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# Effect of "Local Viscosity" on Translational Friction and Viscosity $B$ Coefficients for a Spherical Molecule in Solution

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The translational friction and the viscosity $B$ coefficients for a spherical molecule in solution are calculated from the Navier–Stokes equation for a continuum with space-dependent viscosity. We test three functions for the space dependence of the viscosity as models for the "local viscosity". Each function is a smooth function of distance from the solute center and approaches the viscosity in the bulk at an infinite distance. For all the three functions studied, the translational friction and the viscosity $B$ coefficients decrease with decreasing viscosity in the vicinity of the solute, and the effect of the space-dependent viscosity is larger for the $B$ coefficient than for the translational friction coefficient. These results can explain the observed shortcomings of the ordinary continuum model with space-independent viscosity. This confirms the validity of the use of the viscosity $B$ coefficient as a measure of the structure-breaking effect which is closely related to the idea of the "local viscosity".

The continuum model with spatially uniform solvent properties (the uniform continuum model UCM) has been widely used to explain dynamical properties of electrolytes and nonelectrolytes in solutions. Typical examples are the Stokes law[1,2] for the translational friction coefficient and the Einstein law[2] for the viscosity of solution. Although UCM usually predicts the correct order of magnitude for transport properties and their dependence on pressure and temperature,[3—6] its applicability shows obvious limitations which are believed to originate from the disregard of the molecular nature and liquid structure of the solvent. In order to overcome the limitations, solution chemists have introduced modifications into UCM. Among such modifications, the "solvation radius" and the "local viscosity" are the most important and the most popular ones. These parameters are introduced rather intuitively and their applicabilities have to be justified on a physical basis. For this purpose, Ibuki and Nakahara[7] discussed the validity of the idea of the "solvation radius" for the case of ions in terms of the dielectric friction theory.[8,9] Here we focus our attention on the problem of the "local viscosity".

The idea of the "local viscosity" is usually employed to explain observed friction coefficients smaller than UCM predictions. However, the relation between a small friction coefficient and a viscosity reduction around a solute is not so clearly understood on a physical basis. It should be recognized that the Stokes and Einstein laws tell nothing about the effect of the "local viscosity", since these laws are based on spatially uniform solvent properties. The "local viscosity" is a space-dependent property, so that its analysis should be based on an equation in which the space-dependent properties of the solvent are taken into account. In the present paper, we calculate friction coefficients for a spherical solute in a continuum starting from the Navier–Stokes equation with space-dependent viscosity (the nonuniform continuum model NUCM). The properties calculated are the translational friction and the viscosity $B$ coefficients. The present calculation reveals how the idea of the "local viscosity" is useful for interpreting transport properties in solutions. This kind of analytical study is valuable for a deeper understanding of the limitations of the structureless model, and can stimulate the development of molecular theories of transport properties in solution.

An attempt to evaluate the effect of the "local viscosity" was made by Gierer and Wirtz.[10] In their model, the solvent flow around a solute is divided into concentric layers each with thickness equal to the diameter of the solvent molecule. Such an artificial model is unsatisfactory from both the hydrodynamic and molecular points of view. Another attempt was made by Stiles and Hubbard.[11] As pointed out earlier by Hubbard,[9] the dielectric friction makes the solvent near an ion more viscous due to the dynamic polarization effect. In this sense, Stiles and Hubbard calculated the translational friction coefficient with a space-dependent viscosity which is caused by the dielectric friction and the electrostriction. Although their theory was derived on a concrete physical basis, it can explain only a local viscosity larger than that in the bulk.

When we discuss the effect of the "local viscosity", the viscosity $B$ coefficient is of great importance. The idea of the "local viscosity" is closely related to the structure-breaking effect of ions in aqueous solutions,[12—15] and the negative $B$ coefficients observed for medium-sized ions like the halide ions are considered to be a good measure of the breaking effect. To the authors' knowledge, however, no attempt has been made to explain the validity of the use of the $B$ coefficient as a measure of the breaking effect. In the present paper, we discuss the validity on the basis of the nonuniform continuum model.

