Density, Viscosity, and Conductivity of [VAIM][TFSI] in Mixtures for Lithium-Ion Battery Electrolytes

Cai, Yingjun; von Solms, Nicolas; Zhang, Suojing; Thomsen, Kaj

Published in:
Journal of Chemical and Engineering Data

Link to article, DOI:
[10.1021/acs.jced.9b00648](https://doi.org/10.1021/acs.jced.9b00648)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Cai, Y., von Solms, N., Zhang, S., & Thomsen, K. (2020). Density, Viscosity, and Conductivity of [VAIM][TFSI] in Mixtures for Lithium-Ion Battery Electrolytes. *Journal of Chemical and Engineering Data*, 65(2), 495-502.
<https://doi.org/10.1021/acs.jced.9b00648>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Density, viscosity, and conductivity of [VAIM][TFSI] in mixtures for lithium ion battery electrolytes

Yingjun Cai^{†,‡}, Nicolas von Solms[†], Suojiang Zhang[‡], Kaj Thomsen^{†*}

[†]Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, 2800, Kgs. Lyngby, Denmark

kth@kt.dtu.dk*

[‡]Beijing Key Laboratory of Ionic Liquids Clean Process, CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China

ABSTRACT

A novel unsaturated and amide-based ionic liquid [VAIM][TFSI] (3-(2-amino-2-oxoethyl)-1-vinylimidazolium bis(trifluoromethylsulfonyl)amide) was synthesized using a two-step method. Its structure was confirmed by nuclear magnetic resonance (NMR), and its water content was determined by Karl Fischer titration to be below 0.03 wt %. Density, viscosity, and conductivity of the pure ionic liquid and its binary mixtures with acetonitrile were measured at various temperatures and at ambient pressure. Both density and viscosity increase with the mole fraction of ionic liquid and decrease with decreasing temperature. Excess molar volumes and viscosity deviations were calculated from the experimental results. The electrical conductivities in mixtures with different content of ionic liquid were investigated at different temperatures. The highest conductivity of binary mixtures is achieved at 0.07 mole fraction, the value is $\sim 3.32 \text{ S} \cdot \text{m}^{-1}$ at 298.15 K. The conductivity of an electrolyte consisting of acetonitrile, LiTFSI, and ionic liquid was measured to determine the optimal ionic liquid content. The suggested concentration is 3 wt% ionic liquid in this electrolyte giving a conductivity of $\sim 4.11 \text{ S} \cdot \text{m}^{-1}$ at 298.15 K.

Keywords: Ionic liquids, Imidazolium-based, Lithium ion battery, Physicochemical property, Conductivity.

Introduction

Ionic liquids (ILs) are a class of molten salts that are composed entirely of large organic cations and organic or inorganic anions. Due to their unique properties, such as low melting point (below 373K), high thermal stability, non-flammability and negligible vapor pressure,¹⁻⁴ ILs have been

widely employed in numerous fields such as separations,^{5,6} catalysis,⁷ and chemical reactions.^{8,9} Applications of ILs also have been introduced in electrochemistry, especially related to electrochemical storage^{10,11} and electrodeposition,¹² owing to their promising special properties, for instance, high electrical conductivity,^{13,14} suitable electrochemical stability, and large electrochemical window.¹⁵

Ionic liquids form a gigantic system. Billions of different ionic liquids can be synthesized. Ionic liquids with imidazolium based cations are often selected as a component of electrolytes due to their lower viscosity and melting point.¹⁶⁻¹⁹ Pal and Ghosh,²⁰ Wang et al.²¹ and Yang et al.²², reported the use of these ionic liquids in gel polymer electrolytes. Nevertheless, these ionic liquids were usually used as additives in liquid electrolytes in spite of their higher density and viscosity than electrolytes. Nguyen et al.²³ synthesized a series of imidazolium-based zwitterionic ionic liquids as additives for lithium battery electrolytes to improve their cyclic performance. Wang et al.¹ prepared functionalized ILs based on imidazolium cations with vinyl or allyl groups as film-forming additives to enhance the capacity of lithium batteries. Recently, new studies²⁴ have focused on multifunctional ionic liquids to enhance the performance of lithium batteries.

Acetonitrile has a convenient liquid range and a high dielectric constant (38.8).²⁵ It is therefore often used as solvent in electric devices such as lithium batteries and supercapacitors.²⁶ Acetonitrile can easily dissolve solutes exhibiting excellent ionic conductivity that may contribute to the development of fast-charging lithium batteries. Yamada et al.²⁵ developed a series of acetonitrile-based superconcentrated electrolytes for fast-charging lithium batteries. Nilsson et al.²⁷ used highly concentrated LiTFSI- acetonitrile electrolytes to stabilize graphite electrodes in lithium-ion batteries. Mo et al.²⁸ enhanced the cyclic stability of supercapacitors using acetonitrile electrolytes.

In this work we present the synthesis path for a new type of multifunctional imidazolium based ionic liquid, 3-(2-amino-2-oxoethyl)-1-vinylimidazolium bis(trifluoromethylsulfonyl)amide ([VAIM][TFSI]). The reason why we chose this IL was that it contains two functional groups that are expected to be beneficial for the Li-ion battery. One functional group is unsaturated and is expected to be able to contribute to the formation of the SEI film. The other group is the alkaline group which might help to decrease the content of water and HF. Thermodynamic, electrochemical and transport properties of the pure ionic liquid were determined. Properties of binary mixtures of [VAIM][TFSI] and acetonitrile were measured at temperatures from 298.15 to

333.15 K and at ambient pressure. Effects of different content of ionic liquid in acetonitrile on density, viscosity and conductivity were investigated, enabling the choice of a suitable content of ionic liquid used in the electrolytes.

Experimental methods

Chemicals and Materials. 1-vinyl imidazole (99.0%, Sigma-aldrich) and 2-chloroacetamide (98.0%, Sigma-aldrich) were used to synthesize an intermediate product for the ionic liquid. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.5%), purchased from DoDochem Co., was used for the final product. Acetonitrile (99%, Sigma-aldrich) was used as reaction solvent and as a component of the binary mixtures. Ethanol from Sigma-aldrich was used to wash glasses. Ultrapure water directly from Direct-Q 3 ultrapure water system was used as reaction solvent for the final ionic liquid and for its purification. All chemicals were used directly without further purification. Data on the reagents used are summarized in Table 1.

