

**Figure 15.** Fluorescence spectra of (a) the SP8S monolayer on water at 40 mM/m and (b) the LB film (4 layers) deposited at the same surface pressure onto the nonfluorescent glass plate.

### Conclusion

As can be expected, the amphiphiles having the pyrenyl groups at the hydrophilic head parts can provide more stable and well-ordered monolayers compared with the pyrene fatty acids whose pyrenyl groups are bound to the

hydrophobic tails of the alkyl chains. Since no condensed phases appear in the monolayers of the pyrene fatty acids themselves, the pyrenyl groups at the tails may be able to fluctuate in the liquid expanded phases, leading to irregular orientation of the pyrene chromophores. Meanwhile, in the SP6S and SP8S monolayers, the freedom of the arrangement of the pyrene chromophores should be restricted at the air-water interface, and the compression of the monolayers may force the pyrene chromophores to orient regularly. In addition, the monolayer of the amphiphiles having the chromophores at the hydrophilic head parts can easily be affected by the conditions of the subphase.  $\text{Ca}^{2+}$  in the subphase stabilizes the SP8S monolayer to form the condensed phase and prevents the expulsion of the monolayer component in the liquid expanded phase. In this work, we used 1-stearylpyrenesulfonates as the monolayer components. The  $\text{SO}_3\text{Na}$  group may not be suitable to prepare well-condensed and well-ordered monolayers because of the strong electrostatic repulsion between the head groups at the water surface. We are examining the replacement of the  $\text{SO}_3\text{Na}$  group with the  $\text{COOH}$  group.

**Registry No.** SP6S, 120665-95-4; SP8S, 120665-96-5; ARA, 506-30-9;  $\text{CaCl}_2$ , 10043-52-4;  $\text{NaHCO}_3$ , 144-55-8.

## Diffusion of Charged Micelles through Charged Microporous Membranes

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The effects of micelle/pore interactions (e.g., electrostatic, hydrodynamic, and steric) on intrapore micelle diffusion coefficients were studied experimentally and compared with calculations for the hindered diffusion of charged spheres in charged cylindrical pores. Interactions between the micelle and the pore wall were important, since micelle diffusion was studied in pores whose radii were as small as 10 times the micelle radius and in solutions with low ionic strengths, where the Debye length was significant when compared to the pore size.

### Introduction

The diffusion of nonionic surfactant micelles through microporous membranes (e.g., Celgard, Millipore, and Nuclepore) has been the subject of several recent studies.<sup>1-4</sup> Stroeve et al. were the first to report on this topic with their study of a poly(oxyethylene) alkylphenol surfactant micelle diffusing in Celgard and Mitex filters.<sup>1</sup> The diffusion coefficients of nonionic micelles measured in microporous membranes were less than the diffusion coefficients of these surfactant aggregates in free solution.<sup>1-4</sup> In other words, the mobility of a micelle was less inside a membrane pore even though the micelle radius was 10 times smaller than the pore radius. This phenomenon is known as hindered diffusion and is observed in porous membranes when the size of a particle (e.g., polystyrene

latex sphere, asphaltene, or globular polymer) is significant when compared to the size of the pore.<sup>5-9</sup> In general, as the ratio of the particle to pore radii increases, the diffusion coefficient of a particle in the pore decreases. Theoretical studies of hindered diffusion, using hard spheres in cylindrical pores as model systems, have yielded analytical expressions for the ratio of the intrapore to free solution

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particle diffusion coefficients as a function of particle to pore radii ratio.<sup>10-14</sup>

If there is a charge on the particle and a charge on the pore, the analysis of a particle diffusion through the pore is more complicated. For example, if the particle and pore have opposite charges, they will attract each other, and the concentration of particles in the pore may be greater than that for an uncharged sphere. However, if the charges on the particle and pore are the same, they will repel each other, and the concentration of particles in the pore may be less than that for an uncharged sphere. Electrostatic effects on polystyrene latex sphere<sup>15,16</sup> and globular polymer<sup>17</sup> diffusion in microporous membranes have been studied. However, there have been no studies on the diffusion of charged micelles through microporous membranes.

In the present work, the diffusion of tetradecyldimethylammonium chloride (TBAC) and cetylpyridinium chloride (CPC) micelles through Nuclepore membranes with nominal pore diameters of 300 Å was studied as a function of supporting electrolyte concentration. The experimental results were compared to calculations of hindered diffusion by using the model of Smith and Deen<sup>17</sup> to calculate the partition coefficient of the charged micelle into the charged membrane pore.

### Theory

The diffusion coefficient of a hard sphere in a cylindrical pore ( $D_p$ ) relative to the diffusion coefficient of the same particle in free solution ( $D_\infty$ ) is given by the following expression:<sup>13</sup>

$$D_p/D_\infty = 1 - 2.1044\xi + 2.089\xi^3 - 0.948\xi^5 \quad (1)$$

where  $\xi$  is the ratio of the particle to pore radii. Equation 1 is valid for all values of  $\xi$  less than 0.4 and assumes that the particle diffuses along the axis of the pore.

