SUPPORTING INFORMATION

Dynamic electroosmotic flow and solute dispersion through nanochannel filled with electrolyte surrounded by layer of dielectric and immiscible liquid

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Nomenclature

H	Half height of the nanochannel
δ	Thickness of the dielectric liquid layer
E_0	Magnitude of the applied oscillatory electric field
ω	Angular frequency of the electric field
t	Time
N_0	Concentration of the additional mobile ions present in the dielectric liquid layer
Z	Valence of the additional mobile ions present in the dielectric liquid layer
σ	Charge density along the liquid-liquid interface
κ^{-1}	EDL thickness at the interface side of aqueous medium
κ_d^{-1}	Equivalent EDL thickness towards the liquid-liquid interface
z	Valence of the electrolyte ions
n_0	Bulk electrolyte concentration

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$\eta_d,\ \eta_e$	Viscosity of the membrane and electrolyte later, respectively
$\epsilon_d,\ \epsilon_e$	Dielectric permittivity of the membrane and electrolyte later, respectively
k_B	Boltzmann constant
e	Elementary charge
T	Absolute temperature
F	Faraday constant
N_A	Avogadro's number
$n_i(y)$	Concentration of the ith ionic species
$n_d(y)$	Concentration of the additional mobile ions present in the dielectric liquid layer
R	Gas constant
$\psi(y)$	Electrostatic potential
r	Radius of the ion
ψ_D	Donnan potential
$\rho_d(y),\ \rho_e(y)$	Net volumetric charge of the electrolyte ions inside and outside of the dielectric liquid layer
f	Ion partitioning coefficient
$u(y,t)$	Time dependent axial flow velocity component
$\tilde{\rho}_d,\ \tilde{\rho}_e$	Mass density of the liquid in the peripheral layer and electrolyte solution, respectively
U_{HS}	Helmoltz-Smoluchowsky reference velocity
$C(x,y,t)$	Concentration distribution of solutes
D_0	Diffusivity constant
Pe	Péclet number
$K(t)$	Time dependent dispersion coefficient
K_{avg}	Time-averaged effective dispersion coefficient
τ_0	One oscillation period
Re	Oscillating Reynolds number
K_{eff}	Effective dispersion coefficient

S.1 Spatial distribution of concentration of additional mobile ions present in the dielectric liquid layer

Considering the finite ion size, the electrochemical potential of the additional ions (other than electrolyte ions) is given as

$$\mu_d(y) = \mu_d^0 + ZF\psi(y) + RT\ln\Big(\gamma_d(y)n_d(y)\Big) \tag{S1}$$

2

where μ_d^0 is a constant. The quantities $\gamma_d(y)$, Z and $n_d(y)$ refer to the the ion activity coefficient, valence, and concentration distribution of additional ions present in the liquid layer, respectively. In equilibrium the electrochemical potential may be constant and thus,

$$ZF\psi(y) + RT \ln \left(\gamma_d(y) n_d(y) \right) = \ln(N_0 B) \tag{S2}$$

where N_0 represents the bulk molar concentration of the additional mobile ions in the peripheral liquid layer and the normalization factor B may be deduced later in this section. Using equation (S2) we may deduce the explicit form of concentration $n_d(y)$ of additional ion, given as

$$n_d(y) = \frac{N_0 B}{\gamma_d(y)} \exp\left(-\frac{ZF\psi(y)}{RT} \right) \tag{S3}$$

Note that the spatial distribution of concentration of additional ion must satisfies the following relation

$$\int_{-H}^{-H+\delta} n_d(y) dy = N_0 \delta \tag{S4}$$

In fact the equation (S4) represents the balance of the net volume charge of the additional ions presents in the peripheral liquid layer. Substituting the equation (S3) into equation (S4), we may deduce the explicit form of the normalization factor B, given as

$$B = \frac{\delta}{\int_{-H}^{-H+\delta} \frac{\exp(-ZF\psi(y)/RT)}{\gamma_d(y)} dy} \tag{S5}$$

Substituting (S5) into (S3) yields

$$n_d(y) = \left\{ \frac{N_0 \delta}{\int_{-H}^{-H+\delta} \frac{\exp(-ZF\psi(y)/RT)}{\gamma_d(y)} dy} \right\} \left\{ \frac{\exp\left(-\frac{ZF\psi(y)}{RT} \right)}{\gamma_d(y)} \right\} \tag{S6}$$

Note that the position dependent volume fraction of the additional ions presents in the peripheral liquid layer may be deduced as

$$\phi_d(y) = \frac{4\pi a_d^3}{3} N_A n_d(y) \tag{S7}$$

where N_A and a_d represent the Avogadro number and the radius of the additional ions presents in the peripheral liquid layer, respectively. Thus, the mean volume fraction of the additional ions ϕ_d may be deduced from the given relation

$$\phi_d = \frac{4\pi a_d^3}{3\delta} N_A \int_{-H}^{-H+\delta} n_d(y) dy = \frac{4\pi a_d^3}{3} N_A N_0 \tag{S8}$$

