Supplementary Information Molecular Simulation of Osmometry in Aqueous Solution of BMIMCl Ionic Liquid: A Potential Route to Forcefield Parameterization of Liquid Mixtures

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1 CONTROLLED SIMULATIONS

1.1 Osmotic Pressure of NaCl-Water Solution

Prior to the calculation of osmotic pressure for ionic liquid (IL)-water mixture, a few controlled simulations with NaCl in water are performed. Subsequently, the data are compared with the previous literature reports by Roux and coworkers.¹ The simulation details are exactly same as they used in their study with the forcefield (FF) before corrections.



Figure S1 Comparison of the osmotic pressure obtained from our simulation of NaCl in water with the literature data (Ref. 1). Note that the data are compared for the unmodified FF of NaCl-water mixture. Errorbars represent the standard deviations calculated by dividing the simulation trajectory into 5 blocks.

1.2 Finite Size Effect

To make sure our simulations don't have finite size artifacts, the volume of the pure water region of the simulation box are changed and osmotic pressures are calculated.



Figure S2 System-size effect on the calculation of osmotic pressure (II). Keeping the central part of the simulation box ($4.8 \times 4.8 \times 4.8 \text{ nm}^3$) same for all, the length of the water reservoir is increased or decreased ($4.8 \times 4.8 \times z \text{ nm}^3$) by changing the number of water molecules inside the simulation box (z-direction of the box-length changes accordingly). The value of II with change in z-direction of the simulation box is plotted for the IL concentration of $m \approx 2.52$ mol kg⁻¹. Note that the average value of II from all the box-length is shown by dashed line.

2 COMPUTATIONAL DETAILS

2.1 MD Set1: For Original-FF

Table S1 Details of the number of ion-pairs and water molecules considered in the simulation box in molecular dynamics simulations of osmometry with original IL-FFs. The number of cations and anions are specified by $N_{\rm BMIM^+}$ and $N_{\rm Cl^-}$ respectively. Total number of water molecules are taken in the simulation box is denoted by $N_{\rm w}^{\rm box}$. The average number of water molecules, $N_{\rm w}^{\rm wall}$ inside the central region of the box (4.8 × 4.8 × 4.8 nm³) is counted by dividing the total production simulation trajectory into 5-blocks. The errorbars corresponding to that is given by ${\rm Err.}_{N_{\rm w}^{\rm wall}}$. *m* refers to the molal concentration in osmotic pressure simulation in this study. The errorbars in molal concentration (Err._m) is also given in the next coloumn.

IL Forcefield	$N_{\rm BMIM^+}/N_{\rm Cl^-}$	$N_{\rm w}^{\rm box}$	$N_{\rm w}^{\rm wall}$ (Avg.)	$\mathrm{Err.}_{N_{\mathrm{w}}^{\mathrm{wall}}}$	$m \;({\rm mol}\;{\rm kg}^{-1})$	$\operatorname{Err.}_m$
FF-SA	5	7500	3633.40	0.54772	0.076386	0.000012
	25	7200	3484.80	0.83666	0.398218	0.000096
	50	7200	3299.60	0.89443	0.841138	0.000228
	75	7000	3113.80	1.30384	1.336993	0.000560
	100	6400	2931.00	1.58114	1.893838	0.001022
	125	6400	2748.80	2.38747	2.524211	0.002192
	150	6250	2569.00	2.91548	3.241053	0.003674
FF-LP	5	7500	3633.40	0.89443	0.076386	0.000019
	25	7200	3484.20	0.44721	0.398286	0.000051
	50	7200	3299.60	1.14018	0.841138	0.000291
	75	7000	3117.20	1.09545	1.335535	0.000469
	100	6400	2937.20	1.92354	1.889840	0.001237
	125	6400	2758.00	2.54951	2.515791	0.002326
	150	6250	2582.80	3.42053	3.223737	0.004271

2.2 MD Set1: For Reparameterized-FF

As mentioned in the main article, the number of water molecules $(N_{\rm w}^{\rm wall} \text{ (Avg.)})$ inside the central region of the box may differ after the modification of the original-FF, and hence, we have taken such consideration while calculating the molality (m) of the solution Here, we present the corresponding values and errorbars related to them. Note that the starting simulation setup $(i.e. N_{\rm BMIM^+}/N_{\rm Cl^-} \text{ and } N_{\rm w}^{\rm box})$ is same as for the original-FF.

