ABSTRACT: The viscosity of water under an external electric field of 0.00−0.90 V/nm was studied using both molecular dynamics simulations and atomistic modeling accounting for intermolecular potentials. For all temperatures investigated, the water viscosity becomes anisotropic under an electric field: the viscosity component parallel to the field increases monotonically with the field strength, E, while the viscosity perpendicular to the field first decreases and then increases with E. This anisotropy is believed to be mainly caused by the redistribution of hydrogen bonds under the electric field. The preferred orientation of hydrogen bonds along the field direction leads to an increase of the energy barrier of a water molecule to its neighboring site, and hence increases the viscosity in that direction. However, the probability of hydrogen bonds perpendicular to the electric field decreases with E, together with the increase of the average number of hydrogen bonds per molecule, causing the perpendicular component of water viscosity to first decrease and then increase with the electric field.

1. INTRODUCTION

Charged or electrified liquids are commonly encountered in nano- and microfluidic devices,1−11 including labs-on-a-chip,1 inkjet2 and electrostatic printing3 and nanofluidic devices,4−6 where the viscosity of liquid is important in determining the device functionalities. For example, in electrospinning, viscosity plays an important role in preventing the nanothreads from breaking up into droplets.7 The strength of the electric fields in these devices (e.g., in ion channels10,11 and membranes12 and around electrospraying needles5) can sometimes reach up to 0.2−1.0 V/nm.6,10−12

Experiments have been conducted to investigate the effect of electric field on liquid viscosity since more than 60 years ago. Some of these studies have reported enhanced viscosity under electric field for polar liquids.8−11 For example, Andrade and Hart13 and Andrade and Dodd14 used capillary viscometry to measure the viscosity of both nonpolar and polar liquids confined in a rectangular channel under external electric fields perpendicular to flow for up to 4.2 × 10−5 V/nm. Their results showed a negligible effect of electric field on viscosity of nonpolar liquid (benzene) but a −0.5% increase for polar liquids (monochlorobenzene, chloroform, and amyl acetate). Capillary viscometry was also used by Ostapenko15 to study the viscosity of polar and nonpolar liquids with an electric field of 0.0 to 0.01 V/nm. When eliminating the influence of electric currents, the viscosity of polar liquids (acetone, nitrobenzene, chlorobenzene, and toluene) increases by 5−40%, but the increase in viscosity of nonpolar liquids (hexane and decane) never exceeds 4%. Kimura et al.16 studied the shear viscosity of deionized water using a modified coaxial rheometer and found that the viscosity subtly increases under an electric field up to 6.0 × 10−6 V/nm and credited this slight increase in viscosity to electrohydrodynamic convection. In contrast, experimental evidence has shown the reduction of liquid viscosity due to an external electric field. Using high resolution quasi-elastic neutron scattering, Diallo et al.17 observed the enhanced translational diffusion of water molecules confined in silica pores under an electric field of 2.5 × 10−3 V/nm, indicating a decrease in water viscosity with an electric field. Raraniet al.18 and Tao and Tang19 also reported decreased viscosities of ethylene glycol and crude oil, respectively, under an electric field. Existing literature on experimental studies of liquid viscosity under electric fields13−21 has shown poor reproducibility and contradicting results, possibly caused by the dependence of viscosity on temperature and the purity of liquid, among others. Furthermore, the field strength applied in most experimental studies is much lower than those encountered in nano- and microfluidic devices which can go up to 0.2−1.0 V/nm.

It is well recognized that the intermolecular interactions play a key role in determining the liquid viscosity. Andrade and
Hart and Andrade and Dodd attributed the viscosity increase with an electric field to the increase in the energy barrier of a molecule interacting with its adjoining empty site. However, a quantitative relationship between the energy barrier and the electric field is unclear. Ostapenko postulated that the increase in viscosity under an electric field is mainly due to the enhancement in the intermolecular interactions. Both the energy barrier and intermolecular interaction arguments require atomic level knowledge, which is difficult to probe experimentally.

Molecular dynamics (MD) simulation is a powerful tool in investigating nano/micromechanics and has been widely used to study the viscosity of pure liquids and mixtures. Using nonequilibrium molecular dynamics simulations, McWhirter studied the viscosity of a dense simple dipolar fluid where the reduction of viscosity was observed with an electric field perpendicular to flow. The effect of electric field on the viscosity of water, a common working fluid in electrospinning, labs-on-a-chip, and micro electrical discharge machining, is expected to be much more complex due to the unique hydrogen bonds between water molecules but has not been fully investigated.

