Conductance of Potassium Iodide in Supercooled Water

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The conductance of potassium iodide was measured in water as a function of concentration (between 2×10^{-3} and 10^{-2} mol dm^{-3}) and temperature (between −6 and 0 °C). The effect of temperature on the mobility of such halide ions as I^- and Cl^- ions was discussed by taking the ionic residual friction coefficient $\Delta\zeta$, which was defined as the overall friction coefficient subtracted by the Stokes one for slip, instead of the conventional Walden product. We compared the experimental results with the predictions due to the Hubbard-Onsager dielectric friction theory. Of the monovalent ions so far studied, the iodide ion shows the largest negative value of $\Delta\zeta$ with the largest positive temperature coefficient; their signs are opposite to those theoretically predicted. These findings were explained in terms of the special ionic transport mechanism called the passing-through-cavities.

The conductivity measurement in electrolyte solution has made a great contribution to our understanding of the dynamic and static properties of electrolyte solution because of its high sensitivity and the availability of the single-ion property. We can probe the ion-ion and ion-solvent interactions through the concentration dependence of molar conductance and its limiting value, respectively; the latter quantity is involved in a theoretical equation of conductance to be determined experimentally. As reviewed elsewhere,[2,3)] however, our attention is now focused on the dynamics of the ion-solvent interaction as a result of the stimulation due to the recent advances in the theory of ion mobility.[4—7)]

The modern dielectric friction theory of ionic motion in solution developed by Hubbard and Onsager (HO)[4,5)] has been tested systematically against experiments on ion mobility (translational motion) under a variety of conditions in the previous papers.[8—16)] In the extensive test,[9—16)] the residual friction coefficient ($\Delta\zeta$), which is defined as the overall ionic friction coefficient subtracted by the Stokes one for slip,[9,17)] has been used successfully instead of the conventional Walden product, and led to the elucidation of the reliability and limitations of the HO theory; although the HO theory can describe the charge effect for small ions with a large surface charge density, it is unsuccessful in explaining the negative values of $\Delta\zeta$ for such medium-sized ions as the larger alkali metal and the halide ions in hydrogen-bonded solvents.

The validity of the HO theory indicates that the classical Stokes-Einstein-Walden framework for interpreting ion mobility has to be replaced by the modern HO framework as soon as possible. On the other hand, the disclosed limitations of the HO theory suggests the necessity of a new theory where the molecular nature and the liquid structure of solvent are taken into account in some manner. To explain the essential limitations of the continuum theory for ion transport, such a jump mechanism as the passing-through-cavities (PTC) has been proposed.[9—12,16)] The idea on the PTC mechanism has been hinted in the first study on conductances of the alkali metal ions in supercooled water.[9)] This important work is extended here to such halide ions as I^- and Cl^- to have more insights into the PTC mechanism.

Theoretical

We use the HO continuum model as a reference system to elucidate the effect of the solvent structure on the mechanism of ion transport process. For this purpose, first of all, we show in brief the significance of the HO theory and the procedure for its application.

Although the Stokes-Einstein-Walden (SEW) framework based on the Navier-Stokes (NS) hydrodynamic equation of motion is in general use in the interpretation of ion mobility, in principle, the NS hydrodynamic equation is inapplicable to ionic systems of our interest. HO have overcome the fundamental limitations of ordinary hydrodynamics by developing the dielectric friction theory and inventing the epoch-making electrohydrodynamic equation for migrating ions as follows:

$$\eta\nabla^2\boldsymbol{v}=\nabla p-\tfrac{1}{2}[\boldsymbol{E}_0\times(\nabla\times\boldsymbol{P}^*)+\boldsymbol{E}_0(\nabla\cdot\boldsymbol{P}^*)], \qquad (1)$$

where η is the solvent viscosity, $\boldsymbol{v}$ the velocity field in the fluid, p the pressure, $\boldsymbol{E}_0$ the electrical field at $v=0$, and $\boldsymbol{P}^*$ the polarization deficiency. In this equation $\boldsymbol{P}^*$ expresses the departure of the orientational polarization of the Debye type from that at $v=0$ due to slow dielectric relaxation of the flowing solvent. Thus HO extended the NS hydrodynamic equation to ionic systems in a self-consistent manner by adapting the Debye dielectric relaxation theory to the flow system involving a charged sphere.

