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Supporting Information

Intrinsic Electric Fields in Ionic Liquids Determined by Vibrational Stark Effect Spectroscopy and Molecular Dynamics Simulation

Shiguo Zhang,[a] Rui Shi,[b] Xiangyuan Ma,[a] Liujin Lu,[a] Yude He,[a] Xiaohu Zhang,[b] Yanting Wang,*[b] and Youquan Deng*[a]

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Experimental section

All ionic liquids (ILs) studied in this work were synthesized and purified according to the well-established procedures,[1] and dried under vacuo at 80 °C for 10 h prior to NMR analysis and spectral analysis. EtSCN-ILs solutions were made by adding 10 μL EtSCN to 1 mL ILs. Infrared absorption spectra were recorded on a Thermo-Nicolet 5700 FTIR spectrometer relative to a background taken with pure ILs. Sample cell was equipped with KBr windows separated with a Teflonspacer of 160 μm. All EtSCN-ILs solutions were used directly for ^{13}C NMR spectra measurement (Bruker AMX FT 400-MHz NMR spectrometer) without deuterated solvents. The ^{13}C NMR spectra were collected in a capillary tube inserted into the NMR tube using TMS as an external standard. All measurements were performed at room temperature.

Theoretic method

All-atom MD simulations were performed to study the electric fields in nine different ILs. The force field parameters for all the imidazolium-based cations were taken from the AMBER force field,[2] whereas partial charges were taken from our previous study.[3] In the case of anions, the parameters of [Cl] and [NO_3] were taken from the AMBER force field and the paper of Yan et al,[4] respectively. Those of [BF_4] anion were taken from the model developed by Andrade.[5] The [PF_6] and [NTf_2] anions were modeled with the force fields developed by Canongia Lopes *et al*.[6-7]

All the systems studied in this work contain 512 ion pairs in a cubic box with the periodic boundary conditions applied in all three dimensions. The cutoff distances for the van der Waals and electrostatic interactions were set to be 15 angstrom and the particle-mesh Ewald method[8] was used to calculate the electrostatic interactions. All simulations were carried out by using the GROMACS package,[9-10] with a time step of 1 fs.

Some random configurations at their experimental densities were initially equilibrated with a constant *NVT* ensemble by a simulated annealing process with 5 sequential steps: 200 ps at T = 2000 K, 300 ps at 1500 K, 500 ps at 1000 K, 1ns at 700 K, and 1 ns at 500 K. Then the MD simulations with a constant *NPT* ensemble were performed at T = 300 K and P = 1 atm for 2 ns. With the system sizes fixed to those determined from the last 1ns *NPT* trajectories, constant *NVT* production runs were followed at T = 300 K for 1 ns. A total of 1000 configurations were sampled during the production runs.

The electric fields experienced by the cations, anions, headgroups, and tail carbon atoms were calculated using the "rerun" function in the GROMACS package with all the intramolecular and van der Waals interactions turned off. The electric fields were calculated using the following equation:

$$\langle E \rangle = \frac{1}{N \times M} \sum_{i}^{N} \sum_{j}^{M} \frac{\left| \sum_{k}^{L} f_{ijk} \right|}{q_{ij}} \qquad \text{(S1)}$$

Where f is the electrostatic force experienced by each atom, q is the net charge of each ion, L is the number of atoms in one ion, M and N are the number of ions in the system and the number of sampled configurations, respectively.

Results

Table S1. NMR chemical shifts *d*(^{13}CN) and vibrational frequencies ?C=N of EtSCN in molecular solvents and ILs, and relative electric fields in molecular solvents and ILs by taking [BMIm][Cl] as a reference determined by the VSE experiments.

No.	ILs/solvents	$?_{\mathrm{CN}}$ (cm^{-1})$^{(a)}$	*d*(^{13}CN) (ppm)	? $?_{\mathrm{CN}}$ (cm^{-1})	? E_{VSE} (MV/cm)
(1)	DMSO	2151.7		2.1	-2.9
(2)	DMF	2153.2		3.6	-5.0
(3)	acetone	2155.9		6.3	-8.8
(4)	CD_2Cl_2	2157.2		7.6	-10.6
(5)	THF	2155.8		6.2	-8.6
(6)	$CDCl_3$	2158.2		8.6	-11.9
(7)	toluene	2157.1		7.5	-10.4
(8)	cyclohexane	2161.1		11.5	-16.0
1	[BMIm][NTf_2]	2155.6	112.343	6.0	-8.3
2	[BMIm][PF_6]	2154.5	112.746	4.9	-6.8
3	[BMIm][BF_4]	2153.8	112.887	4.2	-5.8
4	[BMIm][NO_3]	2152.1	113.249	2.5	-3.5
5	[BMIm][Cl]	2149.6	113.375	0	0
6	[EMIm][BF_4]	2153.8	113.040	4.2	-5.8
7	[HMIm][BF_4]	2153.9	112.614	4.3	-6.0
8	[OMIm][BF_4]	2154.2	112.435	4.6	-6.4
9	[DMIm][BF_4]	2154.4	112.286	4.8	-6.7

(a) Data of molecular solvent were from ref. [11].

