Thermophysical Properties of Imidazolium-based Binary Ionic Liquid Mixtures using Molecular Dynamics Simulations

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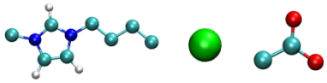
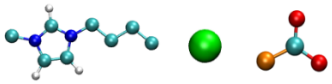
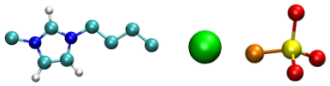
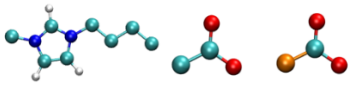
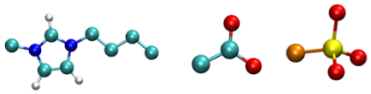
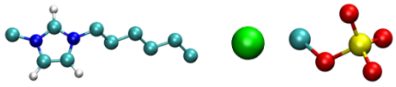
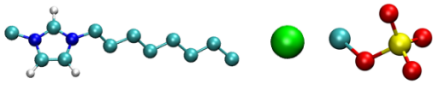
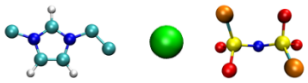
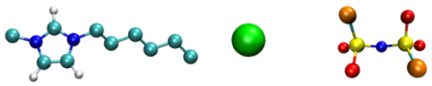
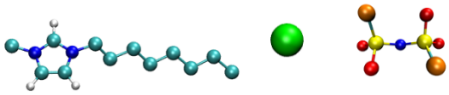
Abstract

Until very recently, task-specific ionic liquids have been designed by altering the chemistry of either the cation, anion or both. An alternative approach, that is gaining considerable momentum, is to consider ionic liquids that are derived from mixing two different ionic liquids and varying the molar composition of such blends to exert precise control over the desired physicochemical and biological properties. As the number of ionic liquids that result from mixing is projected to be close to a billion, it is highly desirable to predict *a priori* whether ionic liquid mixtures can be considered as ideal solutions of their pure analogues. Towards this end, we employ molecular dynamics simulations to predict the density, molar volumes, excess molar volumes, self-diffusion coefficients, and ionic conductivities for eleven ionic liquid systems as a function of mole fractions spanning the entire range of compositions of the constituent ionic liquids. The ionic liquid mixtures investigated here are 1-n-butyl-3-methylimidazolium [C mim] chloride Cl paired with [C mim] acetate [CH COO] /[OAC] , [C mim] trifluoroacetate [CF COO] /[TFA] and [C mim] trifluoromethanesulfonate [CF SO] /[TFS] , and [C mim][OAC] combined with [C mim][TFA] and [C mim][TFS]. The effect of change in the alkyl chain length on the thermophysical properties of ionic liquid mixtures containing anions as Cl – methylsulfate [MeSO] , and Cl – bis(trifluoromethanesulfonyl)imide [NTf] is evaluated by coupling with 1-ethyl-3-methylimidazolium [C mim] , 1-n-hexyl-3-methylimidazolium [C mim] and 1-n-octyl-3-methylimidazolium [C mim] cations. The deviation of the property trend from the linear mixing rule is discussed in terms of the difference in the properties of pure ionic liquid analogues.

Introduction

a priori

Table 1: List of Imidazolium-based Binary Ionic Liquid Mixtures Investigated. (Please note that united-atom (UA) representations are used for representing the molecular structure, as per the employed UA force field.)