It is important to note that  $D_p$  is the intrapore particle diffusion coefficient based on the concentration of particles in the pore. The intrapore particle diffusion coefficient based on the bulk concentration of particles ( $D$ ) is the product of  $D_p$  and the ratio of the concentration of particles in the pore relative to the concentration of particles in the bulk ( $K$ ). In general,  $K$  is given by the expression<sup>17</sup>

$$K = 2 \int_0^{1-\xi} \exp[-E(\theta)/kT] \theta \, d\theta \quad (2)$$

where  $\theta$  is the ratio of the distance of the particle's center from the center line of the pore to the pore radius and  $E(\theta)$  is the electrostatic free energy of the particle, relative to that in the bulk solution, at the dimensionless pore position  $\theta$ . The minimum value of  $\theta$  is zero when the center of the particle is on the pore axis, and  $\theta$  can become as large as  $1 - \xi$  if the particle's surface touches the pore wall. Values of  $K$  can be calculated from eq 2 by using the model of Smith and Deen<sup>17</sup> to determine  $E(\theta)$ . If  $E(\theta) = 0$  (i.e., the particle experiences no electrical potential), then eq 2 becomes

$$K = (1 - \xi)^2 \quad (3)$$

which describes the partitioning of an uncharged hard sphere into an uncharged cylindrical pore. Multiplying both sides of eq 1 by  $K$  produces the expression

$$D/D_\infty = K(1 - 2.1044\xi + 2.089\xi^3 - 0.948\xi^5) \quad (4)$$

where  $D$  is the intrapore particle diffusion coefficient based on the bulk concentration of particles.

To calculate  $D$  for an uncharged hard sphere in an uncharged cylindrical pore from eq 4,  $D_\infty$ , the particle radius, and the pore radius must be known. If there are charges on the sphere and pore wall, the surface charge density on the sphere, the surface charge density on the pore, and the ionic strength of the solution must also be determined to calculate  $K$  from eq 2.<sup>17</sup> A description of the experimental procedures used to determine parameters required for calculations, to characterize membranes, and to measure micelle diffusion coefficients in microporous membranes is in the next section.

### Experimental Section

**Materials.** The reagents cetylpyridinium chloride (CPC, Aldrich), tetradecyldimethylbenzylammonium chloride (TBAC, Alpha), hydrocortisone (Sigma), sodium chloride (Baker), and potassium chloride (Baker) were used as received. Polycarbonate microporous membranes, with nominal pore diameters of 300 Å, were purchased from Nuclepore.

**Diffusion Measurements.** The diffusion cell (with stirrers rotated at 300 rpm) has been described in a previous study.<sup>4</sup> Both sides of the cell, maintained at  $25 \pm 1$  °C, were filled with surfactant solution above the cmc such that one side had a higher concentration of surfactant than the other. The cmc values of CPC and TBAC in deionized distilled water, as determined by a break point in solution conductance, were 1.02 and 1.95 mM, respectively. These cmc values are in agreement with previous studies.<sup>18</sup> Surfactant micelles will diffuse across the membrane to reduce the concentration gradient. Surfactant monomers are assumed to make a negligible contribution to surfactant diffusion since the monomer concentration on both sides of the membrane is the same. Since the volume of the membrane was much smaller than the volume of the cell, a pseudo-steady-state approximation was made to obtain the following expression for the surfactant concentration differences across the membrane (see Appendix):

$$\ln [\Delta C_{S0}/\Delta C_S(t)] = \beta D_M t \quad (5)$$

where  $\beta$  is the cell constant,  $D_M$  is the intrapore micelle diffusion coefficient, and  $\Delta C_{S0}$  and  $\Delta C_S(t)$  are the concentration differences of surfactant across the cell initially and at time  $t$ , respectively. The cell constant is

$$\beta = A/[L(1/V_1 + 1/V_2)] \quad (6)$$

where  $A$  is the pore area,  $L$  is the membrane (pore) thickness, and  $V_1$  and  $V_2$  are the volumes of sides 1 and 2 of the diffusion cell, respectively. In this work,  $V_1$  and  $V_2$  are both 19.5 mL. It is important to note that experiments were run for times much greater than  $L^2/D_M$  (generally, 18 h). Surfactant concentrations, from 1-mL samples drawn from each side of the diffusion cell, were determined by ultraviolet absorbance spectrophotometry (Perkin-Elmer Model 576 spectrophotometer). After the concentration of the sample was determined, it was immediately replaced in the diffusion cell. If  $\ln [\Delta C_{S0}/\Delta C_S(t)]$  is plotted versus time, the slope will be the product of  $D_M$  and  $\beta$  (see eq 5). The standard deviation of the data from these experiments was between 6% and 8%. Determination of the cell constant is described below.

**Membrane Characterization.** The ratio of pore area to pore length (membrane thickness),  $A/L$ , for a membrane was measured by hydrocortisone diffusion ( $D = 4.24 \times 10^{-6}$  cm<sup>2</sup>/s) through the membrane.<sup>19</sup> The cell constant  $\beta$  was obtained from the slope of a plot of  $\ln [\Delta C_0/\Delta C(t)]$  for hydrocortisone versus time. Since

