Supplemental Material

Effect of Concentration on Like-Charge Pairing of Guanidinium Ions and on the Structure of Water: An All-Atom Molecular Dynamics Simulation Study

Dibyendu Bandyopadhyay[1], K. Bhanja[1], Sadhana Mohan[1], Swapan K. Ghosh[2] and Niharendu Choudhury[2]*

[1]Heavy water Division, [2]Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India

*Address for correspondence:

Dr. Niharendu Choudhury
Theoretical Chemistry Section,
Bhabha Atomic Reasearch Centre,
Mumbai 400 085, India
Ph. +91-22-25585089, Fax: +91-22-25505151
Email: nihcho@barc.gov.in
niharc2002@yahoo.com
niharc2007@gmail.com

Supplemental Material Text

In this Supporting Information we have three parts namely Part A, Part B and Part C. In Part A, we present results obtained from the TIP3P water model and in Part B the results obtained from the 65 ns simulation of around 6 M GdmCl solution with a larger box length (L=5.021 nm) containing 500 GdmCl and around 2350 water molecules are presented. It is meant to check the reported results obtained from smaller simulation size and time against system size and finite time dependence. In Part C, we have shown how mean squared displacements of different species in solution are varying with concentration of GdmCl.

Part-A

Results Obtained from TIP3P Water Model:

A. Radial Distribution Functions: The RDFs of the carbon atom of Gdm moieties around the carbon atom of a central Gdm moiety at three different concentrations of GdmCl have been shown in Figure S1. The water model used here is TIP3P. Although considerable change in peak heights of the RDF at different concentration is observed, numbers of Gdm moieties within the first and the second solvation shells as calculated by integrating the g(r) up to appropriate distances are shown in the inset of Figure S1.

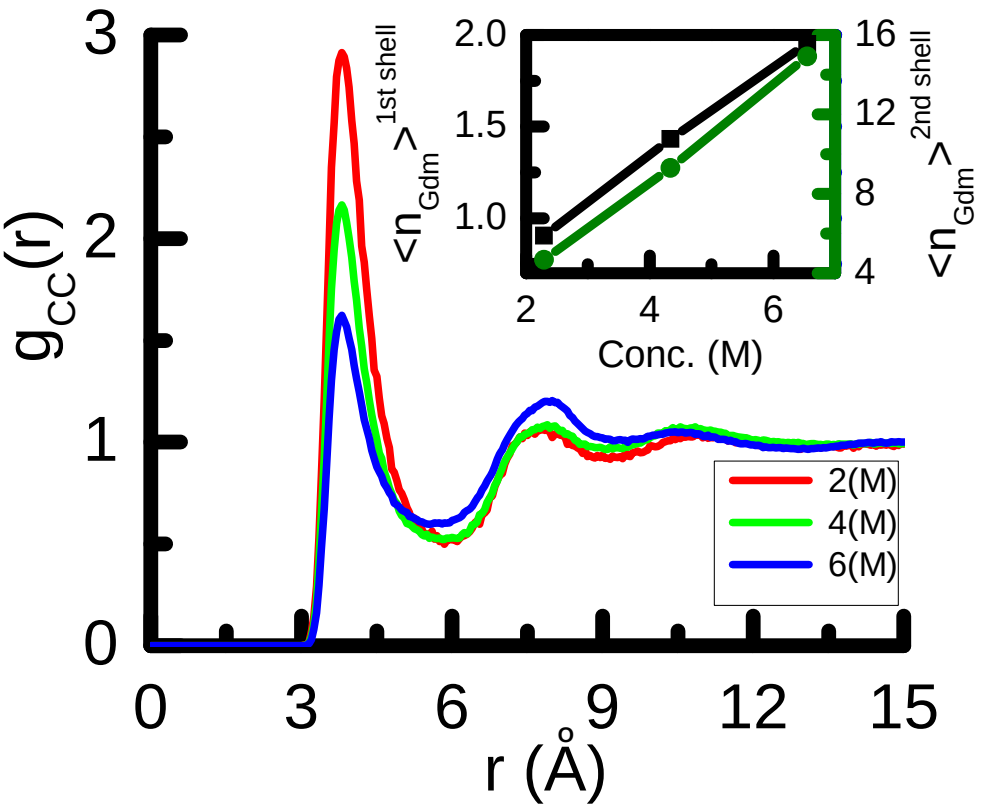

Figure S1: Radial distribution functions of Gdm^+-Gdm^+ moieties at three different guanidinium chloride concentrations. The radial distance *r* is measured as the distance between carbon atoms of two Gdm moieties. Inset: Average numbers of Gdm ions presents in 1st solvation shell (black line, left hand side axis) and in 2nd solvation shell (green line, right hand side axis) respectively (inset). Water model used here is TIP3P.