Compound	Molecular Structure	Abbreviation
1-n-butyl-3-methylimidazolium chloride — 1-n-butyl-3-methylimidazolium acetate		$[C_4mim]Cl_x[OAC]_{1-x}$
1-n-butyl-3-methylimidazolium chloride — 1-n-butyl-3-methylimidazolium trifluoroacetate		$[C_4mim]Cl_x[TFA]_{1-x}$
1-n-butyl-3-methylimidazolium chloride — 1-n-butyl-3-methylimidazolium trifluoromethanesulfonate		$[C_4mim]Cl_x[TFS]_{1-x}$
1-n-butyl-3-methylimidazolium acetate — 1-n-butyl-3-methylimidazolium trifluoroacetate		$[C_4mim][OAC]_x[TFA]_{1-x}$
1-n-butyl-3-methylimidazolium acetate — 1-n-butyl-3-methylimidazolium trifluoromethanesulfonate		$[C_4mim][OAC]_x[TFS]_{1-x}$
1-ethyl-3-methylimidazolium chloride — 1-ethyl-3-methylimidazolium methylsulfate		$[C_2mim]Cl_x[MeSO_4]_{1-x}$
1-n-hexyl-3-methylimidazolium chloride — 1-n-hexyl-3-methylimidazolium methylsulfate		$[C_6mim]Cl_x[MeSO_4]_{1-x}$
1-n-octyl-3-methylimidazolium chloride — 1-n-octyl-3-methylimidazolium methylsulfate		$[C_8mim]Cl_x[MeSO_4]_{1-x}$
1-ethyl-3-methylimidazolium chloride — 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide		$[C_2mim]Cl_x[NTf_2]_{1-x}$
1-n-hexyl-3-methylimidazolium chloride — 1-n-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide		$[C_6mim]Cl_x[NTf_2]_{1-x}$
1-n-octyl-3-methylimidazolium chloride — 1-n-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide		$[C_8mim]Cl_x[NTf_2]_{1-x}$

Force Field Description

$$E \quad \sum K \quad r - r \quad \sum K \quad \theta - \theta$$

$$\sum K \quad n\chi - \delta \quad \sum K \quad n\psi - \delta$$

$$\sum \sum \left\{ \epsilon \left[\left(\frac{\sigma}{r}\right) - \left(\frac{\sigma}{r}\right) \right] \left(\frac{q\,q}{r}\right) \right\}$$

$K \quad K \quad K \quad K$

$\sigma \quad \epsilon \quad i \quad j$

q

$\pm$

Computational Details

NVT

NPT

NPT

τ τ

Results and Discussion

Liquid Densities

$<$ $<$ $<$

Molar Volumes

$$V \qquad \frac{M}{\rho} - x \; \frac{M}{\rho} - x \; \frac{M}{\rho}$$

ρ x M i

n

$\sim$

V

Self-Diffusion Coefficients

D

$$D \quad - \quad \frac{d}{dt}\left\langle \sum \vec{r} \;\; t \;\; - \vec{r} \qquad \right\rangle$$

$\langle \ldots \rangle$ N

$t \quad \vec{r} \;\; t$

$<$ $<$ $<$ $\sim$ $<$

Table 2: Self-diffusion coefficients ($D \times$ cm /sec) of ions for pure ionic liquids, obtained from simulations in this work and compared with literature at 353 K

. ± .	. ± .	.			
. ± .	. ± .	.	.		
. ± .	. ± .	.	.	−	−
. ± .	. ± .	−	−	−	−
. ± .	. ± .	.	.		
. ± .	. ± .	.	.		
. ± .	. ± .				.
. ± .	. ± .	−	−	−	−
. ± .	. ± .	−	−	−	−
. ± .	. ± .	−	−	−	−
. ± .	. ± .	−	−	−	−
. ± .	. ± .	−	−	−	−
. ± .	. ± .	−	−	−	−

$$D \quad \underline{D \qquad xD \qquad\qquad - x \;\; D}$$

$$D \quad x\underline{D \qquad D} \qquad\qquad - x \;\; \underline{D \qquad D}$$

Ionic Conductivity

σ

σ

$\langle \ldots \rangle$

$$\sigma \quad \frac{}{k \;\; VT} \qquad \frac{d}{dt} \left\langle \sum \sum q \, q \;\; \vec{r} \;\; t \;\; - \vec{r} \qquad . \vec{r} \;\; t \;\; - \vec{r} \qquad \right\rangle$$

$$\sigma \qquad \frac{N}{Vk \;\; T} \left(q \;\; D \qquad q \;\; x \;\; D \qquad x \;\; D \quad \right)$$

