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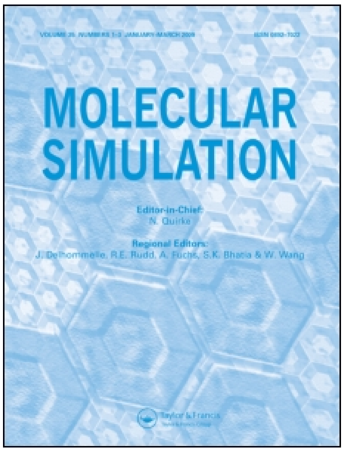

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Chan, Kwong-Yu , Tang, Yuk W ai and Szalai†, István(2004) 'Ion Transport in Simple Nanopores', Molecular Simulation, 30: 2, 81 — 87

To link to this Article: DOI: 10.1080/0892702031000152235

URL: http://dx.doi.org/10.1080/0892702031000152235

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Molecular Simulation, Vol. 30 (2–3), 15 February–15 March 2004, pp. 81–87

Ion Transport in Simple Nanopores

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(Received November 2002; In final form December 2002)

Equilibrium and non-equilibrium molecular dynamics (EMD and NEMD) simulations are reported for the study of ion transport in an infinite long cylindrical nanopore. Results are compared for 3 models of electrolytes including the restricted primitive model (RPM), the solvent primitive model (SPM), and the extended simple point charge model (SPC/E). In EMD simulations, the mean square displacements are used to yield diffusion coefficients. Conductivity can be obtained through the Nernst–Einstein relation. Current and conductivity are calculated directly in NEMD simulations in which an external field is present along the pore axis. The effects of confinement on the ion transport are studied for the 3 model electrolytes. Comparing the EMD results and the NEMD results show that the Nernst–Einstein relation fails for the 3 models of electrolytes in very narrow nanopores.

In addition to direct current NEMD simulations, alternate current (AC) NEMD simulations are performed to investigate the frequency dependence of ion transport. Towards high frequencies, a pore-size independent behavior is observed with vanishing conductivity and a phase lag approaching 90°. The effect of confinement is more evident at low frequencies and an electrical capacitor like behavior is observed in the narrowest pores, as indicated by the conductivity, the phase lag and the Cole–Cole plot. The narrowest pores show a combined reactance–resistance–capacitance (LRC) character and a maximum conductivity can be seen at the resonance frequency.

Keywords: Non-equilibrium molecular dynamics; RPM; SPM; SPC/E; Nanopores; Electrolytes; AC conductivity

INTRODUCTION

In recent years, there has been a rapid development of nanoscale technology in a wide range of applications. Progress in nano-technology includes fundamental understanding in areas of biophysics and materials. The transport of ions in a solution confined in the nanometer scale is critical for the function of inorganic and biological membranes. In the nanometer scale, the transport properties are different from the bulk state. In reality, porous electrodes and biological ion channels have complex geometries. To focus on the effect of nano-confinement, it is useful to investigate ionic transport by computer simulations. To reduce computational time, simple models of electrolytes can be used.

Molecular dynamics simulations of simple electrolytes confined in infinitely long nanopores have been performed [1–5]. By equilibrium molecular dynamics simulations (EMD), Lynden-Bell and Rasaiah [1] have reported diffusion coefficients of different monovalent ions at infinite dilution inside neutral channels of 0.15–0.55 nm using the extended simple point charge model (SPC/E). Lo *et al.* [2] have reported some EMD results for a 0.1 M 1:1 primitive model electrolyte in pores with surface charges. In the EMD simulations, mean square displacement is used to calculate diffusion coefficients. Ionic conductivity is obtained from the diffusion coefficients by the Nernst–Einstein relation. Simulations with a steady-state current in an infinite nanopore were reported using non-equilibrium molecular dynamics (NEMD) [3,4]. As opposed to the EMD approach, current and conductivity are explicitly obtained in the simulation without relying on the Nernst–Einstein relation. The effect of confinement on the validity of the Nernst–Einstein relation was investigated by comparing EMD and NEMD results [4].

