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Trialkyl-Substituted Imidazolium-Based Ionic Liquids for Electrochemical Applications: Basic Physicochemical Properties

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The trialkyl-substituted imidazolium-based ionic liquids (ILs) are considered to be promising as supporting electrolytes for electroplating and other electrochemical applications because of their increased stability compared to that of dialkyl-substituted compounds. Basic properties like density, viscosity, and conductivity of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($BMMImBF_4$), 1-butyl-2,3-dimethylimidazolium azide ($BMMImN_3$), and their mixtures were measured. The thermal stability of the azide IL permits its use up to 423.15 K, whereas the upper temperature limit for telrafluoroborate IL extends to 623.15 K. The electrochemical stability with regard to cathodic reduction was the same for both ILs; the decomposition potential was about −1.9 V versus the Ag/AgCl reference electrode. However, the resistance to electrochemical oxidation at the anode was much lower for the azide IL. The decomposition potential was 0.5 V against 2.05 V for the tetrafluoroborate IL.

Introduction

Imidazolium-based ionic liquids (ILs) have gained considerable interest. Hydrogen in the imidazolium group can be easily substituted; therefore, a variety of properties are achievable. The most famous group of imidazolium-based ILs is probably 1,3-alkyl-substituted ILs because of their low melting point, relatively low viscosity, and high conductivity. Their physical properties and some chemical properties have been studied.[1,2] The relatively low cathodic stability of the disubstituted imidazolium cation limits their application in electrochemical purposes[3,4] because the cations undergo cathodic dimerization, and dialkylation reactions occur that involve the acidic proton in the two position.

In the present work, two trisubstituted imidazolium ILs have been studied, both based on the 1-butyl-2,3-dimethylimidazolium cation with BF_4^- ($BMMImBF_4$) and azide ($BMMImN_3$) anions.

Because of the absence of an acidic proton in the two position, 1,2,3-trialkylated imidazolium cation-based ILs show superior electrochemical stability compared with the 1,3-substituted ILs.[5] Therefore, their use in electrochemical applications, for example, as electrolytes for the deposition of metals, is preferable to the disubstituted imidazolium-based ILs. However, basic knowledge of the physicochemical properties (density, viscosity, conductivity, thermal and electrochemical stability) is required to find optimal application conditions.

Another significant factor that should be elucidated is the effect of the nature of the anion on the properties of the electrolyte. In particular, it is interesting to know the changes in properties that result from mixing the liquids with a common cation and two different anions (one "ball"-shaped and the other "rod"-shaped).

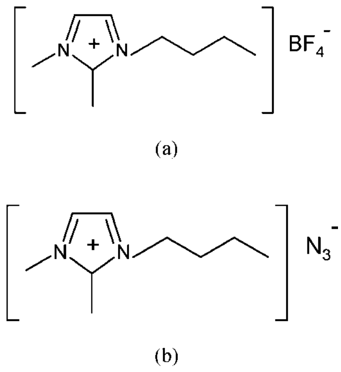

Figure 1. Structure of (a) 1-butyl-2,3-dimethyl imidazolium tetrafluoroborate ($BMMImBF_4$) and (b) 1-butyl-2,3-dimethyl imidazolium azide ($BMMImN_3$).

Therefore, gaining the information that is of primary interest for electrochemical applications of the two ILs with trisubstituted imidazolium cation was the aim of the present work.

Experimental Section

The ILs under study were 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($BMMImBF_4$) and 1-butyl-2,3-dimethylimidazolium azide ($BMMImN_3$, University of Innsbruck, Institute of General, Inorganic and Theoretical Chemistry, Austria) (Figure 1). (More detailed information on the properties and characterization of $BMMImN_3$ can be found in: Bentivoglio, G. New Ionic Liquids for Material Science Applications. Diploma Thesis, 2005.)

The liquids were dried under vacuum (0.022 mbar) at 338.15 K overnight before use. After drying, a Karl Fischer titration (Metrohm 756 KF Coulometer) was performed, resulting in a mass fraction of water of $16.6 \cdot 10^{-6}$ and $7.9 \cdot 10^{-6}$ in $BMMImBF_4$ and $BMMImN_3$, respectively. Mixtures of the two ILs were prepared to study the influence of the anion on the properties of the ILs. The mole ratios were as follows: 75 %, 25 %, and 50 % of $BMMImN_3$.

