Modeling of Electrohydrodynamic Flow Around a Single Particle on an Electrode with Alternating Current

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An approximate model for the velocity due to electrohydrodynamic flow of electrolyte in the vicinity of a dielectric sphere near an electrode is described. The model considers the interaction of a lateral electric field, caused by the presence of the sphere, with free charge produced in the diffusion layer near an electrode when alternating current is passed through it. An equation based on the model predicts that adjacent dielectric particles aggregate or separate depending on the relative magnitude of the individual ionic conductivities and the frequency of oscillation in the case of a binary electrolyte. If the anion reacts and its conductance exceeds the cation conductance, the particles repel each other; the particles aggregate if the reverse is true. The equation also predicts that separation or aggregation depends on frequency of oscillation of the current. The model accounts for observed effects of frequency and particle size found in the literature. Finally, a dimensionless group that places a constraint on the frequency at which electroneutrality remains a good assumption for calculating electrohydrodynamic flow in oscillating systems is derived.

The electrohydrodynamic response of electrolyte in the vicinity of a dielectric particle on an electrode is a complex phenomenon with strong frequency-dependent effects. The first insight afforded by this model is the effect of frequency. Frequency governs the relationship between the diffusion layer thickness and the particle size as expressed by the dimensionless ratio $\delta^* = (D/\omega a^2)^{1/2}$. D is the binary electrolyte diffusivity, w is the frequency of hte alternating current, and a is the particle radius. Values of $\delta^* >> 1$ mean that the particle is well within the diffusion layer where the electric field surrounding the particle can interact with the laplacian of the concentration. $\delta^* << 1$ means that most of the particle is outside the region of concentration variation. Furthermore, frequency governs the distribution of current between the double layer capacitance and the faradaic reaction, depending on $\Gamma^* = \omega R_{ct} C_{dl}$. R_{ct} and C_{dl} are the charge transfer resistance and double layer capacitance of the electrode's equivalent circuit consisting of linear elements. If $\Gamma^*>>1$, most of the current goes through the capacitance rather than through the faradaic reaction, and *vice versa*.

Comprehending the interplay between these two parameters is the key to understanding the electrohydrodynamic effects:

• If $\delta^* >> 1$ and $\Gamma^* << 1$ at a particular frequency, the direction of flow is in the primary direction set, as discussed below, by the parameter $\hat{t}$. In this case the magnitude of the charge imbalance increases with the square root of frequency because the diffusion layer shrinks toward the particle diameter as the frequency is increased. The force density distribution in the vicinity of the particle is relatively constant under these conditions.

• If $\delta^* << 1$ and $\Gamma^* << 1$, the direction of flow remains the same, but the velocity is reduced because the diffusion layer is confined to a range much smaller than the particle diameter and the free charge is proportional to the inverse square root of frequency.

• If $\delta^* >> 1$ and $\Gamma^* >> 1$ much of the total current goes through the capacitance and hence the concentration effects are reduced so the velocities are lower. The overall flow is still negative.

• If $\delta^* << 1$ and $\Gamma^* >> 1$, the combination of a small diffusion layer and a shift of current to the capacitance of the double layer causes substantial positive force density to appear, enough so that the overall flow reverses.

The second insight is the effect of particle size on the observed behavior. Higher electric fields are necessary for smaller particles and that two observers could come to different conclusions about aggregation and repulsion of particles at low frequency if one is using relatively large or small particles. At frequencies below 100 Hz particles 1 μm in radius separate while particles 5 μm in radius strongly aggregate. This effect again points out the complex interaction of the particle size, the electrical behavior, and the mass transfer.

A model for electrohydrodynamic flow near a dielectric sphere on an electrode undergoing ac polarization accounts for several disparate observations in the literature. The decrease of velocity and even flow reversal with increasing frequency are a result of the complicated interplay of the thickness of the diffusion layer with the particle size and the electrodics of the system. The primary direction of flow depends on the transport properties of the electrolyte and the details of the electrode reaction. Specific issues to be investigated are:

1. The predictions should be independent of particle charge.
2. The strength of the effects should be proportional to the square of the electric field.
3. One should observe reversal of flow upon a suitable change of counterion if the reacting species remains the same.
4. Particle size is a key parameter. Perhaps the best chance to observe the maximum in velocity magnitude predicted at low frequencies is to use particles that are less than 5 microns in diameter. Use of small particles pushes the position of the velocity maximum out to larger frequencies where the electrode kinetics are more linear, in keeping with the assumptions of the model.
5. There should be a search for different electrode/electrolyte combinations that allow confirmation of the effects of charge transfer resistance and the transference parameter.