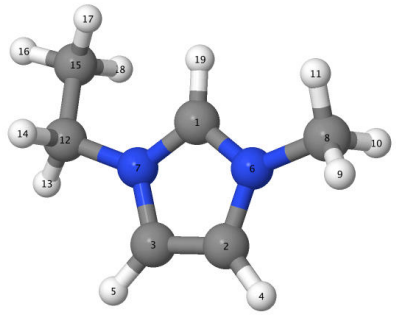
Supporting Information:

Simulations of Water Exchange Dynamics on Lanthanide Ions in 1-Ethyl-3-Methylimidazolim Ethyl Sulfate ([EMIm][$EtSO_4$]) Ionic Liquid and Water

Yi-Jung Tu, Matthew J. Allen, G. Andrés Cisneros*

Department of Chemistry, Wayne State University, Detroit, Michigan, USA, 48202

A. Intra-molecular parameters for [EMIm]



1. Bonds

Bond	AMOEBA		MP2
	K_b, kcal/mol	r_{b0}, Å	r_{b0}, Å
C1-N6,7	653.90	1.3450	1.338
C1-H19	370.50	1.0810	1.076
C2,3-N6,7	653.90	1.3450	1.372
C2-C3	539.60	1.3520	1.374
C2,3-H4,5	370.50	1.0810	1.078
N6,7-C8,12	399.70	1.4487	1.468
C8-H9,10,11	402.87	1.0911	1.090
C12-H13,14	402.87	1.0911	1.092
C12-C15	385.10	1.4980	1.517
C15-H16,17,18	385.00	1.1120	1.092

2. Bond angle bending

Angle	AMOEBA		MP2
	K_Θ, kcal/mol rad^2	Θ_0 (degree)	Θ_0 (degree)
N6-C1-N7	28.78	112.10	108.4
C1,1-N6,7-C2,3	86.03	107.85	108.9
C1,1-N6,7-C8,12	67.19	124.04	124.7
C2-C3-N7	47.48	107.00	106.9
C3-C2-N6	47.48	107.00	106.8
C2,3-N6,7-C8,12	67.19	124.04	125.8
N6,7-C1,1-H19	38.13	122.50	125.7

N6-C8-H9,10,11	51.66	105.53	108.3
H9-C8-H10	32.07	112.24	110.6
N7-C12-C15	79.47	111.24	111.9
N7-C12-H13,14	32.07	112.24	106.3
H13,14-C12-C15	38.12	109.66	110.8
H13-C12-H14	32.07	112.24	110.7
C12-C15-H16,17,18	39.49	107.23	110.0
H16-C15-H18	40.57	107.60	108.9

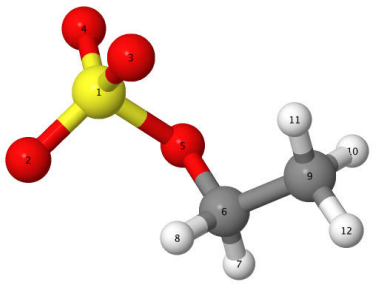
3. Torsions

	Amplitude	Phase 1	Amplitude	Phase 2	Amplitude	Phase 3
C1-N6-N2-N3	0	0	14.000	180	0	0
C1-N6-N2-H4	0	0	7.000	180	0	0
N6-C2-C3-N7	0.900	0	15.000	180	0	0
N6-C2-C3-H5	0.755	0	10.000	180	0	0
C2-N6-C1-N7	0	0	15.000	180	0	0
C2-N6-C1-H19	0	0	7.000	180	0	0
C8-N6-C2-C3	0	0	4.120	180	0	0
C8-N6-C2-H4	-0.530	0	3.000	180	0	0
C8-N6-C1-H19	-0.530	0	3.000	180	0	0
C8-N6-C1-N7	0	0	4.120	180	0	0
H9,10,11-C8-N6-C1,2	0	0	0	0	0.380	0
C12-N7-C1-N6	0	0	4.120	180	0	0
C12-N7-C1-H19	-0.530	0	3.000	180	0	0
C12-N7-C3-C2	0	0	4.120	180	0	0
C12-N7-C3-H5	-0.530	0	3.000	180	0	0
H13,14-C12-N7-C1,3	0	0	0	0	0.380	0
C15-C12-N7-C1,3	-0.800	0	-0.100	180	-0.550	0
H16,17,18-C15-C12-N7	0	0	0	0	0.500	0
H16,17,18-C15-C12-H13,14	0	0	0	0	0.238	0

4. Out of plane deformations

Out of plane deformations	K_{out}
H5-C3-N7-C2	0.59
H4-C2-N6-C3	0.59
H19-C1-N7-N6	0.59

B. Intra-molecular parameters for [$EtSO_4$]



1. Bonds

Bond	AMOEBA		MP2
	K_b, kcal/mol	r_{b0}, Å	r_{b0}, Å
S1-O2,3,4	570.00	1.4780	1.466
S1-O5	605.58	1.6698	1.688
O5-C6	464.51	1.4154	1.432
C6-H7,8	399.82	1.0681	1.095
C6-C9	385.22	1.4999	1.517
C9-H10,11,12	385.00	1.1120	1.093

2. Bends angle bending

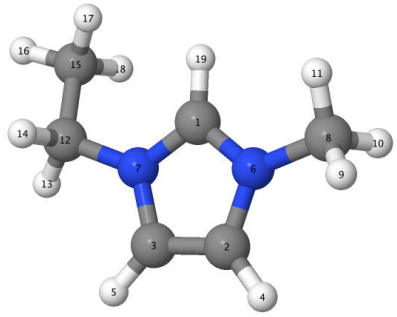
Bend	AMOEBA		MP2
	K_θ, kcal/mol rad^2	Θ_0	Θ_0
O2-S1-O3	161.37	115.30	115.2
O2,3,4-S1-O5	88.25	103.15	102.9
S1-O5-C6	80.19	114.49	114.1
O5-C6-H7,8	54.32	106.25	107.9
H7-C6-H8	32.66	107.67	107.9
O5-C6-C9	88.02	110.78	111.1
C6-C9-H10,11,12	38.57	109.12	110.0
H10-C9-H11	40.57	107.60	108.9

