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Transient characteristics of electric double layer charging and the associated induced-charge electrokinetic flow

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This paper presents a detailed numerical analysis of the transient characteristics of electric double layer (EDL) charging and the associated induced-charge electrokinetic (ICEK) flow around an ideally polarizable cylinder. To this end, we solved numerically the coupled Poisson-Nernst-Planck and Navier-Stokes equations with the finite element method. The numerical simulation provides an unprecedented full-field (including the EDL region) characterization of the transient evolutions of ion transport, electric potential, and fluid flow during the EDL charging. The simulation results show that the EDL charging is driven by the electric current normal to the cylinder surface. With EDL being charged, the charge density in the EDL counteracts the local external electric field on the cylinder surface to reduce the electric current, which then leads to the slowing down of the EDL charging. At the steady state, the EDL becomes fully charged and the charge density in EDL exactly counteracts the external electric field, and then the EDL charging stops. During the EDL charging, the interaction of the external electric field with the charge density in the EDL drives the liquid in the EDL to move first, and then as time evolves, the liquid in the bulk electrolyte sets in motion because of the momentum transfer between the EDL and the bulk. These findings are conducive to the understanding of the transient dynamics of ICEK phenomena around polarizable objects. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5055866>

I. INTRODUCTION

Electrokinetic phenomena refer to a large class of phenomena (electroosmosis, electrophoresis, streaming potential, and sedimentation potential) which arise due to the so-called electric double layer (EDL) attached to a charged solid surface. Normally, a higher charge density on the solid surface leads to a higher charge density of EDL, and thus the associated electrokinetic phenomena would be stronger. Electrokinetic phenomena were originally discussed in colloid chemistry, and now is undergoing renaissance in microfluidics and nanofluidics for liquid, particle, and ion manipulations during the past few decades.^{1–3} The classic theory of electrokinetic phenomena assumes that the solid surface is electrically non-polarizable (equivalent to a zero electric permittivity) and the charge on the solid surface is determined by physicochemical properties of both the solution and surface (e.g., the pH and concentration of solution, the composition and density of surface chemical groups, and the extent of ion adsorption on the solid surface), but independent of the external electric field. However, most solid surfaces in practice are electrically polarizable (i.e., nonzero electric permittivity), and in this case even if the physicochemical surface charge is zero, the electric charge still can be induced on the solid surfaces due to

the polarization of the surface by the external electric field. The polarization-induced surface charge plays a role similar to the physicochemical charge, and also it can lead to the formation of EDL around the solid surfaces and the development of numerous induced-charge electrokinetic (ICEK) phenomena. Originally, the idea of ICEK phenomena was suggested by Levich⁴ more than 50 years ago, and around 20 years ago the Ukrainian colloid community observed the phenomena in the form of vortical flows around polarizable particles induced by external electric fields.^{5–7} In the past two decades, ICEK phenomena were introduced in the realm of microfluidics and nanofluidics because of their flexibility and readiness in inducing & controlling the microscale flows and microparticle motion.^{8,9} Furthermore, the term “induced-charge electrokinetic phenomena” was suggested by Bazant and his co-workers to differentiate this type of electrokinetic phenomena from the conventional electrokinetic phenomena and also to highlight the essential role of the surface charge induced by electric polarization. The ICEK phenomena hitherto have found myriads of microfluidic and nanofluidic applications, such as particle manipulations,^{10–12} liquid pumping,^{13,14} solute mixing,^{15–17} liquid flow control^{18,19} and electrolyte ion selection,^{20,21} etc.

It is noticed that ICEK phenomena discussed above share similar physics with the field effect electroosmosis.^{22,23} They both utilize the external electric field to modulate the polarization as well as the electric charge on solid surfaces. The

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only difference is the setup of the external electric fields. In the setup of the ICEK phenomena, the external electric field is produced by two electrodes. The solid surface stays in this field and becomes polarized to induce the surface charge. The polarization charge on the solid surface can be controlled by modulating the field strength (voltage applied on the two electrodes). In the setup of the field effect electroosmosis, the external electric field is produced by three electrodes. Two of the three electrodes are used to generate the electric field for driving the electrokinetic phenomena and the remaining one is used to generate the electric field for modulating the polarization charge on the solid surface. However, from the physics perspective, the surface charge in the ICEK phenomena and field effect electroosmosis is both due to the electric polarization; or in other words, both are induced by external electric fields, then the field effect electroosmosis is essentially one type of ICEK phenomena. Due to the same reason, the widely studied AC electrokinetic flow over coplanar electrodes also belongs to ICEK phenomena.^{24,25} Figure 1 summarizes the three types of electrokinetic phenomena due to the surface charge induced by the electric polarization. Because of the induced origin of the surface charge, the three types of electrokinetic phenomena are essentially ICEK phenomena.

