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On the Effect of the Finite Size of the Solvent Molecule in Dielectric Friction Theory

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By considering the charge distribution function around the ion, the effect of the finite size of the solvent molecule can be introduced in the homogeneous dielectric continuum model. A very simple and useful model is presented. The results of this model are compared quantitatively with the experimental Walden products of some simple cations in water, methanol, ethanol, acetone, and acetonitrile solutions, and found to be satisfactory.

There has been a lot of theoretical work on the dielectric friction using the continuum model.[1–5] It has been shown that some of these theories succeed qualitatively.[6–7] Most of the authors of these works regarded the surrounding medium as a dielectric continuum extending up to the surface of the ion. Due to this assumption, dielectric continuum theories do not consider the short range order around the ion correctly. The finite size of the solvent molecule has not yet been properly treated in dielectric continuum theories.

In this article, we will develop a dielectric continuum model without empirical parameters by taking the finite size of the solvent radius into consideration. By introducing the similar treatment of the molecular theory by Wolynes[8] into the dielectric continuum model, we can achieve a very simple and useful model for the dielectric friction theory. We will show that this model is successful for some ion-solvent systems.

Description of the Dielectric Drag Coefficient

We will start from the consideration of the polarization of a volume element at point $\boldsymbol{r}$ due to the electric field originating from the ion. The force exerted on the ion by this induced polarization at point $\boldsymbol{r}$, $\boldsymbol{f}(\boldsymbol{r})$, can be written as[8]

$$\boldsymbol{f}(\boldsymbol{r}) = -2q^2\frac{\varepsilon_0-\varepsilon_\infty}{4\pi\varepsilon_0{}^2}\frac{\boldsymbol{r}}{r^5}, \tag{1}$$

where q is the charge of the ion, ε_0 the static (low frequency) dielectric constant of the solvent, ε_∞ the optical (infinite frequency) dielectric constant of the solvent, and $r=|\boldsymbol{r}|$.

On the other hand, when the ion moves in a potential with relaxation time τ_d, the drag coefficient, $\Delta\zeta$, originating from this electrostatic interaction is expressed by[8]

$$\Delta\zeta = k\tau_d. \tag{2}$$

Here k is the force constant of this potential and the harmonic potential is assumed. This constant, k, can be derived from the differential coefficient of the total electrostatic force, $\boldsymbol{F}$, which acts on the ion, when the ion is displaced a small distance δz from the center of this potential. Namely,

$$k = \left(\frac{\partial \boldsymbol{F}}{\partial z}\right)_{z=0}, \tag{3}$$

where the total force, $\boldsymbol{F}$, is expressed by the sum of the contribution of the polarizations, $\boldsymbol{f}(\boldsymbol{r})$, which are induced on each volume element. When we carry out this summation, we must consider the charge distribution around the ion. For the use of Eq. 1, we will introduce the charge distribution function $\rho(\boldsymbol{r})$ which is normalized in such a way that $\rho(\boldsymbol{r})$ is equal to 1 at large r. Therefore, k can be expressed by the following equation:

$$\begin{aligned} k &= \int \mathrm{d}^3 r\rho(r)\left(\frac{\partial f(r)}{\partial z}\right)_{z=0} \\ &= \int_0^\infty \mathrm{d}r\int_\Omega \mathrm{d}\Omega\rho(r)\left(\frac{\partial f(r)}{\partial z}\right)_{z=0}, \end{aligned} \tag{4}$$

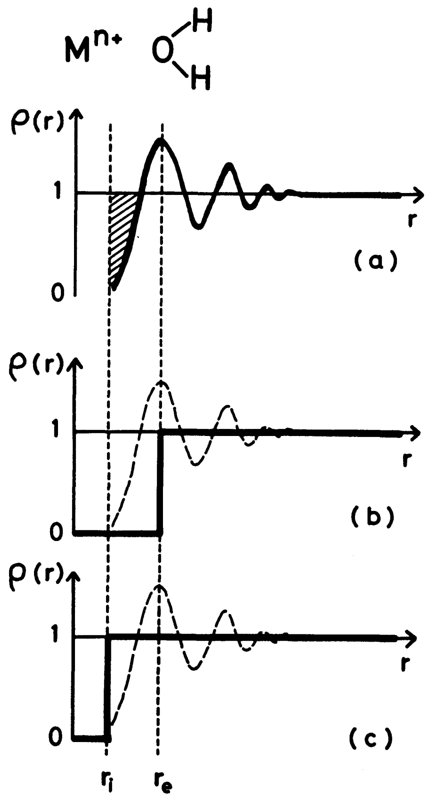

Fig. 1. Schematic charge distribution function around the ion, $\rho(r)$. (a) "Exact" charge distribution. The shaded region indicates the underestimated region of the previous works. (b) Step-wise charge distribution for $r_e=R_{M-O}$. (Eq. 5) (c) Charge distribution for the previous works.

