Dielectrophoresis of Submicrometer Latex Spheres. 1. Experimental Results

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A nonuniform electric field exerts a force on a polarizable particle through the Coulomb interaction with the electric dipole induced in the particle, resulting in a motion termed dielectrophoresis. The magnitude of the force depends on the dielectric properties of both the particle and the medium it is suspended in. As a result, measurement of the dielectrophoretic force provides information about the internal and surface dielectric properties of the particle. This paper presents the first detailed measurements of the dielectrophoretic response of submicrometer particles as a function of electrolyte composition and conductivity, applied field frequency, and particle size. Comparisons are made between the experimental results and the classical theory of the dielectrophoretic force derived from Maxwell–Wagner interfacial polarization. For particles of 557 nm diameter, good agreement is obtained between the experimental results and theory of interfacial polarization taking into account the effects of surface conductance. However, the results for smaller sizes of particle (93, 216, and 282 nm diameter) demonstrate that the theory does not adequately explain the dielectric or dielectrophoretic behavior of colloidal particles. The existence of a second low-frequency dispersion is also apparent in the data, attributable to the polarization of the double layer. The data were compared with a theoretical plot generated by modeling the dispersion in terms of a single Debye relaxation.

1. Introduction

Dielectrophoresis (DEP) can be used as a means of analyzing the dielectric properties of single particles. While much effort has been directed at measuring the properties of particles larger than a few micrometers in diameter, there is little data on colloidal particles. The ability to move and study submicrometer particles by dielectrophoresis is now an established fact. While the effects of Brownian motion on these particles. However, the underlying physical mechanisms that govern the dielectric properties of single particles remain to be explored in detail. Accordingly, we have investigated the dielectrophoretic properties of single submicrometer latex particles over a wide range of applied electric field frequencies and electrolyte compositions and concentrations. In part 1 of this paper, we present detailed experimental results and preliminary examinations of the data in light of the Maxwell–Wagner interfacial polarization mechanism as well as the lower frequency relaxation associated with the electrical double layer.

2. Dielectric Theory of an Interface

A dielectric particle suspended in a dielectric medium polarizes following the application of an electric field. The polarization of the interface between the two dielectrics creates an effective dipole moment in the particle. As is the case for all polarization mechanisms, the interfacial mechanism has an associated relaxation time generally referred to as the Maxwell–Wagner relaxation frequency or \( \beta \)-dispersion. For the particular case of linear, isotropic dielectrics and a spherical particle, the effective dipole moment \( \mathbf{m} \) is given by

\[
\mathbf{m} = 4\pi a^3 \varepsilon_\text{sp} \varepsilon_0 \mathbf{E}
\]  

where \( a \) is the radius of the particle, \( \varepsilon_\text{sp} \) is the permittivity of the medium, and \( \mathbf{E} \) is the electric field. The factor \( f_\text{CM} \) represents the frequency dependence of the effective polarizability of the particle (the Clausius–Mossotti factor), given by

\[
f_\text{CM} = \frac{\varepsilon_\text{p} - \varepsilon_\text{m}}{\varepsilon_\text{p} - 2\varepsilon_\text{m}}
\]

where \( \varepsilon \) indicates a complex permittivity given by \( \varepsilon = \varepsilon - i\sigma /\omega \) where \( \varepsilon \) is the permittivity, \( K \) is the conductivity, \( \omega \) is the frequency of the electric field, and \( i = (-1)^{1/2} \). The subscripts \( m \) and \( p \) refer to the suspending medium and particle, respectively. The magnitude of this complex factor varies with the applied field frequency, and an example of the variation of the real part is shown in Figure 1. In calculating this plot, the following parameters were used: \( \sigma_\text{m} = 2.55, \varepsilon_\text{m} = 78.5, K_\text{m} = 0.01 \text{ S/m and } K_\text{p} = 0.001 \text{ S/m.} \) For a single interface system, there is a single relaxation with a relaxation time that depends on the combined dielectric properties of the medium and the particle. This relaxation time is given by

\[
\tau_\beta = \frac{\varepsilon_\text{p} + 2\varepsilon_\text{m}}{K_\text{p} + 2K_\text{m}}
\]