In this paper, the effect of an external electric field (in the range of 0.00–0.90 V/\text{nm}) on the viscosity of water is investigated using MD simulations at various temperatures. The viscosity components both perpendicular and parallel to the electric field are calculated. The results are compared with atomistic modeling based on the intermolecular interactions between water molecules, including van der Waals interactions, dipole–dipole interactions, and hydrogen bonds. Both methods show interesting anisotropic behaviors of water viscosity under an electric field.

2. METHOD

2.1. Molecular Dynamics Simulations. The viscosity of water with and without an external electric field at various temperatures was studied using MD simulations. A total of 17,064 simple point charge/extension (SPC/E) water molecules with parameters listed in Table 1 were equilibrated in a periodic box with an initial size of 8 × 8 × 8 nm. In the SPC/E model, the interactions between two water molecules (denoted as a and b) are calculated by

\[
\omega(r_{ab}) = 4\epsilon \left( \frac{\sigma}{r_{ab}} \right)^6 - \left( \frac{\sigma}{r_{ab}} \right)^{12} + \frac{1}{4\pi\epsilon_0} \sum_i \sum_j q_i q_j r_{ij},
\]

where the first term on the right-hand side is the standard 12-6 L-J potential for oxygen–oxygen interactions, with \( \epsilon = 0.6502 \) kJ/mol, \( \sigma = 3.166 \) Å, and \( r_{ab} \) the distance between the oxygen atoms of the two interacting water molecules. The second term describes the Coulombic force between the charged atoms, where \( r_{ij} \) is the distance between atom \( i \) (on a) and \( j \) (on b), \( \epsilon_0 \) the vacuum permittivity, and \( q_i \) and \( q_j \) the charges on atoms \( i \) (on a) and \( j \) (on b), respectively. The water molecules were kept rigid by the SHAKE algorithm. The cutoff distance for all simulations was 1.5 nm, and the long-range Coulombic force was calculated using the particle–particle particle-mesh (PPPM) technique. When an external electric field is present, an additional force \( f_{el} = q_i E \) is applied to each atom in the direction along positive \( z \) with a magnitude of \( E = 0.00, 0.20, 0.30, 0.50, 0.70, \) and 0.90 V/\text{nm} (in the range encountered in ion channels and electrospinning).

The MD simulations were performed using the LAMMPS package. The system was first equilibrated using an NPT (in the number of atoms, \( P \) the pressure, and \( T \) the temperature) ensemble at 1 atm for 500 ps and subsequently an NVT (in the volume) ensemble for 500 ps. Simulation runs for viscosity analysis were then conducted for 3 ns in an NVT ensemble. For cases with an external electric field, the electric field was presented at the beginning of the NPT relaxation. The time step was 1 fs in all cases. The calculated densities of water at various temperatures at 1 atm without an external electric field are shown in Figure S1 in good agreement with MD simulations of Fennell et al. and experiments.

The shear viscosity, \( \mu \), was calculated using the Stokes–Einstein relation, commonly used for determining liquid viscosity:

\[
\mu = \frac{k_B T}{3\pi \eta_w D}
\]

where \( r_w \) is the effective molecule diameter which is a function of the size and shape of the molecule (for water molecules, \( r_w = 1.7 \) Å). \( D \) the self-diffusion coefficient, \( k_B \) the Boltzmann constant, and \( T \) the temperature. It is noted that eq 2 was developed for Brownian motions of finite-size particles under a uniform temperature. Here, the water molecules are treated as Stokes particles with an effective molecule diameter \( r_w \). This treatment has been widely adopted in MD simulations which yield accurate predictions of liquid viscosity. In eq 2, three independent components of the self-diffusion coefficient, i.e., \( D_x \), \( D_y \), and \( D_z \) representing \( x \), \( y \), and \( z \) components respectively, can be calculated from the asymptotic slope of the time-dependent mean-square displacements (MSD) following:

\[
\begin{align*}
D_x &= \frac{\langle (r_w^2(t + \tau) - r_w^2(t_0))^2 \rangle}{2\tau} \\
D_y &= \frac{\langle (r_w^2(t + \tau) - r_w^2(t_0))^2 \rangle}{2\tau} \\
D_z &= \frac{\langle (r_w^2(t + \tau) - r_w^2(t_0))^2 \rangle}{2\tau}
\end{align*}
\]