$>$

$>$ $>$

$Y \quad \sigma \quad \sigma$

Y

Y

Y

Y

Conclusion

Acknowledgement

Supporting Information Available

http://pubs.acs.org/

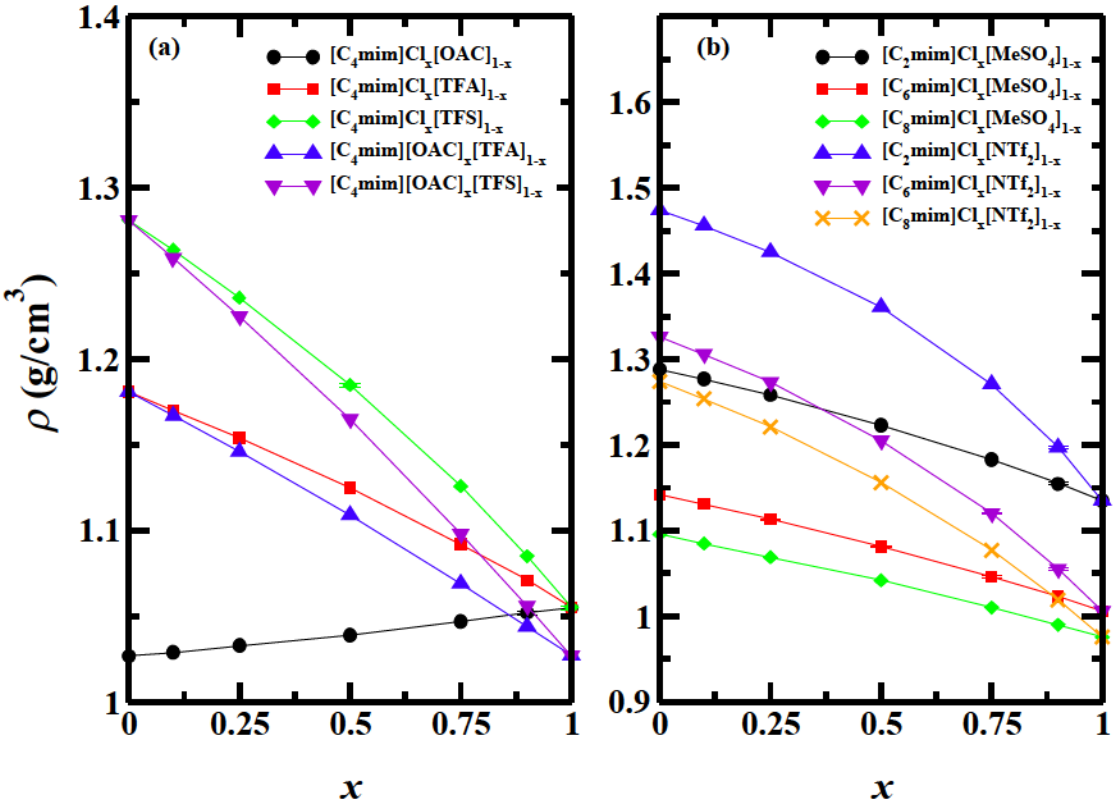
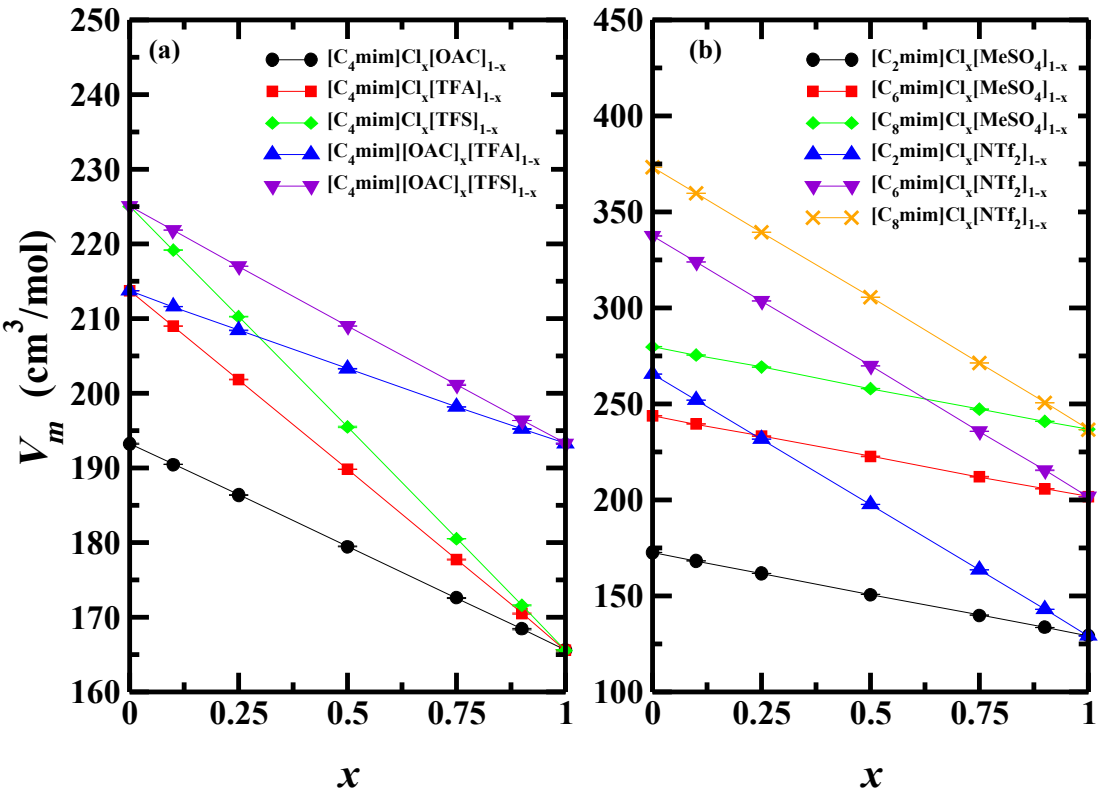