## Theoretical

**1. Space-Dependent Viscosity.** Unfortunately, we have so far no reliable model which analytically expresses a functional form of space-dependent local viscosity. It seems, however, that solution chemists implicitly suppose some conditions for the functional form. To discuss the conditions, a classical model for the structure of aqueous electrolyte solutions proposed by Frank and Wen[13] is helpful. In their model, solvent water around an ion is divided into three parts. The innermost part is a solvation shell in which water molecules are strongly oriented towards the central ion. The outermost part is the bulk water region. Between the two parts, there is an intermediate region in which the solvent is less structured and less viscous than in the other two, though there is no well-defined boundary between the intermediate and outer region. In the case of a medium-sized ion for which the breaking effect is most pronounced, it is considered that the innermost region disappears and the ion is directly immersed in the intermediate region. From this model, we can extract the following conditions for the functional form of the position $\boldsymbol{r}$ dependent "local viscosity" $\eta(r)$: (1) At a sufficiently long distance from the solute, $\eta(r)$ is identical with the viscosity $\eta_0$ in the bulk. (2) Near the solute, $\eta(r)$ is less than $\eta_0$ in average, while $\eta(r)$ must be positive everywhere. (3) $\eta(r)$ is a smooth function of $r$. (4) The difference between $\eta(r)$ and $\eta_0$ decays with distance either monotonously or oscillatory. (5) For a spherical solute, $\eta(r)$ is spherically symmetric around it.

The origin of the breakdown of the solvent structure in the intermediate region is ascribed to an incompatibility between the hydrogen-bonded network in the bulk water and the electrostatic ordering of water molecules towards the central ion. Then we suppose here that the degree of structure-breaking is proportional to the ion-dipole interaction. This assumption results in the following functional form for $\eta(r)$:

$$\eta(r) = \eta_0 \left(1 - \alpha \frac{R^3}{r^3}\right), \tag{1}$$

where $r$ is the distance from the center of the solute, $R$ the solute radius, and $\alpha$ a constant which characterizes the degree of the local viscosity reduction. The value of $\alpha$ is less than unity since the viscosity is always positive; $\alpha=1$ for the zero minimum viscosity, $\alpha=0$ for the space-independent viscosity, and $\alpha<0$ for the local viscosity larger than that in bulk. This function satisfies all the conditions discussed above.

Although Eq. 1 is our first choice, we employ two more functions for $\eta(r)$ in order to show that the validity of our results does not depend on the particular choice of the functional form. One is

$$\eta(r) = \eta_0 \left(1 - \alpha \frac{R^3}{r^3} \cos^2 \left[\frac{\pi}{2}\left(\frac{r}{R} - 1\right)\right]\right). \tag{2}$$

With this function, we can check whether an oscillatory behavior of $\eta(r)$ affects our results. Although the deviation of $\eta(r)$ from $\eta_0$ is not necessarily negative everywhere, we model (Eq. 2) to avoid positive deviations, because positive deviations must be small, even when they exist, in view of the condition (2) mentioned above. We set the period of oscillation as the diameter $2R$ of the solute for each function, because the size of an ion for which the structure-breaking effect is important is usually comparable to the size of a water molecule.

The other is

$$\eta(r) = \eta_0 \left(1 - \alpha \frac{R^6}{r^6}\right). \tag{3}$$

This function supposes the case that the local reduction of the viscosity is governed by a shorter ranged interaction than the ion-dipole one.

The position dependences of the model functions given by Eqs. 1, 2, and 3 are depicted in Fig. 1 for the case of $\alpha=0.5$.

**2. Equation of Motion for a Continuum with Space-Dependent Viscosity.** The Navier–Stokes equation with space-dependent viscosity is given[16] by

