Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Structure and dynamics of Li^+ ion in water, methanol and acetonitrile solvents: Ab-initio molecular dynamics simulations

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Table S1: Calculated values of diffusion coefficients with periodic boundary condition (D_{PBC}) and corrected diffusion coefficients (D_O) of solvent molecules for the various studied systems.

System	Diffusion coefficient ($10^{-5}cm^2/s$)			
	Species	Expt.	AIMD (This work)	
			D_{PBC}	D_0
LiCl - 64(H_2O)	O	1.98[s1]*	0.33	1.06
LiCl - 64(CH_3OH)	O	2.36[s2]	0.52	1.43
LiCl - 64(CH_3CN)	N	2.71[s3]*	1.35	2.72

*Values determined by scanning the plots in cited papers

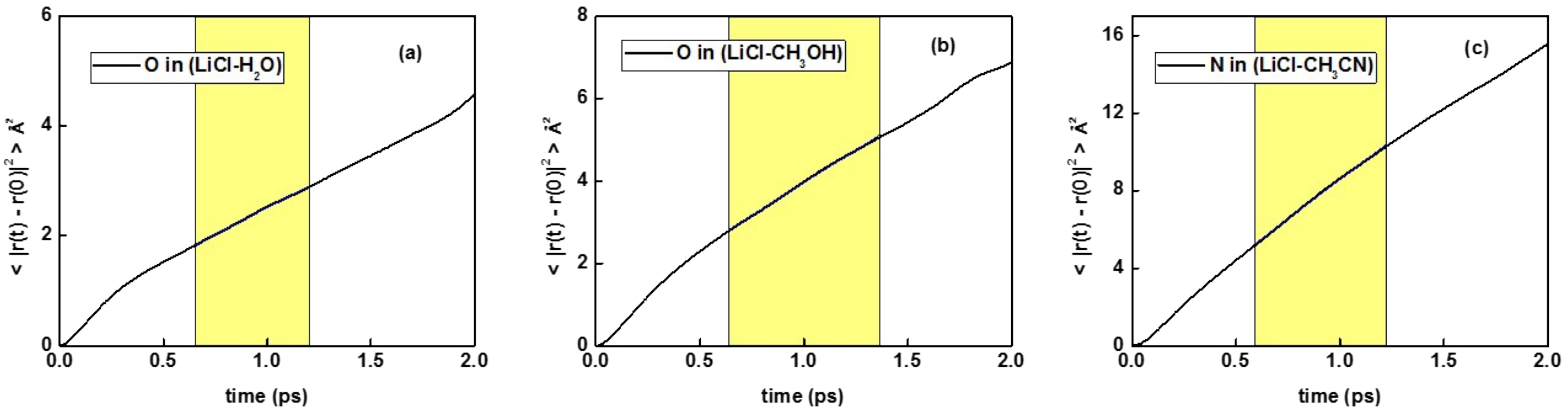

Figure S1: Mean squared displacement plots for (a) water, (b) methanol and (c) acetonitrile.

