Mobility of nanometer-size solutes in water driven by electric field

Mohammadhasan Dinpajooh [a], Dmitry V. Matyushov [b],*

[a] School of Molecular Sciences, Arizona State University, PO Box 871604, Tempe, AZ 85287, United States
[b] Department of Physics and School of Molecular Sciences, Arizona State University, PO Box 871504, Tempe, AZ 85287, United States

H I G H L I G H T S

- Mobility of nanoparticles in liquids is affected by the interfacial dipolar order.
- Zero-charge particles experience a non-zero electric force.
- Electrokinetic charge exceeds the charge of adsorbed ions.
- Mobility of nanoparticles can be inverted by photoexcitation.

A R T I C L E   I N F O

A B S T R A C T

We investigate the mobility of nanometer-size solutes in water in a uniform external electric field. General arguments are presented to show that a closed surface cutting a volume from a polar liquid will carry an effective non-zero surface charge density when preferential orientation of dipoles exists in the interface. This effective charge will experience a non-vanishing drag in an external electric field even in the absence of free charge carriers. Numerical simulations of model solutes are used to estimate the magnitude of the surface charge density. We find it to be comparable to the values typically reported from the mobility measurements. Hydrated ions can potentially carry a significant excess of the effective charge due to over-polarization of the interface. As a result, the electrokinetic charge can significantly deviate from the physical charge of free charge carriers. We propose to test the model by manipulating the polarizability of hydrated semiconductor nanoparticles with light. The inversion of the mobility direction can be achieved by photoexcitation, which increases the nanoparticle polarizability and leads to an inversion of the dipolar orientations of water molecules in the interface.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Electrophoretic mobility is the drag experienced by a dissolved, usually colloidal, particle in a uniform external electric field. Mobility of oil drops and air bubbles in water has been known for a long time [1] and is traditionally linked to preferential adsorption of ions. Their counterions form the diffuse double layer. The overall charge measured by mobility is determined by an incomplete compensation between the charge of the adsorbed ions and the part of the diffuse layer within the shear surface. The latter encircles the stagnant layer of the electrolyte moving together with the dissolved particle. While the overall force acting on the ions of the electrolyte is zero, the electrokinetic drag is the result of choosing a limited volume

---

* Corresponding author.
  E-mail address: dmitrym@asu.edu (D.V. Matyushov).

within the electrolyte, surrounding the colloidal particle, with an uncompensated charge. The dragging force is thus the product of the average charge $\langle Q_R \rangle$ within the shear surface with the electric field acting on the charges. We show here that the idea of a limited volume cut from the liquid and producing an excess charge can be extended to the dipolar polarization of the interface. While the dielectric surrounding the nanoparticle is neutral overall, like the electrolyte in the standard models, the divergent polarization of the interface produces an uncompensated bound charge when integrated over a finite volume.

The excess of the adsorbed charge over the diffuse-layer charge, i.e., uncompensated charge $\langle Q \rangle_R \neq 0$, is reflected in the sign of the ζ-potential at the shear surface [2]. A negative ζ-potential, typically recorded for oil drops and air bubbles in water, has been attributed to the excess of the adsorbed negative charge, with the hydroxide anion being a long-time favorite [3–6].

Recent calculations [7,8] and measurements by surface-sensitive second-harmonic generation techniques [9–12] do not support excessive adsorption of hydroxide to the oil–water [10] and air–water [9,11] interfaces. In addition, the total X-ray reflection fluorescence spectroscopy [13] provides the upper estimate for the free surface charges at the air–water interface at the level of 0.002 (e/nm^2). Depending on the pH and other conditions, this estimate is up to two orders of magnitude below the surface charge density of 0.02–0.4 (e/nm^2) extracted from mobility [3,5,10,12]. It seems plausible that either the formalism of estimating the surface charge density from mobility requires modification or alternative mechanisms of mobility, not involving ion adsorption, might be involved.

The possibility of charge-free electrophoretic mobility in water has been discussed in the literature [14–16,10,17–19]. The main idea here is that the microscopic structure of the interface, allowing molecular order within the hydration layers, can either produce an effective electrokinetic charge, not related to charges of free carriers, or substantially modify the effect of adsorbed ions on the overall mobility. This proposal has faced two difficulties. From the theoretical side, there is no established framework of how to translate the microscopic structure of the interface, captured by atomistic numerical simulations, into the macroscopic current. Care is required in implementing correct cutoff/boundary conditions [20–22] and statistical ensembles adequately representing the conditions of mobility measurements (as discussed briefly below). In addition, the field strengths required to produce sufficient sampling in simulations are significantly higher than experimental fields [23] and can potentially modify the structure of the solution. From the experimental side, it is not clear how to connect the results of surface-sensitive spectroscopies, which directly report on the polarization structure of the interface [24,25], with measured mobilities.

Here we address the calculation of the force acting on a nanometer-size particle dissolved in water and placed in a uniform external field. We do not directly calculate the current produced in response to the external field assuming that, once the force is known, the mobility can be calculated by applying standard equations of hydrodynamics [26,11] (as shown for the capillary flow in the Appendix A). Mobility of the hydrated solute is typically expressed, through Smoluchovski's equation (Eq. (2)), in terms of either the ζ-potential or its effective charge. We derive a relation between the effective mobility (electrokinetic) charge and the interfacial structure of the water dipoles represented by the first-order orientational order parameter of the interface. This parameter is in principle accessible by surface-sensitive spectroscopies [24,25,27,28] and by equilibrium computer simulations of solutions [29,30].

This model shows that the effective charge of the solute responding to the uniform external field is not equal to the charge of the free carriers. It is therefore possible that the effective electrokinetic charge reported by mobility measurements significantly overestimates the number of adsorbed ions. The orientational structure of interfacial dipoles is the key in understanding these differences. Since the interfacial structure and dipolar orientations in the interface can be altered by modifying the solute/substrate [29,31,10], one gains the means to experimentally test both the effect of the interface on the effective electrokinetic charge and the hypothesis of charge-free mobility. In particular, we suggest that changing the polarizability of a (semiconductor) nanoparticle by exciting electron–hole pairs can invert the sign of the mobility. This effect is driven by the relation between the orientation of dipoles in the hydration layer with the nanoparticle polarizability [32] manipulated by light [33].

2. Interfacial structure and particle mobility

2.1. General arguments

We start by considering a single spherical ion with the charge q at its center and with the radius a. It is placed in a polar liquid with the bulk static dielectric constant ϵ_s. We will further consider a spherical liquid sample with the macroscopic radius L and place the ion at its center to simplify the geometry. The instantaneous charge density in the sample is

$$\rho = \rho_i + \rho_b, \tag{1}$$

where $\rho_i = q\delta(\mathbf{r})$ and $\rho_b(\mathbf{r}) = \sum_j q_j \delta(\mathbf{r} - \mathbf{r}_j)$ is the density of bound charge at a given instantaneous configuration of the liquid with the atomic partial charges q_j located at the coordinates $\mathbf{r}_j$. Based on charge conservation [34], $\rho_b = -\nabla \cdot \mathbf{P}$ is expressed in terms of the polarization density field $\mathbf{P}$. No specific approximation, such as the dielectric boundary value problem, is assumed here. The instantaneous polarization field is given by the microscopic expression [35,36]

$$\mathbf{P}(\mathbf{r}) = \sum_j \mathbf{m}_j \delta(\mathbf{r} - \mathbf{r}_j) - \frac{1}{3}\nabla \cdot \sum_j \mathbf{Q}_j \delta(\mathbf{r} - \mathbf{r}_j) + \cdots. \tag{2}$$