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ISSN 0892-7022 print/ISSN 1029-0435 online
DOI: 10.1080/0892702031000152235

Transient response of electrolytes to alternate current (AC) voltage can also be studied by NEMD. Svishchev and Kusalik [6,7] have studied the AC conductivity in bulk electrolytes by NEMD. Tang *et al.* have reported the frequency dependent conductivity in a nanopore using the restricted primitive model (RPM) [5] and a solvent primitive model (SPM) [8]

In this paper, we attempt to summarize the recent results of the RPM and SPM model electrolytes confined in a simple infinite nanopore. Additional new results of the SPC/E model will be provided for further comparison. The focus will be on two issues. Firstly, the validity of the Nernst–Einstein relation in nanopores is explored by comparing results of EMD and NEMD simulations. Secondly, the effect of confinement of the frequency dependent transient response will be discussed from the AC-NEMD simulation results.

MODELS AND SIMULATION METHOD

Simulations were performed for 3 electrolyte models. The SPM assumes the solvent as neutral spheres. The electrostatic effect of the solvent is implicitly represented by using a dielectric constant $\varepsilon_r = 78.3$ to mediate the ion–ion interaction. The RPM can be viewed as a limiting case of SPM with zero solvent density and with symmetrical cation and anion parameters. A soft-core repulsion is used between all particles i and j of types α and β as

$$u_{\alpha\beta}^{\text{core}}(r_{ij}) = \begin{cases} 4\varepsilon_{\alpha\beta}\left[\left(\frac{d_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{d_{\alpha\beta}}{r_{ij}}\right)^{6}\right] + \varepsilon_{\alpha\beta} & \text{if } r_{ij} \le r_{\min}(\alpha,\beta) \\ 0 & \text{if } r_{ij} > r_{\min}(\alpha,\beta) \end{cases} \quad (1)$$

where r_{ij} is the distance between two particles i and j and $\varepsilon_{\alpha\beta}$ and $d_{\alpha\beta}$ are the energy and distance parameters of the potential. Coulomb pair potential between ions is given by

$$u_{\alpha\beta}^{q}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}} \quad (2)$$

where q_i is the electric charge on particle i, ε_0 is the permeability of free space, and ε_r is the relative permeability with a value 78.3 in the case of primitive model. The total ion–ion interaction is therefore,

$$u_{\alpha\beta}(r_{ij}) = u_{\alpha\beta}^{\text{core}}(r_{ij}) + u_{\alpha\beta}^{q}(r_{ij}) \quad (3)$$

and the ion–solvent and solvent–solvent interactions are

$$u_{\alpha\beta}(r_{ij}) = u_{\alpha\beta}^{\text{core}}(r_{ij}). \quad (4)$$

In the SPC/E, explicit charges are placed on the hydrogen and oxygen atom of the water molecule and the oxygen acts as the mass center of the water molecule. The charge, size and energy parameters of the SPC/E model are well documented [9]. The Lennard–Jones (LJ) potential for particle–particle core interactions is given by

$$u_{\alpha\beta}^{\text{LJ}}(r_{ij}) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{d_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{d_{\alpha\beta}}{r_{ij}}\right)^{6}\right] \quad (5)$$

Equation (1) is a cut and shift version of Eq. (5). The total ion–ion, ion–solvent and solvent–solvent interaction is same as Eqs. (3) and (4) with u^{core} replaced by u^{LJ}.

Particle–wall interaction is calculated using the shifted LJ type wall potential proposed by Tjatjopoulos *et al.* [9] and details of the computation are given previously [2].

The transport properties of ions are calculated in EMD simulations using a NVT ensemble. The system temperature is kept constant by implementing a Gaussian thermostat [10]. Periodic boundary conditions are applied in the axial direction of the pore and the axial diffusion coefficient of ions are calculated by the Einstein relation. The Einstein relation is given by:

$$D_\alpha = \frac{1}{2}\lim_{t\to\infty}\frac{\langle |z_{\alpha i}(t) - z_{\alpha i}(0)|^2\rangle}{t} \quad (6)$$

where the brackets $\langle\ldots\rangle$ denotes the ensemble average of the mean axial displacement of α type species in z direction. The electrical conductivity of ions is computed using the Nernst–Einstein relation,

$$\sigma = \frac{e^2 N_A}{kT}\sum_\alpha z_\alpha^2 c_\alpha D_\alpha \quad (7)$$

where N_{A} is the Avogadro number, k is the Boltzmann constant, z_α is the charge valance of different ions, c_α is the concentration of different ions and e is the elementary charge. Electrical conductivity of ions can be obtained directly using NEMD with the presence of an external electric field in the axial direction. The heat generated by the external field was removed by adding a constraint parameter in non-Newtonian equations of motion. The definition of induced electric current density in the axial direction in response to the electric field is

$$J_z = \frac{1}{V}\sum_{j=1}^{N_i} q_j v_{j,z} \quad (8)$$

where $v_{j,z}$ is the axial component of the velocity of the j th ion, V is the volume of the pore and N_{i} is the total number of ions. The electric conductivity can be defined by a simple limit as

$$\sigma = \lim_{E_z\to 0}\frac{J_z}{E_z} \quad (9)$$

The conductivity is calculated by extrapolating the electric conductivity at various electric fields in the linear response region.

