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Influence of the anion on ionic liquids mixtures properties: A molecular dynamics study

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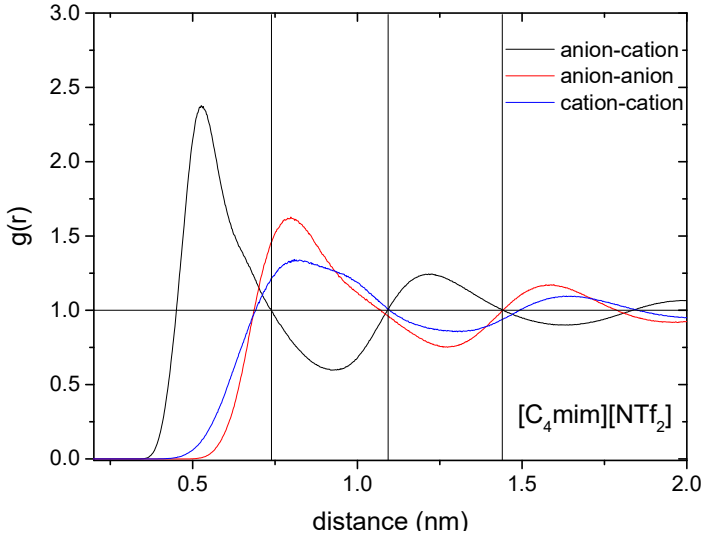


Figure S1. Period estimation – intersection with asymptote on the example of ionic liquid $[C_4mim][NTf_2]$

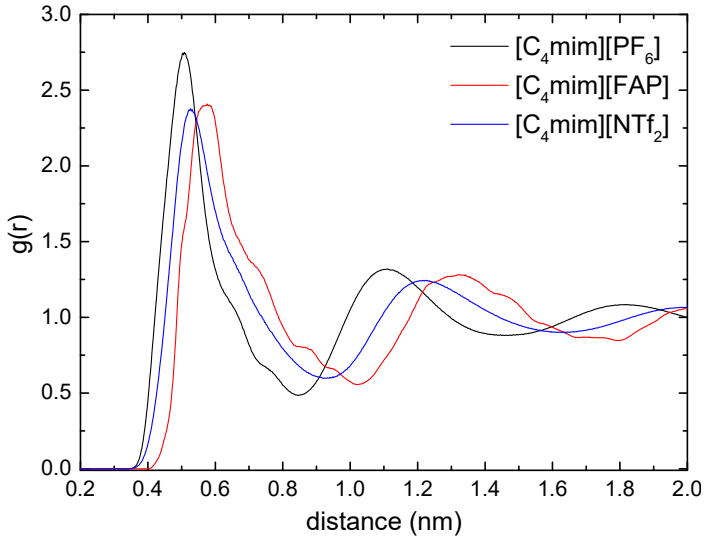
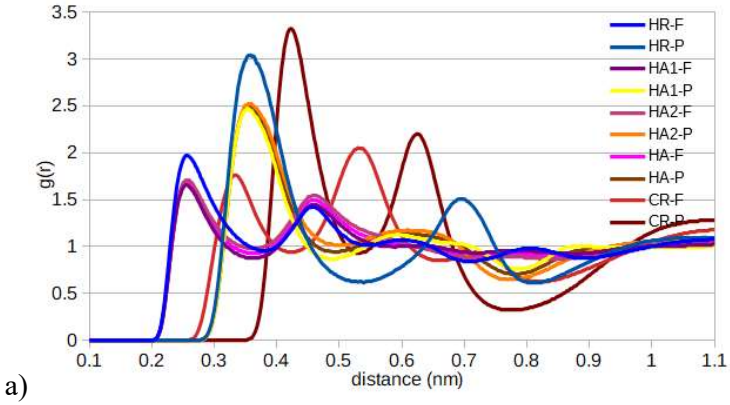