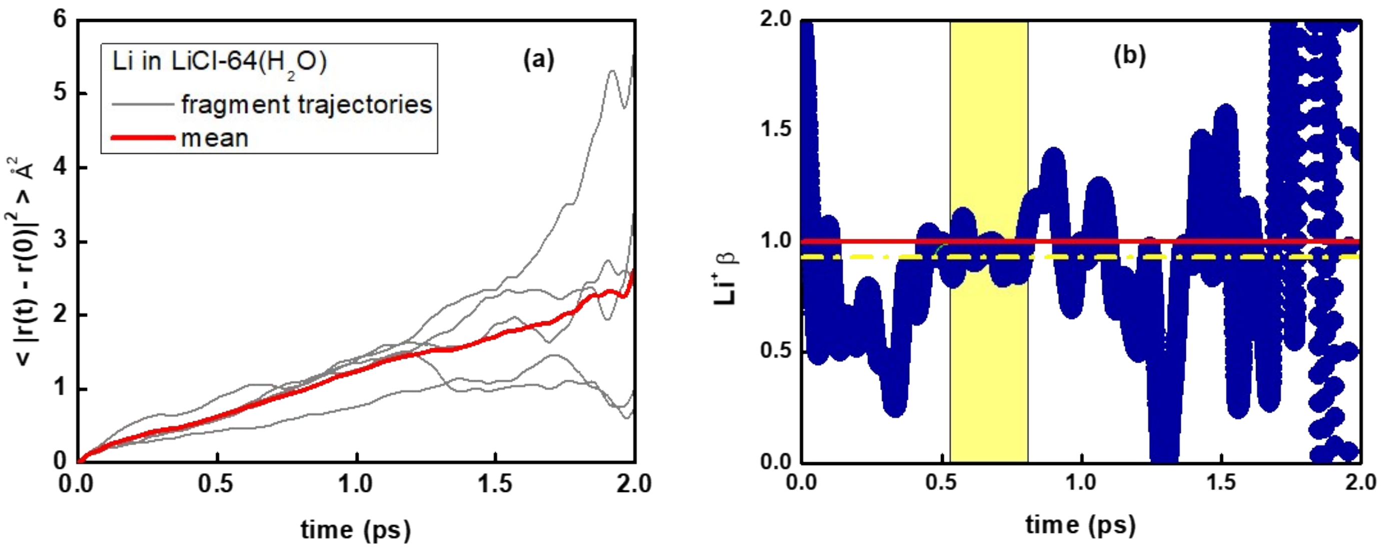

Figure S2: (a) MSD plots for five fragment trajectories (grey) and their mean plot (red) for Li^+ in water. (b) Exponent (β) of Li^+ vs time plot corresponding to MSD of Li^+ ion in water.

Figure S2(a) represents the various MSD plots of Li^+ ion in water that have calculated from the five fragment trajectories of 2ps each. A 10ps trajectory from the equilibrated system was fragmented into 5 trajectories of 2ps and then all these trajectories were averaged to one trajectory of 2ps which was used to calculate the diffusion coefficient (see Figure 9(a)). Since, only one Li^+ ion was present in the simulated system, doing this can be considered equivalent to average Brownian motion of five Li^+ ions for the same concentration. This has been done to improve the averaging of the calculated diffusion property and to reduce the extent of fluctuations in the plot revealing the true nature of diffusion. The linear part of the MSD plot to calculate diffusion coefficient was further determined by plotting the exponent (β) vs time plot following the procedure that had been explained by Nikhil V. S. Avula et al. in their study of physical properties of ionic liquid electrolytes[s4]. The exponent $\beta(t)$ can be used to determine the diffusive region of the MSD which can then be fitted to calculate the diffusion coefficient and is given in equation S1:

$$\beta(t) = \frac{d(\ln(MSD(t)))}{d(\ln(t))} \#(S1)$$

where, ln() is the natural logarithm, MSD(t) is the mean squared displacement at time 't' and β(t) is the exponent at that time.

Figure s2(b) represents the plot of exponent (β) vs time for MSD corresponding to Li^+ ion in water for the system LiCl-64(H_2O). The red line represents β = 1 while the dashed yellow line represents the average value of β from the selected part to calculate diffusion. Similar averaging has been done for diffusion of Li^+ in methanol and acetonitrile represented in Figure 9(b) and 9(c) respectively.