In a nonuniform electric field, a force is exerted on the dipole moment of the particle giving rise to movement referred to as dielectrophoresis (DEP). If the field is not very nonuniform, the time-averaged dielectrophoretic force \( F_\text{dep} \) is given by the equation

\[
F_\text{dep} = \text{Re}(\mathbf{m} \cdot \nabla \mathbf{E})
\]

For a dielectric sphere with the properties outlined above and in low-frequency ac electric fields (\(<10^6 \text{ Hz})\), the Clausius–Mossotti factor is positive and the force acts to move the particle.
to regions of high field strength. At high frequencies (>10⁶ Hz), the Clausius–Mossotti factor is negative and the particle moves toward regions of low field strength; see Figure 1. The movement is referred to as positive and negative dielectrophoresis, respectively.

The surface charge density of a particle has been shown to be important in governing its behavior, and the effects on the dielectrophoretic properties of particles are discussed in detail in ref 1. Although latex has a low intrinsic conductivity, dielectric measurements have demonstrated that the measured value of the particle conductivity is high. Researchers in the field attributed the anomaly to the presence of a surface conductance component caused by the movement of counterions to the surface charge on the particle. For a sphere with a uniform surface charge density, \( \lambda \), and associated counterion mobility \( \mu \), O’Konski defined the surface conductance as

\[
\lambda = \sigma \mu
\]

and derived the following expression for the total particle conductivity:

\[
K_p = K_{\text{int}} + \frac{2\lambda}{a} \tag{6}
\]

where \( K_{\text{int}} \) is the internal particle conductivity and the last term in this expression is the surface conductivity. The presence of this extra component of conductivity increases the Maxwell–Wagner relaxation frequency without introducing an extra dispersion.

Dielectric measurements also indicate that there is a dispersion at frequencies lower than the Maxwell–Wagner, with its origin also attributed to a surface charge effect. This second polarization mechanism involves changes in the charge density of the electrical double layer generated by the surface potential of the particle. The relaxation of this polarization mechanism, called the \( \alpha \)-relaxation, occurs at a frequency that is proportional to the particle radius squared.

Accurate measurement of the dielectrophoretic force is difficult to achieve for colloidal particles owing to the effects of Brownian motion and electrically induced fluid flow. The presence of the \( \alpha \)-relaxation at low frequencies also complicates simple analysis of the system. Comparatively, the measurement of the frequency at which the dielectrophoretic force is zero or the “crossover point” is simple and can provide information about the internal and surface dielectric properties of the particle. The crossover point is defined to be the frequency at which \( \text{Re}((\varepsilon_p - \varepsilon_m)(\varepsilon_p + 2\varepsilon_m)) = 0 \), where \( \text{Re} \) indicates the real part.

Figure 2 shows plots of the variation of crossover frequency with electrolyte conductivity where the dielectric properties of the particle have been varied as indicated on the figure. The crossover point was numerically calculated from the Clausius–Mossotti factor using a simple binary search algorithm. It can be seen from Figure 2a that varying the particle permittivity (with constant particle conductivity) produces a shift in the crossover frequency across the entire electrolyte conductivity range, but the transition conductivity above which only negative DEP occurs remains unaltered. The effect of changing the
The SEM analysis showed that the samples were uncontaminated and that the variation in size of the spheres was within the uncertainty quoted by the manufacturer. The surface charge density of the spheres was determined using a Coulter \( \zeta \) potential analyzer to measure the particle mobility. This was related to the \( \zeta \) potential using the Helmholtz–Smoluchowski equation, and the surface charge density was calculated by applying the Gouy–Chapman/Grahame theory of the double layer. 5,18