Table S2 Details of the number of ion-pairs and water molecules taken in the simulation box in molecular dynamics simulations of osmometry with modified IL-FFs. The number of cations and anions are specified by $N_{\rm BMIM^+}$ and $N_{\rm Cl^-}$ respectively. Total number of water molecules taken in the simulation box is denoted by $N_{\rm w}^{\rm box}$. The average number of water molecules, $N_{\rm w}^{\rm wall}$ inside the central region of the box (4.8 × 4.8 × 4.8 nm³) is counted by dividing the total production simulation trajectory into 5 blocks. The errorbars corresponding to that is given by ${\rm Err}_{N_{\rm w}^{\rm wall}}$. *m* refers to the molal concentration in osmotic pressure simulation in this study. The errorbars in molal concentration (Err._m) is also given in the next coloumn.

IL Forcefield	$N_{\rm BMIM^+}/N_{\rm Cl^-}$	$N_{\rm w}^{\rm box}$	$N_{\rm w}^{\rm wall}$ (Avg.)	$\mathrm{Err.}_{N_{\mathrm{w}}^{\mathrm{wall}}}$	$m \;({\rm mol}\;{\rm kg}^{-1})$	$\operatorname{Err.}_m$
FF-SA	5	7500	3626.67	0.57735	0.076528	0.000012
	25	7200	3453.20	0.83666	0.401862	0.000097
	50	7200	3239.20	1.30384	0.856822	0.000345
	75	7000	3028.00	1.41421	1.374877	0.000642
	100	6400	2816.80	1.48324	1.970619	0.001037
	125	6400	2607.20	1.48324	2.661303	0.001514
	150	6250	2401.00	1.87083	3.467830	0.002701
FF-LP	5	7500	3626.80	0.83666	0.076525	0.000018
	25	7200	3455.20	0.83666	0.401629	0.000097
	50	7200	3244.20	1.78885	0.855502	0.000472
	75	7000	3035.20	1.30384	1.371616	0.000589
	100	6400	2529.00	1.87083	2.194875	0.001623
	125	6400	2625.00	1.87083	2.643257	0.001883
	150	6250	2420.40	3.50714	3.440039	0.004979

2.3 MD Set2: FF-SA, both Original and Reparameterized-FF

This set of simulations are performed to evaluate the reparameterized-FF as compared to the original-FF in yielding thermodynamic, dynamic, and structural properties of BMIMCl-water mixture. Note that with original-FF at very high molality (18.503 mol kg⁻¹), the system takes too long to properly equilibrate in simulation, may be, due to very high viscosity and presence of heterogeneity in the system. As most of the properties of our interest need properly equilibrated simulations, we did not consider m = 18.503 mol kg⁻¹ with original-FF as part of our any analysis. One should note that our motivation here is just to compare the simulated properties

before and reparameterization over a concentration range.

Table S3 Details of the system size and observables calculated from equilibrium molecular dynamics simulation for FF-SA. The number of cations and anions are specified by $N_{\rm BMIM^+}$ and $N_{\rm Cl^-}$ respectively. The number of water molecules used for simulation is denoted by $N_{\rm w}$. The corresponding molal concentration of IL is denoted by m. Solution density, thermal expansion coefficient, isothermal compressibility, self diffusion coefficient, viscosity and radial distribution functions are denoted by ρ , α_P , κ_T , D, η and rdfs respectively. For any molal concentration if the specific observable is calculated it is checked by " \checkmark " otherwise denoted by "-".

$N_{ m BMIM^+}/N_{ m Cl^-}$	$N_{\rm w}$	$m \pmod{\mathrm{kg}^{-1}}$	IL-FF	ρ	α_P	κ_T	D	η	rdfs
0	3800	0.00	-	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
5	3633	0.07639	original-FF reparameterized	\checkmark	- -	- -	- -	- -	- -
25	3485	0.3982	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
50	3300	0.8411	original-FF reparameterized	\checkmark	-	-	-	- -	-
75	3114	1.3370	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
100	2931	1.8938	original-FF reparameterized	\checkmark	-	-	- -	- -	-
125	2749	2.5240	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
150	2569	3.2411	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
200	1600	6.9386	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
250	1200	11.564	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
250	750	18.503	original-FF reparameterized	-	- √	- √	-	- √	- √

