

Mean First Passage Times of Ions between Charged Surfaces

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Analytic expressions for the mean first passage times of ions diffusing in the electric double layer between two planar charged surfaces have been derived. The theory is based on the Smoluchowski–Poisson–Boltzmann model in which the diffusing ion is assumed to move in the potential field given by the non-linear Poisson–Boltzmann equation. Numerical results for the mean first passage times of co-ions and counter-ions calculated under the non-linear Poisson–Boltzmann model are given for a range of surface separations, surface potentials and ionic concentrations. Two simple analytic methods for calculating the mean first passage times are also presented.

1. Introduction

In understanding diffusion-controlled chemical kinetics and the transport of ionic species in the vicinity of charged surfaces, it is necessary to obtain a quantitative measure of the diffusion times of ions in the electric double layer generated by charged surfaces. Very early work in this area has employed linear approximations and numerical solutions^{1,2} or neglected the many-body screening effects of the electrolyte altogether.^{3,4} Any realistic model that aspires to describe ionic transport phenomena should include effects due to the non-uniform distribution of ionic concentrations near charged surfaces.

The description of the dynamical properties of non-uniform primitive model electrolytes can begin with the many-body Fokker–Planck equation in an external field. This starting point requires that (1) the relaxation of ionic and solvent momenta and of solvent configurations is fast compared to the timescale for relevant changes in the ionic configurations; (2) the interaction potentials between the various ionic species are slowly varying over the ionic momentum correlation length $[D(m/k_B T)]^{1/2}$, where D is the diffusion constant and m the ion mass; and (3) the solvent-mediated dynamic coupling between the ions and with the surface may be neglected. With these not too restrictive assumptions, it is possible to integrate out all but one of the particle coordinates to obtain a one-particle equation involving an effective external field that is time-dependent.⁵ This time dependence arises from the possibility of correlation of ionic positions at different times due, for example, to Coulombic interactions. However, if we further assume that as the tagged ion moves, the remaining ions in the system can adjust their configurations without any time lag then such time correlations can be ignored and the result is a one-particle diffusion equation in which the tagged ion moves in the one-particle equilibrium potential of mean force arising from the presence of the charged interfaces. This neglect of time-dependent correlation effects has been referred to as the instantaneous relaxation approximation.⁵ The resulting diffusion equation for the one-particle propagator $P(\mathbf{r}, t | \mathbf{r}_0)$, the probability density of finding the particle at position \mathbf{r} at time t , given an initial position \mathbf{r}_0 at $t = 0$, is of the form

$$\partial P(\mathbf{r}, t | \mathbf{r}_0) / \partial t = D \nabla \cdot \{ [\nabla + \nabla \beta w(\mathbf{r})] P(\mathbf{r}, t | \mathbf{r}_0) \} \quad (1.1)$$

where D is the single-ion diffusion constant in the solvent and $\beta = 1/k_B T$. In the instantaneous relaxation approximation

$w(\mathbf{r})$ is the exact one-particle equilibrium potential of mean force.

The Gouy⁶–Chapman⁷ or Poisson–Boltzmann model has proved to be extremely functional in describing the equilibrium properties of the electric double layer. It can also serve as a useful basis in providing a working model for the transport properties of ionic species in the double layer. In this context, the exact one-particle potential of mean force is approximated by the product of the ionic charge ($v_i e$) and the mean electrostatic potential $\psi(\mathbf{r})$, where $\psi(\mathbf{r})$ satisfies the Poisson–Boltzmann equation:

$$\nabla^2 \psi(\mathbf{r}) = (4\pi e/\epsilon_r) \sum_i n_i v_i \exp[-\beta v_i e \psi(\mathbf{r})] \quad (1.2)$$

with ϵ being the relative permittivity of the solvent and n_i the number per unit volume of ions of species i in the bulk electrolyte. Eqn (1.1) and (1.2) define the Smoluchowski–Poisson–Boltzmann approximation for describing the diffusion of a single tagged ion near charged surfaces.

In this paper, we study the diffusion of a single tagged ion belonging to a symmetric ($v : v$) electrolyte bounded by two identically charged surfaces. In particular, we derive analytic results for the mean first passage times of ions to arrive at the mid-plane (the plane of symmetry) and/or at the charged surface. More recent studies of the ion-diffusion problem have focussed on electrolytes without co-ions confined between two charged surfaces⁸ as well as electrolyte systems in a semi-infinite domain.^{9,10} In the next section, we derive general expressions for the various absorption models of interest. General relations between the various mean first passage times and explicit results are given in Sections 3 and 4, and numerical results are given in Section 5. In Section 6, we propose two simple approximate methods based on the superposition principle for evaluating the mean first passage times. One method is quite accurate (with error less than 1% for the most interesting cases) but involves more numerical calculations, while a second method is almost analytic and very simple but incurs a higher error of *ca.* 10% for the interesting cases considered.

2. General Formulation

Consider the general solution of the non-linear Poisson–Boltzmann for a symmetric ($v : v$) electrolyte located between two identically charged surfaces bearing a uniform surface charge. The surfaces are located at a distance ($2b$) apart as shown in Fig. 1. Without loss of generality, we assume the surface charge is positive.

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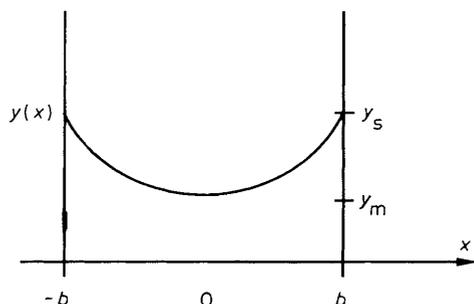


Fig. 1 The potential profile between two identically charged surfaces

The non-dimensional electrostatic potential at position x between the surfaces

$$y(x) = ve\psi(x) \quad (2.1)$$

obeys the Poisson–Boltzmann equation ($\kappa^2 \equiv 8\pi\beta nv^2 e^2/\epsilon_r$ is the Debye screening parameter)

$$y''(x) = \kappa^2 \sinh(y) \quad (2.2)$$

The solution of which can be written in the form

$$\exp[-y(x)] = \exp(-y_m) \text{cd}^2(u|m) \quad (2.3)$$

where $\text{cd}(u|m)$ is a Jacobi elliptic function¹¹ with

$$u = (\kappa x/2) \exp(y_m/2) \quad (2.4)$$

The mid-plane potential $y_m = y(0)$ and the surface potential $y_s = y(b)$ are related by the equation

$$\kappa b/2 = K(\alpha) - F(\phi|\alpha) \quad (2.5)$$

The functions $K(\alpha)$ and $F(\phi|\alpha)$ are, respectively, the complete and incomplete elliptic integrals of the first kind, with α being the modular angle and ϕ the amplitude¹¹ defined by

$$\sin \alpha = \exp(-y_m) = k = \sqrt{m} \quad (2.6)$$

$$\sin \phi = \exp[-(y_s - y_m)/2] \quad (2.7)$$

Here k is the modulus and m the parameter associated with the elliptic integrals. Definitions for these elliptic integrals are given in the Appendix. If we specify the distance b and the reduced surface potential y_s and we can solve eqn (2.5) for the mid-plane potential y_m . Eqn (2.5) has only one solution in the range $0 < y_m < y_s$. For systems with a negative surface charge, all the above equations will hold for the magnitude of the potentials.

Now that we have explicit expressions for the one-particle potential given by eqn (2.3) we can solve eqn (1.1) and (1.2) for the propagator $P(x, t|x_0)$, which now only depends on one spatial variable. The solution of the Smoluchowski–Poisson–Boltzmann equation can be reduced to the Lamé equation whose solution is known.¹² However, mean first passage times can be obtained directly from the one-particle potential without first obtaining explicit forms for the propagator $P(x, t|x_0)$. This result is well known and has appeared in a number of different forms. We follow the derivation and notation of ref. (8). For a particle confined within the diffusion domain $x_1 < x < x_2$, the probability that the particle, located initially at x_0 , has not yet been absorbed at time t is obtained by integrating over the diffusion domain, *i.e.*

$$Q(t|x_0) = \int_{x_1}^{x_2} dx P(x, t|x_0) \quad (2.8)$$

Clearly $Q(t=0|x_0) = 1$ and, unless both boundaries at x_1 and x_2 are reflecting, $Q(t=\infty|x_0) = 0$. If $F(t|x_0) dt$ is the probability that the particle is absorbed during the time interval t to $t + dt$ then

$$F(t|x_0) = -\frac{\partial Q(t|x_0)}{\partial t} \quad (2.9)$$

The mean first passage time or average time for a particle, initially at x_0 , to be absorbed is then given by

$$\tau_{pq}(x_0) = \int_0^\infty dt F(t|x_0) = \int_0^\infty dt Q(t|x_0) \quad (2.10)$$

where the first subscript p indicates the type of boundary at x_1 and the second subscript q indicates the type of boundary at x_2 . These subscripts are assigned the value R for reflecting boundaries and A for absorbing boundaries.

