

Mixtures of Ionic Liquids as Possible Electrolytes for Lithium Ion Batteries

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Due to their unique properties like incombustibility, low vapor pressure, large electrochemical stability, wide liquid range and high thermal stability, ionic liquids have a great potential as components of electrolytes for lithium ion batteries. Lithium ion batteries with electrolytes on the basis of ionic liquids are safer than those with conventional electrolytes. Unfortunately, ionic liquids normally possess a higher viscosity and lower conductivity than conventional electrolytes. In order to decrease the viscosity and increase the conductivity of electrolytes based on ionic liquids, we prepared mixtures of ionic liquids. We could show that the viscosity of ionic liquids can be significantly reduced by using eutectic mixtures. Therefore, the conductivities of some mixtures were significantly higher than those of the pure ionic liquids. In addition, we could increase the conductivity by introducing functional groups in the side chain of the ionic liquids.

1. Introduction

Lithium ion batteries are today not only used as power sources for mobile electronic devices but also for a growing amount of electronic means of transportations [1]. The electrolyte of a lithium ion battery has a great influence on the performance of lithium ion batteries. Important requirements for the electrolyte of lithium ion batteries are a large electrochemical stability, a wide liquid range, a high thermal stability, a low vapor pressure, incombustibility, a low viscosity, a high lithium ion conductivity, a high capacity and high cycling rates [2,3]. The major problems of lithium ion batteries with conventional electrolytes are that short circuits often lead to overheating and ignition of the organic solvents, which are part of conventional electrolytes [4].

Ionic liquids possess a unique combination of properties, like a wide liquid range and a high thermal stability. In particular their low vapor pressure and their incombustibility make them safer alternatives for low volatile organic solvents, which are an important component of conventional electrolytes for lithium ion batteries [5]. Therefore, ionic liquids based electrolytes became more and more important and thus part

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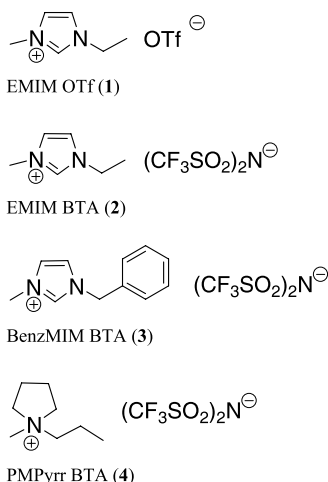


Fig. 1. Chemical structure of the investigated ionic liquids.

of many investigations during the last years [6–13]. Ionic liquids can also be used as additives for increasing the conductivity of conventional electrolytes [14–16]. In order to obtain insight in the nature of the solid electrolyte interface (SEI) layer between the electrolyte and the electrode *in situ* transmission electron spectroscopy [17] and impedance spectroscopy [18] of lithium ion batteries with ionic liquids based electrolytes were performed. Investigations of interfacial layers between ionic liquids and Au(111) surfaces were performed by Endres *et al.* [19].

Despite their advantages, most ionic liquids-based electrolytes show lower conductivities than conventional electrolytes. This is mostly due to the higher viscosity of ionic liquids in comparison to conventional organic solvents. In order to decrease the viscosity and to increase the conductivity of ionic-liquid based electrolytes, we investigated for this short paper some mixtures of ionic liquids.

2. Results and discussion

At first we were interested in the viscosity and the conductivity of binary mixtures of ionic liquids. The increased entropy of the components of an eutectic mixture usually leads to a decrease of the melting temperature [20]. The optimal mixtures of ionic liquids should possess a low viscosity and a high conductivity to overcome transport limitations. In particular ionic liquids based on the bis(trifluoromethylsulfonyl)amide or trifluoromethylsulfonate anion are interesting candidates due to their high electrochemical stability. In this work, we chose 1-ethyl-3-methylimidazolium trifluoromethylsulfonate (EMIM OTf, **1**), 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylamide (EMIM BTA, **2**) and 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonate) (PMPyrr BTA, **4**) as contents of our binary mixtures, because these small ionic liquids have relatively low viscosities (Fig. 1). The advantage of ionic liquids with pyrrolidinium cations compared to

