

# The Application of a Dynamic Stern Layer Model to Electrophoretic Mobility Measurements of Latex Particles

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## Introduction

Electrokinetic methods provide an essential tool for the study of the charging properties of colloidal particles and interfaces. This information can often be used to correlate with phenomena such as colloid stability or flow behaviour in colloidal suspensions. One commonly used technique is micro-electrophoresis, in which an electric field is applied and the resulting migration velocity of charged colloidal particles is measured. The purpose of the measurement is to determine the zeta potential, the average electrokinetic potential at the surface of shear, but the interpretation of the measurement is by no means straightforward. Whilst it is now over a quarter of a century since O'Brien and White<sup>1</sup> presented the exact calculation of the electrophoretic mobility of a spherical particle in an electrolyte solution, questions are still raised about the completeness of the standard electrokinetic theory. Whilst the model has had a degree of success, a number of authors have discussed extensions to this model to account for discrepancies between its predictions and experiment<sup>2,3</sup>. One such extension would be to take into account transport processes within the Stern layer. Applying the techniques of O'Brien and White, Mangelsdorf and White<sup>4</sup> presented a rigorous mathematical treatment for a general dynamic Stern-layer model in which the original theory is the special case of an immobile Stern layer.

Polystyrene and polymer lattices have the potential to provide ideal model systems with which to test electrokinetic theory. However despite appearing to be the best candidates to show ideal kinetic properties, these systems have shown anomalies, some of which are thought to be caused by surface conduction effects inside the Stern layer. This, together with the large body of data in the literature make them an interesting systems to study and assess Dynamic Stern-layer model extensions to the standard electrokinetic model.

## Theory(1)- Immobile Stern layer

Before describing transport in the Stern layer, we give a brief review of the theory developed by O'Brien and White.

Consider a particle immersed in an electrolyte composed of  $N$  ionic species of charge  $z_i e$ , bulk density  $n_i^0(\infty)$  and drag coefficient  $\lambda_i$  ( $i = 1 \dots N$ ).

To describe the system we require the electrostatic potential,  $\Psi(r)$ , the ion number densities  $n_i(r)$  and drift velocities  $v_i(r)$  and the fluid velocity  $u(r)$ , and pressure  $P(r)$ . The axes of the co-ordinate system are fixed at the centre of the particle, so that fluid velocity is zero at the particle surface and far from the particle moves with velocity  $-\mu E$ , where  $\nabla\Psi(r) \rightarrow -E$  as  $r \rightarrow \infty$ . Since ions cannot penetrate the particle surface, the component of the ion drift velocity normal to the particle surface must vanish at the particle surface,  $v_i \cdot \hat{r} = 0$  at  $r = a$ . In what follows  $\varepsilon$  and  $\eta$  are the medium's permittivity and viscosity respectively.

These quantities are governed by the following equations:-

### Poisson's Equation

$$\nabla^2 \Psi = -\frac{1}{\varepsilon_r \varepsilon_0} \rho(r) \quad \text{where} \quad \rho(r) = \sum_{j=1}^N z_j e n_j(r)$$

**Navier Stokes equation** (Steady, incompressible, low Reynolds number flow)

$$\eta \nabla^2 u - \nabla P = \rho \nabla \Psi \quad \text{with} \quad \nabla \cdot u = 0$$

### Ion Force Balance

$$-\lambda_i (v_i - u) - z_i e \nabla \Psi - k_B T \nabla \ln n_i = 0$$

### Ion Continuity Equation

$$\nabla \cdot (n_i v_i) = 0$$

These equations form a coupled set of non-linear partial differential equations. To solve them they must be linearised, and the problem decomposed into two simpler ones – the particle held fixed in the flow field - U the particle held fixed in an electric field E. For a spherical particle the problem can then be reduced to a set of ordinary differential equations that may be solved numerically.

## Theory (2) – Dynamic Stern Layer

To go beyond the model described earlier, more assumptions have to be made about the Stern layer. The classical model of the region behind the slipping surface, is illustrated in fig.0.