3. Torsions

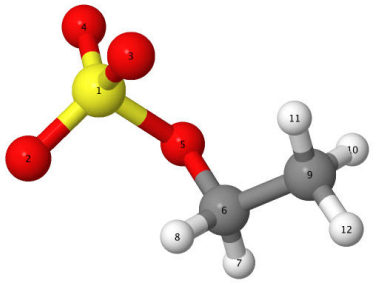
	Amplitude	Phase 1	Amplitude	Phase 2	Amplitude	Phase 3
S1-O5-C6-C9	-1.437	0	-0.744	180	0.357	0
S1-O5-C6-H7,8	0	0	0	0	0.403	0
O2,3,4-S1-O5-C6	0	0	0	0	0.590	0
O5-C6-C9-H10,11,12	0	0	0	0	0.495	0
H7,8-C6-C9-H10,11,12	0	0	0	0	0.238	0

C. Inter-molecular parameters for [EMIm][$EtSO_4$]

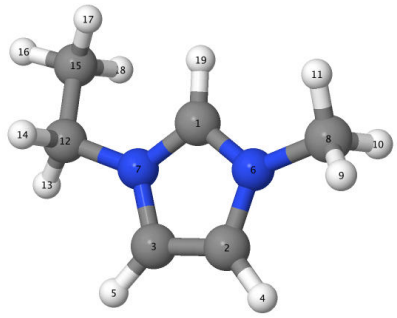
1. Definition of [EMIm] local frame for multipole GEM-DM

Optimized geometry for [EMIm]	N	Name	Axis type	Z	X	Y
	1	C	Bisector	6	7	0
	2	C	Z-then-X	6	3	0
	3	C	Z-then-X	7	2	0
	4	H	Z-then-X	2	6	0
	5	H	Z-then-X	3	7	0
	6	N	Z-then-X	1	2	0
	7	N	Z-then-X	1	3	0
	8	C	Z-then-X	6	9	0
	9	H	Z-then-X	8	6	0
	10	H	Z-then-X	8	6	0
	11	H	Z-then-X	8	6	0
	12	C	Z-then-X	7	15	0
	13	H	Z-then-X	12	7	0
	14	H	Z-then-X	12	7	0
	15	C	Z-then-X	12	16	0
	16	H	Z-then-X	15	12	0
	17	H	Z-then-X	15	12	0
	18	H	Z-then-X	15	12	0
	19	H	Z-then-X	1	6	0

2. Definition of [$EtSO_4$] local frame for multipole GEM-DM

Optimized geometry for [EMIm]	N	Name	Axis type	Z	X	Y
	1	S	Z-then-X	2	3	0
	2	O	Z-then-X	1	2	0
	3	O	Z-then-X	1	2	0
	4	O	Z-then-X	1	2	0
	5	O	Z-then-X	1	6	0
	6	C	Z-then-X	5	9	0
	7	H	Z-then-X	6	5	0
	8	H	Z-then-X	6	5	0
	9	C	Z-then-X	6	10	0
	10	H	Z-then-X	9	6	0
	11	H	Z-then-X	9	6	0
	12	H	Z-then-X	9	6	0

3. GEM-DM multipoles for [EMIm] (4G)[a]



Local frame definition

Permanent multipoles

Multipoles	atom1	atom2	atom3	q		
Atom Type	T1	T2	T3	Dx	Dy	Dz
				Qxx		
				Qxy	Qyy	
				Qxz	Qyz	Qzz

Requirements: Qxx+Qyy+Qzz=0

Where q, D, Q are the point charge, dipole, and quadrupole, respectively

Bisector-then-X

T1 T2 -T3

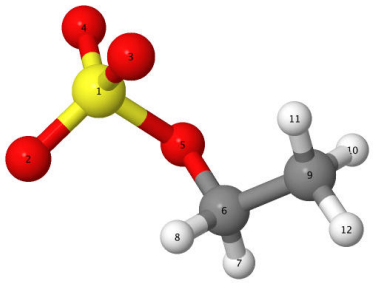
Results from the fitting to the electrostatic potential (EP)

multipole	1	6	7	0.41689		
Atom Type	351	-354	-354	-0.16792	0.08646	-0.48509
				-0.83832		
				-0.16931	-0.71924	
				0.21953	0.45075	1.55756
multipole	2	6	3	0.31536		
Atom Type	352	354	352	-0.58570	0.06193	-0.12795
				-0.14986		
				0.26184	-0.22330	
				1.19425	-0.21140	0.37316
multipole	4	2	6	-0.19224		
Atom Type	353	352	354	0.02833	0.00044	-0.30489
				0.14427		
				0.06298	-0.04460	
				-0.09714	0.00541	-0.09967
multipole	6	1	2	0.03706		
Atom Type	354	351	352	-0.08903	0.14053	0.04527
				-0.00508		
				-0.00066	0.62938	
				-0.60992	0.22096	-0.62430
multipole	8	6	9	0.56495		
Atom Type	355	354	356	0.02283	0.06216	0.08695
				0.19932		
				-0.45032	0.10659	
				0.05749	-0.14183	-0.30591
multipole	9	8	6	-0.10274		
Atom Type	356	355	354	-0.04119	0.00658	-0.34946
				0.19526		
				-0.03567	0.07322	
				-0.12395	0.01216	-0.26848
multipole	12	7	15	0.50303		
Atom Type	357	354	359	0.04646	0.03781	0.18524
				-0.93077		
				0.94546	1.17660	
				0.74281	-0.40468	-0.24583