For frequency dependent conductivity, the external electric field applied to the system has a sinusoidal waveform. The electrical conductivity is obtained from the average current density of Eq. (8). In the linear response range, the real part of the electrical conductivity $\sigma(\omega)$ is computed as,

$$\sigma(\omega) = Re[\sigma(\omega)] = \lim_{E_{zo}\to 0} Re\left[\frac{J_{zo}e^{i(\omega t+\varphi)}}{E_{zo}e^{i\omega t}}\right] = \lim_{E_{zo}\to 0}\frac{J_{zo}}{E_{zo}}\cos\varphi \tag{10}$$

where relations between zero point current density in the z-direction, J_{zo} and applied electric field, E_{zo} are affected by a phase angle φ.

All simulations were carried out at 298 K and the time interval of a simulation step is 1 fs. All ions in the RPM and SPM simulations have the parameters of a sodium ion with diameter 3 Å and mass 23 a.u. The LJ energy parameters for ions and solvent particles are 4.369×10^{-21} and 1.080×10^{-21} J, respectively. Concentration of ions in the RPM and SPM is 0.1 and 0.5 M in SPC/E. In the SPM, solvent particles have packing fractions of 0.2 and 0.3. In the SPC/E model, the actual parameters of potassium and chloride ions are used. The sizes of K^+, Cl^- and H_2O are 3.25, 3.785 and 3.169 Å, respectively, and the LJ energy parameters are 8.700×10^{-22} J for ions and 1.080×10^{-21} J for water molecules. The density of water is 997 kgm^{-3} in the SPC/E model. Periodic boundary conditions were applied at both ends of the pore. The radii of cylindrical pore ranges from 4.5 to 45 Å and length of pore is at least 7 times that of the radius so that the long range interaction force is negligible compared with interaction forces among particles inside the pore.

In the NEMD simulations, external fields with field strength between 9.09×10^5 and 1.82×10^6 Vm^{-1} were applied to the pore in RPM, and a field strength between 9.09×10^6 and 5.45×10^7 Vm^{-1} were applied to the SPM. In the SPC/E model, the field strength varies between 1.06×10^8 and 6.38×10^8 Vm^{-1}.

Applied field frequencies in the AC-NEMD simulations are set in a higher range compared with experimental settings in order to show the relaxation range in the frequency dependent conductivity spectrum. The applied field frequency ranges between 1.13×10^8 and 1.26×10^{12} Hz in RPM simulations and between 1.13×10^{11} and 3.16×10^{13} Hz for SPM simulations.

RESULTS AND DISCUSSIONS

The electrical conductivities of ions obtained by direct current (DC-NEMD) simulations for different models are shown in Fig. 1. Concentration of electrolyte in the RPM and SPM is 0.1 M while that in SPC/E model is 0.5 M. The packing fraction of solvent directly affects the mobility of ions and the RPM model ($\eta_s = 0$) gives an unrealistic conductivity which is three orders of magnitude above experimental values. Even though the ion concentration is higher, the total density of particles in the SPC/E model is still higher than all cases of SPM model studied here. Hence the conductivity of the 0.5 M SPC/E electrolyte has the lowest value. Except for the RPM model, a general trend of a decrease in conductivity with decreasing pore size is observed. The decrease of diffusivity is due to a confinement effect from the wall of the pore. In our work the particle–wall interactions are represented by a potential that is like a smooth wall. In the case of an atomically structured wall, transport properties of electrolytes in the pore will be affected by the scattering and spectral reflection. Somers and Davis [11] reported that axial diffusion coefficients of particles in a pore with a smooth wall is larger than that with a rough wall if the pore radius is smaller than 2.75 times the size of the particle. Therefore, smaller values of transport coefficients and a stronger confinement effect would be expected in the narrow pores if rough walls are used. For pores diameters larger than three nanometers (about 10 times the size of the ions), a constant conductivity is observed and is close to the value of the bulk electrolyte. The usual increase of conductivity in the RPM model with decreasing pore size can be