Table 1. CAS Registry Number, Source and Mass Fraction Purity of the Chemicals

IUPAC Name	CAS Reg. No.	Source	Purity	Analysis Method
1-Ethenylimidazole	1072-63-5	Sigma-Aldrich	0.99	GC ^a
2-Chloroacetamide	79-07-2	Sigma-Aldrich	0.98	HPLC ^b
Lithium bis(trifluoromethylsulfonyl)azanide	90076-65-6	www.DoDochem.com	0.995	ICP ^c , IC ^d
Acetonitrile	75-05-8	Sigma-Aldrich	0.99	GC ^a
Dichloromethane	75-09-2	Sigma-Aldrich	0.99	GC ^a
3-(2-amino-2-oxoethyl)-1- vinylimidazolium bis(trifluoromethylsulfonyl)amide	2365111-84-6	Self-synthesized	>0.99	NMR ^e

^aGas Chromatograph; ^bHigh-performance Liquid Chromatography; ^cInductively Coupled Plasma; ^dIon Chromatography; ^eNuclear magnetic resonance.

Preparation of [VAIM][TFSI]. The target ionic liquid was synthesized using a two-step process. Firstly, 40 g 1-vinyl imidazole and 45 g 2-chloroacetamide were dissolved in acetonitrile at 323.15K for about 30 minutes, then reacted in a flask under stirring at 343.15 K for 1 h. A white blocky intermediate, 3-(2-amino-2-oxoethyl)-1-vinylimidazolium chloride was obtained. It was washed and filtered with acetonitrile after being crushed, and dried in vacuum oven for 2 hours. In the second step, 32.8 g 3-(2-amino-2-oxoethyl)-1-vinylimidazolium chloride and 51.2 g lithium bis(trifluoromethylsulfonyl) imide were dissolved in water and reacted in a flask at room

temperature for 2 hours. After the reaction, the solution separated in two layers. The upper layer was a water phase, and the lower layer was the ionic liquid phase. The desired ionic liquid [VAIM][TFSI] was washed with water under the protection of a layer of dichloromethane until chloride ions could not be detected in the wash water using AgNO_3 .²⁹ The ionic liquid was dried in a vacuum oven at 343.15 K for more than one week before its physicochemical properties were measured. The ^1H NMR spectrum showed almost no impurity peaks except for water. The chemical shifts of the peaks corresponded to the structure of [VAIM][TFSI] shown in Figure S1. The water content of this sample was measured to be less than 0.03 wt % by Karl Fischer titration (Mettler-Toledo C20X). Characteristic peaks and ^1H NMR data for [VAIM][TFSI] are shown in the Supporting Information. The synthesis pathway and the structure of [VAIM][TFSI] are shown in Figure 1.

Figure 1. The synthesis pathway and the structure of ionic liquid [VAIM][TFSI].

Thermal Analysis. The thermal decomposition temperature of the pure ionic liquid [VAIM][TFSI] was determined on a Discovery TGA from TA Instruments in a nitrogen atmosphere with a heating rate of 10 K min⁻¹ from room temperature to 1173.15 K. The glass transition point of pure ionic liquid was measured on a differential scanning calorimetry (DSC) System (Ta Instruments) in a nitrogen atmosphere with a heating and cooling rate of 10 K min⁻¹ from 213.15 K to 273.15 K, with an accuracy of ± 0.1 K.

Conductivity Measurements. The conductivities of the ionic liquid and its binary mixtures were measured in a three-electrode electrolytic cell connected with a CHI 660E Electrochemical Workstation. The cell was immersed in a thermostatic silicone oil bath, in which the temperature was kept constant with a ± 0.01 K accuracy. The cell constant ($C = 324.56 \pm 0.01 \text{ m}^{-1}$) was determined using standard aqueous potassium chloride solutions ($\sigma = 1.28 \pm 0.005 \text{ S} \cdot \text{m}^{-1}$, at 298.15

K).^{30, 31} This corresponds to a relative standard uncertainty of 0.04 %. All solutions were prepared using an analytical balance (Mettler Toledo AB204) with an accuracy of 0.1 mg.

Density Measurements. The densities of the pure ionic liquid were measured using a 5 mL glass pycnometer, which was placed in a thermostatic bath with an accuracy of 0.01 K. The pycnometer was calibrated by ultra pure water at all temperatures in the relevant range with a precision of $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$. The densities of binary mixtures were measured with the use of Anton Paar DMA 4100 Density meter from 298.15 K to 333.15 K. The density measurements were compared to previously published data³² for pure acetonitrile for validation. The average deviation between the two data sets is 0.065 % (AARD). The data is shown in Table S1.

Viscosity Measurements. The viscosity of pure ionic liquid was measured on a Discovery HR-1 equipment using a disk from 298.15 K to 333.15 K. The viscosities of binary mixtures were determined by a PAAR AMV 200 Viscosity meter which is a falling ball automated viscometer using standardized glass capillaries from 298.15 K to 333.15 K, with an accuracy of 0.01 K. The measurement was carried out in four capillaries (diameters 1.6 mm, 1.8 mm, 3.0 mm and 4.0 mm, respectively) and a matching ball (diameter 1.5 mm, 1.5 mm, 2.5 mm and 3.0 mm, respectively). The viscosity measurements were compared to previously published data³³ for pure acetonitrile for validation. The data is shown in Table S2.

Results and discussion

Thermal Properties of pure ionic liquid [VAIM][TFSI]. The thermal properties of pure ionic liquid [VAIM][TFSI] were evaluated by DSC and TGA analysis. The TGA trace related to the decomposition of [VAIM][TFSI] is shown in Figure S2. The ionic liquid starts decomposing slowly at temperatures near 573.15 K, and the decomposition increases rapidly above 573.15 K. The decomposition reaches a weight loss percentage of $\approx 80\%$ at 673.15 K. The DSC curve in Figure S3 shows that the glass transition point of pure ionic liquid [VAIM][TFSI] is as low as $-243.15 \text{ K} \pm 5 \text{ K}$. The analysis with TGA in combination with DSC shows that the ionic liquid has a conveniently large stable liquid range, useful for a wide temperature adaptability in lithium-ion batteries.