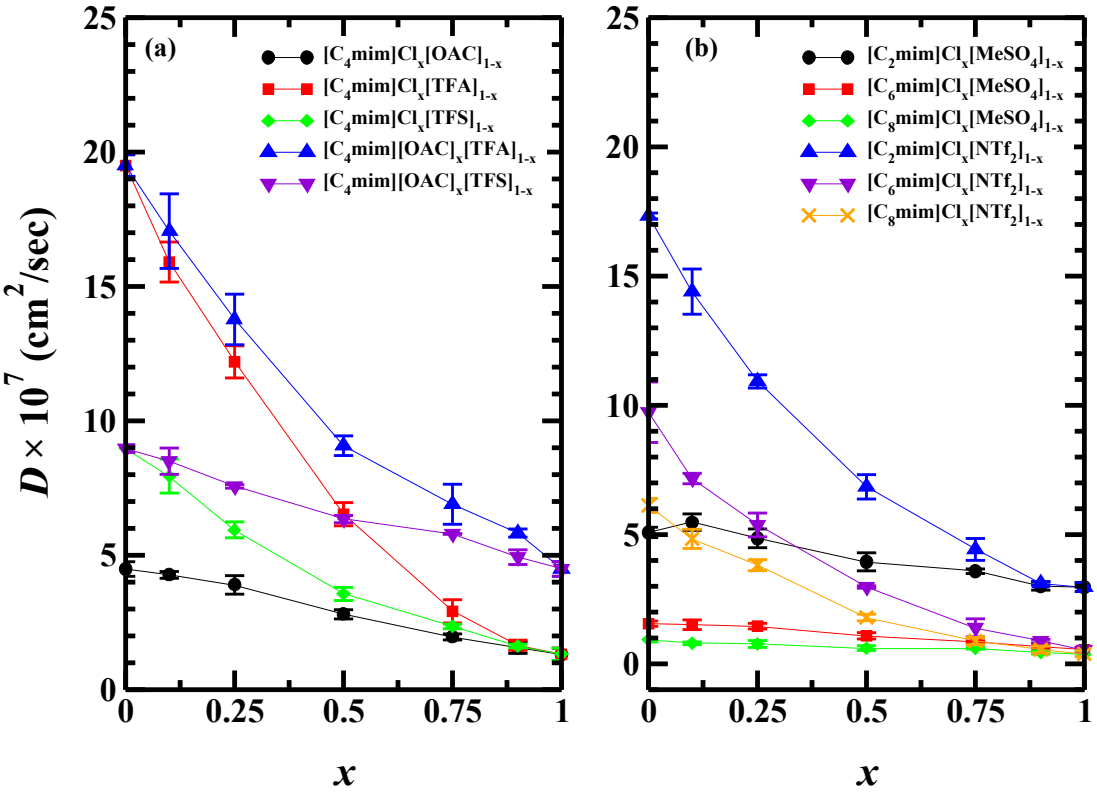
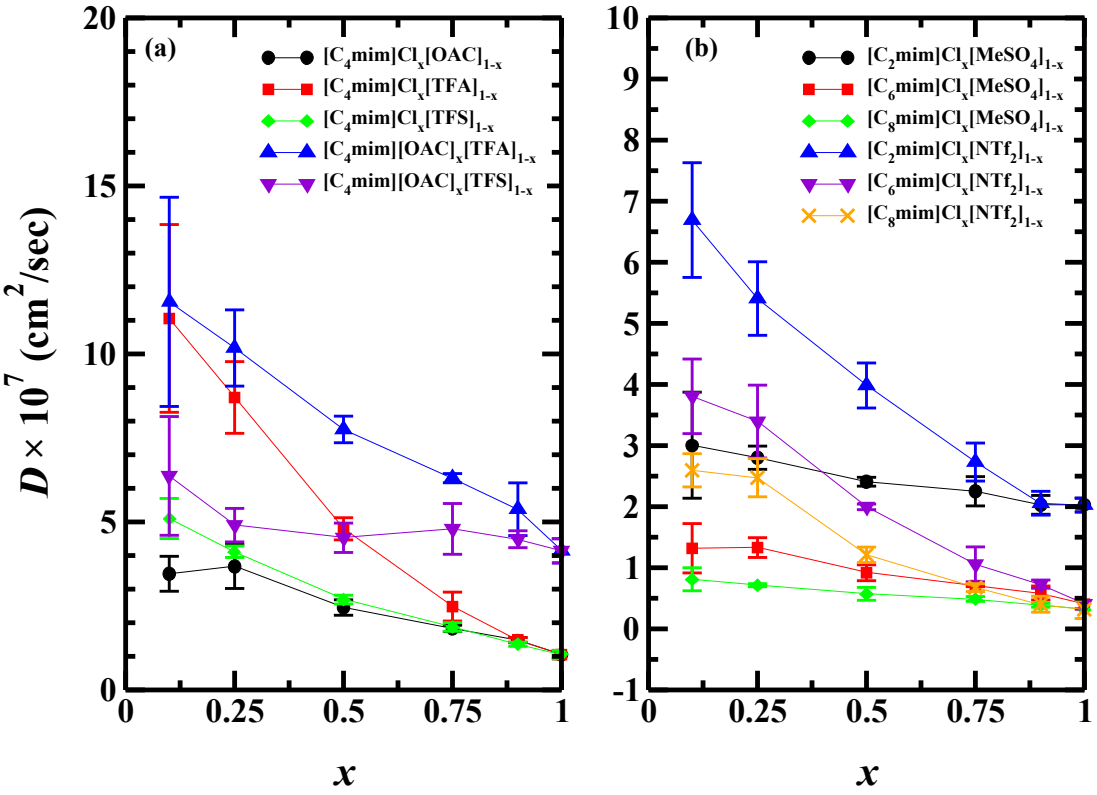
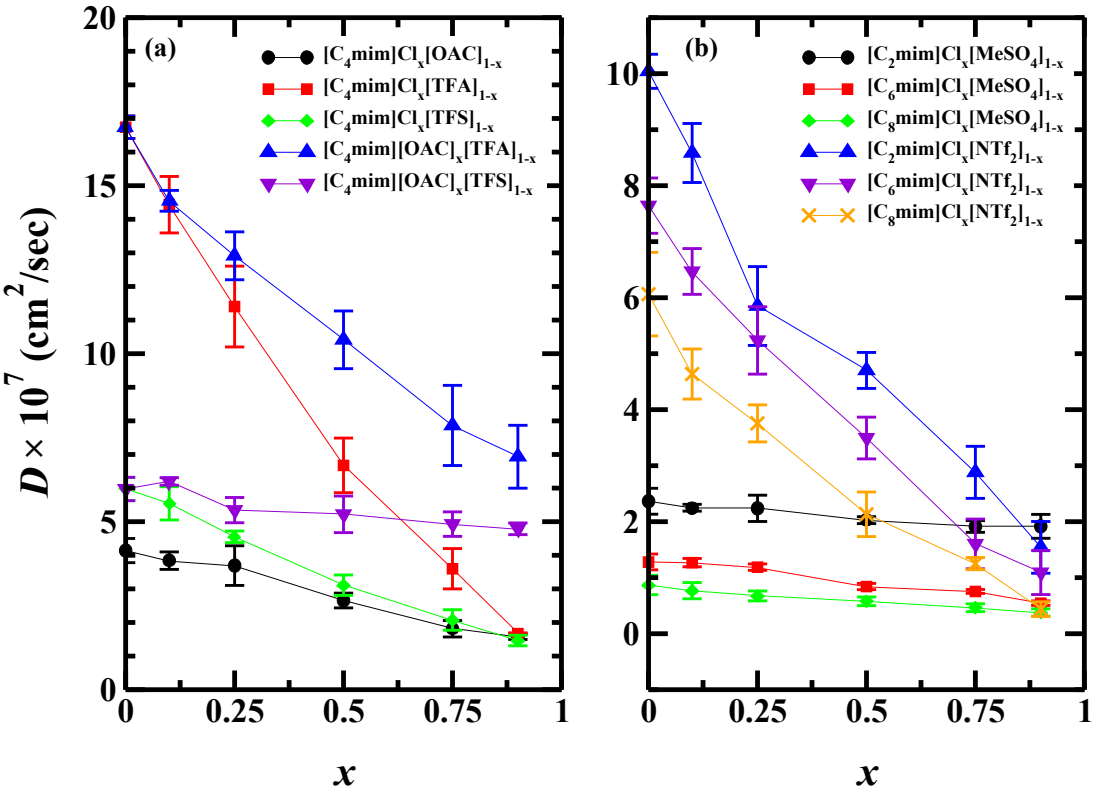