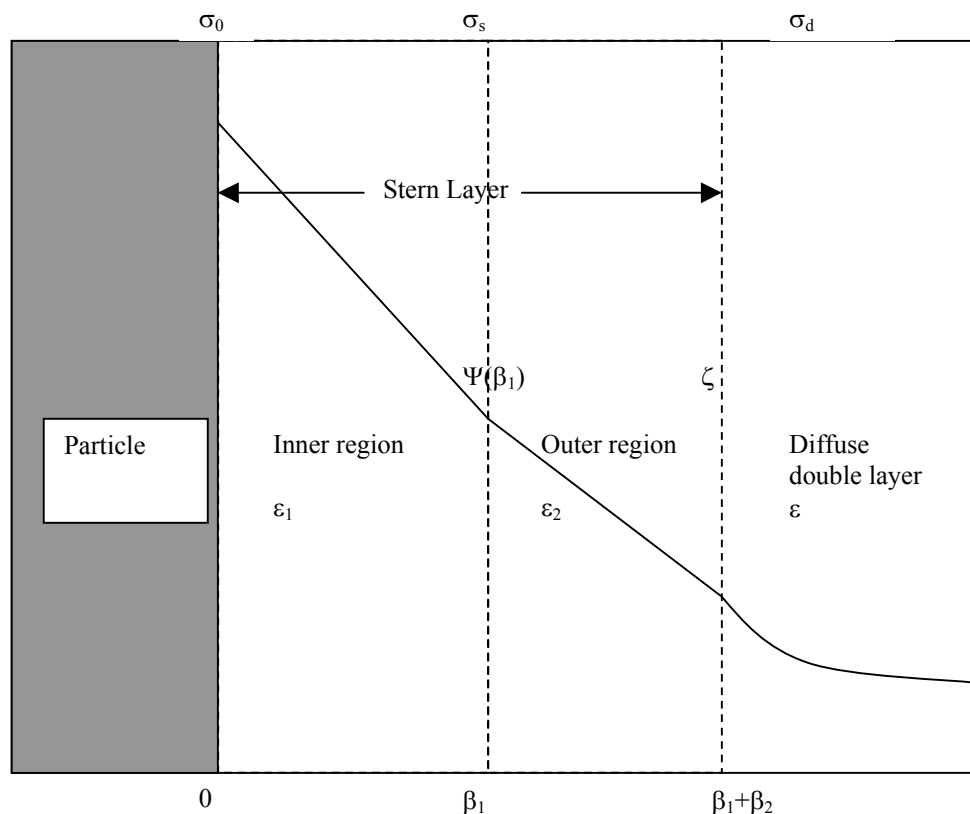


Figure 0

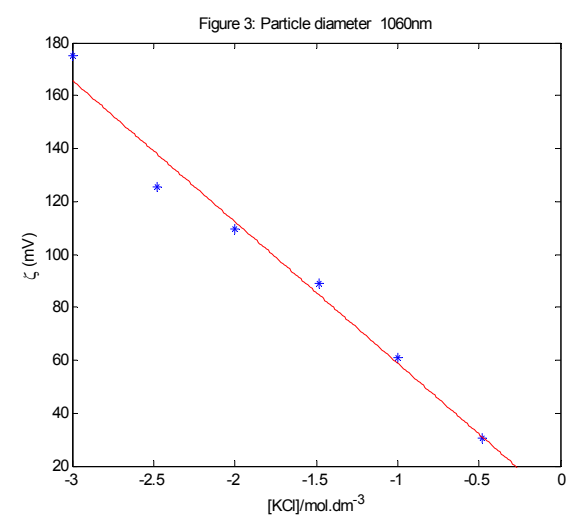
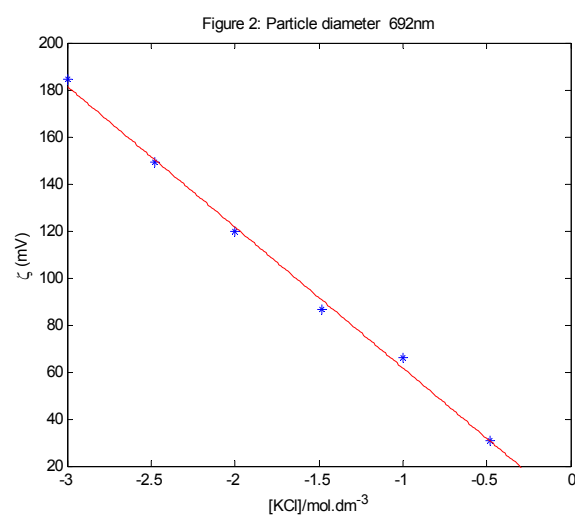
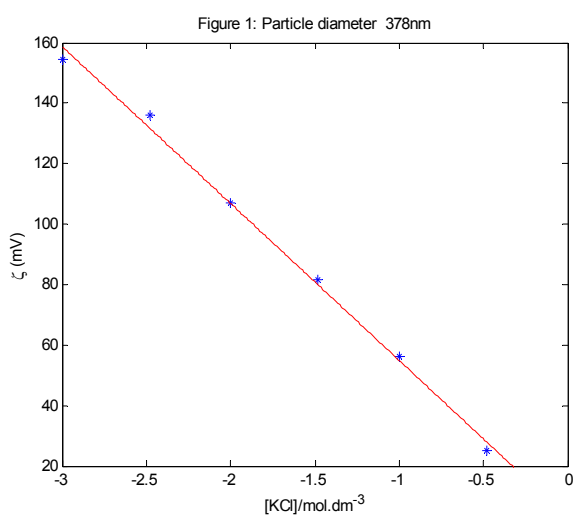
The true particle interface  $\sigma_0$  has a 'titratable' charge density due to fixed ionic species on the surface. The slipping plane at  $\beta_1 + \beta_2$  represents the closest approach of double layer ions. The plane  $\beta_1$  represents the distance of closest approach of an ion that has lost part of its hydration sheath and having some strong surface interaction. In this model, the surface charge  $\sigma_0$  is confined to plane at  $0$ , whilst the Stern layer charge density  $\sigma_s$  is confined to the plane at  $\beta_1$ . It is implicitly assumed that the Stern layer is thin compared with the particle dimensions or the double layer thickness, and that consequently the fluid velocity is approximately zero within the Stern layer, but ions may move behind the slipping plane. The equations governing the motion of ions within the Stern layer can be converted into boundary conditions on the slipping plane, and the formalism of O'Brien and White previously described can be used in its entirety with modified boundary conditions relating to the ion velocities at the slipping plane. The formalism is completely general. The only thing specific to a particular model is the description of the Stern layer charge density - hence the only difference between models is in the nature of the Stern layer adsorption isotherm. There are two main classes of model— those where adsorption is onto available free surface area and those where counter ions are adsorbed is onto specific surface sites.

The theory is in one sense more ambitious than the original model of O'Brien and White, in that it seeks to provide quantitative insight into the Stern region. It does so at a cost – there are a significant number of additional parameters that must be provided. For each ion, its maximum Stern-layer charge, ion drag coefficient ratio, and pK of dissociation must be known. In addition to these, the outer Stern-layer capacitance must also be provided. However the model is now able to calculate the Stern-layer charge density as well as the diffuse layer charge, allowing the surface charge  $\sigma_0$  to be deduced directly.