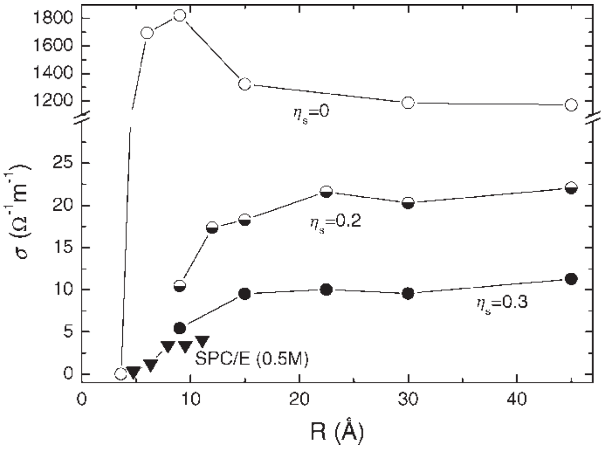

FIGURE 1 DC electrical conductivity of different electrolyte models in nanopore of different sizes. The SPM model has different solvent packing fractions, η_s and the RPM model is the limiting case of SPM with $\eta_s = 0$. The concentration of the symmetric univalent electrolyte is 0.1 M in the SPM and RPM model but a 0.5 M KCl electrolyte is modeled by the SPC/E with results denoted by triangles.

explained by the weakening of the average ion–ion Coulomb interaction due to the increase in ion–ion distance in the one-dimensional geometry [2]. This effect is diminished in electrolytes modeled with realistic high packing fraction of solvent particles. For a very small nanopore that ions cannot pass around each other, conductivity will drop to zero, even in the RPM model. The trend of transport properties of particles with increasing pore size agrees with the previous literature result [1].

To investigate the validity of the Nernst–Einstein relation for electrolytes in nanopores, diffusion coefficients of ions are obtained in EMD simulations. The mean square displacement Eq. (6) was calculated in the EMD simulations for the electrolytes. Conductivities of ions are calculated from diffusivities using Eq. (7). Figure 2 shows the comparison of the EMD conductivity (x-value) and the DC-NEMD conductivities (y-value). If the data points lie on the 45° diagonal line, the Nernst–Einstein relation appears to be valid. From the figure, all the data points for the SPM fall below the 45° line. In SPC/E models, the same behavior is observed for the results of pore with $R \leq 6.34\,\text{Å}$. The conductivities obtained with an explicit field and current are lower than that obtained from EMD simulations with the assumption of the Nernst–Einstein relation. In addition, the magnitude of the discrepancy is not uniform for all pore sizes and is different in different electrolyte models. The observations do not encourage the use of EMD simulations to study accurately the conductivity in small nanopores.

From Figs. 1 and 2, the results of the SPC/E model seem to follow the general trend of the SPM model, except that it has a high density. The asymmetry and polarity of the solvent did not appear to affect the general trend of the confinement effect. The orientation of the SPC/E solvent can be investigated. Figure 3(a) shows the 3 point charges representing hydrogen atoms and oxygen atom in a water molecule. The average orientation of the water molecule can be tracked by computing the probability of orientation.

$$P(\alpha) = P_i(\alpha) \Big/ \sum_i P_i(\alpha) \tag{11}$$

where

$$P_i(\alpha) = P_i(\theta = \alpha)/\sin\alpha \tag{12}$$

and α the angle is between the direction of pore axis and the vector between the two OH bonds, as shown in Fig. 3(a).

Figure 3(b) shows the probability distribution of orientation of the first layer of SPC/E water molecule along the wall in EMD and NEMD simulation for $R = 4.75\,\text{Å}$. In the EMD simulation, two preferred orientations at 30° and 150° are observed. These two orientations appear to be symmetrical, representing dipole up and dipole down orientations. The water molecules appear to tilt away from the wall to attain a more favorable structure in a nanopore. Such orientations are not seen in wider pores, where highest portion of water molecules have an orientation of either 0° or 180°.When the external field in the axial direction is turn on in a NEMD simulation, only