Figure 1: The liquid phase density as a function of molar composition at 353 K: (a) common cation $[C_4mim]^+$ paired with different anions namely Cl^-–$[OAC]^-$, Cl^-–$[TFA]^-$, Cl^-–$[TFS]^-$, $[OAC]^-$–$[TFA]^-$, and $[OAC]^-$–$[TFS]^-$; (b) cations $[C_2mim]^+$, $[C_6mim]^+$, and $[C_8mim]^+$ coupled with different anions Cl^-–$[MeSO_4]^-$ and Cl^-–$[NTF_2]^-$. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the continuous lines joining data points are only guide to the eye.


(a)
[C4mim]Clx[OAC]1-x
[C4mim]Clx[TFA]1-x
[C4mim]Clx[TFS]1-x
[C4mim][OAC]x[TFA]1-x
[C4mim][OAC]x[TFS]1-x
Vm (cm3/mol)
x
(b)
[C2mim]Clx[MeSO4]1-x
[C6mim]Clx[MeSO4]1-x
[C8mim]Clx[MeSO4]1-x
[C2mim]Clx[NTf2]1-x
[C6mim]Clx[NTf2]1-x
[C8mim]Clx[NTf2]1-x
x


(a)
[C4mim]Clx[OAC]1-x
[C4mim]Clx[TFA]1-x
[C4mim]Clx[TFS]1-x
[C4mim][OAC]x[TFA]1-x
[C4mim][OAC]x[TFS]1-x
(b)
[C2mim]Clx[MeSO4]1-x
[C6mim]Clx[MeSO4]1-x
[C8mim]Clx[MeSO4]1-x
[C2mim]Clx[NTf2]1-x
[C6mim]Clx[NTf2]1-x
[C8mim]Clx[NTf2]1-x
D × 10^7 (cm^2/sec)
x
x
0
5
10
15
20
25
0
0.25
0.5
0.75
1


