Supporting Information for

NMR Measurements of Solute Diffusion in Ionic Liquids

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A. Viscosity Parameterizations: Viscosity data were collected in 5 K increments over the temperature range 278 – 338 K and fit to the equation:

$$\ln(\eta / \text{cP}) = A + \frac{B}{(T - T_0)} \qquad (1)$$

Parameters of these fits and the value calculated for 25 °C are listed in Table SI-1. The present parameterizations of the $[Pr_{n1}][Tf_2N]$ series liquids are all new measurements; we believe them to be more accurate than those previously reported Ref. [1]. In order to render the fit parameters more meaningful, when fitting to Eq. 1 we include a point at the glass transition temperature with an estimated viscosity of 10^{13} mPa s, as recommended by Angel and coworkers. [2]

Table SI-1: Parameters of Temperature-Dependent Viscosity Fits

Ionic Liquid	T_g[(a)] / K	A	B / K	T_0 / K	η(25 °C) / mPa s	Ref.
$[Pr_{31}][Tf_2N]$	183	-1.998	868	156	60.4	this work
$[Pr_{41}][Tf_2N]$	184	-2.029	901	156	73.6	this work
$[Pr_{51}][Tf_2N]$	187	-2.272	965	157	95.7	this work
$[Pr_{61}][Tf_2N]$	191	-2.079	920	162	109	this work
$[Pr_{81}][Tf_2N]$	190	-2.395	1026	158	139	this work
$[Pr_{10,1}][Tf_2N]$	191	-2.568	1096	157	183	this work
$[Pr_{14,6,6,6}][Tf_2N]$	197	-2.025	1047	164	327	this work
$[Im_{41}][BF_4]$	188	-2.468	1025	156	114	1
$[Im_{41}][PF_6]$	191	-2.586	1108	157	196	1
$[Im_{41}][Tf_2N]$	186	-1.819	781	161	48.8	1

(a) Glass transition temperatures of the $[Pr_{n1}][Tf_2N]$ series from unpublished measurements by James Wishart and that for $[Pr_{14,6,6,6}][Tf_2N]$ from Ref. 3.

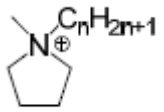
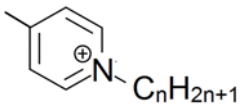
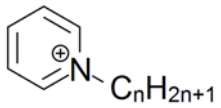
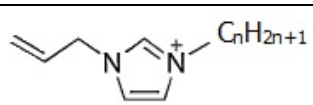
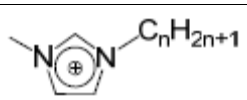
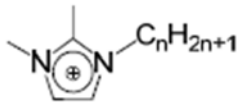
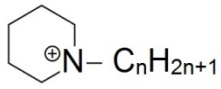
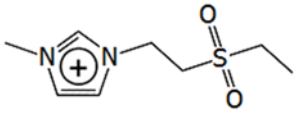
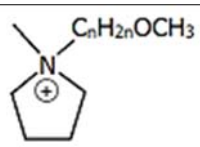
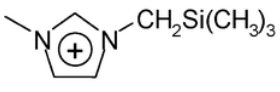
B. Comparisons to Literature Diffusion Coefficients: Comparison is only made to literature data with ±5 K of the default temperature 298 K. Differences in temperature are compensated by comparing the group $D\eta/T$, which is expected to be approximately constant over small temperature ranges.

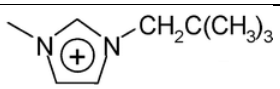
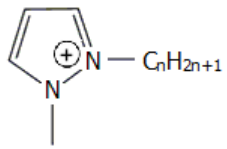
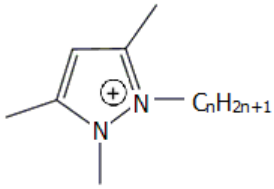
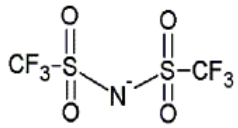
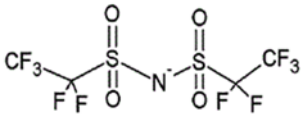
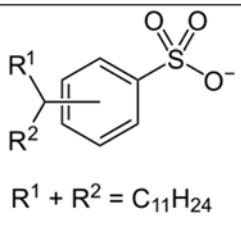
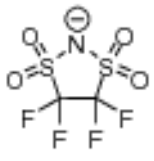
Table SI-2: Comparison of NMR-Based Measurements of Dilute Solute Diffusion Coefficients to Literature Values