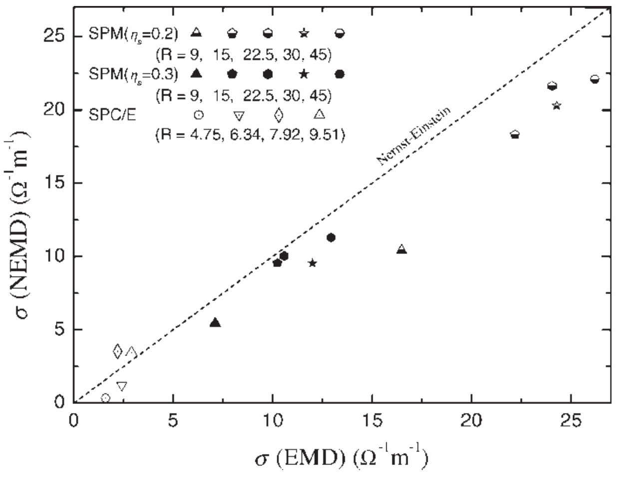

FIGURE 2 Comparison of the electrical conductivities obtained by NEMD and EMD for the SPM and SPC/E models.

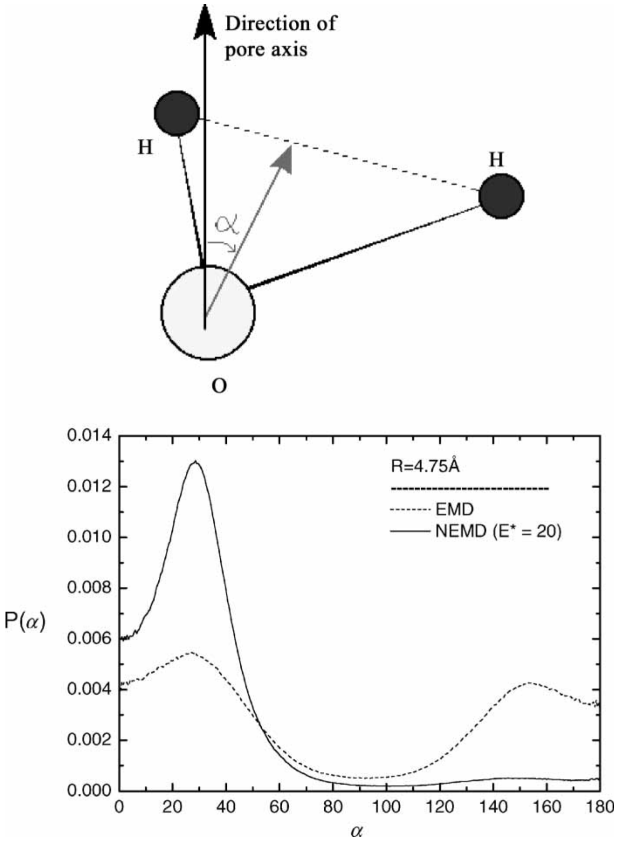

FIGURE 3 (a) Definition of the angle α between the water dipole and the axial direction of the pore. (b) Probability density function of α in a pore of $R = 4.75\,\text{Å}$. The dotted line is the angle distribution for water dipole in EMD simulation and the solid line is the NEMD result.

one orientation is preserved with a sharper peak. Similar dipole orientation graphs were used previously by Shelley and Patey [12]. How the orientation and solvation of the SPC/E water molecules affect the ionic conductivity in a nanopore can be further studied in greater details in the future.