where \( r_w \) is the position of atom \( i \), (\ldots) represents ensemble average, and \( \langle (r_w^2(t + \tau) - r_w^2(t_0))^2 \rangle \) are the MSD of the water molecule along \( x \), \( y \), and \( z \) directions, respectively. Since the electric field is applied along the \( z \) direction for all simulations, the shear viscosity perpendicular to the electric field, \( \mu_z \), was calculated using eq 2 with \( D = (D_x + D_y)/2 \), and the shear viscosity parallel to the external electric field, \( \mu_y \), was obtained by setting \( D = D_z \).

In addition, the reverse nonequilibrium molecular dynamics (rNEMD) method was also used to calculate the viscosity of water. In the rNEMD method, the shear viscosity, \( \mu \), is evaluated by imposing a shear stress tensor on the bulk liquid to generate a velocity gradient following:

\[
\tau = \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)
\]

Table 1. Parameters of SPC/E Water Model.

<table>
<thead>
<tr>
<th>( r_{OH} ) (Å)</th>
<th>( \theta_{HOH} ) (deg)</th>
<th>( q_0 ) (e)</th>
<th>( q_1 ) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>109.47</td>
<td>-0.8476</td>
<td>0.4238</td>
</tr>
</tbody>
</table>
To calculate the shear viscosity perpendicular to the electric field, the simulation system was evenly divided into 40 slabs along the electric field direction in $z$. A shear stress $\tau_\perp = -\mu_\perp \partial u_\perp / \partial z$ was imposed along $x$ by swapping the maximum velocity in negative $x$ direction of a water molecule in the middle $z$-slab with the maximum velocity in positive $x$ direction of another molecule in the bottom $z$-slab every 500 time steps.\(^{26}\) By calculating the total momentum exchange, $P_\mu$, of the system, it follows that $\tau_\perp = P_\mu / 2tA_{xy}$, where $t$ is the simulation time and $A_{xy}$, the cross-sectional area in the $xy$ plane.\(^{45}\) The resulting equilibrium velocity gradient, $\partial u_\perp / \partial z$, was evaluated by averaging the velocity in each $z$-slab, and the viscosity component perpendicular to the electric field, $\mu_\perp$, was hence obtained. Similarly, the shear viscosity parallel to the external electric field, $\mu_\parallel$, was obtained by imposing a momentum exchange along $z$ following $\mu_\parallel = - (P_\mu / 2tA_{zy}) / (\partial u_\parallel / \partial x)$.

Figure 1 shows the viscosity of water calculated by the Stokes–Einstein relation\(^{37}\) and the rNEMD method\(^{42}\) at various temperatures at 1 atm without an external electric field where error bars are obtained using the standard deviations of six separate simulation runs with different random velocity seeds for temperature initializations. It is observed that, in the absence of an electric field, for both methods, the difference between the shear viscosity parallel ($\mu_\parallel$) and perpendicular ($\mu_\perp$) to the $z$ direction is within the range of error for all simulated temperatures ranging from 298 to 338 K, indicating anisotropic water viscosity without an electric field. Consistent with MD calculations based on the Stokes–Einstein relation\(^{37}\) of Thomas and McGaughey\(^{38}\) and Li et al.,\(^{25}\) the present MD results using the Stokes–Einstein relation overestimate the viscosity of water compared with experimental measurements,\(^{46}\) which may be caused by treating nonspherical water molecules as perfect spheres for calculating the viscosity in eq 2. On the contrary, the rNEMD method underestimates the viscosity of water, which agrees well with the previous studies of Kuang and Gezelter\(^{35}\) and Müller et al.\(^{34}\) Nonetheless, the maximum relative error between the MD-calculated (using both Stokes–Einstein relation and rNEMD methods) and experimentally determined water viscosity is less than 15% for the temperature range considered.