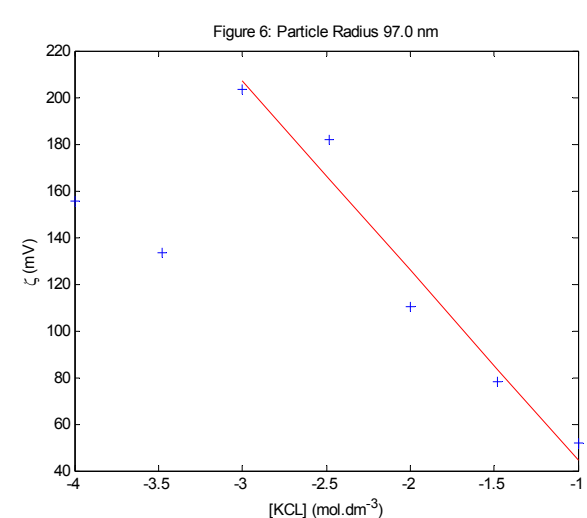
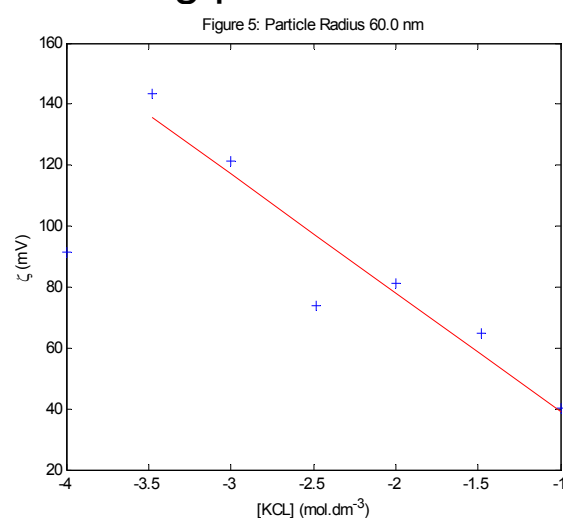
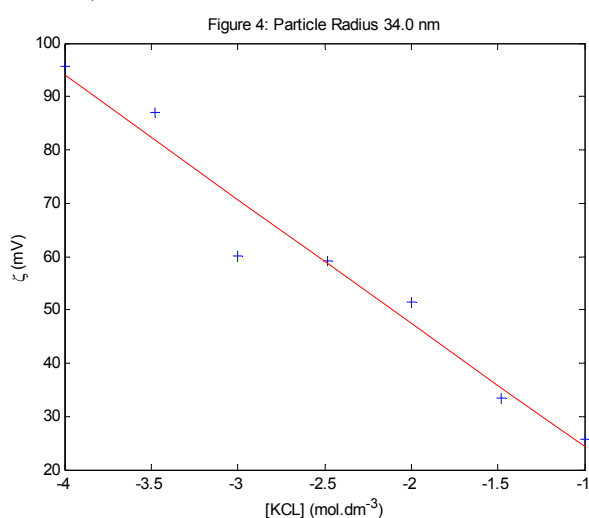
## Results: Immobile Stern Layer

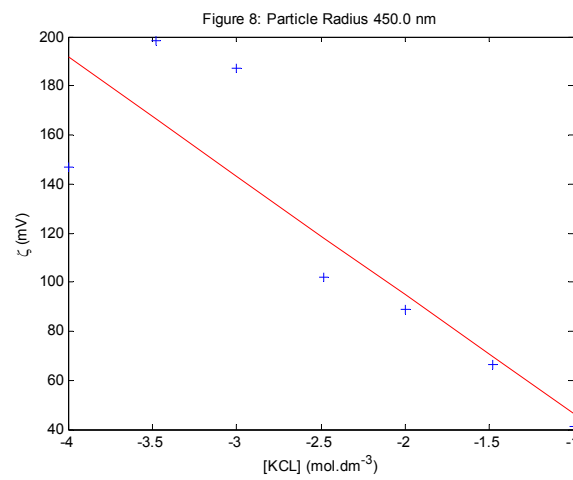
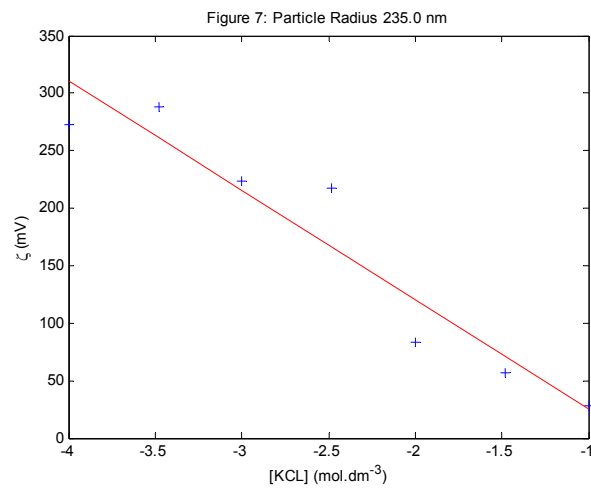
In this section we compare the model predictions of the theory using an immobile Stern layer with electrophoretic mobility data obtained from the literature. After all, if the standard electrokinetic model can adequately describe data, there is little justification for using a more complicated model requiring extra assumptions.