The fundamental understanding of ICEK phenomena awaits further advancement, albeit its fast development in recent years. Particularly, the transient development of the surface charge and the EDLs around polarizable surfaces subject to a suddenly applied electric field is fundamental for understanding the characteristics of ICEK phenomena. The general conception is that electric current in the bulk electrolyte solution upon the application of external electric field gradually leads to the formation (or charging) of EDL around the solid surface, and then induces the electric charge on the solid surface.¹⁴ At the steady state, the electric current in the bulk solution vanishes and the EDL becomes fully charged. The external field at this stage is completely shielded from the solid surface, making the solid surface effectively a perfect insulator. Squires and Bazant found that the time scale of the EDL charging under a weak electric field is the so-called resistor-capacitor (RC) time scale, $\lambda_D L_{ref}/D$ (wherein λ_D is the Debye length measuring the thickness of EDL, L_{ref} is the characteristic dimension of the solid surface, and D is the diffusivity of ions). Later, Bazant, Thornton, and Ajdari²⁶ and Chu and Bazant²⁷ conducted more detailed analyses for the transient charging of EDL around planar and cylindrical conductors, respectively. In addition to the primary RC time scale, they identified that a secondary time scale, L_{ref}^2/D , emerges for a moderately high external electric field strength. The appearance of this time scale is due to the

significant depletion of the electrolyte near the solid surface under moderately high electric fields. Transient analysis of EDL charging was further expanded to a more general situation with an arbitrarily polarizable solid surface.²⁸ It was found that the time scale of EDL charging correlates with the polarizability of the solid surface, and the time scale increases from the so-called Debye time scale, λ_D^2/D , to the RC time scale $\lambda_D L_{ref}/D$ as the dielectric constant of the surface increases. The most recent investigation revealed that the transient characteristics of EDL charging under extremely high electric fields become more complicated and the chaotic ICEK flow appears.²⁹

The aforementioned investigations about the transient characteristics of EDL charging under a suddenly applied electric field all involved certain assumptions, such as thin EDL,^{14,28} the decoupling of ion transport and fluid flow,^{14,26–28} and equal diffusivity of cations and anions.^{14,26,27,29} Some or all of these assumptions were widely used in the analyses of other aspects of ICEK phenomena.^{15,30–38} Actually, these assumptions are “standard” assumptions in analyses of electrokinetic phenomena, which greatly simplify the studied problem and thus make the analysis of the problem much easier. Yet, the practical situations witness frequent violation of these assumptions, and the adoption of these assumptions could lead to inaccurate or even wrong conclusions.

To avoid the use of the “stand” assumptions, the full numerical model consisting of coupled Poisson-Nernst-Planck and Navier-Stokes equations has been recently formulated to investigate ICEK phenomena.^{20,21,29,39,40} Apart from the work of Davidson *et al.*, other studies considered only the steady state characteristics of ICEK phenomena. Davidson *et al.* performed a transient numerical simulation of ICEK phenomena around a cylindrical conductor under extremely high electric fields, and their main focus was the discovery of chaotic ICEK flow and the discussion of its characteristics. At present, to the best of our knowledge, there is still a lack of detailed investigations for the transient characteristics of EDL charging in the ICEK phenomena under a suddenly applied electric field. In this work, we perform a detailed analysis of the transient characteristics of EDL charging and ICEK flows around perfectly polarizable (conducting) solids based on the numerical solution of the coupled Poisson-Nernst-Planck and Navier-Stokes equations. With our numerical simulation, the detailed information (ion concentration, electric potential, and velocity) inside the EDL during the EDL charging process is revealed for the first time, and the ICEK flow field associated with the EDL charging is also investigated and discussed. The findings are helpful for the fundamental understanding of ICEK phenomena.

FIG. 1. Three types of electrokinetic phenomena due to the surface charge induced by electric polarization. (a) The ICEK flow around a conducting cylinder or particle; (b) ac electrokinetic flow over a pair of coplanar electrodes; and (c) Field effect electroosmosis. The grey areas denote the electrodes, and the white areas denote the insulating substrate or channel wall. The red arrow lines represent the flow. All three types of electrokinetic phenomena are essentially ICEK phenomena.

II. NUMERICAL MODELLING

A. Simulation domain and governing equations

We consider a conducting cylinder of radius a immersed in an unbounded electrolyte solution domain (Fig. 2). The conducting cylinder is assumed to be ideally polarizable, and thus there is no electrochemical reactions occurring on the cylinder surface. As soon as the cylinder is subject to an external electric field E_0 , it becomes polarized instantaneously to induce negative (positive) electric charges on the left (right) half of the cylinder surface. Such induced surface charges immediately attract counterions in the surrounding electrolyte to induce an electric current for the charging of EDL around the cylinder. To model the transient characteristics of EDL formation (or charging) around the cylinder floating in the external electric field, we take a square simulation domain with the cylinder located at its center, as shown in Fig. 2. In order to avoid the influence of the size of the imaginary square domain on the simulation results, we compared the numerical results for several sizes of the square domain and found that the domain size effect is insignificant as the lateral length of the square domain is 100 times the cylinder radius. We consider a binary electrolyte in the present study. The cation (anion) valence, concentration, and diffusivity are denoted by z_1 (z_2), $c_{1\infty}$ ($c_{2\infty}$), and D_1 (D_2), respectively. The ionic strength of the electrolyte solution is then $I = 0.5(z_1^2 c_{1\infty} + z_2^2 c_{2\infty})$. Due to electroneutrality, $z_1 c_{1\infty} + z_2 c_{2\infty} = 0$ must be satisfied in the bulk electrolyte solution. The concentration of electrolyte is low (order of millimolarity) and therefore the physical properties of the electrolyte solutions (viscosity, permittivity, and density) are identical to those of the room temperature ($T = 298$ K) water.