where d^3r is the differential volume element and $d\Omega$ is the angular part of the differential volume element. Considering the effect of the finite size of the solvent radius corresponds to the consideration of the oscillation of $\rho(\boldsymbol{r})$ (see Fig. 1). In Wolynes' treatment, $\rho(\boldsymbol{r})$ was calculated by the molecular dynamics method. It can be seen that the distribution function of their model was selected strictly. By introducing a suitable model, we can take the effect of the oscillation of $\rho(\boldsymbol{r})$ into the continuum theory. For simplicity, we will take the step function for $\rho(\boldsymbol{r})$ as

$$\rho(\boldsymbol{r}) = \rho\,(r) \begin{cases} = 0 & \text{for } r < r_c \\ = 1 & \text{for } r \geq r_e, \end{cases} \tag{5}$$

where r_e is the first peak position of the charge distribution function contributing to the induced polarization. This step function, Eq. 5, can take roughly the effect of the first trough of $\rho(r)$ which is shown by the shaded region of Fig. 1-a. The value of $\rho(r)$ at the first peak is larger than 1 and that at the second trough is smaller than 1, *etc.* Therefore, the use of the step function, Eq. 5, possibly underestimates the effect of the first peak and overestimates that of the second trough, *etc.* But these effects partly cancel with each other. So we can use this equation as a first approximation.

By referring to Eq. 5, the drag coefficient, $\Delta\zeta$, is expressed by the following equation:

$$\begin{aligned} \Delta\zeta &= \tau_d \int_0^\infty dr \int_\Omega d\Omega \rho(r) \left(\frac{\partial f(r)}{\partial z}\right)_{z=0} \\ &= \tau_d \int_{r_e}^\infty dr \int_\Omega d\Omega \left(\frac{\partial f(r)}{\partial z}\right)_{z=0} \\ &= \frac{2}{3} q^2 \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0^2} \frac{\tau_d}{r_e^3}. \end{aligned} \tag{6}$$

If we replace r_e with the radius of the ion in Eq. 6, this formula will be identical with the results obtained by Zwanzig's theory,[4] which can be regarded as the essence of the dielectric friction theories.

The values of r_e can be obtained from the distance between the center of the ion and the center of the atom that belongs to the first nearest neighbor molecules, *i.e.*, in the case of the aqueous solution, the distance between the ion and the oxygen atom, R_{M-O}. We can take the R_{M-O} data of some of the electrolyte aqueous solutions from X-ray diffraction analyses.[9–14] The R_{M-O} data from the X-ray studies agree well with the sum of the crystalline ion radius and the van der Waals' radius of an oxygen atom.

Results and Discussion

We will examine Eq. 6 with the R_{M-O} values which are used for r_e. R_{M-O} values are taken as the sum of the crystalline ion radius and the van der Waals' radius of the nearest atom of the first nearest neighbor molecule. The other parameters used in the following results are taken from Refs. 15—23. The results of the calculations using the Walden product,[24] $\lambda_0\eta$, are shown in Figs. 2 and 3 in the case of aqueous solutions. Here λ_0 is limiting ionic equivalent conductance: $\lambda_0 = Fq/\zeta$ (F is the Faraday constant) and $\zeta = 4\pi\eta r_i + \Delta\zeta$ (η is the bulk viscosity of the solvent). The results in the case of the solution of some other solvents are also shown in Figs. 4 and 5.