Density and excess molar volume. The experimental densities (ρ) of the pure ionic liquid and its binary mixtures with acetonitrile were measured from 298.15 K to 333.15 K. Table 2 shows the density data of the binary mixtures as a function of mole fraction of ionic liquid at different

temperatures. The densities of samples increase along an asymptotic line with increasing mole fraction. The experimental values of binary mixtures as a function of temperature were fitted with an empirical equation as following:

$$\rho = A + BT \quad (1)$$

where A and B are adjustable parameters, B is a negative value. The densities decrease linearly with increasing temperature, which reflects that the numbers of ions per unit volume reduce with temperature.

From the experimental density values, the molecular volume, V_m of the pure ionic liquid at 298.15 K can be calculated by using the following equation:

$$V_m = M / (N \cdot \rho) \quad (2)$$

where M is the molar mass of the pure ionic liquid [VAIM][TFSI] = 432.1768, N is Avogadro number, ρ is the average experimental density of pure ionic liquid = 1607.1 kg·m⁻³ at 298.15 K. The calculated molecular value V_m of [VAIM][TFSI] is 0.4465 nm³.

The excess molar volume (V^E) of a binary mixture is defined from experimental values using the following equation:³⁴

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (3)$$

In which ρ represents the density of the binary mixture, ρ_1 and ρ_2 represent the densities of ionic liquid and acetonitrile, M_1 and M_2 are the molar masses of ionic liquid and acetonitrile, x_1 and x_2 are the mole fractions of ionic liquid and acetonitrile.

Table 2. Densities (ρ , kg·m⁻³) of the binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

x _{IL}	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K	T = 333.15 K
0.0100	825.6	820.1	814.6	809.1	803.6	798.0	792.4	786.7
0.1000	1090.5	1085.0	1079.6	1074.0	1068.6	1063.0	1057.5	1052.0
0.2010	1258.4	1253.0	1247.7	1242.3	1237.0	1231.6	1226.3	1220.9
0.3026	1361.3	1356.0	1350.8	1345.5	1340.3	1334.7	1329.0	1323.2
0.4011	1426.7	1421.6	1416.4	1411.3	1406.1	1400.9	1395.7	1389.8
1.0000	1607.1	1601.2	1594.4	1588.1	1580.8	1573.7	1567.9	1561.1

^aStandard uncertainties are $u(x_{IL}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Expanded uncertainty for density is $u(\rho) = 1$ kg·m⁻³ (0.95 level of confidence). x_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

The excess molar volumes of mixtures of [VAIM][TFSI] and acetonitrile against mole fraction of ionic liquid are listed in Figure 2 and Table 3. Generally, the excess molar volume is mainly influenced by the intermolecular forces and the differences in size and shape between component molecules.^{35,36} From the molecular masses of the components of mixtures, the large difference in size between acetonitrile molecules and the ions of ionic liquid results in a negative contribution to the excess molar volume V^E values. The small acetonitrile molecule can fit into the free volume between the large ions. The excess molar volumes decrease in magnitude with increasing amount of ionic liquid. This implies that the intermolecular interactions with the ionic liquid become stronger. The most effective packing in the mixture was obtained at about $x_{IL} = 0.3$. At higher IL fractions, the excess molar volumes increase with increase in ionic liquid fraction, and the intermolecular interactions with the ionic liquid become weaker.

Figure 2. Excess molar volumes, V^E , of the binary mixtures [VAIM][TFSI] and acetonitrile as a function of mole fraction of IL at different temperatures: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; ◀, 323.15 K; ▶, 328.15 K; □, 333.15 K, at 0.1 MPa. The lines are tendency lines.

Table 3. Excess Molar Volumes ($V^E \cdot 10^6, \text{m}^3 \cdot \text{mol}^{-1}$) of the binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 333.15 K.

x_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0100	-0.480	-0.490	-0.508	-0.527	-0.551	-0.568	-0.591	-0.609
0.1000	-0.878	-0.937	-1.025	-1.094	-1.198	-1.288	-1.371	-1.474
0.2010	-1.127	-1.211	-1.341	-1.450	-1.606	-1.751	-1.867	-2.013
0.3026	-1.083	-1.183	-1.345	-1.475	-1.671	-1.826	-1.911	-2.042
0.4011	-0.737	-0.858	-1.037	-1.195	-1.417	-1.630	-1.760	-1.892
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

^aStandard uncertainties are $u(x_{IL}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Expanded uncertainty (u) for excess molar volumes is $u_r(V^E) = 0.002 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ (0.95 level of confidence). x_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

In the mixture, the partial molar volume of the ionic liquid was calculated according to the method used by Sastry et al.³⁷ Table 4 shows the calculated partial molar volume of ionic liquid. The partial molar volume of IL, $\bar{V}_{IL}$ increases with increasing concentration of ionic liquid and temperature. This performance indicates stronger interactions between acetonitrile and [VAIM][TFSI] at high concentration of ionic liquid and temperature. The small acetonitrile molecule fits into the free volume between large ions.

Table 4. partial molar volume ($\bar{V}_{IL} \cdot 10^6, \text{m}^3 \cdot \text{mol}^{-1}$) of [VAIM][TFSI] at different temperatures from 298.15 K to 323.15 K, at 0.1 MPa.

x_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K
0.0100	254.7938	254.9314	254.7395	255.0320	254.7437	255.3537
0.1000	258.1710	258.4904	258.6366	259.0320	259.1203	259.6021
0.2010	261.7471	262.2887	262.8128	263.3412	263.8542	264.2584
0.3026	263.7753	264.5238	265.2811	266.0242	266.8195	267.5966
0.4011	264.1029	265.0125	265.8295	266.8425	267.7422	269.2925

^aStandard uncertainties are $u(x_{IL}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Expanded uncertainty (u) for partial molar volume is $u_r(\bar{V}_{IL}) = 0.002 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ (0.95 level of confidence). x_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

Viscosity. The viscosity of pure ionic liquid is shown as a function of temperature in Table 5. It can be seen from the values that the viscosity decreases with increasing temperature. The viscosity follows the fitting asymptotic equation from experimental values $y = a - b \times c^x$, with $a = 3.3850 \pm 0.0001$, $b = -9.4440 \times 10^3 \pm 0.0001$, and $c = 0.8683 \pm 0.0001$. The viscosity of pure ionic liquid was difficult to measure at low temperatures, but it can be calculated from the asymptotic equation. The calculated viscosity is $280.657 \pm 0.001 \text{ Pa} \cdot \text{s}$ at 298.15 K and $140.301 \pm 0.001 \text{ Pa} \cdot \text{s}$ at 303.15 K, respectively. The viscosities of the binary mixtures are lower. These were measured using a

falling ball automated viscometer. As can be seen from Table 5, the viscosities of the mixtures increase with increasing mole fraction of ionic liquid resulting in a much higher viscosity than that of pure acetonitrile.