Eqn (2.10) for the first passage times can be evaluated by repeated integration of the diffusion equation together with the appropriate boundary conditions.¹³ The result is⁸ [see eqn (36) of ref. (8)]

$$\tau_{pq}(x) = \frac{1 + \kappa_1 f(x_1) J_1(x_1, x) + \kappa_2 f(x_2) \bar{J}_1(x, x_2) + \kappa_1 \kappa_2 f(x_1) f(x_2) [J_0 J_1(x_1, x) - J_0(x_1, x) J_1]}{\kappa_1 f(x_1) + \kappa_2 f(x_2) + \kappa_1 \kappa_2 f(x_1) f(x_2) J_0} \quad (2.11)$$

where, for $n = 1$ or 2 ,

$$J_n(x', x'') = \int_{x'}^{x''} \frac{d\xi}{Df(\xi)} \left[\int_{\xi}^{x_2} d\xi f(\xi) \right]^n \quad (2.12)$$

$$\bar{J}_n(x', x'') = \int_{x'}^{x''} \frac{d\xi}{Df(\xi)} \left[\int_{x_1}^{\xi} d\xi f(\xi) \right]^n \quad (2.13)$$

while J_n and \bar{J}_n (without arguments) are the above integrals with $x' = x_1$ and $x'' = x_2$. The constants κ_1 and κ_2 are absorption coefficients at the boundaries x_1 and x_2 :

$$\kappa_i = \begin{cases} 0, & \text{perfectly reflecting} \\ \infty, & \text{perfectly absorbing} \end{cases} \quad i = 1, 2 \quad (2.14)$$

Other positive values of κ_i , which correspond to partially reflecting surfaces, will not be considered here. The function $f(x)$ is the normalized equilibrium probability of finding a co-ion or a counter-ion at position x . Since the surface is taken to be positive, co-ions are positive and so the normalized probability of finding a co-ion at x is

$$f_+(x) = \frac{\exp[-y(x)]}{\int_{x_1}^{x_2} \exp[-y(x)] dx} \quad \text{co-ions} \quad (2.15)$$

similarly the normalized probability of finding a counter-ion at x is

$$f_-(x) = \frac{\exp[y(x)]}{\int_{x_1}^{x_2} \exp[y(x)] dx} \quad \text{counter-ions} \quad (2.16)$$

The explicit form for the function $y(x)$ is given by eqn (2.3). Although we have assumed that the surface is positively charged and hence the co-ions are positive and counter-ions are negative, it is clear from symmetry considerations that any result we derive for co- or counter-ion will be independent of the actual sign of the surface or ionic charge for the symmetric electrolyte considered here.

To give a specific example, we write down from eqn (2.11) the expression for the mean first passage time for diffusion in

the domain $(x_1, x_2) = (0, b)$ subjected to a reflecting boundary at $x = 0$ ($\kappa_1 = 0, p = R$) and an absorbing boundary at $x = b$ ($\kappa_2 \rightarrow \infty, q = A$)

$$\tau_{RA}(x) = \bar{J}_1(x, b) = \int_x^b \frac{d\zeta}{Df(\zeta)} \int_0^\zeta d\xi f(\xi). \quad (2.17)$$

That is, for a diffusing particle starting at x , it will, on average, reach the charged surface at $x = b$ after a time period of $\tau_{RA}(x)$. We simply replace $f(x)$ by $f_+(x)$ or $f_-(x)$ depending whether we require the mean first passage time for a co-ion or a counter-ion.

In many cases, the initial position of the diffusing ion is not known but the accessible quantity is the mean first passage time that has been averaged over all possible initial positions of the ion. This averaging procedure is based on the normalized equilibrium probability distribution $f(x)$, of finding an ion at position x . This position-averaged mean first passage time is defined by

$$\bar{\tau}_{pq} = \int_{x_1}^{x_2} dx \tau_{pq}(x) f(x) \quad (2.18)$$

The subscripts p and q are assigned the value R for reflecting boundaries or A for absorbing boundaries. The diffusion domain is $x_1 < x < x_2$ and a different normalized equilibrium distribution function $f(x)$ will be needed in eqn (2.18) for co-ions and counter-ions.

3. Relations between Mean First Passage Times

We derive a number of general relations between the various mean first passage times which will simplify their actual evaluation as well as provide a check on the consistency of numerical results.

Consider diffusion in the domain $0 < x < b$. Various mean first passage times can be written down from eqn (2.11) depending on the choice of boundary conditions at $x = 0$ which corresponds to the mid-plane between the two surfaces and at $x = b$ where the charged surface is located. There are three cases:

(i) Reflecting at $x = x_1 = 0$. Absorbing at $x = x_2 = b$.

$$\tau_{RA}(x) = \bar{J}_1(x, b) = \int_x^b \frac{d\zeta}{Df(\zeta)} \int_0^\zeta d\xi f(\xi) \quad (3.1)$$

(ii) Absorbing at $x = x_1 = 0$. Reflecting at $x = x_2 = b$.

$$\tau_{AR}(x) = J_1(0, x) = \int_0^x \frac{d\zeta}{Df(\zeta)} \int_\zeta^b d\xi f(\xi) \quad (3.2)$$

(iii) Absorbing at $x = x_1 = 0$. Absorbing at $x = x_2 = b$.

$$\tau_{AA}(x) = J_1(0, x) - \frac{J_1(0, b)}{J_0(0, b)} J_0(0, x) \quad (3.3)$$

The first result we wish to establish relates $\tau_{AR}(x)$ and $\tau_{RA}(x)$. From eqn (3.2) we have

$$\begin{aligned} \tau_{AR}(x) &= \int_0^x \frac{d\zeta}{Df(\zeta)} \int_\zeta^b d\xi f(\xi) \\ &= \left\{ \int_0^b \frac{d\zeta}{Df(\zeta)} - \int_x^b \frac{d\zeta}{Df(\zeta)} \right\} \left\{ \int_0^b d\xi f(\xi) - \int_0^\zeta d\xi f(\xi) \right\} \\ &= \int_0^x \frac{d\zeta}{Df(\zeta)} - \tau_{RA}(0) + \tau_{RA}(x) \\ &= \tau_D(x) - \tau_{RA}(0) + \tau_{RA}(x) \end{aligned} \quad (3.4)$$

The third equality of eqn (3.4) follows from the fact that $f(x)$ [eqn (2.15) or (2.16)] is a normalized probability so that

$$\int_0^b dx f(x) = 1 \quad (3.5)$$

In the last line of eqn (3.4) we have defined [see also eqn (2.12)]

$$\tau_D(x) \equiv J_0(0, x) = \int_0^x \frac{d\zeta}{Df(\zeta)} \quad (3.6)$$

Eqn (3.4) is the required relation between $\tau_{AR}(x)$ and $\tau_{RA}(x)$. We see that once $\tau_{RA}(x)$ is known, the calculation of $\tau_{AR}(x)$ then involves the evaluation of one more integral, namely $\tau_D(x)$.

We can also derive simple identities involving different first passage times for particles located initially at the boundaries: $\tau_{AR}(b)$ and $\tau_{RA}(0)$. From eqn (3.1) we have the obvious results

$$\tau_{RA}(b) = 0 \quad (3.7)$$

and

$$\tau_{RA}(0) = \int_0^b \frac{d\zeta}{Df(\zeta)} \int_0^\zeta d\xi f(\xi) \quad (3.8)$$

Also from eqn (3.4) and (3.7) we can write

$$\begin{aligned} \tau_{AR}(b) &= \int_0^b \frac{d\zeta}{Df(\zeta)} - \tau_{RA}(0) \\ &= \int_0^b \frac{d\zeta}{Df(\zeta)} - \int_0^b \frac{d\zeta}{Df(\zeta)} \int_0^\zeta d\xi f(\xi) \quad \text{using eqn (3.1)} \\ &= \int_0^b \frac{d\zeta}{Df(\zeta)} \left\{ 1 - \int_0^\zeta d\xi f(\xi) \right\} \\ &= \int_0^b \frac{d\zeta}{Df(\zeta)} \int_\zeta^b d\xi f(\xi) \\ &= \int_0^b d\xi f(\xi) \int_\zeta^b \frac{d\zeta}{Df(\zeta)} \quad \text{interchanging orders of integration} \end{aligned} \quad (3.9)$$

We can now write down the explicit form of $\tau_{AR}(b)$ for co-ions and $\tau_{RA}(0)$ for counter-ions by using eqn (2.3), (2.4), (2.15), (2.16), (3.8) and (3.9):

$$\begin{aligned} D\tau_{AR}^{\text{co-ion}}(b) &= \int_0^b d\zeta \text{cd}^2(\bar{\kappa}\zeta | m) \int_0^\zeta d\xi \text{dc}^2(\bar{\kappa}\xi | m) \\ &= D\tau_{RA}^{\text{counter-ion}}(0) \end{aligned} \quad (3.10)$$

where $\text{dc}(u|m) = 1/\text{cd}(u|m)$ is also a Jacobi elliptic function and $\bar{\kappa}$ is the constant

$$\bar{\kappa} = (\kappa/2)\exp(y_m/2) \quad (3.11)$$

A similar result can be obtained between $\tau_{AR}(b)$ for counter-ions and $\tau_{RA}(0)$ for co-ions

$$\begin{aligned} D\tau_{AR}^{\text{counter-ion}}(b) &= \int_0^b d\zeta \text{dc}^2(\bar{\kappa}\zeta | m) \int_0^\zeta d\xi \text{cd}^2(\bar{\kappa}\xi | m) \\ &= D\tau_{RA}^{\text{co-ion}}(0) \end{aligned} \quad (3.12)$$

Eqn (3.10) and (3.12) are the results we require between $\tau_{AR}(b)$ and $\tau_{RA}(0)$. These identities are useful in checking the consistency of numerical results.