Using equations (S3) and (S8) into (S7), we may write

$$\phi_d(y) = \frac{\phi_d}{N_0} n_d(y) = \frac{B\phi_d}{\gamma_d(y)} \exp\left(-\frac{ZF\psi(y)}{RT} \right) \tag{S9}$$

3

We may write the explicit form of ion activity coefficient based on Carnahan-Starling model [1], given by [2]

$$\gamma_d(y) = \exp\left\{\frac{\phi_d(y)\left(8 - 9\phi_d(y) + 3\phi_d^2(y)\right)}{\left(1 - \phi_d(y)\right)^3}\right\} \tag{S10}$$

Substituting equation (S10) into equation (S9) yields

$$\phi_d(y) = B\phi_d \exp\left\{-\frac{\phi_d(y)\left(8 - 9\phi_d(y) + 3\phi_d^2(y)\right)}{\left(1 - \phi_d(y)\right)^3}\right\} \exp\left(-\frac{ZF\psi(y)}{RT}\right) \tag{S11}$$

Note that the presence of free charges (other than electrolyte ions) within the peripheral liquid layer may lead to non-zero charge density along the liquid-liquid interface. Thus, two EDLs may forms at the interface, one along the water side and other one towards the liquid layer. The thickness of EDL towards the water side and liquid layer sides are denoted as κ^{-1} and κ_d^{-1}, respectively. A detailed description of κ^{-1} is indicated in the main manuscript. Note that thickness of the EDL towards the liquid layer side depends on the electrolyte concentration as well as concentration of additional ions present in peripheral liquid layer. The explicit form of κ_d^{-1} may be deduced as [3, 4]

$$\kappa_d^{-1} = \frac{1}{\sqrt{\left(\frac{F^2}{\epsilon_d RT}\right)\left\{ZN_0 + \sqrt{Z^2 N_0^2 + 4f^2 z^2 n_0^2}\right\}}} \tag{S12}$$

In our present study we consider the concentration of additional molar concentration is moderate to high. Thus, for the undertaken range of concentration of electrolyte and additional ions within the peripheral liquid layer, EDL thickness κ_d^{-1} is in general lower that the thickness of the peripheral liquid layer. For such a case, the EDL potential within the peripheral liquid layer may be approximated by the Donnan potential ψ_D and ion activity coefficient $\gamma_d(y)$ can be approximated to γ_d (which is the value of $\gamma_d(y)$ at $\psi(y) \approx \psi_D$). Thus, the expression for normalization constant B and ion activity coefficient γ_d may be deduced as follows

$$B = \gamma_d \exp\left(\frac{ZF\psi_D}{RT}\right) \tag{S13}$$

and

$$\gamma_d = \exp\left\{\frac{\phi_d\left(8 - 9\phi_d + 3\phi_d^2\right)}{\left(1 - \phi_d\right)^3}\right\} \tag{S14}$$

Substituting equations (S13) and (S14) into equation (S11), we may write

$$
\phi_d(y) = \phi_d \exp \left\{ -\left(\frac{\phi_d(y)\Big(8 - 9\phi_d(y) + 3\phi_d^2(y)\Big)}{\Big(1 - \phi_d(y)\Big)^3} - \frac{\phi_d\Big(8 - 9\phi_d + 3\phi_d^2\Big)}{\Big(1 - \phi_d\Big)^3} \right) \right\} \times \\
\exp \left\{ -\frac{ZF}{RT}(\psi - \psi_D) \right\} \tag{S15}
$$

The first order approximation $\phi_d(y)$ yields

$$
\phi_d(y) = \phi_d \frac{\exp\left\{ -\frac{ZF}{RT}(\psi - \psi_D) \right\}}{(1 - \Omega) + \Omega \exp\left\{ -\frac{ZF}{RT}(\psi - \psi_D) \right\}} \tag{S16}
$$

where $\Omega = 8\phi_d/(1 + 8\phi_d)$. Note that the above expression is valid under the limit $\phi_d \leq 0.1$, which is however reasonable. So, the modified Boltzmann distribution for finite sized additional mobile ions may be deduced as follows

$$
n_d(y) = N_0 \frac{\exp\left\{ -\frac{ZF}{RT}(\psi - \psi_D) \right\}}{(1 - \Omega) + \Omega \exp\left\{ -\frac{ZF}{RT}(\psi - \psi_D) \right\}} \tag{S17}
$$

Note that if $\phi_d \to 0$ then the equation (S17) correctly merged with the standard Boltzmann distribution applicable for the spatial distribution of point-like ions.

