Micelle Formation in Aqueous Solutions of Room Temperature Ionic Liquids: a Molecular Dynamics Study

J.M. Vicent-Luna[†], J.M. Romero-Enrique[‡], S. Calero[†], and J.A. Anta[*,†]

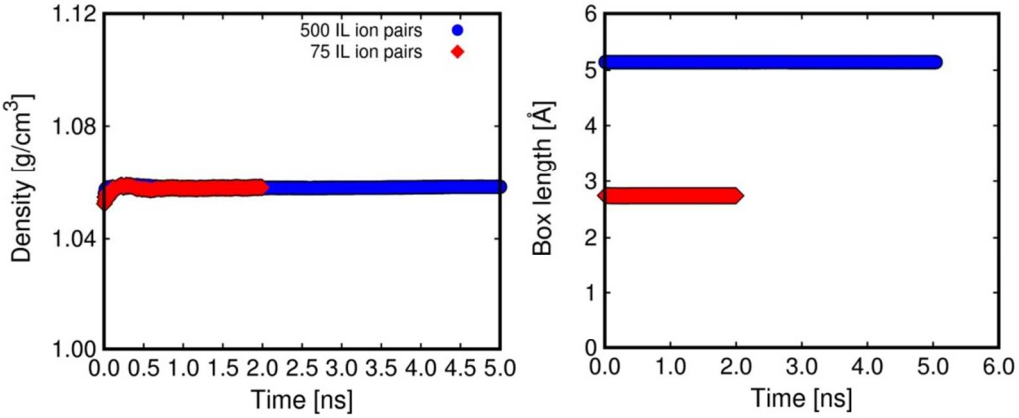
[†]Department of Physical, Chemical, and Natural Systems. Universidad Pablo Olavide. Ctra. Utrera km. 1, ES-41013, Seville, Spain

[‡] Departamento de Física Atómica, Molecular y Nuclear, Área de Física Teórica, Universidad de Sevilla, Avenida de Reina Mercedes s/n, Sevilla, Spain

*E-mail: anta@upo.es. Tel.: +34-954349314

System size effect

Figure S1. Time evolution of the average density and average cell length of water/IL mixtures containing 75 and 500 $[C_4MIM]^+$ IL ion pairs.



Simulation time effect

Figures S2-3 compare the resulting data from two independent simulations with different time scales for a system containing 200 $[C_{12}MIM]^+Cl^-$ ion pairs and 6000 molecules of water. MSD of cations and water depicted in Figure 1 show similar trend for the simulations of 5 and 50 ns respectively. The obtained self-diffusion coefficients of cations in both simulations are $1.18 \cdot 10^{-10}$ and $1.49 \cdot 10^{-10}$ m^2/s, respectively. These values are in line with the values obtained for systems containing $[C_{12}MIM]^+$ cations in the range of 0.51-1.35 M, which fluctuates between $1.02 \cdot 10^{-10}$ and $1.54 \cdot 10^{-10}$ m^2/s. The deviation of the self-diffusion coefficients of water varying the simulation time scale is insignificant. In addition, the diffusive regime can be examined computing the time-dependent parameter: $\beta(t)=dLn(MSD(t))/dLn(t)$. When $\beta(t)$ is close to the unity, the system is in a linear diffusive regime. These values are shown in the bottom graph of Figure S2. According to this approximation, the systems are in the diffusive regime in the time scales used to extract the self-diffusion coefficients (between 1 and 3 ns and 10 and 30 ns for simulations of 5 and 50 ns respectively), as can be seen in the figure. Water describes a more linear behavior, since it has a larger diffusion constant and better statistics due to the high number of molecules considered in the simulations. Figure S3 shows no dependence with the time scale of the structural properties analyzed in Figures 6, 8, 9, and 10 of the main text.

Figure S2. Log-log and linear representations of the mean squared displacement of $[C_{12}MIM]^+$ (top) and water (center) at different simulation timescales and their corresponding first derivatives (bottom) as a function of time.

