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Geminate recombination in proton-transfer reactions. III. Kinetics and equilibrium inside a finite sphere

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The kinetics of reversible dissociation of a single ion pair inside a finite sphere is described by the transient solution of the Debye–Smoluchowski diffusion equation, with backreaction boundary conditions at contact, and a reflective boundary condition at the sphere's radius. At long times the solution tends to an equilibrium state. A simple analytic expression for the equilibrium coefficient is derived. For an infinitely large sphere ("infinite dilution") it reduces to an expression similar to that of Fuoss, while its dependence on the sphere's radius is qualitatively similar to the concentration dependence of activity coefficients.

I. INTRODUCTION

In the present series of papers¹ we have treated the reversible dissociation–recombination reaction of an excited state acid, 8-hydroxypyrene 1,3,6-trisulfonate (HPTS), on which much picosecond work has been done in the past.² These experiments were performed at low HPTS concentration in solution, so that the space in which the relative proton–anion diffusion occurs could be considered infinite on the time scale of the experiments. The initial population of the excited-state acid therefore decays to zero due to the ongoing dissociation process.

The situation is different inside a microcavity which restricts the extent of the diffusive motion. Under these conditions, even a single dissociating molecule is expected to reach an equilibrium state, where (averaged over an ensemble of many such systems) the concentrations of the acid and anion become finite and time independent. The exact nature of this equilibrium state depends on the nature of the microcavity: Its size, geometry, and possible interactions with the reactants and products.

The general theory of chemical reaction rates in a microcavity is applicable to many experimental situations, such as reactions in porous materials, in micelles, liposomes, and possibly many biochemical systems,³ ranging from enzymes to cells. Preliminary experimental results are available³ for the dissociation of HPTS inside soybean phospholipid liposomes.

The present work deals with the simplest situation, where a single acid molecule is confined to a spherical microcavity of a given radius R_m with the anion located in the center of the sphere whose walls are completely reflective towards the diffusing proton. The protic dissociation, recombination, and diffusion is described, as before,¹ by the transient solution of the Debye–Smoluchowski equation⁴ (DSE) with backreaction boundary conditions⁵ at the proton–anion contact distance a and with the additional reflective boundary condition imposed at R_m . While the transient solution can be obtained only numerically, the equilibrium concentration of the proton as $t \rightarrow \infty$ can be derived analytically. This yields a new expression for the dependence of the

equilibrium coefficient on the sphere's radius, or volume. This "concentration dependence" of the equilibrium coefficient is qualitatively comparable with that of ions in electrolyte solutions,^{6,7} as manifested by their activity coefficients.

II. THEORY

Our starting point is the diffusion (Smoluchowski) equation⁴ with backreaction boundary conditions.⁵ More precisely, we consider the diffusional flux for spherical symmetric diffusion in three dimensions in the presence of a field of force

$$J(r,t) = -4\pi D r^2 \exp[-V(r)] \frac{\partial}{\partial r} \exp[V(r)] p(r,t). \quad (1)$$

Here $a \leq r \leq R_m$ is the relative separation of the dissociated particles, $p(r,t)$ their density (i.e., the probability of being separated by a distance r at time t), D the relative diffusion coefficient, and $V(r)$ their mutual interaction potential divided by $k_B T$. For two ions with charges z_1 and z_2 , $V(r)$ is the Coulomb potential in dimensionless units:

$$V(r) = \frac{z_1 z_2 e^2}{\epsilon k_B T r} \equiv \text{sgn}(z_1 z_2) \frac{R_D}{r}. \quad (2)$$

In the above equations k_B is Boltzmann's constant and T the absolute temperature. e is the electronic charge, and ϵ the dielectric constant of the solvent. Equation (2) also defines the "Debye radius" R_D which measures of the extent of the Coulomb interaction. For singly charged ions in water at 25 °C, the dielectric constant is 78.3, and $R_D = 7.13$ Å. sgn is the sign function, which is negative for oppositely charged particles and positive if they both have the same charge. The time-dependent DSE can be written as a continuity condition

$$4\pi r^2 \frac{\partial p(r,t)}{\partial t} = -\frac{\partial J(r,t)}{\partial r}. \quad (3)$$

The two ions are considered to react at a finite distance $r = a$, which is called the "distance of contact". At this distance we assume that both dissociation and association may occur. This leads to the backreaction boundary condition⁵

$$J(a,t) = \kappa_d [1 - Q(t)] - 4\pi a^2 \kappa_r p(a,t). \quad (4)$$

κ_d and κ_r are the intrinsic dissociation and recombination rate coefficients. These constants, which describe the

