Physical Chemistry Chemical Physics

SUPPOTING INFORMATION

A Molecular Dynamics Study on Magnetic Imidazolium-based Ionic Liquids: Effect of an External Magnetic Field

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Table S1. Force field parameters for $[emim]^+$, $[bmim]^+$, $[hmim]^+$, and $[FeCl_4]^-$ ions used in this work. Atom labeling used in this table is the same as those in Figure 1.

The general form of the applied force field is:

$$E = \sum_{bonds} K_b \left(r - r_{eq}\right)^2 + \sum_{angles} K_\theta \left(\theta - \theta_{eq}\right)^2 +$$

$$\sum_{dihedrals} \frac{1}{2}(K_1\left[1+\cos\varphi\right] + K_2\left[1-\cos(2\varphi)\right] + K_3\left[1+\cos(3\varphi)\right] + K_4\left[1-\cos(4\varphi)\right] +$$

$$\sum_{impropers} K_\varphi\left[1+d\cos(n\varphi)\right] + \sum_{i=1}^{N-1}\sum_{j>1}^{N}\left\{4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right\}$$

Lenard-Jones parametrs		
$[emim]^+$		
atom	**σ_{ii}(Å)**	**ε_{ii}(kcal.mol^{-1})**
C1	3.50	0.066
CE	3.50	0.066
CR	3.55	0.070
CW	3.55	0.070
HA	2.42	0.030
HC	2.50	0.030
H1	2.50	0.030
NA	3.25	0.170
$[bmim]^+$		
C1	3.50	0.066
C2	3.50	0.066
CR	3.55	0.070
CS	3.50	0.066
CT	3.50	0.066
CW	3.55	0.070
HA	2.42	0.030
HC	2.50	0.030
H1	2.50	0.030
NA	3.25	0.170

Table S1. Continued.

Lenard-Jones parametrs		
[hmim]$^+$		
atom	**σ_{ii}(Å)**	**ε_{ii}(kcal.mol^{-1})**
C1	3.50	0.066
C2	3.50	0.066
CR	3.55	0.070
CS	3.50	0.066
CT	3.50	0.066
CW	3.55	0.070
HA	2.42	0.030
HC	2.50	0.030
H1	2.50	0.030
NA	3.25	0.170
[$FeCl_4$]$^-$		
Fe	2.08	0.134
Cl	3.47	0.265

Table S1. Continued.

Bond parameters			
$[emim]^+$, $[bmim]^+$, and $[hmim]^+$			
atom	**atom**	**r_{eq} (Å)**	**K_b (kcal.mol^{-1}.Å^{-2})**
CR	HA	1.08	331
CW	HA	1.08	331
C*	H*	1.09	331
CR	NA	1.315	477
CW	NA	1.378	427
CW	CW	1.341	520
NA	C1	1.466	337
C*	C*	1.529	268
$[FeCl_4]^-$			
Fe	Cl	2.26	78.46

Table S1. Continued.

Angle parameters				
[emim]$^+$, [bmim]$^+$, and [hmim]$^+$				
atom	**atom**	**atom**	θ_{eq}**(deg)**	K_θ**(***kcal.mol*$^{-1}$*.rad*$^{-2}$**)**
CW	NA	CR	108.00	69.93
CW	NA	C1	125.60	69.93
CR	NA	C1	126.40	69.93
NA	CR	HA	125.10	34.97
NA	CR	NA	109.80	69.93
NA	CW	CW	107.10	69.93
NA	CW	HA	122.00	34.97
CW	CW	HA	130.90	34.97
NA	C*	H*	110.70	74.86
C*	C*	H*	110.70	74.86
NA	C*	C*	112.70	100.0
C*	C*	C*	112.70	100.0
H*	C*	H*	107.80	65.99
[FeCl$_4$]$^-$				
Cl	Fe	Cl	111.32	232.74

Table S1. Continued.

Dihedral parameters							
[emim]$^+$							
atom	**atom**	**atom**	**atom**	K_1(kcal.mol^{-1})	K_2(kcal.mol^{-1})	K_3(kcal.mol^{-1})	K_4(kcal.mol^{-1})
X	NA	CR	X	0.000	4.651	0.000	0
X	CW	CW	X	0.000	10.75	0.000	0
X	NA	CW	X	0.000	2.999	0.000	0
CW	NA	C1	H1	0.000	0.000	0.131	0
CR	NA	C1	H1	0.000	0.000	0.000	0
CW	NA	C1	CE	-1.377	1.059	0.210	0
CR	NA	C1	CE	-0.772	0.000	0.000	0
NA	C1	CE	HC	0.000	0.000	0.000	0
H*	C*	C*	H*	0.000	0.000	0.318	0
[bmim]$^+$ and [hmim]$^+$							
X	NA	CR	X	0.000	4.651	0.000	0
X	CW	CW	X	0.000	10.75	0.000	0
X	NA	CW	X	0.000	2.999	0.000	0
CW	NA	C1	H1	0.000	0.000	0.131	0
CR	NA	C1	H1	0.000	0.000	0.000	0
CW	NA	C1	C2	-1.377	1.059	0.210	0
CR	NA	C1	C2	-0.772	0.000	0.000	0
NA	C1	C2	CS	0.176	-0.163	0.244	0
NA	C1	C2	CT	0.176	-0.163	0.244	0
NA	C1	C2	HC	0.000	0.000	0.000	0
C*	C*	C*	H*	0.000	0.000	0.366	0
H*	C*	C*	H*	0.000	0.000	0.318	0
C*	C*	C*	C*	0.174	-0.157	0.279	0

Table S1. Continued.

Improper parameters						
[emim]$^+$, [bmim]$^+$ and [hmim]$^+$						
atom	**atom**	**atom**	**atom**	K_ϕ**(kcal.mol^{-1})**	***d***	***n***
X	NA	X	X	1.000	-1	2
X	CW	X	X	1.100	-1	2
X	CR	X	X	1.100	-1	2

Table S2. NBO atomic charges obtained by B3LYP/6-311++G [LANL2DZ] method for [emim][$FeCl_4$], [bmim][$FeCl_4$] and [hmim][$FeCl_4$] ionic pairs.**

$[emim]^+$	*q*(e)	$[FeCl_4]^-$	*q*(e)
NA	-0.33076	Fe	0.41112
NA	-0.34134	Cl	-0.34835
CE	-0.58472	Cl	-0.42303
HC	0.23337	Cl	-0.28747
HC	0.19316	Cl	-0.32303
C1	-0.16576	Total charge	-0.97076
H1	0.20101		
H1	0.23685		
C1	-0.36192		
H1	0.20597		
H1	0.25023		
H1	0.22251		
CR	0.30113		
HA	0.27260		
CW	-0.02841		
HA	0.23510		
CW	-0.02402		
HA	0.23529		
HC	0.22047		
Total charge	0.97076		

Table S2. Continued.