In order to explore the molecular packing structures of water with and without an electric field, the spatial distribution functions (SDFs) $g(r_{\beta\gamma})$ were calculated from the MD results. Here, $r$, $\beta$, and $\gamma$ are the radial distance, polar angle, and azimuthal angle of the spherical coordinate around a water molecule. Following Svishchev et al.\(^{46}\) the SDFs were determined by dividing the spherical space around each molecule into $360 \times 360$ radial sectors, where the oxygen–oxygen distribution was evaluated. Radial distribution function (RDF) $g(r)$ can be obtained by averaging SDFs in the polar and azimuthal directions following

$$g(r) = \frac{1}{2\pi^2} \int_0^\pi \int_0^{2\pi} g(r, \beta, \gamma) \sin(\beta) \, d\beta \, d\gamma$$

### Figure 1. Comparison between MD simulations and experiments of water viscosity without external electric field at temperature from 298 to 338 K. Experimental data (Exp) are taken from ref 36.

### Figure 2. (a) Principal frame coordinates for calculating the spatial distribution function (SDF) of water. The water molecule lies in the $y$–$z$ plane. The SDF for water (b) without and (c) with an electric field of $E = 0.9$ V/nm at $T = 298$ K. The green, blue, black dots, and red surface represent $g(r_{\beta\gamma}) = 1, 2, 4$, and 6, respectively.

2b and 2c show the three-dimensional spatial distribution function, $g(r_{\beta\gamma})$, for water without and with an applied electric field of strength $E = 0.9$ V/nm, respectively. In Figure 2, the green, blue, black dots, and red surface represent $g(r_{\beta\gamma}) = 1, 2, 4$, and 6, respectively, where $g(r_{\beta\gamma})$ of unity denotes the bulk water density. The red surfaces (i.e., $g(r_{\beta\gamma}) = 6$) in both Figures 2b and 2c reveal the tetrahedral structure of water\(^{46}\) even under an electric field strength of 0.9 V/nm (Figure 2c).
However, unlike ice, the tetrahedral structure in liquid water is disordered and labile, and an "empty site" or "hole" can be formed if a water molecule moves away from its initial location. If such a hole is formed, the central molecule, which is also the adjoining molecule of its neighbors as well as the hole, may move to fill the hole and meanwhile leaves a new hole in its original central location.

As shown in Figure 3, a water molecule moving from its initial central site to an adjoining empty site (or a "hole") needs to overcome an energy barrier or activation energy, $\Delta G$, caused by the difference in the potential energy states. Eyring related the liquid viscosity with the energy barrier using

$$\mu = A \exp \left( \frac{-\Delta G}{k_B T} \right)$$  \hspace{1cm} (5)

where $A$ is a pre-exponential constant. Since both the initial central position and the "hole" are equilibrium positions for water molecules, the water molecule experiences the highest potential energy at the intermediate state of $l = 2b$, where $l$ is the moving distance of a water molecule from its original central position and $2b$ is the distance between its original central position and the adjoining empty site. As indicated by eq 5, the viscosity of liquid is a function of both the temperature and this energy barrier. For water molecules, this energy barrier $\Delta G$ includes the contributions from the van der Waals interactions, $\Delta G_{vdW}$ dipole–dipole interactions, $\Delta G_{\text{polar}}$ and hydrogen bonds between the electron-depleted hydrogen atoms and the highly polar OH groups, $\Delta G_{\text{HB}}$, following

$$\Delta G = \Delta G_{vdW} + \Delta G_{\text{polar}} + \Delta G_{\text{HB}}$$  \hspace{1cm} (6)

Figures 4a, 4b, and 4c show the schematics of a water molecule (denoted as M1, and M4 stands for the intermediate state of M1) moving from its initial central position ($l = 0$) to an adjoining empty site (denoted as M2 at $l = 2b$), overcoming the energy barrier caused by van der Waals interactions, dipole–dipole interactions, and hydrogen bonds, respectively. In Figure 4, the orientation angles $\psi_1$, $\psi_2$, and $\psi_3$ are defined as the angle between the moving direction of the central molecule and the direction of the van der Waals force, the dipole–dipole force, and the hydrogen bond between the central molecule and the adjoining molecule (M3), respectively. Here, $R_{oo}$ (or $R_{oot}$), $R_{dd}$ (or $R_{dtd}$), and $R_{hd}$ (or $R_{htd}$) are distance parameters between the M1 and M3 (M4 and M3) states for calculating the van der Waals interactions, the dipole–dipole interactions, and the hydrogen bond interactions, respectively. The dipole position of a water molecule is assumed to be in the middle of the positive and negative charge centers. For a central water molecule with an adjoining empty site, the following assumptions are applied:

(i) There is no adjoining molecule at $\psi_1 > \pi/2$ ($\psi_2 > \pi/2$ or $\psi_3 > \pi/2$), and the distributions of the three adjoining molecules for $\psi_1 < \pi/2$ ($\psi_2 < \pi/2$ or $\psi_3 < \pi/2$) are the same as in bulk water where the oxygen and dipole distributions are uniform both with and without an electric field (but the dipole directions may change due to the electric field).