AC-NEMD simulations were carried out for RPM ($\eta_s = 0$) and SPM ($\eta_s = 0.3$). An alternating electric field of a certain frequencies was applied along the axial direction of the pore. The current density of ions was measured at every time step by equation (8). From the current density response curve, the magnitude of the current density can be found by measuring the peak value in the sinusoidal waveform. The phase difference between current response and applied field is also measured. The AC electrical conductivities of electrolytes were computed for different field strengths to extrapolate to the zero field conductivity. The ohmic conductivity and phase shift for different pore sizes are plotted in Fig. 4 for the SPM and the RPM models. Conductivities of RPM electrolytes of different pore sizes measured in AC NEMD simulations (Fig. 4a, left) are plotted in solid lines. At high frequencies, the AC-conductivities vary in a same manner for all pore sizes and decrease rapidly to zero in the same frequency range. This appears to be a high frequency relaxation phenomenon of bulk electrolyte and therefore present in all pore sizes. At low frequencies and towards zero frequency, the AC-NEMD results approaches the values of static field DC-NEMD results (plotted as open symbols). The maximum DC conductivity observed in the RPM model for $R = 6$ and $9\,\text{Å}$, (also shown in Fig. 1) can be explained by the weakening of ion–ion interaction in a one dimensional geometry. In the narrowest pores ($R = 4.5\,\text{Å}$), the highest AC conductivity is observed but the DC conductivity is the lowest, among the pore sizes simulated. For DC-NEMD in such smallest nanopores, oppositely charged ions need to pass each other, as they migrate in opposite directions. The severe confinement, however, prevents a DC current. When an alternate field is applied, however, the ions moved back and forth following the direction of the field without head on collisions. A higher conductivity can therefore be obtained. Frequency dependent conductivity for electrolytes in SPM shows similar trends for different pore sizes (Fig. 4a, right), though conductivities are orders of magnitudes lower. The general rapid decline of conductivity for all pore sizes is also observed but at 10-fold higher frequencies compared with the RPM results. Conductivity of ions in the narrowest pore increases and then decreases with increasing frequency. As opposed to the RPM results, conductivity is monotonically decreasing with pore size for the whole frequency range. Again, the high packing fraction of solvent particles reduced the weakening effect of ion–ion Columbic interaction in the one dimensional geometry. The approach of the AC-conductivity of the SPM model at low frequencies does not meet the DC-NEMD results, except for the case of the largest pore. It could be due to the insufficient simulations at very low frequency and they require much more CPU time for sufficient cycles.

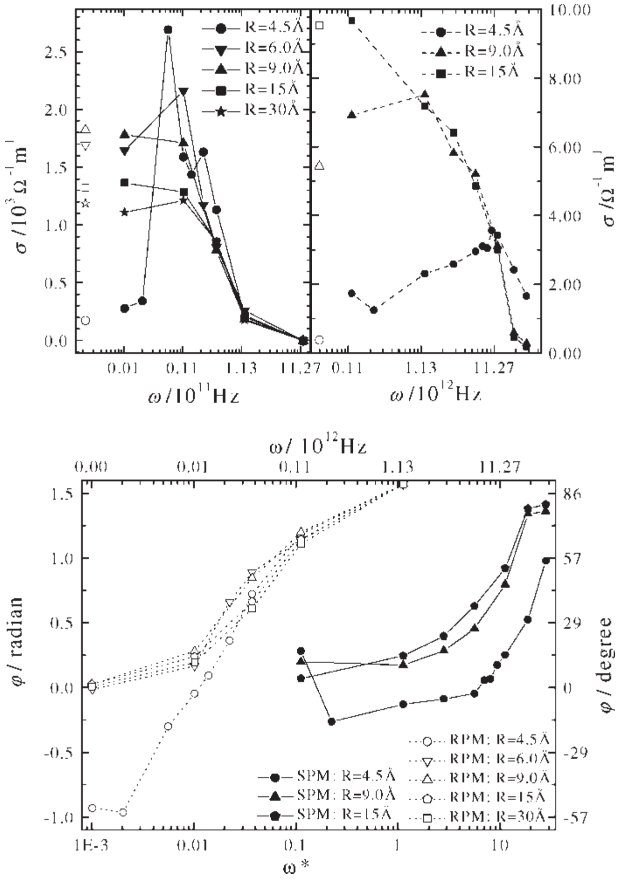

FIGURE 4 (a) Frequency dependent conductivity for RPM (left panel) and SPM (right panel) from AC-NEMD results. (b) Phase difference between the current and the applied electric field in AC-NEMD results.

The phase lags of current response to applied electric field in different frequencies are plotted in Fig. 4b. The phase difference increases monotonically from 0 to $\pi/2$ radian for all pore sizes except in the case of $R = 4.5\,\text{Å}$. The rapid approach of the phase lag to $\pi/2$ occurs at the same frequency range of rapid decline of conductivity in Fig. 4(a). For the narrowest pore, the phase of current leads (negative phase shift) the applied electric field at low frequencies, both for the RPM and SPM electrolytes. For the severely confined electrolytes, the resonance peak conductivity and the negative phase shift suggests electrical behavior like a LRC circuit with inductance, resistance and capacitance components. The capacitance property only appears in a very narrow pore when the ions cannot get past each other and accumulate as an ion pair (like a tiny double layer). The ion-pairing effect was recently discussed by Nicholson and Quirke [13]. At a certain frequency, the inductance effect appears and the electrolyte is in the resonance state where maximum conductivity is observed. For larger pores, the capacitance property is absent and only a LR circuit behavior is observed.