$[bmim]^+$	q(e)	$[FeCl_4]^-$	q(e)
NA	-0.32912	Fe	0.40742
NA	-0.33659	Cl	-0.34374
C2	-0.38652	Cl	-0.41278
HC	0.20499	Cl	-0.29065
HC	0.19172	Cl	-0.32842
C1	-0.17107	Total charge	-0.96817
H1	0.20245		
H1	0.24755		
CS	-0.37288		
HC	0.18592		
HC	0.20435		
CT	-0.56810		
HC	0.20459		
HC	0.18910		
HC	0.19757		
C1	-0.36113		
H1	0.22582		
H1	0.24754		
H1	0.20556		
CR	0.29728		
HA	0.27042		
CW	-0.02397		
HA	0.23436		
CW	-0.02691		
HA	0.23524		
Total charge	0.96817		

Table S2. Continued.

$[hmim]^+$	q(e)
NA	-0.33075
NA	-0.33628
C2	-0.38539
HC	0.22548
HC	0.18665
C1	-0.16477
H1	0.20202
H1	0.23510
CS	-0.37690
HC	0.18192
HC	0.20697
CS	-0.37321
HC	0.18130
HC	0.19490
C1	-0.36143
H1	0.20583
H1	0.24842
H1	0.22398
CR	0.29995
HA	0.27038
CW	-0.02731
HA	0.23562
CW	-0.02436
HA	0.23497
CS	-0.36684
HC	0.19091
HC	0.18300
CT	-0.56862
HC	0.19833
HC	0.18803
HC	0.19329
Total charge	0.97119
$[FeCl_4]^-$	q(e)
Fe	0.40157
Cl	-0.33894
Cl	-0.28586
Cl	-0.41595
Cl	-0.33201
Total charge	-0.97119

Table S3. Transport numbers, t, of the cation and anion, and electrical conductivity, σ, as a function of temperature for the studied MILs.

T(K)	t_+	t_-	σ(mS.cm^{-1})
	[emim][FeCl$_4$]		
293.15	0.582	0.418	2.552
313.15	0.599	0.401	6.692
333.15	0.604	0.396	15.59
353.15	0.641	0.359	31.39
403.15	0.582	0.418	81.45
453.15	0.554	0.446	149.9
	[bmim][FeCl$_4$]		
293.15	0.572	0.428	0.597
313.15	0.556	0.444	1.996
333.15	0.548	0.452	5.776
353.15	0.521	0.479	15.31
403.15	0.516	0.484	45.89
453.15	0.508	0.492	86.26
	[hmim][FeCl$_4$]		
293.15	0.529	0.471	0.229
333.15	0.513	0.487	2.444
353.15	0.505	0.495	6.833
403.15	0.502	0.498	29.27
453.15	0.500	0.500	70.05

Table S4. The density, ρ, and diffusion coefficients, D, of the cation and anion of [bmim][FeCl$_4$] at T=293.15 K with and without charge modification.

	ρ(g.cm^{-3})	D_+(10^{11} m^2.s^{-1})	D_-(10^{11} m^2.s^{-1})
without charge modification	1.332	0.227	0.170
with charge modification	1.333	0.254	0.154

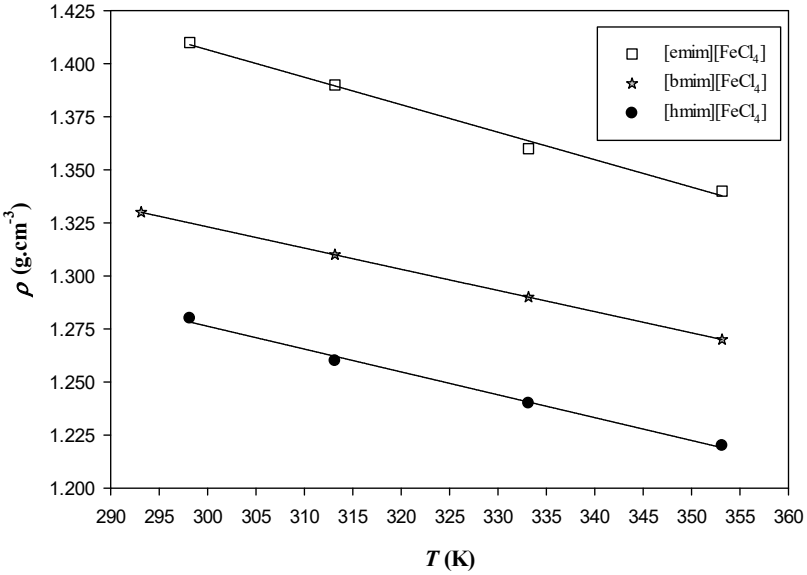

Fig. S1 Temperature dependence of the simulated densities of the studied MILs. The lines denote the linear regression of the corresponding simulated data.

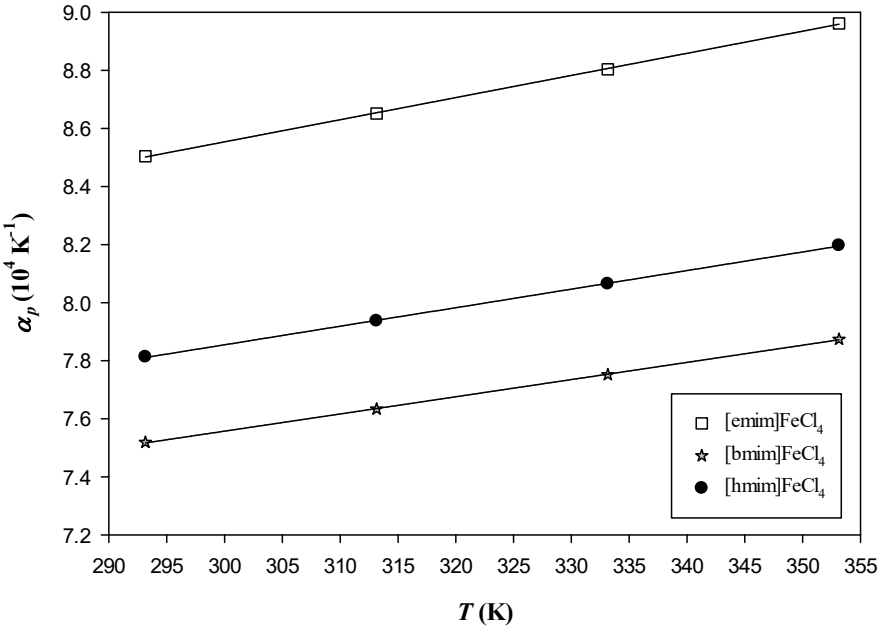

Fig. S2 Calculated isobaric expansion coefficients, α_p, for the studied MILs fitted by a linear regression.