The temperature dependence of the viscosities of the mixture of ionic liquid and acetonitrile can be calculated by the Vogel–Fulcher– Tammann (VFT) equation.³⁸

$$\eta(T) = A \exp \left(\frac{-B}{T-T_0} \right) \quad (4)$$

Where $\eta(T)$ is viscosity, A, B and T_0 are adjustable parameters. The best fitted parameters and the average absolute relative deviation (AARD %) are listed in Table 6. It was shown that, a remarkable agreement is observed between the calculated and the experimental viscosity data, by using VFT equation. The overall average absolute relative deviation is smaller than 3.05 %.

The experimental viscosity deviations of the binary mixtures are calculated using the Redlich-Kister equation:⁸

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (5)$$

where η , η_1 and η_2 are the viscosities of pure ionic liquid and acetonitrile, x_1 and x_2 are the mole fractions of pure components, ionic liquid and acetonitrile. The viscosity deviation diagrams against x_1 are shown Table 7. It can be seen that the viscosity deviation values are negative over the whole range of mixtures. The minimum value was found at $x_1 \sim 0.5$, at all temperatures. The negative values may be attributed to hydrogen bonding, van der Waals' forces, molecular size and shapes of the components.^{4,39}

Table 5. Viscosities of binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 333.15 K at 0.1 MPa.

Viscosities (η_1 , mPa·s) of the binary mixtures [VAIM][TFSI] and acetonitrile								
x_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.0100	0.67	0.64	0.61	0.57	0.55	0.52	0.48	0.47
0.0500	2.88	2.84	2.71	2.49	2.39	2.26	2.17	2.01
0.1000	10.27	9.97	9.16	8.17	7.74	7.02	6.62	6.07
0.2010	75.29	68.64	59.58	50.56	45.90	40.19	36.78	32.69
0.3026	275.66	246.55	202.32	162.65	142.30	118.63	105.39	89.93
0.4011	805.91	683.34	549.20	423.76	351.61	288.09	232.95	192.74
Viscosities (η_2 , Pa·s) of pure ionic liquid [VAIM][TFSI]								
1.0000	280.66	140.30	71.51	35.30	19.85	12.53	8.60	6.21

^aStandard uncertainties are $u(x_{IL}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty for viscosity is $u_r(\eta) = 0.10$. x_{IL} = mole fraction of ionic liquid. T is the Kelvin Temperature.

Table 6. Fitted Values of the VFT Parameters, A, B and T_0 and AARD for the Viscosities of binary mixtures [VAIM][TFSI] and acetonitrile.

x_{IL}	A	B	T_0	AARD(%)
0.0100	0.069	-415.35	116.64	0.94
0.0500	0.760	-125.91	207.68	1.60
0.1000	3.351	-45.96	261.00	3.05
0.2010	0.632	-747.88	143.59	1.45
0.3026	0.363	-1076.04	137.96	2.10
0.4011	0.037	-1995.16	100.00	1.87

Table 7. Experimental viscosity deviations ($\Delta\eta$, mPa·s) of the binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 318.15 K.

x_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0100	-2806.24	-1402.70	-714.84	-352.68	-198.26	-125.04	-85.82	-61.86
0.1000	-28111.82	-14048.49	-7156.81	-3528.70	-1981.72	-1248.64	-855.74	-616.17
0.2010	-56336.94	-28132.12	-14314.95	-7044.08	-3944.64	-2478.37	-1692.85	-1215.26
0.3026	-84651.24	-42208.76	-21437.98	-10517.99	-5865.21	-3672.87	-2498.40	-1788.70
0.4011	-111765.62	-55591.59	-28135.17	-13733.46	-7611.33	-4737.50	-3218.31	-2297.33
1.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

^aStandard uncertainties are $u(x_{IL}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Expanded uncertainty (u) for viscosity deviation is $u_r(\Delta\eta) = 0.02$ mPa·s (0.95 level of confidence). x_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

Conductivity.

The experimental conductivities of the binary mixtures are listed as functions of the concentration of ionic liquid in Figure 3. The values show increasing conductivity at IL mole fractions below 0.07 and decreasing conductivity at higher IL mole fraction. In the beginning, with the increase of ionic liquid mole fraction, the conductivity increases in the dilute solutions.

In dilute solutions, the amount of charge carriers depends directly on the amount of dissolved solute, and the restriction of molecular motion is lower. Therefore, the conductivity increases with the mole fraction of ionic liquid.

At high ionic liquid concentration, the mixture viscosities are high and the mobility of the charge carriers decrease sharply, the conductivity decrease with the increasing of ionic liquid mole fraction after passing a maximum value at $x_{IL} \sim 0.07$. According to the research of Dorbritz et al.,³⁶ at high concentration of ionic liquid, it can be proved that the amount of charge carriers is

reduced due to aggregate formation. The conductivity increases with increasing temperature in all binary systems.

Conductivities were converted into molar conductivities and are given as a function of ionic liquid concentrations in Table 8. It is shown that the molar conductivity decreases with increasing concentration of ionic liquid at all temperatures.

Figure 3. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the binary mixtures ionic liquid [VAIM][TFSI] and acetonitrile at different temperatures, at 0.1 Mpa. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; ◀, 323.15 K; ▶, 328.15 K; □, 333.15 K. The lines are tendency lines.

Table 8. Molar conductivities ($\Lambda \cdot 10^4$, $\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$) of the binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

χ_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.020	26.670	27.964	29.394	30.688	31.906	33.141	34.364	35.518
0.047	17.327	18.212	19.308	20.293	21.205	22.065	22.964	23.774
0.070	14.064	14.865	15.823	16.765	17.614	18.465	19.382	20.266
0.080	12.750	13.593	14.576	15.477	16.331	17.180	18.039	18.693
0.100	10.615	11.370	12.241	13.178	13.966	14.763	15.600	16.388
0.200	4.132	4.581	5.113	5.645	6.155	6.668	7.218	7.753
0.393	0.831	1.026	1.282	1.563	1.846	2.149	2.493	2.862

^aStandard uncertainties are $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainties (u) for molar conductivity is $u_r(\Lambda) = 0.04$. χ_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

Figure 4. Conductivities (σ , $\text{S} \cdot \text{m}^{-1}$) of electrolytes, with (0 %, 3 wt %, 5 wt % and 44 wt %, respectively) [VAIM][TFSI], variable mass fraction of LiTFSI, and the remaining part acetonitrile at different temperatures, at 0.1 MPa. a) is electrolyte without ionic liquid, b) is electrolyte with 3 wt % ionic liquid, c) is electrolyte with 5 wt % ionic liquid and d) is electrolyte with 44 wt % ionic liquid: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; ◀, 323.15 K; ▶, 328.15 K; □, 333.15 K. The lines are tendency lines.