(a)
[C4mim]Clx[OAC]1-x
[C4mim]Clx[TFA]1-x
[C4mim]Clx[TFS]1-x
[C4mim][OAC]x[TFA]1-x
[C4mim][OAC]x[TFS]1-x
D × 10^7 (cm^2/sec)
x
(b)
[C2mim]Clx[MeSO4]1-x
[C6mim]Clx[MeSO4]1-x
[C8mim]Clx[MeSO4]1-x
[C2mim]Clx[NTf2]1-x
[C6mim]Clx[NTf2]1-x
[C8mim]Clx[NTf2]1-x
x


(a)
[C4mim]Clx[OAC]1-x
[C4mim]Clx[TFA]1-x
[C4mim]Clx[TFS]1-x
[C4mim][OAC]x[TFA]1-x
[C4mim][OAC]x[TFS]1-x
D × 10^7 (cm^2/sec)
x
(b)
[C2mim]Clx[MeSO4]1-x
[C6mim]Clx[MeSO4]1-x
[C8mim]Clx[MeSO4]1-x
[C2mim]Clx[NTf2]1-x
[C6mim]Clx[NTf2]1-x
[C8mim]Clx[NTf2]1-x
x

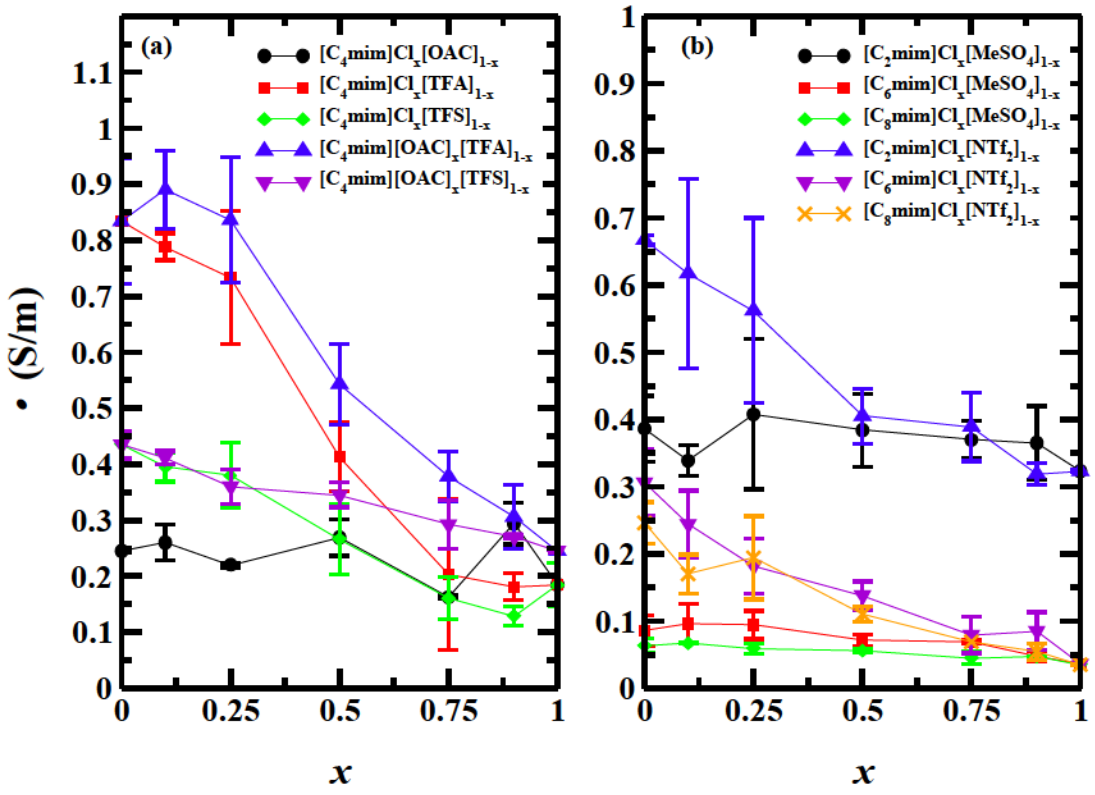


Figure 6: Ionic conductivity computed the Einstein relation (eq. 6) as a function of composition at 353 K: (a) common cation $[C_4mim]^+$ paired with different anions namely Cl^-–$[OAC]^-$, Cl^-–$[TFA]^-$, Cl^-–$[TFS]^-$, $[OAC]^-$–$[TFA]^-$, and $[OAC]^-$–$[TFS]^-$ (b) cations $[C_2mim]^+$, $[C_6mim]^+$, and $[C_8mim]^+$ coupled with different anions Cl^-–$[MeSO_4]^-$ and Cl^-–$[NTF_2]^-$. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the continuous lines joining data points are only guide to the eye.