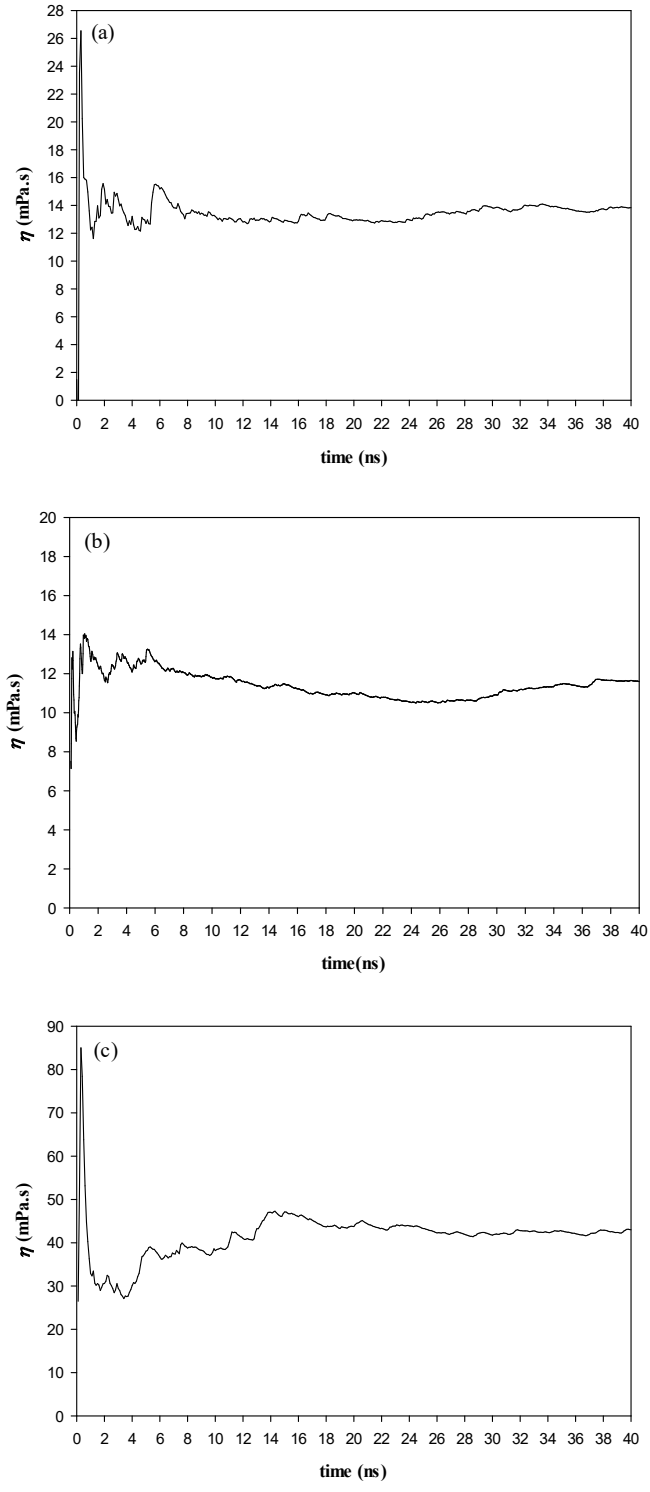

Fig. S3 The viscosity calculated by Green-Kubo method for (a) [emim][$FeCl_4$], (b) [bmim][$FeCl_4$] and (c) [hmim][$FeCl_4$] at T=353.15 K and P=0.1MPa.

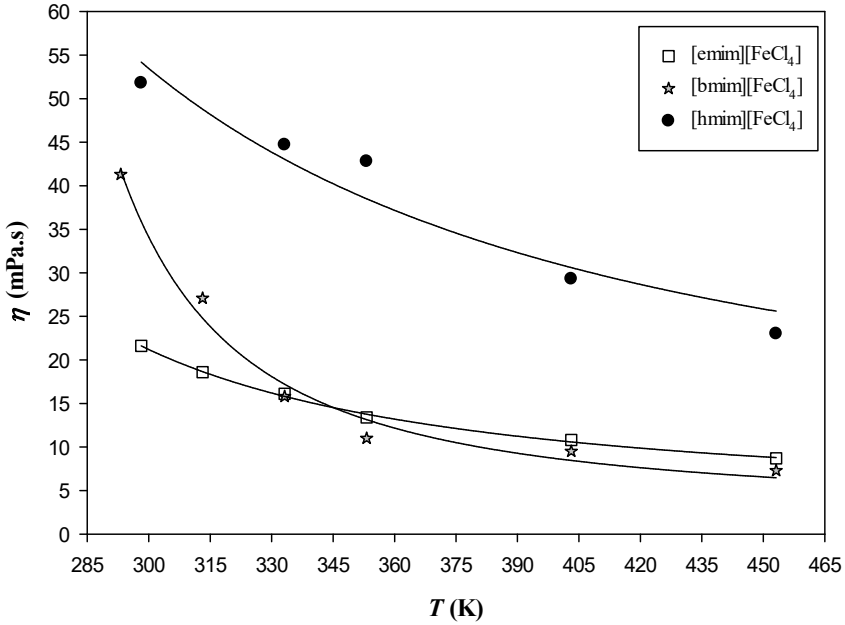

Fig. S4 The calculated viscosities of the studied MILs as functions of temperature using Green-Kubo formulation. The lines show VFT regression of data.