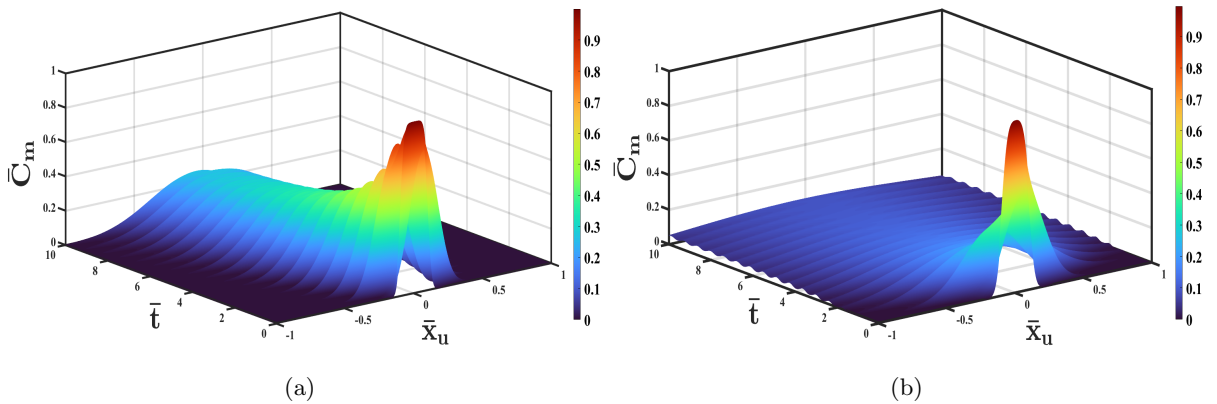## S.2 Additional results to support the findings

(a)

(b)

Figure S.1: The time evolution of cross sectional averaged scaled mean concentration distribution $\bar{C}_m$ is shown as a functions of moving co-ordinate system $\bar{x}_u$ and scaled time $\bar{t}$ for (a) Pe = 15 and (b) Pe = 5. Other model parameters are same as considered in Fig. 7 appearing in main manuscript (MS).
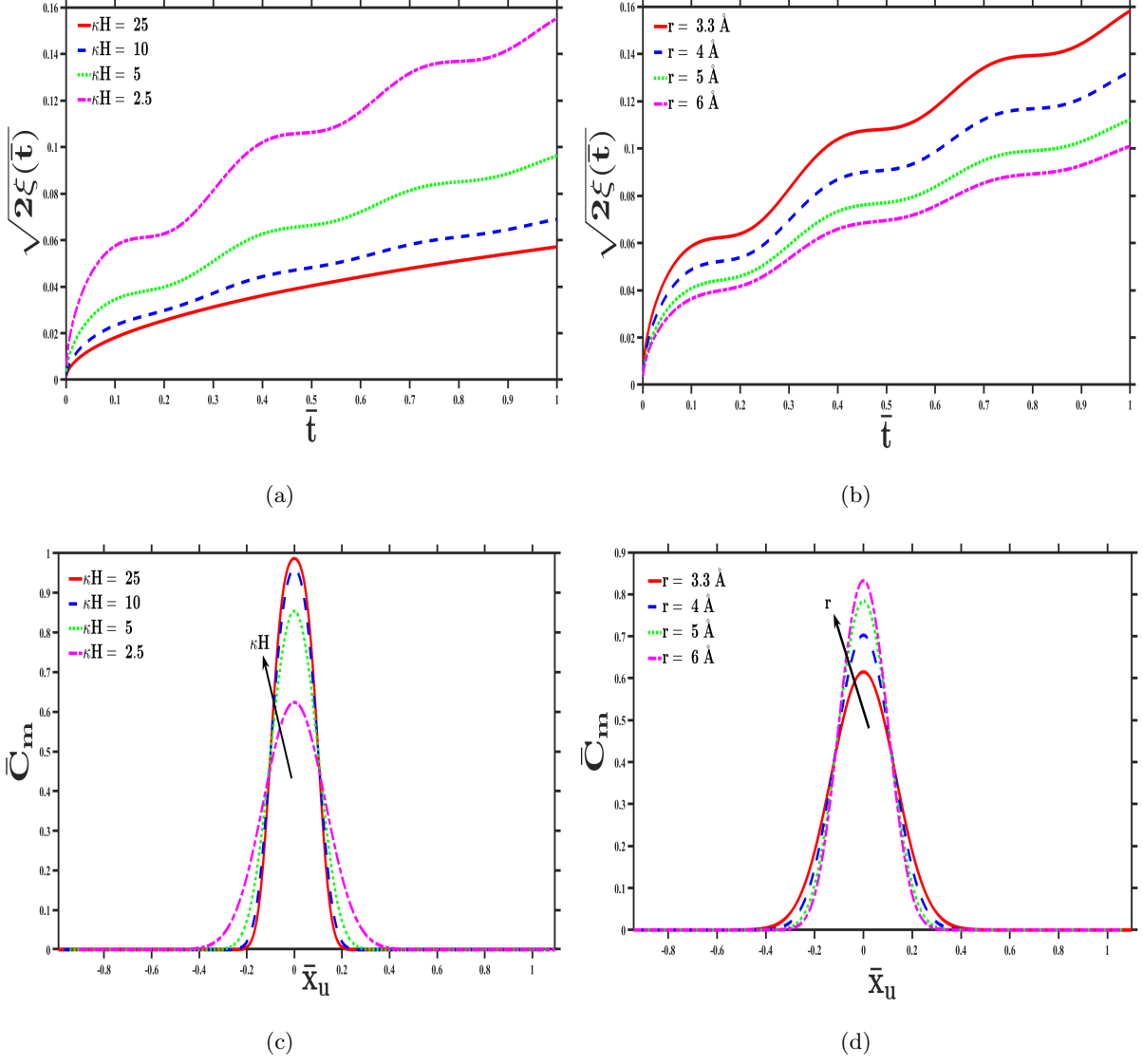
(a)