We first use the data of Midmore, Pratt and Herrington<sup>5</sup>, who reported linear plots of Zeta potential against ionic strength and three sizes of latex. They used O'Brien's closed form approximation rather than the full computer solution. We show the results of our fit in figure 2. As can be seen, the fits are linear with slopes approximating the Nernst constant : -53.5 , -51.9 and -59.9mV for the 1060, 378 and 692 nm lattices respectively.



Next we use the data of Borkevec, Behrens and Semmler<sup>6</sup>. They measured mobilities of 5 different sizes of latex with varying ionic strengths of electrolyte concentration. They reported that whilst the agreement between experiment and the standard electrokinetic model were acceptable for larger particles, for smaller particles the agreement was less satisfactory. We show the results of our calculations in figures 4,5,6,7,8, where we attempt to plot zeta potential against ionic strength. As can be seen, the results for the points of lowest ionic strength consistently fail to fit well (ie at concentrations less than 0.001 mol/dm<sup>3</sup>) for the smaller particles, and for the very smallest particle size the working concentration range was even less. It is interesting to note that in this was also reported and attributed to anomalous surface conduction<sup>3</sup>. Indeed, Borkevec et al themselves, speculated that the discrepancies they observed could be explained by surface conduction. Another problem, discussed by Herrington et al<sup>3</sup>, is the choice of which branch of the solution to use to obtain the solution and without any other information there is some degree of arbitrariness as to what points correspond to the 'correct' zeta potential. The general rationale has been where possible to use points which remove the maximum by taking the zeta potential from the upper branch. In the case of points low ionic strength, where they clearly do not form part of a trend, we do not include them in the fitting process.