(ii) The oxygen–oxygen distance between the central molecule and its adjoining site, $R_{oo} = 2b$, is assumed to be the distance between the reference oxygen and the location of the first peak of the oxygen–oxygen radial distribution function in bulk water.

(iii) Only the interactions between the central molecule and its adjoining molecules are considered while neglecting the interactions with molecules that are farther apart. In addition, the central molecule experiences the highest potential energy when moving to a distance $l = b$, the midpoint between the original central location and its adjoining empty site.

It is noted that the hydrogen–hydrogen and hydrogen–oxygen van der Waals forces are much weaker than the oxygen–oxygen van der Waals interactions, and they are therefore neglected, as in most other water models. The
activation energy due to van der Waals interactions between the central molecule and its three closest neighbors is given by

$$\Delta G_{vdW} = \frac{1}{2} \int_{0}^{\pi/2} 3\left(\alpha_{vdW}(R_{oo}) - \alpha_{vdW}(R_{oo}^0)\right) F_{oo}(\psi_t) \, d\psi_t \biggr|_{0}^{\pi/2}$$

where $\alpha_{vdW}(R)$ is the van der Waals interaction energy between two water molecules, $R_{oo} = R_{oo}^0$ and

$$R_{oo}^0 = \sqrt{(R_{oo}^0 \sin \psi_t)^2 + (R_{oo}^0 \cos \psi_t + b)^2}$$

(as shown in Figure 4a) are the distances of the oxygen–oxygen atoms at the initial central position and when moving to the position of $l = b$, respectively, and $F_{oo}(\psi_t)$ is the distribution probability of an adjoining oxygen in the direction of $\psi_t$. Assuming that the distribution of the adjoining oxygen atoms at $\psi_t < \pi/2$ is uniform as in bulk water yields the normalized $F_{oo}(\psi_t) = \sin \psi_t$.\(^\text{54}\) As shown in Figure S5, the calculated oxygen–oxygen–oxygen radial distribution functions are not significantly affected by the electric field with the strength up to 0.9 V/nm. The first peak of $g_{oo}(r)$ is at $R_{oo} = 0.276$ nm at 298 K, which is found to be within statistical uncertainty without and with an electric field. Similarly, Kiselev and Heinzing\(^\text{55}\) has shown the independence of $R_{oo}$ with an electric field for strength up to 10 V/nm.\(^\text{55}\) The calculated energy barrier due to van der Waals interaction is $-12.072$ kJ/mol at 298 K and is independent of the external electric field.

Unlike van der Waals interactions, the dipole–dipole interactions are a function of not only their distance but also the orientations of the two dipole moments.\(^\text{19}\) For freely rotating dipoles, the average dipole–dipole interaction (or angle-averaged dipole–dipole interaction) can be calculated using

$$-\frac{u_1^2 u_2^2}{2} \rho \frac{3(4\pi\varepsilon_0)^2 k_B T^2}{\sin^2 \theta_{12}}$$

the so-called Keesom interaction.\(^\text{49}\) where $u_1$ and $u_2$ are the two interacting dipoles and, for two water molecules, $u_1 = u_2 = 6.17 \times 10^{-30}$ C·m.\(^\text{98}\) $\rho$ is the distance between the two dipoles. When an external electric field is applied to prevent free dipole rotations, based on the potential distribution theorem,\(^\text{17,58}\) the angle-averaged dipole–dipole interaction energy, $\omega(r,\Omega)$, can be obtained from averaging the angle-dependent potential $\omega(\theta,\rho)$ via $e^{-\omega(r)/k_B T}$.\(^\text{59}\) Here, the angle set $\Omega = \{\theta_1, \theta_2, \theta_{12}, \phi\}$ includes $\theta_1$ and $\theta_2$ denoting the angles between each of the two dipoles and the direction linking two dipole centers, $\theta_{12}$ the angles between the dipoles and the electric field, and $\phi$ the angle between the two dipoles, with details shown in the Supporting Information. Using this theorem, the angle-averaged dipole–dipole interactions with an electric field were calculated using (detailed derivations are shown in the Supporting Information)