	multipole	13	12	7	-0.15230		
	Atom Type	358	357	354	-0.05449	0.05883	-0.52850
					0.25596		
					0.01999	0.30735	
					-0.12977	-0.06216	-0.56330
	multipole	15	12	16	0.46549		
	Atom Type	359	357	360	-0.21296	-0.36438	-0.08871
					0.95255		
					0.27236	-0.06369	
					-0.18626	0.01045	-0.88886
	multipole	16	15	12	-0.12116		
	Atom Type	360	359	357	0.00535	-0.02861	-0.34059
					0.27696		
					-0.07650	0.05101	
					0.00753	0.08168	-0.32797
	multipole	19	1	6	-0.29442		
	Atom Type	361	351	354	0.00013	0.04186	-0.29608
					0.10931		
					0.08112	0.02100	
					-0.31807	-0.04714	-0.13031
	polarize	351			1.334	354	361
	polarize	352			1.334	353	354
	polarize	353			0.496	352	
	polarize	354			1.073	351	352
	polarize	355			1.334	356	
	polarize	356			0.496	355	
	polarize	357			1.334	358	
	polarize	358			0.496	357	
	polarize	359			1.334	360	
	polarize	360			0.496	359	
	polarize	361			0.496	351	

[a] 4G indicates four polarizable groups

4. GEM-DM multipoles for [$EtSO_4$] (4G)[a]



Local frame definition

Multipoles atom1 atom2 atom3
ATOM TYPE T1 T2 T3

Permanent multipoles

q
Dx Dy Dz
Qxx
Qxy Qyy
Qxz Qyz Qzz

Requirements: Qxx+Qyy+Qzz=0
Where q, D, Q are the point charge, dipole, and quadrupole, respectively

Bisector-then-X
T1 T2 -T3

Results from the fitting to the electrostatic potential (EP)

multipole	1	2	3	2.13865		
Atom Type	362	363	363	-0.37750	0.23771	0.03617
				-0.20081		
				1.31528	0.25189	
				-0.37888	-0.17795	-0.05108
multipole	2	1	2	-0.93408		
Atom Type	363	362	363	0.12712	0.09351	-0.29322
				-0.09824		
				-0.01188	-0.08333	
				-0.04962	0.18382	0.18156
multipole	5	1	6	-0.31293		
Atom Type	364	362	365	0.72255	-0.09493	0.04881
				0.27339		
				0.51631	-0.77295	
				-1.56949	-1.59096	0.49956
multipole	6	5	9	0.24070		
Atom Type	365	364	367	-0.17935	0.01130	-0.33196
				-0.17610		
				0.21086	0.07838	
				-0.25144	-0.24116	0.09772
multipole	7	6	5	-0.14156		
Atom Type	366	365	364	0.04591	0.01126	0.15443
				-0.36383		
				-0.09835	-0.15149	
				-0.13517	-0.09004	0.51532
multipole	9	6	10	0.26365		
Atom Type	367	365	368	-0.11750	0.15967	0.62775
				-0.56727		
				0.05343	-0.10564	
				-0.22792	0.03076	0.67291
multipole	10	9	6	-0.08157		
Atom Type	368	367	365	-0.04615	-0.00233	-0.14585
				0.01470		
				-0.06316	0.06853	
				0.00129	0.00303	-0.08323

	polarize	362	3.300	363
	polarize	363	0.837	362
	polarize	364	0.837	
	polarize	365	1.334	366
	polarize	366	0.496	365
	polarize	367	1.334	368
	polarize	368	0.496	367

[a] 4G indicates four polarizable groups

5. Optimal λ parameters and the corresponding auxiliary basis sets from the fitting results

	Analytical, λ	auxiliary basis sets	Total charge, e
[EMIm]	0.014	A2DG for H, C, N atoms	+1.0
[$EtSO_4$]	0.003	A2DG for H, C, and O atoms; A2 for the S atom	-1.0

6. van der Waals parameters[a] for [EMIm]

Atom type	Atom class	R_{min}, Å	ε, kcal/mol
351	92	3.7800	0.1010
352	92	3.7800	0.1010
353	93	3.0000	0.0240
354	91	3.7100	0.1050
355	102	3.820	0.1010
356	42	2.9800	0.0240
357	102	3.820	0.1010
358	42	2.9800	0.0240
359	40	3.8200	0.1010
360	41	2.9600	0.0240
361	93	3.0000	0.0240

[a]All parameters were taken from the parameter list of AMOEBA force field.

7. van der Waals parameters[a] for [$EtSO_4$]