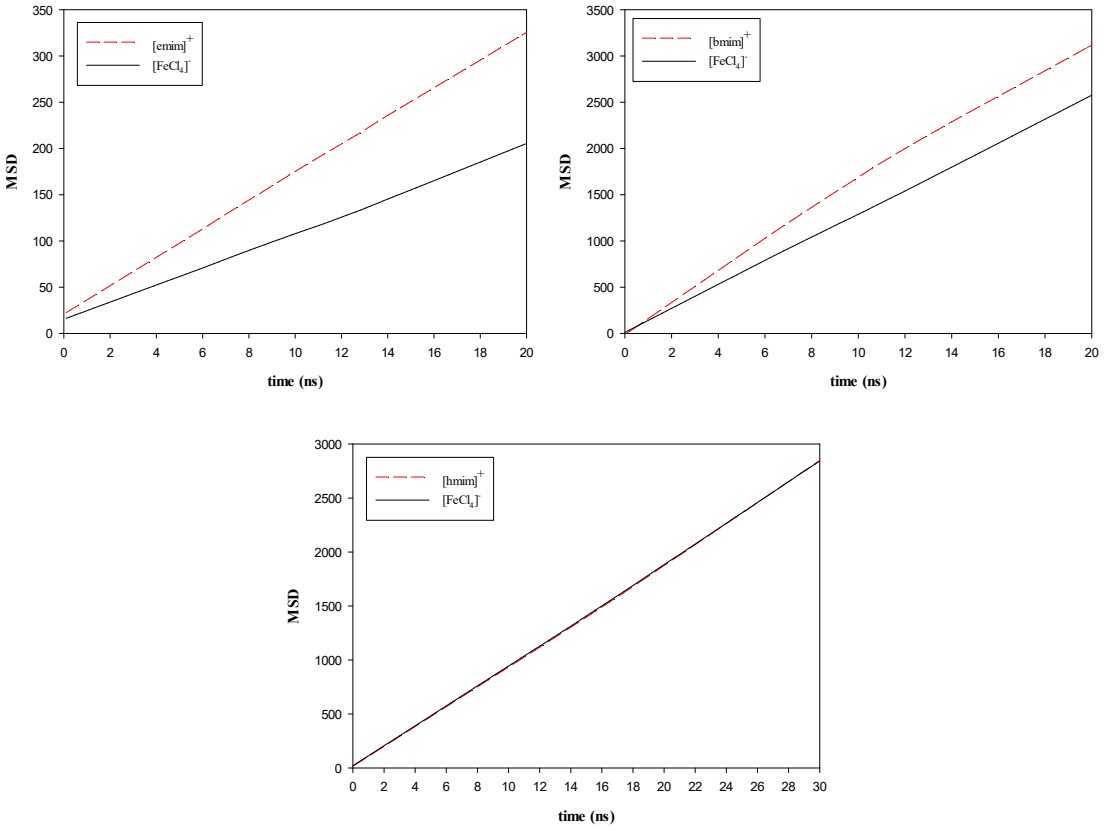

Fig. S5 Mean square displacement (MSD) plots of the cation and anion of each studied magnetic ionic liquids at 403.15 K and 0.1 MPa.

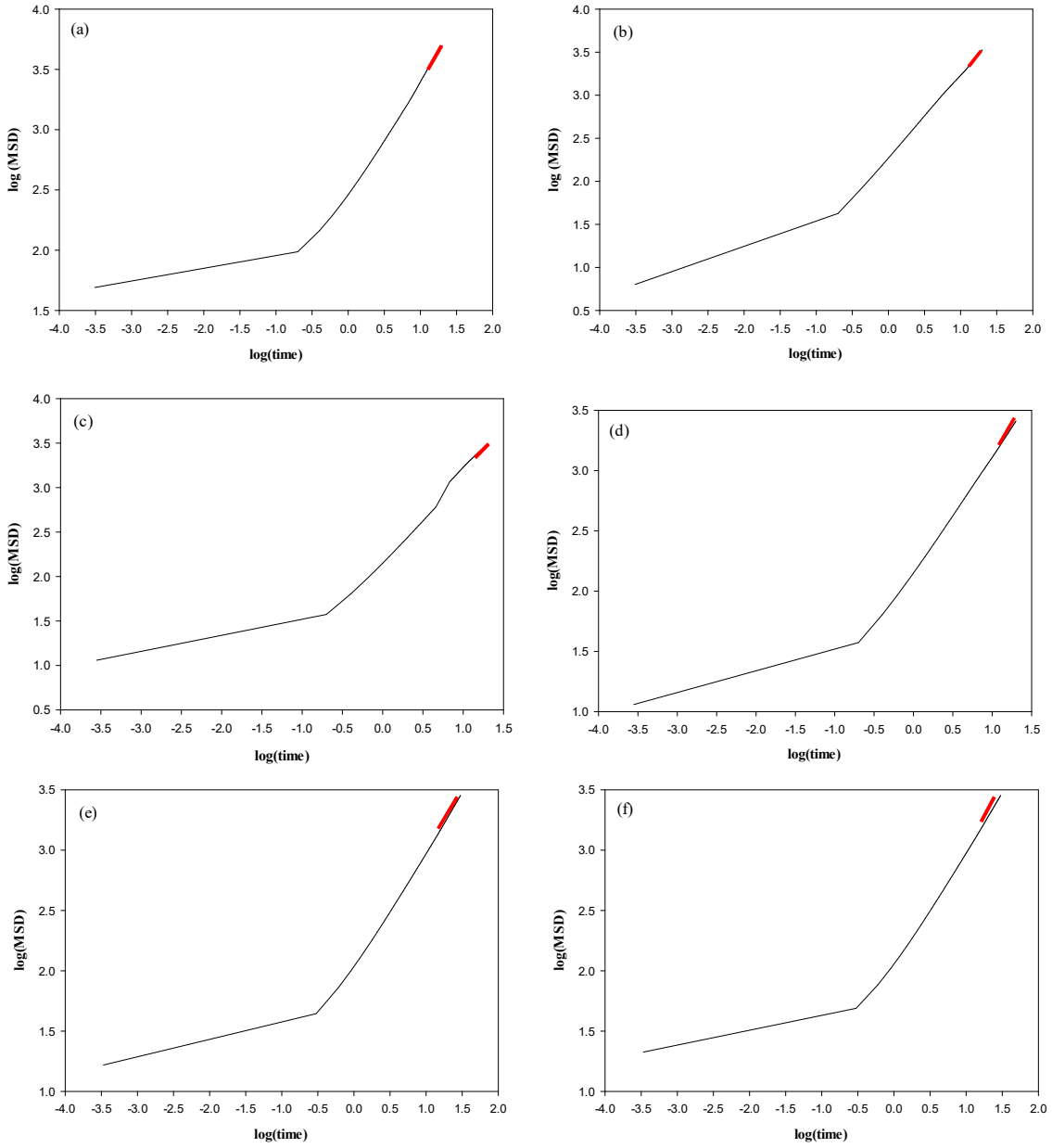

Fig. S6 log(MSD) versus log(time) for (a) cation and (b) anion of [emim][$FeCl_4$], (c) cation and (d) anion of [bmim][$FeCl_4$], and (e) cation and (f) anion of [hmim][$FeCl_4$] at 403.15 K.

