

## Electrokinetic Phenomena and Anomalous Conduction

*Dudley A. Saville*

*Princeton Center for Complex Materials  
and  
Department of Chemical Engineering, Princeton University,  
Princeton NJ 08544, USA*

Received February 9, 1998; accepted April 30, 1998

The effects of immobilizing a thin layer of water adjacent to the surface of a colloidal particle are calculated using the Dynamic Stern Layer model introduced by Zukoski and Saville.<sup>1</sup> Supposing water is immobilized by, for example, unreacted monomer or polymer chains dangling from the particle surface allows one to divide the diffuse layer into two regions, an outer region where transport is by convection, electromigration and diffusion and a region near the surface where counterions move only by electromigration and diffusion. The present calculations account for all the relevant processes in a mathematically rigorous fashion. Even a thin layer has dramatic effects in diminishing particle mobility and increasing the dielectric response.

### INTRODUCTION

A central problem in colloid science concerns the dichotomy between theory and experiment regarding the electrokinetic behavior of colloidal particles. The presence of a »fuzzy layer« on the particle surface is sometimes advanced to reconcile this schism. Such a layer could immobilize solvent and shift the shear surface outward, occluding a portion of the diffuse layer. Accordingly, electromigration and diffusion within the immobilized layer would alter the electrokinetic behavior. Dukhin and Semnikhin<sup>2</sup> provided

---

This article is dedicated to Professor Egon Matijević on the occasion of his 75<sup>th</sup> birthday.

an asymptotic theory for the effect of such processes on the electrophoretic mobility. The present contribution revisits the problem; here dielectric and conductivity increments are calculated in addition to electrophoretic mobility. For this purpose the Dynamic Stern Layer Model originally set out by Zukoski and Saville<sup>1</sup> is used. This is a general model, applicable irrespective of the size of the particle charge and diffuse layer thickness. As stated in the original paper, the model envisions a dynamic equilibrium between ions »adsorbed« behind the shear surface and the diffuse part of the double layer. Nevertheless, as has been noted, there are a number of ways of interpreting the parameters in the model.<sup>3,4</sup>

The formulation adopted here is similar to Dukhin and Semenikhin's.<sup>2</sup> Accordingly, the problem statement begins with a sphere of a certain radius and surface potential. Given the surface potential, the equilibrium double layer structure follows from the Gouy-Chapman model. For a bare surface this potential is identical with the  $\zeta$ -potential. Next, a layer thickness is stipulated. Diffuse layer ions residing between the surface and the edge of the layer are »assigned« to an infinitesimally thin dynamic Stern layer. Ion movement within the layer by electromigration and diffusion is governed by the Nernst-Planck expression; the ion mobility may be different from that in the bulk. The parameters describing the surface layer are the equilibrium ion density, valence, and mobility. The response of a typical particle is computed by solving the dynamic equations numerically.<sup>3</sup> It should be emphasized, however, that the model is non-specific as to the details of the physical and chemical processes which lead to transport within the Stern layer. Insofar as mathematics is concerned, the layer is infinitesimally thin.

Although results are presented for but one set of conditions, other calculations not reported here indicate that qualitative generalizations are justified. The presence of mobile ions retards the electrophoretic mobility and enhances the dielectric and conductivity responses. A noteworthy result is the large magnitude of the mobility retardation and the dielectric and conductivity increments enhancements. It also appears that mobile ions behind the shear surface set an upper limit on the  $\zeta$ -potential which can be inferred from mobility measurements. The mobility of ions inside the »fuzzy layer« has a dramatic effect on the increments.

## METHODOLOGY AND RESULTS

Computations were carried out for 300 nm particles in aqueous 1 mM KCl solutions so the diffuse layer thickness is 9.62 nm and  $\alpha\kappa = 15.6$ . A »fuzzy layer« thickness of 2.23 nm was chosen so the surface layer »occludes« a little over 20% of the diffuse layer. The electrostatic properties of surfaces

with different potentials are shown in Figures 1–3. Figure 1 shows the relation between the surface potential and the  $\zeta$ -potential (the potential at the edge of the hypothetical »fuzzy layer«). Note how the  $\zeta$ -potential saturates as the surface potential increases due to the addition of charge. Figures 2