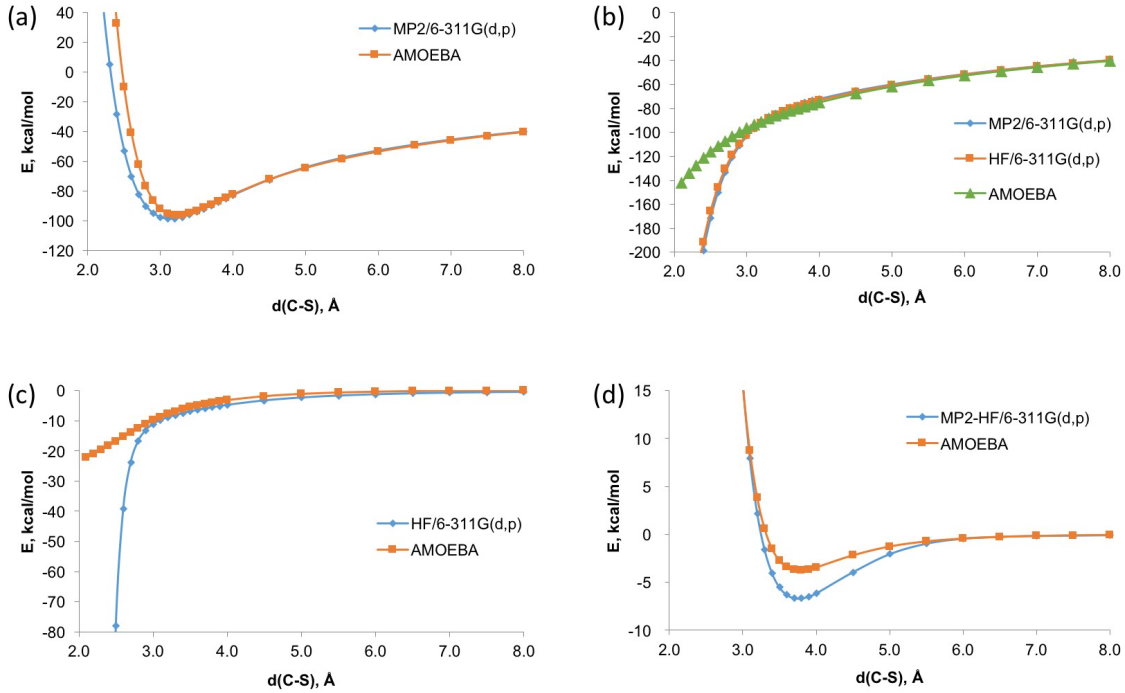
Atom type	Atom class	R_{min}, Å	ε, kcal/mol
362	76	3.8930	0.4370
363	77	3.4930	0.1530
364	103	3.393	0.1240
365	104	3.818	0.1100
366	105	2.780	0.0280
367	40	3.8200	0.1010

368	41	2.9600	0.0240

[a] parameters of atom types 367 and 368 were taken from the parameter list of AMOEBA force field, and parameters for atom types 362–366 were obtained after the van der Waals fitting.[1]

D. AMOEBA intermolecular interaction energies for [EMIm][$EtSO_4$] ionic pair

Comparison of interaction energies for [EMIm][$EtSO_4$] ionic pair using GEM-DM multipole force fields with ab initio data from MP2/6-311G(d,p) level. (a) Total intermolecular interaction energy, (b) Coulomb energy, (c) Polarization energy, and (d) van der Waals energy.



E. Density and heat of vaporization of [EMIm][$EtSO_4$] at 298 K

	MD simulation	Experiments
Density (g/cm^3)	1.240	1.2376[2]
Heat of vaporization (kJ/mol)	153.2	152.6;[3] 155.9;[3] 164[4]

F. Intermolecular interaction energies for lanthanide-water dimers

1. Total interaction energies (kcal/mol) of lanthanide-water dimers (Ln–H_2O)

	AMOEBA[a]		MP2	
	Ln–O distance	Total interaction	Ln–O distance	Total interaction
Gd^{3+}–H_2O	2.171	-101.3952	2.179	-111.34
Dy^{3+}–H_2O	2.165	-102.3076	2.140	-114.82
Ho^{3+}–H_2O	2.164	-102.3767	2.136	-114.48

[a] The structures of lanthanide-water dimers were optimized by NEWTON in TINKER[5] program. [b] AMOEBA total interaction energies were calculated using ANALYZE in TINKER program.

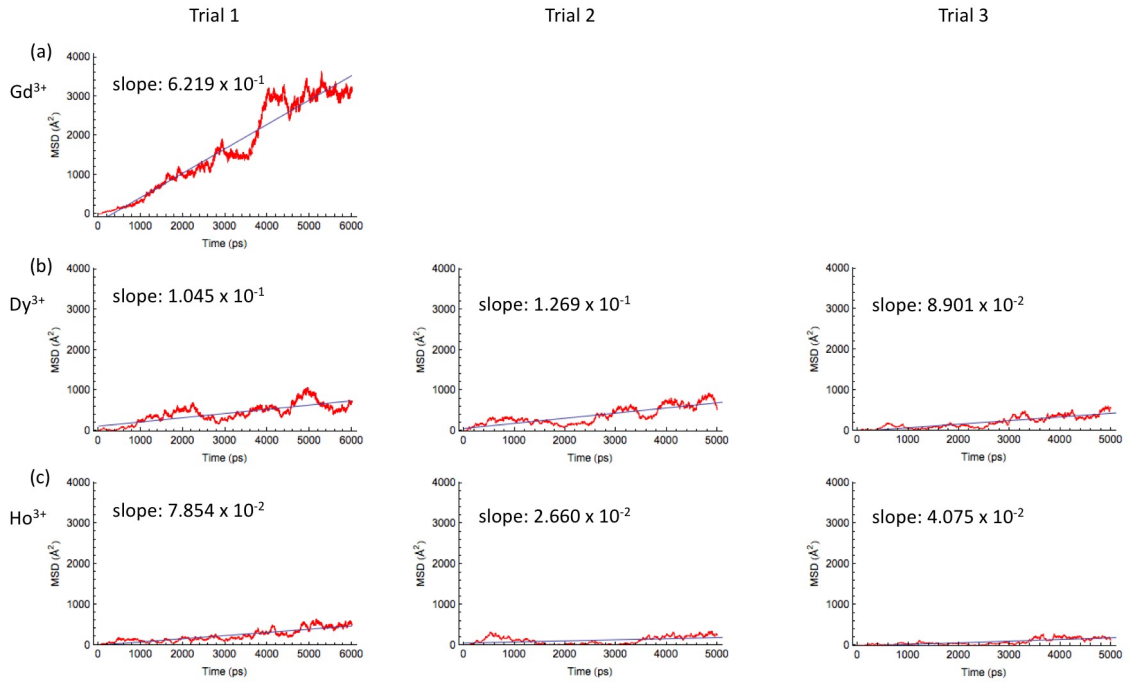
2. AMOEBA intermolecular interaction energies