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**Table I. Pore Size, Density, and Length for Nucleopore Membranes Used in This Study**

membrane	$r_p$ , Å	$n$ , pores/cm <sup>2</sup> × 10 <sup>-8</sup>	$L$ , μm
1	315	5.72	5.97
2	296	7.13	6.05

the volumes of each half-cell were known (19.5 mL),  $A/L$  was easily calculated by using eq 6. The ratio of membrane area to pore length is given by

$$A/L = A_m(\pi n r_p^2)/L \quad (7)$$

where  $A_m$  is the membrane area exposed between the gaskets (1.9-cm i.d.),  $n_p$  is the pore density,  $r_p$  is the pore radius, and the factor  $\pi n r_p^2$  is the membrane porosity.  $L$  can be determined by measuring the membrane weight  $W$  and correcting for the porosity and the pores that were not aligned normal to the surface (0–29° from the normal) as follows:<sup>20–22</sup>

$$L = 1.068W / [(1 - \pi n_p r_p^2) \rho A_d] \quad (8)$$

where  $A_d$  is the area of the membrane disk (3.7-cm diameter),  $\rho$  is the density of polycarbonate (1.19 g/cm<sup>3</sup>), and the factor 1.068 accounts for pore alignments deviating from the normal. The Poiseuille equation for fluid flow through the membrane pores is<sup>21</sup>

$$V_f/\Delta P = \pi n_p r_p^4 A_m / (8 \mu L) \quad (9)$$

where  $V_f$  is the flow rate,  $\Delta P$  is the pressure drop across the membrane, and  $\mu$  is the viscosity of the fluid. Equations 7–9 are a set of three equations with three unknowns ( $n_p$ ,  $r_p$ , and  $L$ ) that can be solved with data from the following experiments: (1) hydrocortisone diffusion to determine  $A/L$ , (2) weighing the membrane to determine  $W$ , and (3) measurement of water flow through the membrane under an applied pressure gradient to determine  $V_f/\Delta P$ . The values of  $n_p$ ,  $r_p$ , and  $L$  for the two membranes used in this study are in Table I. The standard deviation of the data from hydrocortisone diffusion and pressure drop/flow rate experiments was approximately 4% and 3%, respectively. On the basis of a previous study of boundary layer resistance for the stirrer configuration at 300 rpm,<sup>4</sup> it was determined that the membrane used in the present study accounted for approximately 97% of the mass-transfer resistance across the diffusion cell.

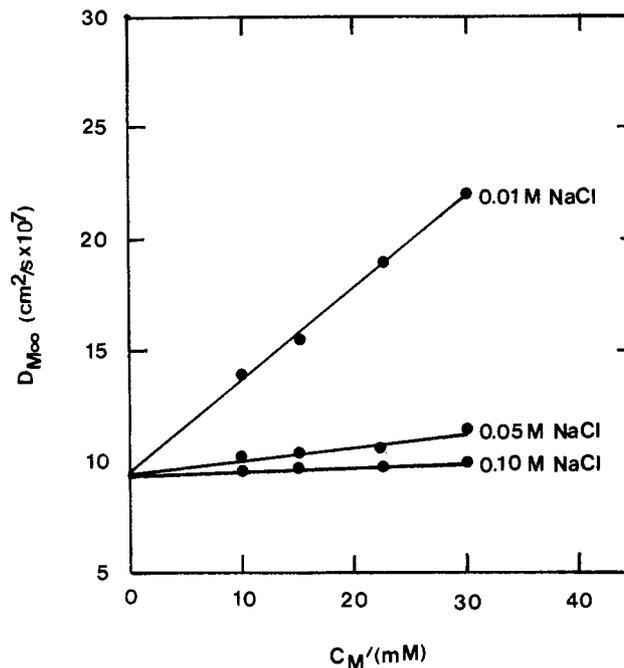
#### Micelle Radii and Free Solution Diffusion Coefficients.

The free solution diffusion coefficients  $D_{M\infty}$  and hydrodynamic radii  $r_M$  of micelles were determined by quasi-elastic light scattering or QELS.<sup>23–25</sup> A 3-W Spectra Physics argon ion laser (514.5-nm line) was used in conjunction with a Brookhaven Instruments Model BI30 64-channel digital correlator. Sample temperatures were kept at 25 ± 0.1 °C. Data were analyzed by using software from the manufacturer. Prior to light-scattering experiments, all surfactant solutions were passed through a filter (0.2-μm pore diameter) to remove dust. For spherical micelles,  $D_{M\infty}$  is related to the hydrodynamic radius by the Stokes–Einstein equation:

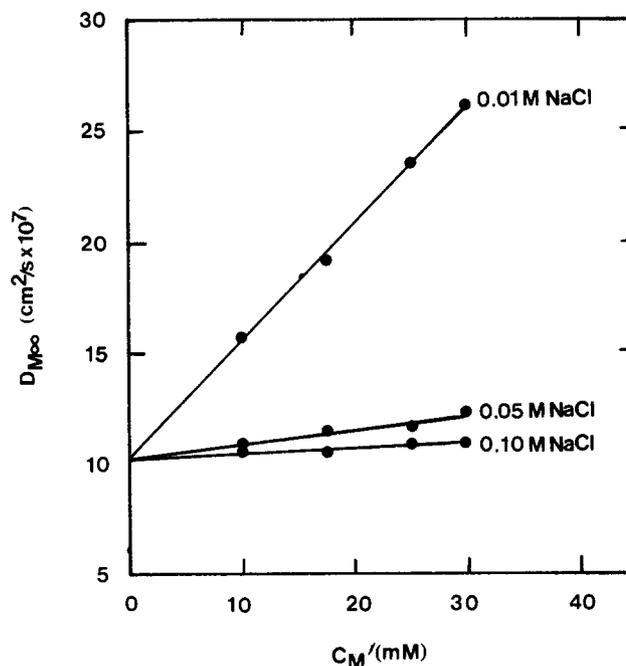
$$D_{M\infty} = kT / (6\pi\mu r_M) \quad (10)$$

where  $k$  is Boltzmann's constant and  $T$  is temperature.

