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The electrophoretic mobility of an uncharged particle

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Richard W. O'Brien *, James K. Beattie, Alex M. Djerdjev

School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

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ABSTRACT

Hypothesis: It has been claimed that *uncharged* particles can have negative electrophoretic mobilities, and so a negative mobility need not imply a negative particle charge. We show that although a steady electrophoresis may be possible for the uncharged infinite slabs studied in Molecular Dynamics simulations, it is *not* possible for a finite particle.

Experiments and theory: An uncharged particle may initially move when the field is turned on, but our analysis shows that this motion ceases as charges of opposite sign build up on the front and back of the particle. Uncharged particles may move in alternating electric fields, but their mobility is predicted to increase with electrolyte conductivity. Experimentally, however, the mobility of hexadecane oil drops in water at pH 9 decreases with increasing NaCl concentrations.

Findings: Our results are consistent with the usual compression of the double layer with added salt, and with the traditional interpretation, that hydrophobic particles have negative mobilities because they are negatively charged. Uncharged particles may have a transient mobility but it is quickly quenched by polarisation of the double layer.

1. Introduction

Hydrophobic particles have negative electrophoretic mobilities at pH values above about 4 if there is no added surfactant, and this is usually taken to imply that the particles carry a negative charge [1]. Beattie and coworkers claim that this charge comes from preferential adsorption of hydroxide at the water-hydrophobic surface, and they have developed a theory that fits the measured mobilities of oil droplets as a function of pH [2]. This theory also accounts for the measurements of the hydroxide uptake as oil is emulsified in water at fixed pH [3].

But this explanation is at odds with Molecular Dynamic (MD) simulations which indicate that hydronium, rather than hydroxide ions, should be preferentially adsorbed at the hydrophobe–water interface [4]. In an attempt to resolve this discrepancy between the MD simulations and the electrophoresis observations, some workers have claimed that *uncharged* particles can have negative mobilities, and so a negative mobility need not imply a negative charge. This assertion is supported by some MD simulations which indicate that an uncharged slab of decane in water moves in the opposite direction to a tangential applied field [5]. It has been suggested that this motion comes about because the first few layers of water molecules at the surface carry electric charges, due to "dangling hydrogen bonds" unevenly shared between the layers [6–8]. A tangential electric field will tend to push these oppositely

charged layers in opposite directions, and the resulting shear forces will generate an electro-osmotic motion, provided the layers are free to slide over each other.

One problem with these MD simulations is that the results are very model-dependent. Bonthuis et al. [9] showed that the electrophoretic motion calculated by Knecht and co-workers [10] was caused by a discontinuity in the Lennard–Jones potential they used in their simulation; when the discontinuity was removed, the electrophoretic motion vanished. Although a subsequent simulation by Knecht et al. [5] using a different model restored the electrophoretic motion, the uncertainty remains.

In this paper we subject this uncharged electrophoresis proposal to further scrutiny, both theoretical and experimental.

In the following section we show that although a steady electrophoresis may be possible for uncharged infinite slabs it is *not* possible for a finite particle. The uncharged particle may initially move when the field is turned on, but the motion will only be temporary, for the sliding water layers will inevitably carry electric charge with them, and so charges of opposite sign will build up on the front and back of the particle. Ions from the surrounding electrolyte will then be drawn down to form diffuse layers that balance the surface charges. As the drops of voltage across these diffuse layers build up, the tangential driving field at the surface is reduced until the motion eventually ceases. In Section 3 we calculate the time it will take for this motion to cease.

This does not rule out the possibility that uncharged particles may move in alternating electric fields, and indeed many of the measurements of hydrophobic particle electrophoresis have been

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* Corresponding author.
E-mail address: obrien_r@chem.usyd.edu.au (R.W. O'Brien).

made in this way, so to test for this possibility, we carried out measurements of the dynamic electrophoretic mobility for surfactant-free oil droplets in water at pH 9 as a function of added electrolyte. The results of these measurements and the theory for the electrolyte dependence for an uncharged particle are set out below. In theory, the mobility of an uncharged particle should be *increased* by the addition of indifferent electrolyte, but instead we find that the mobility drops dramatically with increasing electrolyte, a result that is completely consistent with the standard interpretation of a negative charge on the oil droplets. Thus there is no experimental evidence of significant uncharged electrophoresis in this case.

2. Calculating the motion of an uncharged spherical particle in a time-dependent electric field

Electrophoretic motion is driven by electrical forces, so to generate this motion it is necessary to have regions of non-zero charge in the colloid. The charge in this case is believed to come, not from adsorbed ions but from an unequal sharing of electrons among the first few water layers. Thus when the electric field is first turned on, the tangential component of the field at the surface pushes the surface water layers in opposite directions. What happens next depends on whether the layers can carry charges with them. If the induced charge separation is only due to dipole molecule alignment, then the field will just cause a reorientation of the surface molecules and that will be the end of the motion, but if the electrons associated with the H-bond induced charge transfer can undergo migration, then the layers will be free to slide over each other [6–8]. In this case the electric field will drive a tangential current. As we will show, this current then influences the field distribution around the particle, and this in turn alters the particle mobility.