$$\omega_{\text{polar}}(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_0)^2 k_B T^2} \left[ -\frac{E_0^2}{2k_B T} \left( u_1 + u_2 - \frac{1}{3} u_1^2 + \frac{1}{3} u_2^2 \right) \right]$$

$$+ \frac{E_0(u_1 + u_2)}{3k_B T} \left[ u_1^2 - \frac{E_0(u_1 + u_2)}{3(4\pi\varepsilon_0)^2 k_B T^2} \right]$$

(8)

where $E_0 = 3E/(\varepsilon_e + 2)^{\text{60}}$ is the actual field strength in water caused by the external electric field. Here $\varepsilon_e = 80$ is the relative dielectric constant of bulk water. The first term on the right-hand side of eq 8 is the Keesom interaction,\(^\text{97,99}\) while the other terms are results of the electric field. The activation energy due to dipole–dipole interactions, $\Delta G_{\text{polar}}$, can then be calculated by

$$\Delta G_{\text{polar}} = \frac{1}{2} \int_{0}^{\pi/2} 3[\alpha_{\text{polar}}(R_{oo}) - \alpha_{\text{polar}}(R_{oo}^0)] F_{\text{dipole}}(\psi_t) \, d\psi_t \biggr|_{0}^{\pi/2}$$

where $R_{oo}^0 = R_{oo}$ and

$$R_{\text{dipole}} = \sqrt{(R_{\text{dipole}} \sin \psi_t)^2 + (R_{\text{dipole}} \cos \psi_t + b)^2}$$

(as shown in Figure 4b) are the distances between the dipoles at the initial central position and at $l = b$, respectively, and $F_{\text{dipole}}(\psi_t)$ is the distribution of dipole position in the direction of $\psi_t$. Assuming that the distribution of dipole positions at $\psi_t < \pi/2$ is uniform in bulk water yields $F_{\text{dipole}}(\psi_t) = \sin \psi_t$.

Although there is no simple expression for the potential energy of hydrogen bonds, it is well accepted that the hydrogen bond is predominantly an electrostatic interaction which can be approximated by the following expression for the charge–dipole interaction:

$$\omega_{\text{HB}}(r, \varphi) = -\frac{Q u \cos \varphi}{4\pi\varepsilon_0 r^2}$$

(10)
where \( r \) is the distance between the charge and the dipole, \( \varphi \) the angle between the dipole and the direction linking the charge and the dipole center, and \( Q \) is the charge. For hydrogen bonds in water, the charge and dipole refer to the hydrogen that forms the bond and the water molecule that provides the oxygen of the bond, respectively, and \( r = R_{oo} = 0.226 \text{ nm}, Q = 0.4 \times 10^{-19} \text{ C}, \) and \( \varphi = 0^\circ \) at the initial central position, where \( R_{oo} \) is the distance between the hydrogen atom and the adjoining molecule dipole at \( l = 0 \), as shown in Figure 4c. The activation energy due to hydrogen bonds or the so-called structure activation energy, \( \Delta G_{HB} \), is given by

\[
\Delta G_{HB} = \frac{1}{2} \int_0^{\pi/2} \int_0^{\varphi_{oo}^b} \frac{[\psi_{oo}^b(R_{oo}^b, \varphi_{oo}^b) - \alpha_{oo}(R_{oo}^b, 0)] F_{HB}(\psi_i) d\psi_i}{\int_0^{\pi/2} F_{HB}(\psi_i) d\psi_i}
\]

(11)

where the coefficient \( 3/4 \) is introduced to account for the adjoining empty site (a central molecule with an adjoining empty site owns 3 adjoining molecules rather than 4), \( \langle n_{HB} \rangle \) is the average hydrogen bonds per molecule,

\[
R_{bd}^b = \sqrt{(R_{bd} \sin \psi_3)^2 + (R_{bd} \cos \psi_3 + b)^2}
\]

(as shown in Figure 4c) is the distance between the hydrogen atom and the adjoining molecule dipole at \( l = b \), and \( \varphi_{bd}^b \) is the angle between the adjoining molecule dipole and the direction linking the hydrogen and the dipole center at \( l = b \) and

\[
\frac{b}{\sin \varphi_{bd}^b} = \frac{R_{bd}^b}{\sin \psi_3}
\]

