Diffusion-Controlled Reactions: Hydrodynamic Interaction between Charged, Uniformly Reactive Spherical Reactants

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In this work, different models of hydrodynamic interaction (HI) are examined in the diffusion-controlled reaction between uniformly reactive charged spherical particles. In addition to Oseen "stick" and "slip" models of HI, one is considered that accounts for the disturbance of fluid flow by the ions around one reactive partner as they interact with a neighboring reactive species. This interaction is closely related to the "electrophoretic effect" in electrokinetics and can be described by a fairly simple electrophoretic, or E-tensor. These models are applied to the electron-transfer quenching reaction of $Ru(bpy)_3^{2+}$ and methyl viologen (MV^{2+}) over a wide range of NaCl concentrations (Chiorboli, C. et al., *J. Phys. Chem*. **1988**, *92*, 156). The back reaction is also considered. From a comparison of the salt dependence of the model and experimental rates, it is concluded that the "E-tensor" model works best and ignoring HI altogether works worst. The Oseen "stick" and "slip" models fall between these.

Introduction

The rates of bimolecular reactions in solution are limited by the rate of diffusional encounter between reactive species. This upper bound "diffusion-controlled reaction" rate has been the subject of extensive investigation that has its origins in Smoluchowski theory.[1,2] In this theory, the reactant partners are assumed to be spherical, uniformly reactive, and move through a viscous medium by simple diffusion. In addition, direct and hydrodynamic interactions are ignored. The importance of direct electrostatic interaction was recognized early and incorporated into the Smoluchowski theory by Debye.[3] Since many reactions that approach diffusion control are enzyme−substrate reactions, where at least one of the species is reactive only over a part of its surface, considerable attention has been devoted to modeling where at least one of the reactants, both assumed spherical, is reactive only over a portion of its surface.[4−7] To deal with still more complex features, such as irregularly shaped reactants bearing arbitrary charge distributions, Brownian dynamics trajectory methods have been developed and successfully applied to a range of problems.[8−10]

As two reactants diffuse toward each other in solution, the intervening solvent is perturbed in different ways, and this produces "hydrodynamic interaction". Most, but not all, biomolecular transport phenomena, translational and rotational diffusion constants in particular, have been accurately accounted for by detailed modeling that employs "stick" hydrodynamic boundary conditions on the model structures.[11−13] In the case of "stick" boundary conditions, fluid and particle velocities match at the (local) fluid/particle interface.[14] For "slip" boundary conditions, on the other hand, only the local normal component of the fluid and particle velocities match at the interface. In addition, there is no tangential component of the fluid stress tensor at the interface.[15] In the case of *rotational* diffusion of small molecules in aqueous solution, boundary conditions intermediate between stick and slip appear to be appropriate.[16]

In the theory of diffusion-controlled reactions, hydrodynamic interaction (HI) has proven to be problematic. In what shall be referred to in the present work as the "conventional treatment" of HI, fluid stresses are assumed to have their source in surface contact forces that act at the fluid−particle interface. Subject to the assumptions of this "conventional treatment", the diffusion-controlled reaction rate between uniformly reactive spheres in the absence of direct interactions is predicted to vanish when HI is accounted for using stick boundary conditions.[17] In past work, this apparently spectacular failure of hydrodynamics has been dealt with in several ways. One way has been to approximate HI using the Oseen tensor[18] with stick boundary conditions. In the framework of the "conventional treatment", this approach is exact in the limit of large separation.[19,20] An alternative approach has been to approximate HI using slip boundary conditions,[17] but otherwise retain the assumptions of the "conventional treatment". For uniformly reactive spherical species in the absence of direct forces, this model gives diffusion-controlled reaction rates that are smaller than the Smoluchowski rate, which ignores HI, but larger than the rate predicted using the Oseen tensor with "stick" boundary conditions.[17] The objective of the present work is to propose a simple and yet realistic alternative to both Oseen "stick" and "slip" representations of HI discussed above.