The second term on the right side of Eq. 1 represents the contribution of dielectric friction which is coupled to viscous friction. The full coupling of the two kinds of frictions renders the HO theory superior to ordinary hydrodynamics and the early dielectric friction theory[18,19)] in the treatment of ion dynamics in solution, as clearly shown elsewhere.[15,16,20,21)]

The essential difference between the modern (HO) and classical (NS) continuum models mentioned above is understandable from Eq. 1. When the charge on an ion is neglected ($\boldsymbol{E}_0=0$), Eq. 1 reduces to the linearized form of the NS equation given by

$$\eta \nabla^2 v = \nabla p. \qquad (2)$$

This equation leads to the following well-known Stokes law of the friction coefficient for a sphere with the radius R:

$$\zeta_S = 4\pi\eta R, \qquad (3)$$

where ζ_S is the Stokes friction coefficient for the slip boundary condition. As mentioned elsewhere,[14] the slip boundary condition seems preferable to the stick on the molecular level, and R is usually taken to be the crystallographic radius of the ion.[22] Thus only the size effect of the solute can be handled by the NS hydrodynamic equation, whereas the charge effect as well as the size effect is treated by the HO electrohydrodynamic equation in a self-consistent manner.

The ionic friction coefficient ζ is related to the limiting conductance λ° as:

$$\zeta = |e| F/\lambda^\circ, \qquad (4)$$

where F is the Faraday constant and e is the ionic charge. By using Eqs. 3 and 4 we can define the residual friction coefficient[9,17] as

$$\Delta\zeta = \zeta - \zeta_S. \qquad (5)$$

Since the purely hydrodynamic friction is taken as a reference in Eq. 5, $\Delta\zeta$ reflects mainly the dielectric friction and all the other factors neglected in the primitive hydrodynamic model for ζ_S. As elucidated previously,[17] the residual friction coefficient is much more useful and meaningful than the so far widely used Walden product.

The numerical solutions to the linearized form of Eq. 1 are given in terms of the dimensionless quantity of the form

$$x = \zeta/\eta R_{HO}, \qquad (6)$$

where R_{HO} denotes the Hubbard-Onsager radius, and x depends only on R and R_{HO}. A kind of solvent parameter R_{HO} is defined as

$$R_{HO} = \left[\frac{e^2}{16\pi\eta\varepsilon_0^2}(\varepsilon_0 - \varepsilon_\infty)\tau\right]^{1/4}, \qquad (7)$$

where τ, ε_0 and ε_∞ are the dielectric relaxation time, the static, and high-frequency dielectric constants, respectively.

The HO theoretical value of the residual friction coefficient is expressed in the polynomial form[14,15]

$$\Delta\zeta = \eta(xR_{HO} - yR) = \eta R_{HO} \sum_{j=1}^{4} a_j (R_{HO}/R)^j, \qquad (8)$$

where $y = 4\pi$ for the slip boundary condition considered here and the universal coefficients are given as follows:

$$a_1 = -2.7866,$$
$$a_2 = 8.6216,$$
$$a_3 = -3.3425,$$

and

$$a_4 = 0.39550,$$

for $R/R_{HO} > 0.3$, which is satisfied by the I^- ion in water. When the physical properties of solvent involved in the HO radius expressed by Eq. 7 are all available, the HO value of the residual ionic friction coefficient $\Delta\zeta$ can be calculated for the ion characterized by the radius R and the charge e according to Eq. 8 under any conditions.