(b)

(c)

(d)

Figure S.2: In Fig. (a-b) we have shown the time evolution of $\sqrt{2\xi(\bar{t})}$ for various choices of (a) κH (= 2.5, 5, 10, and 25) with fixed $r = 3.3$ Å and (b) r (= 3.3 Å, 4 Å, 5 Å, and 6 Å) with fixed $\kappa H = 2.5$. We have further shown the results for $\bar{C}_m$ in Fig. (c-d) for similar choices of other model parameters as in Fig. (a,b) at a fixed time $\bar{t} = 0.5$. Other model parameters values are same as Fig. 8 appearing in main MS.
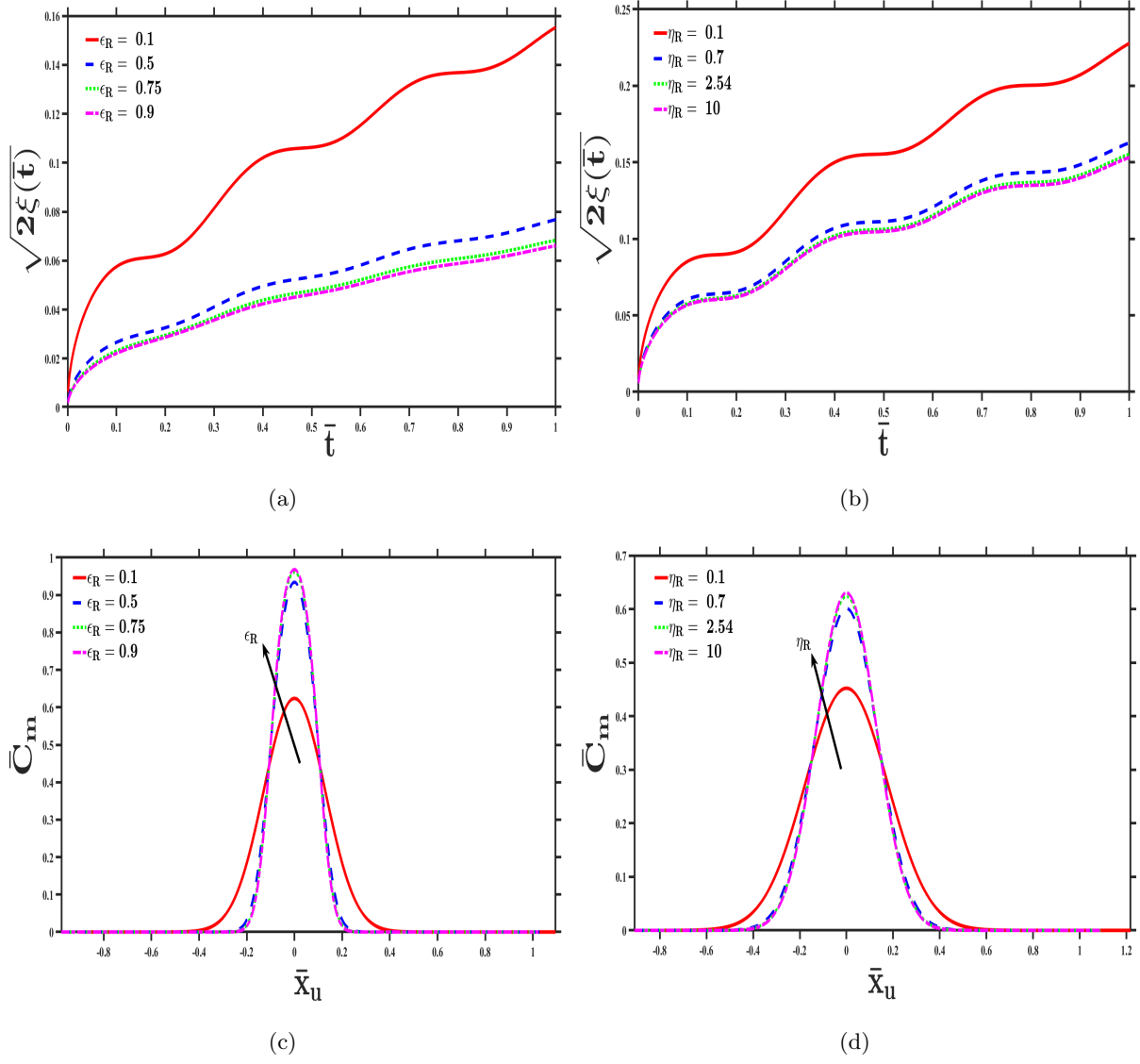