The mean first passage time $\tau_{AA}(x)$ corresponding to absorbing boundaries at $x = 0$ and $x = b$, can be written in terms of $\tau_{RA}(x)$ and $\tau_D(x)$. By combining eqn (2.12), (2.13), (3.1) and

(3.3)–(3.6) we find

$$\begin{aligned}\tau_{AA}(x) &= \tau_{AR}(x) - \frac{\tau_{AR}(b)}{\tau_D(b)} \tau_D(x) \\ &= \frac{\tau_{RA}(0)}{\tau_D(b)} \tau_D(x) + \tau_{RA}(x) - \tau_{RA}(0)\end{aligned}\quad (3.13)$$

From the definitions of $\tau_D(x)$ and $\tau_{RA}(x)$ we can check from eqn (3.13) that $\tau_{AA}(x)$ does indeed vanish at $x=0$ and at $x=b$ as expected, and once $\tau_D(x)$ and $\tau_{RA}(x)$ are known, $\tau_{AA}(x)$ can readily be found.

We observe that the results in eqn (3.4) and (3.13) are quite general, while eqn (3.10) and (3.12) apply only to ion diffusion in a symmetric electrolyte in the Smoluchowski–Poisson–Boltzmann model or to the case of free diffusion.

Turning now to diffusion in the domain $-b < x < b$, owing to the symmetry of the problem, the only mean first passage of interest is the case in which absorbing boundary conditions prevail at both surfaces at $x = \pm b$. We denote this first passage time by $\tau_{AA}(x| -b, b)$ where the diffusion domain is indicated explicitly. From symmetry we know that $\tau_{AA}(x| -b, b)$ is an even function of x . By identifying the general diffusion domain limits as $x_1 = -b$ and $x_2 = b$ we can now write down the expression for $\tau_{AA}(x| -b, b)$ in terms of the normalized equilibrium probability $f(x| -b, b)$ of finding a particle at x :

(iv) Absorbing at $x = x_1 = -b$. Absorbing at $x = x_2 = b$.

$$\tau_{AA}(x| -b, b) = J_1(-b, x) - \frac{J_1(-b, b)}{J_0(-b, b)} J_0(-b, x) \quad (3.14)$$

where the integrals $J_n(x', x'')$ are given by eqn (2.12) with $f(x)$ replaced by $f(x| -b, b)$. Since $f(x| -b, b)$ is also an even function of x , we can rewrite all the integral definitions of $J_n(x', x'')$ to range over the interval $(0, b)$ to give

$$J_0(-b, b) = 2 \int_0^b \frac{d\xi}{Df(\xi| -b, b)} = 2J_1(-b, b) \quad (3.15)$$

$$J_0(-b, x) = \int_0^b \frac{d\xi}{Df(\xi| -b, b)} + \int_0^x \frac{d\xi}{Df(\xi| -b, b)} \quad (3.16)$$

$$\begin{aligned}J_1(-b, x) &= \frac{1}{2} J_0(-b, x) \\ &+ \int_x^b \frac{d\xi}{Df(\xi| -b, b)} \int_0^\xi d\xi_1 f(\xi_1| -b, b) \\ &= \frac{1}{2} J_0(-b, x) + \tau_{RA}(x)\end{aligned}\quad (3.17)$$

where $\tau_{RA}(x)$ is the mean first passage time for diffusion in the domain $0 < x < b$, given by eqn (3.1). Eqn (3.17) holds because for x in the range $(0, b)$ the normalized probability $f(x)$, apart from a factor of 2 in the normalization constant, has the same x -dependence as the normalized probability $f(x| -b, b)$. For negative values of x in the interval $(-b, 0)$, eqn (3.17) will still hold provided we replace x by $|x|$. Thus by combining eqn (3.14)–(3.17) we have the result

$$\tau_{AA}(x| -b, b) = \tau_{RA}(x) \quad (3.18)$$

In summary, the key results in eqn (3.4), (3.13) and (3.18) relate all three other mean first passage times to $\tau_{RA}(x)$ and the function $\tau_D(x)$.

4. Expressions for $\tau_{RA}(x)$ and $\tau_D(x)$

We now derive expressions for the mean first passage time $\tau_{RA}(x)$ in terms of elliptic functions and integrals. As we have seen in section 3, all other first passage times can be written

in terms of $\tau_{RA}(x)$ and the function $\tau_D(x)$. For notational convenience we introduce the following dimensionless variables:

$$\beta \equiv \kappa b \quad (4.1)$$

$$\xi \equiv \kappa x \quad (4.2)$$

and work in terms of non-dimensional mean first passage times:

$$\tau^* \equiv D\tau/b^2 \quad (4.3)$$

In the free-diffusion limit [$y(x) = 0$], the equilibrium probability density is

$$\begin{aligned}f(x) &= 1/b \quad \text{for diffusion in the domain } 0 < x < b \\ &= 1/2(b) \quad \text{for diffusion in the domain } -b < x < b\end{aligned}\quad (4.4)$$

Corresponding to this limit, the various mean first passage times are

$$\left. \begin{aligned}\tau_{RA}^*(x) &= [1 - (x/b)^2]/2 \\ \tau_{AR}^*(x) &= [2(x/b) - (x/b)^2]/2 \\ \tau_{AA}^*(x) &= [(x/b) - (x/b)^2]/2 \\ \tau_D^*(x) &= x/b \\ \tau_{AA}^*(x| -b, b) &= [1 - (x/b)^2]/2\end{aligned}\right\} \text{free diffusion} \quad (4.5)$$

It is easy to verify that these results satisfy all the relations between the various mean first passage times derived in the previous section.

Using the above notation together with eqn (2.3), (2.4), (2.15), (2.16) and (3.1) we have

$$\beta^2 \tau_{RA}^*(x) = 4m \int_\xi^\beta du \, dc^2 u \int_0^u dt \, cd^2 t \quad \text{co-ions} \quad (4.6)$$

$$\beta^2 \tau_{RA}^*(x) = 4m \int_\xi^\beta du \, cd^2 u \int_0^u dt \, dc^2 t \quad \text{counter-ions} \quad (4.7)$$

where we have suppressed the dependence on the modulus m in the Jacobi elliptic functions.

(i) $\tau_{RA}(x)$ for Co-ions

Consider the expression for $\tau_{RA}^*(x)$ for co-ions given by eqn (4.6). The inner integral can be evaluated using eqn (A6)

$$\begin{aligned}\beta^2 \tau_{RA}^*(x) &= 4m \int_\xi^\beta du \, dc^2 u \int_0^u dt \, cd^2 t \quad \text{co-ions} \\ &= 4 \left\{ \int_\xi^\beta duu \, dc^2 u - \int_\xi^\beta duE(u) \, dc^2 u \right. \\ &\quad \left. + m \int_\xi^\beta du \, sn \, u \, dc \, u \right\}\end{aligned}\quad (4.8)$$

The first integral in eqn (4.8) can be simplified using integration by parts and the results in the Appendix

$$\begin{aligned}\int_\xi^\beta duu \, dc^2 u &= [u\{u - E(u) + sn \, u \, dc \, u\}]_\xi^\beta \\ &- \int_\xi^\beta du\{u - E(u) + sn \, u \, dc \, u\} \\ &= [u\{u - E(u) + sn \, u \, dc \, u\} - u^2/2]_\xi^\beta \\ &+ \int_\xi^\beta duE(u) - \int_\xi^\beta du \, sn \, u \, dc \, u\end{aligned}\quad (4.9)$$

The second integral in eqn (4.8) can also be simplified using integration by parts together with the formulae in the Appendix

$$\begin{aligned} \int_{\xi}^{\beta} du E(u) dc^2 u &= [E(u)\{u - E(u) + sn u dc u\}]_{\xi}^{\beta} \\ &\quad - \int_{\xi}^{\beta} du dn^2 u\{u - E(u) + sn u dc u\} \\ &= [E(u)\{u - E(u) + sn u dc u\} \\ &\quad - uE(u) + \frac{1}{2}E^2(u) - (m/2) sn^2 u]_{\xi}^{\beta} \\ &\quad + \int_{\xi}^{\beta} du E(u) - (1 - m) \int_{\xi}^{\beta} du sn u dc u \end{aligned} \quad (4.10)$$