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“chemical” (as opposed to the “diffusional”) part of the process, are (together with the contact distance a) the free parameters in this treatment. Q is the survival probability of the separated ion pair

$$Q(t) = 4\pi \int_a^{R_m} p(r,t) r^2 dr. \quad (5)$$

R_m is the maximal possible separation, as determined by the size of the porous sphere. At R_m one assumes a reflective boundary condition

$$J(R_m, t) = - \frac{\partial [\exp(V)p(r,t)]}{\partial r} \Big|_{r=R_m} = 0. \quad (6)$$

As $t \rightarrow \infty$, $Q(t)$ tends to its equilibrium value, which is the degree of dissociation designated by $\alpha \equiv \lim_{t \rightarrow \infty} Q(t)$.

The equilibrium solution obtained by setting $J = 0$ in Eq. (1) is of the form $p^{\text{eq}}(r) = A \exp[-V(r)]$. This result is, of course, much more general than the particular form for the flux given in Eq. (1), and holds true for any stochastic equation of motion admitting an equilibrium solution. The constant A is obtained by inserting p^{eq} into the back-reaction boundary condition, Eq. (4). The degree of dissociation is then easily determined from Eq. (4) as

$$\alpha = \frac{\int_a^{R_m} \exp[-V(r)] r^2 dr}{\int_a^{R_m} \exp[-V(r)] r^2 dr + \exp[-V(a)] a^2 \kappa_r / \kappa_d}. \quad (7)$$

κ_d / κ_r is an “intrinsic” dissociation constant. When it is very large (as, for example, for strong electrolytes) the degree of dissociation α tends to unity.

The equilibrium dissociation coefficient for a given value of R_m is

$$K(R_m) = \frac{\alpha^2}{(1 - \alpha)v N_A}, \quad (8)$$

where

$$v \equiv 4\pi R_m^3 / 3 \quad (9)$$

is the sphere's volume, and $N_A = 6.02 \times 10^{23}$ molecules/mol is Avogadro's number, used for converting to units of moles.

Assuming that $V(r)$ tends to zero fast enough as $r \rightarrow \infty$, the integral in the numerator of Eq. (7) diverges as the volume in Eq. (9). Hence, for infinite dilution one has

$$K_\infty \equiv K(R_m = \infty) = \frac{\kappa_d \exp[V(a)]}{4\pi a^2 \kappa_r N_A} \quad (10)$$

or, written explicitly for dissociation into oppositely charged ions

$$K_\infty = \frac{\kappa_d \exp(-R_D/a)}{4\pi a^2 \kappa_r N_A}. \quad (10')$$

If $K_1 \equiv \frac{1}{2} \kappa_d / \kappa_r$ is interpreted as the dissociation constant into a “complex” at contact, and K_2 is the dissociation of the complex into two particles at infinite separation, then $K_\infty = K_1 K_2$, and

$$K_2 = \frac{3 \exp[V(a)]}{4\pi a^3 N_A}. \quad (11)$$

For a Coulomb potential, this agrees with the expression given by Fuoss.⁸ Note that the Debye-Hückel theory⁷ is not

needed in deriving Eq. (11), and that its interpretation is the dissociation constant of the ion-pair complex. The infinite-dilution dissociation constant for the parent molecule, Eq. (10), is derived here for the first time. For ionic dissociation Eq. (10') predicts a linear dependence of $\ln K_\infty$ on $1/\epsilon$ [cf. Eq. (2)] only if κ_d / κ_r does not depend on ϵ . Such a linear dependence has been observed experimentally [see Table 14.2 and Figure 14.3 in Ref. 6(a)], but may not represent the most general case.

More interesting is the dependence of K on R_m for a finite sphere. For large R_m and/or for almost complete dissociation (i.e., $\kappa_r / a \ll \kappa_d$) one may write

$$K(R_m) \approx \left[4\pi v^{-1} \int_a^{R_m} \exp[-V(r)] r^2 dr \right] K_\infty. \quad (12)$$

For a dissociation of a neutral molecule into oppositely charged ions, the (mean) activity coefficient γ_\pm would be defined as $\gamma_\pm^2 \equiv K_\infty / K$. Hence, for a strong electrolyte

$$\gamma_\pm^2 = \frac{\int_0^{R_m} r^2 dr}{\int_a^{R_m} \exp(R_D/r) r^2 dr}. \quad (12')$$

