The influence of Stern layer conductance on the dielectrophoretic behaviour of latex nanospheres

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Running title: Stern layer conductance in dielectrophoresis

Abstract:

The influence of the Stern layer conductance on the dielectrophoretic behaviour of sub-micrometre sized latex spheres is examined. The dielectrophoretic response of the particles is measured and analysed in terms of a model of surface conductance divided into discrete components related to the structure of the double layer. The effect of both co- and counter-ions in the bulk solution on the Stern layer conductance is demonstrated.

A polarisable particle suspended in a non-uniform electric field experiences a force due to the interaction of the field and the induced dipole moment. The resulting movement of the particle is referred to as Dielectrophoresis (1,2). The dielectrophoretic force is *positive* (particles attracted to regions of high field strength) or *negative* (particles repelled) when the particle is more or less polarisable than the medium respectively.

An example of dielectrophoresis is shown in figure 1, with fluorescent latex spheres suspended in KCl on a quadrupole electrode structure (3,4). At low frequencies, the spheres are attracted to regions of high field at the edges of electrodes and between adjacent electrodes. At high frequencies the particles are repelled to the local low field region at the centre of the electrode array (3).

This type of latex sphere, suspended in an electrolytic solution, undergoes a single interfacial relaxation process at a frequency related to the properties of particle and medium (2). The particles have a high surface charge density and therefore a polarisability greater than the aqueous suspending medium at low frequencies. As a result, the particles experience positive dielectrophoresis at low frequencies. At high frequencies the permittivity of the particle is significantly lower than that of water, the particles are therefore less polarisable and experience negative dielectrophoresis. The dielectrophoretic force changes sign at a characteristic frequency, generally referred to as the *crossover* frequency. Analysis of the crossover frequency as a function of medium conductivity can be used to characterise the polarisability and as a result the dielectric properties of a particle. This method of dielectrophoretic analysis has been demonstrated on sub-micrometre particles such as latex beads (5,6) and viruses (7-9).

Previous work (5,10) has showed that the dielectrophoretic behaviour of sub-micrometre latex spheres is dominated by the effects of charge movement across the particle surface. In this paper we demonstrate that conductance in the double layer is influenced not only by the movement of counterions at the particle surface, but also by the net mobilities of both counterions and coions in the bulk medium.

The dielectrophoretic force $\mathbf{F}_{DEP}$ acting on a homogeneous, isotropic dielectric sphere is given by (2):

$$\mathbf{F}_{DEP} = 2\pi r^3 \varepsilon_m Re[f_{CM}]\nabla|\mathbf{E}|^2 \qquad [1]$$

where a is the particle radius, ε_m is the permittivity of the suspending medium, $\mathbf{E}$ the local RMS electric field and $Re[f_{CM}]$ the real part of the Clausius-Mossotti factor, given by:

$$f_{CM} = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \qquad [2]$$

where ε_m^* and ε_p^* are the complex permittivities of the medium and particle respectively and a general complex permittivity is given by $\varepsilon^* = \varepsilon - i\sigma/\omega$, with ω the angular frequency of the applied field, σ the conductivity and ε the permittivity. This factor describes the frequency dependence of the dipole moment of the particle and the resulting dielectrophoretic behaviour of the particle.

Experimental measurement of the dielectrophoresis of colloidal latex particles has demonstrated that for very small particles (less than 500nm in diameter) the effective particle conductivity varies as a function of the medium conductivity (5,10). Recent work by Hughes et al. (10) has demonstrated that the effective conductivity of a latex particle can be described as the sum of three components: the bulk conductivity of the particle, σ_{pbulk} ; and surface components due to the movement of charge in the diffuse double layer (conductance K_s^d) and the Stern layer (conductance K_s^i). The total conductivity of the particle is then written as

$$\sigma_p = \sigma_{pbulk} + \frac{2K_s^i}{r} + \frac{2K_s^d}{r} \qquad [3]$$

For latex spheres, the bulk conductivity is negligible and the effective conductivity of the particle is dominated by the surface conductance. The conductance of the diffuse layer can be expressed as (11):

$$K_s^d = \frac{\left(4F^2cz^2D^d\left(1+3m/z^2\right)\right)}{RT\kappa}\left(\cosh\left[\frac{zF\zeta}{2RT}\right]-1\right) \qquad [4]$$

where D^d is the ion diffusion coefficient, z the valency of the counterion, F the Faraday constant, R the molar gas constant and T the temperature. κ is the reciprocal Debye length, given by $\kappa = \sqrt{\left(\frac{2czF^2}{\varepsilon RT}\right)}$,c is the electrolyte concentration (mol m^{-3}), and ζ is the electrostatic potential at the boundary of the slip plane. The