Figure S.3: In Fig. (a,b) the time evolution of $\sqrt{2\xi(\bar{t})}$ is shown for various values of (a) ϵ_R (= 0.1, 0.5, 0.75, and 0.9) with fixed $\eta_R = 2.54$ and (b) η_R (= 0.1, 0.7, 2.54, and 10) with fixed $\epsilon_R = 0.1$. For similar choices of parameters as in Fig. (a,b) we have shown the cross sectional averaged concentration $\bar{C}_m$ in Fig. (c,d) at fixed time. Other model parameters are same as Fig. 9 appearing in main manuscript MS.
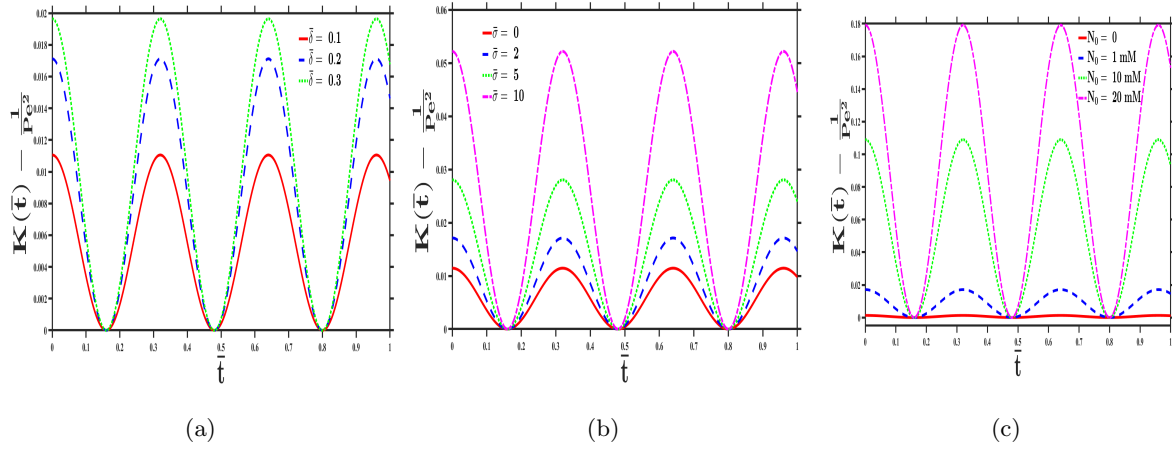
(a)   (b)   (c)