3. Experimental Section

Electrolytes for the dielectrophoresis experiments were made from three different salts: potassium chloride (KCl), sodium chloride (NaCl), and potassium phosphate buffer, pH 7.2 (KPO4). The salt used most frequently in the literature for dielectric measurements is potassium chloride (KCl), a symmetrical electrolyte, both in terms of charge (the two ions have equal valency) and in terms of mobility (the potassium ion and the chloride ion have less than a 4% difference in mobility). The other two salts were used in order to determine the effect on the DEP properties of the particles of altering the mobility of either ion in solution. Fluorescent latex spheres (Molecular Probes, Eugene, Oregon) were supplied in a 2 mM azide solution, in sealed containers to prevent contamination. Four sizes of sphere were used in the experiments, with diameters of 557, 282, 216, and 93 nm and were supplied carboxylate-modified with a high net negative charge at neutral pH. Samples were prepared by diluting the manufacturer’s supplied solution either 1:1000 or 1:10000 in each salt solution.

Dielectrophoretic measurements were performed on hyperbolic polynomial electrodes6–7,21,22 with the center separation varying from 5–50 \( \mu \)m and with a range of applied voltages from 1 to 10 V peak-to-peak provided by analogue or digitally synthesized signal generators.

4. Results

4.1. Size and surface charge measurements. Samples of the spheres were placed on silicon wafers, dried, sputter-coated with metal, and imaged by scanning electron microscopy to determine both if the solutions were contaminated and to check the manufacturer’s data on sphere size. Figure 3 shows an SEM of 557 nm diameter spheres forming close-packed structures. The SEM analysis showed that the samples were uncontaminated and that the variation in size of the spheres was within

Figure 4. Plot of the electric field magnitude in a plane 100 nm above the surface of a 50 \( \mu \)m diagonal gap polynomial electrode, with an applied potential of 10 V peak-to-peak between adjacent electrodes. The highest field regions (3 \( \times \) \( 10^6 \) V/m) are found along the electrode edges. In the center of the electrode array, there is a low-field region surrounded by high-field regions that acts as a negative dielectrophoretic potential-energy minimum.
the electrodes are noticeably curved, were repelled from the electrode edge into the center of the array. After 9 s, the spheres collected at the center of the array (Figure 5d). Figure 5b–d clearly shows that spheres at the edge of the image, where the electrode edges are almost parallel, moved upward and away from the electrodes rather than into the center. For both cases of positive and negative DEP, the trapped spheres remained in position as long as the electric field was maintained at the same frequency and potential.

As a result of the high electric fields required to produce discernible movement of the particles, heat is dissipated in the electrolyte. In certain circumstances, this gives rise to fluid motion that can affect the particle trajectory.\(^5,20\) Under the experimental conditions used in this work, fluid flow was not significant. When present, detailed observation of the patterns of particle movement could be used to clearly distinguish fluid-driven from DEP-driven particle motion.

4.4. Crossover Measurements. To characterize the dielectric properties of the latex spheres, the crossover frequency of individual particles in a low-volume fraction suspension was measured. This was determined by measuring the range of frequencies over which no dielectrophoretic response of either type was observed. Typically 15–20 particles were analyzed for each conductivity; each point plotted on the figures represents the average of two to six separate measurements using different electrodes. The error in the measurements was less than 1%, and the bars shown in the figures represent the frequency range over which no dielectrophoretic response was observed. The data points without error bars represent the highest frequency at which positive DEP was observed in the case of electrolytes in which no negative DEP was observed. No variation in the mean crossover frequency was observed with voltage, although the frequency range was longer for lower voltages. For conductivities less than \(10^{-2}\) S/m and for high electric fields, fluid flow was observed for frequencies below 10–50 kHz. However, the dielectrophoretic behavior of the particle could be analyzed in the presence of fluid flow, since the flow patterns were distinct and different from particle behavior induced by DEP. This was also the case for higher electrolyte conductivities at frequencies up to 0.5 MHz.

