Article

Molecular Diffusion of lons in Nanoscale Confinement

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In applications where rapid diffusion of ions is important, it would therefore be advisable to not prewet a confined space with pure water. We attribute this phenomenon to the effect of the electrical potential of the confining walls. Unscreened surface potential in a thin film severely hinders the diffusion of the fluorescein ion. As salt diffuses into the thin film, the electrostatic double layer shrinks in thickness and further diffusion of ions is less hindered. On the other hand, diffusion of ions into the film is only weakly affected by the Debye length of the solution, provided that the surface potential inside a thin film is initially screened by even a low concentration of electrolyte inside the film. The time evolution of the concentration profile for different Debye lengths matches a diffusion model developed with the finite difference method (FDM).

INTRODUCTION

Diffusion is important in many confined aqueous systems, including drug delivery,¹ polymeric membranes,² and enhanced oil recovery.^{3,4} Molecular diffusion under nanoscale confinement by solids may differ from bulk diffusion because of interactions with the walls. If the molecule is sufficiently large compared to the confined space, then there will be an increased viscous drag.⁵ Fields from the walls may also affect diffusion. Electrostatic fields are particularly significant in aqueous solutions where the high dielectric constant of water allows a significant electrical potential to build at the solid–water interfaces. The length scale of the field exerted on ions, the Debye length, can be much greater than the hydrated ion radius, and therefore, confinement effects on diffusion should be felt in aqueous films that are much thicker than the ion size.

an equilibrium distribution of fluorescein was 10 times longer without the inert electrolyte than when the electrolyte was present.

The diffusion of molecules is driven by the gradient of chemical potential. For charged ions, both the gradient in concentration and the gradient in electrical potential contribute to diffusion, as described by the Nernst–Planck equation⁶

$$\frac{\partial c_{i}}{\partial t} = D_{i} \nabla \cdot \left(\nabla c_{i} + c_{i} \frac{Z_{i} e}{k_{\rm B} T} \nabla \psi \right)$$
(1)

where subscript i denotes the species of the molecule, c is the concentration, Z is the valence, D is the diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, and ψ is the electrostatic potential. The first term is the entropic diffusion described by Fick's law, and the second term is the diffusion that is driven by an external field. Here, we consider the field that arises from the spontaneous charging of the confining

walls. This contrasts with electrophoresis⁷ where the field is externally applied and with a streaming potential⁸ that is caused by externally applied convective flow.

Chan and co-workers used analytical methods to describe the diffusion of ions near charged surfaces in the 1980s,⁹⁻¹¹ but experimental studies of diffusion in nanoscale confinement were not achieved until the development of nano- and microfabrication. Several studies^{1,12,13} investigated the diffusion of protein or nanoparticles within a nanochannel, concluding that the apparent diffusion coefficients for these bulky particles were reduced by hydrodynamic interaction with the wall and interaction with wall electrostatic fields. Reduced surface diffusion of a polycation in a nanoslit was also reported as the slit width was reduced.¹⁴ Siwy et al.¹⁵ found asymmetric diffusion through conical nanopores. The Debye-lengthdependent results were explained in terms of depletion of surface co-ions. Bluhm et al.¹⁶ studied transport of radioactive cations across porous alumina membranes. They found that the apparent diffusion coefficient for various cations was 1 order of magnitude lower than the bulk value and found a small change in diffusion coefficient with increasing ionic strength. These results were also explained by the exclusion of ions by electrical double-layer interactions inside the nano-

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pores. Wang et al.¹⁷ used conductance measurements (i.e., ions driven by an external potential) to measure the diffusion of potassium chloride in a 65 nm channel. The authors concluded that the apparent diffusion coefficient of KCl in the channel was significantly lower than in bulk value when its concentration was less than 1 mM. This was attributed to the effect to the slow equilibration of surface charge.