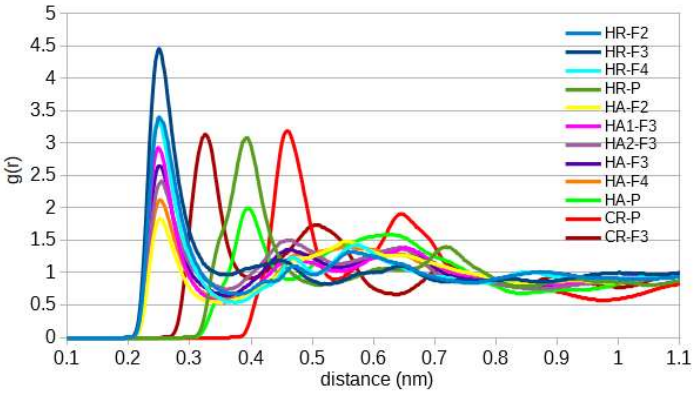
Figure S2. Comparison of cation-anion center-of-mass RDFs in $[C_4mim][PF_6]$ (black), $[C_4mim][FAP]$ (red), and $[C_4mim][NTf_2]$ (blue).

Table S1. Comparison of anion radii, obtained in this work, with literature values.

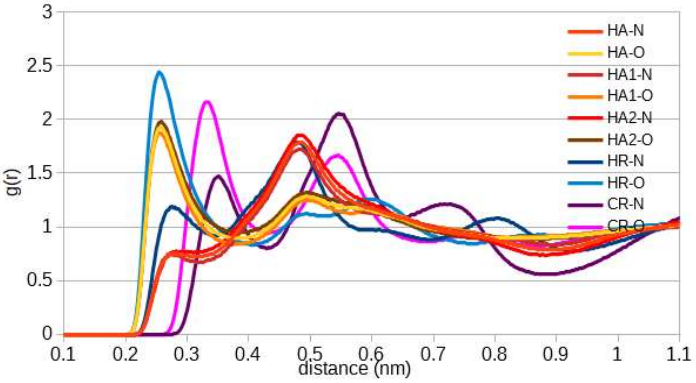
Anion	This work, nm	Literature calculated, nm	Method	Reference
$[PF_6]^-$	0.318			
		0.254	MM2	J. Electrochem. Soc., 141 (12), p.3336, 1994
		0.254	MM2	J. Electrochem. Soc., 149 (10), A1385-A1388, 2002
		0.291	COSMO	Electrochim. Acta 114, p. 95 (2013)
$[NTf_2]^-$	0.356			
		0.325	MM2	J. Electrochem. Soc., 141 (12), p.3336, 1994
		0.327	MM2	J. Electrochem. Soc., 149 (10), A1385-A1388, 2002
		0.39	AAV	Fluid Phase Equilibr., 263 (1), p. 26 (2008)
$[FAP]^-$	0.447			
		0.425	COSMO	Electrochim. Acta 114, p. 95 (2013)



a)



b)



c)

Figure S3. Atom-atom RDFs for between the most important sites of cation and anion $[PF_6]^-$ (a), $[FAP]^-$ (b) and $[NTf_2]^-$ (c). As it can be seen, RDFs, involving atoms HA1 and HA2 are not distinguishable. Therefore, for further analysis the sites HA, HR, CR, as well as P and F for $[PF_6]^-$, O for $[NTf_2]^-$, and P and F3 for $[FAP]^-$ were chosen.