The mathematical problem is to calculate the electric field around an uncharged spherical particle in a spatially uniform ambient field $\boldsymbol{E}_a(t)$. The particle is in an electrolyte solution with a double-layer thickness small compared to the particle radius a. The calculation of the field distribution is the first step in the calculation of the particle mobility, but it is all that is needed here, for the electrophoretic velocity is proportional to the average tangential electric field over the particle surface [11].

The electric field in the liquid or particle can be written as:

$$\boldsymbol{E} = -\nabla \psi \tag{1}$$

where the electrical potential ψ satisfies Laplace's equation:

$$\nabla^2 \psi = 0 \tag{2}$$

along with the outer boundary condition that the field is uniform far from the particle, that is:

$$\psi \to -\boldsymbol{E}_a(t) r \cos \theta \tag{3}$$

as $r \to \infty$, where distance r is measured from the particle centre and θ is the angle between the position vector $\boldsymbol{r}$ and the direction of the ambient field $\boldsymbol{E}_a$.

The potential must also satisfy two boundary conditions at the particle surface. The first of these comes from the application of Poisson's equation and the charge conservation constraint to a thin slabbed-shaped volume on the particle surface [12]:

$$\left(K + \varepsilon \frac{\partial}{\partial t} \right) \frac{\partial \psi}{\partial r} \bigg|_0 + K_s \nabla_s^2 \psi_i = \varepsilon_p \frac{\partial}{\partial t} \frac{\partial \psi}{\partial r} \bigg|_i \tag{4}$$

Here K and ε are the electrical conductivity and permittivity of the solvent and ε_p is the permittivity of the particle. The quantity K_s is the surface conductance associated with the motion of the water layers at the surface. As we shall show, this conductance leads to a

buildup of charge over the particle surface, and this draws diffuse countercharge down from the surrounding electrolyte. The subscripts o and i denote the values on the top and bottom of the slab. The top surface of the slab lies just above the double layer and the bottom surface lies just inside the particle. Finally, the quantity ∇_s^2 is the surface Laplacian, obtained by removing the r derivatives in the usual Laplacian in spherical polar coordinates. The first term on the left and right hand sides of the above equation represent the current (free charge plus displacement) flowing through the top and bottom of the slab while the remaining term, involving K_s is the net tangential current flowing out through the sides of the slab.

The second boundary condition comes from the fact that the diffuse charge in the double layer is equal to its capacitance C per unit area times the voltage drop across the double layer. On taking the time derivative of this formula and using the fact that all the diffuse charge is conducted in from the neighbouring electrolyte, we get:

$$-C \frac{\partial}{\partial t} (\psi_i - \psi_o) = K \frac{\partial \psi}{\partial r} \bigg|_0 \tag{5}$$

where the double layer capacitance per unit area is given by [13]:

$$C = \varepsilon \kappa \tag{6}$$

for the low charge surfaces of interest here. As usual the quantity κ here denotes the inverse Debye length.

From the symmetry and linearity of this problem it follows that the potential function must take the form of a function of r times $\cos\theta$. Substituting this form into Laplace's equation and solving for that function of r we find that:

$$\psi = A(t) r \cos\theta \tag{7}$$

inside the particle and

$$\psi = \left[-\boldsymbol{E}_a(t) r + \frac{B(t)}{r^2} \right] \cos\theta \tag{8}$$

outside the double layer. These forms satisfy Laplace's equation and the outer boundary condition (3).

The functions $A(t)$ and $B(t)$ are determined by the boundary conditions (4) and (5) at the particle surface. From (4) we find:

$$\left[\varepsilon' \frac{d}{dt'} + 2\lambda \right] A + 2 \left[\frac{d}{dt'} + 1 \right] \frac{B}{a^3} = -\left[\frac{d}{dt'} + 1 \right] E_a \tag{9}$$

while (5) yields,

$$\kappa a \frac{dA}{dt'} - \left[\kappa a \frac{d}{dt'} + 2 \right] \frac{B}{a^3} = \left[1 - \kappa a \frac{d}{dt'} \right] E_a \tag{10}$$

Here

$$t' = \frac{Kt}{\varepsilon} \tag{11}$$

is a non-dimensional time,

$$\lambda = \frac{K_s}{Ka} \tag{12}$$

is a non-dimensional surface conductance and,

$$\varepsilon' = \frac{\varepsilon_p}{\varepsilon} \tag{13}$$

is the ratio of particle to solvent permittivity.

Thus the calculation of the field distribution around an uncharged sphere for an arbitrary applied field involves the solution of the pair of coupled differential Eqs. (9) and (10) for the coefficient functions A and B. The quantity of greatest interest to us is $A(t)$, since this determines the tangential electric field at the particle surface, the field that acts on the charged water layers and thereby generates the electrophoretic motion.