The free solution micellar diffusion coefficients as a function of surfactant concentration at various concentrations of NaCl are in Figures 1 and 2. At low concentrations of supporting electrolyte (NaCl), the diffusion coefficients of these micelles increase with surfactant concentration due to electrostatic interactions.<sup>26,27</sup> As the salt concentration is increased, the slopes of these plots decrease and approach slopes of negligible value due to the screening



**Figure 1.** Free solution diffusion coefficient of CPC micelles ( $D_{M\infty}$ ) measured by QELS versus the surfactant concentration minus cmc ( $C_M'$ ) at various concentrations of a supporting electrolyte (NaCl).



**Figure 2.** Free solution diffusion coefficient of TBAC micelles ( $D_{M\infty}$ ) measured by QELS versus the surfactant concentration minus cmc ( $C_M'$ ) at various concentrations of a supporting electrolyte (NaCl).

of electrostatic interactions by the electrolyte. Even though interparticle interactions affect the diffusion coefficient at low supporting electrolyte concentrations, the Stokes–Einstein equation may be applied if the values of diffusion coefficients at various micelle concentrations are extrapolated to zero micelle concentration or infinite dilution. The diffusion coefficients at infinite dilution for CPC and TBAC micelles remained almost constant with increasing salt concentration and are 9.4 and 10.2 × 10<sup>-7</sup> cm<sup>2</sup>/s, respectively. Using eq 10, the hydrodynamic radii for CPC and TBAC micelles ( $r_M$ ) were calculated to be 26 and

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**Table II. Comparison of Micelle Diameters Determined from QELS and Thickness of Adsorbed Surfactant Layer on Membrane Pore Wall**

surfactant	micelle diameter, Å	thickness of adsorbed surfactant layer, Å
CPC	52	48
TBAC	48	45

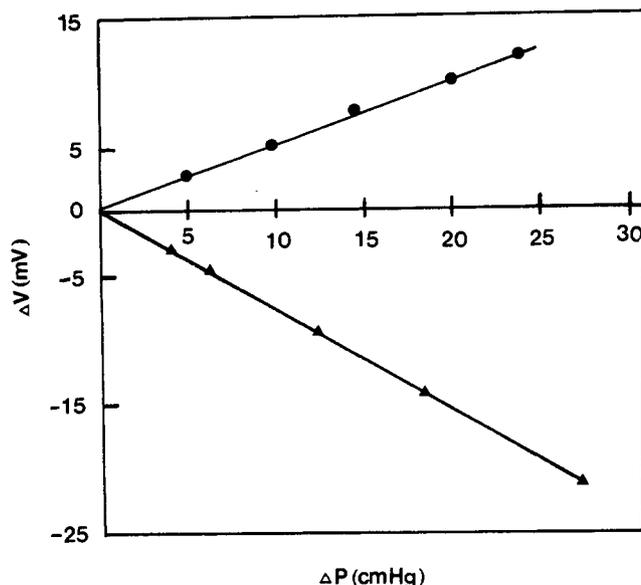
24 Å, respectively. The value of  $r_M$  for CPC is in agreement with results reported by Anacker.<sup>28</sup>

**Membrane Surface Charge Measurements.** The surface charge of Nuclepore membranes was determined from streaming potential measurements.<sup>29</sup> The same diffusion cell was used for electrokinetic measurements where the only modification was a set of plastic supports on both sides of the membrane that protected the membrane against damage by high pressures. Silver/silver chloride electrodes were used because they are reversible to the chloride ion. Electrodes were produced by anodizing 1-cm-long silver wires in 0.1 M KCl with 1 mA/wire for 45 min. A piece of copper tubing was connected to the negative pole of the current source. The biases of the electrodes produced were always less than 0.5 mV.

After assembling and filling both sides of the cell with the electrolyte solution, we inserted an electrode in each side through the sample port, making a tight seal. The streaming potential was determined by applying pressure to one of the half-cells while the other was open to the atmosphere. Pressure (from compressed nitrogen) was applied through a bottle of stock solution and measured by a mercury-air manometer. The potential produced was measured with a Keithley Model 642 electrometer. Five different pressures were applied on each half-cell. Three measurements were made from the lowest to the highest pressure, and then two measurements were made between the first three. The last two measurements were made to detect any hysteresis in the  $\Delta V/\Delta P$  plot that would be an indication of membrane damage due to pressure. No hysteresis was observed. The slope of the  $\Delta V$  versus  $\Delta P$  plot was used with the approximate solutions of the Poisson-Boltzmann equation from Christoforou et al.<sup>30</sup> to calculate the surface charge density on the pore wall. The standard deviation of data from these experiments was approximately 3%.

## Results and Discussion

**Effect of Ionic Surfactant on Pore Walls.** The Nuclepore membranes used in the present study were made of polycarbonate that dissociates at a pH of 3.9 to give the surface of the pores a negative charge.<sup>31</sup> All diffusion experiments were performed in a pH range of 7–8.5. Bisio et al.<sup>31</sup> demonstrated that cationic surfactants adsorb on the surface of polycarbonate membranes forming a bilayer that reduces the pore radius by approximately the length of two surfactant monomers and reverses the sign of the surface charge. The first layer adsorbs because of the electrostatic interaction of the positively charged head group with negatively charged membrane surface, and the second layer adsorbs by hydrophobic interactions. The membrane parameters  $n_p$ ,  $r_p$ , and  $L$  were measured before the pores were exposed to the surfactant solution, as described in the previous section. Since the pore density and length would not be affected by the surfactant, only one measurement was required after the membrane was exposed to surfactant to determine the reduced pore radius. After exposure to the surfactant, the pressure drop/flow rate relationship for the solution through the membrane was remeasured, and this allowed the calculation of the reduced pore radius. The calculated adsorbed surfactant