	Total interaction	Coulomb	Polarization	van de Waals	Pol% [a]
Gd^{3+}–H_2O	-101.3952	-77.4282	-51.2140	27.2470	50.50%
Dy^{3+}–H_2O	-102.3076	-77.8353	-51.4074	26.9351	50.25%
Ho^{3+}–H_2O	-102.3767	-77.8619	-51.0788	26.5640	49.89%

[a] Pol% = (polarization energy / total interaction energy)×100%

G. Self-diffusion coefficients for water molecules and lanthanide ions

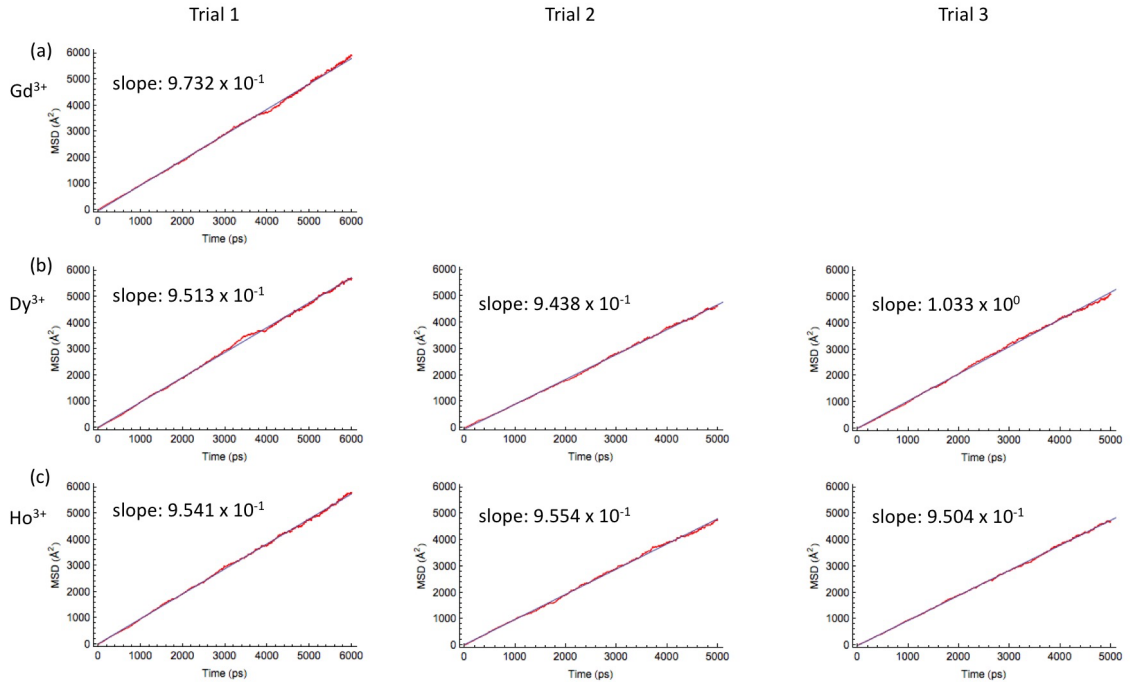
1. MSD plots for lanthanide ions in water



The averaged diffusion coefficient of lanthanide ions (D_{Ln}) from three independent simulation trajectories

metal ion	Average slopes of MSD plots ($Å^2$/ps)	Diffusion coefficient (cm^2/s)	Standard deviation of D_{Ln} (cm^2/s)
Gd^{3+}	6.22E-01	1.04E-05	
Dy^{3+}	1.07E-01	1.78E-06	1.90E-06
Ho^{3+}	4.86E-02	8.11E-07	2.69E-06

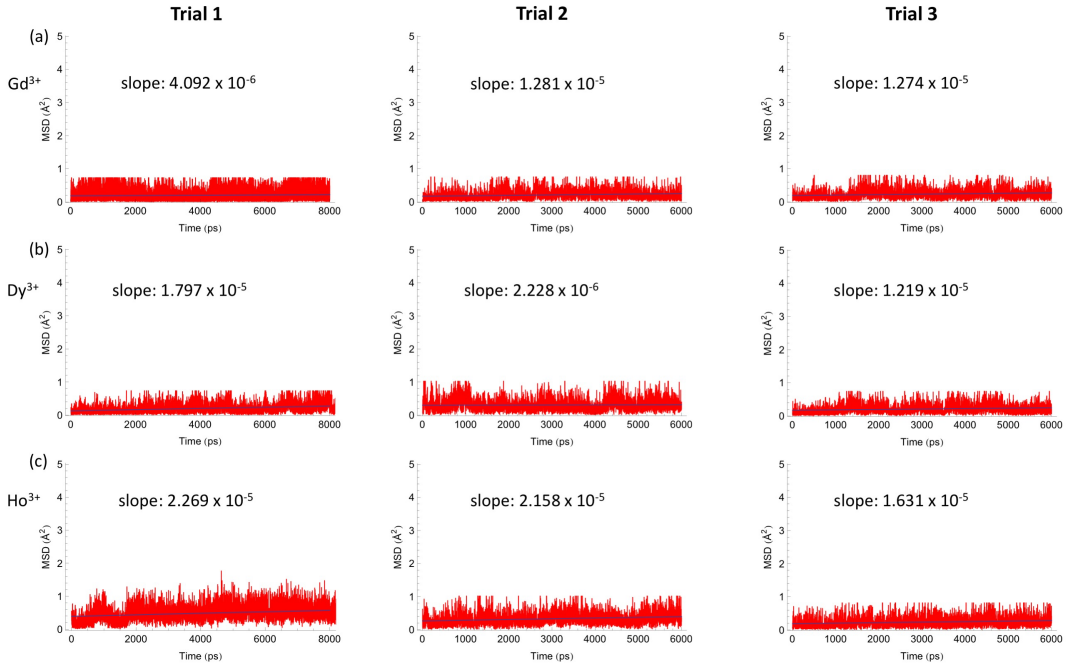
2. MSD plots for water molecules in water