dimensionless parameter m describes the electroosmotic contribution to K_s^d and is given by (11)

$$m = \left(\frac{RT}{F}\right)^2 \frac{2\varepsilon_m}{3\eta D^d}$$ [5]

where η is the viscosity. In previous work (10) the conductance of the Stern layer was given by the expression:

$$K_s^i = u\mu_s^i$$ [6]

where u is the surface charge density and μ_s^i is the mobility of the counterion. However, analysis of experimental results using latex spheres suspended in different electrolytes with identical counterions but different coions (5), shows that equation [6] does not describe these experimental results correctly.

Returning to the definition of the Stern layer conductance, the Dukhin number Du (11) for a Stern layer containing one ion species i is given by

$$Du = \frac{u\mu_s^i}{2rz^i Fc^i \mu_m^i}$$ [7]

where μ_s^i and μ_m^i are the mobilities of the ion species in the Stern layer and bulk medium respectively. The Dukhin number describes the ratio between surface and bulk conductances and is given by (11)

$$Du = \frac{K_s^i}{r\sigma_m} \qquad\qquad [8]$$

where σ_m is the conductivity of the bulk electrolyte. Combining equations [7] and [8] and rearranging we obtain the following expression for K_s^i:

$$K_s^i = \frac{u\mu_s^i \sigma_m}{2z^i F c^i \mu_m^i} \qquad\qquad [9]$$

If the electrolyte is symmetrical, it is possible to replace the conductivity term and concentration c^i with molar conductivity Λ (S m^2 mol^{-1}):

$$K_s^i = \frac{u\mu_s^i \Lambda}{2z^i F \mu_m^i}. \qquad\qquad [10]$$

Values of Λ are constant for given electrolytes (a table of values is given by Bockris and Reddy (12)). Equation [10] reduces to [6] only if the values of the mobilities of the co- and counterion are equal, in which case the value of $\dfrac{\Lambda}{2z^i F \mu_m^i}$ goes to 1.

The validity of equation [10] was tested by measuring the dielectrophoretic crossover frequency for latex spheres in different electrolytes. The latex spheres (Molecular Probes, Oregon, USA) were 216nm in diameter and loaded with fluorescent dye. The suspending electrolytes were aqueous solutions of KCl and K_2HPO_4-KH_2PO_4 (a 50:50 mixture of monobasic and dibasic potassium phosphate) with conductivities in the

range 10^{-4} to 10^{-2} Sm^{-1}. The pH of the two solutions was measured at 6.5 and 7.1 for the KCl and K$_2$HPO$_4$-KH$_2$PO$_4$ respectively; since the pH of the media are similar, we assume that the number of dissociated carboxyl groups on the beads is similar for the beads in both media. The suspensions of particles were placed on microfabricated electrode structures energised using a signal generator (3-5). The particle movement was observed using a Photonic Science Coolview HS light-intensifying camera and a fluorescence microscope.

The crossover frequencies of the beads in the two media are shown in figure 2. Three key features are used in the best-fit analysis of undescribed homogeneous spheres; the value of the crossover frequency in low conductivity media, the gradient of the rise in crossover as a function of increasing medium conductivity, and the conductivity at which the crossover drops by a decade or more. However, where the internal properties of the particle are known and we are interested in determining the surface properties only, we are interested only in the crossover behaviour *below* the characteristic drop in conductivity. In this region, the dielectrophoretic behaviour is dictated by the surface charge density which determines the low-conductivity crossover, (or "y-intercept" in figure 2) and the ζ potential affects the apparent increase in particle conductivity with medium conductivity (the "slope" of the graph in figure 2). The conductivity at which the frequency drops is a factor of the two surface conductance components and provides no extra information; where the internal properties of the particle are known, we need only use two parameters – the y-intercept and slope – to determine the surface conductances by best-fit methods.