Our numerical simulation starts with the nondimensionalization of the governing equations. To do so, we introduce the

FIG. 2. Sketch of the simulation domain and the coordinate systems. A conducting cylinder with radius a is immersed in an electrolyte solution. Under the external electric field E_0 , the cylinder is polarized with the right (left) half of cylinder surface acquiring positive (negative) charge. Accordingly, the EDL with a charge of the opposite sign forms near the cylinder surface, and the associated ICEK flow develops. The simulation domain is a square with dimensions of $L \times L$. The four boundaries (dashed lines) of the square are where the far field boundary conditions are specified for the Poisson equation, the Nernst-Planck equation, and the Navier-Stokes equation.

following reference parameters for the length, electric potential, surface charge density, concentration, time, velocity, and pressure:

$$\begin{aligned} L_{ref} &= a, \quad \psi_{ref} = \frac{RT}{F}, \quad q_{ref} = \varepsilon \frac{\psi_{ref}}{a}, \quad c_{ref} = 2I, \\ t_{ref} &= \frac{\lambda_D a}{D}, \quad u_{ref} = \frac{\varepsilon \psi_{ref}^2}{\mu a}, \quad p_{ref} = \varepsilon \frac{\psi_{ref}^2}{a^2}, \end{aligned} \quad (1)$$

respectively, as well as the Peclet number and Schmidt number

$$Pe = \frac{u_{ref} L_{ref}}{D} = \frac{\varepsilon \psi_{ref}^2}{\mu D}, \quad Sc = \frac{\mu}{\rho D}. \quad (2)$$

In Eqs. (1) and (2), ψ_{ref} is the so-called thermal voltage with F , R , and T being the Faraday constant, the universal gas constant, and the absolute temperature, respectively. ε , μ , and ρ are the electric permittivity, dynamic viscosity, and density of the electrolyte solution, respectively. λ_D is the Debye length which measures the thickness of EDL and can be defined as $\lambda_D = \sqrt{\varepsilon RT / (2IF^2)}$. D is the average of cation and anion diffusivity, i.e., $D = 0.5(D_1 + D_2)$. The presence of electrolyte ions usually modifies the physical properties of water (such as the dielectric constant and viscosity), especially inside the EDL where the ion concentration is high. These modifications are only noticeable under extreme conditions (highly concentrated solutions or highly charged solid surfaces) which are beyond the scope of the present analysis. Then all physical properties of the electrolyte solution are assumed to be homogeneous inside the entire domain for the current study.

In Eq. (1), the reference time t_{ref} stands for the characteristic time of the EDL charging.^{26,41} It can be considered as the RC time for the circuit with a EDL capacitor, $C = \varepsilon / \lambda_D$, in series with a bulk resistor, $R = a / \sigma$, where σ represents the bulk electric conductivity and can be expressed as $\sigma = 2IF^2 D / (RT)$. The above RC time scale of EDL charging is only applicable to polarizable surfaces under weak electric fields. For a moderately high applied field, prominent surface conduction and bulk diffusion leads to a much larger time scale, a^2 / D . For extremely high electric fields, the situation becomes even more complicated, and the existence of other time scales is possible.²⁹ In the present investigation, we focus on weak applied electric fields, and thus the RC time scale is chosen as the reference for nondimensionalization.

The electric field in the electrolyte liquid domain is governed by the Poisson equation^{42,43} which can be expressed in the nondimensional form as

$$\nabla^2 \psi = - \left(\frac{a}{\lambda_D} \right)^2 (z_1 c_1 + z_2 c_2), \quad (3)$$

where c is the dimensionless concentration of ions (subscript 1 denotes cations, while subscript 2 denotes anions).

Ion transport (concentration) is described by the Nernst-Planck equation^{42,43} which can be written in nondimensional form for cations and anions as

$$\frac{a}{\lambda_D} \frac{\partial c_1}{\partial t} + \nabla \cdot [Pec_1 \mathbf{u} - (1 + \chi) \nabla c_1 - z_1 c_1 (1 + \chi) \nabla \psi] = 0, \quad (4)$$

$$\frac{a}{\lambda_D} \frac{\partial c_2}{\partial t} + \nabla \cdot [Pec_2 \mathbf{u} - (1 - \chi) \nabla c_2 - z_2 c_2 (1 - \chi) \nabla \psi] = 0, \quad (5)$$

where χ is a parameter which quantifies the difference in cation and anion diffusivity and is defined as $\chi = (D_1 - D_2)/(D_1 + D_2)$. The resulting dimensionless electric current density because of the ion transport can be evaluated as

$$\mathbf{i} = z_1 [Pec_1 \mathbf{u} - (1 + \chi) \nabla c_1 - z_1 c_1 (1 + \chi) \nabla \psi] + z_2 [Pec_2 \mathbf{u} - (1 - \chi) \nabla c_2 - z_2 c_2 (1 - \chi) \nabla \psi], \quad (6)$$

where the reference current density is defined as $2FDI/a$.