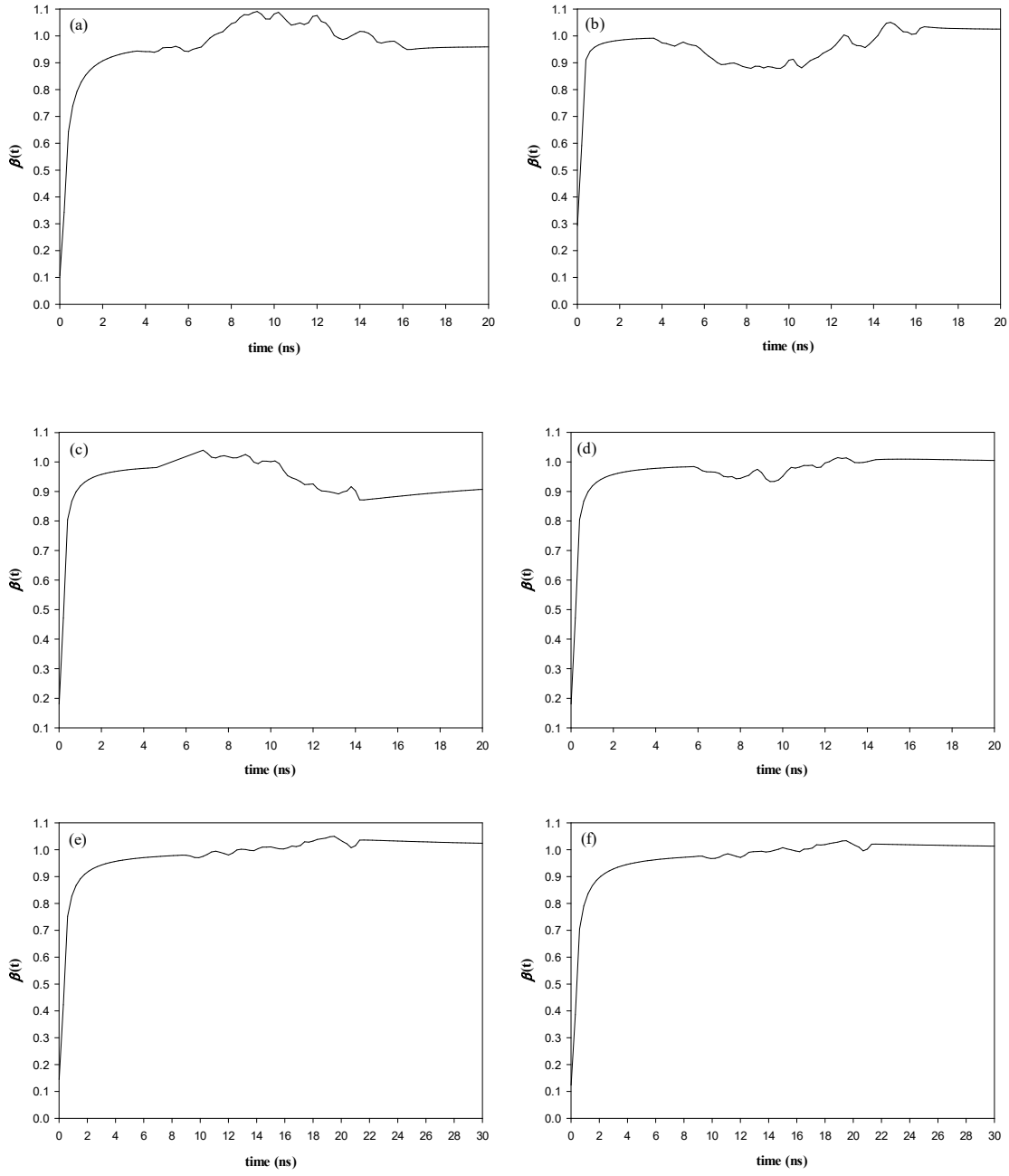

Fig. S7 β(t) versus time for (a) cation and (b) anion of [emim][$FeCl_4$], (c) cation and (d) anion of [bmim][$FeCl_4$], and (e) cation and (f) anion of [hmim][$FeCl_4$] at 403.15 K.

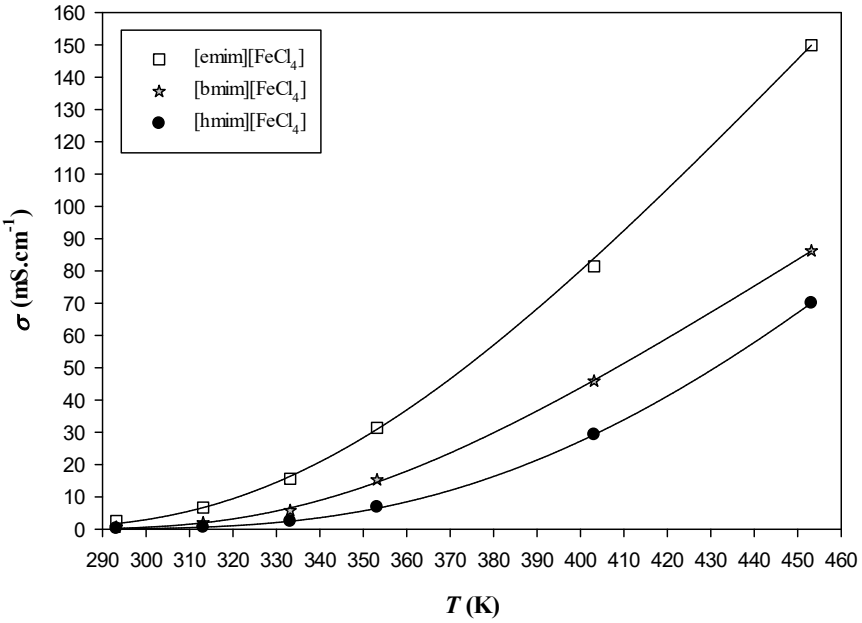

Fig. S8 Temperature dependence of the simulated electrical conductivity of the studied MILs at 0.1 MPa. Lines are fittings with the VFT equation.