The equivalent electric circuits analyses are usually performed with the Cole–Cole plot where the imaginary part of the conductivity is plotted against the real part. The conductivities of the NEMD and EMD results are shown in a Cole–Cole plot in Fig. 5(a) for both the RPM and the SPM. The results of SPM model are orders of magnitude too small and are therefore plotted in Fig. 5(b) with an enlarged scale. In Fig. 5(a), the dotted data of the same pore sizes are connected by dotted lines to aid the reading. In Fig. 5(b), the lines are frequency dependent conductivities derived by Fourier transform of autocorrelation function of current density in EMD simulations [8]. The semi-circle curve for the larger pores of $R = 9$ and $15\,\text{Å}$ is a common feature of a RL circuit. For the narrowest pore of $R = 4.5\,\text{Å}$, the additional semi-circle at low frequencies is the feature of a capacitor and the complete locus is that of a LRC circuit.

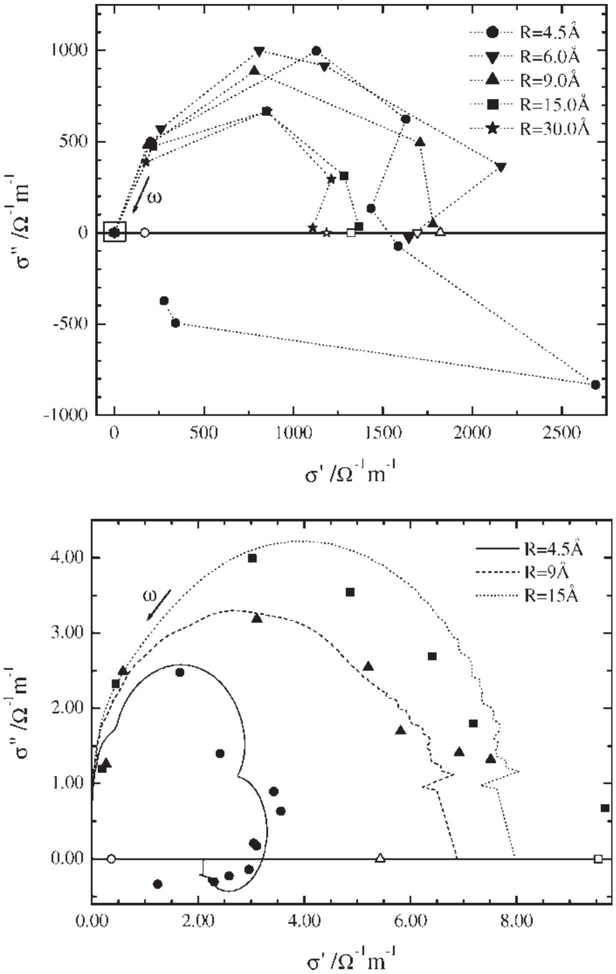

FIGURE 5 (a) The Cole–Cole plots of the frequency dependent conductivity for different field frequencies of various pores. The solid symbols are AC NEMD results while the open symbols are DC NEMD results. (b) Enlarged figure for the SPM results. The lines are obtained from Fourier transforms of autocorrelation functions of current density from EMD simulations.

CONCLUSIONS

The NEMD results of different electrolyte models show a general decrease of conductivity with smaller nanopores due to a confinement effect, which is more serious at high solvent packing. The confinement effect also affects the validity of the Nernst–Einstein relation and the EMD approach is not reliable for small nanopores in calculating current and electrical conductivity. The unrealistically low packing in the RPM model leads to a unique feature of maximum DC conductivity at a certain nanopore size. A LR equivalent circuit behavior is generally observed for electrolytes in large nanopores. But for the smallest pores, a capacitance behavior is observed as indicated by the phase lead at low frequencies and a negative semi-circle in the Cole–Cole plot. The LRC equivalent behavior in the smallest pores is also consistent with the observation of a maximum AC conductivity at a certain resonance frequency.

Acknowledgements

This work was supported by the Research Grants Council of Hong Kong (HKU7213/99P). Prof. I. Szalai received financial supported from the Hungarian National Research Fund (OTKA-TO25884).

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