In this work, we use the fixed geometry of a wedge (Figure 1) to examine aqueous ion diffusion into confinement. The key



Figure 1. (A) Geometry of the crack. The blue-shaded region represents the electrostatic double layer, which will change thickness according to the salt concentration. The depth of the crack (from bulk solution to zero thickness) is about 1 mm with an opening of about 1 μ m at the bulk solution. (B) Schematic of the centerline potential inside the crack. This potential asymptotes to zero when $\kappa^{-1} \ll T$.

concept is that diffusion of ions into the wedge is controlled not only by the concentration gradient but also by the naturally occurring electrical surface potential at each point (eq 1). This electrical potential differs from the bulk value in the doublelayer region adjacent to each wall, which has a thickness characterized by the Debye length

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\epsilon^2 \sum_i Z_i^2 n_{b,i}}}$$
(2)

where ε_0 is the permittivity of free space, ε_r is the dielectric constant, and $n_{b,i}$ is the number density of each ion in bulk. The ability to alter the diffusion should thus depend on the ratio of the Debye length to the film thickness. If the Debye length of the solution is much smaller than the film thickness, T, then there is only slight alteration of diffusion. At the other extreme, a Debye length that exceeds the film thickness should alter the diffusion. Because the Debye length depends on the bulk solution concentration, the diffusion of ions should be a function of the ion concentration.

Here, we examine the diffusion of ions in nanoscale aqueous films between two nearly parallel solid surfaces and show that the diffusion into pure water is dramatically hindered compared to diffusion into an electrolyte solution. This shows that order-of-addition effects are very important in applications involving confinement: prewetting with pure water greatly slows the delivery of dissolved ions into the confined space. In pure water, the surface potential from the confining surfaces exerts an effect far into the solution, which can hinder transport as described by eq 1. As electrolyte diffuses into the double layer, the Debye length decreases, reducing the effect of the surface potential.

EXPERIMENTAL METHODS

Fabrication of Crack. In a class 100 cleanroom, Borofloat 33 wafers (University Wafers, 100 mm diameter, 500 μ m thickness) were cleaned in nanostrip (90% sulfuric acid, 5% peroxymonosulfuric acid, <1% hydrogen peroxide, KMG Electronic Chemicals, Inc.) at 75 °C for 15 min. After cleaning, the wafers were rinsed with DI water and dried in a Verteq SC1600-3 spin rinse dryer to remove any nanostrip residue. Two wafers were then aligned and pushed together by hand until they were weakly bonded from van der Waals forces. Cleanroom conditions were used to prevent the deposition of particles in the crack. From this point on, the crack construct can be removed from the cleanroom because it is difficult for particles to deposit in the formed crack.

The wafers were then thermally bonded in a furnace at 530 °C overnight.¹⁸ Owing to incomplete binding, a wedge-shaped crack was formed along the edge of the wafers. The depth of the fabricated crack is usually about 1 mm with an opening of about 1 μ m, where it enters the solution (as indicated in Figure 1A). The bonded wafer was then cut into small pieces (about 1 cm × 1 cm) with a diamond blade and put into a flow cell (see Figures S1 and S2). Both top and bottom surfaces were attached to coverslips using optically transparent glue, Norland Optical Adhesive 88 (NOA, Norland Products Inc.). The optical glue was cured with a handheld UV lamp for 2 min.

Microscopy Methods. A Zeiss Axio Imager M1 microscope was used with an Excelitas X-Cite 120Q fluorescence lamp as the light source and an EC Plan-Neofluar 20×/0.5 NA objective. The film thickness at each pixel was measured using reflected light interferometric microscopy. A band pass 395 nm filter with 25 nm band width was placed before the camera to narrow the range of wavelength of reflected light from the sample. The thickness at each pixel, i.e., the shape of the crack was determined in air because of the improved refractive index contrast. The position of the crack tip, i.e., where z = 0 for each y position was determined by a fitting procedure described in the Supporting Information (Section S2).