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Even hydrophobic ILs can absorb significant amounts of water from the ambient air.[6] Therefore, all operations with the ILs were performed in a glovebox (MBraun Labstar; mass fraction of H_2O and O_2, $1 \cdot 10^{-6}$). After being handled in the glovebox, the samples exhibited the same water content, which was measured again by KF titration. Conductivity and cyclic voltammetry measurements were made outside after the cell was prepared and sealed in the glovebox. Conductivity measurements were carried out in the temperature range between (303.15 and 368.15) K (Qcond 2400 VWR international; cell constant, 1.05). The heating rate was approximately 0.5 $K \cdot min^{-1}$. The values obtained while the ILs were heated reasonably agreed with the values from the measurements during cooling.

The temperature dependence of the density and viscosity (range (313.15 to 373.15) K) were measured using an SVM 3000 viscosimeter (Anton Paar/A). The reproducibility of the viscosity and density measurements for this instrument was 0.35 % and 0.0005 $g \cdot cm^{-3}$, respectively. The temperature was controlled with a precision of 0.05 K.

Thermal decomposition was studied with Biotage Initiator microwave equipment. (For a detailed description of this instrument, see http://www.biotage.com/.) NMR (^1H and ^{13}C) spectra were run in $CDCl_3$ on a 400 MHz instrument (Bruker Advance). We measured the purity (decomposition in percent) of the samples by calculating the integration of the imidazolium species on the basis of one of the olefinic proton signals versus the total integration of signals in the spectrum. Also, thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA 851 instrument (heating rate 10 $K \cdot min^{-1}$).

Cyclic voltammetry of the pure ILs and their mixtures was used to estimate the electrochemical stability of the ILs. Experiments were carried out in a standard three-electrode electrochemical cell using a Pt disk (area, 0.031 cm) as a working electrode, a glassy carbon rod as an auxiliary electrode, and an Ag/AgCl electrode in oversaturated AgCl in $BMMImBF_4$ solution as the reference. The reference electrode compartment was separated from the electrolyte by means of Vycor glass frit. All of the electrochemical measurements were carried out at 338.15 K using a IMP83PC-60V-5A potentiostat (IPS Schrems/D) in combination with a data acquisition system.

Results and Discussion

Density and Molar Volume. Unlike viscosity or conductivity, density is not a property that is very sensitive to structural changes. It linearly depends on the temperature (Figure 2). $BMMImBF_4$, has a higher density than $BMMImN_3$ because tetrafluoroborate is a heavier anion. This is also true for imidazolium-based ILs with different anions; with an increase in the anion molecular weight, the density increases.[7] The density measured in this work is in good agreement with the literature data.[7,8] Different water content and, in some cases, a small amount of the sample for performing a KF titration are normally the reasons for different values reported in the literature for the same ILs.

In the mixtures, the two different anions do not seem to interact with each other in a different way than they would interact within the same anionic species. Therefore, densities change almost linearly with the composition of the ILs.

To be used as reference data, the density values were approximated by the linear equation

$$\rho = \rho^0[1 - \alpha(T - 273.15)] \qquad (1)$$

where T is given in Kelvin. The values of empirical coefficients ρ^0 and α are represented in Table 1 together with standard deviations for calculations by eq 1. As follows, eq 1 approximates the data with very good precision. Because the dependence of density on the composition at constant temperature is, in fact, linear, the magnitudes of densities for the compositions other than that represented in Table 1 can easily be calculated by simple interpolation.

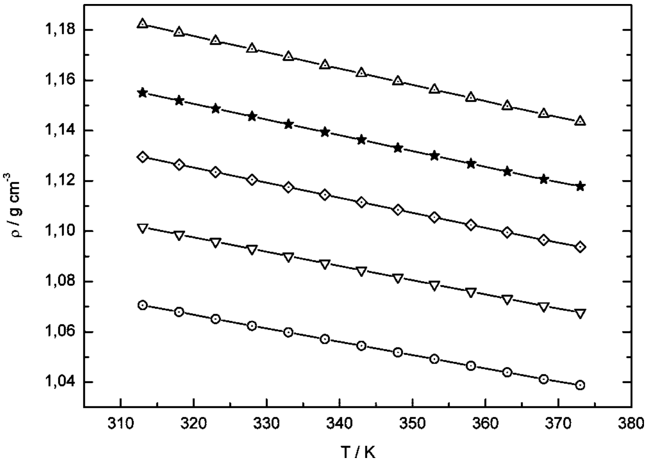

Figure 2. Density dependence of pure ILs and the mixtures with the following molar fractions on the temperature: △, pure $BMMImBF_4$; ★, 0.25 $BMMImN_3$; ◇, 0.5 $BMMImN_3$; ▽, 0.75 $BMMImN_3$; ○, pure $BMMImN_3$.

