# Role of Electrical Interactions in the Rotational Motion of a Charged Solute Molecule in a Polar Solvent

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A continuum theory of the rotational motion of a uniformly charged solute molecule in a polar solvent which takes into account dielectric friction, dielectric saturation, and spatial dependence of the solvent viscosity due to electrostriction is developed. The results are obtained from the solution of the generalized electrohydrodynamic equations for rotational motion. We observe that both dielectric saturation and dielectric friction have a strong impact on the rotational dynamics of the solute, while the effect of the local enhancement of the viscosity is not of the same importance.

It is generally acknowledged that the electrical interactions between a charged solute and a polar solvent are very important in both the rotational and translational motions of solute molecules. Microscopic,[1−4] as well as continuum, theories[5−12] have been developed to address this problem. The microscopic approaches, having the obvious advantage of being "first-principle" theories, usually provide very complicated expressions, which are typically difficult to analyze. On the other hand, the continuum theories ignore the molecular structure of the solvent; however, they generally allow a qualitative and even quantitative analysis of the solute dynamics.[13] These models regard the solvent as a continuous medium with local macroscopic properties (e.g., viscosity, density, etc.), which vary smoothly from point to point in the bulk. The role of the solute−solvent electrical interactions in these continuum theories is 2-fold: Firstly, relaxation of the solvent polarization in the electric field of the solute particle causes a "dielectric friction" effect,[5−11] which augments the hydrodynamic viscous friction. Secondly, electrostriction of the solvent in the vicinity of the solute particle modifies its local viscosity;[14] hence, the viscous drag and torque exerted on a moving particle are also altered.[15] Both the viscosity enhancement ("electroviscosity") and the dielectric friction are accompanied by dielectric saturation of the solvent in the vicinity of the solute particle due to the extremely high electrical field.[11]

The impact of the dielectric friction on the *rotational* motion of solutes was considered for dipolar[16] or charged noncentrosymmetric particles.[17] In references 16 and 17 the first-order approximation for the dielectric friction coefficient was obtained, but the effects of electroviscosity and dielectric saturation were not taken into account. In the present study, we analyze the impact of dielectric saturation, dielectric friction, and electroviscosity on the rotational motion of a charged spherical solute. Our analysis is based on the exact solution of the generalized Hubbard−Onsager equations for a uniformly rotating sphere which has been obtained recently.[18] An approximate analysis of these effects has been performed for the case of translational motion,[12] but to our knowledge no such analysis has yet been done for the rotational motion.

The generalized Hubbard−Onsager equations, which account for the electrostriction, read[18]

$$\nabla[\eta\hat{D} + (\zeta + {}^1/_3\eta)\,\mathrm{div}\,\mathbf{V}] = \nabla\left[p - {}^1/_2\mathbf{E}_0^2\rho\frac{\partial\chi}{\partial\rho}\right] - {}^1/_2\mathbf{E}_0 \times \mathrm{rot}\,\mathbf{P}^* - {}^1/_2\mathbf{E}_0\,\mathrm{div}\,\mathbf{P}^* - {}^1/_2\mathbf{E}_0^2\nabla\chi \quad (1)$$

$$\tau_D^{-1}\mathbf{P}^*(\mathbf{r}) = (\mathbf{V}\cdot\nabla)\chi_D\mathbf{E}_0 + {}^1/_2\chi_D\mathbf{E}_0 \times \mathrm{rot}\,\mathbf{V} \quad (2)$$

Here $\mathbf{V}(\mathbf{r})$ and $p(\mathbf{r})$ are, respectivly, the velocity and pressure fields at point $\mathbf{r}$ in the bulk; $\hat{D} = (\partial V_i/\partial r_j + \partial V_j/\partial r_i)$; $\eta$ and $\zeta$ are the shear and bulk viscosities of the solvent; $\chi = (\epsilon - 1)/4\pi$ and $\chi_D = (\epsilon - \epsilon_\infty)/4\pi$ are total polarizability and orientational polarizability, respectively, of the solvent; and $\epsilon$ and $\epsilon_\infty$ are the low and high frequency dielectric constants. $\mathbf{E}_0(\mathbf{r})$ is the electric field of the solute particle in the dielectric at rest; $\mathbf{P}^*$ is the polarization deficiency (i.e., the difference between the actual polariazation $\mathbf{P}$ and its static value $\chi\mathbf{E}_0$):

