

Ion steric interactions and electrostatic correlations on electro-osmotic flow in charged nanopores with multivalent electrolytes

Shubhra Sahu , Bapan Mondal , and Somnath Bhattacharyya ^{*}

Department of Mathematics, Indian Institute of Technology Kharagpur, Kharagpur 721302, West Bengal, India



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Atomistic and coarse-grained simulations show the formation of a condensed layer of counterions near a charged surface in contact with multivalent or monovalent electrolytes of high concentration. This condensed layer may overscreen the surface charge, and eventually a coion-dominated region may arise within the electric double layer, which again draws a layer of counterions and so on till the charge density approaches zero. Such a type of overscreening and charge density oscillation cannot be predicted through the mean-field based models as it does not account for the correlations between discrete charges. In the present study the mean-field-based model has been extended to consider the many-body interactions to analyze the electro-osmosis and ion transport of multivalent electrolytes in a highly charged nanopore. The ions are considered to be finite-sized, which is accounted for by considering the hydrodynamic steric interactions and modification of the suspension medium viscosity. Consideration of the electrostatic correlation leads to a fourth-order Poisson-Fermi equation for an electric field. Such a type of continuum model is easy to handle and to use to predict the layered structure of the EDL. Our model captures the existing experimental and molecular dynamics simulation correctly. Based on the modified model, we have analyzed the volume flow rate, current density, and ion selectivity of the pore in multivalent electrolytes for different electrostatic conditions. The present model shows that the counterion size has an impact on the condensed layer and hence overscreening. We demonstrate that the EOF reversal of multivalent electrolytes can be suppressed by mixing with monovalent salts.

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I. INTRODUCTION

The form of the Debye layer on the charged confined surfaces across aqueous electrolytes is important in many fundamental and applied research areas. For example, these interactions are crucial for controlling the properties of a colloidal suspension. In biology, many specific functions of cell membranes strongly depend on electrostatic interactions, such as interactions with biomolecules, membrane adhesion, and cell-cell interactions. Studies electrokinetic transport in nanopores and channels with charged surface are extremely important in the context of nanotechnology [1]. Nanopores can be classified into biological nanopores and solid-state nanopores. Mimicking some of the biological functionalities involving transport of ions and fluids on small scales can be made efficiently in synthetic nanopores or channels [2,3]. Besides mimicking biological ionic channels, analysis of the mechanical, chemical, and electrical properties of ion transport through solid-state nanopores has relevance in fabricating nanofluidic devices [4], energy conversion, separation and sensing molecules [5], water purification, and so on. The transport of ions and molecules, such

^{*}Contact author: somnath@maths.iitkgp.ac.in

as DNA and RNA, in nanopores can be suitably tuned by modifying the electrostatic and geometric parameters of nanopores. The electro-osmotic flow (EOF) arises in the charged pore or channel driven by an externally imposed electric field. Controlling the direction and strength of the electro-osmotic flow and ion transport in nanopores is extremely important in a number of nanotechnological applications [6].

The existing studies of nanopores are mostly based on the Nernst-Planck equation for ion transport coupled with the Navier-Stokes equations and Poisson equation for electric field (PNP model). This model considers the ion as a point charge that interacts via a volume-averaged electric force, and the dielectric permittivity as well as the viscosity of the electrolyte medium is considered to be uniform. This mean-field-based approach is found to be inefficient in characterizing the EOF near a highly charged surface. Qiao and Aluru [7] have shown that in a region away from the channel wall with surface charge density above -0.285 C/m^2 the concentration of coions becomes higher and the electro-osmotic velocity for the monovalent NaCl electrolyte is in the opposite direction to that predicted by the classical PNP model. Through the molecular dynamic simulation for EOF of a monovalent electrolyte in a nanotube Chen *et al.* [8] has shown that no surface charge over-screening occurs even at a high surface charge density and a higher concentration of monovalent ions can suppress the charge inversion that occurs in the case of multivalent ions. Suppression of over-screening in a mixed electrolyte is also reported by Van der Heyden *et al.* [9] through an experimental study. However, the molecular dynamics simulation on EOF of an aqueous NaCl solution in a slit channel shows a reversal in electro-osmotic velocity at high values of surface charge density [10]. In this case they found that the counterions over-screen the surface charge and a layer of coions forms, which leads to the electro-osmotic mobility reversal. Over-screening arises due to the excessive accumulation of counterions in the Stern layer.

The transport of multivalent electrolyte in charged pores has relevance in biological systems, which has been addressed by several authors, e.g., Rangharajan *et al.* [11] and Pail *et al.* [6]. The study of Rangharajan *et al.* [11] established a close agreement between the experimental results with the numerical results determined by the standard PNP model for the considered range of bulk ionic concentration and surface charge density. Besteman *et al.* [12] found experimentally the reversal of surface charge polarity upon addition of a charge-asymmetric salt having trivalent and quadrivalent counterions. The over-screening and electro-osmotic flow reversal in a multivalent electrolyte over a highly charged surface has been reported by Telles *et al.* [13]. In this study the dissipative particle dynamics is used to simulate the electro-osmotic flow of multivalent electrolytes in a nanopore at a higher range of surface charge density.

Experimental measurement of electrophoretic mobility and electro-osmosis at a higher salt concentration is difficult due to the manifestation of short-range forces [9]. Several authors analyzed the ion correlations and excluded volume effects going beyond the mean-field formulation by adopting the molecular dynamic (MD) simulations, Monte Carlo simulations, density functional theory, etc. Buyukdagli and Ala-Nissila [14] have characterized electrostatic correlation effects on the ionic selectivity of cylindrical nanopores based on the one-loop expansion of the electrolytic free energy around the PB theory and have demonstrated that an increase in surface charge creates an enhancement in monovalent coion concentration in a multivalent electrolyte. Gupta *et al.* [15] formulated the over-screening, ion concentration oscillations, and effect of electrolyte valence by considering the pair of ions as hard spheres below the distance of closest approach and as point charges otherwise. Counterion condensation and charge inversion in multivalent electrolytes over a charged plate are analyzed by incorporating the excluded volume effect by Agarwal and Wang [16]. In this study, the ion correlation is accounted for through the self-energy of ions.

The large system size necessary to tackle the hydrodynamic time and space scales in molecular dynamic simulation or Monte Carlo simulations lead to a big challenge. The many-body interaction in the mean-field-based model can be incorporated by introducing the ion-ion electrostatic correlations. With this modification the mean-field-based approach for the electrokinetics can capture the surface charge over-screening and ion crowding effects, which arises at a large surface charge density. By incorporating the nonlocal effect in the ion free energy, Bazant *et al.* [17] derived the

fourth-order modified Poisson-Fermi equation, which accounts the electrostatic correlation of ions. This model for electrostatic correlation involves a parameter, the correlation length scaled by the Debye length, which signifies the importance of the correlation effect. The overscreening and ion crowding in the context of the electrophoresis of a charged particle in a multivalent electrolyte can be explained based on this modified model. Subsequently, Storey and Bazant [18] adopted this continuum model which comprises the electrostatic correlations to study the electro-osmotic flow of highly concentrated multivalent electrolytes over homogeneously charged surface and established that the double-layer structure is similar as has been observed by the Monte Carlo simulations or density functional theory. Celebi *et al.* [19] studied the EOF by extending the continuum model to take into account the overscreening and ion crowding effects and established a good agreement between the MD simulation results and continuum predictions for surface charges as large as -0.37 C/m^2 . In this paper the ion distribution is considered to govern by the Boltzmann distribution. However, this continuum model overlooks viscosity variations with ion concentration and incorporates ion steric interactions via the Bikerman model. The continuum model for the electrostatic correlation is used by de Souza and Bazant [20] to demonstrate the mobility reversal of charged colloids in multivalent electrolytes, which accurately reproduces Monte Carlo simulation results. In this paper a power-law expression for the correlation length, which scales by the correlation hole, is proposed.

