Electrokinetics of Diffuse Soft Interfaces. III. Interpretation of Data on the Polyacrylamide/Water Interface

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Electrokinetics of Diffuse Soft Interfaces. III. Interpretation of Data on the Polyacrylamide/Water Interface

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Streaming potential measurements were carried out on a family of polyacrylamide-*co*-sodium acrylate gels cross-linked with *N*,*N*′-methylenebisacrylamide in a homemade electrokinetic cell. Measurements of the ionic conductivity within thin films of these gels allowed the equilibrium Donnan potential difference between the bulk gel and the bulk electrolyte environments to be estimated at various ionic strengths. The resulting Donnan potential data were combined with the directly measurable streaming potential data and used to evaluate the diffuse soft interface model of electrokinetics (*Langmuir* **2004**, *20*, 10324). The model introduces the concept of a gradual decay of polymer density and fixed charge density within a narrow inter-phase at the gel/solution interface. The nature of the decay at the interface has a dramatic effect on the magnitude of the streaming potential as predicted by the diffuse soft interface model. In this investigation, the gradual decay of polymer density within the inter-phase is described with a hyperbolic tangent function. For the gels mentioned, the characteristic length scale of the decay, α, as calculated from the fit to the model, increases significantly with decreasing ionic strength, suggesting an osmotically driven swelling of the loosely cross-linked polymer chains at the interface. The experimental data and the results of the fitting are discussed in terms of the physical picture of the interface and compared to fitting results for a model which assumes a simple step function at the gel−solution interface.

1. Introduction

The electrokinetics of soft surfaces has become a topic of great interest to the physicochemical community over the course of the past decade. Soft surfaces can be formed by chemically cross-linked gels, self-assembled layers, or adsorbed layers of polymers or polyelectrolytes, and the term "soft surface" in principle includes lipid bilayers and biological membranes as well, in which case there is no hard surface support under the soft layer. The common trait of all the examples given above is the presence of a porous interface, which allows ion penetration and limited solvent flow within the polymer matrix. If the polymer chains of the matrix possess fixed charged groups, a potential difference will develop between the bulk polymer environment and the electrolyte solution. When the polymer matrix is thick relative to the Debye length, the electrostatic character of soft surfaces is typically described in terms of an ideal Donnan equilibrium[1] model.

While the electrophoresis of soft colloidal particles has been studied at length in the literature,[2−11] the number of investigations on the electrokinetic properties of soft macroscopic surfaces by streaming current and streaming potential measurements has been considerably more limited. Donath and Voight[12] presented a model of the streaming potential of surfaces covered with a soft, ion-penetrable gel layer. Their work stressed the importance of the enhanced conductivity of the charged gel layers in the streaming potential data for soft surfaces. Somewhat later, Starov and Solomentsev[13,14] created a model which allowed for specific chemical interactions between the soft gel layers and the supporting electrolyte in the medium. The most extensive modeling of the electrokinetics of soft surfaces has come from Ohshima and co-workers.[5−7,15] Ohshima and Kondo[15] published a model of streaming potential for soft surfaces within the Debye−Huckel approximation, which requires two input parameters, that is, the fixed charge density within the polymer layer and a "softness parameter" to characterize the extent of solvent flow in the polymer matrix. All of the models listed above require a homogeneous polymer density in the gel layer with a sharp gel/water interface at which the polymer volume fraction drops precipitously to zero.

The first two articles in this series[16,17] propose a new model, the diffuse soft interface model, which allows for a gradual thinning out of material density at the interface. Not only the polymer segment density but also the charge density and friction coefficient of the polymer network are assumed to decay gradually within a narrow inter-phase at the gel−solution interface. The decay has important consequences for the potential distribution and flow profiles which control the magnitudes of the electrokinetic effects. The present investigation provides an experimental evaluation of the diffuse soft interface model

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for a family of cross-linked polyacrylamide-*co*-sodium acrylate gels, together with a comparison of the merits of the Ohshima−Kondo model.

2. Theory

2.1. Gel Structure. Thin films of cross-linked polymer gel can be modeled as porous networks with fixed charged sites uniformly distributed throughout the structure. The fixed charged groups inside the gel give rise to a potential difference between the bulk gel and the bulk electrolyte solution with which it is in contact. In the present analysis, the assumption is made that the gel thickness, d, is much larger than the Debye length characteristic of the bulk electrolyte solution. The equilibrium value of the Donnan potential difference, Ψ_D, for a gel layer with homogeneously distributed charge groups of number density N and valence z_g in contact with a symmetrical electrolyte of bulk concentration c and valence $z_- = z_+ = z$ can be obtained from the condition of overall electro-neutrality, giving

$$\Psi_D = \frac{RT}{zF}\text{arcsinh}\left(\frac{z_g F N}{2zFc}\right) \tag{1}$$

where R is the gas constant, T is the absolute temperature, and F is the Faraday constant. In the simplest model, as mentioned above, the charge and polymer densities are modeled to be uniform within the gel with a step function to zero at the interface, and the dielectric permittivity within the gel is assumed to be equal to that of water. A more complete model put forth by Duval[16,17] and van Leeuwen[16] explores the effect of a diffuse interface on streaming potential measurements and is described below in detail.