Table 1. Empirical Coefficients for Calculation of Densities by Equation *1*

	ρ^0	$\alpha \cdot 10^4$	standard deviation, 10^{-5}
	$g \cdot cm^{-3}$	K^{-1}	$g \cdot cm^{-3}$
$BMMImN_3$	1.09170	4.8649	9.7
0.75 $BMMImN_3$	1.12413	5.6593	7.2
0.50 $BMMImN_3$	1.15338	5.1850	7.7
0.25 $BMMImN_3$	1.17991	5.2840	7.4
$BMMImBF_4$	1.20798	5.3664	7.3

Molar volumes of the mixtures calculated from density data are plotted versus composition for four different temperatures in Figure 3. The isotherms in Figure 3 are linear.

Transport Properties: Viscosity and Conductivity. Both viscosity and conductivity depend on temperature in a similar way, the first decreasing and the second increasing exponentially as the temperature increases (Figure 4). As expected, the nature of the anion has a small effect on the transport properties because they are mainly determined by the nature of the large cation.[9−11]

Conductivity and viscosity data are often combined into what is called the Walden rule, which is, to some extent, also valid for ILs[9]

$$\eta \cdot \frac{\sigma M}{\rho} = \text{const} \qquad (2)$$

where η is the viscosity, σ is the ionic conductivity, M is the molar mass, and ρ is density of the IL.

Thus, one can expect that the Walden product has to be constant within the range of temperature for the ILs under consideration. However, it only approximately holds true. The Walden product (eq 2) is independent of temperature for pure $BMMImBF_4$ and becomes temperature dependent when $BMMImN_3$ is present in the liquid (Figure 5A). When averaged over the temperature limits ((313.15 to 373.15) K), values of the Walden product pass through a minimum at the mole fraction of 0.5 of $BMMImN_3$ in the mixture (Figure 5B).

In the case of ILs and molten salts, this criterion should be used with caution for the prediction of viscosity or conductivity, provided that one of the values is known.

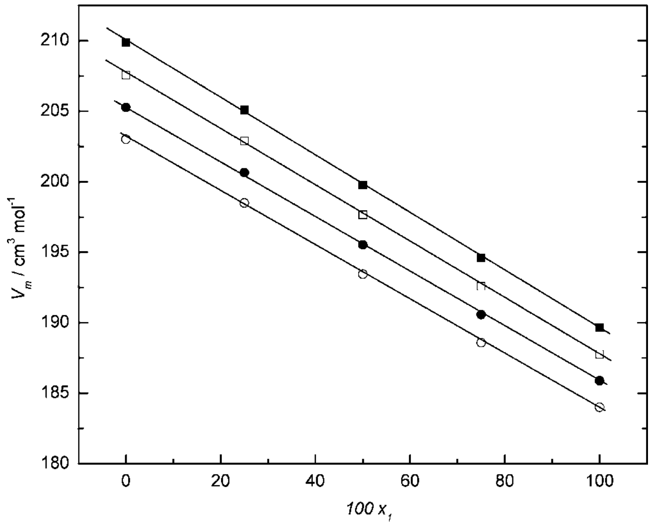

Figure 3. Dependence of molar volume V_m on the mole fraction (x_1) of BMMImN$_3$ at different temperature: ■, 373 K; □, 353 K; ●, 333 K; ○, 313 K.

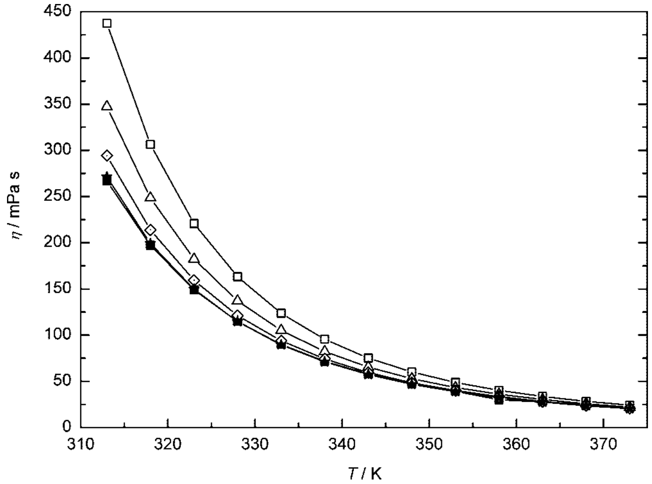

Figure 4. (A) Temperature dependence of viscosity of BMMImN$_3$, BMMImBF$_4$, and its mixtures: ■, BMMImBF$_4$; ★, 0.25 BMMImN$_3$; ⊡, 0.5 BMMImN$_3$; △, 0.75 BMMImN$_3$; □, BMMImN$_3$.