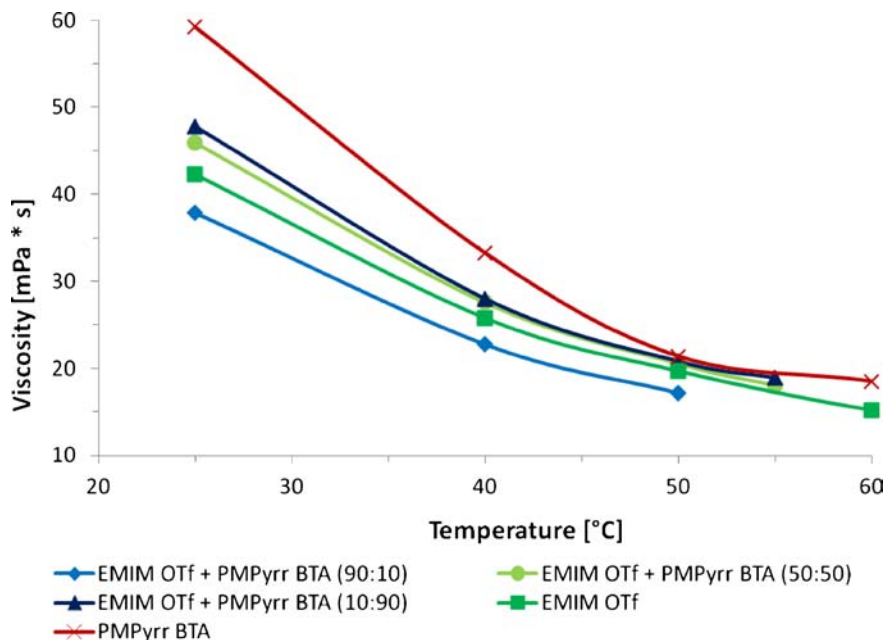


Fig. 2. Temperatur-dependent viscosity of selected mixtures of EMIM OTf (1) with PMPyrr BTA (4) (the ratio is given in mol %).

ionic liquids with imidazolium cations is that these substances have no acidic CH-bond. 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (3) (Fig. 1) has a comparatively high viscosity (112 mPa·s at 25 °C). Even so it shows a good performance in mixtures of ionic liquids.

2.1 Viscosities

The viscosity of ionic liquids is influenced by a combination of van der Waals interactions, coulomb interactions and hydrogen bond formations [21].

Figure 2 shows the temperature-dependent viscosity of EMIM OTf (1), PMPyrr BTA (4), the 90 : 10 mol % mixture of EMIM OTf and PMPyrr BTA, the 50 : 50 mol % mixture of EMIM OTf and PMPyrr BTA and the 10 : 90 mol % mixture of EMIM OTf and PMPyrr BTA.

All measurements were performed under the same conditions under air. Due to the possibility of the absorption of water from the air, the water content of the solutions might have an influence on the results and was therefore measured directly after the last measurement. It was less than 1% after all measurements.

PMPyrr BTA (4) has at 25 °C a significantly higher viscosity than EMIM OTf (1) and the mixtures of EMIM OTf and PMPyrr BTA. The mixtures of 10 : 90 mol % EMIM OTf and PMPyrr BTA and of 50 : 50 mol % EMIM OTf and PMPyrr BTA have a comparable viscosity at room temperature, which is slightly higher than the viscosity