Over the last few years, exhaustive attention has been paid to synthetic pores that mimic several relevant physiological mechanisms carried out by ion channels filled with multivalent electrolytes, i.e., lanthanum chloride in which the typical charge density of a fully ionized surface can exceed 0.3 C/m^2 in magnitude [13]. In such cases of a highly charged channel with multivalent electrolytes, ions interact via a correlated force instead of mean electrostatic force potential. The impact of the electrostatic correlations and hydrodynamic steric interactions of ions on EOF and ion transport in a reservoir-connected nanopore of length on the order of the pore width has not been addressed before. The standard PNP model shows a dominance of the counterions in the nanopore, leading to a strong counterion selectivity of the pore [21]. However, the ion saturation created by the steric interactions and the occurrence of layer of coions in the diffuse layer may attenuate the selectivity of the pore. The selective transport of ions in the nanopore creates depletion and enrichment zones of ions at the two ends of a nanopore. This leads to the ion concentration polarization (ICP), resulting a strong induced electric field which modifies the ion transport and EOF in the nanopore [22]. Thus, the electrostatic correlations will have a profound effect on the ICP in a nanopore.

In this study we developed a continuum model to extend the mean-field based approach to account for the many-body interactions. We adopt the formulation of ion-ion correlation as proposed by Bazant *et al.* [17] in which the energy functional is modified by including the nonlocal Coulombic correlation. The ion crowding effect near a highly charged surface is accounted for by including the volume exclusion due to hydrodynamic steric interaction of ions. Based on the BMCSL equation of state [23] the ion steric interaction of finite-sized ions is incorporated. Through the MD simulation several existing studies [8,19] demonstrated that the medium viscosity is enhanced in the electric double layer due to the hydration of the ions. In the present model the viscosity is considered to vary with the local volume fraction of ions.

The polarization of water molecules near the charged surface by an applied electric field may have an impact on the suspension medium viscosity and dielectric permittivity, which can be accounted for through the viscoelectric (VE) effect [24]. The VE effect may have significance if the magnitude of the EDL electric field exceeds $1.18 \times 10^8 \text{ V/m}$ [25]. It may be noted that the expression governing the VE considers an ion as point charge. Subsequent studies revealed that near a charged surface, the water molecules are oriented along the field lines generated by the counterions that react by the external electric field, leading to a decrease in the dielectric permittivity of the medium [26,27]. In the present study the VE effect is not incorporated, and the dielectric permittivity of the medium is considered to be constant. However, in our model the viscosity of the suspension varies with the local ionic concentration, which depends on the electric field. Thus, the variation of viscosity and hence, diffusivity of ions have implicit dependence on the electric field.

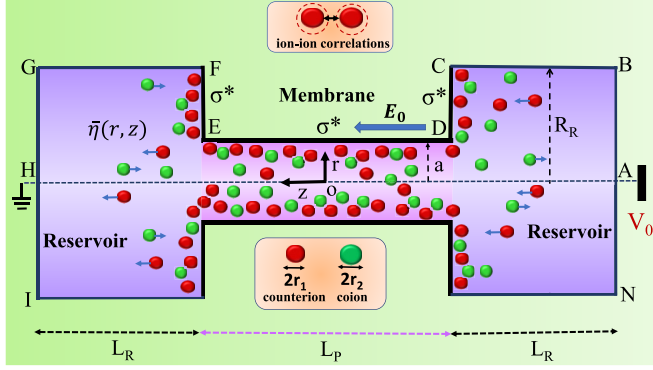


FIG. 1. Schematic of the EOF in a nanopore embedded in a membrane separating two reservoirs.

The governing electrokinetic equations incorporating the finite ion size effects and the ion-ion electrostatic correlations are solved numerically based on a control volume approach. Our numerical solution for EOF in a nanochannel agrees well with existing molecular dynamic simulation as well as existing experimental results. Based on this model we analyze the physical mechanisms of the overscreening of surface charge, and EOF reversal in the nanopore arises for electrolytes of multivalent counterions. Results based on the present modified model are compared with the standard PNP model to highlight the effect of the electrostatic correlations and counterion saturation. The impact of the electrostatic correlations on the average EOF, conductance, and ion concentration polarization (ICP) of the nanopore filled with a non- z : z electrolyte is analyzed. We have demonstrated that the overscreening in multivalent electrolytes can be suppressed by mixing with monovalent electrolytes.

II. MATHEMATICAL MODEL

We consider a cylindrical nanopore of length L_P and radius a drilled through a membrane separating two reservoirs, each of length L_R ($\gg a$) and radius R_R ($\gg a$), which are filled with Newtonian incompressible electrolytes of dielectric constant ϵ_e and density ρ . The inner surface of the perfectly dielectric membrane which is in contact with an electrolyte acquires a constant surface charge density σ^* through the association/dissociation reaction of the surface functional group or adsorption of ions on the wall. The electrostatic charge on the membrane surface creates an electric double layer (EDL) adjacent to the surface. The charged surface together with the EDL forms an electroneutral equilibrium system. When a potential bias V_0 is applied between the two electrodes placed in the two reservoirs a constant axial electric field E_0 develops. We consider the z -axis (Fig. 1) along the direction of the imposed DC electric field E_0 . This imposed tangential electric field interacts with the EDL developed on the pore wall to generate a steady EOF and ion transport within the pore. A cylindrical coordinate system (r, z) with the axis of symmetry $r = 0$ is considered. Similar configuration is adopted by several authors [28–31] to study the steady EOF through a nanopore based on the standard PNP model.

The hydrated ions associated with the aqueous electrolyte are considered as equisized charged hard spheres of finite diameter $2r_i$ and valency z_i for the i th ionic species. The electrochemical potential of the i th ionic species incorporating the volume exclusion effect [32] is governed by

$$\mu_i = \mu_0 + z_i\phi + \ln n_i + \mu_i^{\text{ex}}. \quad (1)$$

Here μ_i is scaled by $k_B T$, μ_0 is the reference electrochemical potential, ϕ is the scaled induced electric potential scaled by the thermal potential $\phi_0 = k_B T / e$, and n_i is the number density of the i th ionic species normalized by the bulk ionic strength $I_\infty = (1/2) \sum_i z_i^2 \bar{n}_i^\infty$ with $\bar{n}_i^\infty$ being the bulk number density of the i th ionic species. If C_0 is the bulk molar concentration of a $z_1 : z_2$ salt, then

the bulk number density of the ionic species is determined as $\bar{n}_1^\infty = |z_2|N_{\text{Av}}C_0$ and $\bar{n}_2^\infty = |z_1|N_{\text{Av}}C_0$, where N_{Av} is Avogadro's number. The excess electrochemical potential $\mu_i^{\text{ex}} = \ln \gamma_i$, where γ_i is the activity coefficient of the i th ionic species arises due to the nonelectrostatic steric interactions, which can be expressed in terms of the local ionic volume fraction $\chi = (4\pi/3)I_\infty \sum_{i=1}^4 n_i r_i^3$. Based on the BMCSL model [23,33], we can express μ_i^{ex} as

$$\begin{aligned} \mu_i^{\text{ex}} = & - \left[1 + 2 \left(\frac{\beta_2 r_i}{\chi} \right)^3 - 3 \left(\frac{\beta_2 r_i}{\chi} \right)^2 \right] \ln(1 - \chi) + \frac{3\beta_2 r_i + 3\beta_1 r_i^2 + \beta_0 r_i^3}{(1 - \chi)} \\ & + \frac{3\beta_2 r_i^2}{(1 - \chi)^2} \left(\frac{\beta_2}{\chi} + \beta_1 r_i \right) - (\beta_2 r_i)^3 \left[\frac{\chi^2 - 5\chi + 2}{\chi^2(1 - \chi)^3} \right] \end{aligned} \quad (2)$$

where $\beta_k = (4\pi/3)I_\infty \sum_i n_i r_i^k$. As the hydrated ions are considered finite-sized charged spheres suspended in the medium, it creates the viscosity to vary with the local ionic volume fraction of the medium [27,34]. The viscosity of the electrolyte η , scaled by the water viscosity η_∞ , varies with the local volume fraction of ions through the Batchelor-Green equation [35] as

$$\eta = \frac{\bar{\eta}}{\eta_\infty} = 1 + 2.5\chi + 5.2\chi^2. \quad (3)$$

Hence, the diffusion coefficient D_i , scaled by its value at the bulk solution D_i^∞ , varies with the local ion volume fraction, i.e.,

$$D_i = \frac{\bar{D}_i}{D_i^\infty} = \frac{1}{1 + 2.5\chi + 5.2\chi^2}. \quad (4)$$

The governing equation for the motion of i th ionic species can be expressed in nondimensional form by applying the conservation law of mass flux as

$$\text{Pe}_i[\mathbf{u} \cdot \nabla n_i] = D_i(n_i \nabla^2 \mu_i + \nabla n_i \cdot \nabla \mu_i) + n_i \nabla D_i \cdot \nabla \mu_i, \quad (5)$$

where $\text{Pe}_i = aU_0/D_i^\infty$ is the ionic Péclet number, which measures the ratio of advective to diffusion transport of ions. Note that the nanopore radius a is taken as the length scale.