Conductivity data for thin films in the electrokinetic cell can be used to estimate Donnan potential differences between the bulk gel and the bulk electrolyte solution.[18] The conductivity of the gel layer, K_g, can be expressed as the integral of the product of the ionic mobilities and ionic population densities in the gel, which are obtained with an equilibrium Donnan correction:

$$K_g = \frac{c}{d}\int_0^d [e^{y(x)}m_-\beta_- + e^{-y(x)}m_+\beta_+]\,dx \tag{2}$$

where $y(x) = F\Psi(x)/RT$ is the reduced potential, m_- and m_+ are the limiting molar conductances of the anion and cation of the symmetrical electrolyte in aqueous solution, and β_- and β_+ are defined as the ratio of the ionic mobility in the gel phase to that in the solution phase for the anion and cation, respectively. When the gel layer is thick relative to the Debye length, that is, $d \gg \kappa^{-1}$, the interfacial effects are negligible and eq 2 can be simplified to

$$K_g = c[m_-\beta_-e^{y_D} + m_+\beta_+e^{-y_D}] \tag{3}$$

where y_D is the reduced Donnan potential, as defined above. The value of β will in principle depend on the total polymer content of the gel, the cross-link density, and the size of the solute. For high water content gels, simple ions such as sodium and chloride typically have values of β between 0.9 and 1.0,[19] although at extremely low ionic strengths somewhat smaller values of counterion mobilities have been reported in moderately charged polymer

systems.[20,21] Eqs 1 and 3 can be used together to estimate Donnan potentials and fixed charge densities from experimental gel conductivity data.[18]

The expressions in eqs 1−3 assume complete ionization of the charge sites within the gel matrix. If the charged sites are weak acids, for example, acrylic acid, the extent of charging will be pH-dependent. At low ionic strengths, the pH inside the gel and, hence, the extent of dissociation, can be substantially affected by the Donnan potential generated by the system. For weak acid fixed charged groups, the effective volume charge density, ρ, will depend on the ionic strength of the bulk solution and can be related to the total density of charged sites, ρ_0, by[5,22]

$$\rho = \frac{\rho_0}{1 + 10^{pK_a-pH}\exp(-y_D)} \tag{4}$$

where pK_a is the negative logarithm of the dissociation constant of the weak acid groups within the gel matrix. The value of ρ_0 is determined by the total number of acid sites within the gel matrix (hence, $\rho_0 = z_g F N$), the dissociated fraction of which is given by ρ/ρ_0; hence, ρ represents the effective charge density of the gel matrix. The electro-neutrality condition within the gel is then given by

$$\frac{\rho_0}{1 + 10^{pK_a-pH}\exp(-y_D)} + czF\exp(-zy_D) -$$
$$czF\exp(zy_D) = 0 \tag{5}$$

If the bulk electrolyte concentration, pH, pK_a of the function groups within the gel, and value of ρ_0 are known (from the synthetic recipe of the copolymer gel, for example), eq 5 becomes a single equation in one unknown, allowing determination of the equilibrium Donnan potential in a manner analogous to eq 1. The conductivity of a weak acid gel can then be calculated with eq 3 above, by substituting in the value of the Donnan potential obtained from eq 5.

2.2. Gel Swelling. Ionic gels swell to varying extents as a function of ionic strength, due to changes in the osmotic pressure. The volume swelling ratio, q_v (defined as the inverse of the polymer volume fraction in the network), can be calculated from the mass swelling ratio q_m (defined as the ratio of the mass of hydrated gel to the mass of dry polymer in a given gel sample) by[23]

$$q_v = 1 + \frac{(q_m - 1)\rho_{m,p}}{\rho_{m,w}} \tag{6}$$

where $\rho_{m,p}$ and $\rho_{m,w}$ represent the densities of polyacrylamide and water, respectively. In the present analysis, a value of 1.35 g/mL was used for $\rho_{m,p}$, and the density of water was assumed to be 1.0 g/mL.

The equilibrium extent of swelling for a polymer gel is subject to the condition of zero net osmotic pressure:

$$\pi = \pi_{mix} + \pi_{el} + \pi_{ion} = 0 \tag{7}$$

where the subscripts *mix*, *el*, and *ion* refer to the polymer−solvent mixing, elastic, and electrostatic contributions to

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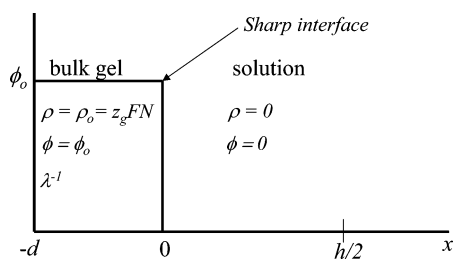(20) Yoshida, N. *J. Chem. Phys.* **1978**, *69*, 4867.
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Figure 1. Schematic diagram of the gel/solution interface as assumed in the Ohshima−Kondo[15] model. Within this model, ϕ, ρ, and λ^{-1} are all assumed to maintain their bulk values up to the sharp interface, where they drop to zero according to a step function.

the osmotic pressure, respectively. Flory−Higgins theory[24] provides an expression for the mixing contribution:

$$\pi_{\text{mix}} = \frac{-RT}{V}[\ln(1-\phi) + \phi + \chi\phi^2] \qquad (8)$$

where V is the molar volume of the solvent, ϕ is the volume fraction polymer in the equilibrium swollen network (i.e., $1/q_v$), and χ is the polymer solvent interaction parameter.

The elastic contribution to the osmotic pressure requires the selection of a model to describe the elastic properties of the polymer network. The simple affine network model[24,25] is selected here, yielding an expression

$$\pi_{\text{el}} = \frac{-RT}{V}X^{-1}\left(\phi^{1/3}\phi_0^{2/3} - \frac{\phi}{2}\right) \qquad (9)$$

where ϕ_0 is the polymer volume fraction at gel preparation and X is the average number of segments between cross-links in the network.

The electrostatic contribution to the osmotic pressure arises from the Donnan partitioning of mobile counterions and is given by[24]

$$\pi_{\text{ion}} = RT\sum_i(c_i^{\,g} - c_i^{\,s}) \qquad (10)$$

where c represents the concentration of ion type i and the subscripts g and s refer to the gel and solution, respectively. Equilibrium swelling is achieved when the total osmotic pressure is zero. In the limit of vanishing electrostatic contributions, eqs 8 and 9 can be combined to estimate the average number of segments between cross-links.