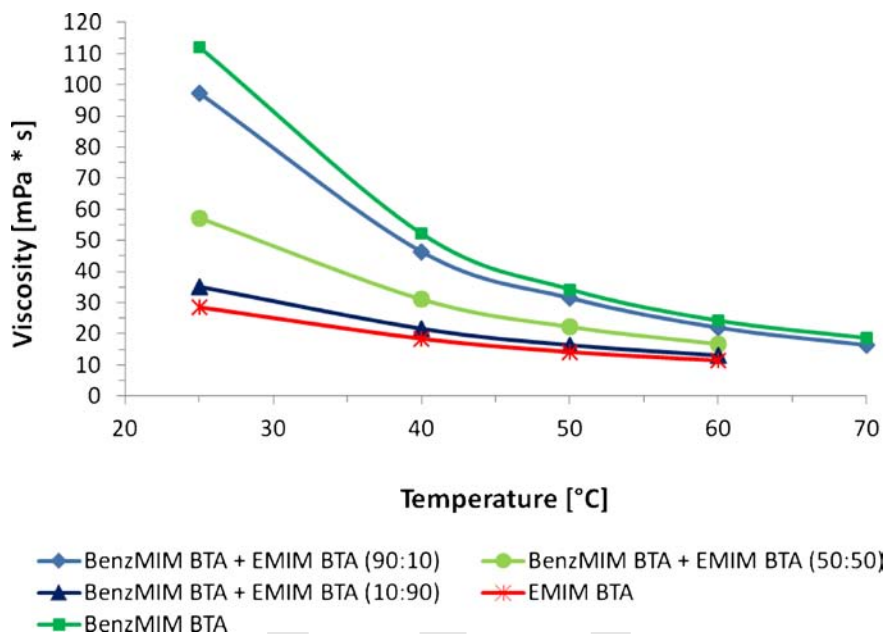


Fig. 3. Temperature-dependent viscosity of selected mixtures of BenzMIM BTA (3) with EMIM BTA (2) (the ratio is given in mol %).

of pure EMIM OTf, while the viscosity of the mixture of 90 : 10 mol % EMIM OTf and PMPyrr BTA is significantly lower than the viscosity of pure EMIM OTf.

The temperature-dependent viscosities of BenzMIM BTA, EMIM BTA and the investigated mixtures of these two ionic liquids are shown in Fig. 3.

EMIM BTA(2) has at 25 °C a significantly lower viscosity than BenzMIM BTA (3). The viscosity of the 90 : 10 mol % mixture of BenzMIM BTA and EMIM BTA is at room temperature slightly lower than the viscosity of pure BenzMIM BTA. The viscosity of the 50 : 50 mol % mixture of BenzMIM BTA and EMIM BTA lies approximately in the middle of the viscosities of the pure ionic liquids and the viscosity of the 10 : 90 mol % mixture of BenzMIM BTA and EMIM BTA is slightly higher than the viscosity of pure EMIM BTA. So in this case we did not observe a significant reduction of the viscosity by mixing.

2.2 Conductivities

The temperature dependent conductivity of EMIM OTf (1), PMPyrr BTA (4) and the selected mixtures of EMIM OTf and PMPyrr BTA are shown in Fig. 4.

All measurements were performed under the same conditions in a sealed measuring cell in order to avoid contact with air and humidity.

The conductivity of the mixture of the 10 : 90 mol % EMIM OTf and PMPyrr BTA is significantly higher than the conductivity of the pure PMPyrr BTA. The mixture of 50 : 50 mol % EMIM OTf and PMPyrr BTA has only a slightly higher conductivity