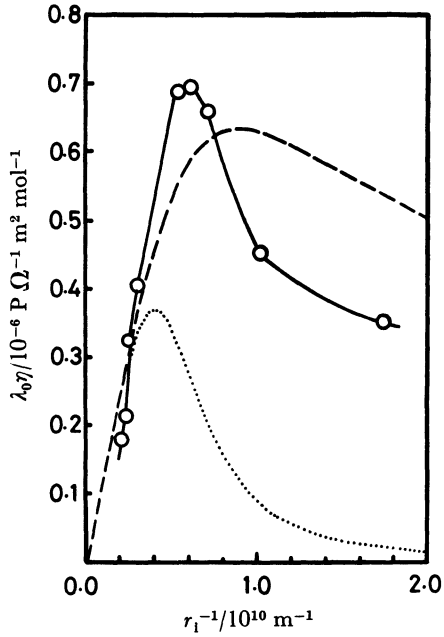

Fig. 2. Experimental (—○—) and calculated (----; $r_e = R_{M-O}$, ······; $r_e = r_i$) Walden products for the alkali metal and tetraalkylammonium ions in water solutions. The experimental values indicate Li^+, Na^+, K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, and $(C_4H_9)_4N^+$, from right side to left side [1 P=0.1 Pa s (in the unit of the vertical axis)].

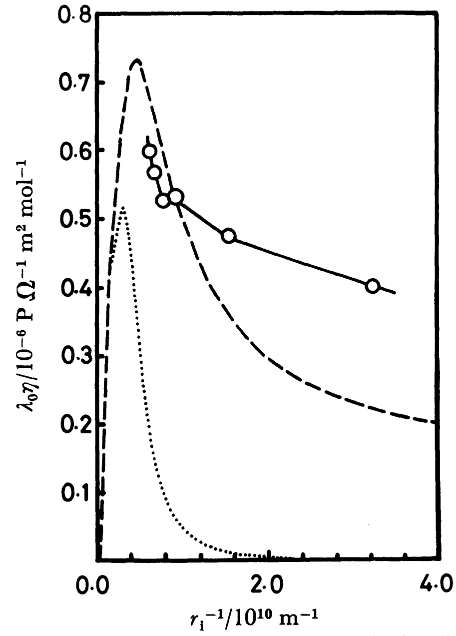

Fig. 3. Experimental (—○—) and calculated (----; $r_e = R_{M-O}$, ······; $r_e = r_i$) Walden products for the alkaline earth metal ions in water solutions. The experimental values indicate Be^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+}, from right side to left side [1 P=0.1 Pa s (in the unit of the vertical axis)].

Figure 2 shows the observed[15,16] and calculated $\lambda_0\eta$

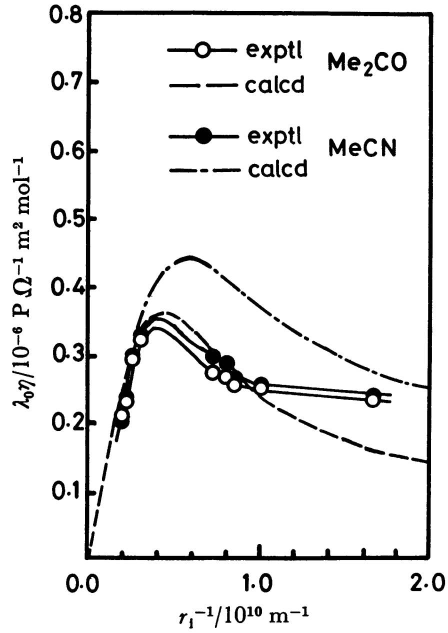

Fig. 4. Experimental and calculated Walden products for the alkali metal and tetraalkylammonium ions in acetone (Me_2CO) and acetonitrile (MeCN) solutions. The experimental values indicate Li^+, Na^+, K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, and $(C_4H_9)_4N^+$, from right side to left side [1 P=0.1 Pa s (in the unit of the vertical axis)].

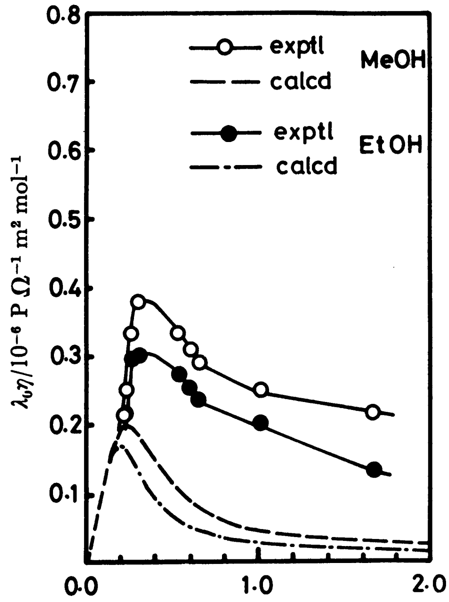

Fig. 5. Experimental and calculated Walden products for the alkali metal and tetraalkylammonium ions in methanol (MeOH) and ethanol (EtOH) solutions. The experimental values indicate Li^+, Na^+, K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, and $(C_4H_9)_4N^+$, from right side to left side. The experimental value of $(C_4H_9)_4N^+$ in ethanol solution is lacked [1 P=0.1 Pa s (in the unit of the vertical axis)].