The electrolyte is an important component in lithium batteries and is usually composed of solvent, lithium salt and additive. Conductivities of electrolytes with different content of ionic liquid as well as lithium salt were measured at different temperatures shown in Figure 4 (a, b, c and d). The conductivity of such electrolytes reflects the migration rate of ions during charging and discharging processes. The conductivity curves of electrolytes with low and high concentration of ionic liquid

have widely different shapes (Figure 4 a, b, c, and d). At low concentration or without ionic liquid, the conductivities are divided into two parts. Firstly, the conductivities increase with increasing lithium salt concentration and reach the highest values at about 30 wt % of LiTFSI, that is because the number density of charge carriers increases with the concentration of lithium salt at lower viscosity and lower density of electrolyte. From Figure 4 (a), it can be seen that the conductivities increase almost linearly as a function of concentration of lithium salt in acetonitrile without ionic liquid. However, the conductivities of the electrolytes with ionic liquid which are affected by both ionic liquid and lithium salt increase nonlinearly shown in Figure 4 (b, c) Subsequently, the conductivities decrease with increasing concentration of lithium salts. That is because the conductivity in this concentration range is affected mainly by viscosity which increases with the concentration of lithium salt. At an ionic liquid concentration of 44 wt %, the conductivity decreases linearly with increasing concentration of lithium salt as shown in Figure 4 (d). From Figure 3, it can be seen that a maximum conductivity value of binary mixtures occurs at an ionic liquid mole fraction $x_{IL} \sim 0.07$ (the weight percent is $\sim 44\%$). The conductivity details of electrolytes with different concentration of lithium salt at various temperatures are listed in Table S4, S5, S6 and S7.

In terms of electrical conductivity, the ionic liquid is better to be used as an additive for lithium batteries from the above values. At low concentration of ionic liquid, the restriction of molecular motion is lower due to the low viscosities of electrolytes. According to marketable electrolytes, the common concentration of lithium salt is from 25 wt % to 30 wt %. During this range, the best concentration of ionic liquid is 3 wt % from the conductivity values of electrolytes. Because of the high viscosity of ionic liquid, the conductivity of electrolyte is much lower at high concentration of ionic liquid. And the high restriction of molecular motion can hinder the diffusion of lithium ions. So we do not recommend adding more ionic liquids.

CONCLUSIONS

The new type of ionic liquid [VAIM][TFSI] was synthesized using a two-step pathway. This kind of ionic liquid exhibits high thermal stability and wide temperature adaptability from 243.15 K to 573.15 K. The densities, viscosities and ionic conductivities of binary mixtures of this ionic liquid in acetonitrile were measured from 298.15 K to 333.15 K. The density of the mixtures increases

with the increasing of ionic liquid mole fraction at all temperatures, and decreases linearly with the increasing of temperature. Similar results were obtained for the viscosity of all systems. The excess molar volumes and viscosity deviations were calculated from experimental data and were all negative. In the binary mixtures with acetonitrile, the molar conductivities decrease with increasing ionic liquid concentration. The highest conductivity of electrolyte with 3 wt % ionic liquid was obtained at a LiTFSI concentration of ~29 wt %. It is suggested from the measured properties that the ionic liquid can be used as an additive in lithium battery electrolyte at a concentration lower than 3 wt % ionic liquid to obtain high mobility and conductivity.

ACKNOWLEDGMENT

The NMR spectrum was measured by Dr. Kasper Enemark-Rasmussen at the NMR Center • DTU supported by the Villum foundation.

FUNDING

The work was supported by the China Scholarship Council and by the Department of Chemical Engineering, Technical University of Denmark.

This work was also supported financially by Major Program of National Natural Science Foundation of China (No. 21890762), Key Research Program of Frontier Sciences, CAS (QYZDY-SSW – JSC011).

Supporting information. ¹H NMR spectrum of [VAIM][TFSI], TGA and DSC curves, density figures, viscosity figures, and conductivity tables.

References

- (1) Shukla, S. K.; Pandey, S.; Pandey, S. Applications of Ionic Liquids in Biphasic Separation: Aqueous Biphasic Systems and Liquid–liquid Equilibria. *J. Chromatogr. A* **2018**, *1559*, 44–61.
- (2) Losetty, V.; Chennuri, B. K.; Gardas, R. L. Synthesis, Spectroscopic Characterization and Acoustic, Volumetric, Transport and Thermal Properties of Hydroxyl Ammonium Based Ionic Liquids. *J. Chem. Thermodyn.* **2016**, *92*, 175–181.
- (3) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303–7306.
- (4) Zhang, Z.; Zhou, Q.; Lu, X.; Qiao, C.; Zhang, S. Densities and Viscosities of Binary Mixtures Containing 1, 3-Dimethylimidazolium Dimethylphosphate and Alcohols. *J. Chem. Eng. Data* **2014**, *59*, 2377–2388.
- (5) Domańska, U.; Wiśniewska, A.; Dąbrowski, Z.; Więckowski, M. Evaluation and Correlation of Separation Heptane/ethanol with Ionic Liquids. Ternary Liquid-Liquid Phase Equilibrium Data. *J. Mol. Liq.* **2018**, *255*, 504–512.
- (6) Myers, C.; Pennline, H.; Luebke, D.; Ilconich, J.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F. High Temperature Separation of Carbon Dioxide/hydrogen Mixtures Using Facilitated Supported Ionic Liquid Membranes. *J. Memb. Sci.* **2008**, *322*, 28–31.
- (7) Zhao, Y.; Tian, L.; Qiu, J.; Li, Z.; Wang, H.; Cui, G.; Zhang, S.; Wang, J. Remarkable Synergistic Effect between copper(I) and Ionic Liquids for Promoting Chemical Fixation of CO₂. *J. CO₂ Util.* **2017**, *22*, 374–381.
- (8) Pires, J.; Timperman, L.; Jacquemin, J.; Balducci, A.; Anouti, M. Density, Conductivity, Viscosity, and Excess Properties of (Pyrrolidinium Nitrate-Based Protic Ionic Liquid + Propylene Carbonate) Binary Mixture. *J. Chem. Thermodyn.* **2013**, *59*, 10–19.
- (9) Wang, X.; Chi, Y.; Mu, T. A Review on the Transport Properties of Ionic Liquids. *J. Mol. Liq.* **2014**, *193*, 262–266.
- (10) Martins, V. L.; Torresi, R. M. Ionic Liquids in Electrochemical Energy Storage. *Curr. Opin. Electrochem.* **2018**, *9*, 26–32.
- (11) Eftekhari, A. Supercapacitors Utilising Ionic Liquids. *Energy Storage Mater.* **2017**, *9*, 47–69.
- (12) Zheng, Y.; Zhang, S.; Lu, X.; Wang, Q.; Zuo, Y.; Liu, L. Low-Temperature Electrodeposition of Aluminium from Lewis Acidic 1-Allyl-3-Methylimidazolium Chloroaluminate Ionic Liquids. *Chinese J. Chem. Eng.* **2012**, *20*, 130–139.
- (13) Borun, A.; Bald, A. Conductometric Studies of 1-Ethyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Tetrafluoroborate in N,N-