2.4 MD Set2: FF-LP, both Original and Reparameterized-FF

Table S4 Details of the system size and observables calculated from equilibrium molecular dynamics simulation for FF-LP. The number of cations and anions are specified by $N_{\rm BMIM^+}$ and $N_{\rm Cl^-}$ respectively. The number of water molecules used for simulation is denoted by $N_{\rm w}$. The corresponding molal concentration of IL is denoted by m. Solution density, thermal expansion coefficient, isothermal compressibility, self diffusion coefficient, viscosity and radial distribution functions are denoted by ρ , α_P , κ_T , D, η and rdfs respectively. For any molal concentration if the specific observable is calculated it is checked by " \checkmark " otherwise denoted by "-".

$N_{ m BMIM^+}/N_{ m Cl^-}$	$N_{ m w}$	$m \pmod{\mathrm{kg}^{-1}}$	IL-FF	ρ	α_P	κ_T	D	η	rdfs
5	3633	0.07639	original-FF reparameterized	\checkmark	- -	- -	- -	- -	-
25	3484	0.3983	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
50	3300	0.8411	original-FF reparameterized	\checkmark	- -	- -	- -	- -	- -
75	3117	1.3356	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
100	2937	1.8900	original-FF reparameterized	\checkmark	- -	- -	- -	- -	- -
125	2758	2.5157	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
150	2583	3.2235	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
200	1600	6.9386	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
250	1200	11.564	original-FF reparameterized	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
250	750	18.503	original-FF reparameterized	- √	- √	- √	- √	- √	- √

3 RESULTS

Herein, we provide a few supplementary figures to complete the discussions and conclusions of the results presented in the main article.



3.1 Reparameterization Based on only Scaling Down the Partial Charges

Figure S3 Reparameterization FF-SA based on only scaling down the partial charges. Scaling factor, $\alpha = 1$ represent the original FF without charge scaling. For IL-molality of m = 2.524 mol kg⁻¹, we first scale down all the partial charges to estimate α (found to be 0.65) which reproduces exact experimental ϕ value. The $\alpha = 0.65$ is used then for all other concentrations studied here (blue linepoints). Black solid linepoints represent the experimental data.² The black dashed line represents $\phi = 1.0$ line.

As mentioned in the parameterization scheme of the main article, we start with a solution of IL-molality of $m = 2.524 \text{ mol kg}^{-1}$ and scale down the partial charges from $\alpha = 1.0$ to 0.80 to 0.74 and so on. We find $\alpha = 0.65$ reproduces the experimental ϕ value. Subsequently, the same α is used for all other concentrations. Note that, in this case we did not modify any of the LJ σ_{ij} parameters. In Figure S3, we observe that most of the points (blue) are way off from the experimental data except $m \approx 2.524 \text{ mol kg}^{-1}$, for which initial reparameterization has been performed. This suggests that acquiring unique FF-parameters, independent of molal concentration is not possible only by scaling down the partial charges of IL atoms.

3.2 Mean Square Displacement (MSD) of IL-Water Solution of Different Molality



3.2.1 IL-FF by Sambasivarao and Acevedo (FF-SA) in SPC/E Water

Figure S4 Log-log plot of the mean square displacement (MSD) obtained from original FF and reparameterized-FF in this study, (a & d) BMIM⁺, (b & e) CI^- , (c & f) water oxygens. Diffusivities are calculated in each case by linearly fitting the diffusive regimes.



3.2.2 Estimation of Diffusive Regime from the Exponent $\beta(t)$: FF-SA

Figure S5 Calculated $\beta(t)$ values for FF-SA before and after reparameterization, (a & d) BMIM⁺, (b & e) Cl⁻, (c & f) water oxygens for the lowest and highest concentration investigated in this study.

Note that, $\beta(t)$ for only the lowest and highest concentrations investigated here are plotted in the figures. The $\beta(t)$ for other concentrations lie in between.



Figure S6 Log-log plot of the mean square displacement (MSD) obtained from original-FF and reparameterized-FF in this study, (a & d) BMIM⁺, (b & e) CI^- , (c & f) water oxygens. Diffusivities are calculated in each case by linearly fitting the diffusive regimes.



3.2.4 Estimation of Diffusive Regime from the Exponent $\beta(t)$: FF-LP

Figure S7 Calculated $\beta(t)$ values for FF-LP before and after reparameterization, (a & d) BMIM⁺, (b & e) Cl⁻, (c & f) water oxygens for the lowest and highest concentration investigated in this study.