Many reactants involved in diffusion-controlled reactions are charged, and consequently electrostatic interactions must be accounted for. The fluid flow in the vicinity of a translating uncharged sphere in a fluid that is stationary at large distances under conditions of stick[14] or slip[17] boundary conditions is very different from that of a translating charged sphere in a salt solution (stationary at large distances) subjected to a constant external electric field.[21] There is a straightforward physical interpretation for these differences that is well-known to investigators in the field of electrokinetics.[22,23] When a charged sphere is subjected to an electric field, the field will exert a direct force on the sphere and this, in turn, gives rise to the variety of hydrodynamic interaction discussed in the previous paragraph. In addition, however, the electric field interacts with the ions that cluster around the sphere, and this interaction gives rise to a hydrodynamic backflow on the host sphere. This is

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the “electrophoretic effect”.[22,23] As mentioned above, Huckel[21] derived the fluid velocity and pressure fields corresponding to this problem many years ago. More recently, the corresponding interaction tensor of a small, weakly charged sphere in an incompressible fluid, placed in a constant external electric field, was derived.[24] This tensor, which shall be called the electrophoretic, or simply E-tensor, reduces to the Oseen tensor in the limit of zero salt. Over the past few years, our lab has made use of this tensor in modeling the electrophoretic mobility of bead arrays[25] and peptides.[26]

In the present work, the E-tensor shall be applied to the problem of diffusion controlled reactions between charged, uniformly reactive spheres. In the next “Theory” section, the relevant equations for diffusion controlled reactions are reviewed and the incorporation of the E-tensor is discussed. In the results section, rate constants are compared for several different models of intersphere HI. In addition, this modeling is applied to the experimental data of an electron-transfer reaction that was carried out over a wide range of salt conditions.[27] It is shown that the E-tensor, like the “slip” Oseen tensor, predicts a smaller reduction in reaction rate due to HI than the “stick” Oseen case. From a comparison with the experimental data, it is concluded that although discrepancies remain, modeling with the E-tensor yields better agreement with experiment than any of the other models. We conclude with a brief discussion of applications of the E-tensor to future studies of diffusion-controlled reactions.

Theory

Consider two uniformly reactive spheres of radii a_1 and a_2, respectively. Let r denote the center-to-center distance between the two spheres that also bear charges qz_1 and qz_2 at their centers, where q is the protonic charge and the z’s are valencies. The solvent is modeled as a continuum and is assumed to be an incompressible, Newtonian fluid of viscosity η and relative dielectric constant ϵ_r. The solvent also contains salt of ionic strength I. The potential of mean force, $U(r)$, between the two spheres is approximated with a Debye−Huckel potential[28]

$$U(r) = \frac{Xq^2 z_1 z_2}{4\pi\epsilon_r r}\,\frac{e^{-\kappa(r-d)}}{(1+\kappa d)} \tag{1}$$

where $X = 4\pi$ (in CGS units) or $1/\epsilon_0$ where ϵ_0 is the permittivity of free space (in MKSA units), d represents an “effective complex radius”, and κ is the Debye−Huckel screening parameter,

$$\kappa = \sqrt{\frac{2q^2 XI}{\epsilon_r k_B T}} \tag{2}$$

In eq 2 above, k_B is Boltzmann’s constant and T is absolute temperature. The Debye−Huckel theory is a continuum mean field theory valid at low electrostatic potentials. If the co- and counterions are not much smaller than than the reactive species, one might question the accuracy of applying such a model to diffusion-controlled reactions between charged species. Brownian dynamics simulations of diffusion-controlled reactions between ions that include co- and counterions explicitly have shown that Debye−Huckel theory is quite accurate in predicting ion distributions as well as the potential of mean force between the reactive partners.[29]

It is assumed that the two spheres instantly react if they approach within a (center-to-center) distance of b. The diffusion-controlled rate constant, $k_D(b)$, in L/(mol s), is given by[30]

$$k_D(b) = \frac{4\pi N_{Av}}{1000}\left[\int_b^\infty \frac{dr\, e^{U(r)/k_B T}}{r^2\, D_M(r)}\right]^{-1} \tag{3}$$

where N_{Av} is Avogadro’s Number, and $D_M(r)$ is the distant-dependent relative diffusion coefficient given by

$$D_M(r) = D_M^0 - 2k_B T\mathbf{n}\cdot\mathbf{T}(\mathbf{r})\cdot\mathbf{n} \tag{4}$$