The flow field in the liquid electrolyte domain is governed by the continuity and Navier-Stokes equations^{42,43} which can be expressed in dimensionless forms as

$$\nabla \cdot \mathbf{u} = 0, \quad (7)$$

$$\frac{1}{Sc} \left(\frac{a}{\lambda_D} \right) \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \nabla^2 \mathbf{u} - \left(\frac{a}{\lambda_D} \right)^2 (z_1 c_1 + z_2 c_2) \nabla \psi. \quad (8)$$

Since the Reynolds number is small for the studied problem (order of 10^{-4}), the nonlinear momentum convection term has been neglected in Eq. (8).

B. Initial/boundary conditions and numerical method

Finally, proper boundary conditions and initial conditions are prescribed for the Poisson equation, Nernst-Planck equation, and Navier-Stokes equation.

For the Poisson equation, on the boundary AB shown in Fig. 2, the far field electric field strength E_0 [normalized by $\psi_{ref}/L_{ref} = RT/(Fa)$] is applied. The boundary CD is taken as the potential reference, namely, $\psi = 0$ is set on the boundary CD. The boundaries AC and BD are in the bulk electrolyte solution and hence the zero electric charge boundary, $\mathbf{n} \cdot \nabla \psi = 0$, is used, where $\mathbf{n}$ denotes the unit outward normal of the corresponding boundary. The cylinder surface is subject to the floating boundary condition, $\oint (\mathbf{n} \cdot \nabla \psi) ds = 0$, which ensures that the cylinder is equipotential in the external electric field.²¹

For the Nernst-Planck equation, the boundaries AB, AC, CD, and BD are in the bulk electrolyte. Accordingly, the concentrations of cations and anions are set to their corresponding bulk concentration, i.e., $c_i = c_{i\infty}$ on the plane AB, AC, CD, and BD. Since the solid boundary is impermeable to electrolyte ions on the cylinder surface, the normal ionic fluxes must vanish, i.e., $\mathbf{n} \cdot [Pec_1 \mathbf{u} - (1 + \chi) \nabla c_1 - z_1 c_1 (1 + \chi) \nabla \psi] = 0$ for cations and $\mathbf{n} \cdot [Pec_2 \mathbf{u} - (1 - \chi) \nabla c_2 - z_2 c_2 (1 - \chi) \nabla \psi] = 0$ for anions.

For the Navier-Stokes equation, the no-slip boundary condition (i.e., $\mathbf{u} = 0$) is set on the cylinder surface. At boundaries AB, AC, CD, and BD, since they are in the bulk electrolyte solution and also there is no externally applied pressure gradient, a normal pressure of $p = 0$ is specified.

The initial conditions are also required for solving the problem. Since the entire electrolyte domain is electroneutral and quiescent at the beginning, $c_i = c_{i\infty}$ is prescribed as the initial condition for the Nernst-Planck equation, and $\mathbf{u} = 0$ is prescribed as the initial condition for the Navier-Stokes

equation. The initial condition for the Poisson equation is prescribed as the solution of the Laplace equation, $\nabla^2 \psi = 0$, which describes the potential distribution of the electroneutral electrolyte domain at $t = 0$.

We use Comsol Multiphysics (COMSOL, Inc.) to solve the highly coupled model. This software is based on the finite element method and features a flexible handling of coupled multiphysical problems. Three modules of the software were used: The Poisson equation, Eq. (3), was solved in the AC/DC module, the Nernst-Planck equations, Eqs. (4) and (5), were solved in the Chemical Species Transport module and the continuity and Navier-Stokes equations, Eqs. (7) and (8), were solved in the Fluid Flow module. A mapped mesh with M uniform points along the azimuthal direction and N points along the radial direction is used in the simulation. To check the mesh independence, three numbers of mesh elements, i.e., 150 000 ($M = 1200, N = 125$), 300 000 ($M = 1200, N = 250$), and 600 000 ($M = 1200, N = 500$) were tested, and we found that the results calculated from the three numbers of mesh elements differ 5% and 0.1% sequentially. Therefore, the total number of mesh elements is chosen to be 600 000 in the current study. To resolve the detailed information of EDL, extremely fine meshes were created near the cylinder surface. The smallest mesh size near the cylinder surface is 1% of the Debye length and then increases by 3% away from the cylinder. For the validation of our model, we computed the transient ICEK slip velocity over the cylinder surface under the conditions of thin EDL ($a/\lambda_D = 1000$) and the weak applied field ($E_0 = 1$), and compared it with the slip velocity model,¹⁴ $u_s = 2E_0^2 \sin(2\theta)(1 - e^{-t})^2$. The numerical solution shows an excellent agreement with the slip velocity model, as is shown in Fig. 3, thereby validating the robustness and accuracy of our numerical model.