It is to note that the results shown here for TIP3P water model are qualitatively the same as those obtained from TIP4P/2005 water model as shown in the main text. (see Figure 1 main text).

B. Average Tetrahedral Order parameter: The average tetrahedral order parameter, $<q_4>$ is calculated in two different ways: (1) by considering four nearest water molecules as the nearest neighbors of the central water molecule and (2) first, we select four nearest neighbors irrespective of whether it is guanidinium ion, chloride ion or water and then calculate q_4 by considering only those water molecules that are within the first four (distance-wise) chosen neighbors. We have used proper normalization for the cases where the number of nearest neighbors is less than four (see Models and Methods section). The water model used here is TIP3P.

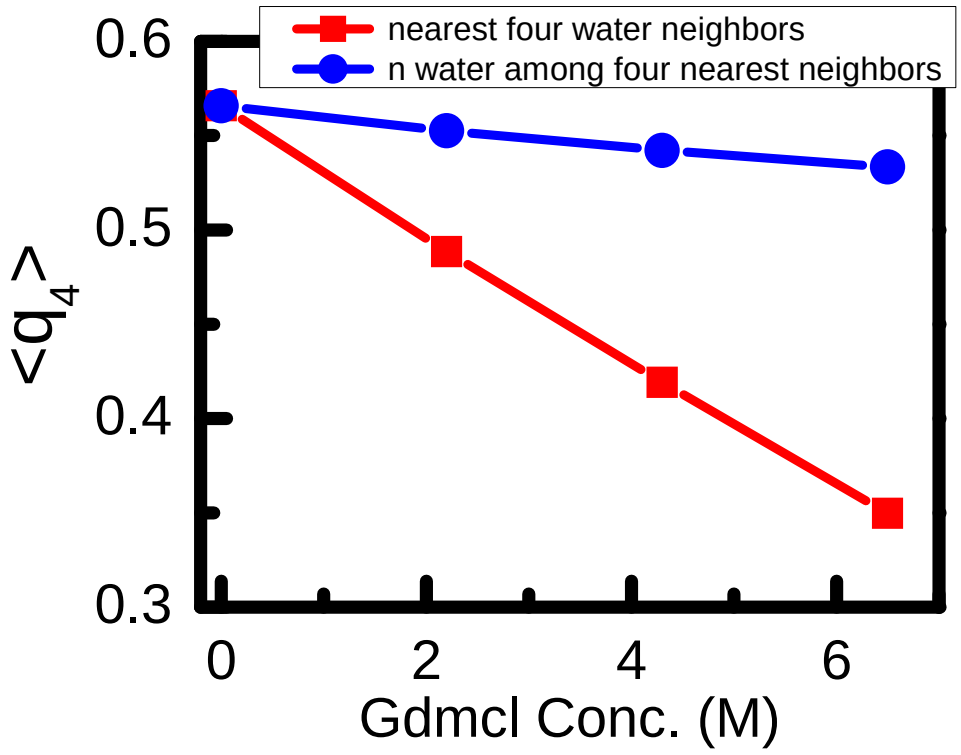

Figure S2: Average tetrahedral order parameter $\langle q_4 \rangle$ as a function of molar concentration of guanidinium chloride. Red line with squares represents results obtained when we choose the first four water molecules as the four nearest neighbors. Blue line with circles represents results obtained by considering n ($n \leq 4$)) water neighbors that are within the first four nearest neighbors. TIP3P water model is used.

C. Distributions of hydrogen bonding angles: The ensemble averaged distribution of the hydrogen bonding (HB) angle (θ_{HB}) made by different "water neighbors" of a central water molecule. In this case while choosing neighbors, Gdm^+ and Cl^- are not considered as probable neighbors. The distributions shown below are obtained from TIP3P water model. This distribution is almost same as those obtained using TIP4P/2005 water model (see Figure 10 of the main text).