(see Figure 4c). As indicated by eq 11, both the average hydrogen bonds per molecule, \( \langle n_{HB} \rangle \), and the distribution probability of hydrogen bonds, \( F_{HB}(\psi_i) \), affect \( \Delta G_{HB} \). In order to better quantify how the external electric field affects \( \Delta G_{HB} \), the average hydrogen bonds per molecule and the distribution probability of hydrogen bonds with various electric field strengths were calculated using MD simulations. In MD simulations, the following geometric criterion \( ^{11,61} \) was used to define the hydrogen bond: hydrogen bond is formed between two water molecules if (a) the oxygen–oxygen distance, \( r_{oo} \), between the two molecules is less than the critical O–O distance \( r_{oo}^c \) (b) the distance \( r_{ob} \) between the hydrogen of the donor and the oxygen of the acceptor is less than the critical oxygen–H distance \( r_{ob}^c \) and (c) the angle \( \alpha \) between the oxygen–oxygen direction and the oxygen–H direction of the donor is less than the critical angle \( \alpha^c \), where H is the hydrogen that forms the bond. The critical parameters are \( r_{oo}^c = 3.6 \text{ Å}, r_{ob}^c = 2.4 \text{ Å}, \) and \( \alpha^c = 30^\circ \) at 298 K. \( ^{11,61} \) The orientation distribution of hydrogen bonds \( G_{HB}(\psi_i) \) is proportional to the lateral area \( S = \pi \alpha^2 \sin \psi_3 \) as shown in the insets of Figure 7. \( ^{54} \) Here, the scaled probability function \( P(\psi_i) \) is used to describe the orientation of hydrogen bonds, following

\[
P(\psi_i) = \frac{F_{HB}(\psi_i)}{\Gamma \sin \psi_3}
\]

(12)

where

\[
\Gamma = \int_0^{\pi/2} F_{HB}(\psi_i) \sin \psi_3 d\psi_i
\]

is used to normalize \( P(\psi_i) \). \( ^{54} \)

Figure 6. (a) Scaled viscosity of water perpendicular, \( \mu_\parallel \), and parallel, \( \mu_\perp \), to the electric field as a function of the electric field strength, \( E_i \), at 298 K; (b) scaled water viscosity perpendicular to the electric field, \( \mu_\parallel \), as a function of electric field strength, \( E_i \), at various temperatures; and (c) scaled water viscosity parallel to the electric field, \( \mu_\perp \), as a function of electric field strength, \( E_i \), at various temperatures. The uncertainties are the standard deviations of six separate simulation runs with different random velocity seeds for temperature initializations.

3. RESULTS AND DISCUSSION

Figure 6a shows the MD-calculated viscosity of water parallel and perpendicular to the external electric field as a function of the field strength at 298 K. The scaled viscosities \( \mu_\parallel \) and \( \mu_\perp \) were used for clarity which are defined as \( \mu_i = \mu_i/\mu_0 \); the superscript 0 stands for the viscosity value in the absence of the electric field, and \( i = \perp \) or \( \parallel \). For both Stokes–Einstein relation and nNEMD methods, the results show that while the viscosity parallel to the electric field, \( \mu_\parallel \), decreases and then increases with electric field \( E \), in addition, the effect of the electric field on \( \mu_\parallel \) is more pronounced than
bonds distributed in the direction parallel to the electric field ($\psi_3 = 0^\circ$ in Figure 7a) than those perpendicular to the electric field ($\psi_3 = 0^\circ$ in Figure 7b). Thus, for a central water molecule moving from the initial position to the adjoining empty site, it needs to overcome more hydrogen bonds parallel to the electric field, resulting in a larger viscosity in that direction.

Figure 8a shows the calculated total activation energy, $\Delta G$, the activation energy due to dipole–dipole interactions, $\Delta G_{\text{polar}}$, and the activation energy due to hydrogen bonds, $\Delta G_{\text{HB}}$, as a function of the electric field. Note that, in the absence of an electric field, the activation energy due to dipole–dipole interactions and hydrogen bonds at 298 K are $\Delta G_{\text{polar}} = 15.103$ kJ/mol and $\Delta G_{\text{HB}} = 17.312 \pm 0.003$ kJ/mol, respectively.