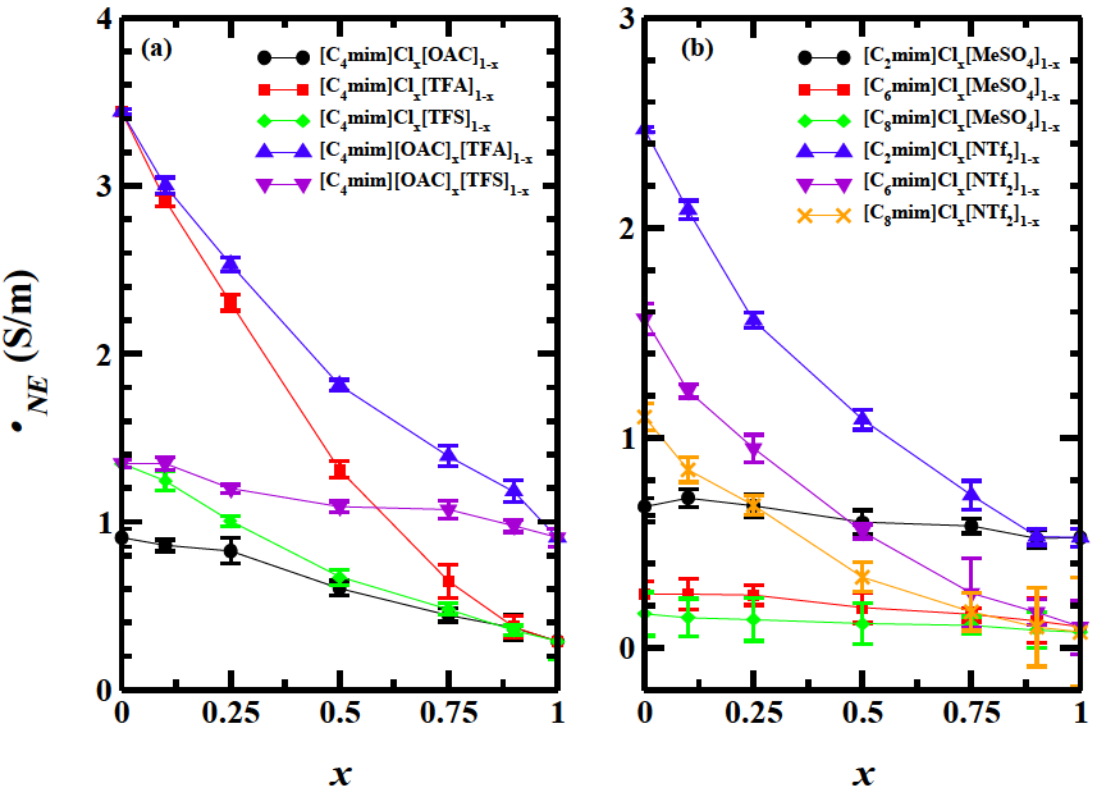


Figure 7: Ionic conductivity computed using Nernst-Einstein (NE) equation (eq. 7) as a function of composition at 353 K: (a) common cation $[C_4mim]^+$ paired with different anions namely Cl^-–$[OAC]^-$, Cl^-–$[TFA]^-$, Cl^-–$[TFS]^-$, $[OAC]^-$–$[TFA]^-$, and $[OAC]^-$–$[TFS]^-$ (b) cations $[C_2mim]^+$, $[C_6mim]^+$, and $[C_8mim]^+$ coupled with different anions Cl^-–$[MeSO_4]^-$ and Cl^-–$[NTF_2]^-$. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the continuous lines joining data points are only guide to the eye.

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