In general, the temperature behavior of transport properties does not exactly obey the Arrhenius equation

$$\ln \eta = \ln \eta_0 + \frac{E_a}{RT} \tag{3}$$

The ILs under consideration are not exceptions. One can see that Arrhenius plots for conductivity deviate from the straight line (Figure 6). Similar deviations are observed in viscosity plots as well.

Nevertheless, the approximation of the data by eq 3 is useful because the fit parameter E_a has clear physical meaning as the activation energy of the transport process (viscous flow or ion transport). The calculated activation energies are given in Table 2 together with the reference data for several dialkyl-substituted imidazolium ILs.

The activation energies, which are practically the same for both viscous flow and conductivity, tend to increase with increasing mole fraction of the azide anion.

Because the activation energy can be related to structural effects of the ions,[17] we consider this tendency to be evidence of the electrostatic interaction prevailing over the van der Waals forces.

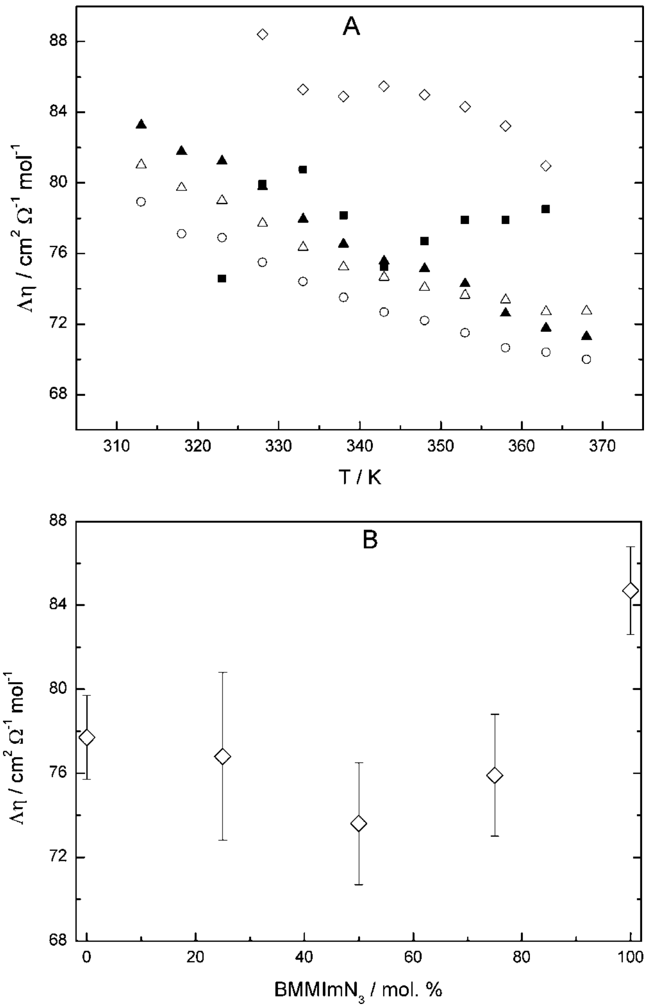

Figure 5. (A) Temperature dependence of Walden product (eq 2) and (B) change in averaged value of Walden product with composition of the mixture. Symbols in A denote: ■, BMMImBF$_4$; ▲, 0.25 BMMImN$_3$; ○, 0.5 BMMImN$_3$; △, 0.75 BMMImN$_3$; ◇, BMMImN$_3$.