2.3. Streaming Potential of "Classical" Soft Surfaces. Ohshima and Kondo[15] developed a theory to describe the streaming potential generated in a thin-layer cell with two parallel plates covered by gel layers. The gel layers are assumed to possess a bulk fixed charge density, polymer chain density, and friction coefficient, which are uniform throughout the layer and which drop precipitously to zero according to a step function at the sharp gel/solution interface. The analytical approach employed is to solve the electrostatic potential distribution and hydrodynamic flow profiles to yield an expression for the overall current density (with contributions from both the pressure driven streaming current and the back current in response to the steady-state potential difference which arises in the cell) and to integrate across the cell. Figure 1 illustrates the situation for one gel/water interface. The gel rests upon a solid surface at $-d$. The gel−solution interface is located at 0, and the halfway point of the cell is located

at $h/2$. The other half of the cell is identical. The pressure gradient is applied along the y axis, parallel to the gel layers. After solving the electrostatic and hydrodynamic distributions, the current density as a function of position in the x direction, $i(x)$, is given by[15]

$$i(x) = \rho(x)\,u(x) + z^2e^2E\left[\frac{c_+(x)}{f_+} + \frac{c_-(x)}{f_-}\right] \qquad (11)$$

where $c_+(x)$ and $c_-(x)$ are the local concentrations of cations and anions, respectively, calculated from the potential distribution assuming a Boltzmann population distribution and f_+ and f_- are the Stokes drag coefficients of the cations and anions in solution. In eq 11, $\rho(x)$ and $u(x)$ represent the mobile charge density and local fluid velocity as a function of x, respectively. Included in the expression for $u(x)$ is the friction coefficient of the polymer network, which determines the magnitude of solvent flow within the gel layer in response to the applied pressure. This is described in terms of a penetration depth, λ^{-1}, defined as $\lambda^{-1} = (\eta/k_0)^{1/2}$, where η is the dynamic viscosity of the solvent and k_0 is the friction coefficient of the polymer network. The value of λ^{-1} provides a measure of solvent flow within the gel. A large value of λ^{-1} indicates significant solvent flow in the gel, while a value of 0 would indicate no flow, with a classical shear plane at the gel/solution interface. The first term on the right-hand side of eq 11 represents the streaming current due to the applied pressure, while the second term reflects the back current which develops due to the potential difference E. The back current can be broken down into a migration contribution, which represents the simple movement of ions in solution in response to the steady-state potential difference which develops along the length of the cell, and an electroosmotic contribution resulting from the action of the field on the diffuse double layer. The electroosmotic component of the back current is negligible provided $d \gg \kappa^{-1}$.[16] The overall net current in the cell, I, is generally given by

$$I = 2\left[\int_{-d}^{0}i(x)\,\mathrm{d}x + \int_{0}^{h/2}i(x)\,\mathrm{d}x\right] \qquad (12)$$

The streaming potential is then the value of the steady-state potential difference, E, determined when the overall net current in the cell is zero. The important parameters which emerge from the model description are the fixed charge density within the gel layer and the penetration depth, λ^{-1}.

2.4. Streaming Potential of "Diffuse, Soft" Surfaces. Duval[16,17] and van Leeuwen[16] have recently proposed an extension to the Ohshima and Kondo theory, which allows for a gradual transition of polymer density, fixed charge density, and friction coefficient at the gel−solution interface. In previous articles,[16,17] the thinning out of polymer density within the inter-phase was assumed to be linear. In the present analysis, the polymer volume fraction is modeled as thinning out at the interface according to a physically more realistic hyperbolic tangent function:
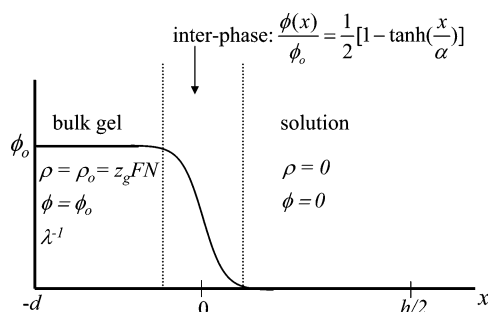
$$\frac{\phi(x)}{\phi_b} = \frac{1}{2}\left[1 - \tanh\left(\frac{x}{\alpha}\right)\right] \qquad (13)$$

where $\phi(x)$ represents the polymer volume fraction at position x, ϕ_b is the polymer volume fraction in the bulk gel, and α is the characteristic distance of the decay. In this analysis, λ^{-1} (and, hence, λ itself) is position-dependent

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Figure 2. Schematic diagram of the gel/solution interface as assumed in the diffuse soft interface model.[16,17] Within this model, ϕ, ρ, and λ^{-1} gradually decay within a narrow inter-phase at the gel/solution interface. The decay is described mathematically with a hyperbolic tangent function.

Cell dimensions: $l = 2.6$ cm $h = 0.2$ mm $L_o = 7.6$ cm

$d \approx 0.29$ mm

Figure 3. Schematic representation of the electrokinetic cell used for streaming potential and conductivity measurements.

within the inter-phase. The dependence of λ on volume fraction is obtained from the Brinkman equation:[26]

$$\lambda(x) = \left\{ \frac{R_s^2}{18} \left[3 + \frac{4}{\phi(x)} - 3\sqrt{\frac{8}{\phi(x)} - 3} \right] \right\}^{-1/2} \quad (14)$$

In this context, R_s represents a model radius of spherical resistance centers, which is necessarily treated as an adjustable parameter. The value of R_s is calculated from the value of λ^{-1} used to describe the bulk gel. When $\phi_b \ll 1$, the position-dependent fixed charge density and friction coefficient follow the same position dependence given for the volume fraction in eq 13.

Figure 2 illustrates the gel layer structure for the soft diffuse interface model. Again, the gel is attached to a hard surface at $-d$ and the center of the cell is located at $h/2$. In this case, however, the polymer density in the network gradually thins out in an "inter-phase" centered around $x = 0$, with a total thickness equal to several α's. In the limit of $\alpha = 0$, the inter-phase would be of zero thickness and the model would reduce to the step-function approach, as is the case in the Ohshima−Kondo theory.