The present model presents a full coupling of the electric potential, ionic transport, and liquid flow and thus can give a detailed, full-field (including EDL region) characterization of transient evolutions of the three coupled fields during the EDL charging. The model solved in COMSOL Multiphysics has been previously used for studying other electrokinetic transport phenomena.^{20,39,44,45}

FIG. 3. Comparison between the numerical ICEK slip velocity and the analytical result $u_s = 2E_0^2 \sin(2\theta)(1 - e^{-t})^2$ under the conditions of thin EDL ($a/\lambda_D = 1000$) and weak applied field ($E_0 = 1$). The circular symbols represent the numerical solutions, and the lines represent the analytical solutions.

III. RESULTS AND DISCUSSION

A. Transient charging of EDL around the cylinder

Figure 4 shows the transient characteristics of the EDL charging around an ideally polarizable cylinder. As shown in Fig. 4(a) for $t = 0.1$, the electric field or electric current density lines in the middle contour plots are perpendicular to the cylinder surface, and this is the classical picture for a conducting cylinder polarized by an external electric field. At this stage, the EDL is being charged by the electric current towards (away from) the left (right) half of the cylinder surface as indicated by the electric current density lines and the contour plot of the magnitude of the electric current density. However, the charge density inside the EDL is still quite low, as is shown in the leftmost and rightmost contour plots in Fig. 4(a) which show the local electric charge density in the EDL near the left and right poles of cylinder surface, respectively. As the EDL charging progresses to $t = 1$, the local charge density near the cylinder surface increases, with the positive (negative) charge density near the left (right) pole of cylinder surface, as is shown in the leftmost and rightmost contour plots in Fig. 4(b). In turn, the charge density inside the EDL begins to counteract the external electric field and distort the local electric field lines near the cylinder surface [see the middle contour plot of Fig. 4(b)]. Accordingly, the electric current density normal to the cylinder surface also declines, leading to the slowing down of the EDL charging. As time evolves further to $t = 2$, the EDL continues to be charged with much higher charge density around the cylinder. At this stage, the charged density inside the EDL distorts the local electric field lines significantly on the cylinder surface, as depicted in the middle contour plot in Fig. 4(c).

FIG. 4. Transient charging process of the EDL around an ideally polarizable cylinder at four instants for an applied electric field of $E_0 = 1$ and $a/\lambda_D = 1000$: (a) $t = 0.1$, (b) $t = 1$, (c) $t = 2$, and (d) $t = 4$. For each instant, the contour plot in the middle shows the magnitude of the electric current density, $|j|$, and the corresponding arrowed lines denote the current density or electric field lines, and the two contour plots beside the middle contour plot show the local electric charge density, c_1 - c_2 , in the EDL near the left and the right poles of cylinder surface, respectively.

FIG. 5. Transient development of the surface charge density of the cylinder for an applied electric field of $E_0 = 1$ and $a/\lambda_D = 1000$.

There is a further declining of the electric current density normal to the cylinder surface, and accordingly the EDL charging is even more decelerated. Till $t = 4$ [Fig. 4(d)], the cylinder is effectively shielded from the external electric field by an EDL “shell,” the charge density inside the EDL becomes high enough to exactly counteract the local external electric field, and thus the charging process ceases. Beyond $t = 4$, it is found that the charge density and the electric field distributions hardly change with time.

The time evolution of the normalized surface charge density of the cylinder corresponding to Fig. 4 is plotted in Fig. 5. It is seen that the surface charge density at each instant follows a cosine-like distribution with respect to the azimuthal angle θ , and the magnitude of the surface charge density increases with time. This feature is quite understandable when

retrospecting the dynamic charging of EDL presented in Fig. 4. During the EDL charging, the charge density inside the EDL grows, which must be neutralized by the increasing surface charge density of the cylinder. After $t = 4$, the surface charge density increases slightly to its steady state value ($t = \text{inf.}$). This suggests that the EDL charging at $t = 4$ is quite close to the steady state, and this is also consistent with the observation in Fig. 4. It is also noticed that the net surface charge is always zero during the charging of the EDL because of the floating boundary condition on the cylinder surface. Unlike the time-independent surface charge in the conventional electrokinetic phenomena, the surface charge in the ICEK phenomena is induced by the electrical polarization and is apparently a transient phenomenon.