In eq 4, $\mathbf{n} = \mathbf{r}/r$, $r = |\mathbf{r}|$, $\mathbf{T}(\mathbf{r})$ is the hydrodynamic interaction (HI) tensor (see below), and D_M^0 is the mutual diffusion constant in the absence of HI. It can be written

$$\mathrm{D}_M^0 = \frac{k_B T}{c\pi\eta}\left(\frac{1}{a_1} + \frac{1}{a_2}\right) \tag{5}$$

where c equals 6 or 4 for “stick” or “slip” hydrodynamic boundary conditions, respectively. In the absence of direct forces, ($U(r) = 0$) or HI ($\mathbf{T}(\mathbf{r}) = \mathbf{0}$ in eq 4), eq 3 reduces to the Smoluchowski value,[1,2] $k_D^0(b)$,

$$k_D^0(b) = \frac{4\pi D_M^0 b N_{Av}}{1000} \tag{6}$$

As discussed in the introduction, the primary focus of the present work is modeling HI between the reactive spheres. In the simplest case, it is simply ignored ($\mathbf{T}(\mathbf{r}) = \mathbf{0}$ in eq 4). In the “conventional treatment” of HI, where fluid stresses arise exclusively from surface contact forces that act at the fluid−particle interfaces, $\mathbf{T}(\mathbf{r})$ can be approximated by the Oseen tensor,[17,18] $\mathbf{T}_O(\mathbf{r})$

$$\mathbf{T}_O(\mathbf{r}) = \frac{1}{8\pi\eta r}[\mathbf{I} + \mathbf{nn}] \tag{7}$$

where $\mathbf{I}$ is the 3 by 3 identity tensor and $\mathbf{nn} = \mathbf{rr}/r^2$ is the unit position dyadic. Equation 7 is valid for both “stick” and “slip” boundary conditions. These two cases differ, however, in the form of D_M^0 as discussed following eq 5.[17] Within the framework of the “conventional treatment”, eq 7 is only exact at large r. It should be emphasized, however, that since charge−charge interactions between the reactive species and ions in the fluid also perturb the fluid flow, the assumptions of the “conventional treatment” render it approximate to begin with.

As an alternative to eq 7, which accounts for the interaction of the charges between the reactive species and ions in the fluid, we turn to the singular solution of a weak point charge subject to a constant external electric field.[24] This, in turn, has its roots in the work of Huckel.[21] From the singular solution, we can define the E-tensor

$$\mathbf{T}_E(\mathbf{r}) = \frac{1}{4\pi\eta}\left\{\left[w_1(\kappa,r) + \frac{1}{\kappa}w_2(\kappa,r) - \frac{1}{\kappa^2}(v_3(r) - w_3(\kappa,r))\right]\mathbf{I} + \left[\frac{3}{\kappa^2}(v_3(r) - w_3(\kappa,r)) - \left(w_1(\kappa,r) + \frac{3}{\kappa}w_2(\kappa,r)\right)\right]\mathbf{nn}\right\} \tag{8}$$

where

$$v_n(r) = \frac{1}{r^n} \tag{9}$$

$$w_n(\kappa,r) = \frac{e^{-\kappa r}}{r^n} \tag{10}$$

In the limit $\kappa \rightarrow 0$, eq 8 reduces to eq 7. Equation 8 is strictly valid for a small sphere placed in a *uniform* electric field. Since the electric field in the vicinity of a "host" reactive sphere due to the presence of a reactive neighbor will vary over the ion atmosphere of the "host" particle, eq 8 is approximate. Nonetheless, it does account, to lowest order, for the contribution of the "electrophoretic effect" to the HI between two charged particles. In cases where eq 8 is used, "stick" boundary conditions are used for D_M^0.

In the following section, $k_D(b)$ is computed for the diffusion-controlled reaction between two charged species. The potential of mean force, $U(r)$, is always approximated using eq 1, but HI is treated differently. For reasonable input parameters, eq 3 is integrated numerically.

Results and Discussion

Consider the bimolecular rate constant, k_q, for the quenching of electronically excited $Ru(bpy)_3{}^{2+}$ by methyl viologen (MV^{2+}) that was extensively studied by Chiorboli and co-workers.[27] The quenching reaction, carried out in aqueous salt solutions, can be summarized

$$*Ru(bpy)_3{}^{2+} + MV^{2+} \xrightarrow{k_q} Ru(bpy)_3{}^{3+} + MV^{+} \quad (11)$$

This reaction approaches the diffusion controlled limit, involves relatively simple reactive species, and was studied over a wide range of salt concentrations. It shall serve as a good test case to assess the various HI models discussed in the previous section. Here, we shall only consider the above reaction in NaCl where the salt concentration is varied from 0.01 to 1.6 mol/L. Many of the parameters used in modeling are taken directly from experiment.[27] These include $T = 293$ K, $\epsilon_r = 80.2$, $a_1 = 0.70$ nm ($Ru(bpy)_3{}^{2+}$), and $a_2 = 0.33$ nm (MV^{2+}). Also, the viscosity of NaCl solutions varies from 1.002 to 1.161 cp as the salt solution varies from 0.01 to 1.6 mol/L. Care is taken to use the correct solvent viscosity in the model calculations of $k_D(b)$.[31]