$$\mathbf{P}^* = -(\mathbf{P} - \chi\mathbf{E}_0)$$

finally, $\tau_D$ is the Debye (orientational) relaxation time for the solvent molecules. In the right-hand side of eq 2 we omit a term associated with the polarization decay due to the translational diffusion of solvent molecules.[8,9] For solvent molecules with shapes that are not extremely aspherical, this contribution is negligible, compared to that of the other terms. Due to local inhomogeneity of the solvent, caused by the electrostriction, the coefficients $\eta$, $\zeta$, $\chi$, $\chi_D$, and $\tau_D$ depend on the distance from the solute particle $r$. Therefore, we generally write $\eta = \eta(r)$, $\zeta = \zeta(r)$, $\chi = \chi(r)$, $\chi_D = \chi_D(r)$, and $\tau_D = \tau_D(r)$.[11,12] For a rotating sphere of radius $R$ with a spherically symmetric (radial) electric field $E_0(r)$, one can solve eqs 1 and 2 and find the rotational friction coefficient $\xi_R$.[18] This relates the angular velocity $\Omega$ of the sphere and the decelerating torque from the solvent $\mathbf{M}$ as $\mathbf{M} = \xi_R\Omega$. For the boundary conditions for the velocity field $\mathbf{V}(\mathbf{r})$ at the surface of the rotating sphere (i.e., at $|\mathbf{r}| = R$) we use:

$$\mathbf{V}(|\mathbf{r}| = R) = \alpha\Omega \times \mathbf{r}$$

where $\alpha = 0$ for the perfect slipping and $\alpha = 1$ for the perfect

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sticking.[16] The result for $\xi_R$ reads[18]

$$\xi_R = \alpha\frac{8\pi R}{3}\left[1+\frac{\tau_D(R)\chi_D(R)E_0(R)}{4\eta(R)}\right]\left[\int_R^\infty \mathrm{d}r\frac{\exp[-\int_R^r \mathrm{d}r' g(r')]}{r^3\eta(r)}\right]^{-1} \tag{3}$$

where

$$g(r) = \frac{1}{r}\frac{1+E_0 r^2 d(E_0\tau_D\chi_D/4r\eta)/\mathrm{d}r}{1+E_0^2\tau_D\chi_D/4\eta} \tag{4}$$

for uncharged particles ($E_0(r) = 0$, $\eta(r) = \eta_0$). Equations 3 and 4 yield the Stokes result, $\xi_{RS} = \alpha 8\pi\eta_0 R^3$. Using the Debye relaxation time $\tau_D = 4\pi\eta a^3/k_\mathrm{B}T$ ($a$ is a radius of the solvent molecule, $k_\mathrm{B}$ is the Boltzmann constant, and $T$ is the temperature), and the Einstein relation for the diffusion coefficient $D_R = k_\mathrm{B}T/\xi_R$ we arrive at

$$D_R = \frac{D_{RS}}{1+BE_0^2(R)}\int_R^\infty \frac{3R^2}{r^3}\frac{\mathrm{d}r}{\eta(r)/\eta_0} \exp\left\{-\int_R^r\left[\frac{1+E_0 r'^2 d(E_0 B/r')/\mathrm{d}r'}{1+BE_0^2}\right]\frac{\mathrm{d}r'}{r'}\right\} \tag{5}$$

here $B = \pi a^3\chi_D/k_\mathrm{B}T$, $\eta_0 = \eta(r \to \infty)$, and $D_{RS} = k_B T/\xi_{RS}$. In order to obtain an estimate for the local viscosity $\eta(r)$ in eq 5, we express it in terms of the pressure-dependent viscosity $\tilde{\eta}(p)$, which is supposed to be known as

$$\eta(r) = \tilde{\eta}(p(r)) \tag{6}$$

The local pressure $p(r)$ may be found within the condition of low compressibility of the solvent. Omitting the terms of the order $\delta\rho/\rho_0$, where $\delta\rho$ is a (small) deviation of the solvent density from the bulk value $\rho_0$, we obtain

$$p(r) = p_0 + {}^1/_2 E_0^2\rho\frac{\partial\chi}{\partial\rho}|_{\rho=\rho_0} \tag{7}$$

where $p_0 = p(r \to \infty)$ is the pressure in the bulk solvent. To account for the dielectric saturation effect, we use the field-dependent dielectric permittivity[10]