As indicated by López-García *et al.* [27], the finite size of the hydrated ions modifies the mass density of the electrolyte medium as, $\rho + (4\pi/3) \sum_i n_i r_i^3 (\rho_i - \rho)$, where ρ_i is the density of the hydrated ionic species i . In most of the electrolytes such as, NaCl the density of Na^+ and Cl^- is equal to that of the water, i.e., 10^3 kg/m^3 . We can treat the effective density of the ions equal to that of the solution [36]. With this we may treat the electrolyte medium as incompressible with constant density ρ . Thus, the fluid flow is governed by the incompressible Navier-Stokes equations, which can be rendered in nondimensional form as

$$\text{Re}[(\mathbf{u} \cdot \nabla) \mathbf{u}] + \nabla p + \eta(\nabla \times \nabla \times \mathbf{u}) - \nabla \eta \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] + \frac{(\kappa a)^2}{2} \rho_e \nabla \phi = 0, \quad (6)$$

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

where, $\mathbf{u}$ is the nondimensional velocity vector scaled by $U_0 (= \epsilon_e \phi_0^2 / a \eta_\infty)$. The pressure p is nondimensionalized by $\eta_\infty U_0 / a$. The parameter $\kappa = \sqrt{2eI_\infty / \epsilon_e \phi_0}$ represents the inverse of the electric double layer (EDL) thickness and $\text{Re} = \rho U_0 a / \eta_\infty$ is the Reynolds number. $\rho_e = \sum_i z_i n_i$ is the scaled charge density.

The induced electric potential is governed by the fourth-order modified Poisson-Fermi equation [17,20], which comprises the ion-ion electrostatic correlation, as

$$\delta_c^2 \nabla^4 \phi - (\kappa a)^2 \nabla^2 \phi = \frac{(\kappa a)^4}{2} \rho_e, \quad (8)$$

where δ_c is the nondimensional correlation length scaled by the Debye length κ^{-1} . The correlation length is fundamentally influenced by both the ion size and the Bjerrum length l_B of the electrolyte.

While most studies have treated the scaled correlation length δ_c as a multiple of the Debye length κ^{-1} , de Souza and Bazant [20] introduced the size of the correlation hole to scale l_c . They derived an expression for δ_c in terms of κ^{-1} and l_B as

$$\delta_c = 0.35(Z^2\kappa l_B)^{2/3} \left(\frac{ea}{2\pi Z^3 \epsilon_e \phi_0 l_B^2 |\sigma|} \right)^{1/8}. \quad (9)$$

Here, $l_B = e/(4\pi\epsilon_e\phi_0)$ represents the Bjerrum length, and Z indicates the magnitude of the counterion valency.

The nanopore wall (DE) and membrane surfaces (CD, EF) possess a uniform surface charge density σ^* . In addition, we impose the condition that the correlation between ions and wall surface charge is negligible [17]. These surfaces are ion-impermeable and no-slip. Thus,

$$\hat{\mathbf{n}} \cdot \delta_c \nabla(\nabla^2 \phi) = 0, \quad \hat{\mathbf{n}} \cdot \nabla \phi = -\sigma, \quad \hat{\mathbf{n}} \cdot \mathbf{N}_i = 0, \quad \mathbf{u} = 0, \quad (10)$$

where $\sigma = \sigma^* a/(\epsilon_e \phi_0)$ is the scaled surface charge density and $\hat{\mathbf{n}}$ is the unit normal to the walls towards the fluid medium. It may be noted that the jump condition for the electric displacement vector as provided in Eq. (2) by Levy *et al.* [37] reduces to the second condition of Eq. (10) for the perfectly dielectric membrane (i.e., the dielectric constant is close to zero), as considered here. Prescribing σ^* instead of the surface potential on the boundary is more appropriate to resemble the model with experimental study. For a measured σ^* of the membrane at a fixed κa the surface potential may differ for a different electrokinetic model as the screening of surface charge depends on the counterion distribution near the surface. Here, $\mathbf{N}_i = n_i \mathbf{u} - (1/\text{Pe}_i) n_i D_i \nabla \mu_i$ is the scaled flux of i th ionic species. The conditions on the insulated side walls of the reservoirs (BC and FG) are

$$\hat{\mathbf{n}} \cdot \delta_c \nabla(\nabla^2 \phi) = 0, \quad \hat{\mathbf{n}} \cdot \nabla \phi = 0, \quad \hat{\mathbf{n}} \cdot \mathbf{N}_i = 0, \quad \mathbf{u} = 0. \quad (11)$$

The reservoirs are considered large enough so that the concentration of each ionic species reaches its bulk concentration at the end of the two reservoirs, i.e., $n_i \rightarrow n_i^\infty$. In the absence of any external pressure gradient and viscous stress across the reservoirs, the far ends of the reservoirs act like open boundaries, i.e., $[(\nabla \mathbf{u}) + (\nabla \mathbf{u})^T] \cdot \hat{\mathbf{n}} = 0$. The electric potential at the right reservoir relative to the left one is considered to be V_0 . Thus, we impose the conditions for ϕ at the two reservoir ends as

$$\phi = 0 \quad \text{on} \quad \text{GI} \quad \text{and} \quad \phi = V_0/\phi_0 \quad \text{on} \quad \text{BN} \quad (12)$$

along with $\hat{\mathbf{n}} \cdot \nabla(\nabla^2 \phi) = 0$ on both GI and BN, which corresponds to zero correlations in the reservoir's uncharged liquid.

III. NUMERICAL METHODS

For numerical modeling we consider that the constant DC electric field is applied for $t \geq 0$, creating a steady electro-osmotic flow after a transient phase. The initial condition ($t = 0$) is governed by the equilibrium situation in which $\mathbf{u} = \mathbf{0}$. Numerical solutions of the nonlinear equations governing the electroosmosis are obtained based on a control volume approach implemented on a staggered grid arrangements. We discretized the governing equations, cast into the conservation-law form, by integrating over each control volume. The transport equations for ions and fluid involve the advection and electromigration terms, governed by first-order derivatives of variables, which can have significant impact when the variables have a sharp change. In to order to impart stability to the numerical scheme for such type of transport equations, we use the total variation diminishing (TVD) scheme to discretize the convective and electromigration terms in the ion transport equations. The TVD scheme prevents spurious oscillations in numerical solutions, ensuring stability. The other terms in the transport equations involving the second-order derivatives are discretized through the linear interpolation of variable values on either sides of the control volume. The discretized equations are solved by the pressure correction-based iterative algorithm SIMPLE (Semi-Implicit Method for Pressure-Linked Equations [38]). This method connects continuity and momentum

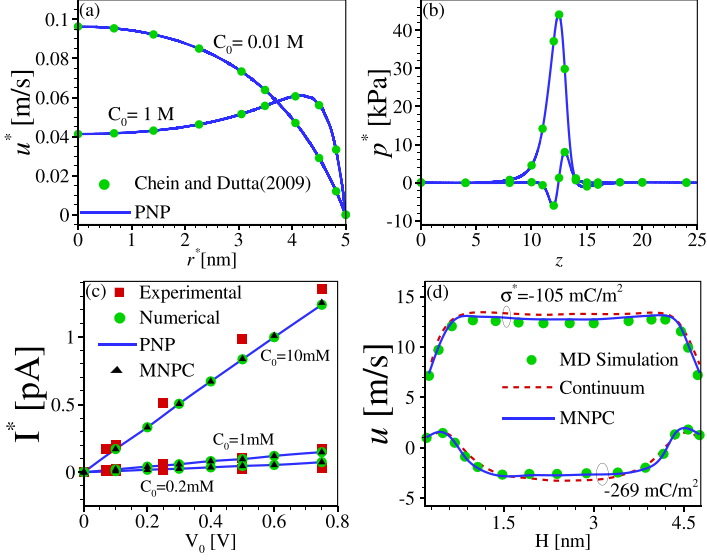


FIG. 2. Comparison of the present results (PNP and MNPC) with (a) numerical results of Chein and Dutta [28] for velocity, (b) Chein and Dutta [28] for pressure in a cylindrical nanopore when $\sigma^* = -30.6$ mC/m², and (c) experimental and numerical results of Rangharajan *et al.* [11] at $\sigma_{\text{pore}} = 0.35$ mC/m², $\sigma_{\text{wall}} = -0.1$ mC/m² for I^* of multivalent salt mixtures in a cylindrical nanopore at different buffer concentrations. Comparison of the present results (MNPC) with (d) (molecular dynamic simulation (symbols) and continuum model (dashed lines) of Celebi *et al.* [19] for velocity profile in a slit channel at various $\sigma^* = -105$ mC/m² ($\delta_c = 0.76$, $\beta = 0.31$ nm), $\sigma^* = -269$ mC/m² ($\delta_c = 1.06$, $\beta = 0.21$ nm) when $C_0 = 1$ M, $E_0 = 0.25$ V/nm.