Combining eqn (4.8)–(4.10), we find that all the remaining unevaluated integrals cancel and we are left with the final result for $\tau_{RA}^*(x)$ for co-ions

$$\begin{aligned} \beta^2 \tau_{RA}^*(x) &= 4[\frac{1}{2}[E^2(u) + u^2] - uE(u) \\ &\quad + [u - E(u)]sn u dc u + (m/2)sn^2 u]_{\xi}^{\beta} \quad \text{co-ions} \end{aligned} \quad (4.11)$$

(ii) $\tau_{RA}(x)$ for Counter-ions

The evaluation of the integrals for $\tau_{RA}(x)$ for counter-ions given by eqn (4.7) follows a similar route. The inner integral can be evaluated using eqn (A7)

$$\begin{aligned} \beta^2 \tau_{RA}^*(x) &= 4m \int_{\xi}^{\beta} du cd^2 u \int_0^u dt dc^2 t \quad \text{counter-ions} \\ &= 4m \left\{ \int_{\xi}^{\beta} duu cd^2 u - \int_{\xi}^{\beta} du E(u) cd^2 u \right. \\ &\quad \left. + \int_{\xi}^{\beta} du sn u cd u \right\} \end{aligned} \quad (4.12)$$

The first integral in eqn (4.12) can be simplified using integration by parts and the results in the Appendix

$$\begin{aligned} \int_{\xi}^{\beta} duu cd^2 u &= \frac{1}{m} [u\{u - E(u) + sn u cd u\}]_{\xi}^{\beta} \\ &\quad - \frac{1}{m} \int_{\xi}^{\beta} du\{u - E(u) + m sn u cd u\} \\ &= \frac{1}{m} [u\{u - E(u) + sn u cd u\} - u^2/2]_{\xi}^{\beta} \\ &\quad + \frac{1}{m} \int_{\xi}^{\beta} du E(u) - \int_{\xi}^{\beta} du sn u cd u. \end{aligned} \quad (4.13)$$

The second integral in eqn (4.12) can also be simplified using integration by parts together with the formulae in the Appendix

$$\begin{aligned} \int_{\xi}^{\beta} du E(u) cd^2 u &= \frac{1}{m} [E(u)\{u - E(u) + m sn u cd u\}]_{\xi}^{\beta} \\ &\quad - \frac{1}{m} \int_{\xi}^{\beta} du dn^2 u\{u - E(u) + m sn u cd u\} \\ &= \frac{1}{m} [E(u)\{u - E(u) + sn u cd u\} \\ &\quad - uE(u) + \frac{1}{2}E^2(u) - \frac{1}{2} sn^2 u]_{\xi}^{\beta} \\ &\quad + \frac{1}{m} \int_{\xi}^{\beta} du E(u) \end{aligned} \quad (4.14)$$

Combining eqn (4.12)–(4.14), we find that all the remaining unevaluated integrals cancel and we are left with the final result for $\tau_{RA}^*(x)$ for counter-ions

$$\begin{aligned} \beta^2 \tau_{RA}^*(x) &= 4[\frac{1}{2}[E^2(u) + u^2] - uE(u) \\ &\quad + m[u - E(u)] sn u cd u + (m/2) sn^2 u]_{\xi}^{\beta} \end{aligned} \quad \text{counter-ions} \quad (4.15)$$

(iii) $\tau_D(x)$ for Co-ions and Counter-ions

We now evaluate the integral for the function $\tau_D(x)$ as defined by eqn (3.6). Using the non-dimensional notation introduced above together with eqn (2.3), (2.4), (2.15), (2.16) and (3.6) we have for the co-ion $\tau_D(x)$

$$\begin{aligned} \beta^2 \tau_D^*(x) &= 4m \int_0^{\beta} du cd^2 u \int_0^{\xi} dt dc^2 t \quad \text{co-ions} \\ &= 4\{\beta - E(\beta) + m sn \beta cd \beta\} \\ &\quad \times \{\xi - E(\xi) + sn \xi dc \xi\} \end{aligned} \quad (4.16)$$

and similarly for the counter-ion $\tau_D(x)$

$$\begin{aligned} \beta^2 \tau_D^*(x) &= 4m \int_0^{\beta} du dc^2 u \int_0^{\xi} dt cd^2 t \quad \text{counter-ions} \\ &= 4\{\beta - E(\beta) + sn \beta dc \beta\} \\ &\quad \times \{\xi - E(\xi) + m sn \xi cd \xi\} \end{aligned} \quad (4.17)$$

The results in eqn (4.11) and (4.15) for $\tau_{RA}(x)$ and in eqn (4.16) and (4.17) for $\tau_D(x)$ together with the general relations given by eqn (3.4), (3.13) and (3.18) will allow us to compute all the mean first passage times. The various elliptic functions and integrals required are readily available in standard library routines or numerical methods texts.¹⁴

5. Results and Discussion

We now present numerical results that illustrate the effects of varying the surface potential and the separation on the various mean first passage times. To provide a reasonable coverage of the range of variations, we shall consider a low-potential case ($y_s = 1$, corresponding to *ca.* 25 mV for a 1 : 1 electrolyte at room temperature) and a high-potential case ($y_s = 4$, *ca.* 100 mV). The surface separation will vary from $\kappa b = 0.5$ to $\kappa b = 30$, which corresponds to a surface separation of 1 Debye length ($1/\kappa$) to 60 Debye lengths ($60/\kappa$). We shall consider the four mean first passage times introduced in section 3 as well as the position-averaged mean first passage times. We examine how these differ from their free-diffusion counterparts as we vary the surface potential and the surface separation.

(i) $\tau_{RA}(x)$: Reflecting at $x = 0$; Absorbing at $x = b$

In Fig. 2 and 3, we show the scaled mean first passage times $[D\tau_{RA}(x)/b^2]$ against the starting position (x/b) at reduced surface potentials $y_s = 1$ and 4. In this case absorption takes place at the charged surface at $x = b$. Since co-ions are repelled from the charged surface and counter-ions are attracted to the surface, we expect the mean first passage times of co-ions to be higher and that of counter-ions to be lower than those in the free-diffusion limit. At a given surface separation deviations from the free-diffusion limit will become larger as the surface potential increases.

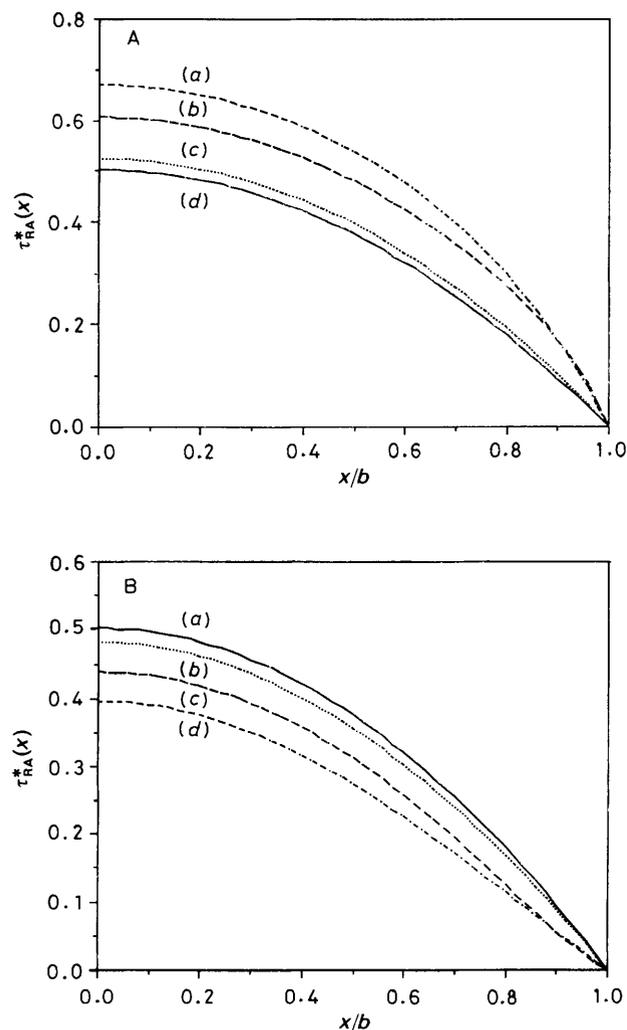


Fig. 2 The scaled mean first passage time $\tau_{RA}^*(x) = [D\tau_{RA}(x)/b^2]$ as a function of initial position for: A, co-ions and B, counter-ions at surface potential $y_s = 1$ and various surface separations: A(a) $2\kappa b = 6$, (b) 20, (c) 1. B(b) $2\kappa b = 1$, (c) 20, (d) 6. The free-diffusion result [A(d) and B(a)] is a function of only (x/b)