$$\epsilon(E) = \epsilon + \frac{\epsilon_0-\epsilon_\infty}{\beta E}L(3\beta E) \tag{8}$$

where $\epsilon_0$ is the low-field value of $\epsilon$ and $L(x)$ is the Langevin function:

$$L(x) = \cot(x) - \frac{1}{x} \tag{9}$$

and the parameter $\beta$ refers to the saturation rate[10]

$$\beta = \frac{9\epsilon_\infty}{4\pi\mu}\frac{m}{\rho_0}\frac{\epsilon-\epsilon_\infty}{(\epsilon_\infty+2)(2\epsilon_\infty+1)} \tag{10}$$

Here $\mu$ is the dipole moment and $m$ is the mass of a solvent molecule. With the use of the relation $E_0(r) = Q/\epsilon(E_0)r^2$ ($Q$ is the solute charge), eq 8 yields

$$(\epsilon-\epsilon_\infty)\,L(3\beta E_0) + \epsilon_\infty\beta E_0 = \beta Q/\epsilon(r)r^2 \tag{11}$$

with $\epsilon(r) = \epsilon\,(E_0(r))$ being the distance-dependent permittivity.

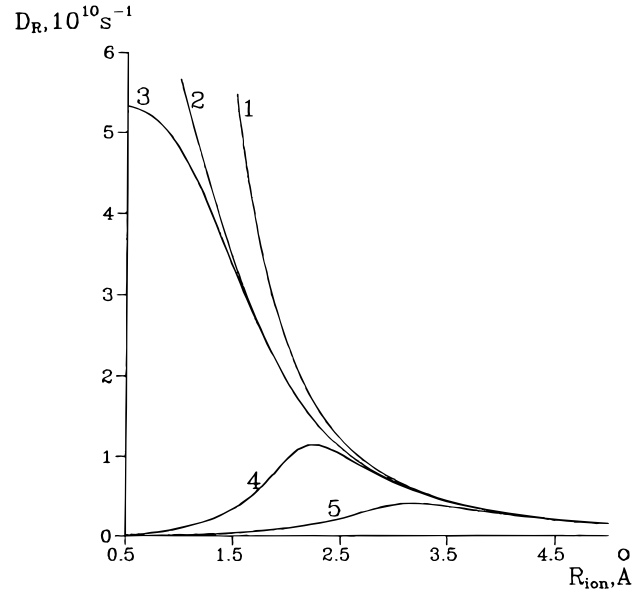


**Figure 1.** The dependence of the rotational diffusion coefficient versus ion radius for aqueous solutions for monovalent ions, curves 1−4, and divalent ions, curve 5. (1) The Stokes dependence, (2) only dielectric friction is taken into account, (3) dielectric friction and electroviscosity are taken into account; (4 and 5) dielectric friction, electroviscosity, and dielectric saturation are taken into account.

The electric field $E_0(r)$ may be found from eq 11 numerically. To calculate $D_R$ one should also know $E_0^2\mathrm{d}(BE_0/r)/\mathrm{d}r$. This may be found from eq 8. Differentiating eq 8 with respect to $r$ we arrive after few manipulations at

$$E_0 r^2\frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{E_0 B}{r}\right] = \frac{BQ^2}{\epsilon^4 r^4}\left[\epsilon_\infty + \frac{2\epsilon}{1+3(\epsilon_0-\epsilon_\infty)L'(3\beta E_0)} - 3\epsilon\right] \tag{12}$$

Here $L'(x) = dL/dx$. Using the Onsager−Kirkwood relation for the dielectric permittivity[19]

$$\frac{(\epsilon-\epsilon_\infty)(2\epsilon+\epsilon_\infty)}{\epsilon(\epsilon_\infty+2)^2} = {}^4/_9\pi(\rho/m)(\mu^2/k_\mathrm{B}T)g_\mathrm{K} \tag{13}$$

where $g_\mathrm{K}$ is Kirkwood $g$-factor, and using eqs 7 and 8 we obtain an expression for the local pressure

$$p(r) = p_0 + \frac{E_0^2(r)}{8\pi}\epsilon(r)\frac{\epsilon_\infty + (\epsilon(r)-\epsilon_\infty)C}{\epsilon_\infty + 3(\epsilon_0-\epsilon_\infty)L'(3\beta E_0(r))} \tag{14}$$

where the constant $C$ is defined as

$$C = \epsilon_0\frac{2\epsilon_0+\epsilon_\infty}{2\epsilon_0^2+\epsilon_\infty^2}\left[\frac{\epsilon_0}{\epsilon_0-\epsilon_\infty} + \frac{2\epsilon_\infty}{\epsilon_\infty+2} - \frac{\epsilon_\infty}{2\epsilon_0+\epsilon_\infty}\right] - \frac{\epsilon_\infty}{\epsilon_0-\epsilon_\infty} \tag{15}$$