equations by transforming the discretized continuity equation into a Poisson equation for pressure correction. At each iteration, the electric potential is obtained by solving the fourth-order Poisson-Fermi equation by transforming it into two coupled second-order elliptic PDEs, which are solved numerically through the successive-over-relaxation (SOR) technique. An iteration procedure is continued till the convergence criteria are satisfied.

We adopt a finer grid distribution near the nanopore wall as a faster change in the variables occur within the EDL. As we move away from the membrane, the grid spacing is gradually increased by an arithmetic progression. The grid spacing in the radial (r) and axial (z) directions, denoted as δr and δz , ranges between 0.001 and 0.003 near the pore wall. Away from the wall, the grid size gradually increases up to 0.015. Further increment in grid size does not alter the electro-osmotic flow within the nanopore.

Based on the numerical algorithm as outlined above, we have developed a custom computer code which is executed on an IBM Power 10 server. Typically, this code takes around 3–4 hours to execute, utilizing 99% of the CPU. The convergence of the current numerical code is confirmed through comparison with various experimental and theoretical findings. Further elaboration of this is presented in the subsequent section.

IV. RESULTS AND DISCUSSIONS

We consider the nanopore of radius $a = 10$ nm and length 50 nm connected two identical reservoirs. For numerical computation we consider the size $L_R \times R_R = 10a \times 10a$ to approximate the large cylindrical reservoir. Further increment in the reservoir size does not alter the results. The dielectric permittivity of the electrolyte ϵ_e is $78.5 \times 8.854 \times 10^{-12}$ F/m. Following the range of the applied electric field considered in existing experimental studies [11, 39–42], we have considered the externally applied bias $V_0 = 200$ mV. Our numerical results show that the variation of electric

TABLE I. Properties of the ions.

Ions	z_i	r_i (Å)	$D_i \times 10^{-9}$ m ² /s
K ⁺	+1	3.31	1.96
Li ⁺	+1	3.82	1.03
Cl ⁻	-1	3.32	2.03
Ba ⁺²	+2	4.04	0.8471
Be ⁺²	+2	4.59	0.599
[Co(NH ₃) ₆] ⁺³	+3	3.96	0.908
La ⁺³	+3	4.52	0.617
Al ⁺³	+3	4.75	0.559

field between 10^4 to 4×10^6 V/m produces a linear increment in the average EOF and ionic current. For this range of E_0 the potential drop across the EDL may not exceed the thermal potential. We have also shown the linear variation of the current density with V_0 in Fig. 2(c). Results are presented based on the MNPC model accounting the ionic correlation, steric interaction and viscosity variation for electrolytes of different ionic size and valence. The MNPC model is compared with the standard PNP model as well as MNP model, in which correlation is neglected. In Table I we provide the electrostatic properties of the electrolytes considered in the present study.

A. Comparison of EOF in a pore with existing results

We begin by comparing the EOF in a pore based on the PNP model for a moderate range of surface charge density and bulk ionic concentrations. In Figs. 2(a) and 2(b) we have compared the velocity profile with Chein and Dutta [28] and the central line pressure distribution for a pore of radius 10 nm at a fixed σ^* for a different bulk ionic concentration (C_0). Our results based on the PNP model are in excellent agreement with those of Chein and Dutta [28]. We find that the axial velocity is higher for a lower C_0 for which the ζ potential is higher. However, the axial velocity near the EDL is higher for a higher C_0 as the number density of the counterions in the EDL is increased. The central line pressure distribution of the pore shows that an adverse pressure gradient is created near the central region of the pore for a lower C_0 and the pressure gradient is favorable for a higher C_0 . A detailed discussion if this is made by Chein and Dutta [28].

In Fig. 2(c) we have compared our results for multivalent electrolyte with the experimental as well as numerical results of Rangharajan *et al.* [11] and established a good agreement. We find no difference between our standard PNP model and the modified MNPC model for this lower range of surface charge density. These results are in excellent agreement with the numerical solution of Rangharajan *et al.* [11] based on the standard PNP model. The maximum percentage difference in ionic current determined by these two models is 1.8%, and the maximum difference from the experimentally measured data is 7%. This provides a validation of our model for multivalent electrolyte. In Fig. 2(c) the electric field is varied between 1.7×10^3 V/m and 0.125×10^6 V/m, and a linear variation of I^* with V_0 at different values of the bulk ionic concentration is evident.

We now compare the present MNPC model with the results based on the molecular dynamic stimulation as well as continuum model of Celebi *et al.* [19] for a higher range of surface charge density and bulk ionic concentration for NaCl electrolyte in a parallel plate channel [Fig. 2(d)]. It may be noted that the continuum model of Celebi *et al.* [19] accounts the ion steric interactions through the Bikerman model and the ion-ion correlations by the BSK model [17]. We find an excellent agreement between our computed solution with the continuum model and a 5.69% deviation from the MD simulation for a higher $\sigma^* = -269$ mC/m². We find a reversal in the EOF velocity for the monovalent NaCl electrolyte away from the EDL at higher σ^* . This occurs due to the overscreening of the surface charge, leading to a larger accumulation of coions outside the EDL, which drives a negative EOF.

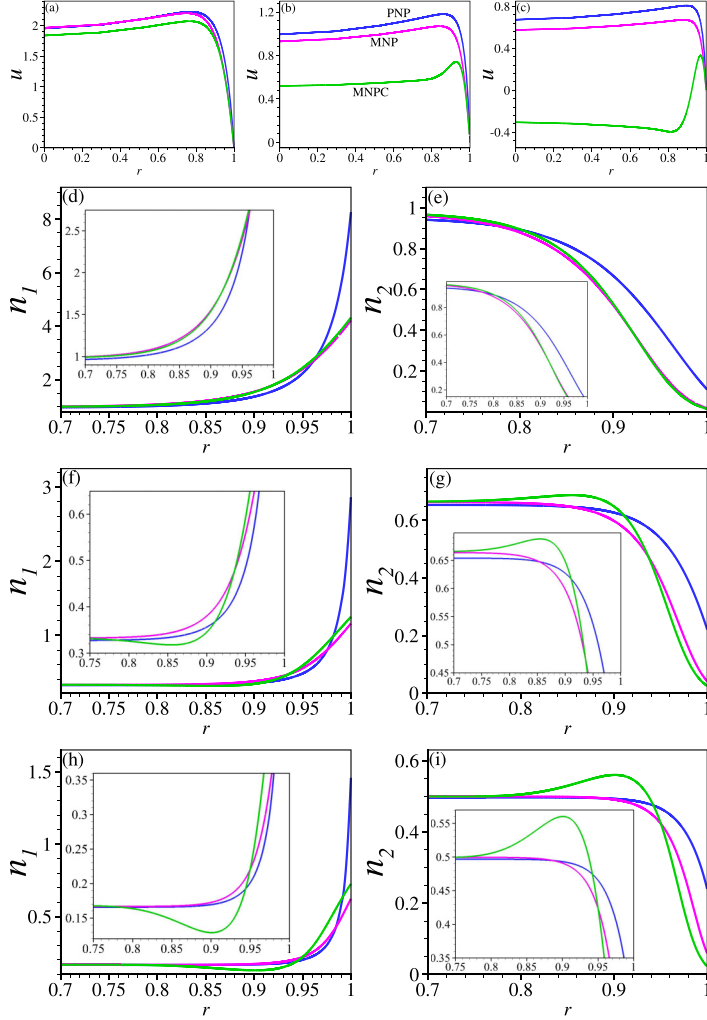


FIG. 3. Radial distribution of (a), (b), (c) velocity, (d), (f), (h) counterion concentration, and (e), (g), (i) coion concentration in three models PNP (blue lines), MNP (pink lines), and MNPC (green lines) for LiCl (a), (d), (e), BeCl₂ (b), (f), (g), and LaCl₃ (c), (h), (i) salts when $C_0 = 300$ mM and $\sigma^* = -80$ mC/m². Inset figures represent the close up near the wall.