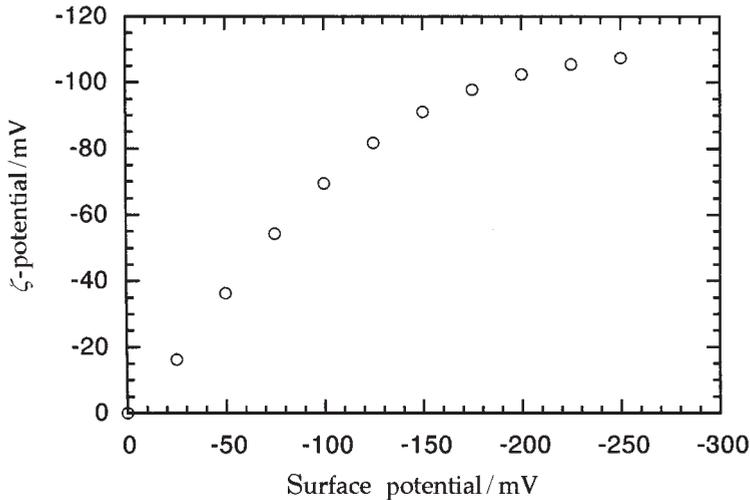


Figure 1. The surface potential –  $\zeta$ -potential relation for 300 nm particles in 1 mM KCl.

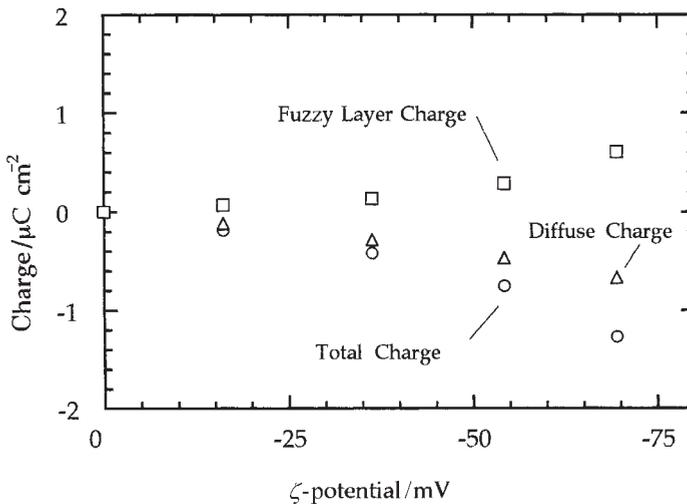


Figure 2. Relationships between charge in the different regions and  $\zeta$ -potential; low potential range.

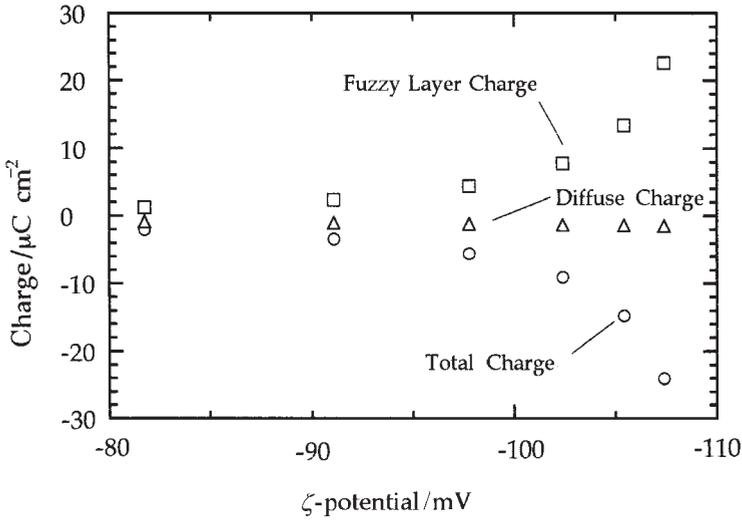


Figure 3. Relationships between charge in the different regions and  $\zeta$ -potential; high potential range.