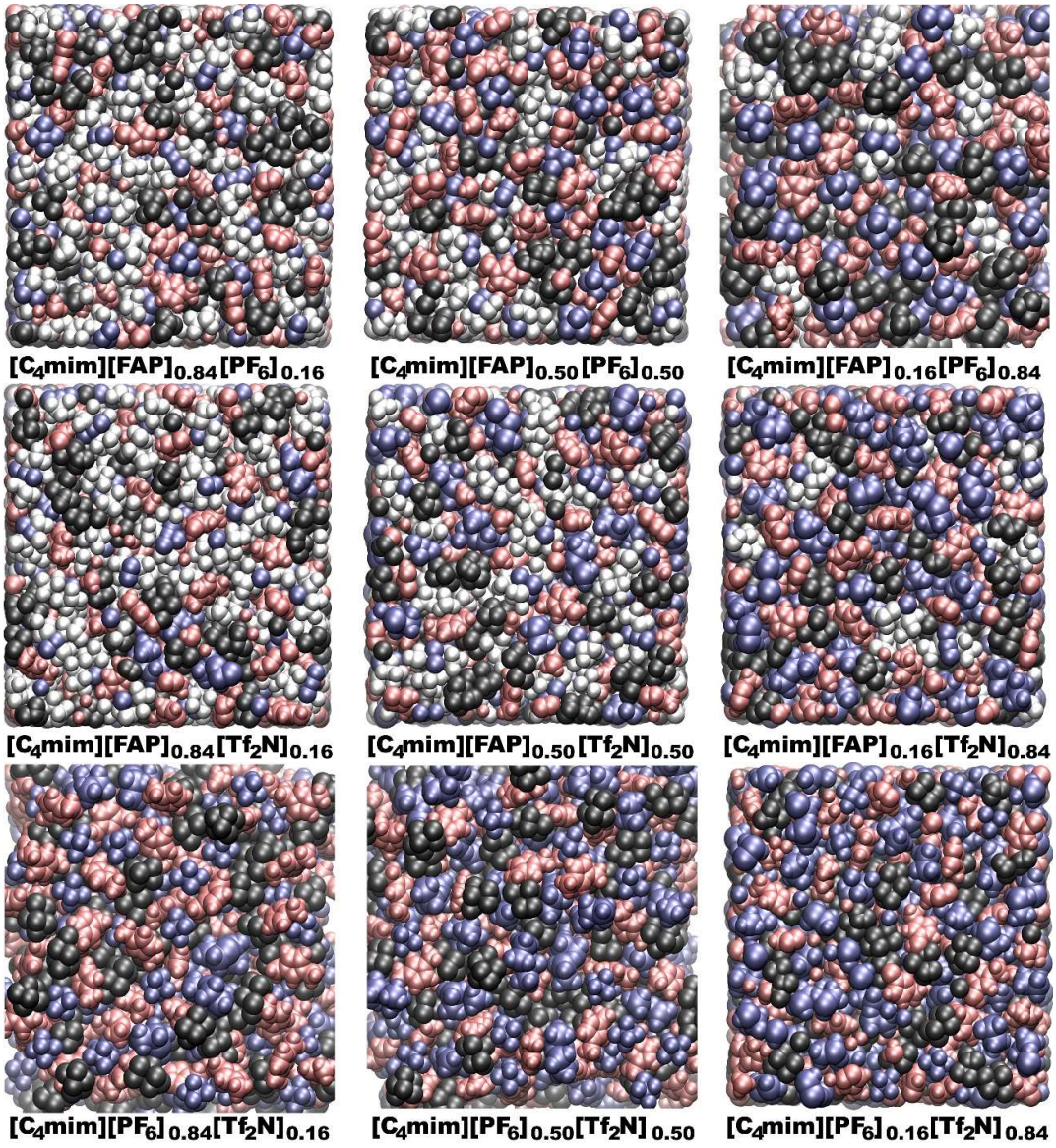
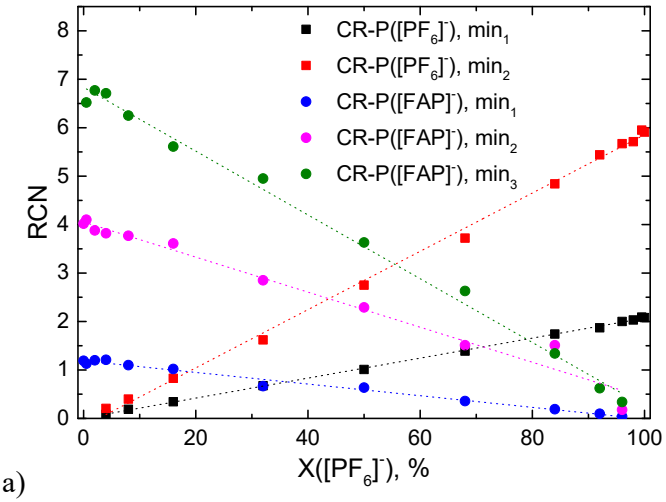
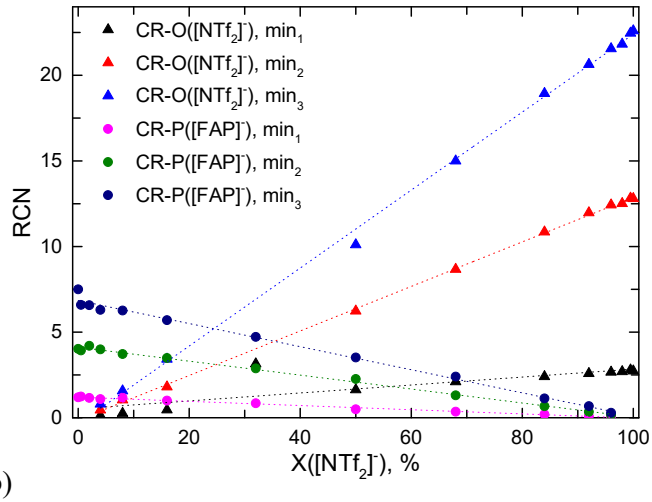