Note that, $\beta(t)$ for only the lowest and highest concentrations investigated here are plotted in the figures. The $\beta(t)$ for other concentrations lie in between.



3.3 Viscosity as a Function of Upper Limit of the Green-Kubo Integral3.3.1 FF-SA in SPC/E Water

Figure S8 Viscosity (η) as a function of upper limit of the Green-Kubo integral. Note that plateau time is always higher with original-FF, whereas it is sufficiently lower for reparameterized-FF. Plateau time also increases with increase in IL concentration in water. Standard deviations are shown as errorbars in each case.



Figure S9 Viscosity (η) as a function of upper limit of the Green-Kubo integral. Note that plateau time is always higher with original-FF, whereas it is sufficiently lower for reparameterized-FF. Plateau time also increases with increase in IL concentration in water. Standard deviations are shown as errorbars in each case.

3.4 Structure of the IL-Water Mixtures Before and After Reparameterization



3.4.1 FF-LP in SPC/E Water

Figure S10 Radial distribution functions (rdf) of different combination pairs in the IL-water solution before (upper panels) and after (lower panels) reparameterization for FF-LP. Each combination pairs are mentioned in each figure.

3.4.2 Water-cluster Analysis

In order to inspect quantitatively whether the size of the water-patches increases after reparameterization of original-FF, here we present histograms of water-cluster distributions at the two concentrations for which the simulation snapshots are provided in the main article. We make use of GROMACS's cluster size distribution tool, " $g_{\rm clustsize}$ " to compute the number of water-clusters and average cluster size present in the system. Although, this tool was introduced to analyze the molecular/atomic cluster in the gas phase, we can employ this for any two component system (as previously used in the literature³⁻⁵), where, during cluster analysis, one can think the second component as a gas phase or the other way around. Water molecules were clustered using a cutoff distance of 3.5 Å between the water oxygens. In figure S11(a), the distribution of number of water-clusters present in 11.564m IL solution is depicted. We see that the number of clusters are higher for original-FF than for the reparameterized-FF. Given that the number of water molecules present in the system is same for both the cases, lower number of clusters for reparameterized-FF indicates that there is an increase in the size of individual water patch. This can also be confirmed by the average water-cluster size distribution presented in Figure S11(b). High frequency peaks at bigger sizes for reparameterized-FF compared to the low frequency peaks at smaller sizes are clear indicative of the presence of bigger water patches after reparameterization. The same two plots for 6.9386m IL solution is presented in Figure S11(c) and (d). At lower concentration, we expect that the difference will not be as subtle as in case of higher concentration because the bulk component of the solution is water and there will only be a very a few clusters present. We observe that the number of water-clusters are slightly lower (Figure S11(c)) for reparameterized-FF, which again indicates the presence of slightly larger water patches after reparameterization. Figure S11(d) (including insets) visualizes that water cluster presents in solution after reparameterization is slightly larger with magnitude of frequency being higher (see red colored histogram, that is for reparameterized-FF) for larger cluster (see inset d3) and lower for smaller cluster (see inset d1).



Figure S11 Histogram plots for water-cluster analysis. Normalized distribution of number of water clusters present in 11.564*m* and 6.9386*m* IL solution (a & c) before (blue) and after (red) reparameterization of FF-SA. Corresponding normalized distribution of average size of the water-cluster at the same two cocentration are shown in (b) (for 11.564*m*) and (d) (for 6.9386*m*). The size of the cluster is represented in terms of number of water molecules present in a certain cluster. In (d) a zommed-in portion of the all the important peaks are shown in the inset (d1-d3). Note that in the inset, ordering of the plots has been changed from the main graph so that histograms for reparameterized-FF (red) appears above the histogram for original-FF. The distributions are calculated over the course of 10 ns NPT production simulation trajectory.





Figure S12 Radial distribution functions (rdfs) of different combination pairs in the IL-water solution before (upper panels) and after (lower panels) reparameterization for FF-SA. Each combination pairs are mentioned in the figure.

3.4.4 rdfs Between Key Components in IL: FF-LP in SPC/E Water



Figure S13 Radial distribution functions (rdfs) of different combination pairs in the IL-water solution before (upper panels) and after (lower panels) reparameterization for FF-LP. Each combination pairs are mentioned in the figure.

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