The total streaming current is described as the sum of the contributions from the bulk gel, inter-phase, and bulk electrolyte environments, each of which is arrived at by integration of the current density across the domain of interest. The back current develops in all three domains. As in the case of the Ohshima-Kondo model, the electroosmotic contribution is negligible provided $d \gg \kappa^{-1}$. The expression for the current density as a function of x is, therefore, identical to the expression in eq 11; however, the specifics of the potential distribution and the fluid velocity distribution are different. The model was described in great detail in recent publications.[16,17] The total current in the cell, I, is then arrived at by integration across the three regions:

$$I = 2\left[\int^{gel} i(x)\,dx + \int^{int} i(x)\,dx + \int^{sol} i(x)\,dx \right] \quad (15)$$

where the superscripts gel, int, and sol refer to the bulk gel, inter-phase, and bulk solution, respectively. The streaming potential is the value of the steady-state potential difference, E_{str}, determined when the overall net current in the cell is zero. The important parameters which emerge are the fixed charge density in the gel layer, the penetration depth, and the characteristic length scale of the inter-phase, α.
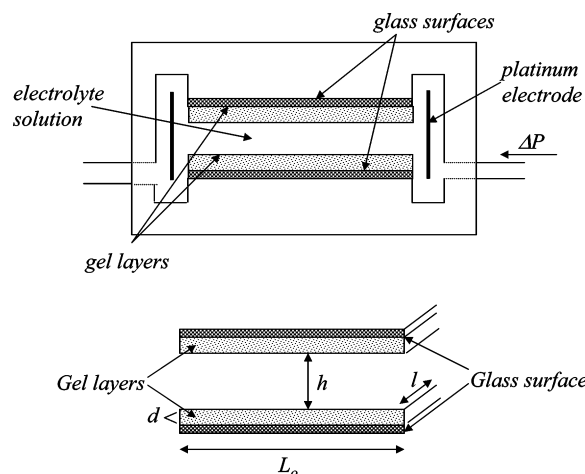
3. Experimental Section

Gels of polyacrylamide cross-linked with N,N'-methylene-bisacrylamide as well as copolymer gels of acrylamide and 0.2, 0.5, and 1.0 mol % sodium acrylate were prepared by free radical polymerization using a recipe based on that of Zhang and Davison.[27] Each gel was prepared from a stock solution with a total monomer concentration of 15.3 g in 100 mL of deionized water. In each stock solution 2% by mass (0.3 g) of the total monomer was methylenebisacrylamide cross-linker. The polymerization was initiated with ammonium persulfate (APS), and tetramethylethylenediamine (TEMED) was used as an accelerant. Acrylamide, methylenebisacrylamide, APS, and TEMED were all obtained from Aldrich and used without further purification. For each gel preparation, 15 mL of stock solution was placed in a beaker, to which 350 μL of APS (10%, w/v) solution and 10 μL of TEMED were added. The contents were thoroughly mixed, then injected between glass plates 0.25 mm apart for setting. After completion of the polymerization, the gels were removed from the glass plates and dialyzed extensively against water, which resulted in swelling relative to the initial gel thickness of 0.25 mm.

Conductivity and streaming potential measurements were made in a homemade streaming potential apparatus.[28] A schematic of the electrokinetic cell is given in Figure 3. The thin films of gel were placed on clean borosilicate microscope slides of the same size (3 in. by 1 in.) and inserted in the parallelepipedic electrokinetic cell. The total separation between glass slides was 0.75 mm, which includes the thickness of the gel layer on each slide and the electrolyte solution between the gel layers. Two platinized electrodes were also present to allow for streaming potential and total cell conductance measurements. Pressure was applied with N_2 gas. At each new ionic strength, the cell was thoroughly flushed with electrolyte solution until a constant total cell conductance was obtained. The characteristic diffusion time, τ ($\tau \approx d^2/D$, where D is the diffusion coefficient of the ion), for a simple electrolyte ion to diffuse through an aqueous film 0.25 mm thick is on the order of 100 s. The time required to reach equilibrium was typically on the order of hours. Total cell conductance was measured with an applied voltage of 10 V between the electrodes. Streaming potentials were measured at a variety of applied pressures, with a maximum of 25 cm Hg. Linearity in streaming potential was observed as a function of applied pressure under all conditions investigated.

Gel swelling measurements were made by preparing small disks of gel, which were weighed immediately after preparation and after hydration and equilibration with NaCl solutions of the

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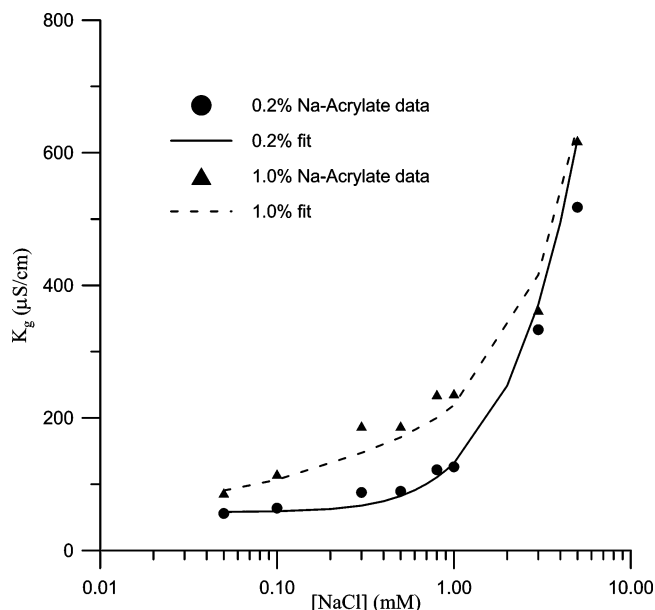(28) van der Put, A. G. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands, 1980.
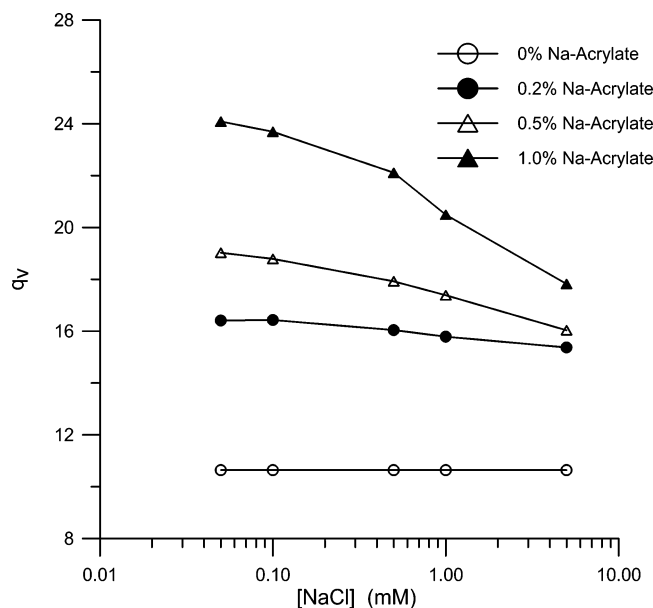
Figure 4. Volume swelling ratio, q_v, of the copolymer gels as a function of sodium chloride concentration at natural pH.