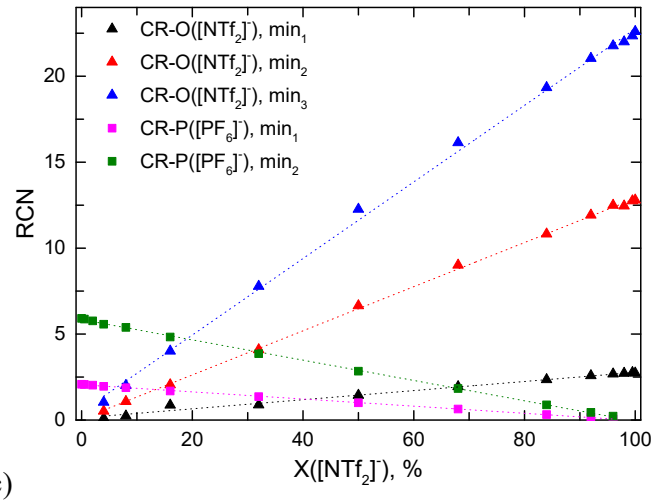
Figure S4. Snapshots of selected simulations cells, containing studied ILs mixtures with different concentrations of respective anions. The color code is as follows: the charged parts of cations (i.e. ring atoms and directly attached to it atoms + methyl group and α-methylene group of butyl-substituent) are pink, the non-polar side chain of cations is grey, the $[PF_6]^-$, $[NTf_2]^-$ and charged part of $[FAP]^-$-anions (phosphorous atom + tree directly attached fluoride atoms) are blue, and the perfluoroalkyl tails of $[FAP]^-$ are white. This color codes facilitate the identification of polar and non-polar domains in the studied mixtures and transition of more nano-segregated systems (mixtures with high content of $[FAP]^-$-anion) to homogeneous mixtures (mixtures with low content of $[FAP]^-$-anion).



a)



b)



c)

Figure S5. Coordination number of anion atoms P([PF_6]$^-$), O, P([FAP]$^-$) in first coordination shell of cation atom CR for Mix1 (a), Mix2 (b), and Mix3(c), obtained from site-site RDFs, resulted from molecular dynamics simulations at 303 K.