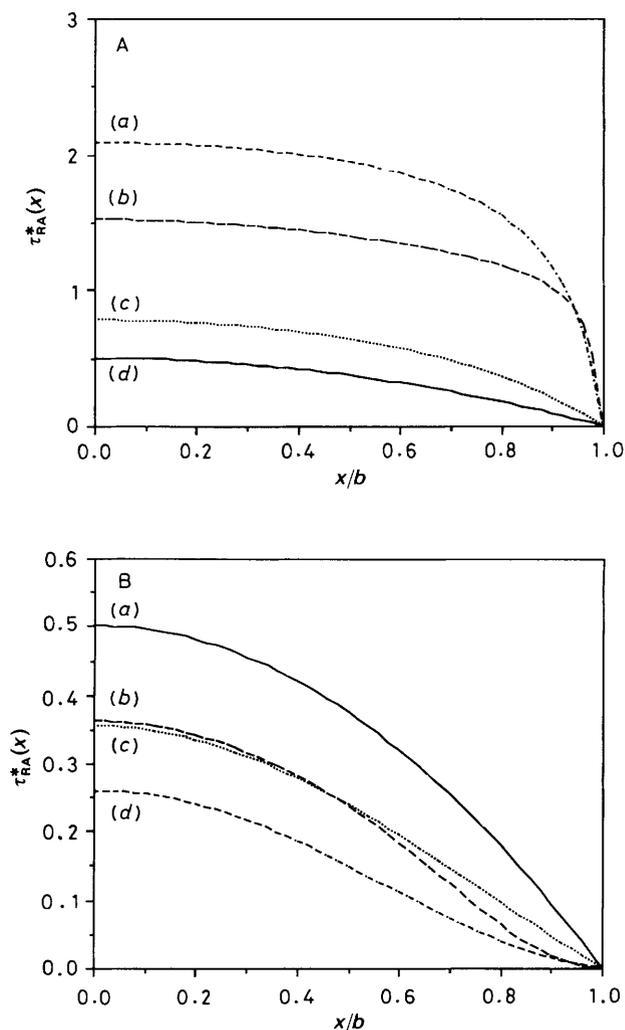


Fig. 3 The scaled mean first passage time $\tau_{RA}^*(x) = [D\tau_{RA}(x)/b^2]$ as a function of initial position for: A, co-ions and B, counter-ions at surface potential $y_s = 4$ and various surface separations: A(a) $2\kappa b = 6$, (b) 20, (c) 1. B(b) 20, (c) 1, (d) 6. The free-diffusion result [A(d) and B(a)] is a function of only (x/b)

Quantitative effects of the surface charge also depend on the surface separation. When the separation is large compared to the Debye length, the diffusing ion is insensitive to electrostatic interactions with the surface until it comes within the influence of the surface, within a Debye length or so. Thus at large separations, the mean first passage time $\tau_{RA}(x)$ will be similar to the free-diffusion result unless the starting position x is near the surface, *i.e.* $x \approx b$. This is evident when comparing the curves for $(2\kappa b) = 20$ with the free-diffusion curves in Fig. 2 and 3.

The effects of electrostatic interactions between the ion and the surface do not increase monotonically as the surface separation decreases. The reason for this can be seen from eqn (1.1). Deviations from free diffusion are controlled by the gradient of the interaction potential between the ion and the surface. When the surface separation is sufficiently small, variations in the electrostatic potential profile across the electrolyte between the surfaces is negligible because the potential profile between the surfaces is essentially a constant function. Consequently, at small separations, the mean first passage time $\tau_{RA}(x)$ will again be similar to the free-diffusion result. This effect is evident in the results in Fig. 2 and 3. Maximum deviation from the free-diffusion result occurs at some inter-

mediate surface separation, which is observed from our numerical calculations to occur when the surfaces are *ca.* 6 Debye lengths apart, $(2\kappa b) \approx 6$.

In view of the general result given by eqn (3.18), the above results are the same as those for the mean first passage time $\tau_{AA}(x| -b, b)$ for diffusion with absorbing boundary conditions at $x = \pm b$, in the domain $-b < x < b$.

(ii) $\tau_{AR}(x)$: Absorbing at $x = x_1 = 0$; Reflecting at $x = x_2 = b$

In Fig. 4 and 5, we show the scaled mean first passage times $[D\tau_{AR}(x)/b^2]$ against the starting position (x/b) at reduced surface potentials $y_s = 1$ and 4.

In this case absorption takes place at the mid-plane at $x = 0$. Since co-ions are repelled from the charged surface towards the absorption plane and counter-ions are attracted towards the surface away the absorption plane, we expect the mean first passage times of the co-ions to be lower and that of the counter-ions to be higher than those in the free-diffusion limit, opposite to the case of $\tau_{RA}(x)$. At a given surface separation deviations from the free-diffusion limit become larger as the surface potential increases.

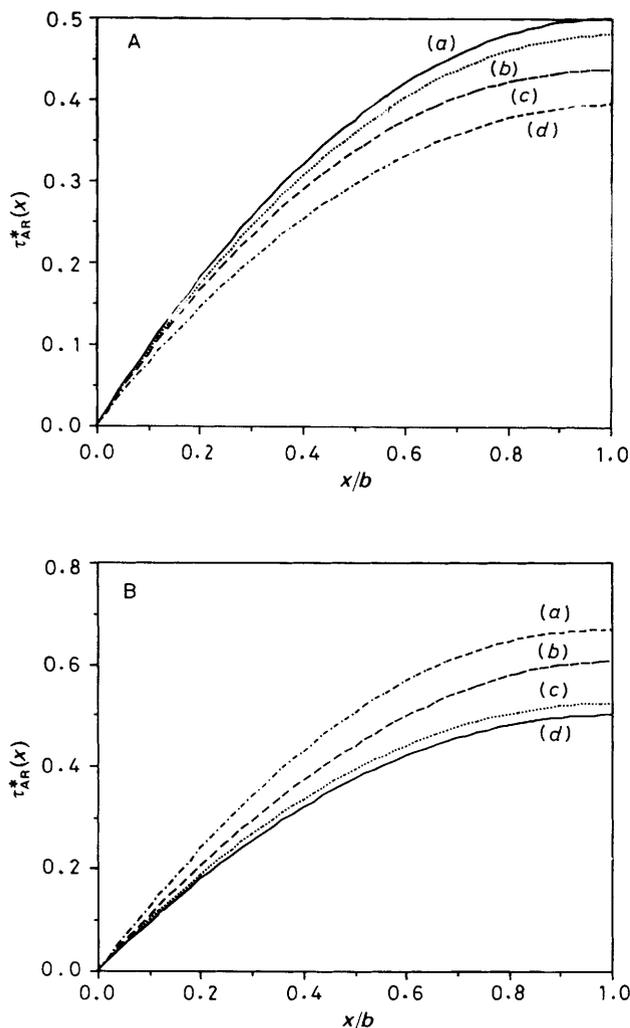


Fig. 4 The scaled mean first passage time $\tau_{AR}^*(x) = [D\tau_{AR}(x)/b^2]$ as a function of initial position for: A, co-ions and B counter-ions at surface potential $y_s = 1$ and various surface separations: A(b) $2\kappa b = 1$, (c) 20, (d) 6. B(a) 6, (b) 20, (c) 1. The free-diffusion result [A(a) and B(d)] is a function of only (x/b)

For exactly the same reasons as described in the case for $\tau_{RA}(x)$, deviation from the free-diffusion result is a maximum at some intermediate separation, observed to occur at around $(2\kappa b) \approx 6$.

(iii) $\tau_{AA}(x)$: Absorbing at $x = x_1 = 0$; Absorbing at $x = x_2 = b$

In Fig. 6 and 7, we show the scaled mean first passage times $[D\tau_{AA}(x)/b^2]$ against the starting position (x/b) at reduced surface potentials $y_s = 1$ and 4.