desired ionic strength. The dry mass of the gels was determined by drying the gel samples at 80 °C until a constant mass was obtained.

4. Results and Discussion

4.1. Gel Swelling. The value of q_v (inverse polymer volume fraction in the gel) of the four gels as calculated with eq 6 is displayed as a function of ionic strength in Figure 4. The 0 and 0.2% sodium acrylate gels show very modest changes in bulk swelling in the experimental window of interest and can be meaningfully modeled with q_v being invariant with ionic strength. The 0.5% and 1.0% acrylate gels, on the other hand, show significant variations in bulk swelling as a function of ionic strength. The enhanced swelling at low ionic strength reflects the influence of the electrostatic contribution to the osmotic pressure. The larger the fixed charge density in the gel phase, the larger will be the electrostatic contribution to the osmotic pressure at any given ionic strength, which is clearly visible in the swelling data in Figure 4.

Under conditions where the electrostatic contribution to the osmotic pressure is negligible (i.e., high ionic strength for the 0% acrylate gel), eqs 8 and 9 can be used to estimate the average number of segments between cross-links in the swollen network, which provides an idea of the mesh size of the porous gel network. As this quantity is a function of the cross-linker concentration in the solution from which the gel is prepared and is unaffected by the sodium acrylate concentration (at least in the limit of such small acrylate concentrations), the value obtained for the 0% gel should in principle apply to all of the networks prepared, subject to the assumption that the polymer–solvent interaction parameter, χ, is not affected by the small quantities of sodium acrylate present in the copolymer gels. The value of χ for polyacrylamide in water has been reported in the literature as 0.48,[29] and that value is typically used for copolymers of acrylamide as well, provided the comonomer mole fraction is low.[29,30] Assuming a value of 0.48 for χ and using the swelling data shown in Figure 3, a value of 400 is obtained for the average

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Figure 5. Gel layer conductivity data for the 0.2% and 1.0% sodium acrylate gels. The lines are fits to eqs 3 and 5, assuming full incorporation of the acrylate as used in the synthetic recipe and a pK_a of 4.6.

number of segments between cross-links in the 0% acrylate gel, and by extension in all of the gel samples. The model for the elastic contribution (eq 9) assumes that the microscopic deformation upon swelling is a linear function of the macroscopic swelling.[30] Because of the approximations involved in the swelling theory, the average cross-link density should not be taken literally in a quantitative sense but rather should be regarded as a qualitative estimate. The estimate is in good agreement with what might be expected from the gel recipe, in which 1 mol % of the monomers are cross-linkers. As not all cross-links will be structurally reinforcing,[25,31–33] a value somewhat larger than 100 is to be expected and is in accord with the trends reported in other investigations.[23,25]

4.2. Conductivity and Donnan Potential. Donnan potentials as a function of ionic strength were estimated from experimental conductivity data using eq 3. Fixed charge densities can then be estimated from the Donnan potential variation with ionic strength using eq 1. Figure 5 shows the experimentally determined gel layer conductivity as function of ionic strength for two of the gel samples, the 0.2% and 1.0% sodium acrylate gels in sodium chloride at the natural pH of 5.8. Fits are shown which account for the incomplete dissociation of the sodium acrylate within the gel, as described by eq 4. The Donnan potentials extracted from the conductivity data, as well as the fixed charge density for the same two gels, are displayed in Table 1. The maximum possible fixed charge density is determined from the synthetic recipe and the swelling, while the effective charge density is extracted from fits to the conductivity data using eqs 3 and 4. At high ionic strength there is quantitative agreement between the charge density from the recipe and the value extracted from the conductivity measurements. A value of 4.6 is used for the pK_a of sodium acrylate,[34] and a value of 0.9 is assumed for the relative mobilities, β, of ions within the gel based on the volume fraction data and

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Table 1. Fixed Charge Density, ρ_0, Donnan Potential, Ψ_D^{exp}, and Dissociation Fraction, ρ/ρ_0, for the 0.2% and 1.0% Sodium Acrylate-*co*-polyacrylamide Gels

C_s (mM)	0.2% sodium acrylate			1.0% sodium acrylate		
	ρ_0 (C/m³) $\times 10^4$	Ψ_D^{exp} (mV)	ρ/ρ_0	ρ_0 (C/m³) $\times 10^4$	Ψ_D^{exp} (mV)	ρ/ρ_0
0.05	−11.14	−78	0.99	−39.02	−92	0.469
0.1	−11.14	−65	1	−39.60	−83	0.657
0.3	−11.26	−45	1	−41.89	−65	0.919
0.5	−11.40	−32	1	−42.39	−55	0.955
0.8	−11.50	−25	1	−43.46	−46	0.99
1	−11.61	−17.5	1	−44.32	−42	1
3	−11.73	>−10	1	−48.64	−15	1
5	−11.90	>−10	1	−52.32	−17	1

literature values for small ion diffusion in polyelectrolyte gels.[19] The data in Table 1 indicate that there is full dissociation across the entire ionic strength range of interest for the 0.2% acrylate gel but that the Donnan potential has a significant effect on the extent of dissociation for the 1.0% acrylate gel at low ionic strength. The corresponding Donnan potential values are listed as well. The entries marked >−10 mV illustrate the detection limit of this technique. The method of fitting the conductivity data and extracting Donnan potentials for all of the gels will be explained in detail in another communication.[35]

The analysis in the present investigation assumes a uniformly smeared out potential within the gel phase. This represents a first approximation and a starting point for the modeling. Consideration of nonuniform charge and potential distributions would introduce additional parameters in the theory. The influence of nonuniform potentials on the model would be a very fruitful future scientific contribution.