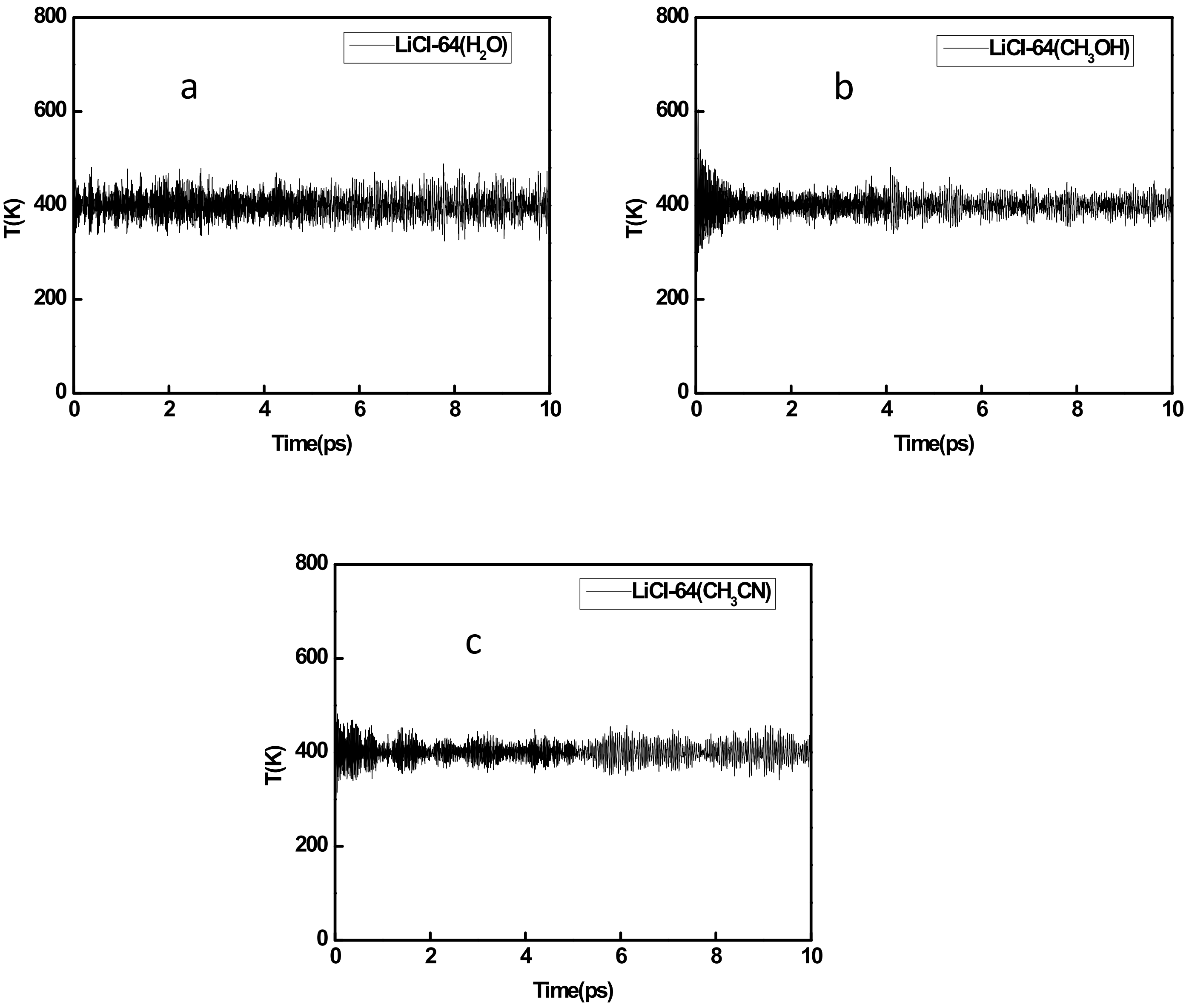

Figure S3: Calculated plot of instantaneous kinetic temperatures (T) versus simulation runs (Time, ps) for all the studied system during AIMD simulation using the PBE functional.

