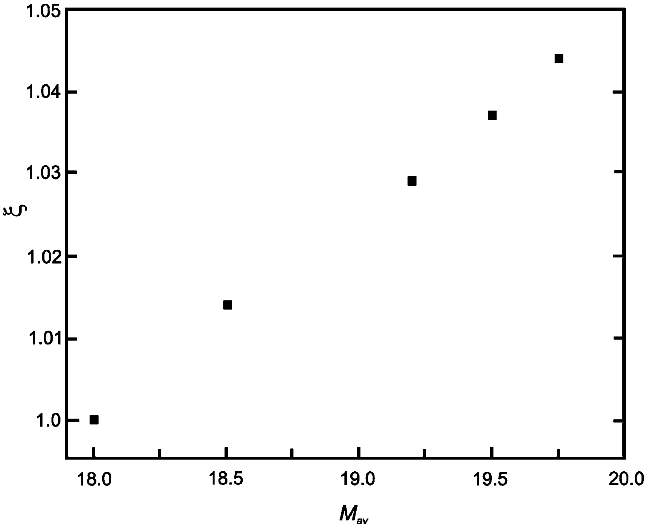

Figure 1. Ratio ξ of the molar conductances defined in eq 1 for an aqueous HCl solution of concentration $C = 0.108$ M as a function of the average relative molar mass M_{av} of water in the ternary $H_2{}^{18}O-H_2{}^{17}O-H_2{}^{16}O$ mixture.

Table 2. Effects of Oxygen Isotopic Substitution on the Molar Electrical Conductance of HCl Solutions at 298.15 K

	atom fraction		
C_{HCl}	^{18}O	^{17}O	$\Lambda(H_2O)/\Lambda(\text{sample})$
0.108 M	0.2513	0.0389	1.014
	0.50.01	0.0773	1.029
	0.7389	0.0283	1.037
	0.8593	0.0330	1.044
	1.0 (extr.)		1.050
0.0485	0.2561	0.0396	1.013
	0.5041	0.0752	1.028
	1.0 (extr.)		1.051
0.0112	0.2112	0.0327	1.012
	0.4801	0.0740	1.026
	0.7502	0.0287	1.038
	100 (extr.)		1.050

At the three HCl concentrations under test, the isotope effect $\Lambda(H_2O)/\Lambda(H_2{}^{18}O)$ agrees within experimental error, suggesting that the ratios $\Lambda^0(H_2O)/\Lambda^0(H_2{}^{18}O)$ of the limiting molar conductances at infinite dilution of HCl possess the same value. This result is not trivial because theoretical relations for the concentration dependence of Λ, such as the well-known Onsager limiting law, involve as input parameters the viscosity and dielectric constant of the solvent as well as the value of Λ^0.[1] For $H_2{}^{18}O$, the resulting concentration dependence of the isotope effect is, however, too small to be detected.

Taking the average of the ratios in Table 1 and considering the experimental uncertainties, we find for HCl in isotopically pure $H_2{}^{18}O$

$$\frac{\Lambda^0_{HCL}(H_2O)}{\Lambda^0_{HCL}(H_2{}^{18}O)} = 1.050 \pm 0.002 \qquad (2)$$

We note that the error of our resistance measurements alone would allow us to determine this ratio with an uncertainty of better than ± 0.0005. In our procedure, the major error results from the precision to which the $H_2{}^{16}O + H_2{}^{18}O$ pair can be matched to the same HCl concentration, which is mainly limited by the uncertainty in the concentration of HCl in $H_2{}^{18}O$. At $C = 0.1$ mol·dm^{-3} this uncertainty is estimated to be smaller than 0.3 %, and at $C = 0.01$ mol·dm^{-3}, it is estimated to be smaller than 0.5 %. The resulting uncertainty in the conductance is at least by a factor of 5 larger than the error caused by the resistance measurements themselves.

According to data by Stokes[1,24] (converted from the international to the absolute Ohm), the limiting conductance of HCl in normal water is $\Lambda^0_{\mathrm{HCl}}(\mathrm{H_2O}) = 425.95\ \mathrm{S\ cm^2 \cdot mol^{-1}}$, with a quoted uncertainty of $\pm\ 0.05\ \mathrm{S \cdot cm^2 \cdot mol^{-1}}$. On the basis of this value, the limiting conductance in isotopically pure $\mathrm{H_2{}^{18}O}$ is

$$\Lambda^0_{\mathrm{HCL}}(\mathrm{H_2{}^{18}O}) = 405.67\ \mathrm{S \cdot cm^2 \cdot mol^{-1}}$$

Error propagation of the uncertainty of the ratio (2) yields for $\Lambda^0_{\mathrm{HCl}}(\mathrm{H_2{}^{18}O})$ an uncertainty of ± 0.7.