- Dimethylformamide at Temperatures from (283.15 to 318.15) K. *J. Chem. Eng. Data* **2012**, *57*, 475–481.
- (14) Kanakubo, M.; Harris, K. R.; Tsuchihashi, N.; Ibuki, K.; Ueno, M. Temperature and Pressure Dependence of the Electrical Conductivity of 1-Butyl-3-Methylimidazolium Bis(trifluoromethanesulfonyl)amide. *J. Chem. Eng. Data* **2015**, *60*, 1495–1503.
- (15) Wang, Z.; Cai, Y.; Dong, T.; Chen, S.; Lu, X. Triethylbutylammonium Bis(trifluoromethanesulphonyl)imide Ionic Liquid as an Effective Electrolyte Additive for Li-Ion Batteries. *Ionics (Kiel)*. **2013**, *19*, 887–894.
- (16) Li, M.; Liao, Y.; Liu, Q.; Xu, J.; Sun, P.; Shi, H.; Li, W. Application of the Imidazolium Ionic Liquid Based Nano-Particle Decorated Gel Polymer Electrolyte for High Safety Lithium Ion Battery. *Electrochim. Acta* **2018**, *284*, 188–201.
- (17) Egashira, M.; Todo, H.; Yoshimoto, N.; Morita, M. Lithium Ion Conduction in Ionic Liquid-Based Gel Polymer Electrolyte. *J. Power Sources* **2008**, *178*, 729–735.
- (18) Egashira, M.; Todo, H.; Yoshimoto, N.; Morita, M.; Yamaki, J.-I. Functionalized Imidazolium Ionic Liquids as Electrolyte Components of Lithium Batteries. *J. Power Sources* **2007**, *174*, 560–564.
- (19) Matsumoto, H.; Sakaebe, H.; Tatsumi, K. Preparation of Room Temperature Ionic Liquids Based on Aliphatic Onium Cations and Asymmetric Amide Anions and Their Electrochemical Properties as a Lithium Battery Electrolyte. *J. Power Sources* **2005**, *146*, 45–50.
- (20) Pal, P.; Ghosh, A. Solid-State Gel Polymer Electrolytes Based on Ionic Liquids Containing Imidazolium Cations and Tetrafluoroborate Anions for Electrochemical Double Layer Capacitors: Influence of Cations Size and Viscosity of Ionic Liquids. *J. Power Sources* **2018**, *406*, 128–140.
- (21) Wang, G.; Yan, C.; Zhang, J.; Hou, S.; Zhang, W. Highly Efficient Solid-State Dye-Sensitized Solar Cells Based on Hexylimidazolium Iodide Ionic Polymer Electrolyte Prepared by in Situ Low-Temperature Polymerization. *J. Power Sources* **2017**, *345*, 131–136.
- (22) Yang, J.; Li, Q.; Jensen, J. O.; Pan, C.; Cleemann, L. N.; Bjerrum, N. J.; He, R. Phosphoric Acid Doped Imidazolium Polysulfone Membranes for High Temperature Proton Exchange Membrane Fuel Cells. *J. Power Sources* **2012**, *205*, 114–121.
- (23) Nguyen, D. Q.; Bae, H. W.; Jeon, E. H.; Lee, J. S.; Cheong, M.; Kim, H.; Kim, H. S.; Lee, H. Zwitterionic Imidazolium Compounds with High Cathodic Stability as Additives for Lithium Battery Electrolytes. *J. Power Sources* **2008**, *183*, 303–309.
- (24) Zhang, J.; Sun, B.; Zhao, Y.; Tkacheva, A.; Liu, Z.; Yan, K.; Guo, X.; McDonagh, A. M.; Shanmukaraj, D.; Wang, C.; Rojo, T.; Armand, M.; Peng, Z.; Wang, G. A Versatile Functionalized Ionic Liquid to Boost the Solution-Mediated Performances of Lithium-Oxygen Batteries. *Nat. Commun.* **2019**, *10*, 1–10.
- (25) Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A. Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for

Fast-Charging Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2014**, *136*, 5039–5046.