Best-fit lines of equation [1], using equations [3] and [4] to describe the particle conductivity are also shown. Relative permittivities for the suspending electrolyte and particle, of 78 and 2.55 respectively, were assumed. The best values were $K_s^i = 0.85nS$ ($\pm0.15nS$) and $\zeta = 110mV$ ($\pm5mV$) for KCl and $K_s^i = 1.25nS$ ($\pm0.1nS$) and $\zeta = 120mV$ ($\pm10mV$) for K_2HPO_4-KH_2PO_4. We can analyse these values to determine the validity of equation [10]. Since carboxylated beads are negatively charged, the ion species involved in surface conduction is K^+. We assume in modelling the data that the parameters for ζ–potential and K_s^i are constant over the range of conductivities studied; in reality, both will reduce slightly as conductivity is increased, but the magnitude of this change over the range of molarities of the electrolytes used should be relatively small (see [11] section 4.6e). For latex spheres suspended in KCl and K_2HPO_4-KH_2PO_4, equation [6] indicates that the Stern layer conductance is the same and that the influence of this conductance on the dielectrophoretic behaviour should also be the same. However, the best-fit values from the experimental data give the ratio between K_s^i in K_2HPO_4-KH_2PO_4 and KCl as 1.47.

If we now consider the definition of the Stern layer conductance given by equation [10], we would expect that the ratio between K_s^i in K_2HPO_4-KH_2PO_4 and KCl to be given by the ratio of the molar conductivities of the two electrolytes, all other factors being equal. The molar conductivities of K_2HPO_4-KH_2PO_4 and KCl are $21.2mSm^2mol^{-1}$ and $14mSm^2mol^{-1}$ respectively (12), giving an expected ratio between the Stern layer conductances of 1.51 in good agreement with the best fit values.

In order to ensure that the effect being observed is not merely the result of the variation in ion concentration for the two electrolytes, the crossover data was analysed

as a function of K$^+$ concentration rather than conductivity; this graph (not shown) demonstrates trends similar to the frequency-conductivity plot shown in figure 2, indicating that the observed effects are not due to the difference in K$^+$ concentrations in the two electrolytes.

Application of the same analysis to the data presented in Green and Morgan (5) for similar latex beads in solutions of KCl, NaCl and K2HPO4-KH2PO4 (not shown) indicates similar results to those presented here. This additional data indicates the same relationship between KCl and K2HPO4-KH2PO4 as described above i.e. matching gives different values for Ksi, for the same counterion but different coions. In addition, the data also indicates that NaCl also can be fitted using the arguments presented in this paper, i.e. that the values of Ksi for NaCl and KCl are similar, for the same counterion but different coions.

Measurement of the electrophoretic mobility of latex spheres of various sizes (5) demonstrated that the surface charge density of latex spheres is in the range 22-40mCm^{-2}, with 33mCm^{-1} falling within the tolerance range of all bead sizes. Considering the above experimental data for beads in KCl and the deduced values of K_s^i, it is possible to estimate the value of the Stern layer mobility. Consider the data for latex beads in KCl presented above. KCl has a molar conductivity of 14.1mSm^{2}mol^{-1} and the bulk mobility of the K$^+$ counterion is 7.69 x 10^{-8} m^{2}V^{-1}s^{-1}. Using these values with the estimated value for K_s^i, we calculate from equation [9] a value for ion mobility within the Stern layer of 2.73x10^{-8} m^{2}V^{-1}s^{-1}, or approximately 35% of the bulk ion mobility. This result is in keeping with Lyklema's assertion (11) that the mobility of counterions in the Stern layer should be "close to, or

somewhat lower than, the corresponding bulk values". If we calculate the value of

$K_s^i = u\mu_s^i$ using the above data we find μ_s^i of 2.575 x 10^{-8} $m^2v^{-1}s^{-1}$, i.e. the value of

$\dfrac{\Lambda}{2z^i F\mu_m^i}$ is approximately 0.95 and the approximation in equation 6 holds. This result

is important in that it demonstrates the mechanism by which the co-ion in solution

affects the Stern layer mobility, and hence the surface conductance, in line with

observed reslts.

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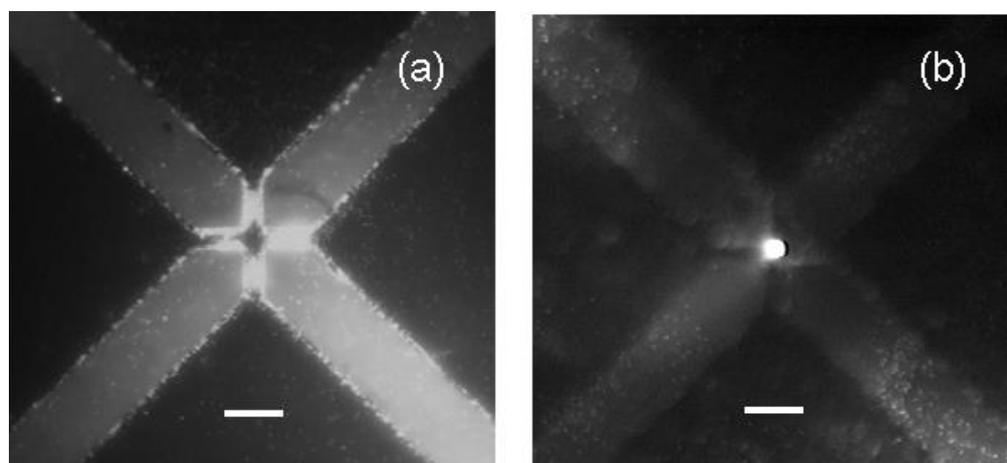
Figure Legends