The amount of fluorescein corresponding to each pixel was measured using fluorescence microscopy. The range of depths (zvalues) at which the emission is sensed by the lens was about 2.5 μ m, which is greater than the thickness of the thin film containing the fluorophore (here, 0-200 nm) such that we always measure the amount corresponding to each pixel for the entire thickness of the film. The average concentration within the area that corresponds to a pixel is the measured amount divided by the area illuminating the pixel divided by the film thickness for that pixel. Fluorescence microscopy utilized a Zeiss 38 HE filter cube (excitation band pass filter 470 \pm 20 nm, a dichroic mirror at 495 nm, and an emission band pass filter at 525 \pm 25 nm). The analysis methods of interference and fluorescence images are similar to that described in Gaddam et al.,¹ except that the geometry here is glass/water/glass. Compared to the work by Gaddam et al., the optical interference is very weak, which simplifies the measurement of the fluorophore concentration and allows us to measure at film thicknesses as great as 200 nm, compared to 65 nm previously. Details of calibration of the amount of fluorophore are provided in the Supporting Information (Sections S3 and S4).

Fluorescein Solutions. Fluorescein sodium (Sigma-Aldrich, used as a fluorescent tracer) solution with four different sodium chloride (Sigma-Aldrich, \geq 99.0%) concentrations was made with a stock NaOH solution with pH = 8.9 to measure the diffusion process of fluorescein. The highest quantum yield for fluorescein is for the 2⁻ state, and the pK for the second dissociation of fluorescein is 6.36.²⁰ The pH was kept at 8.9 (2.5 pH units above the pK) so that the fluorescein was maintained in the highly fluorescent 2⁻ state. Sodium chloride concentrations and corresponding Debye length of the solutions are listed in Table 1. The fluorescence emission was found to be proportional to the fluorescein concentration as measured by a Horiba Fluoromax-4 spectrofluorometer in bulk solution (see Figure S8).

Diffusion Experiment. Diffusion experiments were done with one of two different initial conditions of NaCl concentration: water

Table	1. Salt	Concent	trations	Used	in	Experiments	and
Their	Corres	ponding	Debye	Lengt	hs"	. –	

NaCl conc. (mol/L)	Debye length (nm)
3.7×10^{-1}	0.5
3.7×10^{-3}	5
7.4×10^{-4}	10
1.0×10^{-4}	19
^{<i>a</i>} The calculation includes the contri	bution of fluorescein and NaOH.

pre-equilibrated and NaCl salt pre-equilibrated. For water preequilibration, the flow cell was filled with DI water for 1.5 h to remove any potential residue of fluorescein or NaCl inside the crack. Then, the liquid in the flow cell was replaced by the NaCl/fluorescein solution at time zero, and then both NaCl and fluorescein diffuse into the crack. In order to examine a series of solutions with a single crack, it was necessary to replace the liquid in the fluid cell. To ensure that the solution condition was changed right at the crack opening, the first solution in the flow cell was removed by withdrawing liquid into a syringe such that there was only a small meniscus at the crack entrance (see Figure S4), and then a new solution was added to the flow cell. Any solution within the crack remained in place during this process. Once the replacement was completed, the boundary between diffusing solution and the pre-equilibrated solution was established (as shown schematically in Figure 1A).

For salt pre-equilibration, NaCl solution without fluorescein was first injected into the flow cell for 1.5 h to establish an equilibrated salt environment inside the crack. Then, at time zero, the solution in the flow cell was replaced with fluorescein solution with the same NaCl concentration. In this case, diffusion into the crack is almost exclusively by fluorescein.

Injection of the solution was done off the microscope stage with the flow cell in a vertical orientation so that bubbles would not become trapped in the flow cell. After the solution was injected into the flow cell, it was placed onto the microscope stage in the same location, where the crack geometry was measured. This was achieved with a three-point mounting that allowed replacement within 5 μ m in *x* and *y* dimensions. Images were taken at 30 s intervals over a period of 3 h to observe the diffusion process.