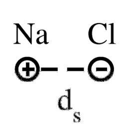
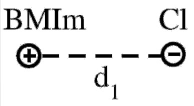
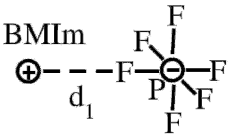
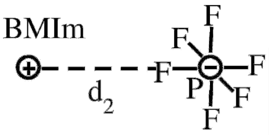
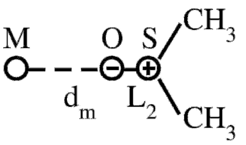
It has been widely accepted that the ionic liquids, consisted of bulky ions, have intrinsic electric fields weaker than molten salts, but much stronger than molecular liquids. However, our results described in the main text indicate that the electric fields of ionic liquids are only slightly stronger but still comparable to that of common polar molecular liquids. To further understand the physical picture behind the structure-dependent electric fields in three common liquids, i.e., molten salts, ionic liquids, and molecular liquids, simple ion (molecule) pair models were employed to estimate the electrostatic interaction between one central ion (molecule) and one of its nearest-neighbours. Although calculating long-range electrostatic interactions should involve all the charges in the system, as what have been done in our MD simulations, the comparison of electric fields based on these simple models can give us a clear picture behind the effect of varying the structure of nearest-neighbours in the first coordination shell. The models and the calculated electric fields are shown in Table S2. We want to emphasize that all the models here describe the structure of central ion (molecule) and its nearest-neighbour in a liquid state, rather than the isolate ion (molecular) pairs in a gas phase.

The molten salt (NaCl) was modelled with positive and negative charges separated by a distance of d_s.[12] Models B, C, D for ionic liquids were taken from our simulation, where L_1 is the P-F bond length, d_1 and d_2 are distances of anion charge center and cationic head group for [BMIm][Cl] and [BMIm][PF_6], respectively, d_P and d_F are the partial charges of P and F atoms. Molecular liquid (dimethl sulfoxide) was taken from the model developed by A. Luzar *et al.*,[13] where d_m is the distance of the charge centers between two molecules, L_2 is the S-O bond length, d_S and d_O are the partial charges of S and O atoms, respectively, and the methyl groups are charge neutral.

Comparing model A with model B, we can see that the electric field experienced by the positive charge is drastically reduced due to larger separation of ions. Although the electric field strength of [BMIm][Cl] is much larger than that calculated by MD simulation (the simple model however gives the strength in the right order of 10 MV/cm), the trend gives us a simple idea that larger separation of ions in the first coordination shell leads to much weaker electrostatic interaction, which is the main reason why ionic liquids with bulky ions typically have very low melting points.

Model C describes the ionic liquid [BMIm][PF_6] with an artificial ion-ion distance d_1 that is chosen to be the same as [BMIm][Cl]. The only difference of models B and C is that the negative charge is delocalized in P and F atoms, resulting in the slight increase of electric field strength. This result indicates that charge delocalization without changing the center-of-mass distance strengthens, rather than weakens, the electrostatic interactions between ions.

Table S2. Intrinsic electric fields exerted by a nearest-neighbour ion (molecule) for (A) molten salts, (B, C, D) ionic liquids, and (E) molecular liquids.

Molten Salts	A Molten NaCl	$d_s=2.6$Å $\delta_{Na}=e$ $\delta_{Cl}=-e$		$E_+= 213$ MV/cm
Ionic Liquids	B [BMIm][Cl] Two-site model	$d_1=4.8$Å $\delta_{BMIm}=e$ $\delta_{Cl}=-e$		$E_+= 63$ MV/cm
	C $[BMIm][PF_6]$ Charge delocalization	$d_1=4.8$Å $L_1=1.606$Å $\delta_P=1.34e$ $\delta_F=-0.39e$		$E_+= 68$ MV/cm
	D $[BMIm][PF_6]$ Charge delocalization Larger sepration of ions	$d_2=5.2$Å $L_1=1.606$Å $\delta_P=1.34e$ $\delta_F=-0.39e$		$E_+= 57$ MV/cm
Molecular Liquids	E Dimethyl sulfoxide	$d_m=4.0$Å $L_2=1.53$Å $\delta_S=0.54e$ $\delta_O=-0.54e$		$E_M= 40$ MV/cm

If only the charge delocalization is considered, $[BMIm][PF_6]$ should have a stronger intrinsic electric field than [BMIm][Cl]. However, both our experimental and simulation results show that the electric field of $[BMIm][PF_6]$ is weaker than that of [BMIm][Cl]. This is because the center-of-mass distance d_2 between opposite ions in the first coordination shell of $[BMIm][PF_6]$ is slightly larger than d_1 of [BMIm][Cl], which effectively weakens the electrostatic interaction between ions, as shown in Model D. The comparison of models B, C, and D provides a simple picture that in ionic liquids, larger separation of ions in the first coordination shell, rather than the delocalization of charge, leads to the reduction of electric field strength.

Moreover, model E shows us an example that polar molecular liquids can also have unexpectedly large electric fields. In model E shown in Table S2, the atom in site M experienced an electric field as strong as 40 MV/cm due to the large dipole moment and short separation of molecules, a little weaker than those in the ILs around 60 MV/cm. Therefore, we learn from those simple models that the polar molecular liquids have electric fields a little weaker but still comparable to those of ionic liquids, in agreement with the VSE experiment results.

Table S1 shows the measured IR frequency and the corresponding relative electric fields by using the VSE spectroscopy. We can clearly see that molecular liquids can also have electric fields comparable to those in ionic liquids.

Table S3: Ion volumes of different anions.

ILs	V_{anion} (nm^3)$^{(a)}$
[NTf_2]	0.232 ± 0.015$^{(b)}$
[PF_6]	0.109 ± 0.008
[BF_4]	0.073 ± 0.009
[NO_3]	0.064 ± 0.011
[Cl]	0.047 ± 0.013

(a) Data from ref. [14]. (b) Data from ref. [15]

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