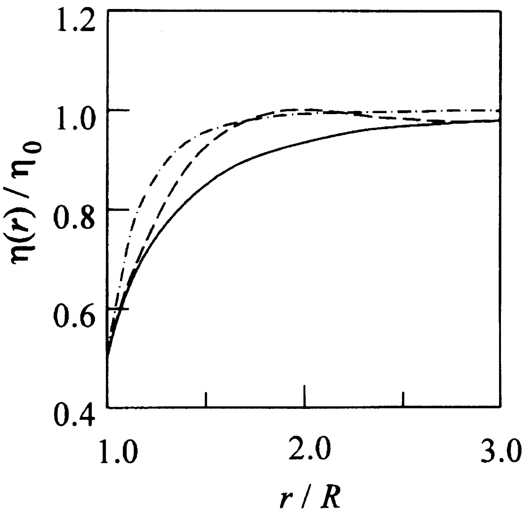

Fig. 1. Distance dependences of the model functions for the space-dependent viscosity for the case of $\alpha=0.5$. Solid, broken, and broken-dashed lines indicate Eqs. 1, 2, and 3, respectively.

$$\rho\left[\frac{\partial \boldsymbol{v}}{\partial t}+(\boldsymbol{v}\cdot\nabla)\boldsymbol{v}\right]=-\nabla p+[\nabla\eta(r)]\cdot\sigma+\eta(r)\nabla^2\boldsymbol{v}. \tag{4}$$

Here, $\rho$ is the density of the continuum, $\boldsymbol{v}$ the velocity field, $t$ the time, $p$ the pressure field, and $\sigma$ the rate-of-strain tensor defined as follows:

$$\sigma_{ij}=\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}, \tag{5}$$

where $x_i=x$, $y$, $z$. To derive Eq. 4, we have used the condition of incompressibility,

$$\nabla\cdot\boldsymbol{v}=0 \tag{6}$$

Although a space dependence of the viscosity might accompany that of the density, we assume a uniform density for simplicity. Stiles and Hubbard[11] calculated the effect of the electrostriction on the translational friction coefficient of an ion based on the dielectric friction theory. According to their theory, the contribution of the electrostriction is smaller than those of the dielectric and purely viscous frictions. In particular, it is very small and negative in water, so that we can assume that a density variation around a solute due to the electrostriction has only a small effect on friction coefficients. Equation 4 is reduced to the ordinary Navier–Stokes equation when the viscosity is independent of space.

We ignore the effect of dielectric friction in Eq. 4 even though the effect of the "local viscosity" is important for ionic solutes. In the case of a medium-sized ion for which the breaking effect is important, however, the Hubbard–Onsager theory tells us that the effect of dielectric friction is much smaller than the effect of viscous friction.[4—9] Furthermore, the effects of dielectric friction and "local viscosity" have opposite directions; it is one of the most serious limitations of the dielectric friction theory that the theory cannot explain the observed friction coefficients smaller than those predicted by the purely viscous friction.[4—6] From these facts we can assume that the effect of dielectric friction is not so important for the ions of interest here. When the solute is a neutral molecule, of course, we can safely ignore the effect of dielectric friction of the first approximation.

As far as slow steady flow is concerned, we can put the left-hand side of Eq. 4 as zero (the Stokes approximation).

$$0=-\nabla p+(\nabla\eta)\cdot\sigma+\eta\nabla^2\boldsymbol{v}. \tag{7}$$

Taking rotation, we get the following equation for the velocity field:

$$0=\eta\nabla^2(\nabla\times\boldsymbol{v})+(\nabla\eta)\times(\nabla^2\boldsymbol{v})+\nabla\times[(\nabla\eta)\cdot\sigma]. \tag{8}$$

This is the basic equation for the calculation of transport coefficients in a continuum with space-dependent viscosity.

**3. Translational Friction Coefficient.** The translational friction coefficient $\zeta_T$ is related to the diffusion constant $D$ as follows:[1]

$$D=\frac{k_BT}{\zeta_T}, \tag{9}$$

where $k_B$ and $T$ are the Boltzmann constant and the absolute temperature, respectively. It is also related to the limiting molar conductance $\lambda^0$ for an ion:

$$\lambda^0=\frac{eF}{\zeta_T} \tag{10}$$

where $e$ and $F$ are the ionic charge and the Faraday constant, respectively.