B. EOF based on different models

We now compare the EOF based on the present model (MNPC) with the standard model (PNP) and the modified model (MNP) where electrostatic correlation is not considered. Counterion correlations are important near the surface where concentration of counterions is high. Figure 3(a) shows that electro-osmotic flow (EOF) for the monovalent electrolyte is reduced when the correlation effect is considered, and this reduction in EOF augments an electrolyte with divalent counterions [Fig. 3(b)]. For a trivalent electrolyte an occurrence of EOF reversal away from the surface is evident from Fig. 3(c). The ion correlation becomes significant as the valence of the counterion is increased, which enhances the screening of surface charge, and eventually a overscreening of surface charge occurs when the correlated force of the ions becomes higher for the trivalent LaCl₃ electrolyte. This overscreening leads to a electro-osmotic mobility reversal, as is seen in Fig. 3(c).

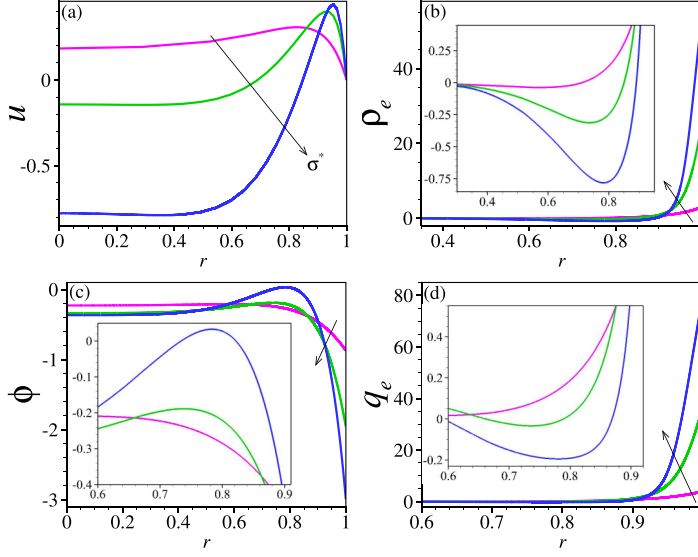


FIG. 4. Radial profile for (a) velocity, (b) charge density, (c) induced potential, and (d) excess ionic strength at various σ^* ($= -10, -40, -80$) mC/m^2 for LaCl_3 electrolyte when $C_0 = 10$ mM. Inset: zoom of the region of charge density reversal.

We find from Figs. 3(d), 3(f), and 3(h) that a relatively less accumulation of counterions compared to the standard PNP model occurs near the surface when the modified model incorporating ion steric interactions (MNP model) is considered. However, the counterion concentration in MNPC model is enhanced compared to MNP model due to the counterion correlation. This difference manifests for multivalent counterions [Figs. 3(f) and 3(h)]. The saturation in ionic concentration near the surface arises due to the consideration of the steric interaction, which attenuates the screening of the surface charge leading to a higher surface potential. A condensed layer enriched with counterions develops near the surface in which a sharp variation in ion distribution occurs. Beyond this layer the counterion concentration reduces and coion concentration enhances. For a multivalent electrolyte a region outside the condensed layer develops, in which the concentration of coion exceeds the counterion concentration, creating a region of opposite electric potential. For a monovalent electrolyte the correlation effect is smaller, and the amount of counterion accumulation near the surface is insufficient to create a reversal in electro-osmotic flow. The profile for coions and counterions obtained by the PNP and MNP models does not show any region where counterions undershoots or coions overshoots their bulk values. In these models the ion density outside the thin layer adjacent to the surface approaches gradually their bulk values. Without the correlation effects, the charge density would decay monotonically from the maximum value to zero far from the wall. However, with the correlation effects included in the model, the charge density oscillates and changes sign. We find that the electrostatic correlations extend the region of the nonzero charge density beyond the Debye screening length κ^{-1} .

C. Overscreening and EOF reversal in multivalent electrolytes

Based on the modified model MNPC we consider the EOF of LaCl_3 electrolyte in Fig. 4 for a moderate to higher range of the surface charge density for the bulk ionic concentration $C_0 = 10$ mM, for which $\kappa a = 8.04$. The correlation length l_c is significant for a higher range of κa and higher valence of the counterion. The electrostatic coupling constant ξ providing a measure of the counterion-counterion interaction with respect to the thermal energy, which is estimated by the ratio

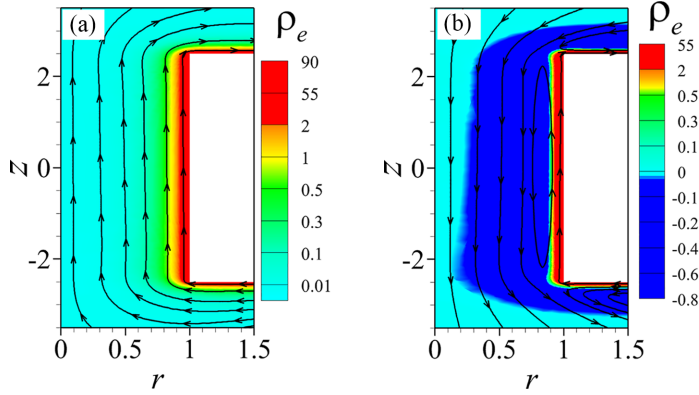


FIG. 5. Streamline pattern and charge density contour of the (a) PNP model and (b) MNPC model in the nanopore for the LaCl_3 electrolyte when $\sigma^* = -80 \text{ mC/m}^2$ and $C_0 = 10 \text{ mM}$.

between the Bjerrum length with the Gouy-Chapman length, i.e., $\xi = 2\pi Z^3 l_B^2 \sigma^*$ [43], increases with the increase of surface charge density for trivalent counterions. A large ξ implies that the counterions are strongly attracted to the charged wall. This creates a larger accumulation of the counterions near the surface, which leads to a manifestation of the correlation effect beyond a moderate σ .

We find that with the increase of σ the axial velocity is enhanced in the vicinity of the surface, and at a higher σ a reversal in velocity occurs as we move away from the surface. This reversal in u enhances with further increase of σ . A similar pattern in velocity profile for a monovalent counterion at a large $\sigma^* (> 0.239 \text{ C/m}^2)$ is found by Celebi *et al.* [19] based on the correlation model. The occurrence of such reversal in velocity can be justified through the charge density and electric potential profiles. The surface potential enhances as the σ is increased, which leads to a larger accumulation of multivalent counterions, leading to net charge density of the mobile ions to become positive near the surface, creating a positive u . An excess accumulation of this multivalent counterions leads to an overscreening of the surface charge. This larger accumulation of counterions overcompensates the surface charge and attracts coions at the outer interface, characterized by a layer of coions ($\rho_e < 0$), leading to $\phi < 0$ within this region. This creates $u < 0$ for the negatively charged surface.

The excess ion distribution measured by $q_e = 0.5(\sum_i z_i^2 n_i - 2)$ shows that near the thin layer adjacent to the surface the concentration of ions compared to the bulk concentration is enhanced by a large margin. Then a depletion region develops, in which the net ionic concentration is lower than the bulk value. It is evident that at a larger σ for which the electrostatic correlation is significant, the double layer extends beyond the Debye screening length κ^{-1} . An increase of the double-layer thickness can, in turn, increase the migration and convection of ions.