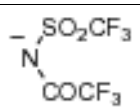
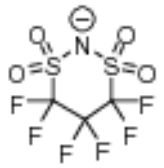
#	Solute	IL	T /K	η /mPa s	$D/10^{-12}$ m^2 s^{-1}	$D\eta/T$	Δ	Reference	Technique
1	ferrocene	$[Im_{41}][BF_4]$	298	114	16.4	6.3	--	this work	^{1}H NMR
			296	**128**	8.7	3.8	-40%	4	cyclic voltammetry
			293	**133**	8.8	4.0	-36%	5	cyclic voltammetry
			299	109	18.3	6.7	+6%	6	chronoamperometry
			295	**123**	4.0	1.7	-73%	7	cyclic voltammetry
2	ferrocene	$[Pr_{41}][Tf_2N]$	298	74	27	6.7	--	this work	^{1}H NMR
			303	**62**	22.1	4.5	-33%	8	rotating disk
			293	94	7	2.2	-67%	9	cyclic voltammetry
			296	81	14.6	4.0	-41%	4	cyclic voltammetry
			299	72	23.1	5.5	-18%	6	chronoamperometry
			298	**67**	34	7.6	+14%	10	chronoamperometry
3	cobaltocinium	$[Im_{41}][BF_4]$	298	115	11.3	4.4	--	this work	^{1}H NMR
			296	**128**	6.1	2.6	-39%	11	cyclic voltammetry
			299	109	11.1	4.1	-7%	6	chronoamperometry
4	cobaltocinium	$[Pr_{41}][Tf_2N]$	298	74	14.2	3.5	--	this work	^{1}H NMR
			299	72	14.5	3.5	-2%	6	chronoamperometry
5	benzophenone	$[Im_{41}][BF_4]$	298	115	13.3	5.1	--	this work	^{1}H NMR
			298	**110**	18	6.6	+29%	12	transient grating
6	benzophenone	$[Im_{41}][Tf_2N]$	298	49	27.7	4.6	--	this work	^{1}H NMR
			298	**55**	34	6.3	+38%	12	transient grating
			293	61	11	2.3	-50%	13	cyclic voltammetry
7	benzophenone	$[Pr_{41}][Tf_2N]$	298	75	22.7	5.7	--	this work	^{1}H NMR
			293	94	25	8.0	+40%	13	cyclic voltammetry
8	anthracene	$[Im_{41}][Tf_2N]$	298	49	28.3	4.6		this work	^{1}H NMR
			293	61	28	5.8	+26%	14	cyclic voltammetry
9	anthracene	$[Im_{21}][Tf_2N]$	298	35	42.1	5.0		this work	1H NMR
			293	42	53	7.7	+54%	14	cyclic voltammetry
10	anthracene	$[Im_{41}][PF_6]$	298	196	10.9	7.2		this work	^{1}H NMR
			293	265	56	50.6	+601%	14	cyclic voltammetry

Viscosities indicated in bold type were those reported with the diffusion data. All other viscosities were calculated using the parameterizations in Table SI-1. Δ denotes the percentage deviation between literature values of $D\eta/T$ and those measured here.

C. Ionic Liquid Abbreviations: Many ionic liquids are represented by several different abbreviations throughout the literature. Here, we identify the abbreviations we have chosen to use for a given ionic liquid or family of ionic liquids. Abbreviations that are not presented here are as given in the reference from which the data derived.

Abbrev. this work	Other Abbrev.	IUPAC name	Structure
Pr_{n1}	P_{n1}, Xmpy, Xmp, XmPYR *See Note	N-Alkyl-N-methyl-pyrrolidinium	
$1Py_n$	Xmpy * See Note	N-Alkyl-4-methyl-pyridinium	
Py_n	Xpy, C_n-py * See Note	N-Alkyl-pyridinium	
Im_{nA}	ABIm	1-Alkyl-3-allyl-imidazolium	
Im_{n1}	$C_n$mim, Xmim * See Note	1-Alkyl-3-methyl-imidazolium	
Imm_{n1}	Xmmim * See Note	1-Alkyl-2,3-dimethylimidazolium	
Pp_{n1}	MXpip * See Note	N-alkyl-N-methyl-piperidinium	
desmim		1-(2-ethylsulfonyl)ethyl-3-methyl-imidazolium	
$Pr_{(no1)1}$	PYR_{1no1} * See Note	N-methoxyalkyl-N-methylpyrrolidinium	
Si-mim		1-Methyl-3-trimethylsilylmethyl-imidazolium	