For the calculation of the translational friction coefficient, we assume that velocity field around a spherical solute can be expressed in the form,[8,9]

$$\boldsymbol{v}(\boldsymbol{r})=\frac{1}{2}\nabla\times[f(r)(\boldsymbol{u}\times\boldsymbol{r})], \tag{11}$$

where $f(r)$ is a scalar function that expresses the perturbation on the velocity field by the presence of the sphere and $\boldsymbol{u}$ is the solvent velocity at an infinite distance. The incompressibility condition is automatically satisfied by this form. Substituting Eq. 11 into Eq. 8, we get the following ordinary differential equation of $f(r)$:

$$\frac{\mathrm{d}^4f}{\mathrm{d}r^4}+\left(\frac{8}{r}+\frac{2}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}^3f}{\mathrm{d}r^3}+\left(\frac{8}{r^2}+\frac{1}{\eta}\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2}+\frac{10}{r\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}^2f}{\mathrm{d}r^2}-\left(\frac{8}{r^3}-\frac{2}{r\eta}\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2}-\frac{2}{r^2\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}f}{\mathrm{d}r}=0 \tag{12}$$

The boundary conditions for $f(r)$ are given as follows:

$$\lim_{r\to\infty}f(r)=1 \tag{13}$$

$$f(R)=0 \tag{14}$$

$$\beta\frac{r}{2}\frac{\mathrm{d}f}{\mathrm{d}r}=\eta\left(\frac{r}{2}\frac{\mathrm{d}^2f}{\mathrm{d}r^2}+\frac{\mathrm{d}f}{\mathrm{d}r}\right),\quad \text{at } r=R. \tag{15}$$

The first condition guarantees that the velocity field becomes a uniform flow $\boldsymbol{u}$ at an infinite distance. The second is the kinematic condition, which means that the normal component of the fluid velocity at the solute surface is zero. The third is the slip-stick condition, which determines the relation between the slip parameter $\beta$ and the tangential component of the fluid velocity at the solute surface. We calculate only two extreme cases for Eq. 15, i.e., the perfect slip case with $\beta=0$ and the perfect stick case with $\beta=\infty$; the former is preferred for a monatomic solute.[4]

The function $f(r)$ should have the same form as that of the Stokes field at a sufficiently long distance where the viscosity is practically constant.

$$f(r)=1-S_1\frac{R}{r}+S_2\frac{R^3}{r^3}, \tag{16}$$

where $S_1$ and $S_2$ are the constants. Then the force $\boldsymbol{F}$ acting on the sphere is given by

$$\boldsymbol{F}=-4\pi\eta_0RS_1\boldsymbol{u}. \tag{17}$$

The validity of this equation is justified by a theorem that the force acting on a domain in an arbitrary closed surface does not depend on the choice of the surface.

It is to be noted that there is a famous paradox called Whitehead's paradox[17] which tells us that the Stokes approximation does not give a proper expression for the velocity field around a sphere at a long distance. This means that Eq. 16 is not a good approximation for the long distance behavior of the velocity field. For a slow and steady flow with a space-independent viscosity, however, the frictional force calculated from Eq. 16, i.e., the Stokes law, is known to be valid.[17] Since the procedures to calculate the frictional force on the solute are the same, our result is considered to be valid within the same level of approximation as the Stokes law.

From Eq. 17, the translational friction coefficient is expressed by,

$$\zeta_T = 4\pi\eta_0 R S_1. \tag{18}$$

**4. Viscosity *B* Coefficient.** The viscosity $B$ coefficient is defined through the Jones–Dole equation[18] for the concentration dependence of the viscosity of dilute electrolyte solutions.

$$\frac{\eta'}{\eta_0} = 1 + A\sqrt{c} + Bc, \tag{19}$$

where $\eta'$ and $\eta_0$ are the viscosities of the solution and pure solvent, respectively, $c$ is the electrolyte concentration in mol dm$^{-3}$, and $A$ and $B$ are the constants. The $A$ coefficient comes from the ion–ion interaction,[19] and the $B$ coefficient for a nonelectrolyte can also be defined through Eq. 19 with the $A$ term omitted. The $B$ coefficient thus obtained is an analogue of the intrinsic viscosity for a polymer solution.