Table 1. Molar Conductances Λ (S^{-1} cm^2 mol^{-1}) of KI in Supercooled Water at Various Concentrations C (mol dm^{-3})

t/°C	$C^{a)} \times 10^3$				
	2.167_6	4.066_1	5.953_0	7.924_2	9.863_6
0	81.09	80.52	80.14	79.85	79.64
−2	76.40	75.88	75.53	75.29	75.09
−4	71.80	71.31	71.00	70.77	70.57
−6	67.29	66.91	66.59	66.41	66.18

a) Concentrations at 0 °C.

Table 2. Limiting Molar Conductances (S^{-1} cm^2 mol^{-1}) of KI, K^+, and I^- in Water and Parameters in Eq. 9 as a Function of Temperature

t/°C	Λ°	$\lambda^\circ(K^+)^{a)}$	$\lambda^\circ(I^-)$	S	E	J
0	83.06	40.63	42.43	48.10	21.26	180
−2	78.22	38.25	39.97	44.97	20.05	176
−4	73.50	35.94	37.56	41.95	18.86	164
−6	68.91	33.67	35.24	39.03	17.72	156

a) From Ref. 9.

Experimental

Potassium iodide of high quality was supplied by Merck. The concentrations of the dilute solutions at 5 °C were determined by weight, and their variation with temperature was corrected by using the density of water. The conductivity of water was in the range of 5×10^{-7}—8×10^{-7} s^{-1} cm^{-1} at 0 °C. Molar conductances of KI measured in this way were reproducible within ±0.1%. The physical properties of water, such as density, dielectric properties, and viscosity, used in the present work are provided elsewhere.[9,23] Details of the experimental apparatus and procedure are described in the previous paper.[23]

Results

Table 1 shows the molar conductance (Λ) of KI in water measured as a function of concentration C (mol dm^{-3}) and temperature t (°C). The limiting molar conductances Λ°(S^{-1} cm^2 mol^{-1}) summarized in Table 2 are obtained by analyzing the conductance data in Table 1 with the aid of the Fuoss-Onsager equation of conductance for unassociated electrolyte[24,25]

$$\Lambda = \Lambda^\circ - SC^{-1/2} + EC \log C + JC, \qquad (9)$$

where the parameters S, E, and J have the usual meaning and depend on the temperature and the solvent properties. Our value of Λ° (KI) at 0 °C agrees with that in the literature.[26]

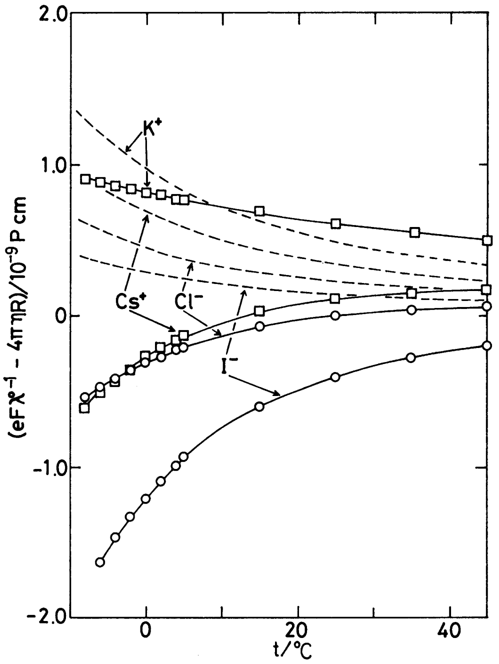

Fig. 1. Plots of the theoretical and experimental residual friction coefficients for several ions in water against temperature. The broken and full lines indicate the theoretical and experimental results, respectively. The square and circle symbols are used for the cations and anions, respectively.

As pointed out elsewhere,[9,11,23,27] the Fuoss-Onsager equation based on the sphere-in-continuum model describes well the concentration dependence of conductance in supercooled water. The validity of the continuum model for this case indicates that the relaxation and electrophoretic effects on ion mobility due to the ion-ion interactions in dilute solution can be presented in terms of the water radial distribution function that is effectively unity at a large ion-ion separation as in the continuum model. As discussed below, however, this is not the case for the ion-solvent interactions acting in the short range.