The averaged diffusion coefficient of lanthanide ions (D_{H2O}) from three independent simulation trajectories

metal ion	Average slopes of MSD plots (Å^2/ps)	Diffusion coefficient (cm^2/s)	Standard deviation of D_{H2O} (cm^2/s)
Gd^{3+}	9.73E-01	1.62E-05	
Dy^{3+}	9.76E-01	1.63E-05	4.95E-06
Ho^{3+}	9.53E-01	1.59E-05	2.59E-07

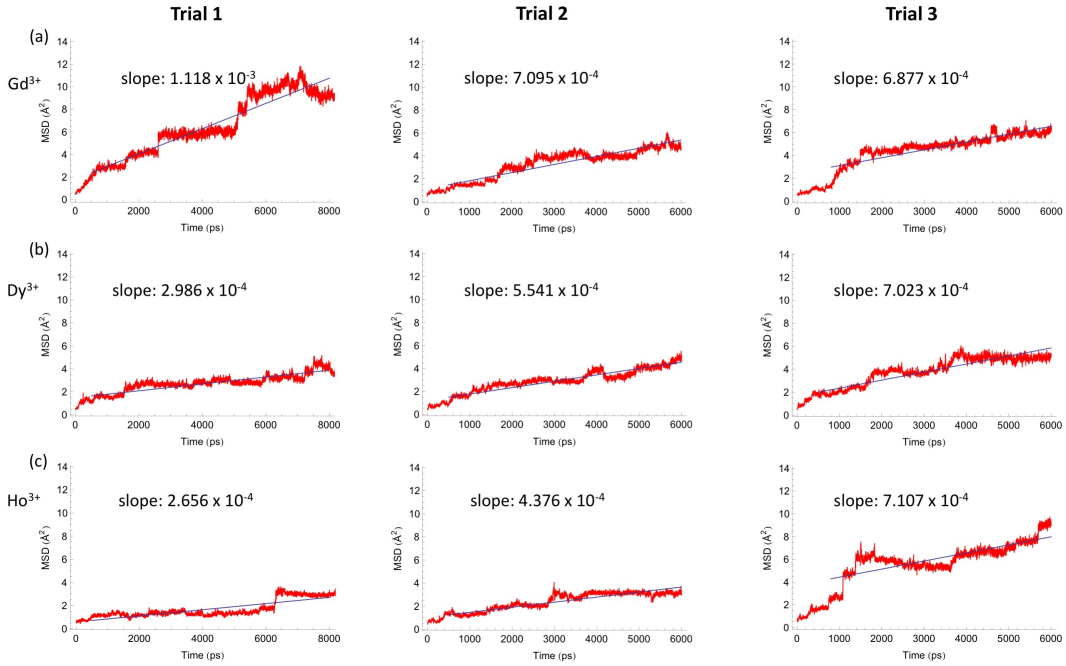
3. MSD plots for lanthanide ions in [EMIm][$EtSO_4$] obtained from the three independent MD trajectories



The averaged diffusion coefficient of lanthanide ions (D_{Ln}) from three independent simulation trajectories

metal ion	Average slopes of MSD plots (Å^2/ps)	Diffusion coefficient (cm^2/s)	Standard deviation of D_{Ln} (cm^2/s)
Gd^{3+}	9.881E-06	1.65E-10	5.01E-10
Dy^{3+}	1.080E-05	1.80E-10	7.96E-10
Ho^{3+}	2.019E-05	3.37E-10	3.41E-10

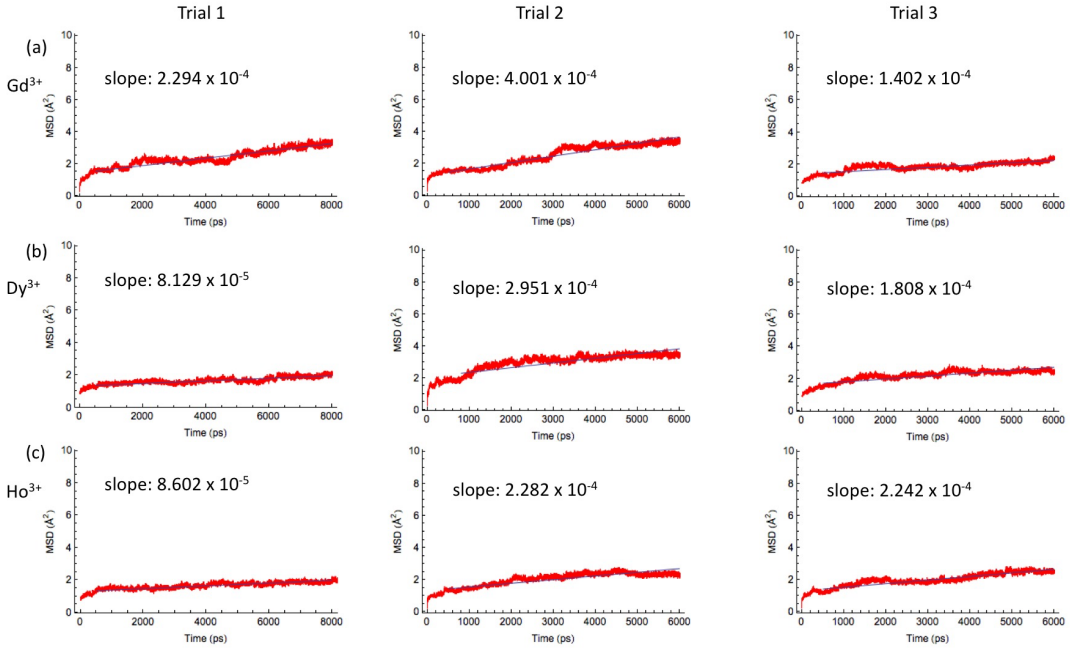
4. MSD plots for water molecules in [EMIm][$EtSO_4$] obtained from the three independent MD trajectories