In this case, absorption takes place at the mid-plane ($x = 0$) as well as at the surface ($x = b$). Electrostatic interactions between the diffusing ion and the charged surface affect the probability of absorption at the charged surface ($x = b$) relative to absorption at the mid-plane ($x = 0$). The co-ions, which are repelled from the charged surface, will therefore have larger mean first passage times than the free-diffusion case because the repulsive interaction with the surface lowers the relative probability of absorption at that surface. On the other hand, counter-ions, which are attracted to the charged surface, will have smaller mean first passage times because of the increased relative probability of absorption at the charged surface. Maximum deviations from the

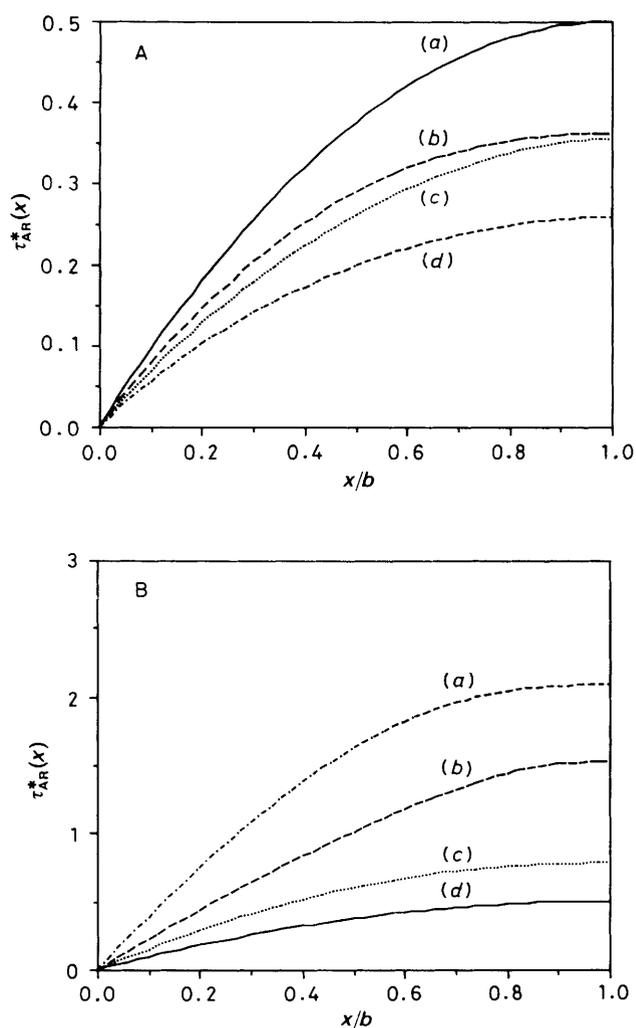


Fig. 5 The scaled mean first passage time $\tau_{AR}^*(x) = [D\tau_{AR}(x)/b^2]$ as a function of initial position for: A, co-ions and B, counter-ions at surface potential $y_s = 4$ and various surface separations: A(b) $2\kappa b = 20$, (c) 1, (d) 6. B(a) 6, (b) 20, (c) 1. The free-diffusion result [A(a) and B(d)] is a function of only (x/b)

free-diffusion results occur at $2(\kappa b) \approx 6$ for counter-ions, but range between $(2\kappa b) = 6$ to 10 for co-ions, depending on the value of the surface potential (see later).

(iv) Variation of $\tau(x)$ with Surface Separation

In Fig. 8 and 9 we show the variation of $\tau_{RA}(0)$, $\tau_{AR}(b)$ and $\tau_{AA}(b/2)$ for co-ions and counter-ions as a function of the half-surface separation (κb) for different surface potentials. The particular x values chosen here are where the maximum values of $\tau(x)$ [or nearly so for $\tau_{AA}(x)$] are located. From eqn (3.10) and (3.12) we recall that

$$\begin{aligned} \tau_{AR}^{\text{co-ion}}(b) &= \tau_{RA}^{\text{counter-ion}}(0) \\ \tau_{AR}^{\text{counter-ion}}(b) &= \tau_{RA}^{\text{co-ion}}(0) \end{aligned} \quad (5.1)$$

These special values of the mean first passage times will approach the following free-diffusion values in the limits $\kappa b \rightarrow 0$ or $\kappa b \rightarrow \infty$

$$\left. \begin{aligned} \tau_{RA}^*(0) &= 1/2 \\ \tau_{AR}^*(b) &= 1/2 \\ \tau_{AA}^*(b/2) &= 1/8 \end{aligned} \right\} \text{free diffusion} \quad (5.2)$$

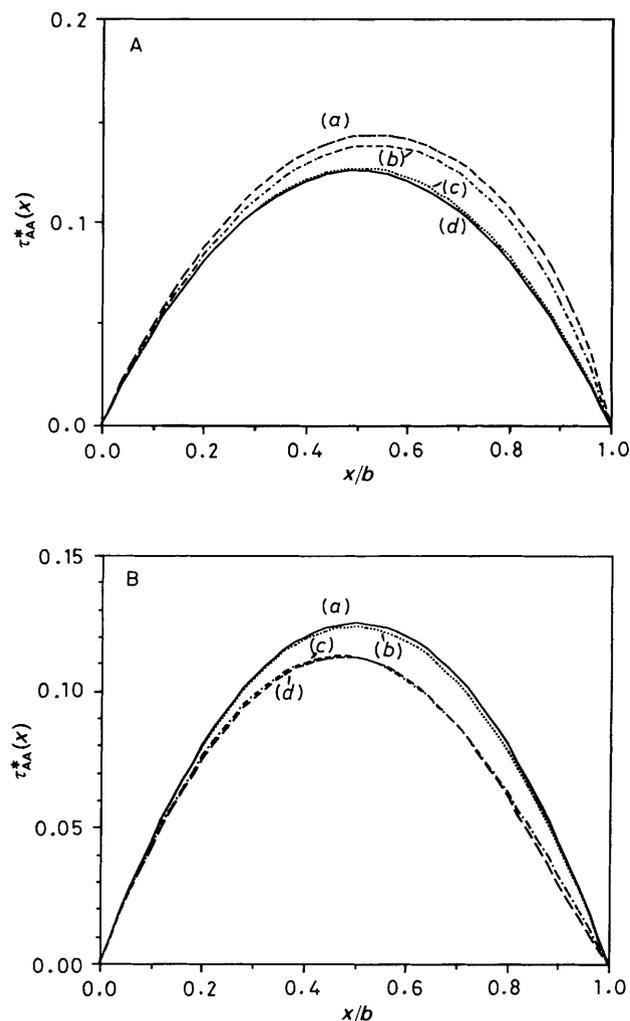


Fig. 6 The scaled mean first passage time $\tau_{AA}^*(x) = [D\tau_{AA}(x)/b^2]$ as a function of initial position for: A, co-ions and B, counter-ions at surface potential $\gamma_s = 1$ and various surface separations: A(a) $2\kappa b = 6$, (b) 20, (c) 1. B(b) 1, (c) 6, (d) 20. The free-diffusion result [A(d) and B(a)] is a function of only (x/b)

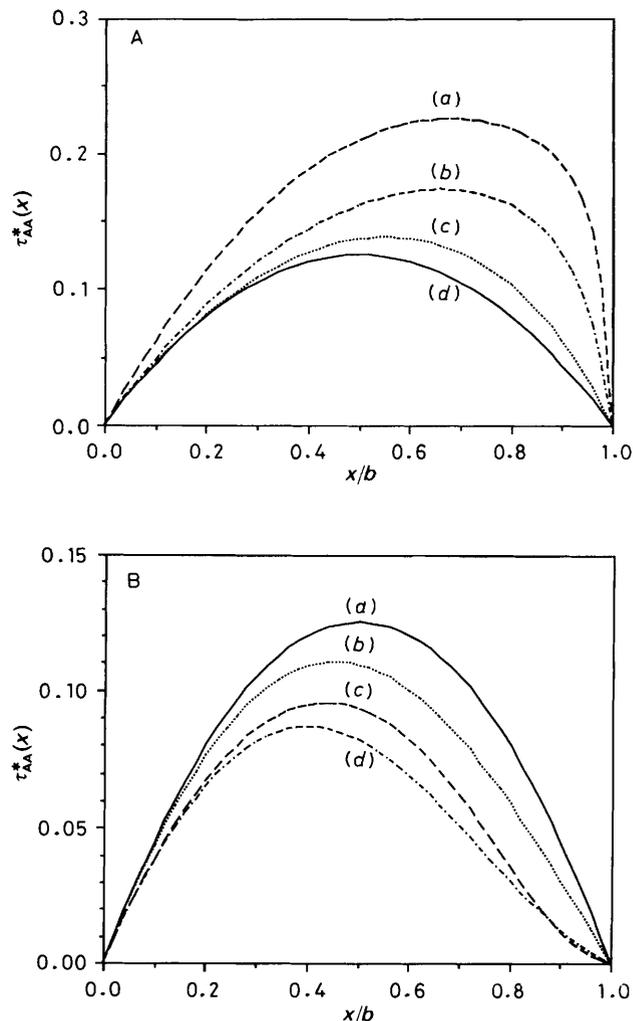


Fig. 7 The scaled mean first passage time $\tau_{AA}^*(x) = [D\tau_{AA}(x)/b^2]$ as a function of initial position for: A, co-ions and B, counter-ions at surface potential $\gamma_s = 4$ and various surface separations: A(a) $2\kappa b = 6$, (b) 20, (c) 1. B(b) 1, (c) 20, (d) 6. The free-diffusion result [A(d) and B(a)] is a function of only (x/b)

The results in Fig. 8 and 9 illustrate the earlier observation that maximum deviations from the free-diffusion limit for both co-ions and counter-ions occur when the surfaces are about $(6/\kappa)$ apart, that is, $(\kappa b) \approx 3$, with the exception of $\tau_{AA}^*(b/2)$, which peaks between $(\kappa b) \approx 6-10$.