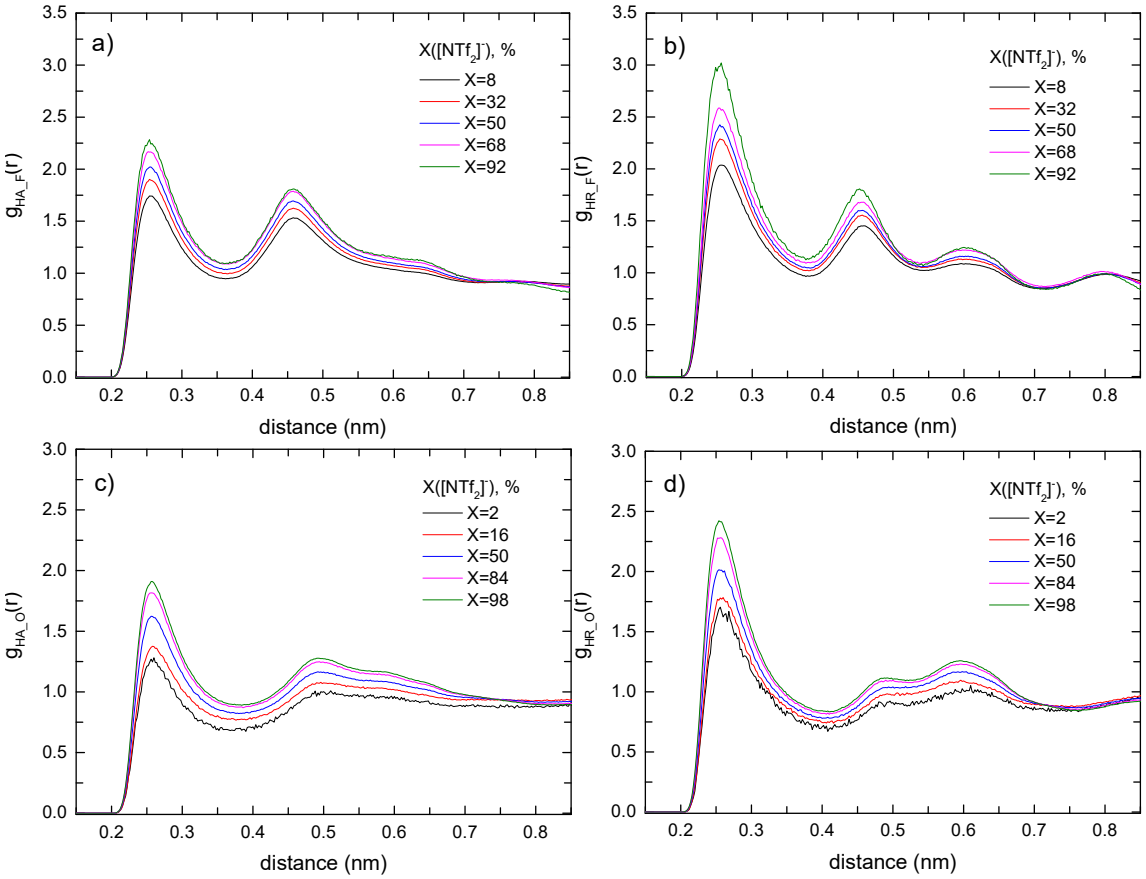


Figure S6. Radial distribution functions between a) HA cation atom and F $[PF_6]^-$-anion atom; b) HR cation atom and F $[PF_6]^-$-anion atom; c) HA cation atom and O $[NTf_2]^-$-anion atom; d) HR cation atom and O $[NTf_2]^-$-anion atom for the $[C_4mim][PF_6]/[NTf_2]$ mixture with a mole fraction of $[C_4mim][NTf_2]$ of 2, 8, 16, 32, 50, 84, 68, 92 and 98%, derived from molecular dynamics simulation at 303 K.

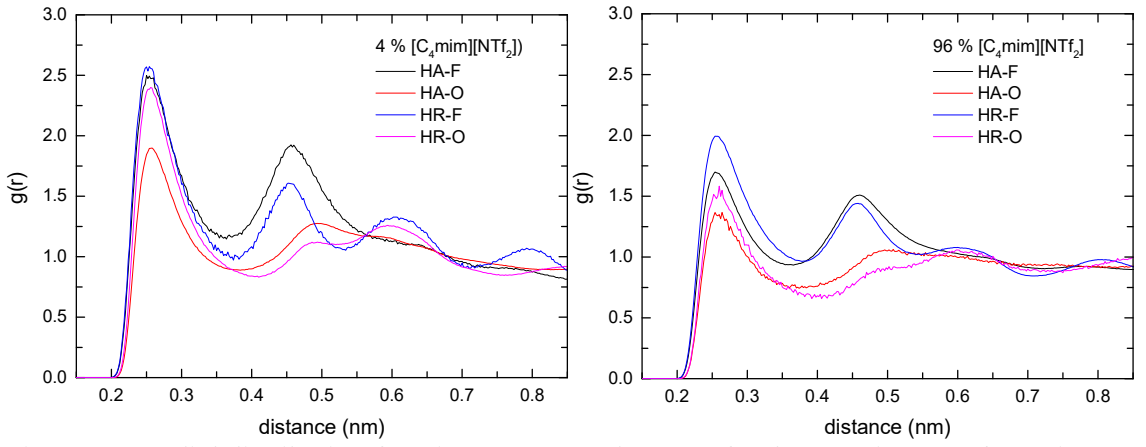


Figure S7. Radial distribution functions, HX-F and HX-O, for the $[C_4mim][PF_6]/[C4mim][NTf_2]$ mixture with a mole fraction of $[C_4mim][NTf_2]$ of 4 % (a) and 96 % (b), derived from molecular dynamics simulation at 303 K.