Figure 1. Fluorescence micrographs showing positive and negative dielectrophoresis of 216nm diameter latex spheres. Four gold electrodes (visible as four bar-shaped, paler regions terminating in points) are energised such that opposing electrodes share the same phase, whilst adjacent electrodes are in antiphase. Figure 1a shows positive dielectrophoresis (particles attracted to regions of high electric field; that is, in the regions inbetween adjacent electrodes), which occurs at lower frequencies; figure 1b shows negative dielectrophoresis (repulsion from regions of high electric field, causing collection at a field null at the centre of the electrodes) which occurs at higher frequencies. The transition frequency between these modes of behaviour is called the crossover frequency, and is related to the dielectric properties of particle and medium. The beads were suspended in a $1mSm^{-1}$ KCl solution, at frequencies of 1MHz and 10MHz, and applied potential $5V_{pk-pk}$, respectively. Scale bar: 20μm.
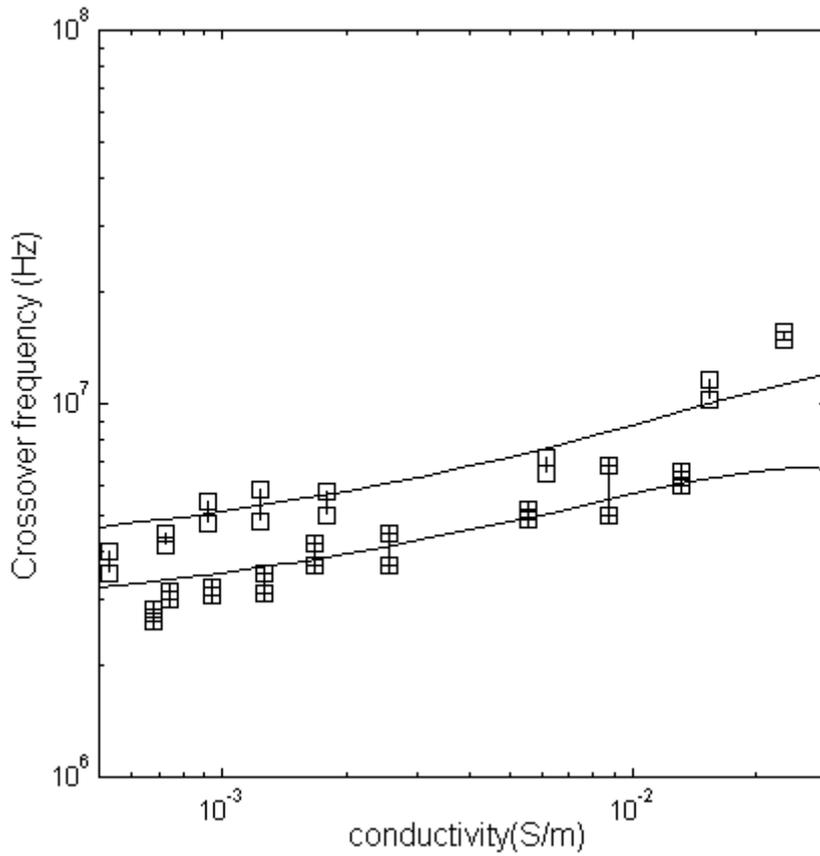
Figure 2. Experimental DEP crossover spectra for 216nm diameter latex beads. The vertical lines show the range of frequencies in which dielectrophoretic crossover was observed for beads suspended in KCl (filled squares) and K_2HPO_4-KH_2PO_4 (empty squares) solutions of varying conductivity. The diagonal curves indicate the best fit model to these data. The values for best fit indicate that the values of K_s^i and ζ are 0.85nS and 100mV for the beads suspended in KCl, and 1.25nS and 120mV in K_2HPO_4-KH_2PO_4 respectively. In both cases the bead permittivity was $2.25\varepsilon_0$ and internal conductivity was negligible.