Figure 6a–d shows the variation in crossover frequency with electrolyte conductivity for 557, 282, 216, and 93 nm diameter latex spheres in KCl (pH 6.2–6.6) with conductivities varying from \(2.88 \times 10^{-4}\) to 3.39 S/m. It can be seen from Figure 6a that the crossover frequency from positive to negative DEP remains constant with electrolyte conductivity up to a transition conductivity (which varies with particle diameter) and drops rapidly over a narrow range of conductivities. This is precisely the behavior expected from a particle exhibiting a single Maxwell–Wagner interfacial relaxation (see Figure 2).

Figures 7a–d and 8a–d show the variation in crossover frequencies for the four sizes of sphere for NaCl and KPO\(_4\), respectively. The conductivity of the NaCl solutions (Figure 7) was varied from \(2.69 \times 10^{-3}\) to 1.09 S/m, and the conductivity of the KPO\(_4\), pH 7.2, (Figure 8) was varied from \(4.27 \times 10^{-4}\) to 1.07 S/m. The crossover frequency—conductivity trends are similar to that shown in Figure 6a–d.

5. Discussion

Each of the figures shows that the particle behavior in nonuniform electric fields conforms in some aspects to theoretical expectations. In general, at low frequencies (down to 10 kHz), particles experience positive DEP, while at high frequencies (up to the maximum measured of 20 MHz) they experience negative DEP. This is consistent with previous observations on the DEP properties of submicrometer latex spheres.\(^5,6\) At low...
electrolyte conductivities and for all of the particles, a crossover frequency in the 1–10 MHz range was observed, which increased with decreasing particle size. As the electrolyte conductivity was increased, the crossover remained relatively constant until, at a value of \( K_m \) around 10\(^{-2}\) S/m, the crossover frequency dropped to the 100 kHz-1 MHz range.

**Interfacial Polarization (\( \beta \)-Dispersion) for Large Particles (557 nm Diameter).** For all three electrolytes, at low conductivities, the 557 nm spheres exhibit behavior consistent with that expected from Maxwell–Wagner theory (Figure 2). The crossover frequency remains constant at 1.5–1.7 MHz, up to a conductivity of approximately 10\(^{-2}\) S/m and then falls at the transition point to a value in the range 10\(^5\) to 5 \times 10^5 Hz. The low conductivity behavior can be matched to the Maxwell–Wagner theory to give values for the particle permittivity and conductivity. Figure 9 shows that the closest theoretical fit to the experimental data (at low electrolyte conductivities) for the 557 nm spheres in KCl gives a value of particle conductivity of \( K_p = 10 \pm 2 \) mS/m. For all the samples, the bulk value of the relative permittivity of latex (\( \varepsilon_p = 2.55 \)) was used. In this plot, the limits of the crossover range are represented by crosses and squares.

For NaCl and KPO₄, best fits were obtained with \( K_p = 8.4 \pm 0.6 \) mS/m and 10 \pm 1 \) mS/m, respectively. The variation in the calculated value is due to the range of frequencies over which the DEP force is too small to produce observable movement. The variation in \( K_p \) was greater than our estimate of experimental error and could be reduced by increasing the DEP force (but this increases fluid flow).

The dielectric response of this size of sphere is largely dominated by surface conductance. Since the value of \( K_p \) is the same for KPO₄ and KCl, the positive ion must be responsible for the surface conductance. The difference between the response for KCl and NaCl can therefore be attributed to the difference in the mobility of the potassium and sodium ions. Assuming that the internal conductivity of the particles is the same in both salt solutions, then using the bulk values for the mobility of the ions [\( \mu_K = 7.69 \times 10^{-8} \) m\(^2\)/(V s), \( \mu_{Na} = 5.24 \times 10^{-8} \) m\(^2\)/(V s)] and adding a scaling factor, \( A \), to eq 6 gives

\[
K_p = K_{in} + \frac{2\sigma a}{a} 
\]

From this equation, the values of \( K_{in} \) and \( \sigma \) can be calculated,
using the values of $K_p$ for KCl and NaCl. The results of this calculation give $K_{int} = 5 \text{ mS/m}$ (which is approximately half of the total particle conductivity) and $\sigma = 9 \text{ mC/m}^2$ (with $A$ set to 1). The measured value for the surface charge density for these particles was $\sigma = 38 \pm 5 \text{ mC/m}^2$, with the uncertainty arising from a spread in the particle mobility rather than experimental error. Substituting this value of $\sigma$ in eq 7 with the bulk value of mobility, gives $A = 0.24$. This implies that, in this simple model, either the surface charge density of counterions (i.e., the surface conductance component) is less than that measured for the particle or that the mobility of the counterions close to the surface is approximately a quarter of the bulk value.