Figure 5(a) for streamlines and charge density distribution within the pore obtained by the PNP model shows that the EOF over the negatively charged surface is along the direction of the electric field ($z > 0$). The formation of the counterion-dominated diffuse layer with positive charge density ($\rho_e > 0$) is evident. The positive charge density decays and approaches zero in the core region of the pore. Results based on the MNPC model [Fig. 5(b)] show that interionic correlation for the trivalent electrolyte leads to an electro-osmotic mobility reversal at a higher surface charge density. Development of a condensed layer of counterions near the charged wall is evident, which drives the fluid to flow along $z > 0$ direction in the vicinity of the membrane. At a higher $-\sigma$ the strong correlations between the counterions enhance the counterion condensation, which leads to an overcharging and eventually a charge inversion occurs. The presence of large coions in the diffuse layer creates a reversal in EOF, i.e., $u < 0$. We find from Fig. 5(b) that a layer of coion-dominated

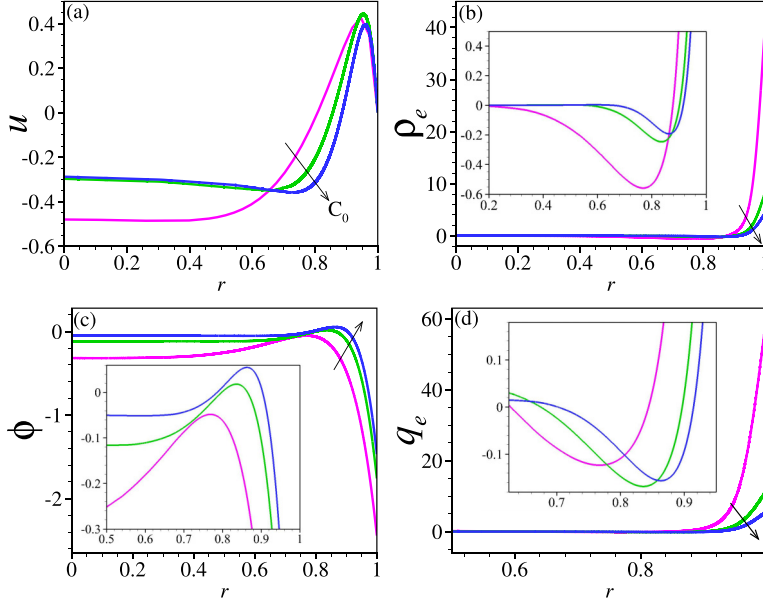


FIG. 6. Radial profile for (a) velocity, (b) charge density, (c) induced potential, and (d) excess ionic strength at various C_0 ($=10, 50, 100$) mM for the LaCl_3 electrolyte when $\sigma^* = -60 \text{ mC/m}^2$. Inset figures refer to the close-up near the pore wall.

region ($\rho_e < 0$) occurs in the MNPC model, which is absent in the PNP model [Fig. 5(a)]. The extension of the Debye layer in the MNPC model compared to the PNP model is evident.

As the bulk ionic concentration increases the correlation length l_c for the electrolyte LaCl_3 with trivalent counterion increases. The strongly correlated fluid near the charged surface attracts more counterions than necessary to neutralize the surface charge (overcharging). This leads to a EOF reversal outside the condensed layer, as is seen in Fig. 6(a). Formation of a correlation-induced condensed layer of counterions with very high ion concentration at the surface is evident from ρ_e distribution [Fig. 6(b)]. This leads to a surface charge overscreening and a flow reversal due to the occurrence of region of excess coions. Outside the condensed layer of counterions a negative ρ_e region develops in which a depletion of ions, i.e., $q_e < 0$ occurs. With the increase of the bulk ionic concentration the axial velocity reduces as the surface potential declines. We find that beyond a moderate C_0 , velocity in the bulk region does not vary appreciably with C_0 . We find that the rate of accumulation of ions is very large near the surface for a lower C_0 , which decreases as we move away from the surface. A region outside the condensed layer forms where the net ionic concentration is lower than the bulk concentration.

We now consider the EOF of electrolytes with trivalent counterions of different size [Figs. 7(a)–7(c)]. As the size of the counterions is increased, the steric force increases and diffusivity declines, leading to a lower accumulation of counterions near the charged surface. This attenuates the screening of the surface charge and enhancement of the surface potential. It is evident that positive EOF velocity near the surface is higher for a larger counterion size. The impact of the ion-ion correlation augments for a smaller counterion size as the number density of counterions near the surface enhances. A larger accumulation of smaller counterions results in a higher ρ_e and q_e in the condensed layer, as is found in Figs. 7(b) and 7(c). This leads to an enhancement in the correlated force, resulting to a stronger overcharging and velocity reversal for smaller counterions. These results show that the correlations between counterions is influenced by the ion size.

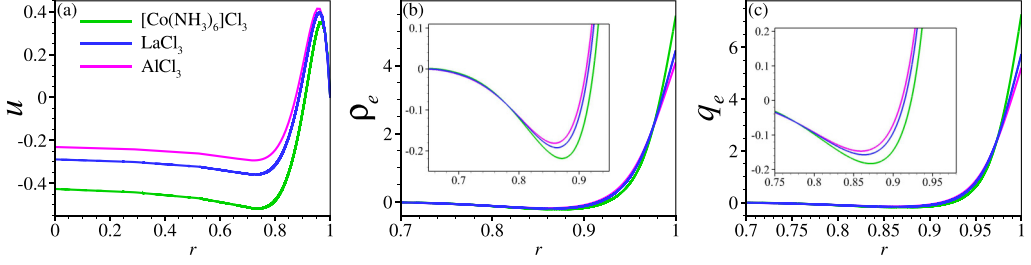


FIG. 7. Radial profile for (a) velocity, (b) charge density, and (c) excess ionic strength when $\sigma^* = -60 \text{ mC/m}^2$ and $C_0 = 100 \text{ mM}$. Inset figures refer to the close up near the pore wall.

D. Volume flow rate, ion selectivity, and ICP for multivalent electrolytes

The volume flow rate through the nanopore is determined by $Q^* = \int_A \mathbf{u}^* \cdot \hat{\mathbf{n}} dA$, where A is any cross section of the nanopore. The ion selectivity of the nanopore, denoted by the parameter S , is measured by the difference between cationic (I_c^*) and anionic (I_a^*) currents, divided by the total current density of the pore, i.e.,

$$S = \frac{|I_c^*| - |I_a^*|}{|I_c^*| + |I_a^*|}, \quad (13)$$

where $I_c^* = e \int_A z_1 \mathbf{N}_1^* \cdot \hat{\mathbf{n}} dA$ and $I_a^* = e \int_A z_2 \mathbf{N}_2^* \cdot \hat{\mathbf{n}} dA$ are the current due to counterions and coions, respectively, passing through the cross section A of the pore. The range of S spans from -1 to 1 with $S = 1$ indicating complete cation selectivity, $S = -1$ signifying complete anion selectivity, and $S = 0$ corresponding to a nonselective nanopore. The ionic current I^* through the cross section A of the nanopore is $I^* = I_c^* + I_a^*$.

In Fig. 8 we present the volume flow rate, net ionic current, pore selectivity, and difference between counterion and coion current through the nanopore by varying the surface charge for

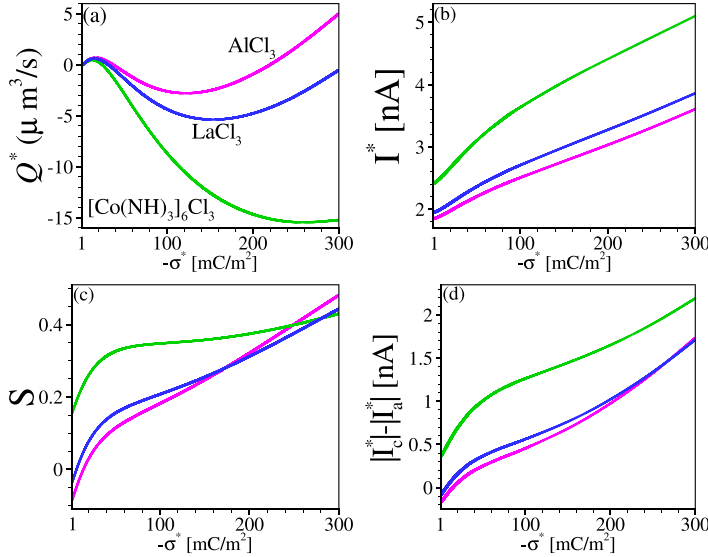


FIG. 8. Variation of the (a) volume flow rate, (b) net ionic current, (c) selectivity, and (d) ionic current difference with σ^* at $C_0 = 50 \text{ mM}$.

electrolytes of trivalent counterions of different size. Results show that Q enhances with σ for a short range of σ in which the counterion correlation is negligible. However, as the surface becomes highly charged ($|\sigma^*| > 10 \text{ mC/m}^2$) the ion-ion correlation becomes significant, which creates a condensed layer of counterions adjacent to the surface and larger accumulation of coions in the diffuse layer. This leads to a decrement in positive Q and eventually a reversal in Q . We find that beyond a larger σ (which varies with bulk ionic concentration), the bulk flow is negative for the negatively charged pore and the magnitude of Q is enhanced for further increase of σ . Reversed EOF arises due to the dominance of the electrostatic correlations. We have seen in Fig. 4(a) that $u > 0$ adjacent to the surface, and it is enhanced as σ is increased, which in turn creates the reversal in Q . As σ increases the accumulation of both counterions and coions are enhanced, leading to a monotonic increment in the current density with σ [Fig. 8(b)].