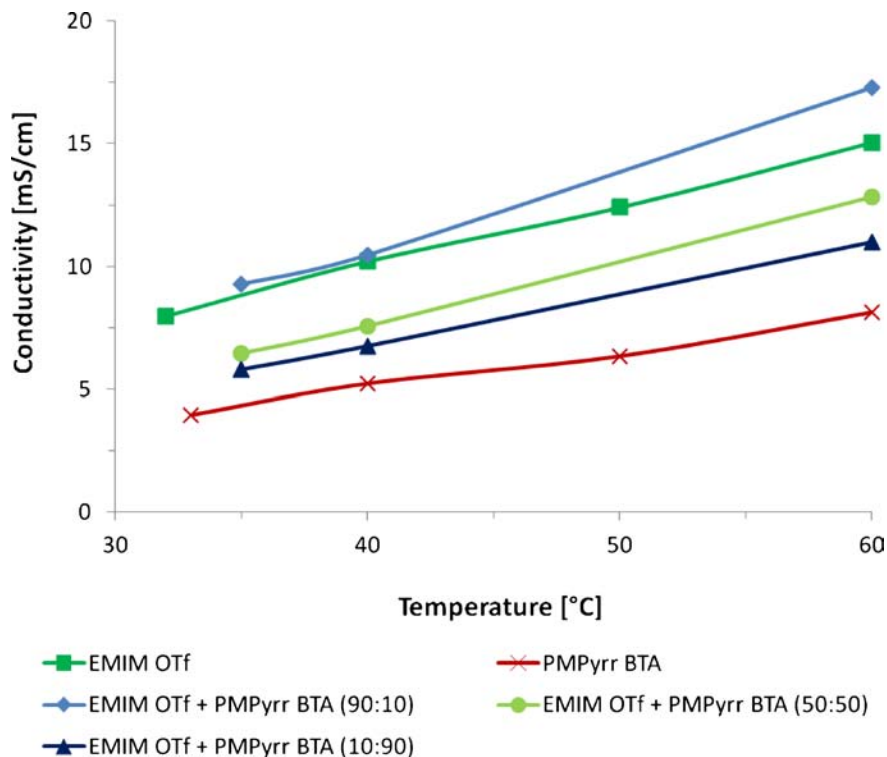


Fig. 4. Temperature-dependent conductivity of selected mixtures of EMIM OTf (1) with PMPyrr BTA (4) (the ratio is given in mol %).

than the mixture of 10 : 90 mol % EMIM OTf and PMPyrr BTA. The highest conductivity is observed for the mixture of 90 : 10 mol % EMIM OTf and PMPyrr BTA. The observed conductivities of the selected mixtures of EMIM OTf and PMPyrr BTA fits well with the expectations from the observed viscosities. But surprising results were obtained for the conductivities of the selected mixtures of BenzMIM BTA and EMIM BTA (Fig. 5).

The mixture of 10 : 90 mol % BenzMIM BTA and EMIM BTA possesses a significantly higher conductivity than pure EMIM BTA even though the viscosity of this mixture is slightly higher than the viscosity of pure EMIM BTA (Fig. 3).

The temperature-dependent conductivity of a mixture of EMIM OTf with PMPyrr BTA and 3 mol % Lithium bis(trifluoromethylsulfonyl)amide (Li BTA) is shown in Fig. 6.

As expected, the conductivity of the pure ionic liquids and of the mixtures is reduced by addition of Li BTA. Interestingly, a higher amount of EMIM OTf leads to a higher reduction of the conductivity by addition of Li BTA. This might be due to the worse miscibility of Li BTA with EMIM OTf in comparison to the miscibility of Li BTA with PMPyrr BTA. The conductivity of pure EMIM OTf is comparable to the conductivity of the mixture of 90 mol % EMIM OTf and 10 mol % PMPyrr BTA after