Interfacial Polarization for Particles of 93–282 nm Diameter. The results for the 282 and 216 nm diameter latex spheres show slight deviations from the expected behavior; the crossover frequency is constant with electrolyte conductivity up to a certain value, as expected, but then rises slightly before decreasing sharply. This effect is not observed for the 557 nm spheres (although probably present) and dominates the behavior of the 93 nm spheres (Figures 6d, 7d, and 8d). This size of sphere has a crossover frequency that is constant over a narrow range of conductivity, then rises continually with electrolyte conductivity.

For the 282 nm spheres, the five lowest data points can be matched to theory with $K_p = 17 \pm 2.5 \text{ mS/m}$, for KCl, $15.5 \pm 2.5 \text{ mS/m}$, for NaCl, and $17.5 \pm 1.5 \text{ mS/m}$, for KPO$_4$. As an example the best fit for the KCl results is shown in Figure 10. A theoretical curve could be fitted to the data for $K_m < 5 \text{ mS/m}$ to give $K_p = 17 \text{ mS/m}$. Figure 10 also shows that the theoretical response with $K_p = 35 \text{ mS/m}$ accurately matches the data points for electrolyte conductivities in the range 15–40 mS/m. Over the range 5–15 mS/m, the crossover frequency increases with $K_m$, a trend that can be seen in the results for the other salts (Figures 7b and 8b). The data for KPO$_4$ can be satisfactorily fitted to theory in the region of the transition point with $K_p = 37 \text{ mS/m}$ (Figure 8b), but the results for NaCl are obscured by the presence of the $\alpha$-relaxation (Figure 7b).

The data for the 216 nm spheres can be analyzed in a similar manner to give values for the low $K_m$ regime of $K_p = 17 \pm 3 \text{ mS/m}$, for KCl, $18.5 \pm 2.5 \text{ mS/m}$, for NaCl, and $20 \pm 3 \text{ mS/m}$, for KPO$_4$. The data points around the transition point
after the rise in crossover frequency can be matched with $K_0 = 45 \pm 5 \text{ mS/m}$, for KCl, $42 \pm 2 \text{ mS/m}$, for NaCl, and $45 \pm 5 \text{ mS/m}$, for KPO$_4$.

There are three possible explanations for the increasing crossover frequency. The first is that, in O’Konski’s theory, the surface conductance arises from the counterions present at the interface. In the derivation of the expression given by eq 6, the counterion density is assumed to be equal to the surface charge density of the particle. This is probably true for the case of a particle with a radius substantially greater than the thickness of the double layer (the Debye length, $\kappa^{-1}$), i.e., thin double layer with $\kappa a \gg 1$. Where this condition does not hold, the total excess charge in the whole double layer is equal to the surface charge density of the particle and, therefore, the counterion density close to the particle surface is smaller. As a result, in cases where the double layer is not thin, the surface conductance may depend on the Debye length.

The second hypothesis concerns the formation time of the double layer. In cases where O’Konski’s theory holds, the frequency of the electric field may be so high that there is insufficient time per cycle for the charge to redistribute and form the double layer. The formation time is given by $\tau = \sigma \epsilon$, implying that the surface conductance should depend on the electrolyte conductivity, as considered by O’Brien. The third explanation concerns the electrical potential across the bound component of the double layer, sometimes referred to as the Stern layer. In low-conductivity solutions, where the Debye length is of the order of 10 nm or greater, the drop in potential across the bound layer is quite large. In concentrated salt solutions, the potential drop across the bound layer is low and the potential at the slip plane (outside the bound layer) is relatively high. For the highly charged spheres, there will be a permanent bound layer of charge at the surface and any perturbations to this layer will occur much faster than $\tau$. As a result, the Maxwell–Wagner theory, which considers the polarization of a particle through calculation of the potential