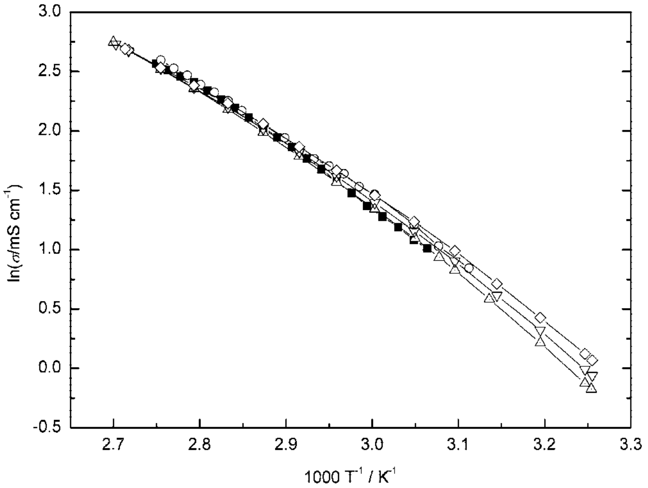

Figure 6. Temperature dependencies of conductivities in terms of the Arrhenius equation: ○, BMMImBF$_4$; ◇, 0.25 BMMImN$_3$; ▽, 0.5 BMMImN$_3$; △, 0.75 BMMImN$_3$; ■, BMMImN$_3$.

Some literature data on activation energies derived from conductivity data for imidazolium ILs are compiled in Table 2. Because of the more complicated structure of the ILs investigated in this study, E_a is higher than the activation energies of most of the disubstituted imidazolium-based ILs mentioned in

Table 2. Activation Energies of Conductivity and Viscosity of Trialkyl-Substituted BMMImN$_3$, BMMImBF$_4$, and Its Mixtures in Comparison with Reference Data on Disubstituted Im-Based ILs

IL[a]	activation energies of transport processes, E_a/kJ σ	 η	refs
BMMImN$_3$	46.0 ± 0.37	46.4 ± 1.0	this work
BMMImN$_3$ 75 %	43.7 ± 0.86	44.3 ± 0.93	
BMMImN$_3$ 50 %	41.9 ± 0.83	42.6 ± 0.85	
BMMImN$_3$ 25 %	40.1 ± 0.79	41.6 ± 0.80	
BMMImBF$_4$	40.1 ± 0.46	41.5 ± 0.85	
EMImTf	17.6		19
EMImTf	15.9		20
EMImNTf$_2$	14.0		20
EMImBF$_4$	18.0		19
EMImPF$_6$	25.5		19
OMImPF$_6$	48.6		18
BMMImNTf$_2$	29.7		18

[a] M, methyl; E, ethyl; B, butyl; O, octyl; Im, imidazolium; Tf, trifluoromethylsulfonate; NTf$_2$, bis(trifluoromethylsulfonyl)imide.

literature so far. For ILs with a larger disubstituted imidazolium cation, as in the case of OMImPF$_6$ (octyl, methyl imidazolium hexafluorophosphate), a higher activation energy of conductivity was reported.[18] Hence, the increased activation energy of the ILs under study is obviously an effect of enlarging the size of the cation upon the introduction of the third substituent to the imidazolium ring.

A much more precise fit for temperature dependencies of viscosity and conductivity can be achieved by the three-parameter equation of Vogel−Tamman−Fulcher (VTF) type

$$\ln \eta = \ln \eta_0 + \frac{k}{T - T_0} \tag{4}$$

or

$$\ln \sigma = \ln \sigma_0 + \frac{k}{T - T_0} \tag{5}$$

where T_0 is related to the ideal glass-transition temperature, and σ_0, η_0, and k are constants.

The VTF equation has previously been successfully used to interpret the temperature behavior of the conductivity of imidazolium-substituted ILs.[2,15,16]

Figure 7 gives an example of temperature dependencies linearized in terms of VTF eq 4. The correlation coefficient is very close to unity (0.999 to 1.000); therefore, the coefficients of VTF approximation can be used as reference values for the reliable calculation of viscosity and conductivity at any particular temperature. These are tabulated in Table 3.

The ideal glass-transition temperature for BMMImN$_3$ is significantly higher than that for BMMImBF$_4$. This is evidence of the IL with a tetrafluoroborate anion possessing a larger free volume between the molecules.

Thermal Stability of BMMImBF$_4$ and BMMImN$_3$. Considering the electrochemical applications of ILs, the thermal regime of the process is very important because it permits the rates of both chemical and electrochemical reactions to be affected and to be varied to optimize, for example, the electrodeposition conditions. Thus, the design of the electrochemical process in an IL requires the temperature range of thermal stability of the ILs to be known. Therefore, data on the thermal stability of BMMImBF$_4$ and BMMImN$_3$ have been acquired.

A thermogravimetric investigation of BMMImBF$_4$ is reported in ref 21. According to these data, the onset of decomposition is observed at 671.15 K, with a heating rate of 10 K·min^{-1}. Thermal decomposition of the azide IL was not yet studied.