The integral in Eq. (12') is similar to that in the Bjerrum theory,⁹ only that the upper limit here is R_m instead of $R_D/2$. It can be easily evaluated, since

$$\begin{aligned} \int_a^{R_m} \exp(R_D/r) r^2 dr &= R_D^3 \int_{R_D/R_m}^{R_D/a} e^x x^{-4} dx \\ &= \frac{1}{6} \left\{ R_m e^{R_D/R_m} (2R_m^2 + R_m R_D + R_D^2) - a e^{R_D/a} \right. \\ &\quad \times (2a^2 + aR_D + R_D^2) + R_D^3 \left[Ei\left(\frac{R_D}{a}\right) - Ei\left(\frac{R_D}{R_m}\right) \right] \Big\} \end{aligned} \quad (13)$$

and the exponential integral $Ei(x)$ is tabulated.¹⁰

III. RESULTS

Using the computer program described in the first paper of this series,^{1(a)} modified to account for a reflective boundary condition at R_m , Eq. (6), one can calculate the transient dissociation kinetics of the HPTS molecule. Figure 1 is an example which uses parameters similar to those of Ref. 1(a). It describes the temporal evolution of the proton-anion distribution. Initially, all the population is in the form of the neutral HPTS molecule. After the laser pulse, protons are discharged at the contact distance, $a = 6.5 \text{ \AA}$.^{1(a)} The proton-anion distance distribution subsequently broadens, until the boundary of the spherical microcavity, at $r = R_m$, is reached. The protons, which are reflected from this boundary, increase their concentration in its vicinity until finally an equilibrium distribution is approached.

The experimentally observed variable is the fluorescence intensity of the undissociated excited-state acid molecules, $1 - Q(t)$ in our notation. This is obtained by integrating the density profiles of Fig. 1. From the result shown in Fig. 2, it is clear that at long times the fluorescence signal should level-off at the equilibrium plateau. The value of this plateau can be evaluated directly from Eq. (7).

An indication of a plateau can be seen in the preliminary

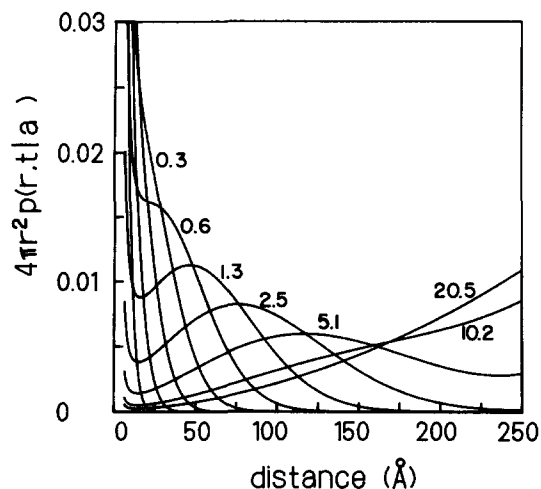


FIG. 1. Temporal evolution of the anion-proton distance distribution for a hydroxypyrene-trisulfonate molecule inside a sphere of radius $R_m = 250$ Å. A reflective boundary condition is set at R_m , and a backreaction boundary condition at the contact radius a . The initial state is that of a completely undissociated molecule (dissociation is triggered by electronic excitation to S_1). The curves are marked by the elapsed time in nanoseconds. The parameters for this calculation are: $D = 930$ Å²/ns, $R_D = 28.3$ Å, $a = 6.6$ Å, $\kappa_d = 9.2$ ns⁻¹, and $\kappa_r = 12$ Å/ns. The grid size is 0.6 Å and the time step 20 ps.

experimental result cited in Fig. 21 of Ref. 3. The time scale of this experiment (~ 1 ns) is too short for the plateau to be clearly visible. The experiments should be repeated more carefully on an extended time scale. For a quantitative comparison with experiment, one must of course multiply our calculated trace by $\exp(-t/\tau)$, where τ is the radiative lifetime of the excited state, and convolute it with the instrument response function. Only then would one be able to determine whether the simplified assumptions describe this system well enough.

The dependence of the activity coefficient, Eq. (12'), on R_m is demonstrated in Fig. 3 for several values of the contact distance a . The behavior is qualitatively similar to the con-

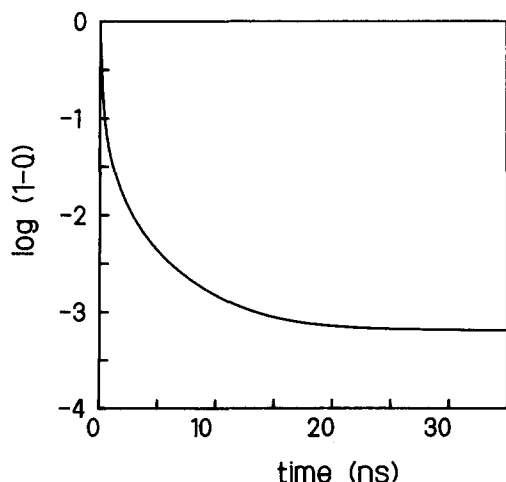


FIG. 2. The survival probability for undissociated HPTS molecules, obtained from a numerical integration of the curves shown in Fig. 1.