To obtain eqs 14 and 15 we omit a small term $\partial(\ln(g_\mathrm{K}))/\partial\rho$. Substituting eq 14 into eq 6 one obtains the local or distance-dependent viscosity $\eta(r)$. In practice we numerically solved eq 11 to obtain $E_0(r)$ and $\epsilon(r)$; these values were then used in the calculations of $p(r)$ and $E_0^2\mathrm{d}(BE_0/r)/\mathrm{d}r$. The pressure dependence of the viscosity $\eta(p)$ was taken from ref 20 and the other molecular constants from ref 21.

Our results are presented in Figures 1−3. Figures 1 and 2 give the dependence of the rotational diffusion coefficient of

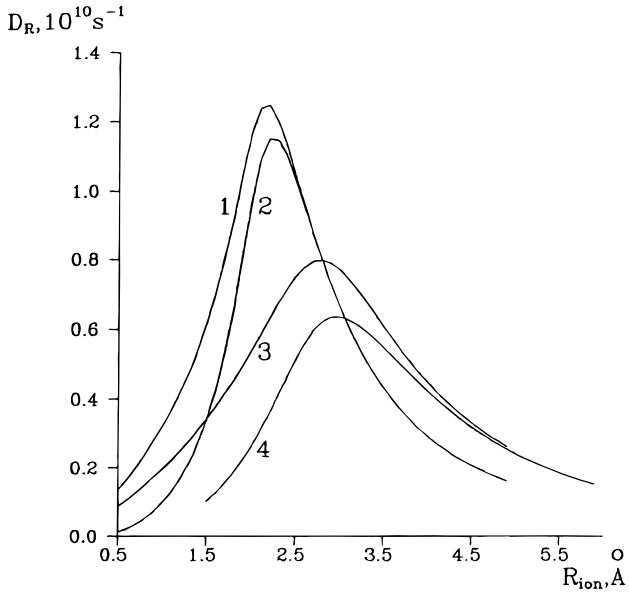


**Figure 2.** The dependence of the rotational diffusion coefficient versus ion radius for monovalent ions in aqueous solutions, curves 1 and 2, and in methanol, curves 3 and 4. For curves 1 and 3, electroviscosity is not taken into account; for 2 and 4, electroviscosity is taken into account.

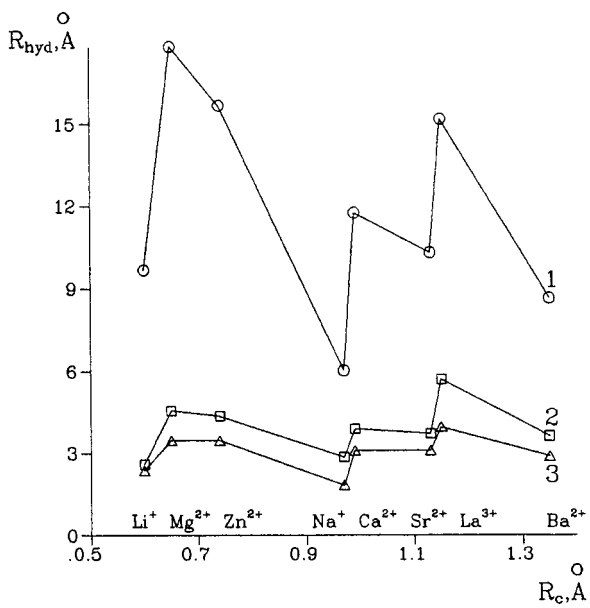


**Figure 3.** The hydrodynamic radius versus crystalline radius for rotational motion (curves 1 and 2) and for translational motion (curve 3). (1) theoretical results for $R_{hyd}$ for the stick boundary conditions on the surface of ion (i.e., at $r = R_c$), (2) theoretical results for the stick boundary conditions at the center of the solvent particle in contact (i.e., at $r = R_c + a$), (3) the experimental data from the ionic conductance.[22]