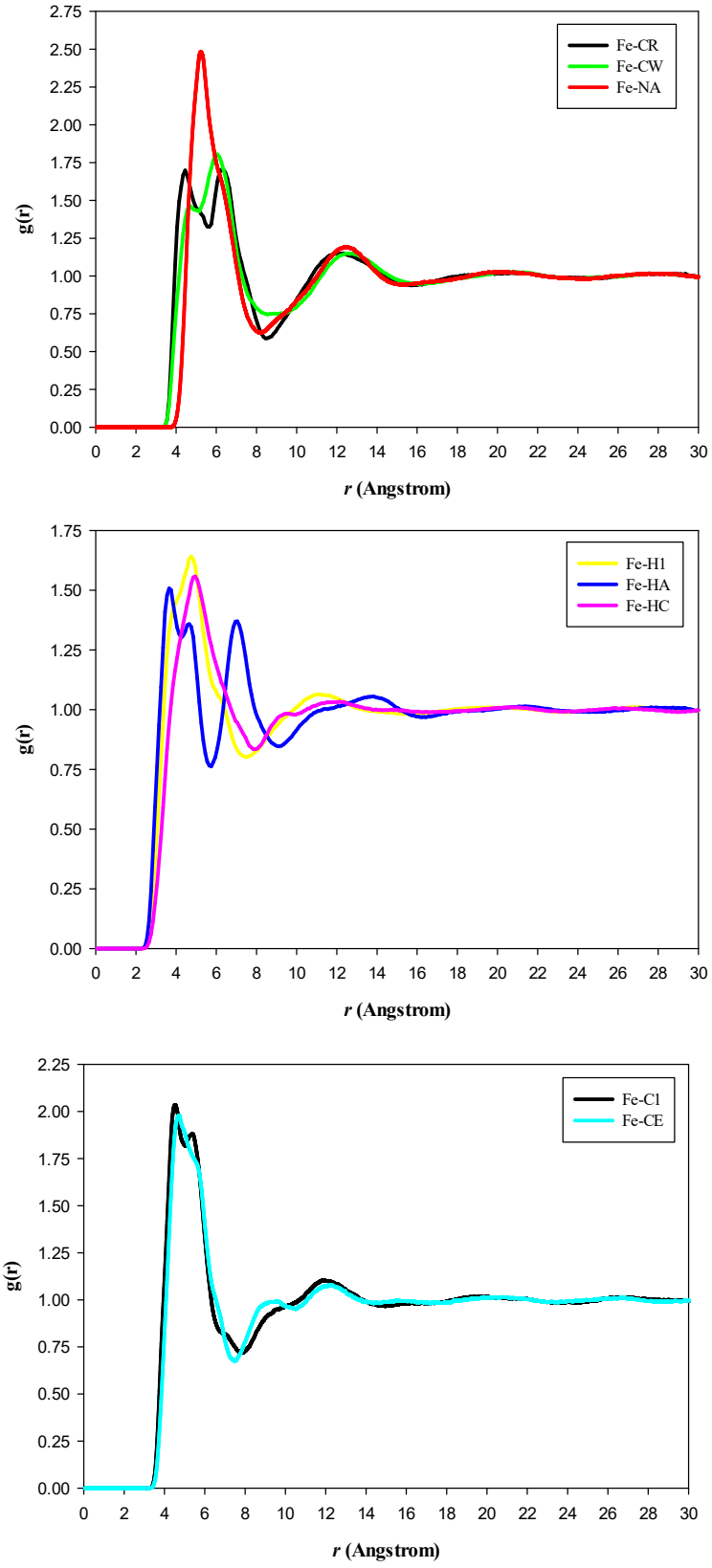

Fig. S9 Site-site radial distribution functions, g(r), for [emim][$FeCl_4$] at 293.15 K and 0.1 MPa.

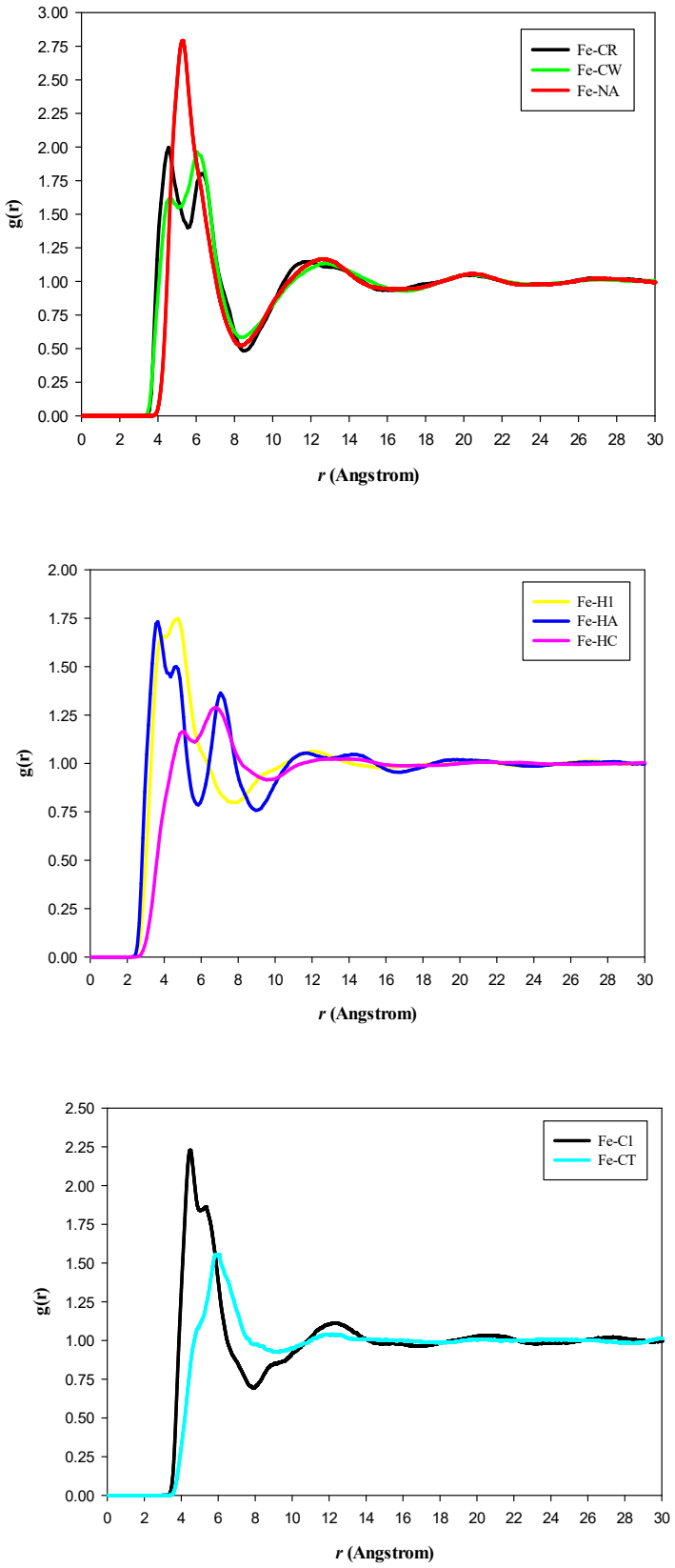

Fig. S10 Site-site radial distribution functions, g(r), for [hmim][$FeCl_4$] at 293.15 K and 0.1 MPa.