We assume the following functional form of the velocity field for the calculation of the viscosity $B$ coefficient:[5]

$$\boldsymbol{v}(\boldsymbol{r}) = \frac{1}{3}\nabla \times [f(r)(\boldsymbol{v}_0 \times \boldsymbol{r})], \tag{20}$$

$$\boldsymbol{v}_0 = \gamma(z\hat{i} + x\hat{k}), \tag{21}$$

where $\boldsymbol{v}_0$ is the solvent velocity at an infinite distance, $\gamma$ is a constant that characterizes velocity gradient, and $\hat{i}$ and $\hat{k}$ are the unit vectors in $x$ and $z$ directions, respectively.

With Eqs. 8, 20, and 21, we get the following ordinary differential equation:

$$\frac{\mathrm{d}^4 f}{\mathrm{d}r^4} + \left(\frac{12}{r} + \frac{2}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}^3 f}{\mathrm{d}r^3} + \left(\frac{24}{r^2} + \frac{1}{\eta}\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2} + \frac{16}{r\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}^2 f}{\mathrm{d}r^2}$$
$$+\left(-\frac{24}{r^3} + \frac{4}{r\eta}\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2} + \frac{14}{r^2}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)\frac{\mathrm{d}f}{\mathrm{d}r}$$
$$+\left(\frac{6}{r^2\eta}\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2} - \frac{6}{r^3\eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)f(r) = 0. \tag{22}$$

The boundary conditions for $f(r)$ are given by

$$\lim_{r\to\infty} f(r) = 1 \tag{23}$$

$$f(R) = 0, \tag{24}$$

$$\beta\frac{r}{3}\frac{\mathrm{d}f}{\mathrm{d}r} = \eta\left(\frac{r}{3}\frac{\mathrm{d}^2 f}{\mathrm{d}r^2} + \frac{4}{3}\frac{\mathrm{d}f}{\mathrm{d}r}\right),\ at\ r = R. \tag{25}$$

The meanings of Eqs. 23, 24, and 25 are the same as those of Eqs. 13, 14, and 15, respectively.

The functional form expected at a sufficiently long distance is

$$f(r) = 1 - S_1\frac{R^3}{r^3} + S_2\frac{R^5}{r^5}. \tag{26}$$

Using this expression, the $B$ coefficient becomes

$$B = \frac{4}{3}\pi R^3 S_1 \cdot \frac{N}{1000}, \tag{27}$$

where $N$ is the Avogadro number.

**5. Numerical Solutions.** We solve the differential equations derived above by a numerical method. The method is similar to that used by Stiles, Hubbard, and Kayser[20] to calculate the dielectric saturation effect on the translational friction coefficient in the dielectric fiction theory. An extension of the method for the calculation of the $B$ coefficient is straightforward.[5] For a space-independent viscosity, our calculation reproduces the Stokes and Einstein laws. The calculation is carried out using a workstation (HP 712/60).

## Results and Discussion

Figures 2 and 3 show the calculated translational friction and viscosity $B$ coefficients, respectively. Each result is depicted as a function of the viscosity reduction parameter $\alpha$ in the range of $0 \leq \alpha \leq 0.5$. Since the idea of the "local viscosity" is usually employed to explain the friction coefficient smaller than that predicted by UCM, we represent results only for positive $\alpha$ values. The results for $\alpha = 0$ are identical with the UCM predictions.

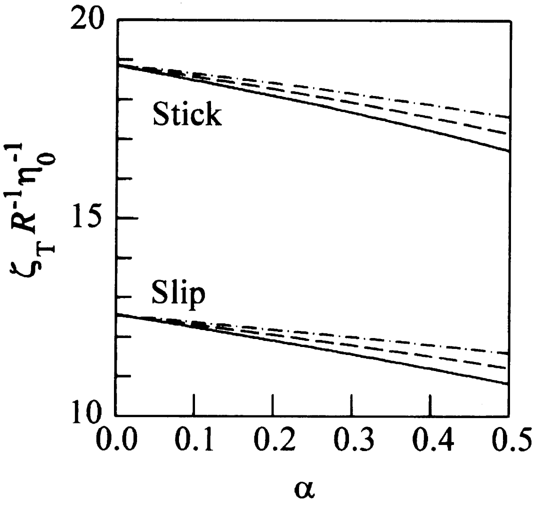

Fig. 2. Translational friction coefficients as functions of the viscosity reduction parameter $\alpha$. Lines have the same meanings as in Fig. 1.