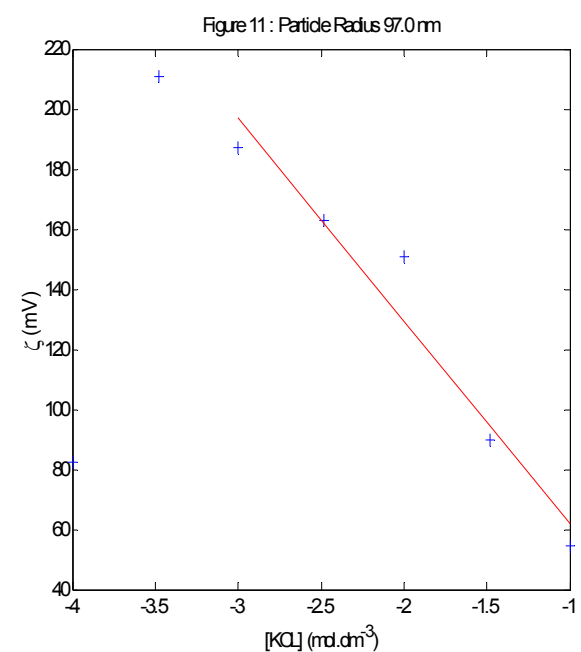
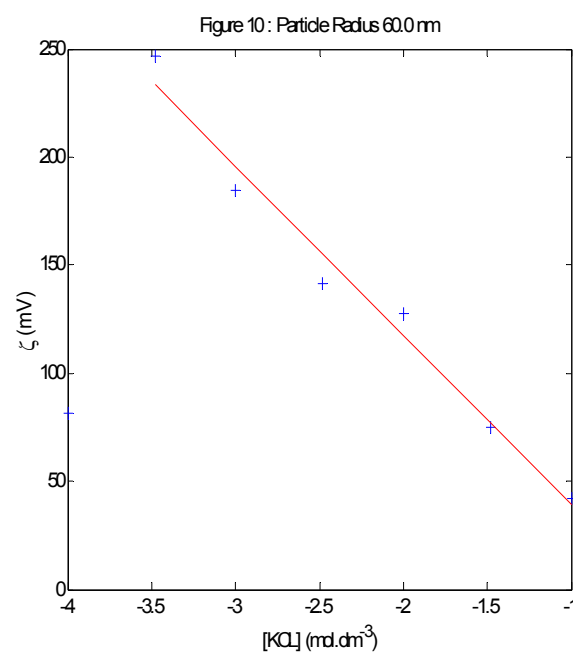
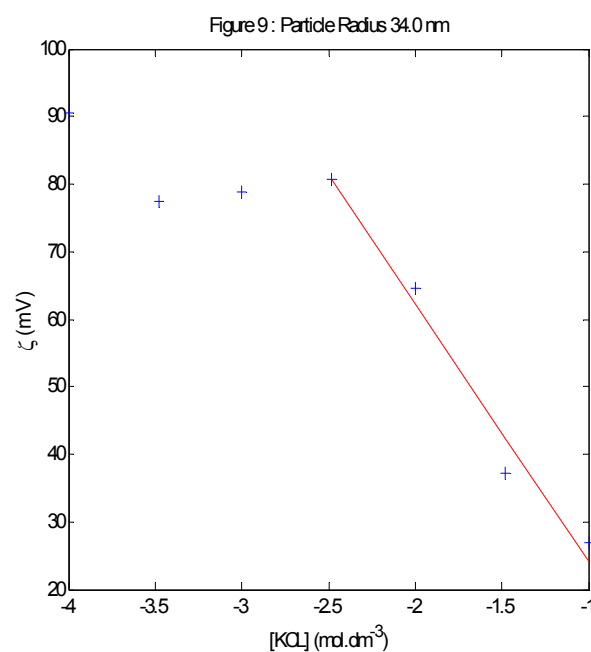
## Results: Dynamic Stern Layer

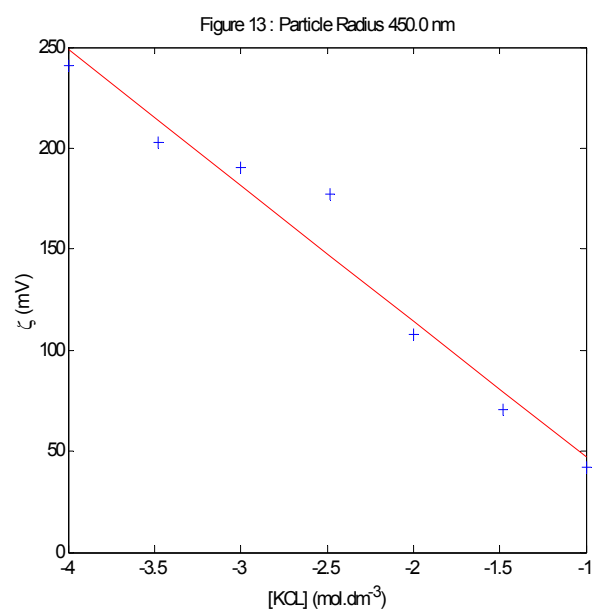
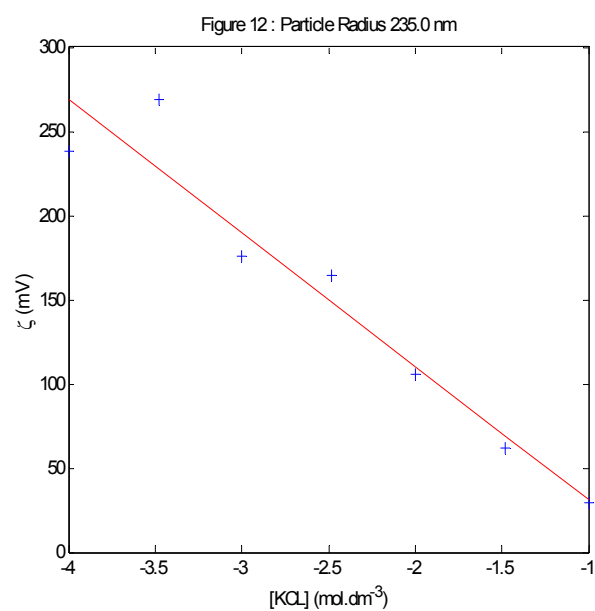
We now repeat our calculations using a Dynamic Stern layer model with the data of Borkevec et al. In view of the large number of parameters that must be specified we make the following assumptions:-