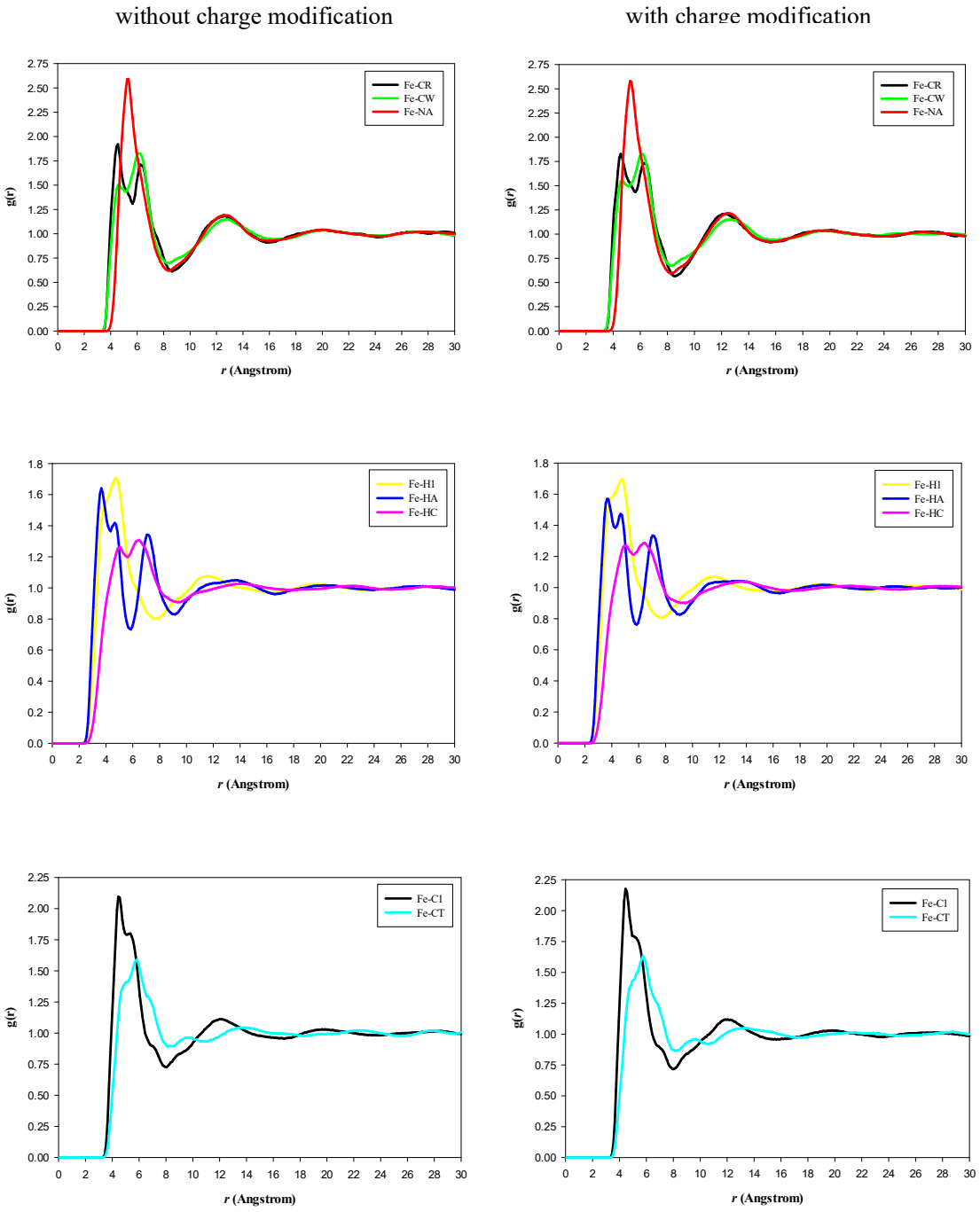

Fig. S11 The effect of asymmetric distribution of charge among the Cl atoms in the $[FeCl_4]^-$ anions on the RDF plots at T=293.15 K.

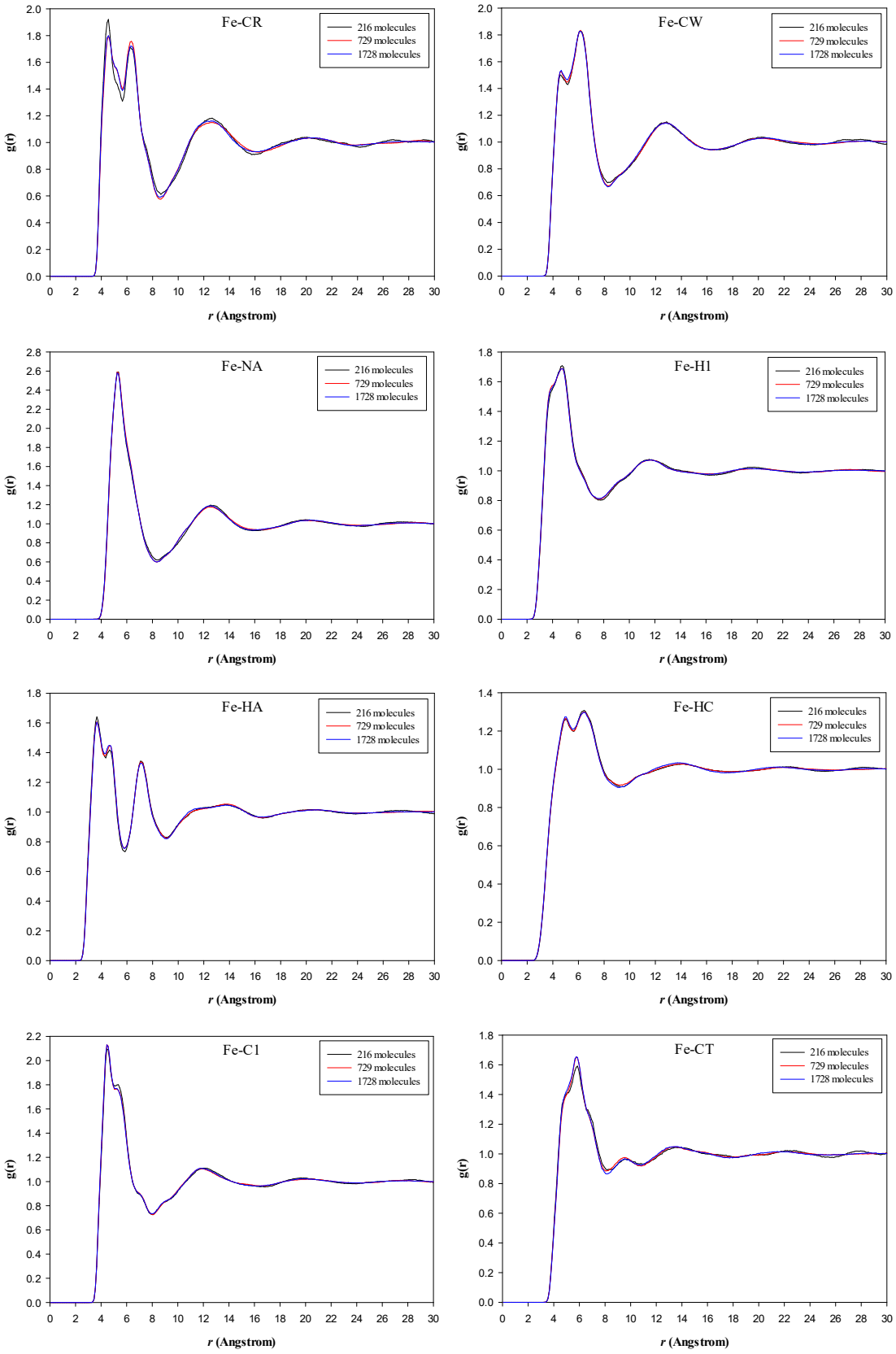

Fig. S12 The effect of system size on the site-site radial distribution functions, g(r), for [bmim][$FeCl_4$] at 293.15 K and 0.1 MPa with $r_{cut\text{-}off}$ = 10 Å.