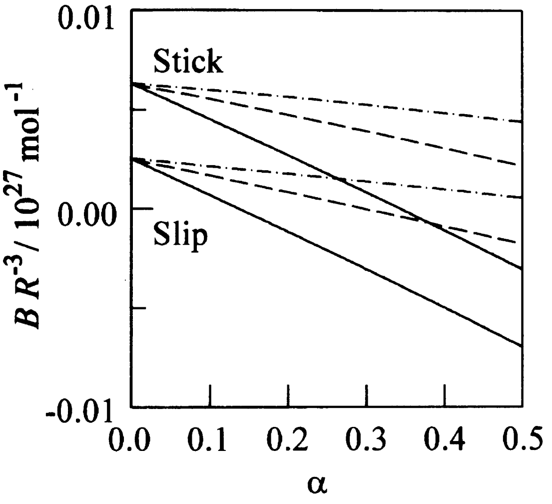

Fig. 3. Viscosity $B$ coefficients as functions of the viscosity reduction parameter $\alpha$. Lines have the same meanings as in Fig. 1.

Quantitatively speaking, the effects of the space-dependent viscosity on the translational friction and the viscosity $B$ coefficients decrease in the order of Eqs. 1, 2, and 3. This indicates that a space-dependent viscosity with a longer-ranged contribution has larger effects on the friction coefficients. Qualitatively speaking, however, the results exhibit similar tendencies irrespective of the functional forms of the space-dependent viscosity and the boundary conditions at the solute surface. (1) Both the translational friction and the viscosity $B$ coefficients decrease monotonously with increasing $\alpha$ parameter. (2) The reduction of the translational friction coefficient from the Stokes low ($\alpha=0$) amounts to less than 15% at $\alpha=0.5$. (3) Although the variation of the $B$ coefficient with $\alpha$ largely depends on the functional form of $\eta(r)$, the degree of its reduction from UCM is larger than those of $\zeta_T$ at the same $\alpha$ value for all the functions studied; the $B$ coefficient becomes even negative for some cases.

The first result indicates that the effect of the " local viscosity" is in the direction that solution chemists expect. The second and the third results tell us about the difference in sensitivity to a local viscosity change between the translational friction and the viscosity $B$ coefficients. To clarify this point, the correlation between the two coefficients is examined in Fig. 4. In this figure, we exhibit results only for the slip boundary condition, because this condition is preferred for monatomic solutes like the halide ions. The UCM prediction is indicated by a closed circle in the figure; since the translational friction and the viscosity $B$ coefficient are normalized by $R\eta_0$ and $R^3$, respectively, the UCM predictions for different solute radii are identical. On the other hand, the NUCM predictions depend on the degree of the viscosity reduction, i.e., the value of the $\alpha$ parameter. The line for $(B/\zeta_T)(\eta_0/R^2)=$const. is also depicted for comparison; this line expresses the correlation curve for the case that the effect of the space-dependent viscosity reduces $\zeta_T$ and $B$ by the same ratio. For all the three functions studied, slopes of the correlation curves are larger than that of the curve for $(B/\zeta_T)(\eta_0/R^2)=$const. This indicates that the $B$ coefficient is more sensitive to a local viscosity change around a solute than the translational friction coefficient. In other words, the breakdown of UCM can be more clearly recognized by $B$ than by $\zeta_T$.

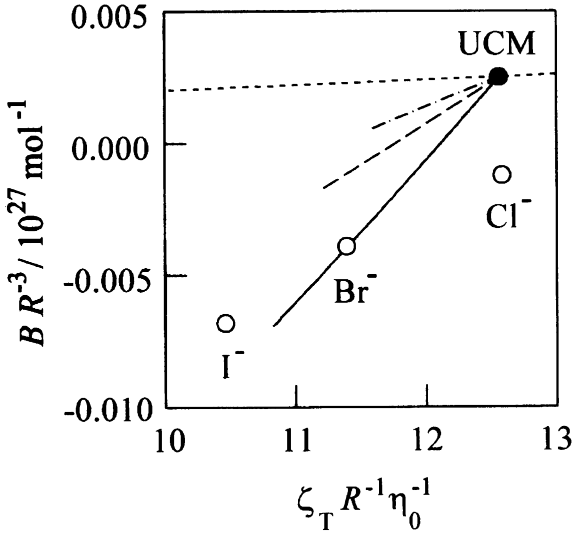

Fig. 4. Correlation between the translational friction and the viscosity $B$ coefficients. Dotted line indicates the line for the case of $(B/\zeta_T)(\eta_0/R^2)=$const. Other lines have the same meanings as in Fig. 1. A closed circle indicates the UCM prediction. Open circles indicate experimental results for the halide ions in water at 25 °C.