RESULTS AND DISCUSSION

Surface Excess of Fluorescein at Equilibrium. We begin by describing the equilibrium distribution of fluorescein ions inside the crack at equilibrium because (a) we can confirm that ion depletion does occur and (b) equilibrium is the final state in diffusion. Figure 2 compares the amount of fluorescein at each film thickness for a range of Debye lengths. Note that the amount is the entire amount between the glass walls at a particular film thickness. If the equilibrium concentration in the crack were equal to the bulk concentration at all thicknesses, then the amount of fluorescein per area would increase linearly with the thickness of the aqueous film. This hypothetical case is shown by the dotted line. Experimental data at each thickness show fewer molecules per area, which is reasonable because both fluorescein and glass are negatively charged at this pH.²¹ It means that the electrostatic potential energy is greater for fluorescein in the thin film. That is, there is a depletion layer or negative surface excess on each surface. The measured data in Figure 2 are linear at large separation where $\kappa^{-1} \ll T$ because the ion depletion zones near each solid do not overlap much and differences in film thickness lead only to changes in the thickness of the bulk solution between the electrical double layers at each interface. At smaller film thicknesses, the depletion zones overlap, and so there is less depletion as the crack narrows.



Figure 2. Equilibrium amount per area of fluorescein ions in solutions of different Debye lengths, as indicated by the legend. The highest amount is 5×10^{-3} molecules/nm². The Debye length was changed by adding NaCl. Circles are the mean of four independent measurements, the error bars are the standard error of the mean, and the small oscillation in data around 50–75 nm that appears in all data is not significant. The solid lines were calculated from the Boltzmann distribution using the best fit of the surface potential calculated from an exact numerical solution of the Poisson–Boltzmann equation. The fitted surface potentials at infinite separation are -86 ± 22 , -83 ± 12 , and -55 ± 3 mV for 5, 10, and 19 nm Debye length, respectively. The uncertainty is the 95% confidence interval. Models to account for the variation in surface potential with ion concentration are presented by Pashley²² and by Miklavic and Ninham.²³

Results at shorter Debye lengths show that the linear region extends to smaller film thickness, and there is less depletion. This is because the overlap of double layers occurs at smaller film thickness, and there is less depletion in the thinner double layer. These qualitative effects are described quantitatively by calculations of amount/area of fluorescein from the Boltzmann distribution using the best fit of the surface potential calculated from an exact numerical solution of the Poisson–Boltzmann equation (Figure 2). The calculation agrees well with the data.

How Debye Length Affects the Diffusion of Fluorescein. We now examine the hypothesis that diffusion of ions in the confined thin film is affected by the Debye length of the solution. We describe experiments where the initial condition was always 50 μ M fluorescein outside the crack and zero inside the crack (Figure 1A). The Debye length of a fluorescein-only solution is 24 nm, and shorter Debye lengths were obtained by the addition of NaCl. There were two types of initial conditions: (1) the initial salt concentration in the crack and in bulk are the same so there is very little diffusion of NaCl and so the screening length in the crack is nearly constant and (2)the crack initially contains only water, so the initial Debye screening length is long and falls with time as NaCl diffuses into the crack. In all cases, the bulk solution volume was so large compared to the film volume that the concentration outside the crack was time invariant.

Initial Condition 1: Constant Salt Concentration and Debye Length in the Crack. We begin by discussing results for case 1 where the salt concentration and Debye length are always almost invariant with time and only fluorescein is diffusing. We write almost because fluorescein is an ion, and so



Figure 3. Effect of salt concentration on the diffusion of fluorescein into a crack. Data are the number of molecules per unit area where the aqueous film is 98 nm thick. Section S3 shows information on calibration and rationale for measuring at 98 nm film thickness, and Section S2 shows how the x = 0 was established. (A) Experimental results where the points are the average of three independent experiments and error bars are the standard error of the mean. The secondary *y*-axis on the plot represents the average molar concentration of fluorescein ions obtained from the measured amount of fluorescein per area divided by the thickness of 98 nm. It represents the average concentration. The distribution of ions is not expected to be uniform in *z*, even at equilibrium. For all of the initial salt conditions, a plateau representing equilibrium is reached after about 10 min. The decline after 10 min in some data is caused by photobleaching (note the logarithmic timescale). (B) Simulation results for 1-D diffusion using the finite difference method. Data and simulation show that the time to reach equilibrium is not sensitive to the initial salt concentration in the crack.