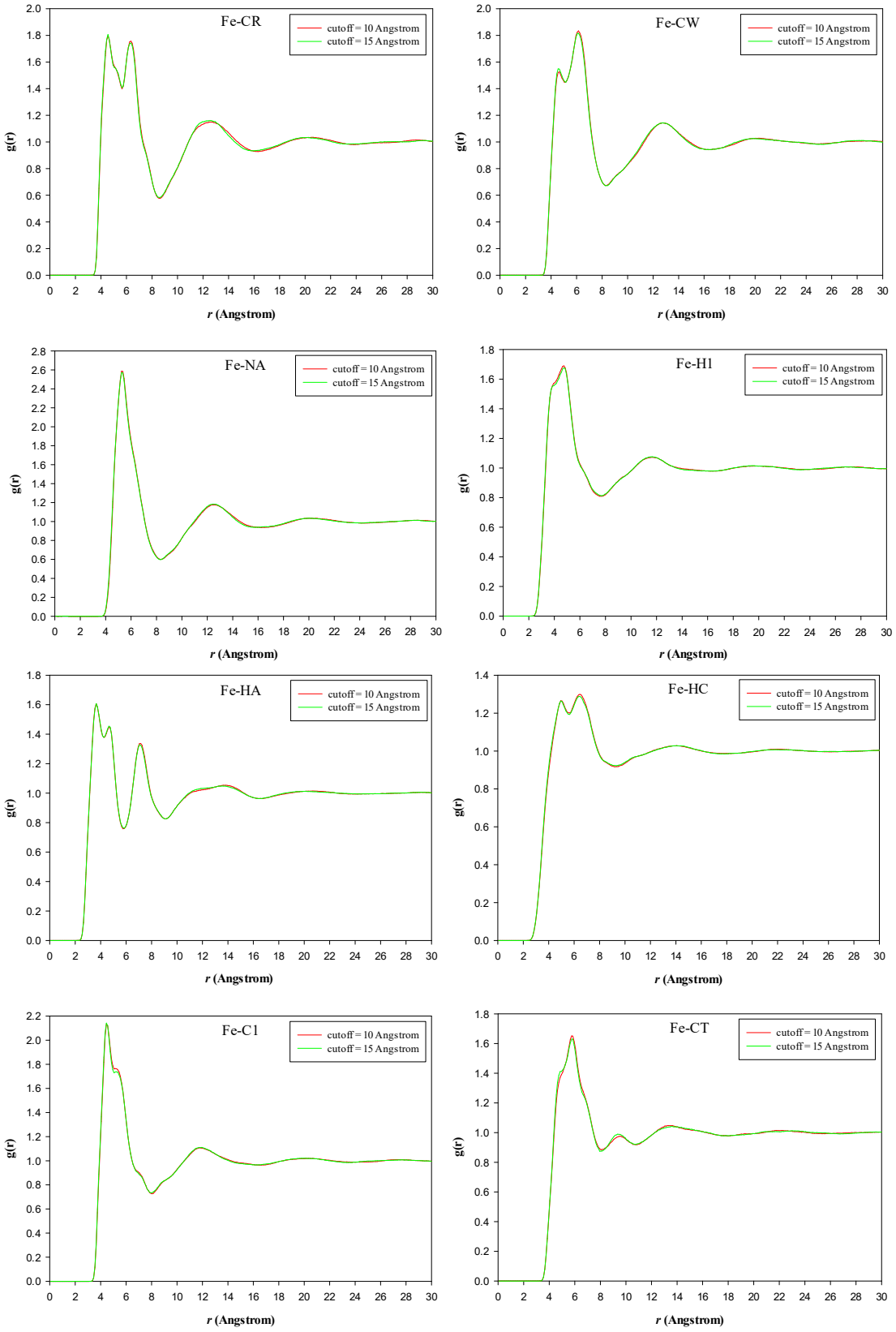

Fig. S13 The effect of cutoff radius on the site-site radial distribution functions, g(r), for the system contains of 729 molecules of [bmim][$FeCl_4$] at 293.15 K and 0.1 MPa.

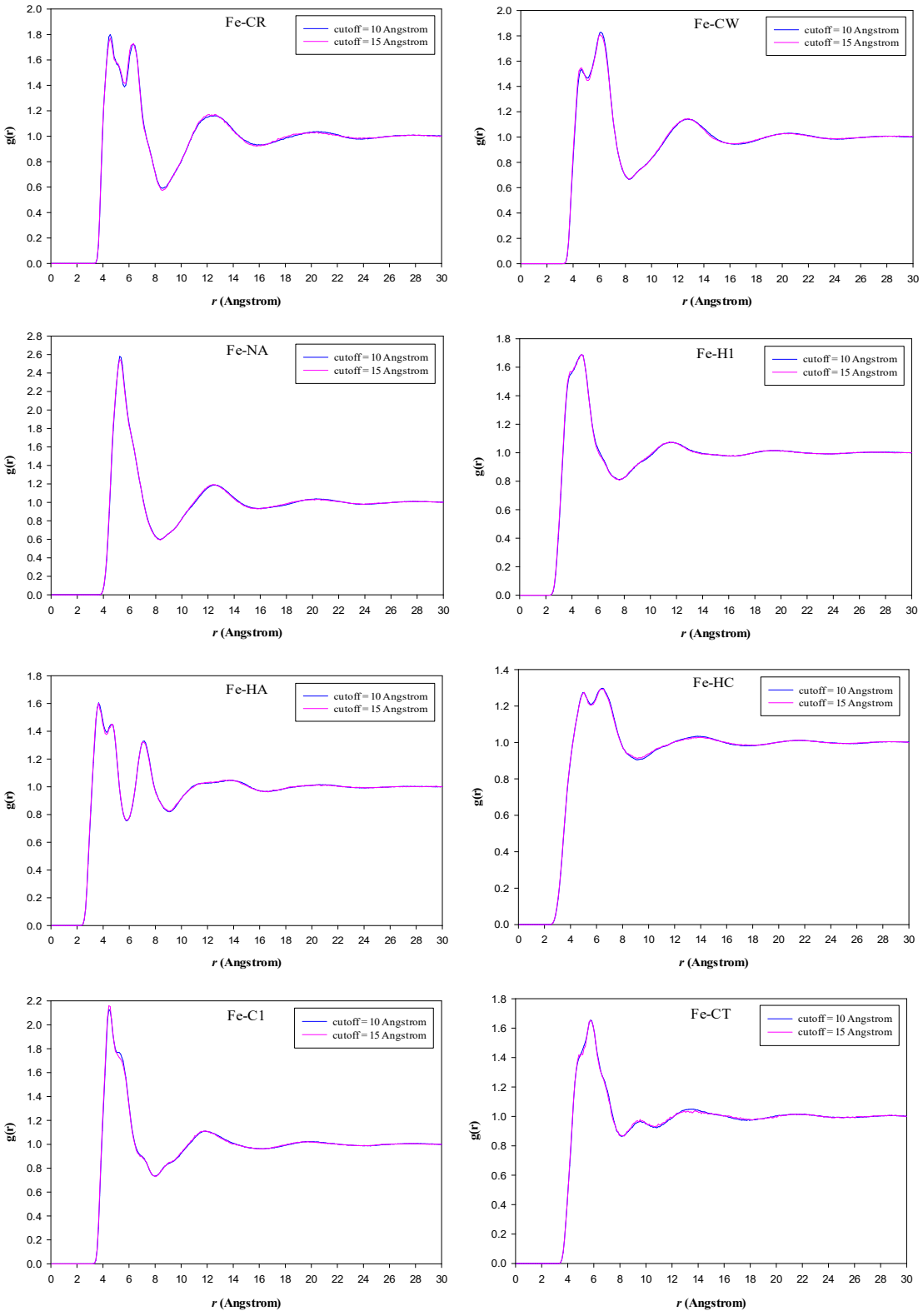

Fig. S14 The effect of cutoff radius on the site-site radial distribution functions, g(r), for the system contains of 1728 molecules of [bmim][$FeCl_4$] at 293.15 K and 0.1 MPa.