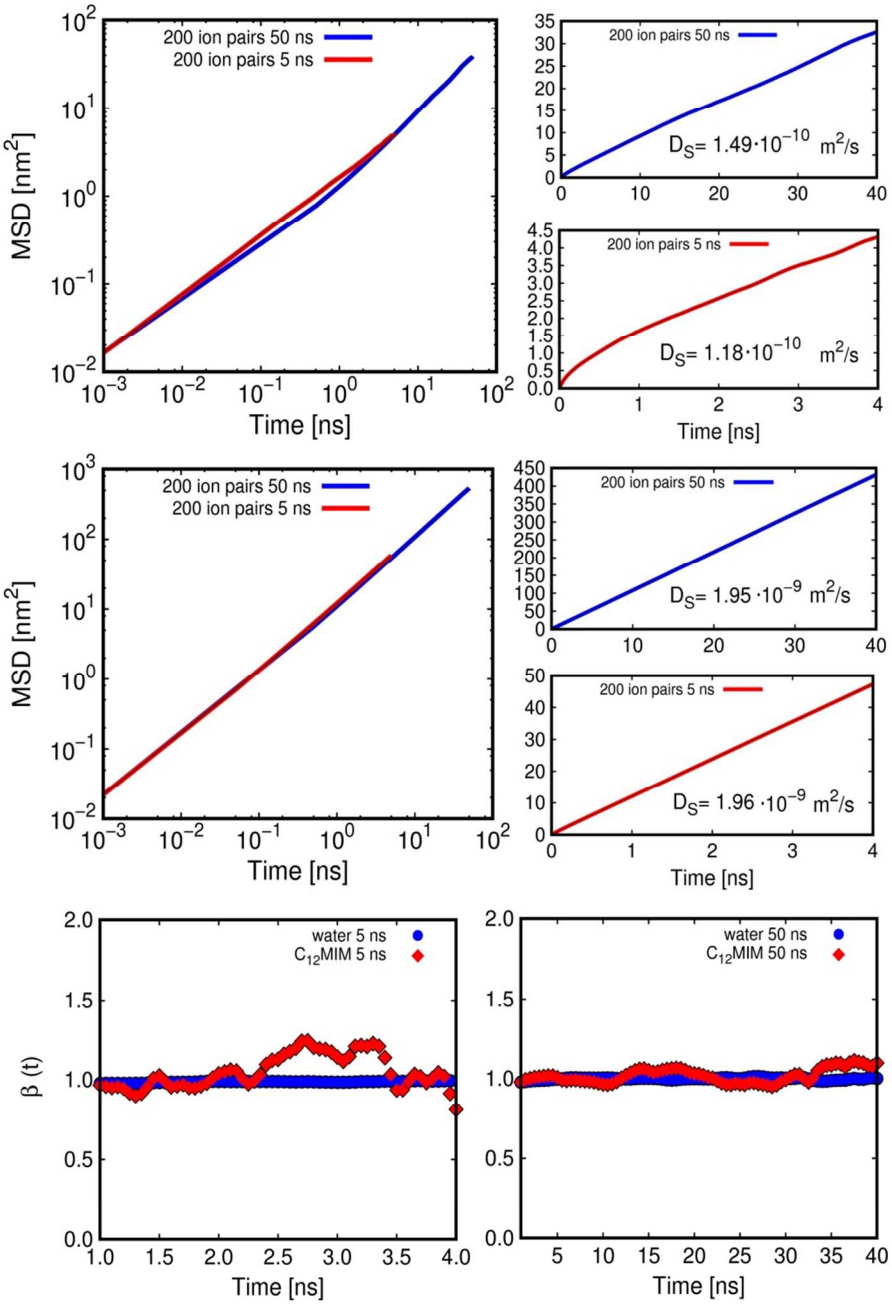


Figure S3. Comparison of the results obtained in this work for a system with concentration corresponding to 200 ion pairs of $[C_{12}MIM]^+Cl^-$ at different simulation time scales. (a) Local density of cations across the x direction (left) and average occupation profiles at low and high concentration of the geometric center of cations in the XY plane (right). (b) Head-head of cations, tail of cations-water, and tail-tail of cations RDFs. (c) Cluster size distribution (number of cations per cluster) and number of cluster distribution.