values for the aqueous solutions of some (1+) ions. It can be seen from Fig. 2 that the calculated values agree well with the observed ones. Figure 2 shows also the calculated values using Zwanzig's formula[4] ($r_e = r_i$). Fig. 3 shows the data of the Walden products for the aqueous solutions of some (2+) ions. It shows better agreement than the case of (1+) ions, except for Be^{2+} and Mg^{2+} ions. We can see from this fact that the contribution of the electrostatic interaction will be the main effect for the case where the ion has larger electronic charge than a (1+) ion with the same radius. Figure 4 shows the observed[15,16,18] and calculated Walden products of the (1+) ions dissolved in acetone or acetonitrile. They agree well, as is the case in water. In the case of methanol and ethanol, however, our results do not agree with the observed results,[15,16] as shown in Fig. 5.

Latimer *et al.*[25] and Stokes[26] discussed the problem of the short range order around the ion on the solvation enthalpy. Considering the small region around the ion whose dielectric constant is different from the "bulk" dielectric constant, they have corrected the Born's equation[1] and fitted the calculated solvation enthalpy to the observed one. It is surely important for the ionic mobility problem also that the physical properties around the ion are different from "bulk" ones. But these treatments have some empirical parameters such as the size of the region. Therefore, in this article, we will discuss the ionic mobility problem without such empirical parameters and consider the importance of the charge distribution around the ion.

Wolynes *et al.* gave the results of their molecular theory on the ionic mobility problem.[8] Our results for the case of water and acetonitrile agree well with theirs. It is surprising that a very simple description of the charge distribution function such as Eq. 5 can express the force exerted on the ion well. The advantage of our approach is that it needs only simple parameters.

A theory that regards the surrounding medium as a dielectric continuum extending up to the surface of the ion, like Zwanzig's,[4] is not sufficient. For example, such a theory gives a Walden product of Li^+ ion about 20 times smaller than the one observed in water solution. As compared with this, our treatment of dielectric friction using the very simple charge distribution function agree quite well with observed data quantitatively. This indicates that the short range order around the ion is important for electrostatic interaction. This can be anticipated from the consideration of the r_e dependence of $\Delta\zeta$ in Eq. 6. The same situation occurs in the other dielectric friction theories.[1–3,5,6]

In contrast with the good agreement of the case of water solution *etc.*, our model for the methanol or ethanol solution does not agree with experimental data quantitatively. An effort to make agreement by varying the R_{M-O} value results in physically unreasonable figures. Therefore, some other effect must be involved in these alcohols. The dielectric relaxation times of methanol (69 ps) and ethanol (144 ps) are 1—2 orders larger than that of water (9.3 ps).[16,17] This indicates that some other relaxation time governs the exerted force relaxation, *e.g.*, the translational relaxation time pointed out by Wolynes.[8] The disagreement of our calculation for methanol and ethanol (Fig. 5) may correspond to this possibility.

The calculated Walden products of Be^{2+} and Mg^{2+} of aqueous solution do not agree with observed ones as well as those for the other (2+) ions (Fig. 3). The ionization potential (IP) data[27] suggests the existence of the specific interaction between Be^{2+} or Mg^{2+} and water molecules. The electron affinities of Be^{2+} (18.2 eV) and Mg^{2+} (15.0 eV) are larger than the first IP of water molecule (12.8 eV). Therefore, it is possible that the charge transfer from water molecule to the Be^{2+} or Mg^{2+} ion occurs in the aqueous solutions. This fact suggests that there are two types of cations, *i.e.* Be^+ or Mg^+ and H_2O^+ ion, in these aqueous solutions. The *ab initio* SCF calculation of Mg^{2+}–H_2O system[28] indicates that the charge transfer from H_2O to Mg^{2+} occurs. The atomic population of Mg^{2+} obtained from this calculation is 10.058.

The results shown here indicate that the charge distribution function must be used when we consider the dielectric friction quantitatively. For closer quantitative discussion, the exact (and/or experimental) charge distribution function is necessary. But the simple treatment of the charge distribution like Eq. 5 is sufficient to describe the dielectric friction quantitatively. This fact suggests that the consideration of the electrostatic interaction at the short range order around the ion is important for the macroscopic dielectric friction theories.

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