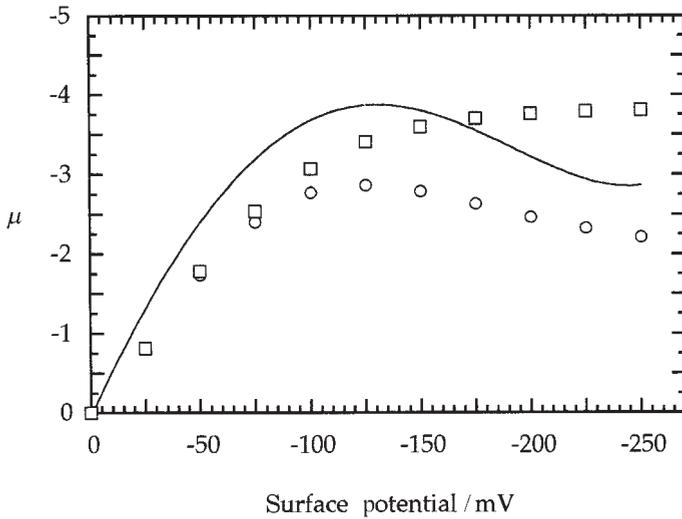


Figure 4. Surface potential *vs.* dimensionless mobility,  $\mu$ , *i.e.*, the velocity per unit field strength scaled on  $2\epsilon\epsilon_0kT/3e\eta$ . The symbols represent:  $\epsilon$  – the dielectric constant of the fluid;  $\epsilon_0$  – the permittivity of free space;  $kT$  – the product of Boltzmann's constant and the absolute temperature;  $e$  – the charge on a proton;  $\eta$  – the fluid viscosity. For water at room temperature the scale factor is 1.33 microns per second per volt per centimeter. (—), without an immobilized layer; ( $\square$ ), immobile counterion charge in the fuzzy layer ( $K^+$  ions); ( $\circ$ ), counterion charge in the fuzzy layer ( $K^+$  ions) has the same mobility as in the bulk.

and 3 show how the charge in the different regions depends on the  $\zeta$ -potential. As expected, most of the additional charge resides in the hypothetical »fuzzy layer« at the higher  $\zeta$ -potentials.

Figure 4 shows how the particle mobility depends on the surface potential with different sorts of charge adjacent to the surface. When a portion of the charge is mobile and the potentials low, polarization and relaxation are negligible and the particle moves as if it simply has a lower  $\zeta$ -potential (or effective charge). As the potential at the edge of the fuzzy layer increases, polarization and relaxation effects appear. With mobile fuzzy layer charge, the mobility decreases due to polarization; polarization is less effective with immobile charge. This is clearly illustrated in Figure 5, which shows the same results plotted in terms of the potential at the edge of the fuzzy layer, *i.e.*, the »effective«  $\zeta$ -potential. With immobile charge, polarization and relaxation effects and deformation of the inner part of the diffuse layer by flow cancel one another. Thus the mobility is no different from that of a particle where all these processes deform the inner part of the diffuse layer. However, when charge inside the shear plane is allowed to polarize and relax, the mobility relation takes its characteristic form, albeit with the maximum at a lower potential. Clearly, the presence of mobile charge inside the shear surface lowers the mobility. Thus, experiments where electrophoretic mobilities exceed the values calculated from the standard model are consistent with the influence of a fuzzy layer.<sup>5</sup>

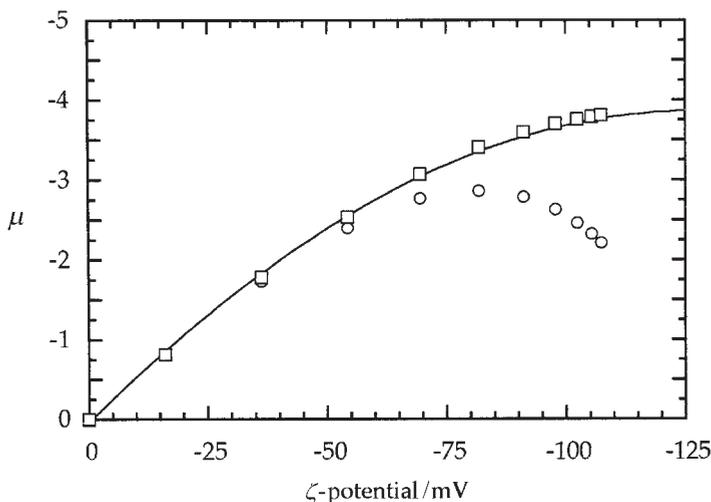


Figure 5.  $\zeta$ -potential *vs.* dimensionless mobility,  $\mu$ . (—), without an immobilized layer; (□), immobile counterion charge in the fuzzy layer ( $K^+$  ions); (o), counterion charge in the fuzzy layer ( $K^+$  ions) has the same mobility as in the bulk.