4.3. Streaming Potential. Streaming potentials for each of the four gels are displayed as a function of ionic strength in Figure 6. The streaming potential as displayed is actually the incremental streaming potential, defined as the slope of the linear plot of streaming potential versus applied pressure (i.e., dE_{str}/dP). The data are not converted to zeta potentials, because soft surfaces do not possess a sharp slipping plane and, hence, the zeta potential is not conceptually appropriate for these systems.[16] As for the conductivity data, the measurements were made in sodium chloride solutions at natural pH (i.e., pH ≈ 5.8). The largest streaming potentials are observed for the 0% acrylate gels and decrease as a function of fixed charge density. The streaming potential and conductivity data illustrate the existence of a nonzero fixed charge density in gels even when no charge groups are intentionally introduced.[18] The charge in such cases primarily arises as a consequence of the ionic initiators used in the preparation of the gel, as well as due to some limited hydrolysis of acrylamide. Some additional charge might be present due to unsymmetrical adsorption of ions from solution as well. The trend from gel to gel (that is, that the largest streaming potential is observed for the lowest charged gel) can be explained in terms of the magnitude of the back current which develops in the cell. At high fixed charge densities, the increased gel conductivity as demonstrated in Figure 5 and the resulting back current effects dominate the opposite effect of a higher double layer potential. As a result, the steady-state streaming potential which develops in the cell is smaller in magnitude for higher charge density gels.

4.4. Ohshima−Kondo Model. In addition to the experimental streaming potential data for the four gels,

(35) Yezek, L. P., submitted to *Langmuir*.
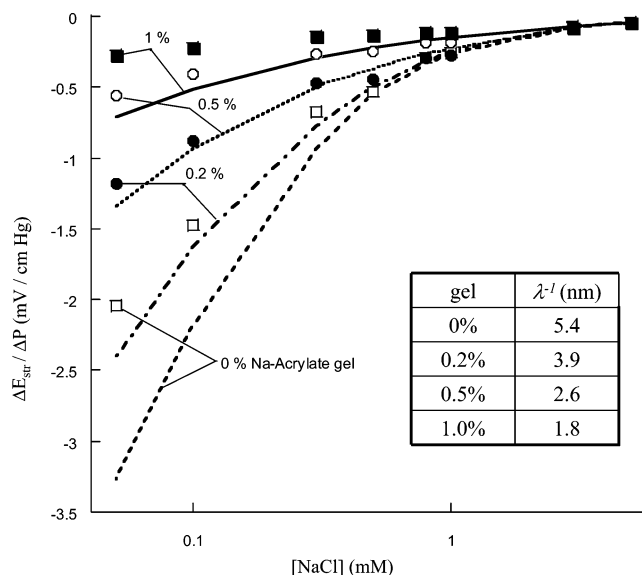
Figure 6. Symbols represent streaming potential data for the four gels as a function of sodium chloride concentration at natural pH. The lines correspond to fits to the model of Ohshima and Kondo.[15] For each gel, a single value of λ^{-1} is assumed over the entire ionic strength regime.
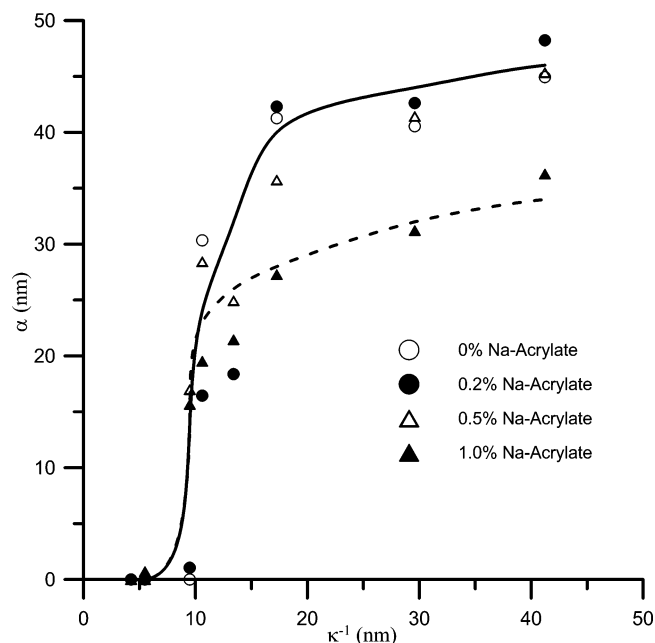
Figure 6 also shows the results of the fitting on the basis of the model of Ohshima and Kondo.[15] The fits employ the fixed charge densities extracted from the conductivity data, while a value of λ^{-1} is selected from the fit to the data at high ionic strength (in this case, 5 mM NaCl). Within the framework of the fitting in Figure 6, the values of λ^{-1} are constant for each gel as a function of ionic strength. As λ can be expressed as a function of polymer volume fraction with eq 14, a constant value of λ^{-1} is consistent with the swelling data for the 0% and 0.2% acrylate gels but represents a somewhat weaker approximation in the case of the higher charge density gels. The data and fits in Figure 6 clearly show good agreement for ionic strengths greater than 1 mM sodium chloride, but the Ohshima−Kondo model overestimates the streaming potential for all four gels at low ionic strength. As the ionic strength is lowered, the discrepancy between model and experiment grows larger for each gel. Since the magnitude of the Donnan potential as a function of ionic strength is known from the conductivity data for each gel, the only parameter in the model which can be varied is λ^{-1}. Increasing the value of λ^{-1}, which amounts to decreasing the friction coefficient, k_0, of the bulk gel, will enhance the magnitude of the bulk gel contribution to the total streaming current (by presenting less resistance to flow in the gel phase, hence, allowing greater fluid flow and, thus, greater electrical current in response to the applied pressure), while leaving the back current unaffected. The net result is a larger streaming potential, creating an even larger discrepancy between model calculations and experimental data at low ionic strength. Raising the value of k_0 and, hence, decreasing the value of λ^{-1} will move the model in the other direction. The agreement will be improved at low ionic strengths, but at the cost of significantly underestimating the streaming potential at high ionic strengths. Hence, there is no single value of λ^{-1} which will fit the data for any of the gels (even qualitatively) across the entire ionic strength range of interest. Although the fits assume a constant value of λ^{-1} for each gel, which might be seen as unrealistic in light of the swelling data for the higher charge density gels, the 0% and 0.2% acrylate gels exhibit no changes in bulk swelling as a function of ionic strength, so there is no a priori reason to expect the