**Figure 3.** Streaming potential ( $\Delta V$ ) across a Nuclepore membrane with a nominal pore diameter of 300 Å versus pressure drop across the membrane ( $\Delta P$ ) before ( $\blacktriangle$ ) and after ( $\bullet$ ) the membrane was exposed to a cationic surfactant (CPC). The electrolyte solution was 1.0 mM NaCl.

layer thicknesses for TBAC and CPC were very close to the micelle diameters ( $\sim$ two monomer lengths) measured by QELS and are in Table II. Such agreement cannot always be expected since micelles are not always spherical (e.g., SDBS micelles<sup>27</sup>).

Figure 3 is a plot of the streaming potential measured across a Nuclepore membrane versus the pressure drop before and after the membrane was exposed to a cationic surfactant. Without the surfactant, the slope of the plot is negative, indicating a negative surface charge on the membrane.<sup>32</sup> However, the slope becomes positive after the surfactant was added, and this change indicates that the membrane pore walls became positively charged after exposure to the cationic surfactant. This is consistent with the bilayer adsorption scheme and agrees with the results of Bisio et al.<sup>31</sup>

From the slope of plots such as those of Figure 3, the surface charge density for the membrane was determined by using the approximate solutions of the Poisson-Boltzmann equation developed by Christoforou et al.<sup>30</sup> The results of these calculations, important for determining the partition coefficient of a charged micelle into the charged membrane pore, are in Figure 4, where  $\sigma_w$  was calculated as a function of NaCl concentration. The values of  $\sigma_w$  for the membrane without surfactant present are in agreement with those found by other researchers.<sup>31</sup> The surface charges when CPC and TBAC were present in the solution below their cmc values (0.2 mM of each surfactant)<sup>18</sup> are also in Figure 4.

**Effect of Electrolytes on Charged Micelle Diffusion in Microporous Membranes.** The diffusion coefficients of ionic micelles in microporous membranes were measured as a function of counterion concentration  $C_C$ , using the procedure described in the previous section, by increasing,  $C_C$ . Because of the concentration dependence of the ionic micelle diffusion coefficients at low ionic strengths (see Figures 1 and 2), small initial concentration differences across the membrane were used ( $\sim$ 0.5 mM) in all experiments.

Diffusion coefficients for cationic CPC and TBAC micelles in Nuclepore membranes with nominal pore diam-

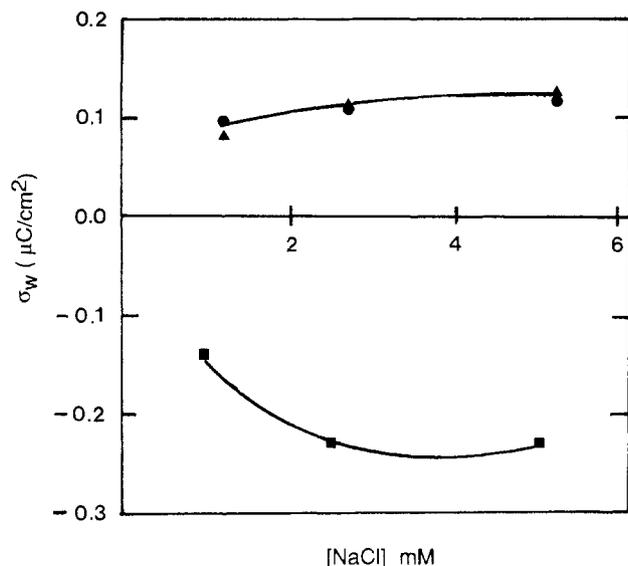
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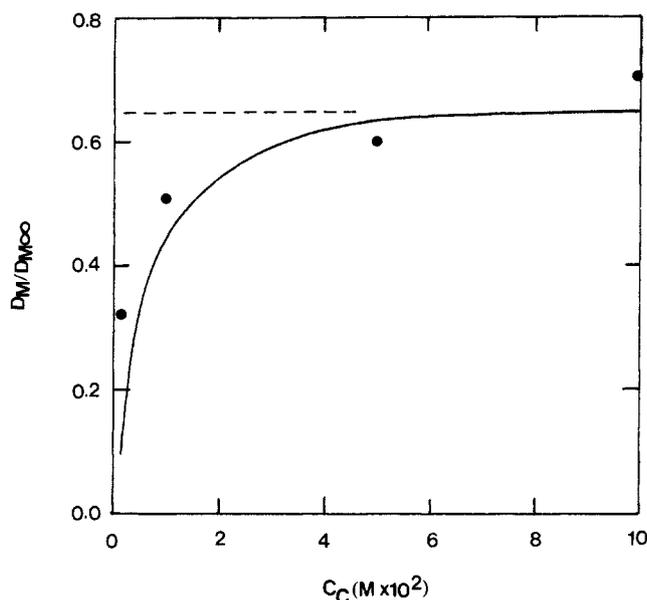
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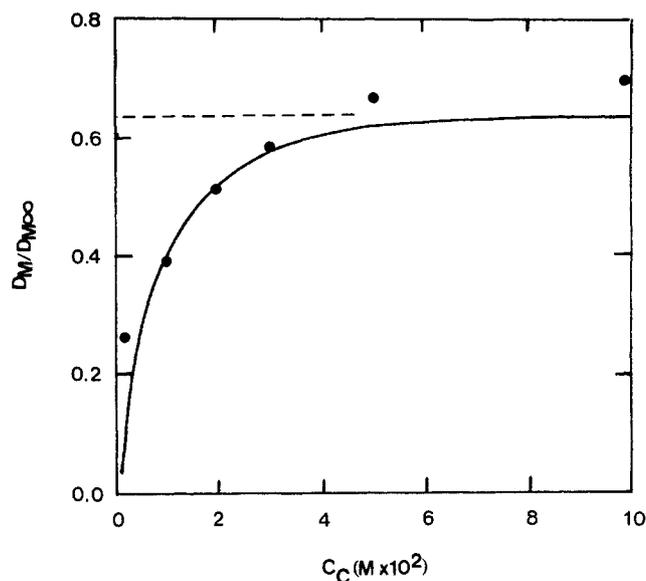