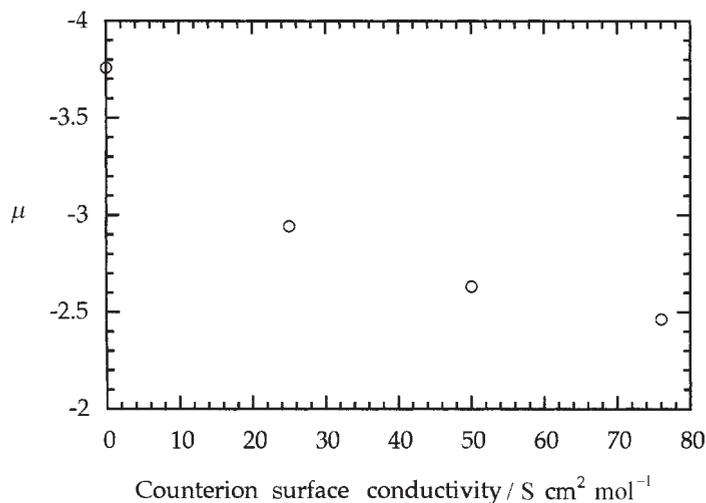


Figure 6. The effect of the counterion surface conductivity on the particle mobility in 1 mM KCl;  $\zeta = -102$  mV.

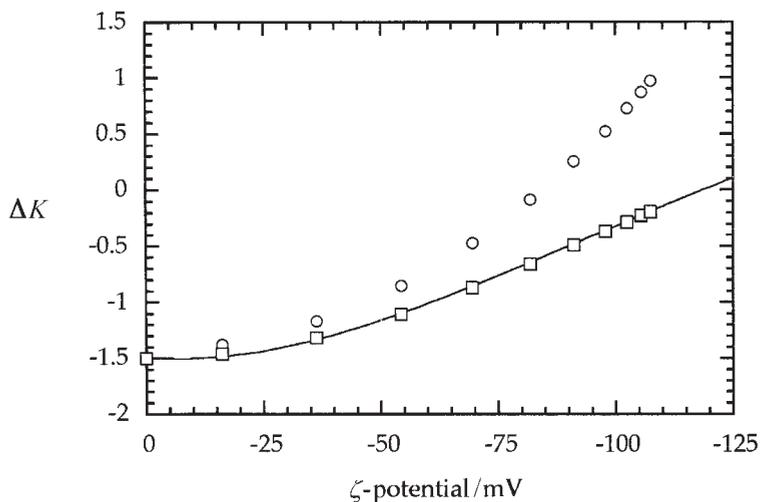


Figure 7. Dielectric increment –  $\zeta$ -potential relationships. Symbols as defined for Figures 4 and 5.

Mobile charge inside the shear plane affects the conductivity and dielectric properties of a suspension dramatically. The conductivity increment reported here,  $\Delta K$ , is defined as the change in the bulk conductivity due solely to the particle dipoles, *i.e.*,

$$\sigma = \sigma_{\infty} (1 + \Delta K \phi) \quad (1)$$

This excludes the important contributions due to added counterions and non-specific adsorption which are not altered by the incident field.<sup>6</sup> Here  $\sigma_{\infty}$  represents the conductivity of the solution without particles and  $\phi$  is the volume fraction of particles. Similarly for the dielectric increment,  $\Delta\varepsilon$ ,

$$\varepsilon = \varepsilon_{\infty} + \Delta\varepsilon \phi \quad (2)$$

where  $\varepsilon_{\infty}$  is the dielectric constant of the solvent. Figure 7 shows the effects of mobile and immobile ions on the low frequency conductivity increment; Figure 8 depicts the behavior of the dielectric increment. Note especially the strong effects of the »fuzzy layer« ion mobility; mobile ions polarized inside the shear surface have a much stronger effect when the solvent is immobilized. To illustrate this point, compare things at a  $\zeta$ -potential of  $-102$  mV where the total surface charge is  $-9.1 \mu\text{C}/\text{cm}^2$ . The 2.2 nm fuzzy layer