- (26) Peng, Z.; Freunberger, S. A.; Hardwick, L. J.; Chen, Y.; Giordani, V.; Bardé, F.; Novák, P.; Graham, D.; Tarascon, J. M.; Bruce, P. G. Oxygen Reactions in a Non-Aqueous Li⁺ Electrolyte. *Angew. Chemie - Int. Ed.* **2011**, *50*, 6351–6355.
- (27) Nilsson, V.; Younesi, R.; Brandell, D.; Edström, K.; Johansson, P. Critical Evaluation of the Stability of Highly Concentrated LiTFSI - Acetonitrile Electrolytes vs. Graphite, Lithium Metal and LiFePO₄ Electrodes. *J. Power Sources* **2018**, *384*, 334–341.
- (28) Mo, D.; Zhou, W.; Ma, X.; Xu, J. Facile Electrochemical Polymerization of 2-(Thiophen-2-Yl)furan and the Enhanced Capacitance Properties of Its Polymer in Acetonitrile Electrolyte Containing Boron Trifluoride Diethyl Etherate. *Electrochim. Acta* **2015**, *155*, 29–37.
- (29) Jin, Y.; Fang, S.; Yang, L.; Hirano, S.; Tachibana, K. Functionalized Ionic Liquids Based on Guanidinium Cations with Two Ether Groups as New Electrolytes for Lithium Battery. *J. Power Sources* **2011**, *196*, 10658–10666.
- (30) Barthel, J.; Feuerlein, F.; Neueder, R.; Wachter, R. Calibration of Conductance Cells at Various Temperatures. *J. Solution Chem.* **1980**, *9*, 209–219.
- (31) William, M. H.; David, R. L. Molar Conductivity of Aqueous HF, HCl, HBr, and HI. *CRC Handb. Chem. Phys.* **2011**, *1*, 90–91.
- (32) Korosi, G.; Kovars, E. Density and surface tension of 83 organic liquids. *J. Chem. Eng. Data* **1981**, *26*, 323–332.
- (33) Moumouzias, G.; Panopoulos, D.; Ritzoulis, G. Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20–23.
- (34) Sastry, N. V.; Vaghela, N. M.; Macwan, P. M. Densities, Excess Molar and Partial Molar Volumes for Water + 1-Butyl- Or, 1-Hexyl- Or, 1-Octyl-3-Methylimidazolium Halide Room Temperature Ionic Liquids at T = (298.15 and 308.15) K. *J. Mol. Liq.* **2013**, *180*, 12–18.
- (35) Mahajan, A. R.; Mirgane, S. R. Excess Molar Volumes and Viscosities for the Binary Mixtures of N-Octane, N-Decane, N-Dodecane, and N-Tetradecane with Octan-2-ol at 298.15K. *J. Thermodyn.* **2013**, *2013*, 1–8.
- (36) Gonçalves, J. C.; Rodrigues, A. E. Thermodynamic Equilibrium of Xylene Isomerization in the Liquid Phase. *J. Chem. Eng. Data* **2013**, *58*, 1425–1428.
- (37) Sastry, N. V.; Vaghela, N. M.; Macwan, P. M. Densities, Excess Molar and Partial Molar Volumes for Water + 1-Butyl- Or, 1-Hexyl- Or, 1-Octyl-3-Methylimidazolium Halide Room Temperature Ionic Liquids at T = (298.15 and 308.15) K. *J. Mol. Liq.* **2013**, *180*, 12–18.
- (38) Garca-Coln, L. S.; del Castillo, L. F.; Goldstein, Patricia. Theoretical basis for the Vogel-Fulcher-Tammann equation. *Physical Review B.* **1989**, *40*, 7040–7044.
- (39) Parsa, J. B.; Haghro, M. F. Excess Molar Volume and Viscosity Deviation for Binary

Mixtures of Polyethylene Glycol Dimethyl Ether 250 with 1,2-Alkanediols (C3-C6) at T = (293.15 to 323.15) K. *J. Chem. Thermodyn.* **2008**, *40*, 782–788.

Supporting information

Density, viscosity, and conductivity of [VAIM][TFSI] in mixtures for lithium ion battery electrolytes

Yingjun Cai^{†,‡}, Nicolas von Solms[†], Suojiang Zhang[‡], Kaj Thomsen^{†*}

[†]Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, 2800, Kgs. Lyngby, Denmark

kth@kt.dtu.dk*

[‡]Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China

The lines in figures S4 to S6 are tendency lines created by OriginLab software.¹

Figure S1. ¹H spectrum for the synthesized ionic liquid [VAIM][TFSI]. Peak integrals are indicated for hydrogen peaks.

The chemical shifts appear as follows: ^1H NMR (400 MHz, DMSO) δ 9.42 (s, 1H), 8.19 (s, 1H), 7.86 (d, $J = 15.1$ Hz, 2H), 7.59 (s, 1H), 7.37 (dd, $J = 15.6, 8.8$ Hz, 1H), 5.98 (dd, $J = 15.6, 2.3$ Hz, 1H), 5.45 (dd, $J = 8.7, 2.3$ Hz, 1H), 4.99 (s, 2H).

Figure S2. TGA curve for pure ionic liquid [VAIM][TFSI] **Figure S3.** DSC curve for pure ionic liquid [VAIM][TFSI]

Figure S4. Densities of the binary mixtures [VAIM][TFSI] and acetonitrile as a function of mole fraction of IL at different temperatures: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; ◀, 323.15 K; ▶, 328.15 K; □, 333.15 K.

Figure S5. Viscosity of pure ionic liquid [VAIM][TFSI] at different temperatures.

Figure S6. Viscosities of the binary mixtures of ionic liquid [VAIM][TFSI] and acetonitrile at different temperatures: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; ◄, 323.15 K; ►, 328.15 K; □, 333.15 K.

Table S1. Densities (ρ , $\text{kg}\cdot\text{m}^{-3}$) of pure acetonitrile at different temperatures (T) from 298.15 K to 333.15 K.

T / K	$\text{kg}\cdot\text{m}^{-3}$, our work	$\text{kg}\cdot\text{m}^{-3}$, Korosi and Kovars ²
298.15	777.7	777.3
303.15	772.3	771.8
308.15	766.8	766.3
313.15	761.3	760.9
318.15	755.7	755.9
323.15	750.2	749.2
328.15	744.5	743.6
333.15	738.9	737.3

^aStandard uncertainties are $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Expanded uncertainty for density is $u(\rho) = 0.5$ $\text{kg}\cdot\text{m}^{-3}$ (0.95 level of confidence). T is the Kelvin temperature.

Table S2. Viscosity (η , $\text{mPa}\cdot\text{s}$) of pure acetonitrile at different temperatures (T) from 298.15 K to 333.15 K.

T / K	mPa·s, our work	mPa·s, Moumouzias et al ³
298.15	0.3441	0.3440
303.15	0.3236	0.3280
308.15	0.3078	0.3080
313.15	0.2926	0.2965
318.15	0.2770	0.2890
323.15	0.2624	0.2715
328.15	0.2462	0.2690
333.15	0.2195	0.2590

^aStandard uncertainties are $u(x_{\text{IL}}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty for viscosity $u_r(\eta)$ is 0.15. T is the Kelvin temperature.