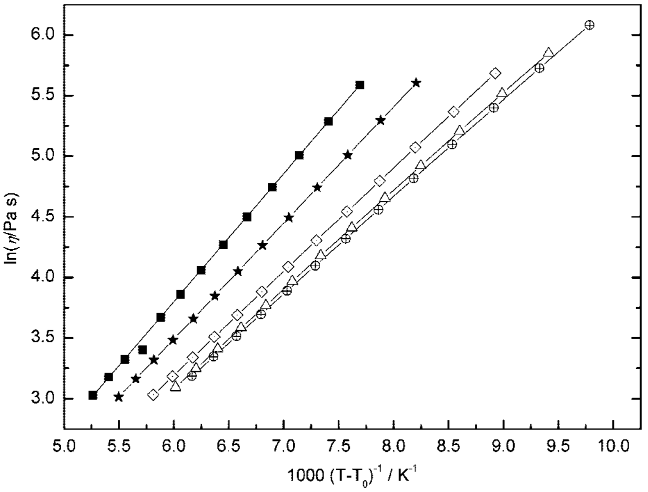

Figure 7. Temperature dependencies of viscosity in terms of three-parameter eq 4: ○, BMMImBF$_4$; ⊕, 0.25 BMMImN$_3$; ▽, 0.5 BMMImN$_3$; △, 0.75 BMMImN$_3$; ■, BMMImN$_3$.

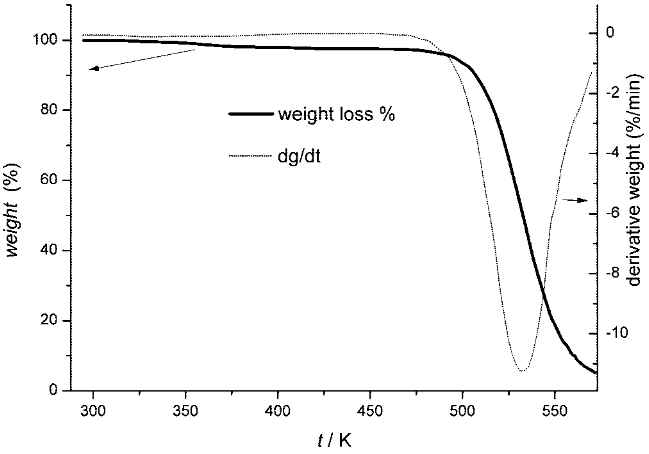

Figure 8. TGA analysis of BMMImN$_3$ ionic liquid (heating rate 10 K·min^{-1}).

Figure 8 shows thermogravimetric curves for pure BMMImN$_3$. As follows from these data, the decomposition begins at around 483.15 K, which is much lower than in the case of fluoroborate compound.

From these data, one may conclude that usage of these salts up to 473.15 K is justified. However, as already stated in the literature,[22] one should be careful about drawing such conclusions from thermogravimetric data alone because a side reaction may occur below the TG decomposition temperature.

Most overlooked side reactions in ILs are dealkylation reactions caused by the nucleophilicity of the anions.[23] To examine the occurrence of such side reactions, we used microwave heating[24] of the samples at various temperature, followed by subsequent analysis of such treated samples by NMR spectroscopy. The following protocol was used: The samples (0.3 mL, neat or mixtures) were placed in (0.2 to 0.5) mL microwave vials, sealed, and heated at 373.15 K, 423.15 K, and 473.15 K for 15 min and were subjected to NMR analysis. The time period of 15 min proved to be sufficient for judging the thermal stability. BMMImBF$_4$ was found to be thermally stable under these conditions. No thermal decomposition was found, even up to 523.15 K (the temperature limit of our instrument), which is in agreement with the results of the TGA measurement.

Treatment of BMMImN$_3$ in the same way revealed a quite different pattern. Though the pure compound was stable at

Table 3. Approximation Coefficients of VTF Equations for Viscosity (Equation *4*) and Conductivity (Equation *5*) Data

	viscosity			conductivity		
IL	$\ln(\eta_0/\text{mPa}\cdot\text{s})$	k/K	T_0/K	$\ln(\sigma_0/\text{mS}\cdot\text{cm}^{-1})$	$-k$/K	T_0/K
$BMMImN_3$	-1.76 ± 0.2	805 ± 5.0	207 ± 0.37	7.33 ± 0.44	701.3 ± 13	216 ± 10
$BMMImN_3$ 0.75	-1.79 ± 0.02	813 ± 6.68	207 ± 0.5	7.88 ± 0.06	890.0 ± 19	197 ± 1.4
$BMMImN_3$ 0.5	-1.92 ± 0.02	852 ± 0.68	201 ± 0.52	7.97 ± 0.07	907.3 ± 19	196 ± 1.5
$BMMImN_3$ 0.25	-2.55 ± 0.02	957 ± 6.77	192 ± 0.51	7.46 ± 0.1	822.0 ± 28	196 ± 2.4
$BMMImBF_4$	-2.17 ± 0.02	1050 ± 7.7	183 ± 3.2	8.74 ± 0.71	1164.6 ± 38	174 ± 6.9