Telles *et al.* [13] based on the DPD simulation as well as Celebi *et al.* [19] through MD simulation have shown that the volumetric flow rate may become positive at a very large surface charge density. In this continuum-based model, we have restricted ourselves to surface charge density up to $\sigma^* = -0.3 \text{ C/m}^2$. We find in Fig. 8(a) that at a high value of surface charge density the volume flow rate either changes its sign from negative to positive or saturates. EOF for AlCl_3 becomes positive for $-\sigma^* > 0.2 \text{ C/m}^2$ as the surface charge creates a stronger Columbic force than the attractive force created by the counterion correlation.

We find from Figs. 8(c) and 8(d) that the difference between the current due to counterions and coions is small as the accumulation of coions within the EDL is high due to occurrence of overscreening. This creates the lower selectivity of the pore. At a lower σ the current due to the coions I_a^* becomes higher than the counterion current I_c^* , creating $S < 0$. The current density and selectivity enhances as the surface charge density is increased.

It is evident from Fig. 8 that $-Q$ and I^* are enhanced for lower size of the counterions. The difference in current produced by coions and counterions is smaller for the smaller counterions. A reduction in counterion size enhances its diffusivity and attenuates the ion steric effect, resulting a larger accumulation of counterions. This leads to an augmentation in the electrostatic correlations, resulting in a larger accumulation of coions in the diffuse layer. For this, the reversed EOF becomes stronger for the smaller ions. As the impact of the ion correlation attenuates for the electrolytes with higher counterion size, Q becomes positive at a higher surface charge density for AlCl_3 whereas it remains negative for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. We find that the ion selectivity is enhanced for the smaller counterions. However, with the increase of σ the selectivity enhances at a faster rate for AlCl_3 . As noted before, smaller counterions enhance the ion-ion correlations, leading to a larger accumulation of coions in the diffuse layer as well. This leads to an increment in I^* but a saturation in S .

In Fig. 9 we consider the effect of bulk ionic concentration on the volume flow rate, current density, and selectivity in the pore. Beyond a moderate value of C_0 the condensed layer of negative counterions grows stronger, which draws coions in the diffuse layer to create an enhanced current density. However, the flow rate saturates with increasing salt concentration. We find that the smaller counterions creates a lower volume flow rate but enhanced current density. As the steric interaction is lower for a smaller counterion, its concentration near the surface becomes higher, leading to a higher screening of surface charge and higher current density. The difference between I_c^* and I_a^* amplifies as C_0 is increased due to a larger accumulation of coions in the diffuse layer. This leads to a saturation in EOF as the momentum created for the electrolyte by the coions and counterions acts oppositely. The ionic current density is enhanced due to the enrichment of ions in the pore, and the rate of increment in I^* attenuates at a higher C_0 .

We find from Fig. 10(a) that the conductance of the pore for a trivalent electrolyte at a smaller range of the surface charge density obtained by the MNPC model differs from the PNP model. The discrepancy from the PNP model grows as the surface charge density is increased as the PNP model does not account the counterion saturation at a higher charge density. The conductance obtained by MNP and MNPC is almost equal with a small reduction in conductance when the correlation effect is considered at a higher σ as the bulk EOF is reduced.

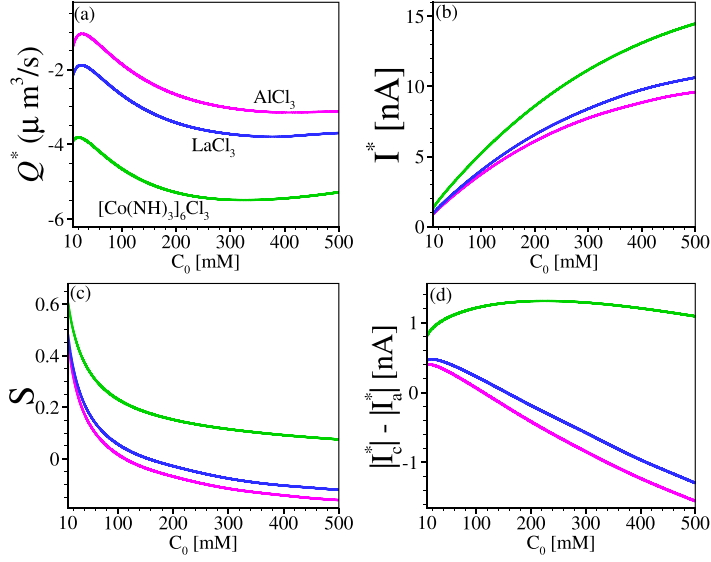


FIG. 9. Variation of the (a) volume flow rate, (b) net ionic current, (c) selectivity, and (d) ionic current difference with C_0 at $\sigma^* = -60 \text{ mC/m}^2$.

The accumulation of ions at the cathode side (right end) of the nanopore and depletion of ions on the other opening, as seen in Fig. 10(b), creates the ion concentration polarization (ICP). This phenomenon occurs when the pore exhibits ion selectivity, i.e., the current density due to counterions is higher than the coions or vice versa. The charge density at the entrance of the pore is negative due to a larger accumulation of coions that arises by the repulsion created by the surface

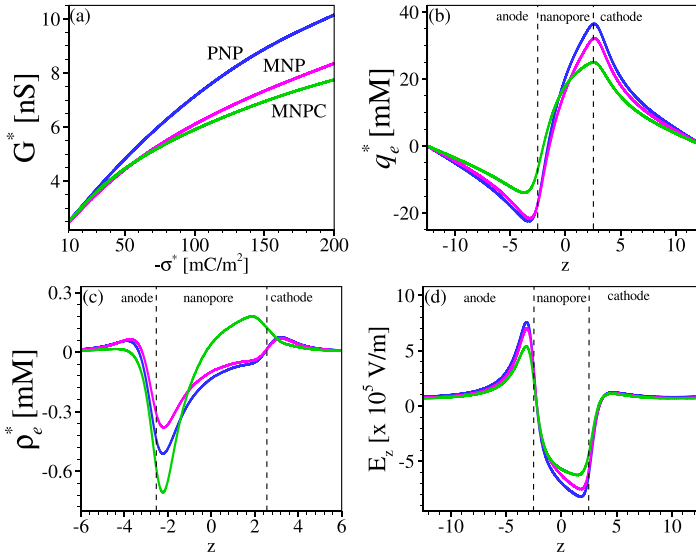


FIG. 10. Variation of the (a) pore conductance ($G^* = I^*/V_0$) with σ^* at $C_0 = 10 \text{ mM}$. Axial profile of (b) excess ionic strength, (c) charge density, and (d) induced electric field along the central line $r = 0$ when $\sigma^* = -60 \text{ mC/m}^2$ and $C_0 = 10 \text{ mM}$.