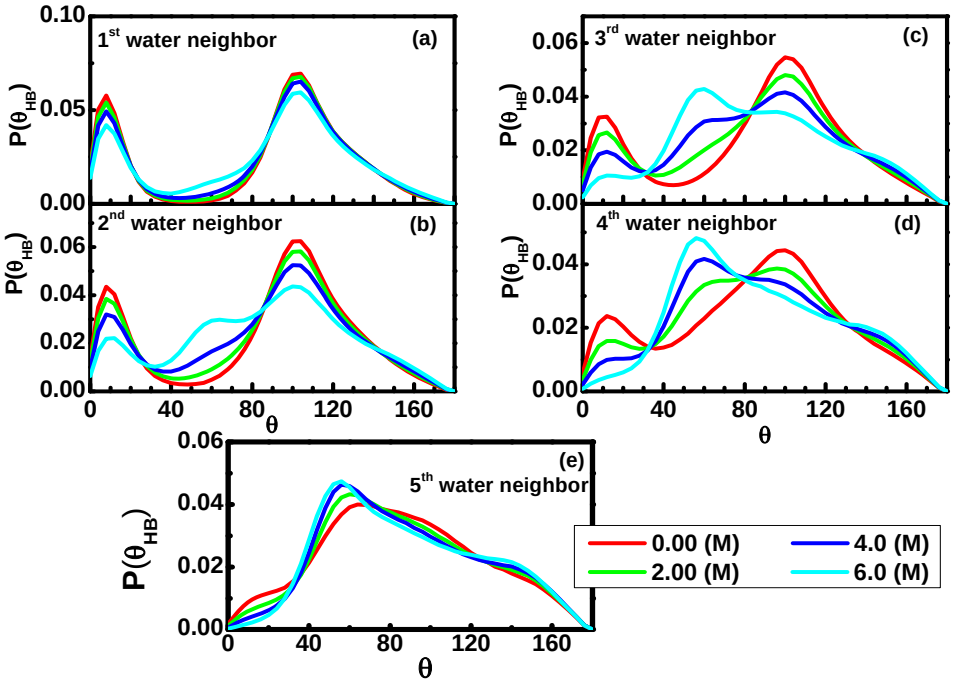

Figure S3. Distributions $P(\theta_{HB})$ of the hydrogen bonding angles θ_{HB} formed by a reference water molecule and one of its neighbors. The distributions for five nearest water neighbors are shown. In this case guanidinium chloride is not considered as a neighbor. The water model used is TIP3P.

Like in the case of tetrahedral order parameter calculation, if we now allow Gdm+ and Cl- also to be probable neighbors of a central water molecule and choose only those water neighbors that are within the first five neighbors for the calculation of HB angle following (Figure S4) distributions are obtained. These distributions are obtained using TIP3P water model and are almost the same as those obtained using TIP4P/2005 water model (see Figure 11 of the main text).

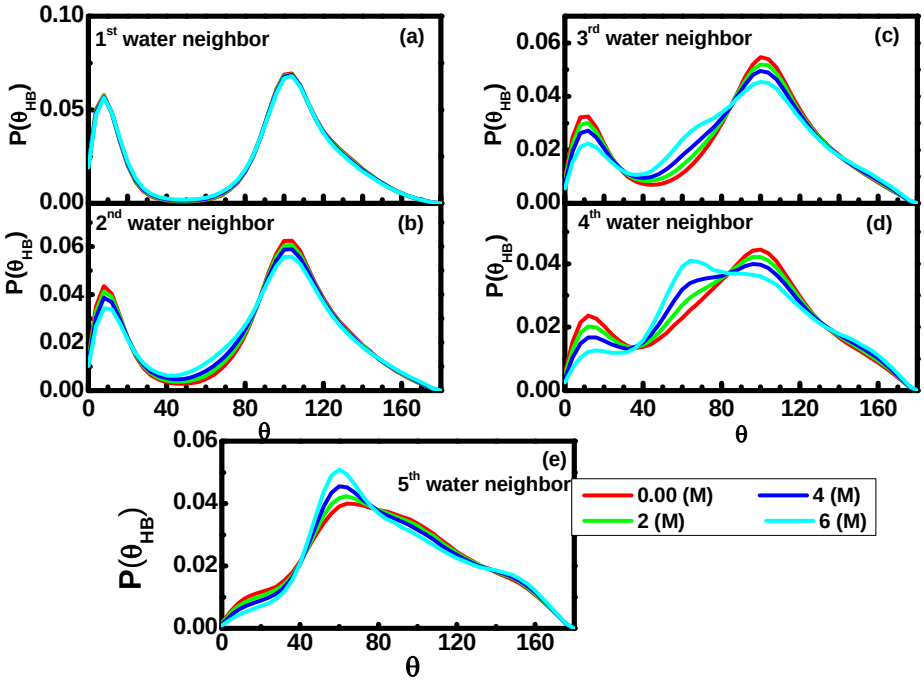

Figure S4. Same as in Figure S3 except that now we choose five nearest neighbors irrespective of whether it is guanidinium ion or chloride ion or water and then calculate the required hydrogen bonding angle between the reference water molecule and that water neighbor, which is within the first five (distance-wise) neighbors. The water model used is TIP3P.

Part B

Here we compare/contrast the results obtained from smaller simulation size and time with those obtained from a simulation with larger system size and longer simulation time.