**Figure 4.** Surface charge density ( $\sigma_w$ ) of a Nuclepore membrane with a nominal pore diameter of 300 Å versus concentration of NaCl for three solutions: no surfactant (■), 0.5 mM CPC (●), and 0.5 mM TBAC (▲).



**Figure 5.** Ratio of the intrapore micelle diffusion coefficient to the micelle diffusion coefficient in free solution ( $D_M/D_{M\infty}$ ) for CPC micelles in a Nuclepore membrane with a nominal pore diameter of 300 Å (no. 1) versus the concentration of a supporting electrolyte (NaCl). The curve is eq 4 where  $K_M$  was calculated for a charged hard sphere by eq 2, using the model of Smith and Deen.<sup>17</sup>

eters of 300 Å as a function of NaCl concentration are in Figures 5 and 6. The points are data from experiments, and dashed lines are the results one would expect for uncharged hard sphere diffusion through the cylindrical pore. The predictions for an uncharged hard sphere in Figures 5 and 6 remained constant over the range of salt concentration studied because the micelle sizes remained constant as the supporting electrolyte concentration was increased (see Figures 1 and 2). Since the micelle and the pore wall have the same charge (positive), they will repel each other, and  $D_M/D_{M\infty}$  is below the uncharged hard-sphere prediction at low salt concentrations. However,  $D_M/D_{M\infty}$  approached the uncharged hard-sphere prediction as the salt concentration was increased since the double-layer thicknesses around the pore wall and the micelle were decreased as the concentration of supporting electrolyte increased. If the electrolyte concentration is high enough,  $\sim 0.1$  M NaCl in Figures 5 and 6, the electrostatic interactions



**Figure 6.** Ratio of the intrapore micelle diffusion coefficient to the micelle diffusion coefficient in free solution ( $D_M/D_{M\infty}$ ) for TBAC micelles in a Nuclepore membrane with a nominal pore diameter of 300 Å (no. 2) versus the concentration of a supporting electrolyte (NaCl). The curve is eq 4 where  $K_M$  was calculated for a charged hard sphere by eq 2, using the model of Smith and Deen.<sup>17</sup>

**Table III. Parameters Used for Calculations in Figures 5 and 6**

surfactant	$r_M$ , Å	$\sigma$ (micelle), <sup>a</sup> $\mu\text{C}/\text{cm}^2$	$r_p$ , <sup>b</sup> Å	$\sigma$ (pore wall), $\mu\text{C}/\text{cm}^2$
CPC	26	2.8	267	0.11
TBAC	24	4.8	251	0.12

<sup>a</sup>Data from ref 35. <sup>b</sup>Corrected for surfactant adsorption to pore wall.

between the micelle and the pore are almost completely screened, and the micelle diffusion coefficient in the pore is comparable to that of a neutral micelle. The screening of electrostatic forces between micelles was observed in the QELS measurements of free solution micelle diffusion coefficients  $D_{M\infty}$  (compare the slopes of lines in Figures 1 and 2 at high salt concentrations to the slopes of lines at low salt concentrations).

The solid lines in Figures 5 and 6 are the results of calculations of  $D_M/D_{M\infty}$  from eq 4, where  $K_M$  was calculated by using the model of Smith and Deen,<sup>17</sup> assuming that the micelle and the pore wall interact at constant surface charge density.<sup>33,34</sup> Values for the micelle and pore wall parameters used in these calculations are in Table III. The calculations are in agreement with the experimental results with the exception of the data points obtained when no salt was present and the counterion concentration was small (i.e.,  $C_C \sim \text{cmc}$ ). There are two reasons for this large error when compared to the results at higher supporting electrolyte concentrations. First, it was assumed that the only contributions to the ionic strength of the solution came from the supporting electrolyte and surfactant monomers while contributions from the micelles were neglected. The ionic strength  $I_S$  is given by<sup>32</sup>

$$I_S = 0.5 \sum z_i^2 C_i \quad (11)$$

Even though the micelle concentration is smaller than the cmc, the valence of a micelle, which is squared in eq 11,

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is about 20 times that of a surfactant monomer. Micelle contributions to the ionic strength are significant when the surfactant monomers at the cmc are the only supporting electrolyte and insignificant at higher NaCl concentrations. Underestimation of the ionic strength leads to an overestimation of the double-layer thickness; hence,  $D_M/D_{M^\infty}$  would be underestimated as in Figures 5 and 6 (specifically, for very low values of  $C_E$ ). A second source of error at low salt concentrations is the assumption that the counterion concentration would be high enough to eliminate the diffusion potential,<sup>36</sup> a potential that would make the micelle diffuse faster. The assumption of sufficient supporting electrolyte concentration to eliminate the diffusion potential was made to obtain eq 5 and facilitate the calculation of micelle diffusion coefficients from the data (see Appendix). At low supporting electrolyte concentrations, the neglect of the diffusion potential could cause  $D_M/D_{M^\infty}$  to be underestimated by the calculations developed by Smith and Deen.<sup>17</sup> In Figures 5 and 6,  $D_M/D_{M^\infty}$  was always severely underestimated when the concentration of supporting electrolyte was at its lowest ( $C_C \sim \text{cmc}$ ).