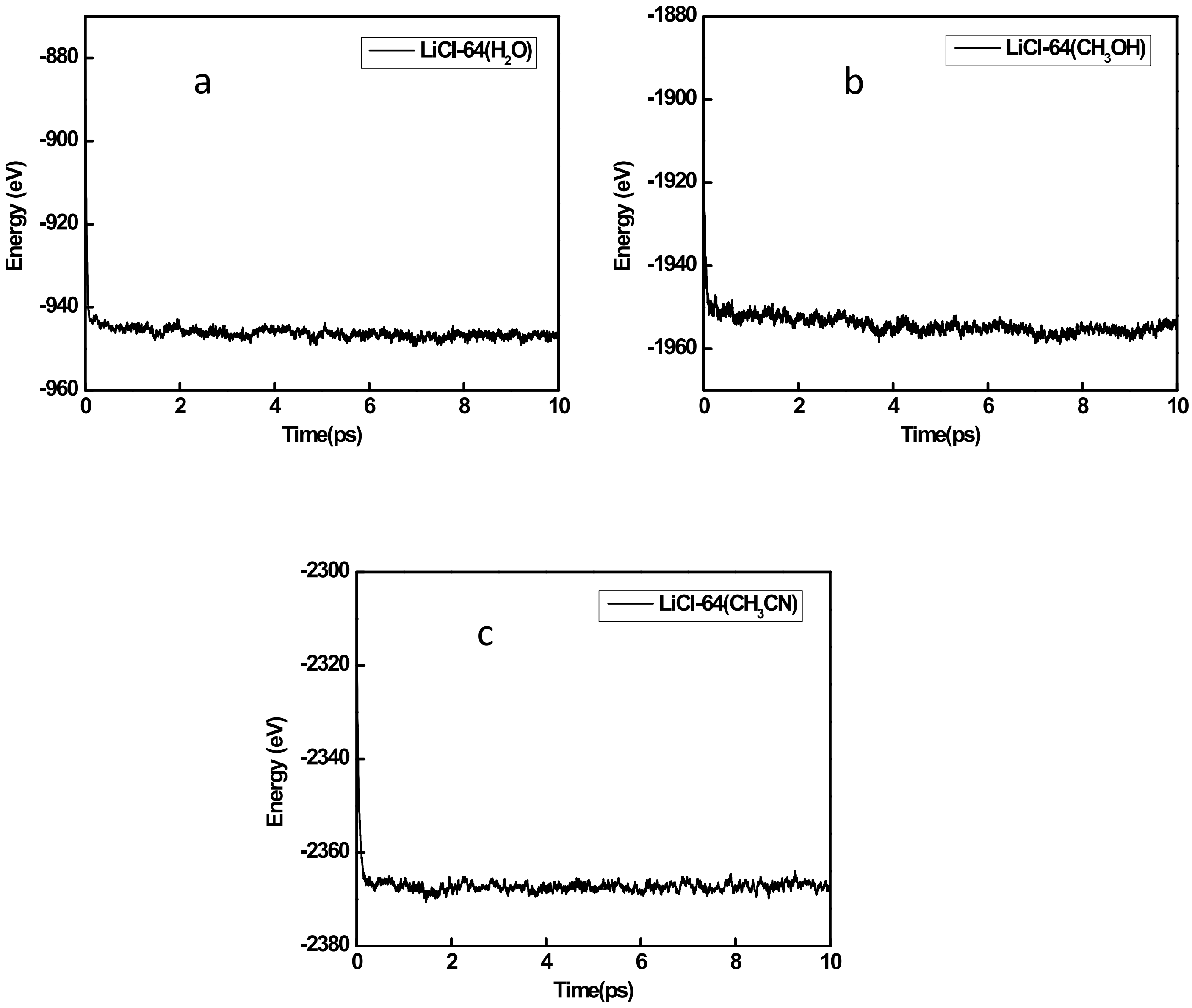

Figure S4: Calculated plot of total energy (E) versus simulation runs (Time, ps) for all the studied system during AIMD simulation using the PBE functional.

S1: Algorithm for calculation of Radial Distribution Function:

Step 1: Determine the distance between the coordinates of all the existing pairs of desired RDF (e.g., Li-O) for first configuration.

Step 2:Do the binning count of the calculated distances i.e., take a total scanning distance of less than the half box length and divide it into different distance intervals (bins), considering PBC. For example, the total number of bins each with a width of say 0.5 Å for a half box length of 6 Å will be 12 (bins = interval * half-box length). So a distance between range 0 to 0.5 Å will increase the count of bin-1 by 1 and distance in range 0.5 to 1.0 Å will add to the count of bin-2 by 1 and so on.