A. Radial Distribution Functions: In this figure different radial distribution functions have been shown in four different panels of Figure S5. In each panel the RDF is calculated from 3 different simulation conditions, namely legend A represents result from L=3.165 nm box averaged over 20-30 ns of the trajectory. Legend B stands for the results obtained from the simulation of a larger box size of 5.021 nm and averaged over 20-30 ns of the trajectory, while Legend C represents results obtained from simulation of the larger box size of 5.021 nm and

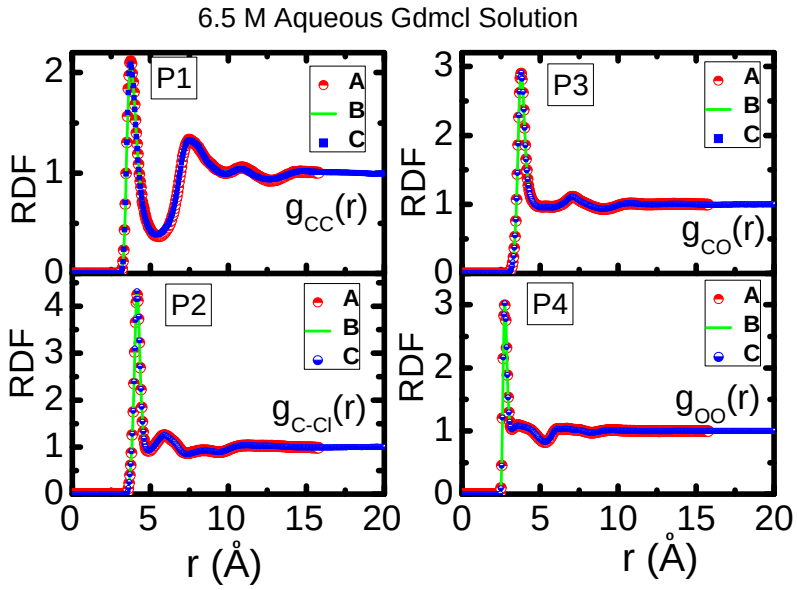

Figure S5. RDFs of (P1) carbon atom of Gdm+ around another Gdm+ carbon, (P2) chloride ion around the carbon atom of Gdm+ (P3) oxygen of water around the carbon atom of Gdm+ and (P4) oxygen atom of water around oxygen atom of another water molecule. In each panel RDFs are drawn for three different simulation conditions, namely Legend A represents result from L=3.165 nm box averaged over 20-30 ns of the trajectory, Legend B is for a larger box size of 5.021 nm and averaged over 20-30 ns of the trajectory, while Legend C is for the larger box size of 5.021 nm and averaged over 60-65 ns of the trajectory.

averaged over 60-65 ns of the trajectory. The RDFs of the carbon atom of Gdm moieties around the carbon atom of a central Gdm moiety for around 6.5 M GdmCl concentration has been shown on panel P1 of Figure S5. The carbon-chlorine, carbon-oxygen and oxygen-oxygen (of water) RDFs are displayed in panels P2, P3 and P4 respectively. In all these cases, RDF shown by the legends A, B and C are almost indistinguishable and thus confirms that the results obtained from smaller simulation systems with shorter trajectory are well converged with respect to both system size and averaging over time scale.

Part C

Here we present our result on translational dynamics of different species present in GdmCl-Water system as a function of GdmCl concentrations.

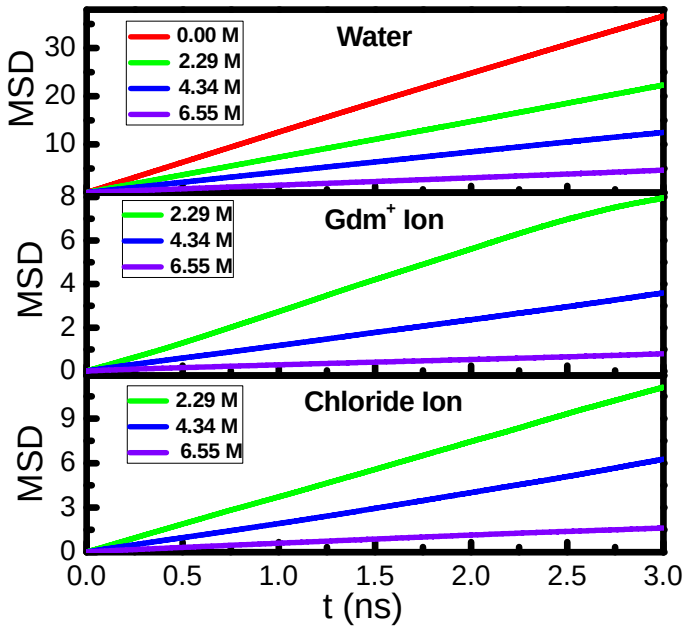

Figure S6. Mean squared displacements of water, Gdm+ ions and Chloride ions in the GdmCl-Water solutions of different concentrations.

Mobility of all the species including water show strong GdmCl concentration dependence. As the concentration of the GdmCl in the solution increases, slope of the MSD curve decreases and therefore translation diffusivity decreases. The diffusivity values are reported in the main text (see Table II).