Figure 4. Effect of salt solutions in the crack when fluorescein was added to the bulk solution. The film thickness is 98 nm for the position where these results are recorded. The Debye length of each figure (A) 0.5 nm, (B) 5 nm, (C) 10 nm, (D) 19 nm is controlled by NaCl concentration in the solutions. Inset in (A) is the data of the first 20 min for 0.5 nm Debye length plotted on a linear *x*-axis. Figures show the time change in the number of fluorescein molecules per nm² at 98 nm film thickness for different Debye lengths and different initial conditions in the crack (indicated by figure legend). The results for the initial DI water differ because the boundary condition (the salt concentration in bulk) varies. The data points are the average of three independent experiments, and the error bars are the standard error of the mean for three independent measurements. Note that the scale of the *x*-axis (time) is logarithmic. The diffusion of fluorescein is about 10 times slower when the initial condition is pure water in the crack than with NaCl solution in the crack, except for the highest salt concentration.

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Figure 5. Effect of salt solutions in the crack when fluorescein was added to the bulk solution. The film thickness is 50 nm in the position where these data were recorded. The Debye length for each figure (A) 0.5 nm, (B) 5 nm, (C) 10 nm, (D) 19 nm is controlled by NaCl concentration in the solutions. The data points are the average of three independent experiments and the error bars are standard error. Note that the scale of the *x*-axis (time) is logarithmic.

its diffusion can change the Debye length. For the most dilute salt, NaCl is 2 times greater than the fluorescein concentration outside the crack. In this case, the Debye length inside the crack goes from 30 nm initially to 19 nm at equilibrium. By capturing an image of the crack, we simultaneously measured the amount of fluorescein for thicknesses in the range 0-400 nm, but Figure 3A shows the data only for one film thickness, 98 nm, over time. We initially expected that the negative electrostatic potential would suppress diffusion of fluorescein into the crack and that the effect would be larger for greater Debye length when more of the crack was under the influence of the crack wall potential. Surprisingly, the time for ions to reach equilibrium for different Debye lengths is about the same, around 10 min. The same trend is observed at other separations, and Figure 5 includes the data at 50 nm thickness (data series with initial condition of NaCl in four plots). This result suggests the counterintuitive conclusion that the lateral diffusion of ions in a confined aqueous film is not hindered by the electrostatic potential from the confining surfaces, i.e., there is no gating effect. This can be understood by considering the geometry. Considering a thin film between two exactly parallel surfaces, the gradient in electrostatic potential (the field) is normal to the overall direction of the ion transport surface and therefore has no effect on diffusion times. In our experiments, the direction of flux is inclined only very slightly relative to the plane of the solid-liquid interface, so the gating effect is small. We would only expect an effect where the angle of inclination was large.

To further understand the effect of the Debye length on diffusion, we numerically calculated the time evolution of concentration arising from diffusion using a one-dimensional (x) solution to Nernst–Planck equation (eq 1) in which the variation in film thickness entered only by setting the electrical potential to be a function of x (for details see Section S5). The electrical potential in the one-dimensional model was set at the midplane (z = 0) potential in the actual two-dimensional system (see Figure 1A for the meaning of *x* and *z* coordinates). Clearly, the real system also has gradients in the z-direction, but we ignore these for now because (a) the z-dimension of the crack is much smaller than the *x*-dimension, so equilibrium should be established much more quickly in the z-direction, and (b) diffusion in the z-direction can only indirectly affect diffusion in the x-direction. The centerline potential was calculated using a constant surface potential of -50 mV and from the low potential solution of the Poisson-Boltzmann equation²

$$\psi_{z=0} = 2\psi_0 \exp\left(-\frac{\kappa T}{2}\right) \tag{3}$$

where ψ_0 is the surface potential. For the model calculations, we assumed that the aspect ratio of the crack is 1000:1 so T = x/1000.