Finally, we estimate the limiting ionic conductances of $\mathrm{H^+}$ and $\mathrm{Cl^-}$. The rigorous separation of the molar conductance $\Lambda^0_{\mathrm{HCl}} = \lambda^0_{\mathrm{H^+}} + \lambda^0_{\mathrm{Cl^-}}$ into its ionic contributions, $\lambda^0_{\mathrm{H^+}}$ and $\lambda^0_{\mathrm{Cl^-}}$, requires data from transference experiments,[1] which are not available. We can exploit, however, the observation that the mobility of $\mathrm{Cl^-}$ in $\mathrm{D_2O}$ reflects within experimental error the viscosity ratio of $\mathrm{D_2O + H_2O}$.[13] Assuming that this condition holds for $\mathrm{Cl^-}$ in $\mathrm{H_2{}^{18}O}$ as well, we immediately find $\lambda^0_{\mathrm{Cl^-}}(\mathrm{H_2{}^{18}O}) = 72.40\ \mathrm{S \cdot cm^2 \cdot mol^{-1}}$ and $\lambda^0_{\mathrm{H^+}}(\mathrm{H_2{}^{18}O}) = 333.27\ \mathrm{S \cdot cm^2 \cdot mol^{-1}}$. Our procedure implies that $\lambda^0_{\mathrm{Cl^-}}(\mathrm{H_2{}^{18}O})$ essentially reflects the accuracy to which the viscosity of $\mathrm{H_2{}^{18}O}$ is known, resulting in an estimated uncertainty of ± 0.05. By error propagation, the uncertainty of $\lambda^0_{\mathrm{H^+}}(\mathrm{H_2{}^{18}O})$ is by at least an order of magnitude larger, ± 0.5 say. Finally, the isotope effect upon the proton conductance is given by

$$\frac{\lambda^0_{\mathrm{H^+}}(\mathrm{H_2O})}{\lambda^0_{\mathrm{H^+}}(\mathrm{H_2{}^{18}O})} = 1.049 \pm 0.002$$

Thus, our results suggest that the $^{18}\mathrm{O}/^{16}\mathrm{O}$ isotope effect upon the proton conductance is somewhat lower than the isotope effect upon the viscosity.

Discussion

The unusually high electrical conductance of HCl in normal water, usually attributed to the so-called Grotthuss mechanism, is maintained in $\mathrm{H_2{}^{18}O}$. The $^{18}\mathrm{O}/^{16}\mathrm{O}$ isotope effect upon the limiting ionic conductance of the proton corresponds roughly to the isotope effect on the viscosity of water. The behavior largely differs from that obtained by $^2\mathrm{H}/^1\mathrm{H}$ substitution in the $\mathrm{H_2O + D_2O}$ pair. The decrease of the excess conductivity in $\mathrm{D_2O}$ markedly exceeds the viscosity effect. It may be noted that $^{18}\mathrm{O}/^{16}\mathrm{O}$ substitution only changes the nature of the surrounding medium but not that of the transferred particle. By contrast, $\mathrm{D_2O}$ substitution changes the nature of the transferred particle (proton/deuteron) as well.

A second difference between $\mathrm{H_2{}^{18}O}$ and $\mathrm{D_2O}$ substitution concerns the conductance variation with the fraction of $\mathrm{H_2{}^{18}O}$ or $\mathrm{D_2O}$ in the mixture. At a given HCl concentration there are substantial negative deviations of the proton/deuteron conductance from a linear dependence on the degree of deuteration.[14] In the equimolar $\mathrm{H_2O + D_2O}$ mixture, the deviation amounts to about 5 %. By contrast, the proton conductance varies linearly with $^{18}\mathrm{O}$ enrichment.

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Literature Cited

(1) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1968.

(2) de Grotthuss, C. J. T. Memoire upon the Decomposition of Water, and on the Bodies which it holds in Solutions, by means of Galvanic Electricity. *Anal. Chim. (Paris)* **1806**, *LVIII*, 54−74; Engl. translation: *Philos. Mag. (London)*, **1806**, *25*, 333−339.

(3) Marx, D. Proton Transfer 200 Years after von Grotthuss: Insights from Ab Initio Simulations. *Chem. Phys. Chem.* **2006**, *7*, 1848–1870.