Figure 8. Graph of the experimentally determined crossover frequency as a function of medium conductivity for different diameter latex spheres in KPO$_4$. Parts a and b show the results for 557 nm and 282 nm diameter spheres. Positive DEP was observed at frequencies below the points and negative DEP above. In the range of frequencies represented by the bars, no DEP was observed for the points below 100 mS/m and both types of DEP were observed for the four points above 100 mS/m. The results for the 216 nm diameter spheres are shown in part c, and in this case, no DEP was observed in the range of frequencies represented by the bars below 200 mS/m and both types of DEP were observed for medium conductivity above 200 mS/m. Again, positive DEP occurred at frequencies above the points and negative DEP below. The results for the 93 nm diameter spheres are shown in part d, where positive DEP was observed below the points and negative DEP was observed at frequencies above the points for medium conductivities below approximately 50 mS/m. In the range of frequencies represented by the bars, both types of DEP were observed and, for medium conductivities above 50 mS/m, only positive DEP was observed, with the maximum frequency of observation represented by a cross.
at, or electric field across, the interface, should be modified to include this intermediate layer.

The results for the 93 nm diameter spheres show that there is a range of electrolyte conductivities, from $10^{-3}$ to 10 S/m over which the crossover frequency increases almost a decade for KCl (Figure 6d). For KPO$_4$ (Figure 8d), it can clearly be seen that there is still a range of conductivities where the crossover frequency, and therefore $K_p$ is constant, occurring at a low value of $K_m$ (Figures 6d, 7d, and 8d). Best fits to the data at low conductivities give $K_p = 32 \pm 6$ mS/m, for KCl, 35 $\pm$ 3 mS/m, for NaCl, and 48 $\pm$ 4 mS/m, for KPO$_4$. Figure 11 shows the cross over frequencies for KCl and KPO$_4$ superimposed on the same two axis plane. This figure indicates that in the conductivity region between $10^{-3}$ and $2 \times 10^{-1}$ S/m, where the crossover frequency increases, the data lie along the same line, even though the low $K_m$ data give different values for $K_p$.

$K_p = K_{int} + (A_1 + A_2 \alpha) \frac{2\sigma_n}{\alpha}$

(8)

This expression includes an additional component of surface conductance that is inversely proportional to the double layer thickness. Figure 12 shows the theoretical line for the 93 nm spheres calculated using this equation, with $K_{int} = 0$, $(2\sigma_n/\alpha) = 32$ mS/m, $A_1 = 0.2$, and $A_2 = 0.1$. In this case, a nonzero value for $K_{int}$ cannot be calculated using eq 7, since the ideal interfacial relaxation model does not fit these sizes of particles. The modification to eq 7 successfully accounts for the increase in crossover frequency with $K_m$, with the slope of the line matching the experimental data. This expression can also be used to fit the data for the larger sizes but with different scaling factors.

Table 1 summarizes the values of $K_p$ for the best fit to the conductivity data where the crossover frequency is constant. The surface charge densities marked as “experimental” were

![Figure 9](image9.png)

**Figure 9.** Plot showing the best fit to the experimental data for 557 nm diameter spheres in KCl, from eq 2, with the following parameters for the particle: $K_p = 10$ mS/m, $\epsilon_p = 2.55$, and $\epsilon_m = 78.4$. The symbols represent the plot of the outer limits of the crossover range: (×) point up to which only positive DEP was observed; (□) point above which only negative DEP was observed.

![Figure 10](image10.png)

**Figure 10.** A plot showing the best fit to the experimental data for 282 nm diameter spheres in KCl, from eq 2, with the following parameters for the particle: $\epsilon_p = 2.55$, $\epsilon_m = 78.4$, and $K_p = 17$ mS/m or $K_p = 35$ mS/m. The symbols represent the plot of the outer limits of the crossover range: (×) point up to which only positive DEP was observed; (□) point above which only negative DEP was observed.