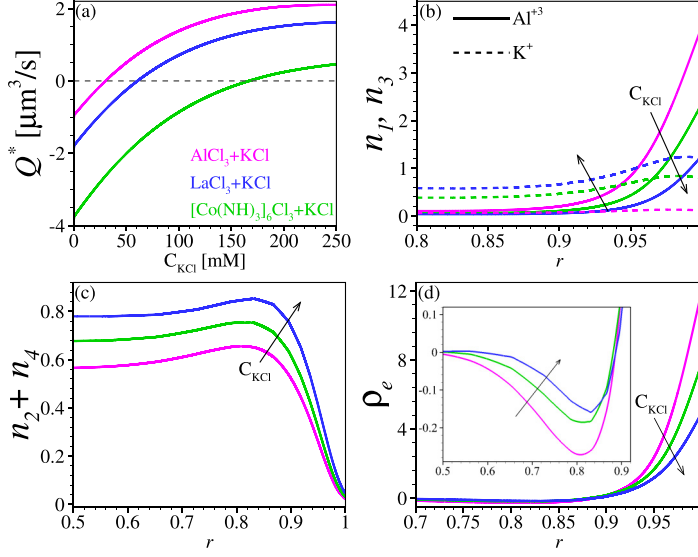


FIG. 11. Variation of the (a) volume flow rate with C_{KCl} when $\sigma^* = -60 \text{ mC/m}^2$ and trivalent $C_0^1 = 30 \text{ mM}$. Radial profile of (b) counterion concentrations, (c) net coion concentration, and (d) charge density for $\text{AlCl}_3 + \text{KCl}$ mixture at various C_{KCl} ($=10, 100, 250 \text{ mM}$) when $\sigma^* = -60 \text{ mC/m}^2$ and $C_0^1 = 30 \text{ mM}$.

charge, which leads to $\rho_e < 0$ [Fig. 10(c)]. This creates an induced electric field [Fig. 10(d)] directed along the imposed field and hence, an enhanced electric field near the pore entrance (anode side). The concentration of the positive counterion enhances within the pore, creating a reduction in the induced electric field. A counterion-enriched zone arises at the cathode side of the pore [Fig. 10(c)] in which $\rho_e > 0$ and $q_e \gg 1$. This enriched counterion region results an induced electric field directed opposite the imposed electric field. We find from Fig. 8(b) that q_e , which measures the excess ion accumulation, is lower in the MNPC model. This implies that both the depletion and enrichment of ions at the two ends is lower in the MNPC model. For this the induced electric field becomes lower in the MNPC model [Fig. 10(d)]. Results show that the ion correlation enhances the space charge density along the central line of the pore, which implies an extension of the EDL compared to the other models.

E. Mixture of electrolytes

We now consider the mixture of a trivalent electrolyte with a monovalent KCl electrolyte. The electrolyte mixtures are abundant in the context of biological, environmental, as well as geological systems [9, 16]. Figure 11(a) shows that a mixture of a small amount of the KCl electrolyte with a different charge-asymmetric electrolyte of counterion valence 3 prevents mobility reversal. Though an increase in bulk concentration of the KCl electrolyte at a fixed amount of trivalent electrolyte increases κa and hence the scaled correlation length δ_c , it attenuates overscreening and hence mobility inversion. Results show that the impact of KCl on the three types of trivalent electrolytes of different counterion size is similar. In the mixed electrolyte with low concentration of KCl the trivalent counterion crowded out the monovalent K^+ near the charged surface due to the higher electrostatic attraction created by the multivalent counterions. This leads to a reduction in the surface potential as the screening effect created by the trivalent counterions is stronger. As the concentration of KCl, i.e., C_{KCl} increased the reversal in EOF declines, and it suppressed at a sufficiently larger C_{KCl} .

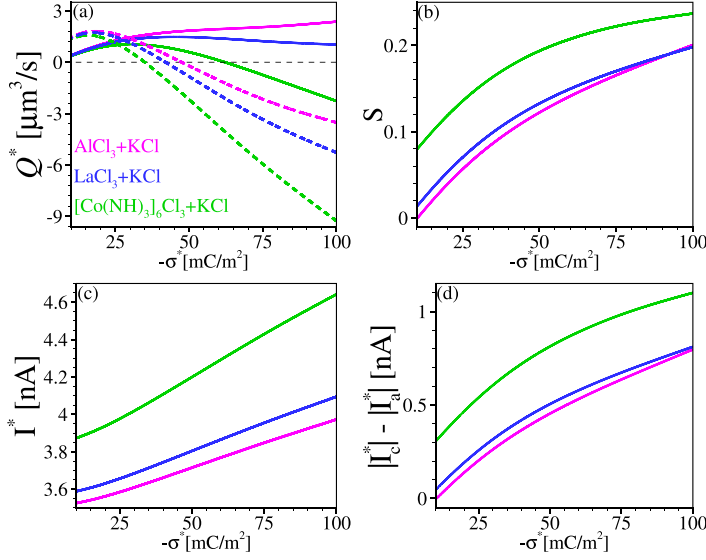


FIG. 12. Variation of the (a) volume flow rate, (b) pore selectivity, (c) net current, and (d) ionic current density with σ^* when $C_0^1 = 30 \text{ mM}$ and $C_{\text{KCl}} = 200 \text{ mM}$. Dashed lines represent the case of $C_{\text{KCl}} = 0$.

Figure 11(b) shows that as the concentration of KCl is increased the concentration of K^+ ions in the condensed layer increases and Al^{+3} decreases, which reduces the correlation effects and hence, overscreening. This is justified by the existing theoretical analysis [8,44] and experimental results of Van der Heyden *et al.* [9] and Martin-Molina *et al.* [45], where it is found that the addition of a small amount of monovalent salt results in a slight increase of the charge reversal. However, for a larger concentration of the monovalent salt this overscreening is suppressed as the multivalent ions concentrate to a bulk electrolyte instead of the charged surface. We find from Fig. 11(c) that the concentration of coions in the EDL increases as C_{KCl} is increased. Figure 11(d) shows that the net charge density in the condensed layer decreases as C_{KCl} is increased, and it also attenuates the overscreening in the diffuse layer, leading to a reduction (or suppression) of EOF reversal. Similar phenomena for EOF in a mixed electrolyte within an infinitely long pore are reported by Agarwal and Wang [16].

The effect of the surface charge density on the EOF in a mixture of monovalent salt KCl into an electrolyte of a trivalent counterion is analyzed in Fig. 12. Figure 12(a) shows that the correlation effect attenuates with the inclusion of KCl into the trivalent electrolyte. Concentration of the trivalent counterions in the condensed layer is suppressed by the monovalent K^+ as the ionic concentration of the later becomes higher. This leads to an attenuation in the interionic correlations near the charged surface, which results in the attenuation of overscreening and hence, reduction of the excess accumulation of coions in the diffuse layer. For this, we find that the critical value of σ^* for EOF reversal increases in the mixed electrolyte.

We find for the electrolyte with higher counterion size that Q remains positive, and it increases with σ . However, the correlation effect is stronger for the trivalent counterion of smaller size, creating $Q < 0$ for a higher range of σ . Figures 11 and 12 demonstrate that the surface charge overscreening and flow reversal in a nanopore by a trivalent electrolyte can be suppressed by suitably mixing with a monovalent electrolyte. This corroborates the experimental findings of Van der Heyden *et al.* [9] and Martin-Molina *et al.* [45].

V. CONCLUSION

We considered the electro-osmotic flow and ion transport through a reservoir-connected nanopore by considering the finite ion size effect and ion-ion correlation. The hydrodynamic steric interactions created by finite-sized ions are accounted for by introducing the volume exclusion term derived from the BMCSL equation of state in the electrochemical potential of the ions. The electrostatic correlations are modeled under the continuum framework by considering the nonlocal contribution to the energy functional. This leads to a fourth-order Poisson-Fermi equation for the electric field. The viscosity of the suspension medium is considered to depend on the local ionic volume fraction, which leads to a modification of the ion diffusivities.

Through this study we have extended the mean-field-based model to analyze the layered structure of the electric double layer and detected the oscillation in charge density that arises in multivalent counterions. The electrostatic correlation is stronger for counterions with higher valence, which results a reversal in volume flow rate beyond a critical surface charge density. Formation of the counterion condensed layer and overscreening creates a larger accumulation of the coions in the EDL, leading to an EOF reversal and attenuation in ion selectivity of the pore. We find that the current density and hence conductivity of the pore attenuates compared to the standard PNP model as the correlation reduces the number density of ions in the EDL. At a sufficiently high surface charge density this reversal in EOF is suppressed or absent. Our results show that the smaller counterions create a stronger electrostatic correlation than a larger counterion as the number density of counterions is enhanced for smaller counterions with higher diffusivity. The overscreening and EOF reversal due to a multivalent electrolyte can be suppressed by mixing with a monovalent salt.

The present model can be extended to incorporate the dielectric decrement that arises due to the polarization of water molecules by the electric field created by counterions, which leads the dielectric constant to depend on the local ionic concentration.

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