friction coefficient (and, thus, λ^{-1}) to vary with salt concentration for those gels. However, the discrepancy between model and experiment follows the same trend for all four of the gels, regardless of fixed charge density.

A brief comment must be made on the values of λ^{-1} as displayed in Figure 6. The Brinkman equation (eq 14) suggests that, as the polymer volume fraction decreases, the value of λ^{-1} should increase, implying a diminishment of the friction coefficient with decreasing polymer volume fraction. Exactly this trend has been reported from experiments which measure solvent flow through poly-acrylamide and other high water-content gels.[36,37] The experiments in those investigations span a range of volume fractions from 2 to 20% or even higher. The variation in λ^{-1} from gel to gel in the present investigation (i.e., a comparison between the 0% and 1% acrylate gels) shows a trend contradictory to the prediction of the Brinkman equation. The 1% acrylate gel has a lower polymer volume fraction and at the same time a smaller penetration depth, λ^{-1}, than the lower charged gels, implying a larger coefficient of friction for the network. The variation of volume fraction from gel to gel (due to differing extents of swelling) in the present study is quite modest, from 5 to 7%. The friction coefficients are calculated from the values of λ^{-1} used to fit the streaming potential data. The values calculated agree on an order of magnitude scale with the values reported elsewhere for polyacrylamide and similar polyelectrolyte gels.[8,36,38] The trend in values of λ^{-1} from gel to gel, which seems contrary to expectation, remains an issue open for resolution. A possible source of inconsistency can be found in the model presented in the Brinkman equation, which describes flow through a lattice of spheres. The polymer networks investigated here are a poor approximation to a collection of spherical resistance centers. Alternatively, some inconsistency, particularly at low ionic strengths, may arise from the selection of a particular function to describe the spatial drop off of polymer volume fraction. The hyperbolic tangent function selected in this investigation assumes a bulk value of λ^{-1} which is independent of ionic strength, even though the bulk networks exhibit some small changes in polymer volume fraction as a function of ionic strength. For the time being, the values of λ^{-1} should, therefore, be regarded as fitting parameters with an approximate physical interpretation as defined above, in a fashion similar to the interpretation of X in the gel swelling calculations.

4.5. Diffuse Soft Interface Model. The experimental streaming potential data and fixed charge density data for each of the four gels were fit using the diffuse soft interface model[16,17] described above. The same values of λ^{-1} as determined at high ionic strength and used in the Ohshima–Kondo model fits are used in this analysis. The introduction of a diffuse interface with a gradual thinning out of polymer density and charge density within a narrow "inter-phase" allows the data for each gel to be fit with a constant bulk value of λ^{-1} and an ionic-strength-dependent value of the characteristic length, α, of the decay of density within the inter-phase. Within the inter-phase itself, λ^{-1} varies as a function of position as described in eqs 13 and 14. For the experimental conditions discussed here, the introduction of the gradual decay in gel density reduces the streaming potential due to the hydrodynamic impact on the velocity profile at the interface.[16] The values of α required to fit the streaming potential data for each gel

(36) Tokita, M.; Tanaka, T *J. Chem. Phys.* **1991**, *95*, 4613.
(37) Klepko, V.; Mel'nichenko, Y.; Shilov, V. *Polym. Gels Networks* **1996**, *4*, 351.
(38) Ohshima, H.; Makino, K.; Kato, T.; Fujimoto, K.; Kondo, T.; Kawaguchi, H. *J. Colloid Interface Sci.* **1993**, *159*, 512.

Figure 7. Characteristic length scales, α, of the inter-phase as calculated from the fit to the diffuse soft interface model.[16,17] For each gel, a constant bulk value of λ^{-1} is assumed over the entire ionic strength regime and in each case is equal to the value used in the fitting in Figure 6. The lines are presented as a guide to the eye.

are plotted as a function of sodium chloride concentration in Figure 7. For each gel, the magnitude of α increases as the ionic strength is lowered, in a manner reminiscent of the behavior of a hairy layer. The bulk swelling data for the four gels provide an average number of segments between cross-links of about 400. For a vinyl polymer, this would correspond to a maximum cross-link separation of about 100 nm,[24] assuming simple additivity of the ~0.25 nm carbon–carbon bond lengths in the polymer chains. Of course, due to the spatial distribution of the polymer chains, the spatial length per segment will depend on the extent of swelling in the network, but the above calculation does provide an order of magnitude estimate of the length between cross-links. In addition, due to the limitations of the swelling model, the 400 segments between cross-links calculation should be understood as a semiquantitative estimate of the average chain length in the network.