In Fig. 4, we also plot experimental results of the translational friction[3] and the viscosity $B$ coefficients[15] for the halide ions in water at 25 °C; we use the crystallographic radius[21] for the ionic radius $R$, and the ionic $B$ coefficients are calculated from the electrolyte $B$ coefficients with the assumption that $B(\text{Cl}^-)=B(\text{K}^+)$.[12,15] The experimental correlation slope is much larger than the slope for $(B/\zeta_T)(\eta_0/R^2)=$const. This qualitatively agrees with the present results. Although the intercepts for the theoretical and the experimental correlation curves differ to some extent, it is difficult to discuss the difference quantitatively since the experimental intercept directly depends on the assumption for the ionic division of the $B$ coefficient; we cannot determine the ionic $B$ coefficient without any arbitrariness. However, the experimental slope is not sensitive to the method of the ionic division. Hence we can consider that the present model explains the observed correlation between the translational friction and the viscosity $B$ coefficients.

The difference in the sensitivity to a local viscosity change can be understood in terms of the difference in the velocity fields from which the friction coefficients are calculated. When we assume the space dependence of the viscosity as a perturbation, the first approximations for the friction coefficients can be calculated from the space-dependent viscosity and the unperturbed velocity fields given by UCM. The equations which characterize the unperturbed velocity fields are Eqs. 16 and 26 for the translational friction and the viscosity $B$ coefficients, respectively. It should be noted that the space dependence in Eq. 16 is longer-ranged than that in Eq. 26; the leading term in Eq. 16 is proportional to $r^{-1}$, whereas that in Eq. 26 is proportional to $r^{-3}$. This indicates that, for the translational friction coefficient, the contribution from a long distance where the viscosity is virtually a constant is much larger than for the $B$ coefficient. In other words, the $B$ coefficient is determined by a shorter-ranged effect and more sensitive to a local viscosity change than the translational friction coefficient.

In view of its sensitivity to a local viscosity reduction, the viscosity $B$ coefficient can be regarded as a good measure of local effects around a solute. This confirms the validity of the use of the $B$ coefficient as a measure for the structure-breaking effect. The relation between the $B$ coefficient and the breaking effect was thoroughly discussed by Gurney[12)] in terms of the "co-sphere" effect. Although he discussed the interrelation between the viscosity $B$ and the translation friction coefficients, he stressed the correlation between the $B$ coefficient itself and the temperature dependence of the electrical conductivity instead of a direct correlation between the two quantities. Necessity of such a subtle choice of correlating variables can be understood by the present result; the translational friction coefficient is insensitive to a local viscosity change and can be roughly approximated by the Stokes law, so that it is difficult to extract information about the limitations of UCM from examinations of the translational friction coefficient itself. On the other hand, Ibuki and Nakahara[6)] pointed out that if we examine deviations from the UCM predictions, we can recognize a direct correlation between the two quantities more clearly.

Once we adopt the space-dependent viscosity, we can interpret the translational friction and the viscosity $B$ coefficients smaller than those predicted by UCM and the correlation between them on the basis of NUCM. The present work is an attempt to answer the question how much local changes in solvent properties affect macroscopic transport properties for different modes of motion. The present results suggest that the investigation of the viscosity of nonelectrolyte solutions as well as electrolyte solutions will give us valuable information about the limitations of UCM in relation to local effects. In theoretical and computer simulation studies, however, it seems that only a little attention has been paid to the viscosity $B$ coefficient compared with the translational friction coefficient. We hope that the origin of the local viscosity change will be elucidated in terms of a molecular theory.

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