the charged solute as a function of the particle radius $R_{ion}$. These figures demonstrate the impact of the various effects of the solute−solvent (electrical) interactions on the rotational motion of charged solute molecules. In Figure 1 the Stokes dependence for the aqueous solutions (curve 1) is compared with the other dependencies, when (i) only the dielectric friction effect is taken into account (curve 2); (ii) dielectric friction and electroviscosity are accounted (curve 3); (iii) the combined effects (i.e., dielectric friction, electroviscosity, and dielectric saturation) are included (curve 4). The curves 1−4 refer to the case of monovalent ions; in Figure 1 we also give the corresponding dependence for the divalent ion (with all the above effects taken into account).

It follows from Figure 1 that dielectric saturation has a strong impact on the the reorientational dynamics of charged solute molecules: When the saturation effect is taken into account a well-pronounced maximum in the $D_R(R_{ion})$ dependence is observed. It is worth noting that a similar maximum is observed in the experimental dependence of the translational diffusion coefficient $D$ as a function of the ion radius (see, e.g., eq 10, where this dependence was plotted for the ionic conductance $\lambda \sim D$). Figure 2 demonstrates the role of the electroviscosity effect. In this case, $D_R(R_{ion})$ is plotted for the aqueous (curves 1 and 2) and methanol (curves 3 and 4) solutions. The curves 1 and 3 refer to the case when electroviscosity is not included, while for the curves 2 and 4 this effect is taken into account. It follows from Figure 2 that the role of the electroviscosity effect in the reorientational motion of solutes is much less important than that of the dielectric friction and dielectric saturation. This happens not only for aqueous solutions where the pressure dependence of the viscosity is relatively weak, but also for methanol solutions, which have a much stronger pressure dependence.

Using the rotational diffusion coefficient $D_R$, which we have obtained, one can estimate an apparent hydrodynamic radius of charged solute molecules, $R_{hyd}$, as a function of its crystalline radius $R_c$ and charge. The definition of hydrodynamic radius follows from the Stokes relation. For the stick boundary condition this reads for the translational motion $R_{hyd} = k_B T/6\pi\eta_0 D(R_c)$.[2] By analogy, one can write for the rotational motion:

$$R_{hyd} = [k_B T/8\pi\eta_0 D_R(R_c)]^{1/3}$$

Figure 3 shows the dependence $R_{hyd}$ versus $R_c$ for the monovalent and divalent ions in aqueous solutions. The crystalline radii $R_c$ were taken from ref 21. The experimental dependence $R_{hyd}(R_c)$ for the translational motion (from the ionic conductance data of ref 22) is also shown in Figure 3. Although the direct comparison of theoretical and experimental dependences is not completely justified (the former refers to the rotational motion while the latter to the translational motion), one notes the close similarity of the two curves. Obviously, the continuum theory overestimates the values of the hydrodynamic radius. This happens because the molecular structure of the solvent was completely ignored, and the boundary conditions for the continuum equations were formulated on the surface of the ion of radius $R_c$. This approximation corresponds to the zero-size limit of the solvent particles. One can attempt to remedy this deficiency of the continuum approach by taking into account the finite size of the solvent molecules. The simplest way to do this is to reformulate the boundary conditions: these should be written not at the surface of the solute ion (i.e., at $r = R_c$) but instead, at the center of the solvent particle in contact (i.e., at $r = R_c + a$). The results of the calculations with the "revised" boundary conditions are also shown in Figure 3. As usual in the continuous approach,[13] we take the solvent radius $a = 1.8$ Å from the molecular volume of water.[13] As it seen from Figure 3, the hydrodynamic radii so obtained agree fairly well with the experimental data.

In conclusion, we have demonstrated that solute−solvent electrical interactions play an important role in the rotational motion of charged solute molecules in polar solvents. The rotational motion of the charged solute was analyzed within the confines of a continuous approach; the effects of dielectric friction, dielectric saturation and electroviscosity (the local enhancement of the solvent viscosity due to the strong electric field of the solute) were considered. We observed that the

nonmonotonic dependence of the rotational diffusion coefficient on the ion radius is similar to that for the translational motion. We also found that dielectric friction and dielectric saturation has a much stronger impact on the rotational motion of charged solutes than that of electroviscosity.

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