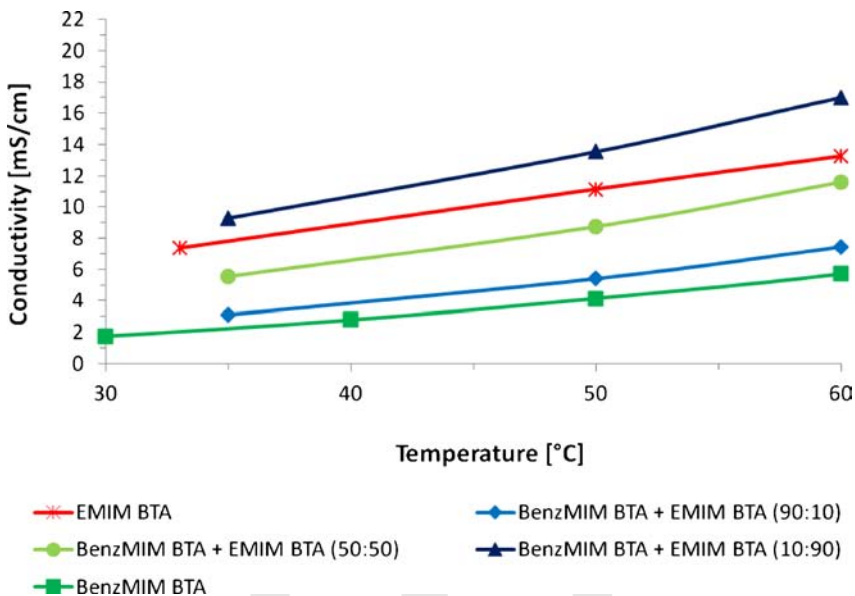


Fig. 5. Temperature-dependent conductivity of selected mixtures of BenzMIM BTA (3) with EMIM BTA (2) (the ratio is given in mol %).

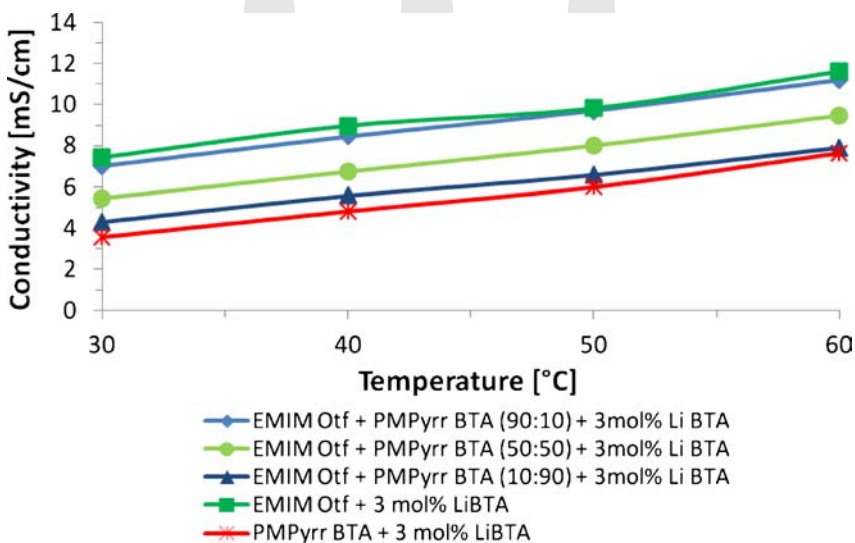


Fig. 6. Temperature-dependent conductivity of selected mixtures of EMIM OTf (1) with PMPyrr BTA (4) (the ratio is given in mol %).

addition of Li BTA, while the pure mixture of 90 mol % EMIM OTf and 10 mol % PMPyrr BTA has at temperatures above 40 °C a slightly higher conductivity than the pure EMIM OTf (see Fig. 4).