Combining with the activation energy due to van der Waals interactions of $\Delta G_{\text{vdW}} = -12.072$ kJ/mol at 298 K, the total activation energy in the absence of an external electric field is $\Delta G^0 = 20.343 \pm 0.003$ kJ/mol, larger than the experimentally measured value of 16.81 kJ/mol. The discrepancy between MD-calculated and experimentally determined values may be caused by (i) the assumption that the water molecules only distribute in $\mu_1 < \pi/2$ (or $\mu_2 < \pi/2$); or (ii) the inaccurate charge–dipole interaction in evaluating the hydrogen bond, i.e., eq 10. As shown in Figure 8a, the $\Delta G_{\text{polar}}$ increases monotonically with the electric field strength, consistent with that reported by Andrade and Hart, Andrade and Dodd, and Ostapenko. In addition, in the presence of an electric field, $\Delta G_{\text{HB}}$ is anisotropic due to the preferential orientation of hydrogen bonds as shown in Figure 7. In the direction parallel to the electric field, $\Delta G_{\text{HB}}$ increases monotonically with the electric field strength, and the amount of increase in $\Delta G_{\text{HB}}$ is more than 3 times the increase of $\Delta G_{\text{polar}}$ under the same electric field strength variation. In the direction perpendicular to the electric field, while the orientation probability of the hydrogen bonds decreases (as in Figure 7b) with increasing electric field strength, the average number of hydrogen bonds per molecule, $\langle n_{\text{HB}} \rangle$, increases with $E$. The combined effects of the orientation distribution of the hydrogen bonds and $\langle n_{\text{HB}} \rangle$ make the activation energy $\Delta G_{\text{HB}}$ first decrease and then increase with the electric field strength, as shown in Figure 8a.

Figures 8b and 8c show the comparison between the MD-calculated (based on the Stokes–Einstein relation and rNEMD methods) and model-predicted scaled viscosities $\mu'_{\parallel}$ and $\mu'_{\perp}$ as a function of an external electric field, respectively. Both MD-calculated and model-predicted results show that $\mu'_{\parallel}$ first decreases and then increases with the electric field strength and $\mu'_{\perp}$ increases monotonically with $E$. The relative differences between the MD-calculated and model-predicted results are less than 10% for viscosity parallel to the electric field and 5% for viscosity perpendicular to the electric field.

4. CONCLUSIONS

The viscosity of liquid water under an external electric field at various temperatures was studied using MD simulations. The viscosity of water becomes anisotropic when an external electric field is applied. The viscosity of water parallel to the electric field, $\mu_{\parallel}$, increases monotonically with the electric field strength, while the viscosity perpendicular to the electric field, $\mu_{\perp}$, first decreases with electric field strength, $E$, but then starts to increase with $E$. The effect of the electric field on $\mu_{\parallel}$ is more pronounced than on $\mu_{\perp}$. The anisotropy of viscosity is mainly caused by the effects of electric field on the orientation distribution of hydrogen bonds. When the electric field is applied, the hydrogen bonds tend to rotate along the electric field.

Figure 7. Scaled probability function of the orientation of the hydrogen bond, $P(\psi_3)$, calculated by eq 12 for the electric field strength of 0.00–0.90 V/nm at 298 K for water moving (a) parallel and (b) perpendicular to the electric field.
field direction, leading to an increase in the activation energy and the viscosity in the direction parallel to the electric field. In the direction perpendicular to the electric field, the orientation probability of hydrogen bonds decreases with the electric field, which, combined with the increase in the average number of hydrogen bonds per molecule, causes the activation energy and viscosity to decrease at first and then increase with the electric field.

Figure 8. (a) The total activation energy, \( \Delta G \), the activation energy due to dipole–dipole interactions, \( \Delta G_{dd} \), and the activation energy due to hydrogen bonds, \( \Delta G_{HB} \), as a function of the electric field strength, \( E \); (b) comparison between the MD-calculated and model-predicted scaled water viscosity perpendicular to the electric field, \( \mu'_{\perp} \), as a function of electric field strength; and (c) comparison between the MD-calculated and model-predicted scaled water viscosity parallel to the electric field, \( \mu'_{\parallel} \), as a function of electric field strength. The uncertainties are the standard deviations of six separate simulation runs with different random velocity seeds for temperature initializations.

**REFERENCES**


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