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Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions

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ABSTRACT

The venerable theory of electrokinetic phenomena rests on the hypothesis of a dilute solution of point-like ions in quasi-equilibrium with a weakly charged surface, whose potential relative to the bulk is of order the thermal voltage ($kT/e \approx 25$ mV at room temperature). In nonlinear electrokinetic phenomena, such as AC or induced-charge electro-osmosis (ACEO, ICEO) and induced-charge electrophoresis (ICEP), several $V \approx 100\, kT/e$ are applied to polarizable surfaces in microscopic geometries, and the resulting electric fields and induced surface charges are large enough to violate the assumptions of the classical theory. In this article, we review the experimental and theoretical literatures, highlight discrepancies between theory and experiment, introduce possible modifications of the theory, and analyze their consequences. We argue that, in response to a large applied voltage, the “compact layer” and “shear plane” effectively advance into the liquid, due to the crowding of counterions. Using simple continuum models, we predict two general trends at large voltages: (i) ionic crowding against a blocking surface expands the diffuse double layer and thus decreases its differential capacitance, and (ii) a charge-induced viscosity increase near the surface reduces the electro-osmotic mobility; each trend is enhanced by dielectric saturation. The first effect is able to predict high-frequency flow reversal in ACEO pumps, while the second may explain the decay of ICEO flow with increasing salt concentration. Through several colloidal examples, such as ICEP of an uncharged metal sphere in an asymmetric electrolyte, we show that nonlinear electrokinetic phenomena are generally ion-specific. Similar theoretical issues arise in nanofluidics (due to confinement) and ionic liquids (due to the lack of solvent), so the paper concludes with a general framework of modified electrokinetic equations for finite-sized ions.

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1. Introduction

1.1. Nonlinear "induced-charge" electrokinetic phenomena

Due to favorable scaling with miniaturization, electrokinetic phenomena are finding many new applications in microfluidics [1–3], but often in new situations that raise fundamental theoretical questions. The classical theory of electrokinetics, dating back to Helmholtz and Smoluchowski a century ago [4], was developed for the effective *linear* hydrodynamic slip driven by an electric field past a surface in chemical *equilibrium* with the solution, whose double-layer voltage is of order the thermal voltage, $kT/e = 25$ mV, and approximately constant [5–10]. The discovery of AC electro-osmotic flow (ACEO) over micro-electrodes [11–13] has shifted attention to a new *nonlinear* regime [14], where the *induced* double-layer voltage is typically several $V \approx 100\, kT/e$, oscillating at frequencies up to 100 kHz, and nonuniform at the micron scale. Related phenomena of induced-charge electro-osmosis (ICEO) [15–17] also occur around polarizable particles [18,19] and microstructures [20,21] (in AC or DC fields), as well as driven biological membranes [22]. Due to broken symmetries in ICEO flow, asymmetric colloidal particles undergo nonlinear, induced-charge electrophoresis (ICEP) [15,23–25]. Some of these fundamental nonlinear electrokinetic phenomena are illustrated in Fig. 1.

A "standard model" (outlined below) has emerged to describe a wide variety of induced-charge electrokinetic phenomena, but some crucial aspects remain unexplained. In their pioneering work 25 years ago in the USSR, which went unnoticed in the West until recently [15,16], V. A. Murtsovkin, A. S. Dukhin and collaborators first predicted

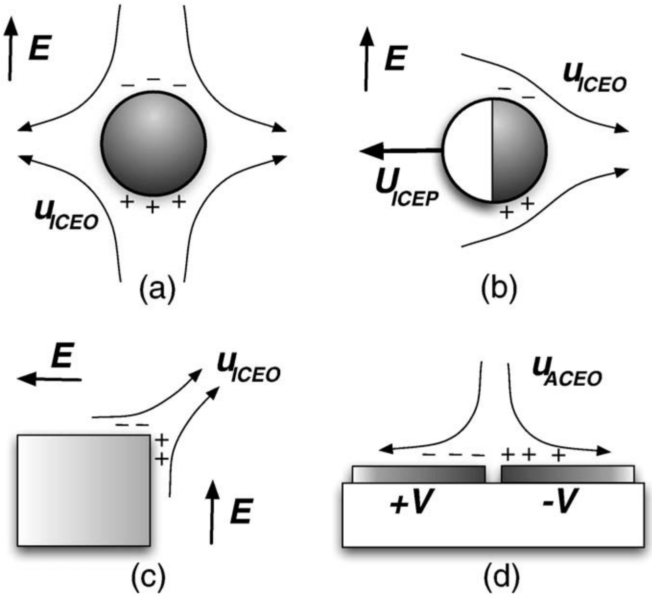

Fig. 1. Examples of nonlinear electrokinetic phenomena, driven by induced charge (+, −) in the diffuse part of the electrochemical double layer at polarizable, blocking surfaces, subject to an applied electric field E or voltage V. (a) Induced-charge electro-osmosis (ICEO) around a metal post [15,16,18,20], (b) induced-charge electrophoresis (ICEP) of a metal/insulator Janus particle [23,25], (c) a nonlinear electrokinetic jet of ICEO flow at a sharp corner in a dielectric microchannel [26,27], and (d) AC electro-osmosis (ACEO) over a pair of microelectrodes [11,12].