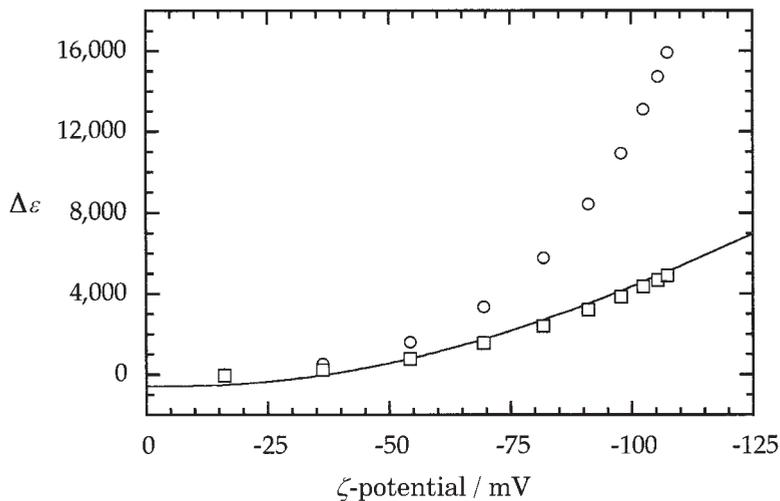


Figure 8. Conductivity increment –  $\zeta$ -potential relationships. Symbols as defined for Figures 4 and 5.

occludes a counterion charge of  $7.8 \mu\text{C}/\text{cm}^2$  leaving a charge of a little over  $-1.3 \mu\text{C}/\text{cm}^2$  outside the fuzzy layer. Restricting solvent motion more than doubles the dielectric increment; the conductivity increment is increased substantially.

## CONCLUDING REMARKS

The calculations reported here demonstrate the decisive effects of, for example, a »fuzzy layer« which immobilizes solvent adjacent to the particle surface. Furthermore, according to calculations based on the Brinkman model for the hydrodynamics of a fluid in a thin polymer layer, only a few polymer segments protruding into the liquid are required to impede solvent motion. The calculations presented here demonstrate a rich variety of behavior with a relatively simple model of transport behind the shear plane. Moreover, inasmuch as the calculations are mathematically rigorous, the observed effects are free of errors arising from mathematical approximations of one sort or another. Evidently processes adjacent to the particle surface have definitive effects on the electrokinetic properties of colloidal dispersions so models which take account of these processes can provide a better understanding of the properties of dispersed systems.

*Acknowledgment.* – This research was supported by awards to the Princeton Center for Complex Materials from the MERSEC Program of the NSF under award DMR-9400362 and to the Department of Chemical Engineering from the NASA Microgravity Science and Applications Program.

## REFERENCES

1. C. F. Zukoski and D. A. Saville, *J. Colloid Interface Sci.* **114** (1986) 32–44 and 45–53.
2. S. S. Dukhin and N. M. Semnikhin, *Kolloidn. Zh.* **32** (1978) 360–366.
3. L. A. Rosen, J. C. Baygents, and D. A. Saville, *J. Chem. Phys.* **98** (1993) 4183–4194.
4. D. A. Saville, *Colloids Surf.* **92** (1994) 29–40.
5. L. A. Rosen and D. A. Saville, *J. Colloid Interface Sci.* **140** (1990) 82–92.
6. D. A. Saville, *J. Colloid Interface Sci.* **91** (1983) 34–50.
7. J. H. Masliyah, G. Neale, K. Malysa, and T. G. M. van de Ven, *Chem. Eng. Sci.* **42** (1987) 245–253.

## SAŽETAK

## Elektrokinetičke pojave i anomalna vodljivost

*Dudley A. Saville*

Efekti imobiliziranja tankog sloja vode na granici s površinom koloidne čestice numerički su obrađeni primjenom modela dinamičkog Sternova sloja koji su predložili Zukoski i Saville. Pod pretpostavkom da je voda imobilizirana neregiranim monomerom ili polimernim lancima koji su jednim dijelom vezani na površinu koloidne

čestice, dopušteno je podijeliti difuzijski sloj u dva područja, vanjsko područje gdje je prijenos određen konvekcijom, električkom pokretljivošću i difuzijom, te područje pri površini čestice, gdje se protuioni gibaju samo električkom pokretljivošću i difuzijom. Pokazani računi opisuju sve bitne procese predloženog modela u strogo definiranom matematičkom obliku.