C-mim		1-Methyl-3-neopentylimidazolium	
Xmpz * See Note		1-Alkyl-2-methylpyrazolium	
Xm_3pz * See Note		1-Alkyl-2,3,5-trimethylpyrazolium	
Tf_2N	NTf_2, TFSI, TFSA, C_1C_1	Bis(trifluoromethylsulfonyl)imide	
BETI	BETA, C_2C_2	Bis(pentafluoroethylsulfonyl)imide	
DBS		Dodecylbenzenesulfonate	
DCA	C_2N_3	Dicyanamide	$(NC)_2N^-$
DEP		Diethylphosphate	$P(OCH_3)_2O_2^-$
$EtSO_4$		Ethylsulfate	$CH3CH2OSO_3^-$
FAP		Tris(pentafluoroethyl)trifluoro-phosphate	$P(C_2F_5)_3F_3^-$
TFA	CF_3OO	Trifluoroacetate	$CO_2CF_3^-$
TfO	OTf, TFMS	Trifluoromethylsulfonate, triflate,	$SO_3CF_3^-$
FTFSI	FTA, C_0C_1	Fluorosulfonyl-(trifluoromethanesulfonyl)imide	$N(SO_2F)(SO_2CF_3)$
CTFSA		1,2,3-dithiazolidine-4,4,5,5-tetrafluoro-1,1,3,3-tetraoxide	

TSAC		2,2,2-Trifluoro-N-(trifluoromethylsulfonyl)acetamide	
FSA	FSI, C_0C_0	Bis(fluorosulfonyl)imide	$N(SO_2F)_2$
C3FSA		1,2,3-dithiazolidine-4,4,5,5,6,6-hexafluoro-1,1,3,3-tetraoxide	
C_1C_2		(Pentafluoroethylsulfonyl) (trifluoromethylsulfonyl)imide	$N(SO_2CF_3)(SO_2C_2F_5)$
C_1C_4		(Nonafluorobutylsulfonyl)(trifluoro methylsulfonyl)imide	$N(SO_2CF_3)(SO_2C_4F_9)$
C_4C_4		Bis(pentafluorobutylsulfonyl)imide	$N(SO_2\ C_4F_9)(SO_2C_4F_9)$

* n = number of carbon atoms in an n-alkyl chain and X= alkyl abbrev. such as "B" for butyl, etc.

D. Data Compilations: Compilations of data measured in this study as well as data collected from literature sources are provided in the form of a separate Microsoft Excel document. Below are some notes to these tables. In all cases we searched the literature to find relevant data measured near to room temperature. We do not attempt to be complete in these data summaries. Rather our purpose was to gather together sufficient data on a broad range of solutes and solvents in order to provide a representative sampling. The volumes in these tables are van der Waal volumes estimated from atomic increments.[15] When a single volume is provided for an ionic liquid solvent it is the average of cation and anion van der Waals volumes. η denotes solution (or solvent) viscosity in units of mPa s.

SI-3: Summary of Literature Data on Diffusion of Constituent Ions of Neat Ionic Liquids: The data summarized in Table SI-3 were all measured using the PFG-NMR method. In many cases parameterized fits of temperature dependent data were available and in such cases values were computed at 298.2 K. With few exceptions, viscosities were taken from the same sources as were the diffusion data.

SI-4: Diffusion Coefficients Measured in This Work: Data in ionic liquids measured here are summarized in Table SI-4. In nearly all cases, ^{1}H PFG-NMR measurements provided both diffusion coefficients of a dilute (<50 mM) solute and the ionic liquid cation. The latter values can be used to assess the uncertainty in the diffusion coefficients and the extent of the perturbation caused by the solute. Hexafluorophosphate anion diffusion coefficients were measured using 31P PFG-NMR.

Table SI-5: **Summary of Literature Data on Dilute Solute Diffusion in Ionic Liquids**:

Table SI-6: Summary of Literature Data on Dilute Solute Diffusion in Conventional Solvents:

Table SI-7: Aromatic Solute Diffusion Coefficients from This Work: These data on diffusion of aromatic solutes in alcohol solvents were collected using 1H-PFG-NMR in order to supplement the literature data displayed in Fig. 8.

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