(v) Position-averaged $\bar{\tau}$

Unfortunately, the position-averaged mean first passage times defined in eqn (2.18) cannot be evaluated in terms of known functions, so the integrals over initial positions involved in their definitions have to be computed numerically. The results are given in Fig. 10-12. With the exception of $\bar{\tau}_{AA}$ for co-ions, all position-averaged mean first passage times show maximum deviation from the free-diffusion result at $(\kappa b) \approx 3$. Maximum deviations of $\bar{\tau}_{AA}$ for co-ions occur at even larger separations.

The above observations have two important consequences. Electrostatic interactions between the diffusing ion and the charged surface can significantly affect the mean first passage time and other diffusion kinetics even when the surface separation is much larger than the extent of the double-layer thickness as measured by the Debye length $(1/\kappa)$. In fact,

maximum deviations from the free-diffusion result occur when the double layers from each surface do not overlap in any significant way. This gives rise to the possibility of constructing approximate methods of calculating diffusion kinetics based on some superposition principle.

6. Two Analytic Approximations

In this section, we propose two simple methods of calculating the mean first passage times based on the superposition principle. The main advantage of these methods is that they circumvent the need to deal with elliptic integrals and elliptic functions. Motivated by the observations of the previous section, we propose the use of two approximate expressions for the reduced electrostatic potential $\psi(x)$ between the charged surface.

(i) The Superposition Approximation

We approximate the reduced potential profile in $-b < x < b$ by the sum of two contributions which are the potential profiles due each surface treated as a single surface in isolation,

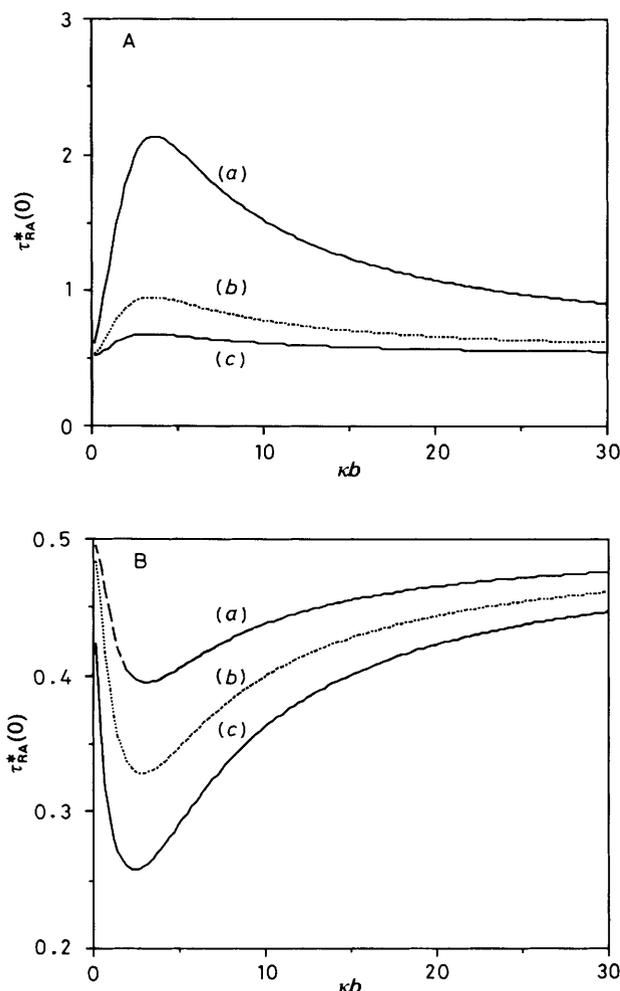


Fig. 8 The scaled mean first passage time $\tau_{RA}^*(0) = [D\tau_{RA}(0)/b^2]$ as a function of half separation (κb) for: A, co-ions and B, counter-ions at various surface potentials: A(a) $y_s = 4$, (b) 2, (c) 1. B(a) $y_s = 1$, (b) 2, (c) 4. These results are related to $\tau_{AR}^*(b)$ by eqn (5.1)

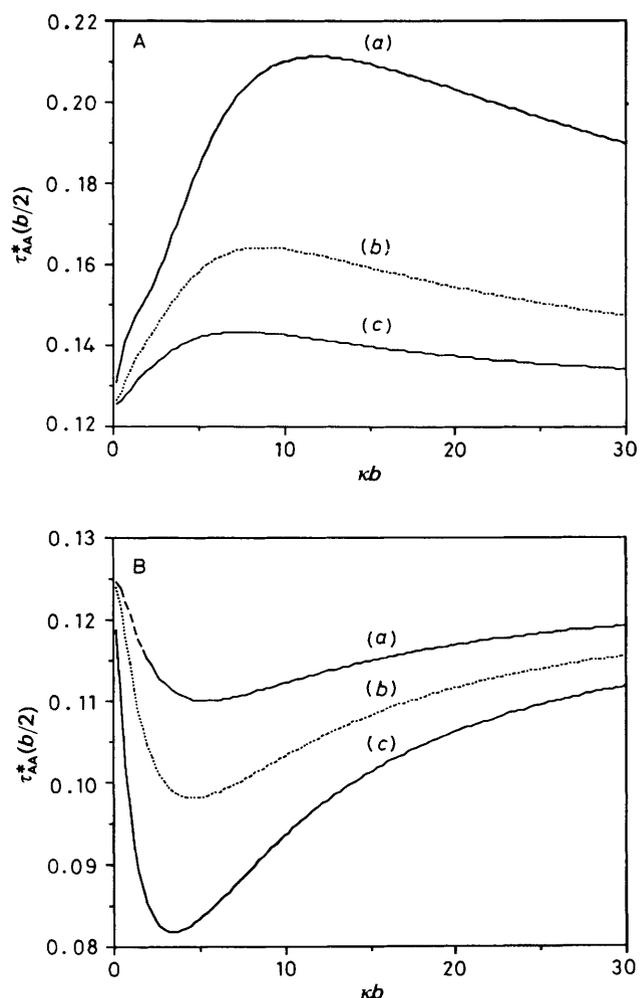


Fig. 9 The scaled mean first passage time $\tau_{AA}^*(b/2) = [D\tau_{AA}(b/2)/b^2]$ as a function of half separation (κb) for: A, co-ions and B, counter-ions at various surface potentials: A(a) $y_s = 4$, (b) 2, (c) 1. B(a) $y_s = 1$, (b) 2, (c) 4

located adjacent to a semi-infinite half-space of electrolyte:¹⁵

$$y(x) = 2 \ln\{\coth[(\alpha + \beta - \xi)/2]\} + 2 \ln\{\coth[(\alpha + \beta + \xi)/2]\} \quad (6.1)$$

The parameters β and ξ are given by

$$\xi \equiv \kappa x, \quad \beta \equiv \kappa b \quad (6.2)$$

and α is related to the reduced surface potential y_s by

$$\alpha \equiv -\ln(\tanh[y_s/4]) \quad (6.3)$$

With this approximate form for $y(x)$, the expressions for the mean first passage times given by eqn (2.18) and (3.1)–(3.3) in terms of iterated integrals have to be evaluated numerically.

This superposition approximation for $y(x)$ gives the correct limit of the mean first passage times as $\kappa b \rightarrow 0$. Although eqn (6.1) gives incorrect function values for $y(x)$, it does provide a reasonable approximation for the gradient of the effective potential that controls diffusion; the incorrect function values in $y(x)$ simply cancel out in the normalization of the equilibrium distribution function $f(x)$. When $\kappa b \gg 1$, eqn (6.1) will obviously give the correct behaviour. Using the superposition approximation the maximum error occurs in the value of $\tau_{RA}^{co-ion}(0)$. At $\kappa b \approx 1$, this error is *ca.* 1% and falls rapidly to less than 1% when κb reaches 2. In practical terms, in the regime where deviations from the free-diffusion limit are

largest, the superposition approximation can give results of acceptable accuracy.

(ii) The One-surface Approximation

If the diffusion domain is $0 < x < b$, and κb is not too small, the first term on the right-hand side of eqn (6.1) is the dominant term. The one-surface approximation simply retains this leading term by setting

$$y(x) = 2 \ln\{\coth[(\alpha + \beta - \xi)/2]\} \quad (6.4)$$

The advantage of this approximation is that the iterated integrals in eqn (3.1)–(3.3) can be evaluated analytically, however, the position-averaged mean first passage time $\bar{\tau}$, defined by eqn (2.18), needs to be evaluated numerically.