Table S3. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the binary mixtures [VAIM][TFSI] and acetonitrile at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

x_{IL}	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.010	1.29	1.34	1.40	1.47	1.53	1.58	1.65	1.69
0.020	2.52	2.64	2.78	2.90	3.01	3.13	3.25	3.35
0.047	3.16	3.32	3.52	3.70	3.87	4.03	4.19	4.34
0.070	3.32	3.51	3.74	3.96	4.16	4.36	4.58	4.79
0.080	3.26	3.47	3.72	3.95	4.17	4.39	4.61	4.77
0.100	3.06	3.28	3.53	3.80	4.02	4.25	4.49	4.72
0.200	1.60	1.77	1.98	2.19	2.38	2.58	2.80	3.00
0.393	0.39	0.48	0.60	0.73	0.86	1.00	1.16	1.33
1.000	0.01	0.02	0.03	0.05	0.07	0.10	0.14	0.20

^aStandard uncertainties are $u(x_{\text{IL}}) = 0.0003$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative uncertainty (u) for conductivity is $u_r(\sigma) = 0.004$. x_{IL} = mole fraction of ionic liquid. T is the Kelvin temperature.

Table S4. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the electrolytes, different mass fraction of lithium salt in acetonitrile, without [VAIM][TFSI] at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

w (salt)	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.1286	2.67	2.79	2.91	3.03	3.14	3.24	3.34	3.47
0.1813	3.11	3.23	3.34	3.47	3.58	3.7	3.81	3.92
0.228	3.53	3.68	3.85	4.01	4.16	4.29	4.43	4.57
0.2696	3.93	4.1	4.25	4.47	4.64	4.81	4.99	5.16
0.307	4.07	4.25	4.45	4.63	4.8	4.97	5.14	5.28
0.3407	3.93	4.12	4.33	4.53	4.7	4.87	5.05	5.24
0.3713	3.82	4.01	4.14	4.35	4.52	4.74	4.95	5.17
0.3992	3.65	3.84	4.05	4.26	4.45	4.63	4.82	4.99

^aStandard uncertainties are $u(w(\text{salt})) = 0.0001$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty (u) for conductivity is $u_r(\sigma) = 0.004$. w (salt) = mass fraction of lithium salt. T is the Kelvin temperature.

Table S5. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the electrolytes with 3 wt % [VAIM][TFSI]. The remaining 97 wt % consists of variable mass fractions of lithium salt in acetonitrile, at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

w (salt)	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.1248	2.73	2.83	2.96	3.07	3.17	3.3	3.4	3.53
0.1759	3.51	3.66	3.82	3.97	4.11	4.25	4.39	4.51
0.2211	3.85	4.02	4.2	4.38	4.53	4.69	4.83	4.97
0.2615	4.03	4.21	4.41	4.6	4.77	4.94	5.1	5.25
0.2978	4.11	4.28	4.51	4.71	4.9	5.08	5.26	5.43
0.3305	3.97	4.15	4.38	4.58	4.77	4.97	5.16	5.34
0.3602	3.8	4	4.22	4.44	4.64	4.83	5.03	5.21
0.3872	3.67	3.86	4.09	4.3	4.51	4.71	4.92	5.13

^aStandard uncertainties are $u(w(\text{salt})) = 0.0001$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty (u) for conductivity is $u_r(\sigma) = 0.004$. $w(\text{salt})$ = mass fraction of lithium salt. T is the Kelvin temperature.

Table S6. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the electrolytes, with 5 wt % [VAIM][TFSI]. The remaining 95 wt % consists of variable mass fractions of lithium salt in acetonitrile, at different temperatures from 298.15 K to 333.15 K, at 0.1 MPa.

w (salt)	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.1222	3.1	3.22	3.36	3.49	3.61	3.73	3.84	3.95
0.1722	3.56	3.7	3.87	4.02	4.18	4.31	4.48	4.6
0.2166	3.82	3.97	4.16	4.33	4.48	4.63	4.77	4.9
0.2561	3.96	4.13	4.33	4.52	4.68	4.85	5.01	5.15
0.2916	4.05	4.22	4.44	4.62	4.8	4.96	5.13	5.28
0.3237	3.98	4.16	4.37	4.56	4.74	4.95	5.13	5.28
0.3527	3.94	4.14	4.37	4.54	4.73	4.92	5.08	5.24
0.3792	3.56	3.72	3.93	4.13	4.31	4.5	4.68	4.85

^aStandard uncertainties are $u(w(\text{salt})) = 0.0001$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty (u) for conductivity is $u_r(\sigma) = 0.004$. $w(\text{salt})$ = mass fraction of lithium salt. T is the Kelvin temperature.

Table S7. Conductivities (σ , $\text{S}\cdot\text{m}^{-1}$) of the electrolytes, with 44 wt % [VAIM][TFSI]. The remaining 56 wt % consists of variable mass fractions of lithium salt in acetonitrile, at different temperatures from 298.15K to 333.15K, at 0.1 MPa.

w (salt)	T =298.15 K	T =303.15 K	T =308.15 K	T =313.15 K	T =318.15 K	T =323.15 K	T =328.15 K	T =333.15 K
0.0720	3.43	3.66	3.92	4.17	4.42	4.67	4.92	5.19
0.1015	3.24	3.48	3.75	4.02	4.28	4.56	4.85	5.15
0.1277	3.05	3.29	3.56	3.81	4.07	4.32	4.61	4.91
0.1510	2.87	3.1	3.36	3.61	3.87	4.13	4.37	4.68
0.1719	2.65	2.87	3.11	3.35	3.58	3.82	4.06	4.3
0.1908	2.47	2.68	2.93	3.16	3.38	3.61	3.85	4.14
0.2079	2.4	2.62	2.86	3.09	3.29	3.52	3.77	4.03

^aStandard uncertainties are $u(w(\text{salt})) = 0.0001$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa. Relative standard uncertainty (u) for conductivity is $u_r(\sigma) = 0.004$. $w(\text{salt})$ = mass fraction of lithium salt. T is the Kelvin temperature.

References

- (1) OriginLab 2018b(9.55) version. Copyright: 1991-2018 OriginLab.
- (2) Korosi, G.; Kovars, E. Density and surface tension of 83 organic liquids. *J. Chem. Eng. Data* **1981**, 26, 323–332.
- (3) Moumouzias, G.; Panopoulos, D.; Ritzoulis, G. Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile. *J. Chem. Eng. Data* **1991**, 36, 20–23.