B. Transient development of the flow field around the cylinder

The transient development of the ICEK flow field around the cylinder corresponding to the EDL charging discussed above is presented in Fig. 6. Initially ($t = 0$), the entire electrolyte solution domain is stationary (not shown in Fig. 6) since the electrolyte solution is electroneutral everywhere and the external electric field does not exert any driving force on the solution. Along with the charging of EDL near the cylinder surface, the external electric field interacts with the EDL to produce an electrostatic body force (or momentum) which drives the liquid solution to move. Since such an electrostatic driving force only exists inside the EDL, the liquid inside the EDL starts to move first. In the present case, the EDL

thickness is only $10^{-3}a$. Basically, the EDL is very thin and effectively attached to the cylinder surface. As time evolves to $t = 1$ [Fig. 6(a)], the momentum generated inside the EDL (or on the cylinder surface) diffuses to the bulk solution due to the finite viscosity of solution, resulting in the motion of the bulk solution. It is clear that the fluid velocity attains the local maximum value very near the cylinder surface. Such a maximal velocity is essentially the Helmholtz-Smoluchowski slip velocity at the outer edge of EDL. With the further charging of EDL, the magnitude of the electrostatic body force in EDL increases, so does the magnitude of Helmholtz-Smoluchowski slip velocity, as shown consecutively in Figs. 6(b)–6(d). At the same time, the momentum generated inside the EDL continues to diffuse to the bulk liquid domain, and thus a larger portion of the bulk solution becomes activated as time evolves. At the steady state shown in Fig. 6(d), the maximal velocity is 1.96, which is only 2% off 2 predicted from the slip velocity model.¹⁴ Such good agreement is expected since for the thin EDL and the weak applied field, the numerical model should be consistent with the slip velocity model, as is shown in Fig. 3.

It is also noted that the basic flow pattern around the cylinder is four vortices which are symmetric with respect to both the x axis and y axis. The two vortices at the upper left corner and at the lower right corner rotate counter-clockwise, while the remaining two rotate clockwise. Since the positive (negative) charge density is induced inside the EDL near the left (right) half of the cylinder surface, the electric field tangential to the cylinder surface interacts with the EDL to induce electrostatic body forces all directing towards $x = 0$ along the

FIG. 6. Contours of the ICEK flow velocity magnitude around the cylinder at four instants for an applied electric field of $E_0 = 1$ and $a/\lambda_D = 1000$: (a) $t = 1$, (b) $t = 2$, (c) $t = 4$, and (d) $t = \text{inf.}$ The arrowed lines denote the stream lines.

cylinder surface. Correspondingly, the fluid is also dragged towards $x = 0$ along the cylinder surface to induce the vortical flow pattern described above.

A further careful examination of Figs. 4–6 shows that the transient development of the ICEK flow field lags behind the transient charging of EDL. This fact can be evidenced by the EDL charging characteristics at $t = 4$ and the flow field at $t = 4$. The EDL charging characteristics at $t = 4$ in Figs. 4 and 5 is not much different from the steady state, while the flow field at $t = 4$ in Fig. 6 is still in development and differs substantially from the steady state. This fact is also consistent with the intuitive understanding that the EDL must be charged before the flow development.

Figures 4–6 are the key results of the present investigation. The results provide a detailed, full-field characterization of transient characteristics of EDL charging and the associated ICEK flow field under a suddenly applied electric field. The distributions of ion concentration, electric potential, and velocity inside the entire domain including the thin EDL region are obtained for the first time. These results are necessary for an in-depth understanding of the ICEK phenomena. Our study here only considers the weak applied fields, namely, $E_0 \sim O(1)$, and this ensures the stability of transient simulation. For high electric fields, $E_0 \sim O(10)$ or beyond, the transient simulation leads to chaos²⁹ which is beyond our current focus.

C. Effects of electrolyte concentration on the ICEK flow field

Figure 7 presents the effect of electrolyte concentration on the steady state ICEK velocity distribution around the cylinder. The concentration effect here is discussed in terms of dimensionless a/λ_D since for a given a , the decrease in a/λ_D means a decrease in electrolyte concentration. It is generally observed from the three contour plots in Fig. 7 that the magnitude of the velocity increases with the increase of a/λ_D (concentration). Such a trend is in accordance with the recent experiment by Feng *et al.*⁴⁶ One also notes that for thin EDL situations (high concentration), such as $a/\lambda_D = 1000$ in Fig. 7(a), the velocity attains the local maximum very near the cylinder surface (effectively on cylinder surface). The numerical result in this case agrees well with the slip velocity model based on the assumption of $a/\lambda_D \rightarrow \infty$.¹⁴ As a/λ_D (concentration) decreases, Figs. 7(b) and 7(c) indicate that the local maximum velocity detaches from the cylinder surface and spreads into the electrolyte domain. Apparently, the slip velocity model by Squires and Bazant fail to describe the velocity distributions in these two cases, and we have to rely on the numerical results.