Step 3:Calculate the Local number density of ith bin:

$$\rho_i(local) = \frac{count\ of\ bin(i)}{Vol.\ of\ bin(i) * no.\ of\ central\ atoms\ per\ configuration(here\ Li)}$$

Step 4:Repeat steps 1 to 3 for each configuration(iteration) and calculate the Average Local number density of ith bin,

$$\rho_i(local) = \frac{Local\ density\ of\ bin(i)}{no.\ of\ iterations}$$

Step 5: Calculate the normalized g(r) such that it goes to 1 for homogeneous system:

$$g(r) = \frac{\rho_i(local)}{\rho(global)}$$

Where; global density,

$$\rho(global) = \frac{(1 + no.\ of\ neighboring\ atoms\ per\ configuration(here\ oxygen))}{Volume\ of\ simulation\ box}$$

('1' in global density expression is for the central atom, the count of which is always 1)

S2: Algorithm for calculation of first shell average coordination number distribution:

Step 1:Take the first minima of RDF for that pair as the distance cutoff limit and calculate the distances between one central atom (here Li) and neighboring atoms (here O).

Step 2: Make a list or an array having elements equal to the number of configurations (steps of iteration). Count the number of neighboring atoms that are within the cutoff distance from the central atom (considering PBC).

Step 3:Put this number as element of array for that particular configuration number. (Take an average of count if more than one central atom present)

Step 4:Repeat Step 2 for all the configurations. Calculate the frequency of each type of configuration and calculate its probability percentage.

S3: Algorithm for calculation of Mean Squared Displacement:

Step 1:Make the coordinates unwrapped if they are initially wrapped (PBC).Take a trajectory containing the same time step (Δt). Calculate the average (if more than one atoms) squared displacement of desired atom for $\Delta t(1)$ i.e., configuration 1 to configuration 2, configuration 2 to configuration 3, …., configuration (n-1) to configuration (n). Take a mean of all the values for $\Delta t(1)$.

Step 2: Calculate the mean of average squared displacement for time steps $\Delta t(2), \Delta t(3), \ldots, \Delta t(n)$ where displacement for $\Delta t(2)$ represents the displacement form configuration 1 to configuration 3, configuration 2 to configuration 4, configuration 3 to configuration 5 and so on.

Step 3: Plot the corresponding values of mean squared displacement for corresponding time step and calculate the slope of this plot to get diffusion coefficient.

S4: Algorithm for calculation of hydrogen bond correlation function:

Hydrogen bond between two molecules can be defined if the following conditions are satisfied:

(i) Oxygen-Oxygen distance is less than 3.6 Å.

(ii) Distance between donor hydrogen and acceptor oxygen is less than 2.4 Å.

(iii) The angle between the vector connecting two oxygen atoms and the vector connecting the donor oxygen and acceptor hydrogen is less than 30°.

Step 1: Make a list or an array of all the possible molecule (e.g. water) pairs for formation of hydrogen bond.

Step 2: For each pair determine the existence of hydrogen bond for each configuration(step) of trajectory. For that pair put '1' if the hydrogen exists for a configuration and '0' if does not. This way each pair will have an array having elements equal to number of steps having values either 1 or 0.

Step 3: Consider arrays only which have at least one hydrogen bond. Format these arrays in such a way that they have values starting from '1' only. (Means for example if a pair has hydrogen bond formed only at step 100 out of total n steps, then discard all the first 99 steps such that the number of elements in that array are 'n-99'; after this it does not matter whether the hydrogen bond breaks or makes again).

Step 4: When done for all the pairs containing hydrogen bonds, make an average array(with whatever number of terms remaining for that element index) from all these arrays and plot against the time of trajectory.

References:

S1 Tanaka, K. and M. Nomura, Measurements of tracer diffusion coefficients of lithium ions, chloride ions and water in aqueous lithium chloride solutions. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1987. 83(6): p. 1779-1782.

S2 Derlacki, Z.J., Easteal, A.J., Edge, A.V.J., Woolf, L.A. and Roksandic, Z., Diffusion coefficients of methanol and water and the mutual diffusion coefficient in methanol-water solutions at 278 and 298 K. The Journal of Physical Chemistry, 1985. 89(24): p. 5318-5322.

S3 Semino, R., et al., Lithium solvation in dimethyl sulfoxide-acetonitrile mixtures. The Journal of chemical physics, 2014. 141(21): p. 214509.

S4 Avula, N.V., Karmakar, A., Kumar, R. and Balasubramanian, S., Efficient parametrization of force field for the quantitative prediction of the physical properties of ionic liquid electrolytes. Journal of Chemical Theory and Computation,2021. 17(7): p. 4274-4290.