(4) Voth, G. A. Computer Simulation of Proton Solvation and Transport in Aqueous and Biomolecular Systems. *Acc. Chem. Res.* **2006**, *39*, 143–150.

(5) Chatzidimitriou-Dreismann, C. A. Complex Scaling and Dynamical Processes in Amorphous Condensed Matter. *Adv. Chem. Phys.* **1991**, *80*, 201–314.

(6) Chatzidimitriou-Dreismann, C. A.; Brändas, E. Quantum Coherence in Disordered Condensed Matter. III Hydrogen Ion and Hydroxide Ionic Conductance and Proton Transfer Reactions in Aqueous Solutions. *Int. J. Quantum Chem.* **1990**, *37*, 155–165.

(7) Chatzidimitriou-Dreismann, C. A.; Brändas, E. Proton Nonlocality and Decoherence in Condensed Matter−Predictions and Experimental Results. *Adv. Chem. Phys.* **1997**, *99*, 393–430.

(8) Baker, W. N.; La Mer, V. K. The Conductance of Potassium Chloride and Hydrochloric-Deuterochloric Acid in $\mathrm{H_2O}$-$\mathrm{D_2O}$ Mixtures. The Viscosity of $\mathrm{H_2O}$-$\mathrm{D_2O}$. *J. Chem. Phys.* **1935**, *3*, 406–410.

(9) Millero, F. J.; Dexter, R.; Hoff, E. Density and Viscosity of Deuterium Oxide Solutions from 5−75 °C. *J. Chem. Eng. Data* **1971**, *16*, 85–87.

(10) Mills, R. Self-Diffusion in Normal and Heavy Water in the Range 1−45 °C. *J. Phys. Chem.* **1973**, 685–688.

(11) Weingärtner, H. Self-Diffusion in Liquid Water. A Reassessment. *Z. Phys. Chem. (München)* **1982**, *132*, 129–149.

(12) Weingärtner, H. Diffusion in Mixtures of Light and Heavy Water. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 47–50.

(13) Swain, C. G.; Evans, F. Conductance of Ions in Light and Heavy Water at 25 °C. *J. Am. Chem. Soc.* **1966**, *88*, 383–390.

(14) Chatzidimitriou-Dreismann, C. A.; Weingärtner, H. Anomalous Proton and Deuterium Conductance in Water−Deuterium Oxide Mixtures. *Nature (London)* **1990**, *346*, 548–550.

(15) Rabinovich, I. B.; Tsvetkov, V. G. Isotopic Effects in the Properties of Oxygen-18-labelled Water. *Zh. Fiz. Khim.* **1971**, *45*, 2675–2676.

(16) Kudish, A. I.; Wolf, D.; Steckel, F. Physical Properties of Heavy-oxygen Water. Absolute Viscosity of $\mathrm{H_2{}^{18}O}$ between 15 and 35 °C. *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 2041–2946.

(17) Harris, R. K.; Woolf, L. A. Pressure and Temperature Dependence of the Self-Diffusion Coefficient of Water and Oxygen-18 Water. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 377–385.

(18) Friedman, H. L. Isotope Effects Upon Motions in Liquids in the Classical Limit. In *Molecular Motions in Liquids*; Lascombe, J., Ed.; Reidel: Dordrecht, 1974; p 87.

(19) Weingärtner, H.; Holz, M.; Sacco, A.; Trotta, M. The Effect of Site-specific Isotopic Substitution on Transport Coefficients of Liquid Methanol. *J. Chem. Phys.* **1989**, *91*, 2568–2574.

(20) Holz, M.; Weingärtner, H.; Sacco, A. Isotope Effects upon Translational Diffusion as a Probe for Translation-Rotation Coupling in Molecular Liquids. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 332–336.

(21) Sacco, A.; Weingärtner, H.; Braun, B. M.; Holz, M. Study of the Structure-breaking Effect on aqueous CsCl Solutions based on $\mathrm{H_2O}$/$\mathrm{D_2O}$ Isotope Effects on Transport Coefficients and Microdynamical Properties. *J. Chem. Soc., Faraday Trans* **1994**, *90*, 849–853.

(22) Gluth, S. Diploma Thesis, Karlsruhe, 1990.

(23) Kell, G. S. Effect of Isotopic Composition, Temperature, Pressure and Dissolved Gases on the Density of Liquid Water. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1109–1131.

(24) Stokes, R. H. The Conductance of Hydrochloric Acid at 25 °C. *J. Phys. Chem.* **1961**, *65*, 1242–1247.

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