Table S2. Self-diffusion coefficient for the Cation, D_{+}, Anion1 (initial), $D_{(anion1)}$, Anion2 (added), $D_{(anion2)}$, and total diffusion, $D_{(total)}$, obtained from MD simulations at 303 K

IL / ILs mixture	D_{+}, $\cdot 10^{-11}$ m^2 s^{-1}	$D_{(Anion1)}$, $\cdot 10^{-11}$ m^2 s^{-1}	$D_{(Anion2)}$, $\cdot 10^{-11}$ m^2 s^{-1}	$D_{(total)}$, $\cdot 10^{-11}$ m^2 s^{-1}
Pure ionic liquids				
$[C_4mim][PF_6]^{*}$	0.47 ± 0.08	0.31 ± 0.07	--	0.78
$[C_4mim][NTf_2]^{**}$	1.01 ± 0.01	0.91 ± 0.03	--	1.92
$[C_4mim][FAP]$	0.025 ± 0.001	0.021 ± 0.002	--	0.046
Mix1; Anion1 = $[FAP]^{-}$, Anion2 = $[PF_6]^{-}$				
$[C_4mim][FAP]_{92}[PF_6]_8$	0.025 ± 0.001	0.017 ± 0.001	0.013 ± 0.002	0.055
$[C_4mim][FAP]_{84}[PF_6]_{16}$	0.029 ± 0.003	0.022 ± 0.002	0.018 ± 0.002	0.070
$[C_4mim][FAP]_{50}[PF_6]_{50}$	0.034 ± 0.002	0.025 ± 0.001	0.021 ± 0.001	0.080
$[C_4mim][FAP]_{16}[PF_6]_{84}$	0.13 ± 0.01	0.035 ± 0.03	0.078 ± 0.04	0.243
$[C_4mim][FAP]_8[PF_6]_{92}$	0.31 ± 0.01	0.11 ± 0.02	0.20 ± 0.01	0.62
Mix2; Anion1 = $[FAP]^{-}$, Anion2 = $[NTf_2]^{-}$				
$[C_4mim][FAP]_{92}[NTf_2]_8$	0.022 ± 0.002	0.021 ± 0.002	0.014 ± 0.002	0.057
$[C_4mim][FAP]_{84}[NTf_2]_{16}$	0.024 ± 0.001	0.023 ± 0.001	0.015 ± 0.002	0.062
$[C_4mim][FAP]_{50}[NTf_2]_{50}$	0.041 ± 0.002	0.033 ± 0.001	0.031 ± 0.001	0.105
$[C_4mim][FAP]_{16}[NTf_2]_{84}$	0.25 ± 0.01	0.15 ± 0.04	0.18 ± 0.03	0.58
$[C_4mim][FAP]_8[NTf_2]_{92}$	0.65 ± 0.06	0.43 ± 0.05	0.58 ± 0.03	1.66
Mix3; Anion1 = $[PF_6]^{-}$, Anion2 = $[NTf_2]^{-}$				
$[C_4mim][PF_6]_{92}[NTf_2]_8$	0.59 ± 0.01	0.29 ± 0.01	0.33 ± 0.03	1.21
$[C_4mim][PF_6]_{84}[NTf_2]_{16}$	0.69 ± 0.02	0.42 ± 0.01	0.56 ± 0.01	1.67
$[C_4mim][PF_6]_{50}[NTf_2]_{50}$	0.51 ± 0.02	0.33 ± 0.04	0.43 ± 0.03	1.27
$[C_4mim][PF_6]_{16}[NTf_2]_{84}$	0.72 ± 0.01	0.54 ± 0.01	0.63 ± 0.09	1.89
$[C_4mim][PF_6]_8[NTf_2]_{92}$	0.74 ± 0.07	0.53 ± 0.08	0.57 ± 0.01	1.84

* - experimental value[1]: $D_{+} = 0.89 \cdot 10^{-11}$ m^2 s^{-1}; $D_{-} = 0.71 \cdot 10^{-11}$ m^2 s^{-1}.

** - experimental value[1]: $D_{+} = 3.4 \cdot 10^{-11}$ m^2 s^{-1}; $D_{-} = 2.6 \cdot 10^{-11}$ m^2 s^{-1}.

1. Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M., How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *The Journal of Physical Chemistry B* **2006,** *110* (39), 19593-19600.