373.15 K (also for prolonged time periods), slight deterioration of approximately 4 % was observed at 423.15 K. The two dealkylation products, 1-butyl-2-methyl- and 1,2-dimethylimidazol, were clearly identified by the comparison of the ^{1}H NMR spectra with the authentic material (characteristic NMR signals of the imidazol protons H-4 and H-5 at (6.88 and 6.89) ppm and (6.78 and 6.79) ppm, the latter being the more abundant. Exposition of the compound to 473.15 K results in almost complete decomposition (Figure 9).

The development of pressure inside the vial caused an automatic shut down after heating for a few seconds. Therefore, the heating time of 15 min could be achieved only by depressurizing the vial.

NMR analysis showed 86 % decomposition of the sample. Again, only the two dealkylated products could be reliably identified, though the spectrum revealed many other minor decomposition products. Because of the complexity of the mixture, further efforts to identify other products gave no certain results.

As expected, the mixtures become more thermally stable as the content of $BMMImBF_4$ in the melt increases. However, even in the 1:1 mixture, decomposition at 423.15 K was noticed (−1 %), whereas at 473.15 K, the degree of decomposition amounted to 41 %.

Our data permit us to conclude that the decomposition of $BMMImN_3$ is initiated by nucleophilic displacement of the N alkyl groups by the azide ion. The observed ratio of 1-butyl-2-methyl- and 1,2-dimethyl-imidazol is in the range that one expects for the nucleophilic displacement on a primary versus a secondary carbon atom. Further decomposition of the transitional alkylazides to nitrenes gives rise to the multitude of minor products observed in the heat-treated samples.

Because we expected that small amounts of impurities generated at temperatures higher than 373.15 K might significantly affect the physical properties of the azide IL and the mixtures, we limited the investigation of the physical−chemical properties within a temperature range up to 373.15 K.

Electrochemical Stability of the Ionic Liquids. Electrochemical windows of the ILs, as well as the presence of electrochemically active impurities, were checked by linear sweep voltammetry. After a constant potential of the Pt electrode in the melt was established, cathodic and anodic curves were consequently recorded. The anodic sweep was started from the equilibrium potential as well.

It was found that the pure $BMMImBF_4$ is electrochemically stable in the range of −1.85 V to +2.05 V and $BMMImN_3$ is electrochemically stable in the range of −1.9 V to +0.5 V versus the Ag/AgCl/$BMMImBF_4$ reference electrode (Figure 10).

The cathodic limit for both ILs is caused by the reduction of the imidazolium-based cation. In the anodic direction, the oxidation of tetrafluoroborate anion with BF_3 and fluorocarbon formation limits the electrochemical window of the $BMMImBF_4$.[9,25] The anodic peak at 1.2 V is attributed to the chloride anion oxidation.[24] The impurity of Cl^- results from the synthesis route.[26]

A slightly higher cathodic stability of $BMMImN_3$ is probably related to the lower water content compared with that of $BMMImBF_4$ IL ((7 and 15) ppm, measured by Karl Fischer Titration).