For better understanding of the transient velocity development in Fig. 7, the transient evolution of the magnitude of the velocity along the radial direction at $\theta = \pi/4$ is depicted in Fig. 8. The analysis shows that the time required to reach the steady state reduces with the decreasing value of a/λ_D . This can be attributed to the fact that for a thick EDL, the surface conduction becomes prominent, which accelerates the redistribution of ions in the EDL and thus the EDL charging process. Therefore, the associated velocity development

FIG. 7. Contours of the steady-state ICEK flow velocity magnitude around the cylinder for three values of a/λ_D with the electric field strength $E_0 = 1$. (a) $a/\lambda_D = 1000$, (b) $a/\lambda_D = 100$, and (c) $a/\lambda_D = 10$.

is also accelerated. It is also relevant to note that for any values of a/λ_D considered, the velocity always increases from zero on the cylinder surface to a local maximal value across the EDL, and then decreases gradually to zero in the far bulk solution. From the plot, we can determine the locations of the local maximal velocity for $a/\lambda_D = 10, 100$, and 1000 to be roughly 2, 3, and 4 times of the Debye length away from the cylinder surface, respectively. Our numerical results provide a detailed characterization of the velocity variation across EDL, which is however neglected in the conventional study of ICEK phenomena due to the assumption of $a/\lambda_D \rightarrow \infty$. Usually, for large values of a/λ_D (e.g., 10^3), the EDL is very thin ($10^{-3}a$), so the detailed velocity variation inside the EDL is not important and thus can be neglected. Then a slip velocity boundary condition is applicable on the cylinder surface. This feature is supported by the good agreement between the

FIG. 8. Transient development of ICEK flow velocity magnitude along the radial direction at $\theta = \pi/4$ corresponding to Fig. 7. The results for different values of a/λ_D are differentiated by different colors: black ($a/\lambda_D = 10$); red ($a/\lambda_D = 100$); and blue ($a/\lambda_D = 1000$). For each value of a/λ_D , different instants are differentiated by different line styles: solid line ($t = 1$); dashed line ($t = 2$); dotted line ($t = 4$); and dashed-dotted line ($t = \text{inf.}$). The circular symbols denote the results from the slip velocity model by Bazant, i.e., $|\mathbf{u}| = 2E_0^2/r^3$.

steady-state numerical result of $a/\lambda_D = 10^3$ outside the EDL and the Bazant's slip velocity model result,¹⁴ $|\mathbf{u}| = 2E_0^2/r^3$, as shown in Fig. 8. However, for the case with small values of a/λ_D (100 and 10), the EDL is relatively thick, so the velocity variation inside the EDL becomes important and cannot be neglected. It is also apparent from Fig. 8 that the slip velocity model substantially overestimates the steady-state velocity for the thick EDL situation. This suggests the invalidity of the slip velocity model for thick EDL situation, and our numerical model has to be used instead.

D. Effects of electric field strength on the ICEK flow field

Figure 9 details the effects of electric field strength on the ICEK flow field at the steady state. The three plots look quite similar, with difference only in the velocity magnitude. It shows that the magnitude of the velocity increases with the increase of the applied electric field. This is understandable because the increase of the externally applied field leads to stronger polarization of the cylinder and thus higher charge density inside the EDL. Then the enhanced charge density interacts with the external field to produce stronger flows. For extremely thin EDL considered here ($a/\lambda_D = 1000$), normally the velocity magnitude is expected to be proportional to the square of external electric field strength, as predicted by the slip velocity model by Bazant,¹⁴ $u_s = 2E_0^2 \sin(2\theta)(1 - e^{-t})^2$. This is the standard scaling of ICEK phenomena and defines its nonlinear nature. For the electric field strength of $E_0 = 1$ shown in Fig. 9(a), the maximum velocity is 1.96 which is only 2% off 2 predicted by the slip velocity model. As the electric field increases to $E_0 = 3$ and 5, the errors between the numerical solution and the slip velocity model increase to 4% and 10%, respectively. This disagreement is due to several assumptions in the slip velocity model, such as the Debye-Hückel linear approximation and the neglect of surface conduction, which becomes invalid as the external electric field

FIG. 9. Contours of the steady-state ICEK velocity magnitude around the cylinder for three values of electric field strength with $a/\lambda_D = 1000$. (a) $E_0 = 1$, (b) $E_0 = 3$, and (c) $E_0 = 5$.

strength increases. Considering the discussion in Fig. 8, the slip velocity model is apparently limited to the thin EDL and the weak applied field condition, but our numerical model has broader applicability.

The transient development of the velocity along the radial direction at $\theta = \pi/4$ corresponding to Fig. 9 is shown in Fig. 10.

FIG. 10. Transient development of ICEK velocity magnitude along the radial direction at $\theta = \pi/4$ corresponding to Fig. 9. The results for different values of E_0 are differentiated by different colors: black ($E_0 = 1$); red ($E_0 = 3$); and blue ($E_0 = 5$). For each value of E_0 , different instants are differentiated by different line styles: solid line ($t = 1$); dashed line ($t = 2$); dotted line ($t = 4$); and dashed-dotted line ($t = \text{inf}$). The circular symbols denote the results from the slip velocity model by Bazant, i.e., $|\mathbf{u}| = 2E_0^2/r^3$.