![Figure 11](image11.png)

**Figure 11.** Mean crossover frequency from Figures 6d (□) and 8d (○) superimposed on the same two-axis plane.

![Figure 12](image12.png)

**Figure 12.** Plot showing the best fit to the experimental data for 93 nm diameter spheres in KCl, from eq 8, with the following parameters for the particle: $\epsilon_p = 2.55$, $\epsilon_m = 78.4$, $K_{int} = 0$, $(2\sigma_n/\alpha) = 32$ mS/m, $A_1 = 0.2$, and $A_2 = 0.1$. The increase in $K_p$ with $K_m$ indicated by the data for the smaller particle sizes can be incorporated into the model of Maxwell—Wagner polarization. Modifying eq 6 to include a term proportional to the ratio of the particle radius to the Debye length gives
calculated from $K_p$ using the bulk value for ion mobility and assuming that the particle conductivity arises solely from surface conductance. The values marked as “measured” were determined from the Coulter particle analyzer. The values for $K_p$ indicate that, for the largest size of sphere, the surface conductance arises from movement of the positive ion near the interface as proposed by O’Konski. For the smaller sizes of spheres, less can be inferred about the mechanism involved except that the effect of the negative ion (co-ion) in the electrolyte appears to have an effect for these sizes. This has not been demonstrated in such a clear and concise experiment previously.

**Low-Frequency Double Layer Relaxation ($\alpha$-Relaxation).**

At high electrolyte conductivity, the crossover data for all particles indicates the presence of a second dispersion at frequencies below the $\beta$-relaxation, due to the relaxation of the double layer (the $\alpha$-relaxation). Using ac impedance methods, this relaxation has been observed for a wide range of particles from cells to latex spheres. The origin of this dispersion is polarization of the double layer charge, either radially or tangential to the particle.\(^{17,18,26–35}\) Whereas much of the published solution-phase dielectric data can be explained in terms of this model, our data on the dielectrophoretic spectrum of single particles cannot. To a first approximation, an empirical fit to the data can be attempted by adding a second independent Debye relaxation of the form $1/(1 + i\omega\tau_a)$, with the time constant of the relaxation given by $\tau_a = a^2/2D$ or $\tau_a = a^2/2DM$, where $D$ is the ion diffusion constant and $M$ is the electroosmotic contribution to the ion flux of the double layer given by $M = 1 + ((F\circ)\tau_{CD})$.\(^{6,29,30}\) The differential capacitance is given by $C_d = \varepsilon_{ik} \kappa \cosh((F\circ)/(2RT))$ where $\zeta$ is the $\zeta$ potential.\(^{29}\) Using the bulk values for the ion mobilities and the measured values of $\zeta$ potentials, the theoretical crossover frequencies for the 282 and 557 nm spheres in KCl are shown in Figure 13. As can be seen, the fit to the data for the case with the electroosmotic flow is better than that where this component is neglected. However, the predicted response clearly does not match the experimental data and a fuller explanation for the double layer polarization mechanism for a single particle is called for.

6. Conclusion

This paper demonstrates that measurements of the dielectrophoretic behavior of single submicrometer latex particles can be used to uniquely characterize their dielectric properties. By measuring the crossover frequency at which the dielectrophoretic force is zero as a function of medium conductivity, we have shown that the dielectric spectrum of a latex particle has two characteristic dispersions. These are related to the well-known $\beta$-dispersion, due to interfacial polarization mechanisms (Maxwell—Wagner polarization), and the $\alpha$-relaxation, which has its origins in the polarization of the double layer surrounding the particle. For larger sizes of particles (~557 nm diameter), reasonable agreement is obtained between the experimental data and the classical theory of interfacial polarization including surface conductance. The $\alpha$-relaxation appears in these data as a crossover at lower frequencies in higher medium conductivities. For the smaller sizes of particles, there is a deviation from the predicted response and the size of the deviation increases with decreasing particle size.

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**References and Notes**