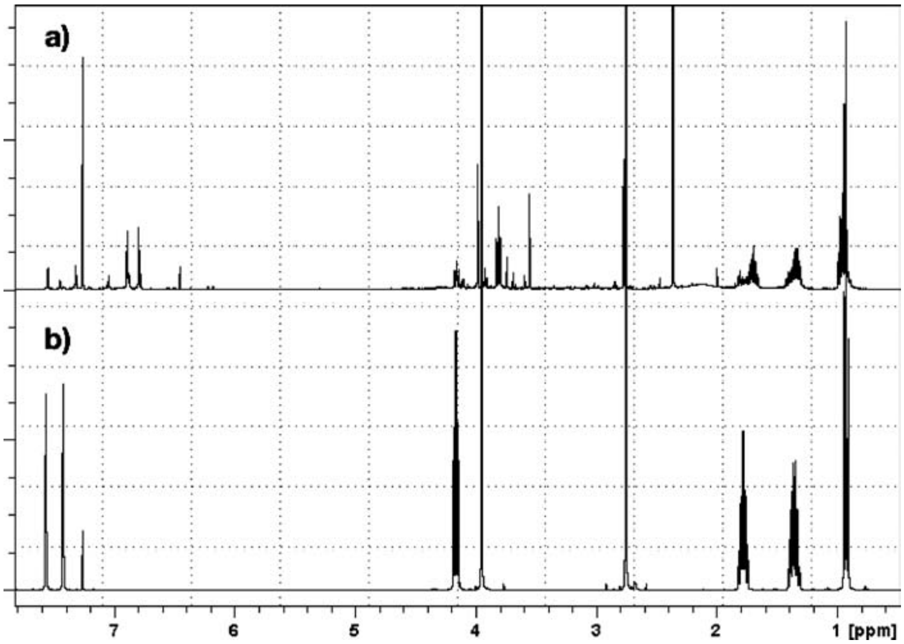

Figure 9. ^{1}H NMR spectra of (a) $BMMImN_3$ after microwave heating for 15 min at 473.15 K and (b) untreated initial substance.

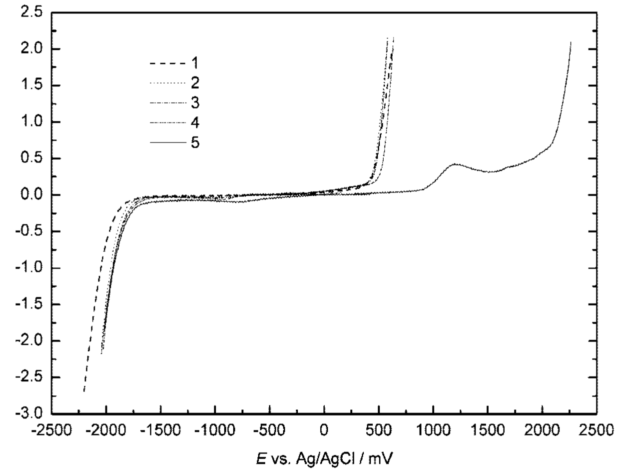

Figure 10. Linear sweep voltammetry of the pure 1-butyl-2,3-dimethyl imidazolium ILs with azide and fluoroborate cations and their mixtures (molar ratios): sweep rate, 100 mV·s^{-1}; temperature, 338 K; Pt working electrode. 1, $BMMImN_3$; 2, 0.75 $BMMImN_3$; 3, 0.5 $BMMImN_3$; 4, 0.25 $BMMImN_3$; 5, $BMMImBF_4$.

The replacement of tetrafluoroborate with an azide anion decreases the anodic stability by 1.5 V.

Their mixtures show, even with low amounts of $BMMImN_3$, a behavior that is quite similar to that of pure $BMMImN_3$ with an anodic decomposition potential of + 0.5 V (Figure 10). The anodic region of the mixtures is limited by the oxidation of the azide anion. In the case of the addition of a 0.25 mol fraction of $BMMImN_3$ to $BMMImBF_4$, the effect of the higher anodic stability of the $BMMImBF_4$ is eliminated. This is probably true for mixtures with a much smaller mole fraction of the $BMMImN_3$ IL. In the cathodic region, for a mixture with 0.25 mol fraction of $BMMImBF_4$, the cathodic stability shifts by 50 mV to the value of pure $BMMImBF_4$.

Conclusions

Because the triakyl-substituted imidazolium-based ILs are of interest as potential electrolyte solvents for electrochemical applications, basic physicochemical, electrochemical, and chemical properties were investigated for two such liquids, $BMMImBF_4$, $BMMImN_3$, and their mixtures. Values of density, conductivity, and viscosity were measured and tabulated in the form of approximative equation coefficients convenient for use as a reference data.

The values of density, molar volumes, and other physical properties indicate that the mixtures of these two salts behave as ideal solutions.

The thermal stability of the azide IL is essentially lower than that in the case of the tetrafluoroborate IL. Whereas $BMMImBF_4$ can be used up to 623.15 K, the $BMMImN_3$ starts to decompose at about 423.15 K.

Cathodic stabilities of both ILs are practically the same with reduction potentials of −1.90 V for azide and −1.85 V for fluoroborate IL. Meanwhile, the azide ion is much less stable, anodically oxidizing via the probable anode reaction

$$2N_3^- \rightarrow 3N_2\uparrow + 2e^- \qquad (6)$$

at a potential + 0.55 V. The much more stable BF_4^- anion oxidizes at a 1.5 V higher potential.

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