The averaged diffusion coefficient of water molecules (D_{H2O}) from three independent simulation trajectories

metal ion	Average slopes of MSD plots ($Å^2$/ps)	Diffusion coefficient (cm^2/s)	Standard deviation of D_{H2O} (cm^2/s)
Gd^{3+}	8.38E-04	1.40E-08	2.42E-08
Dy^{3+}	5.18E-04	8.64E-09	2.04E-08
Ho^{3+}	4.71E-04	7.86E-09	2.24E-08

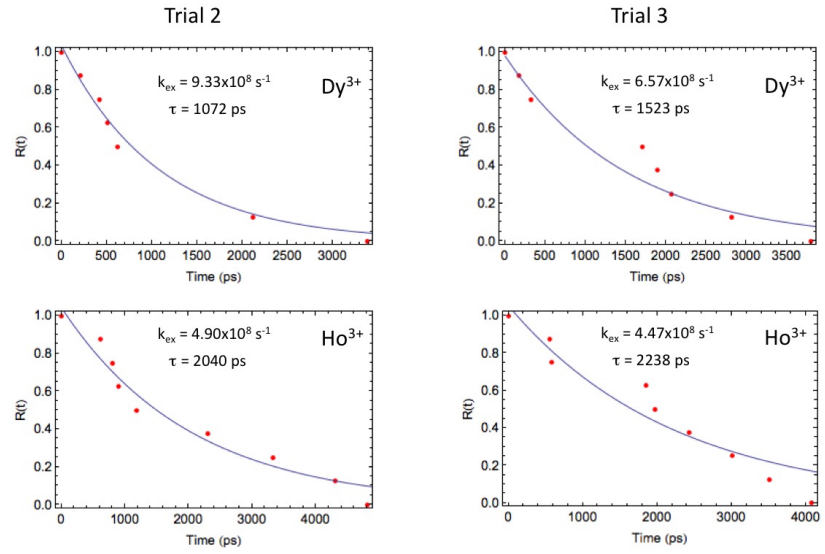
4. MSD plots for $[EtSO_4]^-$ anions in $[EMIm][EtSO_4]$ obtained from the three independent MD trajectories



The averaged diffusion coefficient of $[EtSO_4]^-$ anions (D_{EtSO4}) from three independent simulation trajectories

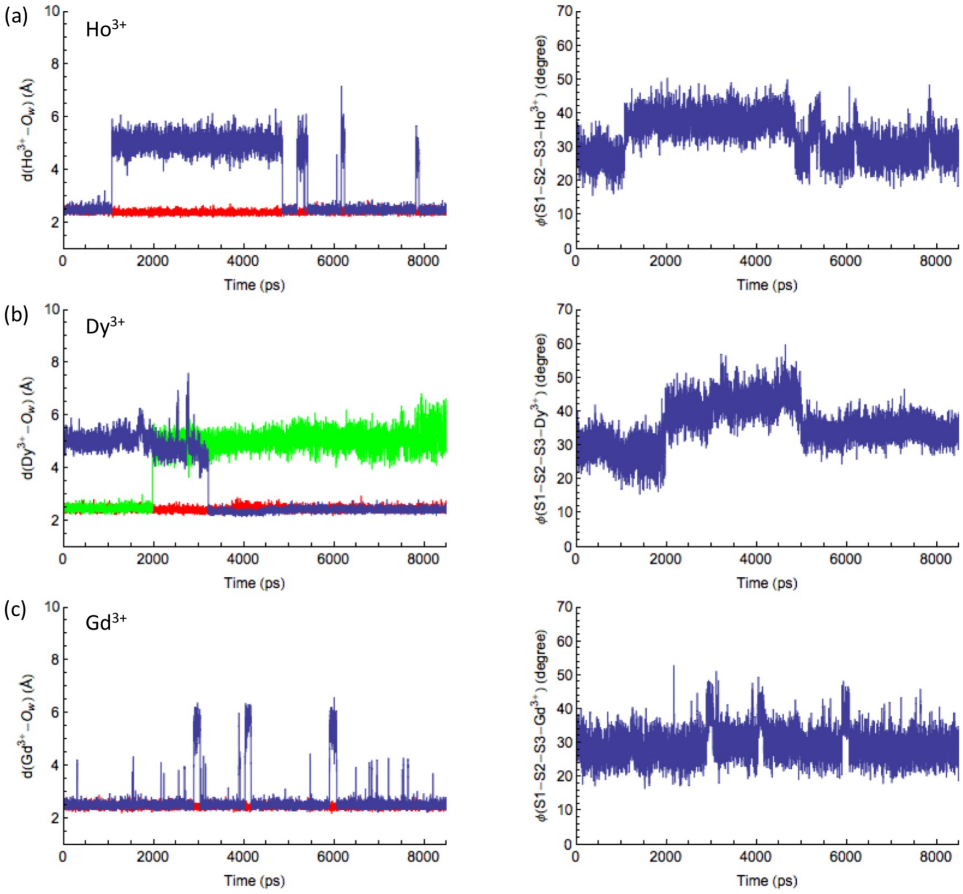
metal ion	Average slopes of MSD plots ($Å^2$/ps)	Diffusion coefficient (cm^2/s)	Standard deviation of D_{EtSO4} (cm^2/s)
Gd^{3+}	2.57E-04	4.28E-09	1.32E-08
Dy^{3+}	1.86E-04	3.10E-09	1.07E-08
Ho^{3+}	1.79E-04	2.99E-09	8.10E-09