### Conclusions

Measurements of ionic micelle diffusion coefficients in microporous membranes were compared with calculations for charged hard spheres diffusing in charged cylindrical pores. In general, the agreement of data on ionic micelles with calculations was good except for ionic micelle diffusion at low concentrations of supporting electrolyte ( $C_C \sim \text{cmc}$ ). This disagreement can be explained by (1) contributions of the diffusion potential and (2) overestimation of the Debye length since micelle contributions to the ionic strength of the solution were neglected.

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### Appendix

Consider a microporous membrane separating two halves of a diffusion cell that contain surfactant solutions above the cmc. Side 1 of the cell has a higher surfactant concentration than side 2. There will be no gradient of monomers since both sides to the membrane are above the cmc. However, there will be a concentration gradient of counterion as well as a concentration gradient of micelles. Following the treatment of a similar problem of Weinheimer et al.,<sup>37</sup> the Nernst-Planck equation is written for the flux  $J_i$  of each ionic species  $i$ :

$$-J_i = D_i dC_i/dx + (F/RT)z_i C_i D_i d\phi/dx \quad (\text{A1})$$

where  $z_i$  is the valence of the ionic species,  $\phi$  is the electrical potential,  $F$  is Faraday's constant, and  $R$  is the gas constant. Equations for the flux of micelles and the flux of counterions can be obtained from eq A1 and then added together to give the following expression for the total surfactant flux  $J_S$ :

$$-2J_S = (n+q)D_M dC_M/dx + (n+q) \times \frac{(F/RT)z_M C_M D_M d\phi/dx + D_C dC_C/dx + (F/RT)C_C z_C D_C d\phi/dx}{(F/RT)C_C z_C D_C d\phi/dx} \quad (\text{A2})$$

where the subscript M stands for micelles, the subscript C stands for counterions,  $n$  is the aggregation number of the micelle, and  $q$  is the number of counterions bound to the micelle. Since eq A2 is the sum of the counterion and the micellar fluxes, and these individual fluxes are equal

to the surfactant molecule flux, the factor 2 appears on the left-hand side. It is important to note that the diffusion coefficient of a counterion ( $D_C$ ) is approximately 1 order of magnitude larger than the diffusion coefficient of a micelle ( $D_M$ ).

Several substitutions can be made to simplify eq A2. The micelle concentration  $C_M$  is defined as

$$C_M = (C_S - \text{cmc})/n \quad (\text{A3})$$

where cmc is the critical micelle concentration. Differentiating eq A3 with respect to  $x$  yields

$$dC_M/dx = (dC_S/dx)/n \quad (\text{A4})$$

The total counterion concentration may be expressed as

$$C_C = C_E + \text{cmc} + \alpha(C_S - \text{cmc}) \quad (\text{A5})$$

where  $C_E$  is the concentration of supporting electrolyte (the same on both sides of the membrane), cmc accounts for the dissociated surfactant monomer (also the same on both sides of the membrane), and  $\alpha$  is the degree of dissociation of the micelle (i.e., number of charges on the micelle divided by the micelle aggregation number, which was 0.31 and 0.21 for TBAC and CPC, respectively.<sup>35</sup> Differentiating eq A5 with respect to  $x$  yields

$$dC_C/dx = \alpha dC_S/dx \quad (\text{A6})$$

Substituting eq A4 and A6 into eq A2 yields

$$-2J_S = [(n+q)D_M/n + \alpha D_C]dC_S/dx + (F/RT)[(n+q)z_M C_M D_M + z_C C_C D_C]d\phi/dx \quad (\text{A7})$$

Since there is no net current flowing across the cell, the micellar and counterion fluxes must satisfy

$$\sum z_i J_i = 0 \quad (\text{A8})$$

therefore

$$0 = z_M D_M dC_M/dx + (F/RT)z_M^2 C_M D_M d\phi/dx + z_C D_C dC_C/dx + (F/RT)z_C^2 C_C D_C d\phi/dx \quad (\text{A9})$$

Substituting eq A4 and A6 into eq A9 and realizing  $z_C^2 = 1$  give the equation

$$0 = [z_M D_M/n + \alpha z_C D_C]dC_S/dx + (F/RT)[z_M^2 C_M D_M + C_C D_C]d\phi/dx \quad (\text{A10})$$

Equation A10 can be solved for  $d\phi/dx$ :

$$d\phi/dx = -(RT/F)[z_M D_M/n + \alpha z_C D_C](dC_S/dx)/[z_M^2 C_M D_M + C_C D_C] \quad (\text{A11})$$

When eq A11 is substituted into eq A7, the following equation is obtained:

$$-2J_S = [(n+q)D_M/n + \alpha D_C]dC_S/dx - \frac{[z_M D_M/n + \alpha z_C D_C][(n+q)z_M C_M D_M + z_C C_C D_C]dC_S/dx}{z_M^2 C_M D_M + C_C D_C} \quad (\text{A12})$$