At the edge of the gel there will be a region of dangling chains sticking out into the electrolyte solution, with charge groups randomly distributed on the chains. This can be thought of as a loosely cross-linked polymer brush extending from the gel surface. The values of α range from close to zero to 40 nm. In the context of the present model of the diffuse interface, which assumes a decay of polymer volume fraction based on a hyperbolic tangent function, as given in eq 13, the actual thickness of the inter-phase region would be approximately 4 times the value of α, which implies an inter-phase thickness which varies with ionic strength from several to some 160 nm. Such a value at full extension suggests that the actual inter-phase region is on the order of two statistical chain lengths thick. The physical picture of the inter-phase region which emerges is illustrated in Figure 8. The region consists of cross-linked charged chains sticking out into solution. The cross-link density in the inter-phase is smaller than that of the bulk gel, giving rise to a smaller elastic contribution to the local osmotic pressure in the inter-phase, which allows for greater swelling in response to an increase in the electrostatic contribution to the
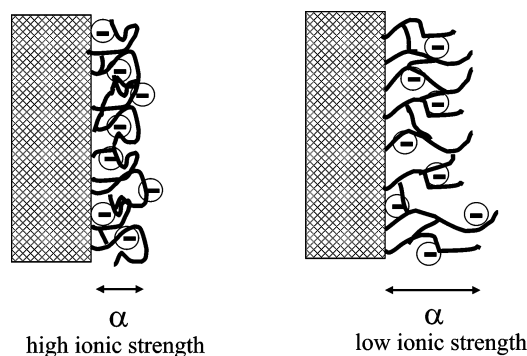
Figure 8. Pictorial view of the diffuse soft interface. At high ionic strengths the polymer chains adopt a compressed configuration. As the ionic strength is lowered, the osmotic pressure within the inter-phase increases, forcing the lightly cross-linked network of chains at the interface to swell.

osmotic pressure. At high ionic strength, the charge groups at the interface are screened and the electrostatic contribution to the osmotic pressure is small, so the chains adopt a random orientation close to the surface. As the ionic strength is lowered, the length scale of the interchain repulsion increases, as does the electrostatic contribution to the local osmotic pressure, resulting in a swelling of the inter-phase region. This is an exact analogy to the changes in bulk swelling observed for the higher charged gels as a function of ionic strength. The magnitude of the swelling is controlled by the balance between the three contributions to the osmotic pressure as presented in eq 7. Since the cross-link density is lower in the inter-phase region, the extent of swelling is larger there and shows variability with ionic strength even for the 0% acrylate (very low charge gel), which shows no variation in bulk swelling. Of course, the charge density is lower in the inter-phase region as well, but it may be that the cross-link density decays faster with respect to position than does the overall chain density.

The values of α for the various gels presented in Figure 7 present a consistent physical picture of the diffuse interface. The values for the 0%, 0.2%, and 0.5% acrylate gels are essentially the same as a function of ionic strength. The fits for the 1% acrylate gels at low ionic strengths (<0.1 mM) deviate in a manner which is difficult to explain physically. Namely, the thickness of the inter-phase as calculated from the fits to the electrokinetic data suggest a thinner region for the highest charge gel. All things being held constant except for the charge density, one would expect a larger value for the 1% gel, or at least the same values, assuming the chains are maximally stretched. However, a glance at Figure 4 clearly illustrates the fact that the bulk swelling of the 1% acrylate gel is significantly enhanced at ionic strengths less than 0.1 mM relative to the value at 5 mM, suggesting that the assumption of a single value of λ^{-1} across the entire experimental window is not applicable. A different value of λ^{-1} at the lowest ionic strengths would change the fitting and would alter the corresponding values of α. Alternatively, it is possible that there are structural differences in the high charged gel at low ionic strengths, which the current modeling does not address.

5. Summary and Conclusions

Streaming potential data for thin films of cross-linked polyacrylamide-*co*-sodium acrylate gels were fit to two models of electrokinetics at soft surfaces. The first model,

put forth by Ohshima and Kondo,[15] assumes a uniform polymer and charge density within the gel layer and a step function to zero at the sharp gel−solution interface. Solvent flow within the gel is described in terms of a softness parameter or penetration depth, which is typically on the order of a few nanometers. The model is able to fit streaming potential data at high ionic strengths (>1 mM) but systematically over-estimates the streaming potential at low ionic strengths.

To more realistically describe the nature of the gel−solution interface, Duval[16,17] and van Leeuwen[16] introduced the diffuse soft interface model, which includes a gradual decay of polymer and charge density within a narrow inter-phase where the gel and solution come into contact. Assuming a decay based on a hyperbolic tangent function within the inter-phase, the conductivity and streaming potential data for the copolymer gels were fit to the diffuse soft interface model. The diffuse inter-phase thicknesses obtained were consistent in a semiquantitative manner with the average chain length in the network, as estimated from the bulk swelling measurements. The physical picture of the inter-phase that emerges is a lightly cross-linked polyelectrolyte brush, which expands at low ionic strength but adopts a more compressed conformation at high ionic strengths. The streaming potential is then dependent on the balance between the streaming current, which develops within the bulk gel, the inter-phase, and the solution phase on one hand, and the back current in the cell on the other. Which of the three contributions to the streaming current dominates is dependent upon the value of the penetration depth. When λ^{-1} is large, the largest portion of the streaming current develops within the bulk gel environment, and the contributions due to the solution phase and the inter-phase are modest, if not negligible. When λ^{-1} approaches zero, a classical shear plane appears at the sharp gel/solution interface, and the streaming current develops only within the bulk solution phase. At intermediate values of λ^{-1}, such as the values reported above, the contributions from all three phases (i.e., the bulk gel, the inter-phase, and the bulk solution) make significant contributions to the total streaming current and, hence, the net streaming potential which develops in the electrokinetic cell. Under such circumstances, the results of the fitting on the basis of the diffuse soft interface model are very sensitive to the mathematical details of the decay profile which is selected to describe the thinning out of the gel at the gel/solution interface. The current investigation assumes a gradual decay, described with a hyperbolic tangent function, which leads to physically reasonable values for the characteristic dimension of the inter-phase layer.

Soft interfaces are by their very nature extremely complex. Describing the electrokinetic effects in a quantitative manner is a difficult task which requires the consideration of many structural parameters which are not subject to direct experimental verification. While the modeling will most assuredly continue to develop in the years to come, the diffuse soft interface model seems to represent a useful step forward in the description of soft interfaces.