Figure S.4: Time periodic dispersion coefficient $K(\bar{t}) - 1/\mathrm{Pe}^2$ are shown as a function scaled time $\bar{t}$ for various values of (a) $\bar{\delta}$ (= 0.1, 0.2, and 0.3) with fixed $\bar{\sigma} = 2$, $N_0 = 1$ mM; (b) $\bar{\sigma}$ (= 0, 2, 5, and 10) with fixed $N_0 = 1$ mM, $\bar{\delta} = 0.2$ and (c) N_0 (= 0, 1 mM, 10 mM, and 20 mM) with fixed $\bar{\sigma} = 2$, $\bar{\delta} = 0.2$. The results are presented for fixed for $\epsilon_R = 0.1$, $H = 25$ nm, $\kappa H = 2.5$ nm, $r = 3.3$ Å, $\rho_R = 1.35$, $\eta_R = 2.54$ and $\bar{\omega} = 10$.
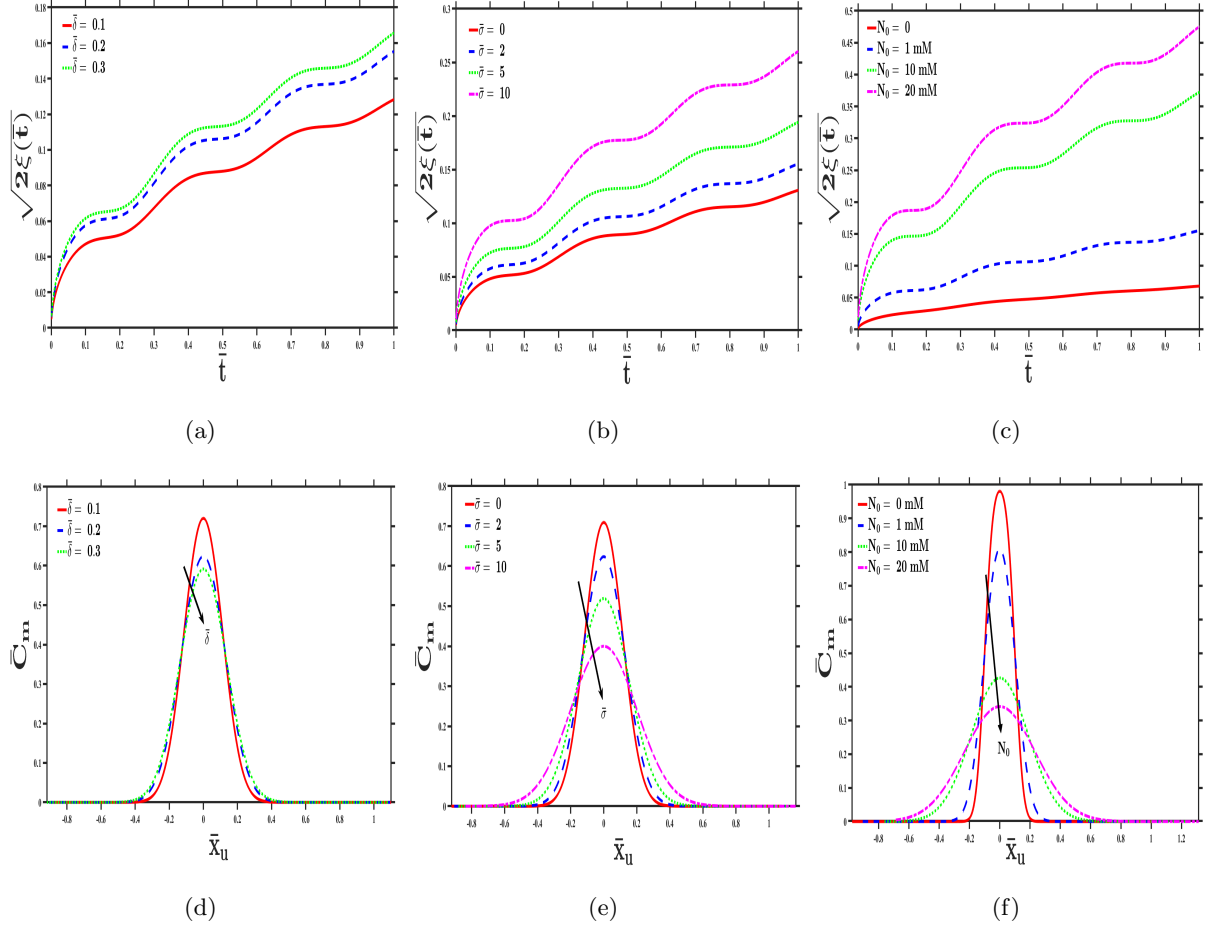
Figure S.5: In Fig. (a,b,c) we have shown the time evolution of $\sqrt{2\xi(\bar{t})}$ for various values of (a) $\bar{\delta}$ (= 0.1, 0.2, and 0.3) with fixed $\bar{\sigma} = 2$, $N_0 = 1$ mM; (b) $\bar{\sigma}$ (= 0, 2, 5, and 10) with fixed $N_0 = 1$ mM, $\bar{\delta} = 0.2$ and (c) N_0 (= 0, 1 mM, 10 mM, and 20 mM) with fixed $\bar{\sigma} = 