Equation A12 may be expressed as

$$-2J_S = D_{\text{eff}} dC_S/dx \quad (\text{A13})$$

where  $D_{\text{eff}}$  is

$$D_{\text{eff}} = (n+q)D_M/n + \alpha D_C - \frac{[z_M D_M/n + \alpha z_C D_C][(n+q)z_M C_M D_M + z_C C_C D_C]}{z_M^2 C_M D_M + C_C D_C} \quad (\text{A14})$$

Equation A14 can be simplified under certain conditions where the concentration of supporting electrolyte is larger than the micelle concentration. If  $|z_C C_C D_C| \gg (n+q)$

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$q)z_M C_M D_M$  and  $C_C D_C \gg z_M^2 C_M D_M$ , then the expression for  $D_{\text{eff}}$  reduces to

$$D_{\text{eff}} = (n + q)D_M/n + \alpha D_C - [z_M D_M/n + \alpha z_C D_C]z_C \quad (\text{A15})$$

But, since  $z_M = (n - q)$ ,  $D_{\text{eff}}$  reduces to  $2D_M$ . Therefore, if  $C_E$  is sufficiently large when compared to  $C_M$ , the flux of ionic surfactant micelles is given by

$$J_S = -D_M dC_S/dx \quad (\text{A16})$$

Since the membrane volume is much smaller than the volume of the diffusion cell, a pseudo-steady-state approximation is made. Such an analysis of the diffusion process leads to the following equation:<sup>36</sup>

$$\ln [\Delta C_{S0}/\Delta C_S(t)] = \beta D_M t \quad (\text{A17})$$

where  $\beta$  is equal to  $A/[L(1/V_1 + 1/V_2)]$ .

### Glossary

$A$	membrane pore area, $\text{cm}^2$
$A_m$	exposed membrane area between the gaskets in diffusion cell, $\text{cm}^2$
$A_d$	area of membrane disk, $\text{cm}^2$
$C_i$	concentration of species $i$
$C_M$	surfactant concentration - cmc
$D_i$	diffusion coefficient of species $i$ , $\text{cm}^2/\text{s}$
$D_{M\infty}$	diffusion coefficient of micelle in free solution, $\text{cm}^2/\text{s}$
$F$	Faraday's constant
$j$	flux, $\text{mol}/(\text{area}\cdot\text{time})$
$k$	Boltzmann's constant
$K$	particle partition coefficient into membrane pore
$K_M$	micelle partition coefficient into membrane pore
$L$	membrane thickness, $\text{cm}$
$n$	micelle aggregation number

$n_p$	pore density, pores/ $\text{cm}^2$
$P$	pressure
$q$	number of counterions bound to micelle
$r_M$	micelle radius, $\text{\AA}$
$r_p$	membrane pore radius, $\text{\AA}$
$R$	gas constant
$W$	weight of membrane disk, $g$
$t$	time
$T$	temperature
$V_1$	volume, side 1 of diffusion cell, $\text{cm}^3$
$V_2$	volume, side 2 of diffusion cell, $\text{cm}^3$
$V_f$	flow rate, $\text{cm}^3/\text{s}$
$z$	valence

### Greek Letters

$\alpha$	degree of dissociation for a charged micelle
$\beta$	diffusion cell constant, $A/[L(1/V_1 + 1/V_2)]$
$\rho$	membrane density, $g/\text{cm}^3$
$\phi$	electric potential, $\text{mV}$
$\sigma$	surface charge density, $\mu\text{C}/\text{cm}^2$
$\theta$	ratio of the distance of the particle's center from the axis of the pore to the pore radius
$\xi$	ratio of particle radius to pore radius
$\mu$	viscosity

### Subscripts

$C$	counterion
$E$	supporting electrolyte
$M$	micelle
$S$	surfactant
$i$	species (e.g., C, E, M, or S)
1	side 1
2	side 2
0	initially, at $t = 0$

Registry No. CPC, 123-03-5; TBAC, 139-08-2; NaCl, 7647-14-5; nucleopore, 12673-61-9.

## The Fractal Dimension of Geometrically Irregular Solid Surfaces: The Role of Attractive Molecule-Surface Interactions

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We have simulated the adsorption of spherically symmetric molecules on deterministic fractal curves in the range of Hausdorff self-similarity dimensions  $1 \leq D \leq 1.5$ . In contrast to previous studies, in this work we have analyzed the role of attractive molecule-surface interactions as well as the influence of the distribution of energetically different centers along the curves on the results of fractal dimension evaluation. The results obtained indicate that within the investigated region of fractal dimensions the fractal dimension of a surface determined from experimentally measured monolayer capacities of a suitably chosen series of spherical adsorbates is relatively insensitive upon the energetic heterogeneity of adsorbing centers.

### Introduction

In recently published papers,<sup>1-14</sup> numerous authors have advocated the use of the so-called fractal theory to describe

physical adsorption of gases on geometrically irregular solid substrates. According to this approach, the monolayer capacity  $N_m$  has been related to the monolayer packing  $\sigma$  via the power law

$$N_m \sim \sigma^{-x} \quad (1)$$

The exponent  $x$  in eq 1 varies in the range 1-1.5, and its physical interpretation is that  $2x$  is the fractal dimension of the geometric adsorbent surface.<sup>15</sup>

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