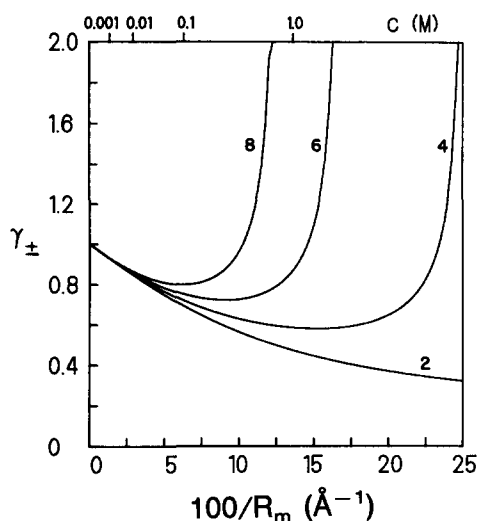


FIG. 3. Activity coefficients, Eq. (12'), for a single strong-electrolyte molecule inside a sphere of radius R_m . Different lines are for various values of the contact distance a (in Å). A concentration scale appears on top of the figure. Note the similarity to experimental results for electrolytic solutions, e.g., Fig. 12-5-2 in Ref. 6(b).

centration (c) dependence of measured activity coefficients for 1-1 strong electrolytes [e.g., Fig. 12-5-2 in Ref. 6(b)]: As $c \rightarrow 0$ ($R_m \rightarrow \infty$) the activity coefficients of all strong electrolytes (in a given solvent) fall on a universal curve which approaches unity. In Fig. 3 we see indeed that the asymptotic slope depends only on R_D , but not on the parameter a , which reflects the chemical identity of the electrolyte.

As the concentration is increased (R_m decreased) γ_{\pm} first decreases and subsequently increases to infinity. The origin of this behavior is clarified upon inspection of Eq. (12'): The initial decrease is due to the fact that the exponent in the denominator is larger than unity; The subsequent increase is due to the lower limit of integration, which is zero for the volume term in the numerator, but equals $a > 0$ for the integral in the denominator. Since a reflects the finite radii of the ions, this ultimate increase in γ_{\pm} is clearly an excluded volume effect. The same effect is seen in some of the measured activity coefficients for 1-1 electrolytes [Fig. 12-5-2 in Ref. 6(b)], e.g., for sodium halides, where the curves fall in the order of increasing halide size: $\text{NaCl} < \text{NaBr} < \text{NaI}$. For electrolytes which are not infinitely strong, this high-concentration behavior depends also on κ_d/κ_r . In both cases it is predicted to depend on the chemical nature of the electrolyte, as is indeed observed.⁶

It is interesting to compare the origin of the concentration dependence of the activity coefficients here and in the theory⁷ of electrolyte solutions.⁶ In the latter case it is basically a many-body problem, the effect due to the interaction of many ions in solution. In the present case the effect is there even for a single ion pair. It has nothing to do with an "ionic atmosphere"⁷ contributed by all other ions, which are simply not there. It is rather due to the restricted geometry and the fact that the ion pair can separate only to a finite distance. It is possible to devise an approximation¹¹ to the behavior of ions in an electrolyte solution, by assuming that

there too they separate to a finite distance, namely their average distance in solution.

IV. CONCLUSION

Reactions in microcavities is a growing field in chemical kinetics and equilibrium.¹² The dissociation of an acid, such as HPTS in its excited state, inside such cavity is characterized by the approach to equilibrium of the fluorescence signal. The kinetics in such a system can be analyzed by the transient DSE with two boundary conditions: One accounting for the chemical reaction and the other for the geometrical restrictions of the cavity. The qualitative comparison of the preliminary experiments in liposomes³ with the simplified model presented here for a spherical reflective liposome are encouraging. It is likely that the model would have to be elaborated when more extensive data becomes available, and a quantitative comparison is attempted.

The determination of the geometry of the cavity may be difficult. In the liposome case, even if the assumption of a spherical geometry is correct, the determination of the sphere's radius R_m may not always be easy. Once the model

for dissociation inside liposomes is perfected, the kinetics may be used as a ruler for determining a liposome's size.

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