- Coion adsorption is relatively un-important:- the model is relatively insensitive to the corresponding Stern-layer parameters ( $eN_+$ ,  $\lambda_+$  and  $pK_+$ )<sup>4</sup>
- The mobility is insensitive to variations in the outer Stern-layer capacitance<sup>4</sup>
- The surface charge is fixed<sup>6</sup>

We found that to obtain a constant surface charge for all ionic strengths we had to use a value of  $pK_+$  of 2 or greater and that model was insensitive to the choice of  $pK_+$  in this range.

This leaves the choice of  $eN_+$  and  $\lambda_+$ . These two parameters appear in the model as a product – hence the mobility is independent of variations of either parameter provided their product remains invariant. To obtain the correct surface charge,  $eN_+$  was the key parameter, particularly with  $pK_+$  values we used, the Stern-layer charge became saturated at the zeta values we were working with. The rationale then, for the choice of these parameters was to find values which gave a surface charge independent of ionic strength and in agreement with values determined by conductometric titration, whilst giving a straight line on a zeta against ionic strength plot.





Finally we show the fitted Nernst slopes (with and without a Dynamic Stern layer), the fitted surface charge and the actual surface charge for the various lattices.

Radius (nm)	Nernst slope (mV) (DSL)	Nernst slope (mV)(SSL)	Cond. Charge (C/m <sup>2</sup> )	Fit. Charge (C/m <sup>2</sup> )
34	-38.2	-23.2	0.048	0.048
60	-78.3	-39.0	0.081	0.080
97	-67.7	-81.3	0.083	0.088
235	-79.4	-95.2	0.159	0.153
450	-67.3	-48.5	0.223	0.220

## Conclusion

The data of Borkevic et al demonstrated that whilst the standard electrokinetic model can describe electrophoretic mobility data quite creditably, there are instances where agreement breaks down. One tentative explanation given was that the discrepancies could be explained by surface conduction. We found that Dynamic Stern-layer extensions to the standard model could give agreement over a broad range of electrolyte concentrations and particle sizes. However for the smallest sizes at the lowest salt concentrations agreement appeared to break down, indicating that surface conduction did not provide a complete explanation. Moreover the number of extra parameters necessary make its use ambiguous and from a scientific point of view not entirely satisfactory. Nevertheless we believe that Dynamic Stern-layer models are a useful addition to the standard theory particularly if a number of transport properties can be measured and thus provide unambiguous inference of surface electrokinetic properties.

<sup>1</sup> R.W.O'Brien, L.R.White. J.Chem.Soc.,Faraday Trans. 2 1978, 77, 1607

<sup>2</sup> Zukoski, C.F;Saville, D.A. J.Colloid Interface Sci. 1985, 107, 322

<sup>3</sup> Midmore, B.R; Hunter, R.J. J.Colloid Interface Sci. 1988, 122, 521

<sup>4</sup> Mangelsdorf, C.S; White. L.R, J.Chem. Soc.,Faraday Trans. 1990, 86(16), 2870

<sup>5</sup> Midmore, B.R;Pratt, G.V; Herrington, T.M, J.Colloid Interface Sci. 1996, 184, 170

<sup>6</sup> Borkovec,M;Behrens,S.H; Semmler,M, Langmuir 2000, 16, 5209