H. Water-exchange rates of lanthanide ions in water

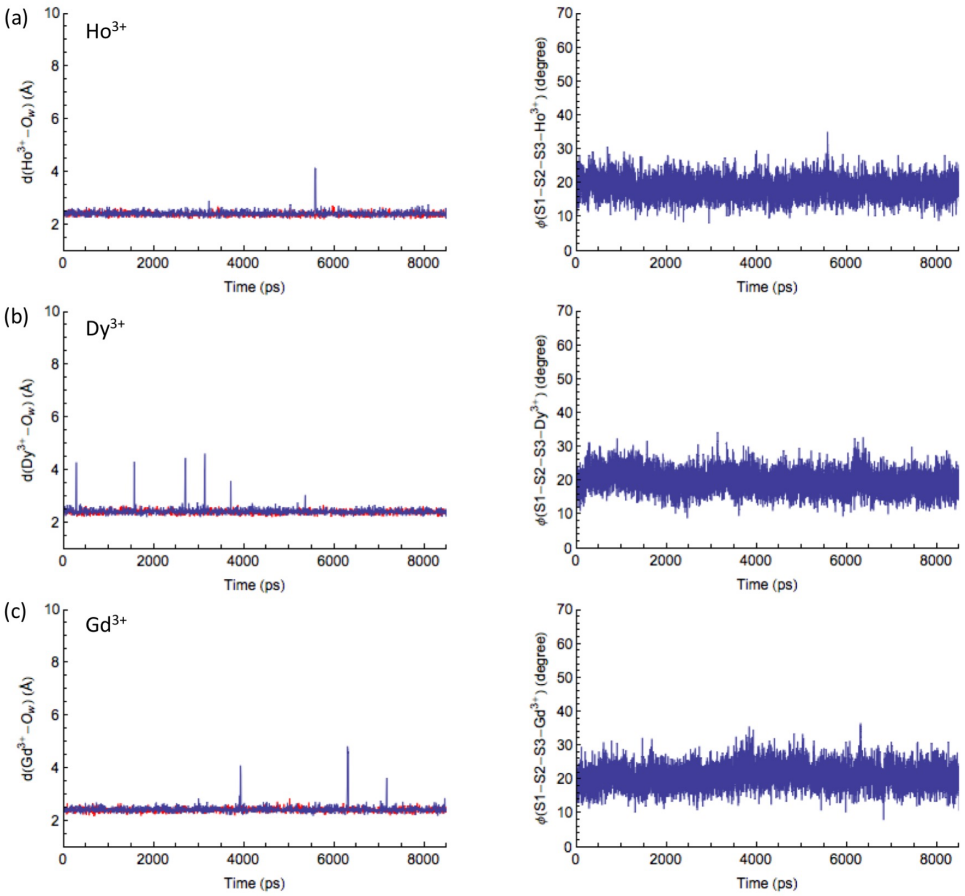


I. The MD trajectories for lanthanide-water oxygen distance and dihedral angle ϕ(S1−S2−S3−Ln) in water/[EMIm][$EtSO_4$]

Trial 2



Trial 3



mean residence time of a water molecule in the first coordination shell of each lanthanide ion

metal ion	mean residence time (ps)	standard deviation
Gd^{3+}	3984.18	2354.29
Dy^{3+}	2382.37	1161.44
Ho^{3+}	1329.65	1161.57

Reference

1. Burger, S. K.; Cisneros, G. A., Efficient Optimization of van der Waals Parameters from Bulk Properties. *J. Comput. Chem.* **2013,** *34*, 2313–2319.
2. Gomez, E.; Gonzalez, B.; Calvar, N.; Tojo, E.; Dominguez, A., Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2006,** *51*, 2096–2102.
3. Zaitsau, D. H.; Fumino, K.; Emel'yanenko, V. N.; Yermalayeu, A. V.; Ludwig, R.; Verevkin, S. P., Structure-Property Relationships in Ionic Liquids: A Study of the Anion Dependence in Vaporization Enthalpies of Imidazolium-Based Ionic Liquids. *Chemphyschem.* **2012,** *13*, 1868–1876.

4. Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J., Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.* **2007,** *9*, 982–990.
5. Ponder, J. W. *TINKER, Software Tools for Molecular Design, version 5.0*, Washington University: St. Louis, MO, 2004.

Complete citation for the Gaussian program:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G. B. V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Parandekar, P. V.; Mayhall, N. J.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian Development Version, Revision H.35 ed.: Gaussian, Inc.: Wallingford CT, 2014.

Complete citation for the AMBER program:

Case, D. A.; Darden, T. A.; Cheatham, T. E., III; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Walker, R. C.; Zhang, W.; Merz, K. M.; Roberts, B.; Hayik, S.; Roitberg, A.; Seabra, G.; Swails, J.; Götz, A. W.; Kolossvaŕy,I.; Wong,K.F.; Paesani,F.; Vanicek,J.; Wolf,R.M.; Liu, J.; Wu, X.; Brozell, S. R.; Steinbrecher, T.; Gohlke, H.; Cai, Q.; Ye, X.; Wang, J.; Hsieh, M.-J.; Cui, G.; Roe, D. R.; Mathews, D. H.; Seetin, M. G.; Salomon-Ferrer, R.; Sagui, C.; Babin, V.; Luchko, T.; Gusarov, S.; Kovalenko, A.; Kollman, P. A. *AMBER 12*, University of California: San Francisco, CA, 2012.