It is seen that the location for the maximal local velocity is hardly different for various magnitudes of electric field strength. As expected in Fig. 9, the velocity increases with the increase of electric field strength. In addition, a careful analysis shows that the velocity reaches the steady state more slowly as the electric field strength increases. This is assumably caused by the onset of bulk diffusion, which introduces a diffusion time scale, a^2/D , larger than the primary RC time scale, $a\lambda_D/D$.^{26,27} In addition, the comparison between the steady-state numerical results and the slip velocity model results for three electric field strengths is shown in the plot, and we can see that as the electric field strength increases, the slip velocity model fails to predict the numerical results. This feature is expected since the slip velocity model is only valid for weak applied fields.

E. Effects of electrolyte type on the ICEK flow field

All the above discussion is limited to the electrolyte solution of KCl. Finally, it is interesting to investigate the effect of electrolytes on the ICEK flow field. In this study, we consider three monovalent electrolytes, LiCl, NaCl, and KCl, which have the common anion Cl^- . It is found that the steady state ICEK flow fields of the three electrolytes for $a/\lambda_D = 1000$ and $E_0 = 1$ have no sensible difference. Therefore, here we did not make a comparison among them since they all are similar to Fig. 9(a). This is reasonable since the current numerical model treats the ICEK phenomenon as a purely physical effect. At the steady state, ion specific parameters are absent from the numerical model, and the charge density in the EDL is only dependent on the ion concentration and ion valences, but not on the ion type. Yet, few experiments did observe significant dependence of ICEK phenomena on the electrolytes.^{46,47} This feature is still difficult to explain at present and probably can be accounted for by taking into account the chemical effects (such as specific ion adsorption and solution chemistry) in the formulation of the numerical model.

FIG. 11. Transient development of ICEK velocity magnitude along the radial direction at $\theta = \pi/4$ for three different electrolytes with $E_0 = 1$ and $a/\lambda_D = 1000$. The results for different electrolytes are differentiated by different colors: black (LiCl); red (NaCl); and blue (KCl). For each electrolyte, different instants are differentiated by different line styles: solid line ($t = 1$); dashed line ($t = 2$); dotted line ($t = 4$); dashed-dotted line ($t = \text{inf}$). The circular symbols denote the results from the slip velocity model by Bazant, i.e., $|\mathbf{u}| = 2E_0^2/r^3$.

Although the types of electrolyte do not have impact on the steady state velocity distribution, they do affect the transient development of the ICEK velocity, as shown in Fig. 11. It is seen that the transient velocity development is the fastest for KCl and slows down for NaCl and LiCl. This is because EDL charging for KCl is the fastest because of the highest diffusivity of K^+ among the three cations, and accordingly, the flow development for KCl is also the fastest. Furthermore, the location of the local maximal velocity seems independent of electrolytes, and this location is roughly 4 times of the Debye length for all the three electrolytes. Expectedly, the slip velocity model agrees well with the steady-state numerical results since in this plot the applied field is weak ($E_0 = 1$) and the EDL is thin ($a/\lambda_D = 1000$).

IV. CONCLUSIONS

In this work, we have formulated a numerical model to describe the transient characteristics of EDL charging and fluid flow around an ideally polarizable cylinder subject to a suddenly applied DC electric field. The model consisting of the coupled Planck-Nernst-Poisson equations and the Navier-Stokes equation provides a detailed, full-field characterization of ion transport (electric current), the electric potential and the flow field during the EDL charging. The numerical results constitute a clear picture of the transient development of EDL charging and the associated ICEK flow under an applied weak electric field. As soon as a DC electric field is applied, the bulk electric current normal to the cylinder surface leads to the EDL charging and then to the induction of electric charges on the cylinder surface. As time evolves, the EDL charge density and the surface charge of the cylinder increase. In turn, the increasing charge density in EDL begins to counteract and distort the local electric field on the cylinder surface, and then the bulk electric current normal to the cylinder surface reduces and the EDL charging is decelerated. As the EDL charge density increases to the extent that it exactly

counteracts the local electric field on the cylinder surface, the EDL charging reaches the steady state and stops. At the steady state, the cylinder is completely shielded from the electric field. The ICEK flow associated with the EDL charging initially develops inside the EDL near the cylinder surface and then spreads into the bulk solution due to the momentum diffusion from the EDL to the bulk solution. The ICEK flow development generally lags behind the EDL charging. These conclusions are instrumental for a better understanding of the ICEK phenomena.

The present investigation also addresses the effects of electric field strength, electrolyte concentration, and the electrolyte type on the transient ICEK phenomena. It is found that the high electric field strength, high electrolyte concentration, and the electrolyte with low ion diffusivity slow down the EDL charging process. The steady state ICEK velocity increases with the increasing electrolyte concentration and external electric field strength and is independent of the electrolytes. The chemical effects (specific ion adsorption or solution chemistry) might need to be taken into account in the numerical model to account for the experimentally observed electrolyte effects in ICEK phenomena.

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