Explicit expressions for the mean first passage times for co-ions are:

$$\beta^2 \tau_{RA}^*(x) = [\{\zeta - 2 \tanh[(\alpha + \beta)/2]\} \times \{\zeta + 2 \coth[(\alpha + \beta - \zeta)/2]\} - \zeta^2/2]_{\zeta=0}^{\zeta=\xi} \quad (6.5)$$

$$\beta^2 \tau_{AR}^*(x) = [(\beta + 2 \tanh[\alpha/2] - \zeta) \times \{\zeta + 2 \coth[(\alpha + \beta - \zeta)/2]\} + \zeta^2/2]_{\zeta=0}^{\zeta=\xi} \quad (6.6)$$

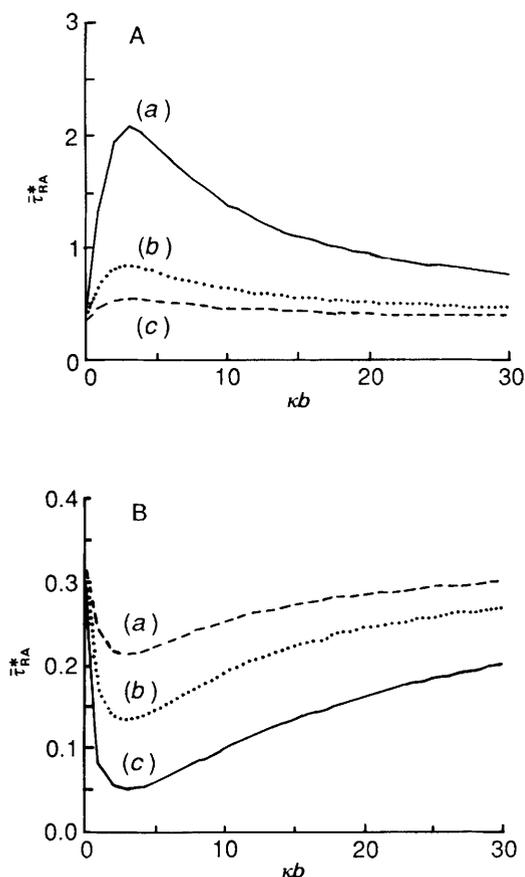


Fig. 10 The position-averaged mean first passage time $\bar{\tau}_{RA}^*$ as a function of half separation (κb) for: A, co-ions and B, counter-ions at various surface potentials: A(a) $y_s = 4$, (b) 2, (c) 1. B(a) $y_s = 1$, (b) 2, (c) 4

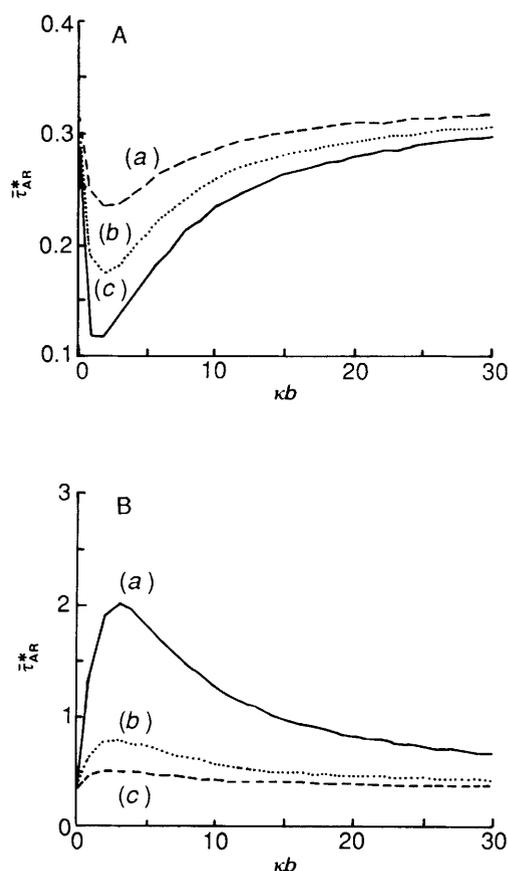


Fig. 11 The position-averaged mean first passage time $\bar{\tau}_{AR}^*$ as a function of half separation (κb) for: A, co-ions and B, counter-ions at various surface potentials: A(a) $y_s = 1$, (b) 2, (c) 4. B(a) $y_s = 4$, (b) 2, (c) 1

$$\beta\tau_D^*(x) = \{\beta + 2 \tanh[\alpha/2] - 2 \tanh[(\alpha + \beta)/2]\} \\ \times \{\xi + 2 \coth[(\alpha + \beta - \zeta)/2] - 2 \coth[(\alpha + \beta)/2]\}. \quad (6.7)$$

The expression for $\tau_{AA}^*(x)$ can be obtained from these results using eqn (3.13). The parameters α , β and ξ are given by eqn (6.2) and (6.3).

The mean first passage times for counter-ions can be obtained from the above results for co-ions by interchanging the hyperbolic functions

$$\tanh[\dots] \leftrightarrow \coth[\dots]$$

wherever they appear in eqn (6.5)–(6.7).

At $\kappa b \approx 3$, where maximum deviations from the free-diffusion result occur, the one-surface approximation is in error by *ca.* 10%. The analytic simplicity of this approximation may in certain circumstances outweigh its inaccuracies. Furthermore, if expressions for the propagators are required, an earlier study of the diffusion kinetics near a single surface⁹ can be extended using the one-surface approximation to give approximate analytic expressions for the propagators.

The calculations and results presented in this paper provided the first quantitative estimate of mean first passage times based on the full non-linear Smoluchowski–Poisson–Boltzmann model. While more sophisticated and rigorous treatments of the diffusion problem are possible, the present model should be adequate for describing diffusion in 1:1 electrolytes.

Appendix: Elliptic Functions and Integrals

This Appendix summarizes the identities and results relating to elliptic functions and elliptic integrals that are needed in Section 4. We use the standard notation for the Jacobi elliptic functions and their ratios.¹¹ In the following, all the moduli m of the different elliptic functions and integrals are the same and will not be written out explicitly. The value of the modulus is related to the mid-plane potential of the Poisson–Boltzmann solution by eqn (2.6).

The incomplete elliptic integral of the first kind is defined by:

$$F(\phi|\alpha) = \int_0^\phi \frac{d\theta}{\sqrt{(1 - \sin^2 \alpha \sin^2 \theta)}} \quad (A1)$$

and the complete elliptic integral of the first kind is

$$K(\alpha) = F\left(\phi = \frac{\pi}{2} \middle| \alpha\right) \quad (A2)$$

The modular angle α and the amplitude ϕ are given by eqn (2.6) and (2.7). These are connected to the Jacobi elliptic functions by

$$\begin{aligned} \operatorname{sn} u &= \sin \phi, & \operatorname{cn} u &= \cos \phi, \\ \operatorname{dn} u &= \sqrt{(1 - m \sin^2 \phi)} \end{aligned}$$

which leads to the following identity which is needed in Section 4

$$\operatorname{dn}^2 u = (1 - m) + m \operatorname{cd}^2 u \quad (A3)$$

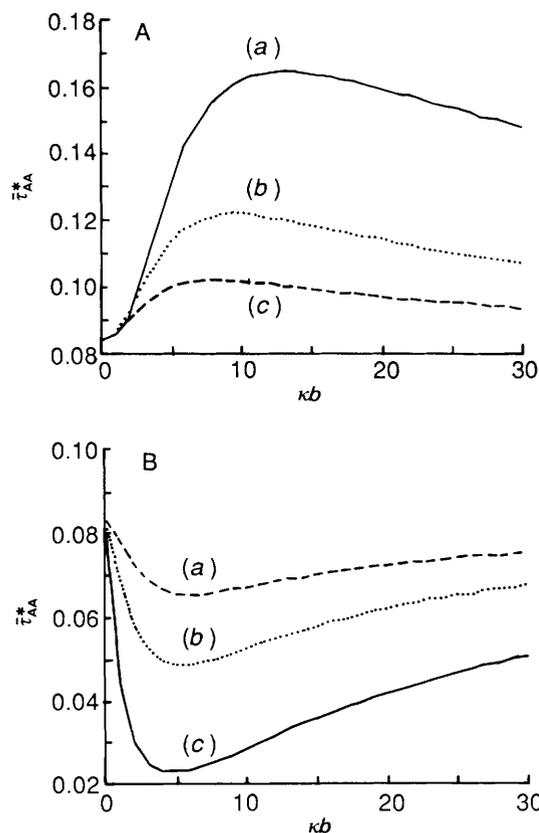


Fig. 12 The position-averaged mean first passage time $\bar{\tau}_{AA}^*$ as a function of half separation (κb) for: A, co-ions and B, counter-ions at various surface potentials: A(a) $y_s = 4$, (b) 2, (c) 1. B(a) $y_s = 1$, (b) 2, (c) 4

The incomplete elliptic integral of the second kind in its different common notation is given by:

$$E(u) \equiv E(u|m) \equiv E(\phi|\alpha) \\ \equiv \int_0^u dt \, dn^2 t \equiv \int_0^{\sin \phi} dt \sqrt{\frac{1-mt^2}{1-t^2}} \quad (\text{A4})$$

or equivalently

$$\frac{dE(u)}{du} = dn^2 u \quad (\text{A5})$$

The following integrals are required in the evaluation of $\tau_{RA}(x)$:

$$\int_0^u dt \, cd^2 t = \frac{1}{m} \{u - E(u) + m \, sn \, u \, cd \, u\} \quad (\text{A6})$$

$$\int_0^u dt \, dc^2 t = u - E(u) + sn \, u \, dc \, u \quad (\text{A7})$$

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Paper 0/02088F; Received 11th May, 1990