2$, $\bar{\delta} = 0.2$. In Fig. (d,e,f) we have further shown the results for $\bar{C}_m$ at a fixed time $\bar{t} = 0.5$ for similar set of pertinent parameters as considered in Fig. (a,b,c). The results are presented here considering layer of CHB solvent adjacent to the supporting walls for fixed channel height $H = 25$ nm and Pe = 25.
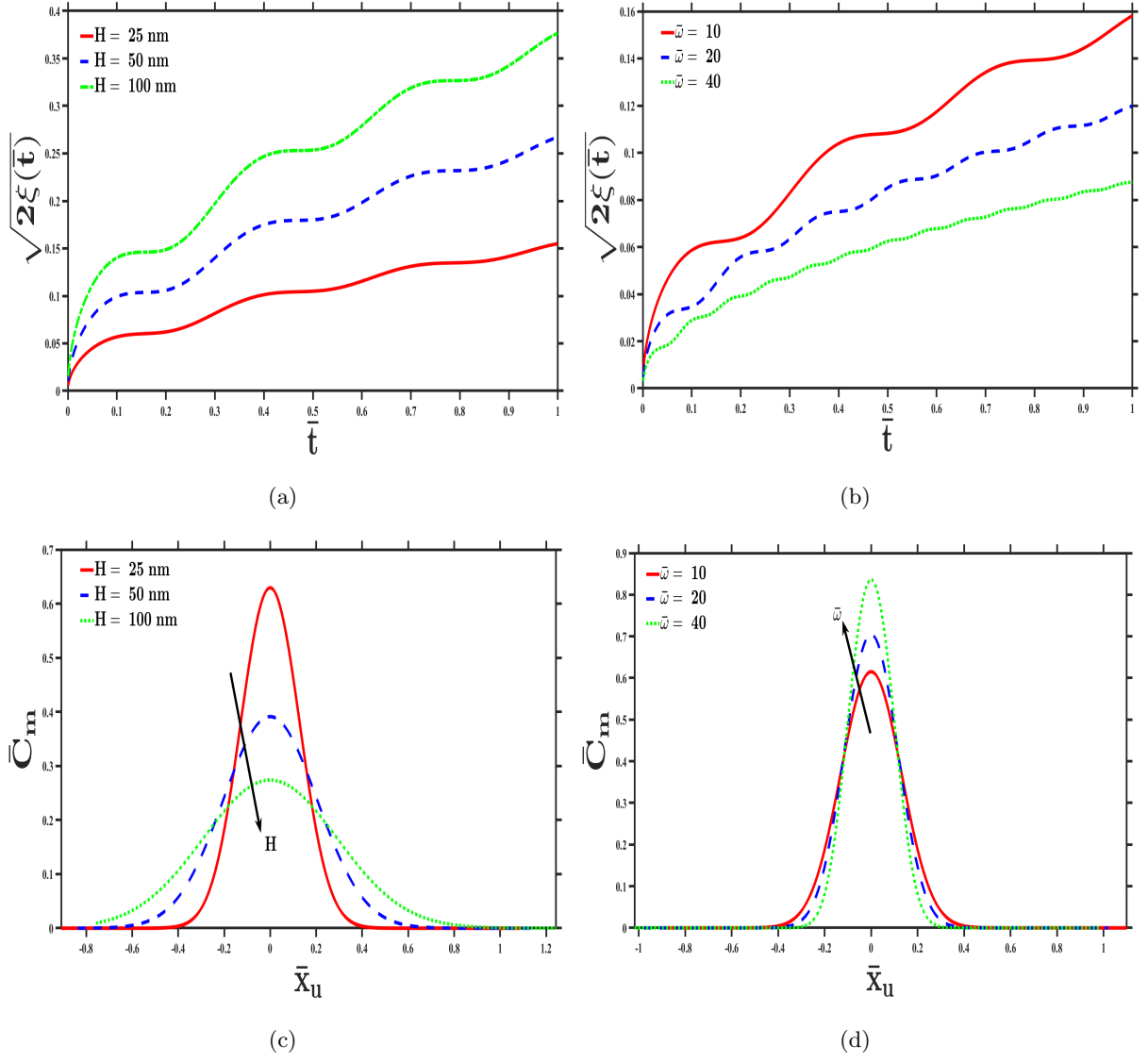
Figure S.6: In Fig. (a,b) we have shown the results for time evolution of $\sqrt{2\xi(\bar{t})}$ with various values of (a) H (= 25 nm, 50 nm, and 100 nm) for fixed $\bar{\omega} = 10$, and (b) $\bar{\omega}$ (= 10, 20, and 40) for fixed $H = 25$. In Fig. (c,d) the cross-sectional averaged concentration $\bar{C}_m$ are shown at fixed time $\bar{t} = 0.5$ for similar set of other parameters as considered in Fig. (a,b). The other model parameters are same as in Fig. 10 in main MS.
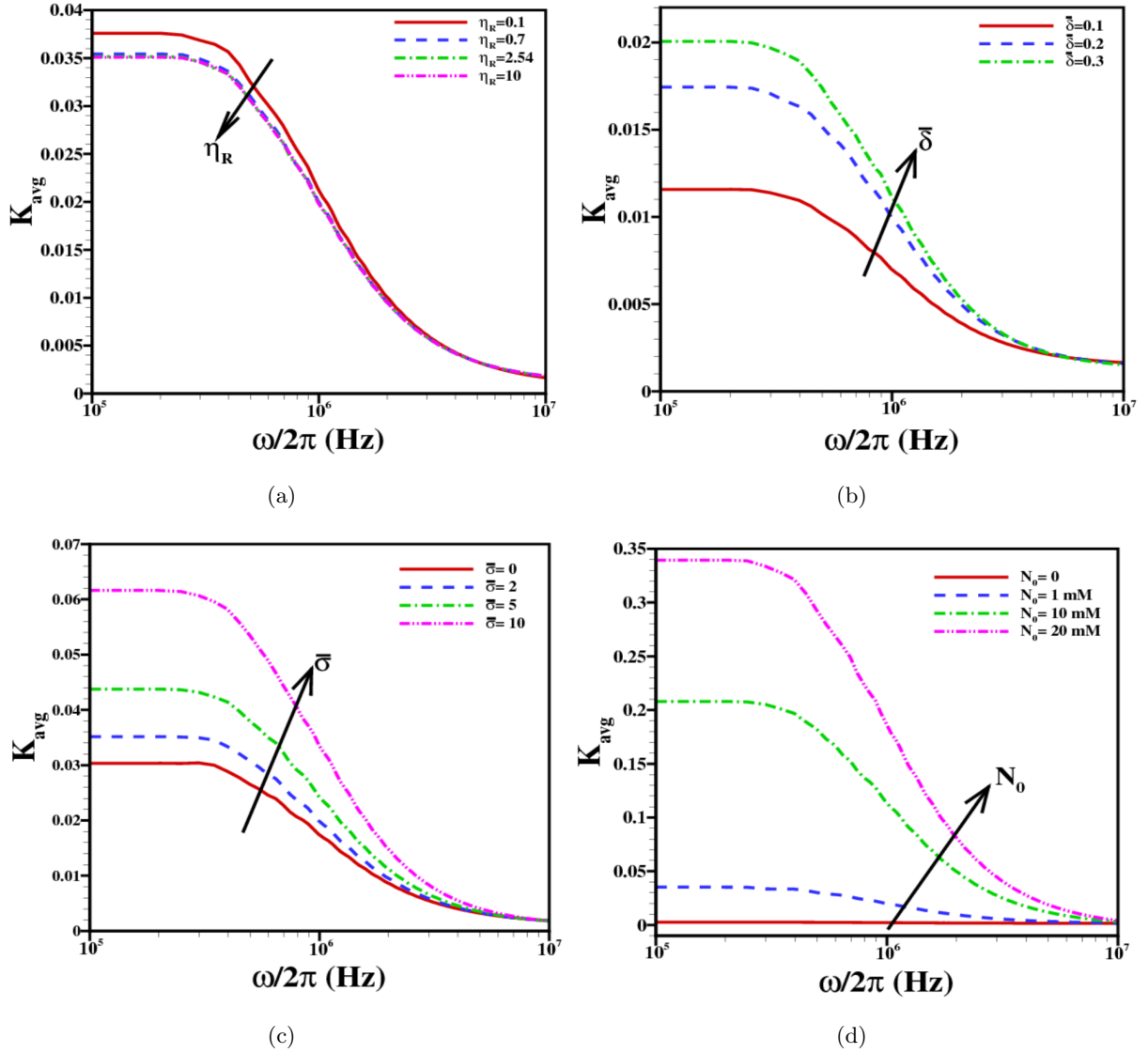