Summarized in Table 1 are model diffusion-controlled rates obtained by numerically integrating eq 3 using the above parameters for four different models of HI. We set $b = d = a_1 + a_2$ in this case. Table 2 contains similar results with $b = a_1 + a_2$, but $d = a_1$. In both cases, the reactive species must diffuse to within 1.03 nm for a reaction to occur, but the ion exclusion radius, d, is larger for the results in Table 1, which accounts for the lower reaction rates. From these tables and for the same model of HI, the ratio of $k_D(b)$ at the highest salt to $k_D(b)$ at the lowest salt falls in the range of 2.2 to 2.7 for all models except for the electrophoretic model, where this ratio equals 3.4−3.5. Thus, the electrophoretic model (which uses the E-tensor) exhibits a stronger salt dependence than the other models. Another observation is that at high salt, model rates using T_E approach those with no HI. In other words, HI is effectively eliminated in the electrophoretic model in the limit of high salt. The model rates in Tables 1 and 2 are all higher than the experimental rates because the latter are not strictly diffusion controlled, perhaps because of additional geometric constraints on reactivity. If we make the reasonable assumption that $k_q/k_D(b)$ is independent of salt concentration, we can make a clearer comparison between experiment and model rates. If the ratio $k_q/k_D(b)$ ($d = a_1 + a_2$ in the model studies) is averaged over the eight different salt concentrations measured experimentally, we obtain 0.300 (no HI), 0.393 (Oseen slip), 0.277 (Oseen stick), and 0.354 (E). Shown in Figure 1 is a plot of model rates, k_{mod}, as well as the experimental rates, k_q, versus salt concentration. In this example, the rates in Table 1 have been scaled by 0.300 (no HI), etc. to bring them into agreement with experiment when averaged overall salt concentrations studied experimentally. For the conditions used in Table 1, the relative discrepancy, $<(k_{mod}/k_q - 1)^2>^{1/2}$, averaged overall salt concentrations, equals 0.408 (no HI), 0.367 (Oseen slip), 0.337 (Oseen stick), and 0.205 (E). If the same procedure is applied to the results from Table 2, a graph almost identical to Figure 1 is obtained.

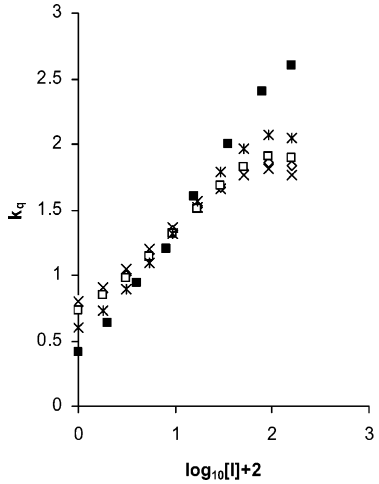

Figure 1. Dependence of k_q on NaCl concentration. Experimental rates are denoted by filled squares. Various model rates are crosses − no HI, diamonds − Oseen tensor with slip boundary conditions, unfilled squares − Oseen tensor with stick boundary conditions, asterisks − E-tensor.

TABLE 1

		$k_D(b)/10^9$ ($d = a_1 + a_2$)		
I (mol/L)	no HI	$\mathbf{T}_O$ (slip)	$\mathbf{T}_O$ (stick)	$\mathbf{T}_E$
0.010	2.658	2.737	1.355	1.705
0.018	3.030	3.136	1.559	2.058
0.031	3.477	3.625	1.811	2.514
0.054	3.990	4.197	2.110	3.077
0.095	4.539	4.825	2.445	3.727
0.168	5.078	5.461	2.793	4.412
0.295	5.548	6.038	3.117	5.050
0.518	5.891	6.483	3.378	5.553
0.910	6.045	6.717	3.531	5.836
1.60	5.910	6.621	3.505	5.793