The limiting molar conductance of the iodide ion $\lambda^\circ(\mathrm{I}^{-1})$ listed in the fourth column of Table 2 is derived at each temperature by using the value of $\lambda^\circ(\mathrm{K}^+)$ previously determined;[9] the Kohlrausch law of independent migration of ions is applied. By using Eqs. 4 and 5 we have transformed the limiting ionic conductances of the iodide ion and some others[9] into the residual friction coefficients and plotted them against temperature in Fig. 1 for comparison with the HO theoretical prediction. The residual friction coefficients above 0 °C in Fig. 1 are computed from the conductance data in the literature.[26,28]

Discussion

Figure 1 shows how the HO dielectric friction theory of ion mobility predicts the temperature and ion-size dependencies of the residual friction coefficients for the medium-sized ions; the theory predicts that the positive ionic residual friction coefficient decreases with an increase in temperature and ion size. Although the K^+ ion ($R=1.33$ Å) has a negative temperature coefficient of $\Delta\zeta$ just as predicted, the I^- ($R=2.16$ Å) and Cl^- ($R=1.81$ Å) ions as well as the Cs^+ ion ($R=1.69$ Å) exhibit a positive temperature coefficient and a large negative value of $\Delta\zeta$ contrary to the theoretical prediction. Of the monovalent ions so far investigated, the iodide ion has the largest negative residual friction coefficient. However, the observed values of $\Delta\zeta$ are in the sequence $\mathrm{K}^+ > \mathrm{Cs}^+ > \mathrm{Cl}^- > \mathrm{I}^-$ in agreement with the HO prediction.

The unpredictable sign of the temperature coefficients of $\Delta\zeta$ for the medium-sized ions is originally related to their large negative values which become more negative as water is supercooled. The negative sign of $\Delta\zeta$ expressed by Eq. 5 indicates that the friction coefficients for these ions are even smaller than the lower limit (Eq. 3) set by the continuum model where the bulk properties of the solvent are used. The essential limitation of the continuum model for solvent is not ascribed to the charge effect of the ion but to the size effect because a similar limitation of the Stokes-Einstein law is found for diffusion of neutral molecules.[3,16,29,30] Thus it turns out that although the HO continuum theory is successful for small ions with a large surface charge density, it exhibits essential limitations for the medium-sized ions because of the neglect of many complicated factors in the vicinity of the ion. To explain the anomalous mobility, such a concept as the passing-through-cavities (PTC) mechanism has been introduced in the previous work.[9,10,12,16]

Figure 1 suggests that the stabilization or development of the hydrogen-bonded network in water favors the PTC mechanism. This is quite reasonable because the PTC process requires the framework formed by the hydrogen-bonded water molecules. The PTC process is assisted by such a cooperative fluctuating motion of the framework that it can reduce the potential barrier or friction for ion migration.[12] The role of the PTC mechanism increases when the extent of hydrogen bonds in water is promoted by any other factors than temperature; the PTC mechanism has so far been confirmed by changing the water structure through temperature,[9,11,12] pressure,[10-13] solvent isotope,[13] and organic cosolvent.[14,15] In this respect, this mechanism is analogous to that seen in the solid electrolyte.[31] Thus the PTC mechanism remains as a memory in the short-range order characteristic of the liquid state even after the long-range order is completely lost by melting. The corresponding limitations of the continuum model are shown also in the study of rotational motion of ions.[20]

Such an ion transport process as the PTC mechanism is expected to be important in highly viscous liquids, liquid crystals, and membranes in view of the features described above. This will be examined in our experimental investigation in progress. Furthermore, a molecular theory of ionic or molecular diffusion in liquids is desired to be developed beyond hydrodynamics. The Wolynes molecular theory$^{6,7)}$ cannot explain the negative value of $\Delta\zeta$ because it relies upon the hydrodynamic relation Eq. 3 in the expression of the friction coefficient due to the hard force-hard force correlation.

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