Figure 3B shows results from the one-dimensional calculation. This simple simulation captures three aspects of the experiment. First, the time to reach equilibrium is on the same order of magnitude. Second, the calculated equilibrium

concentration matches the average concentration of fluorescein from the experiment, shown as the secondary axis in Figure 3A. Note that calculation of the average concentration at a given film thickness from measured number of molecules per unit area assumes that the distribution of fluorescein is uniform along the z-axis in the crack. However, the actual distribution would be depleted of fluorescein ions near the glass walls and is expected to follow the Boltzmann distribution if equilibration in z is much faster than in x because of the high aspect ratio of crack. Third, and most important, the calculation is consistent with the experiments that show that the Debye length only very weakly affects the time to equilibrium in the range measured.

Initial Condition 2: Time-Varying Salt Concentration and Debye Length in the Crack. We now describe results for the diffusion of the ion, fluorescein, where there is pure water in the crack at the start. Under this initial condition, the Debye length of the solution inside the crack is extremely long at the beginning and decreases with time as NaCl diffuses into the crack. Results at 98 nm film thickness are shown in Figure 4, and results at 50 nm film thickness are shown in Figure 5. Note again that we measured all film thicknesses simultaneously but show examples of two thicknesses.

For 5, 10, and 19 nm Debye length solution, the time for fluorescein to reach equilibrium is about 10 times longer when there is no NaCl in the crack for the initial condition. The accumulation rates of fluorescein are also similar among these three Debye lengths.

The data in Figure 4 clearly show that the diffusion of salt causes the delay that hinders the diffusion of fluorescein. When the salt (and fluorescein) is presented with an unscreened potential in the crack, the salt is very slow to diffuse into the crack. With pure water in the crack, the Debye length is set by the autodissociation of water and dissolution of CO_2 and should be around 300 nm, which is much longer than the even the largest film thickness that we describe (200 nm). The long Debye screening length means that the magnitude of electrical potential is high at all *z* positions, and so diffusion of both NaCl and fluorescein is severely hindered.

For very concentrated salt solutions (0.37 M, Debye length = 0.5 nm), the diffusion into water is faster than in the other cases, completed within 20 min, which is presumably because the very large gradient between 0.37 M and pure water causes a large driving force for NaCl diffusion into the crack. The transport of salt rapidly shortens the Debye length and thereby allows further diffusion of NaCl and fluorescein into the crack. The inset of Figure 4A shows the plot on a linear scale for the first 30 min of the diffusion. The diffusion into DI water has a similar accumulation rate as the diffusion into NaCl solution, except that it is delayed by \sim 4 min. This time period is sufficient for concentrated salt to diffuse into the crack and lower the Debye length to a degree where the following diffusion is significantly accelerated.

Figure 5 shows the same result experiments as in Figure 4 but at a location where the film is only 50 nm. For this thinner film, there is stronger depletion of fluorescein at equilibrium so all amounts are smaller. Otherwise, the effects are similar with a much longer time to reach equilibrium for the initial condition of deionized water in the crack.

CONCLUSIONS

We make two conclusions from this work. First, the initial condition of salt can be very important in determining the diffusion of ions into a crack. It takes 10 times longer for an ion to reach equilibrium inside the crack when there is no salt. This is because diffusion of ions is severely hindered by the electrostatic potential in the extremely long Debye length of pure water. Second, provided that the surface potential inside a thin film is initially screened by even a low concentration of electrolyte inside the film, the diffusion of ions into the film is barely affected by the Debye length of the solution.

One can envisage many applications where diffusion into cracks is important and can be manipulated by controlling the initial condition. For example, hair products often consist of charged surfactants that diffuse into thin films between hair fibers. Our results suggest that such diffusion and hence the time to move product into the hair before a rinse might depend critically on whether the hair is wet with water prior to application of the product or whether the product is put directly on the hair. Similarly, when surfactants in water solutions are injected into cracks for oil recovery, the diffusion of charged surfactant would depend critically on the preexisting salt conditions and on the first solution that is put down the oil well.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.2c00248.

Additional experimental details, including photographs of the experimental setup; crack tip detection method; details on fluorescence intensity calibration; relation between fluorescein intensity and its concentration; and details on simulation using 1-D finite difference method (PDF)

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Notes

The authors declare no competing financial interest.

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