Figure S.7: Time average dispersion coefficient K_{avg} are shown as a function frequency $\omega/2\pi$ (Hz) for various values of (a) η_R ($= 0.1,\ 0.7,\ 2.54,\ \text{and}\ 10$) with fixed $\bar{\bar{\delta}} = 0.2$, $\bar{\sigma} = 2$, $N_0 = 1$ mM; (b) $\bar{\bar{\delta}}$ ($= 0.1,\ 0.2,\ \text{and}\ 0.3$) with fixed $\eta_R = 2.54$, $\bar{\sigma} = 2$, $N_0 = 1$ mM; (c) $\bar{\sigma}$ ($= 0,\ 2,\ 5,\ \text{and}\ 10$) with fixed $N_0 = 1$ mM, $\bar{\bar{\delta}} = 0.2$, $\eta_R = 2.54$ and (d) N_0 ($= 0,\ 1$ mM, 10 mM, and 20 mM) with fixed $\bar{\sigma} = 2$, $\bar{\bar{\delta}} = 0.2$. The results are presented here for fixed channel height $H = 25$ nm and Pe $= 25$.

References

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[3] Ohshima, H.; Nomura, K.; Kamaya, H.; Ueda, I. Liquid membrane: Equilibrium potential distribution across lipid monolayer-coated oil/water interface. *Journal of Colloid and Interface Science* **1985**, *106(2)*, 470–478.

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