TABLE 2

		$k_D(b)/10^9$ ($d = a_1$)		
I (mol/L)	no HI	$\mathbf{T}_O$ (slip)	$\mathbf{T}_O$ (stick)	$\mathbf{T}_E$
0.010	2.738	2.826	1.402	1.762
0.018	3.160	3.283	1.637	2.156
0.031	3.680	3.858	1.936	2.677
0.054	4.286	4.544	2.300	3.331
0.095	4.936	5.304	2.713	4.089
0.168	5.560	6.061	3.137	4.873
0.295	6.075	6.715	3.516	5.571
0.518	6.405	7.164	3.790	6.070
0.910	6.493	7.328	3.909	6.290
1.60	6.257	7.103	3.811	6.144

Next, consider the "back" electron-transfer reaction also studied by Chiorboli et al.,[27]

$$Ru(bpy)_3{}^{3+} + MV^{+} \xrightarrow{k_b} Ru(bpy)_3{}^{2+} + MV^{2+}$$

This reaction is modeled in exactly the same way as the quenching reaction considered previously. For $d = a_1 + a_2$, the ratio $k_b/k_D(b)$ averaged over all salt concentrations equals 0.780 (no HI), 0.710 (Oseen slip), 1.362 (Oseen stick), and 0.889

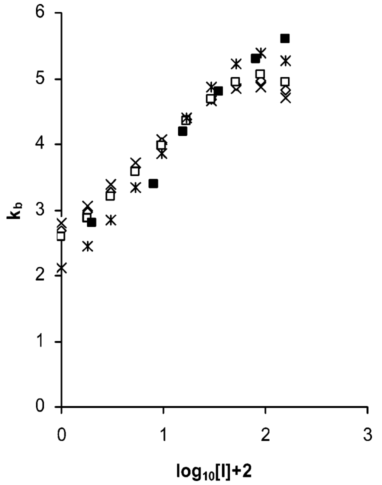

Figure 2. Dependence of k_b on NaCl concentration. Experimental rates are denoted by filled squares. Various model rates are crosses − no HI, diamonds − Oseen tensor with slip boundary conditions, unfilled squares − Oseen tensor with stick boundary conditions, asterisks − E-tensor.

(E). It is interesting to note in this case that the experimental rate actually *exceeds* $k_D(b)$ for the Oseen model with "stick" boundary conditions. Since $k_D(b)$ should represent an absolute upper bound on reaction rate, this result suggests the Oseen stick model overestimates HI. If we repeat the procedure applied to k_q of simply scaling the model $k_D(b)$'s by 0.780 (no HI), etc. to bring model and experimental rates into agreement when averaged over all salt concentrations, Figure 2 is obtained. For the back reaction, the relative discrepancy, $<(k_{mod}/k_b - 1)^2>^{1/2}$, averaged overall salt concentrations, equals 0.112 (no HI), 0.093 (Oseen slip), 0.078 (Oseen stick), and 0.063 (E). Although the Oseen stick results yield a relative discrepancy that is comparable to that obtained using the electrophoretic model, it should also be remembered that the Oseen stick model yields absolute model rates that actually exceed experimental rates which is unphysical.

From Figures 1 and 2, it can be concluded that the HI model using the E-tensor (asterisks) yields a salt dependence in better agreement with experiment (filled squares) than the other models. Perhaps not surprisingly, the model that made no correction for HI yields the poorest agreement with experiment. Both Oseen stick (unfilled squares) and Oseen slip (diamonds) models perform slightly better, but not as well as the E-tensor. It should be emphasized that the Oseen stick and slip models are approximate in the framework of the "conventional treatment" of HI since they are strictly valid only at large *r*. Also, the E-tensor model is approximate since it assumes the external field is uniform over the ionic atmospheres of the reactant spheres. As discussed in the previous paragraph, the Oseen stick model, actually *underestimates* k_b, which is unphysical.

Conclusions

In this work, several models of hydrodynamic interaction have been examined within the framework of diffusion-controlled reactions between charged, uniformly reactive spherical particles. In comparing model rates with experimental rates of an electron-transfer reaction as a function of salt concentration, it is concluded that a model that accounts for the electrophoretic effect (hydrodynamic backflow generated by the interaction of counterions with external electric fields) is in better agreement with experiment than "Oseen" models, or a model that ignores hydrodynamic interaction altogether. On simple physical grounds, we feel this electrophoretic effect should be significant provided the reactant particles bear charges and salt is present. It should be emphasized that this E-tensor model is approximate. Perhaps its greatest shortcoming, when applied to diffusion-controlled reactions, is its failure to account for the variation in the "external" electric field over the counterion atmosphere of a "host" particle. In the future, we plan to extend this treatment to more complex enzyme−substrate reactions, which involves the use of Brownian dynamics.[8−10]

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