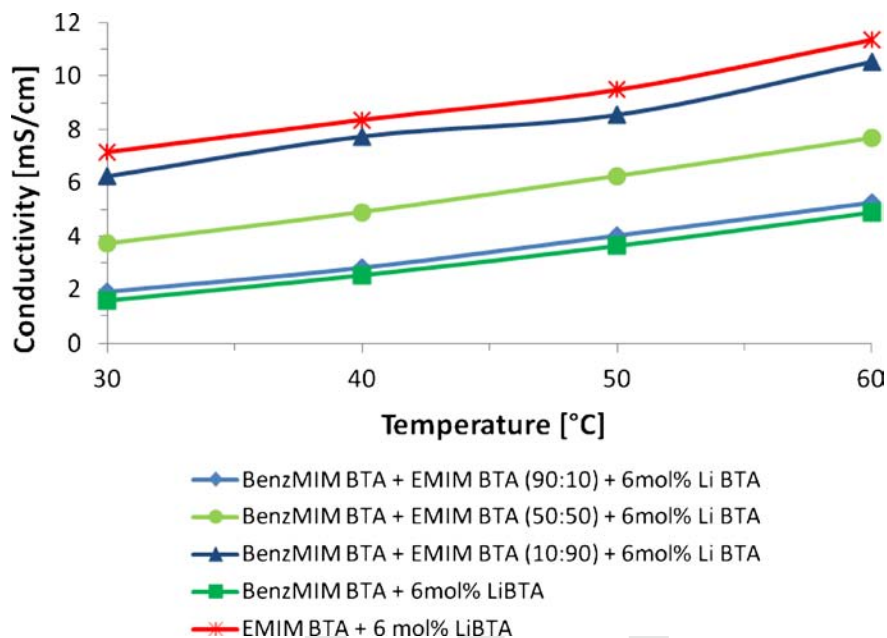


Fig. 7. Temperature-dependent conductivity of selected mixtures of BenzMIM BTA (3) with EMIM BTA (2) (the ratio is given in mol %).

Figure 7 summarizes the temperature-dependent conductivities of BenzMIM BTA, EMIM BTA and selected mixtures thereof. The influence of Li BTA on the conductivity of EMIM BTA is significantly higher than on the conductivity of BenzMIM BTA. At 50 °C the conductivity of EMIM BTA is reduced by 1,657 mS/cm after addition of Li BTA while the conductivity of BenzMIM BTA is only reduced by 0,514 mS/cm. Hence, the decrease of the conductivity of the mixtures is all the more the higher the amount of the EMIM BTA. Due to the high influence of the Li BTA on the conductivity, the mixture of 10 mol % BenzMIM BTA and 90 mol % EMIM BTA has after addition of Li BTA a lower conductivity as the mixture of EMIM BTA and Li BTA, while the same mixture has without Li BTA a slightly higher conductivity than the pure EMIM BTA (see Fig. 5).

Conventional electrolytes for lithium ion batteries have a conductivity of at least 10 mS/cm [22]. All investigated ionic liquids as well as their selected mixtures have after addition of Li BTA a conductivity which is at least 2 mS/cm lower. This shows that further optimizations are necessary before using an electrolyte consisting of pure ionic liquids for commercial lithium ion batteries.

The Arrhenius plot of the investigated mixtures of ionic liquids and the pure ionic liquids is shown in Figs. 8 and 9.

The plots show that the pure ionic liquids as well as the selected mixtures of the ionic liquids deviate from Arrhenius like behavior and fit to a Vogel–Tammann–Fulcher like behavior. A Vogel–Tammann–Fulcher like behavior of pure ionic liquids was already observed by Gores *et al.* [23].

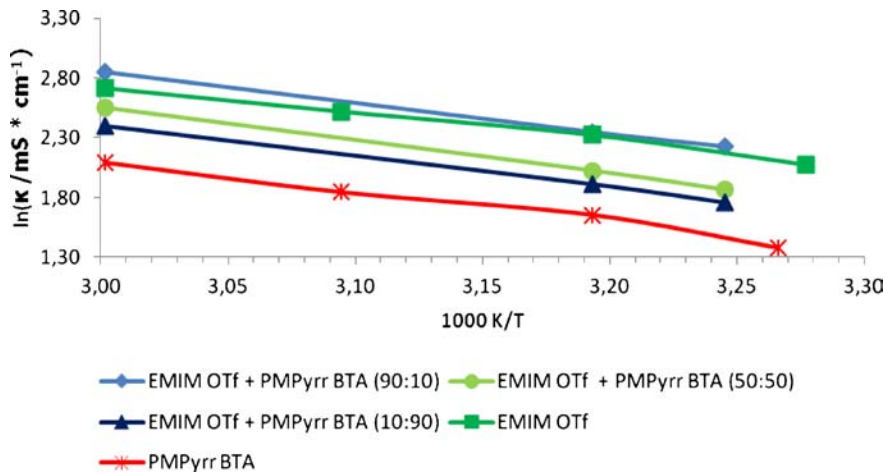


Fig. 8. Arrhenius plot for EMIM OTf, PMPyrr BTA, and the mixtures of EMIM OTf and PMPyrr BTA temperature dependent conductivity.

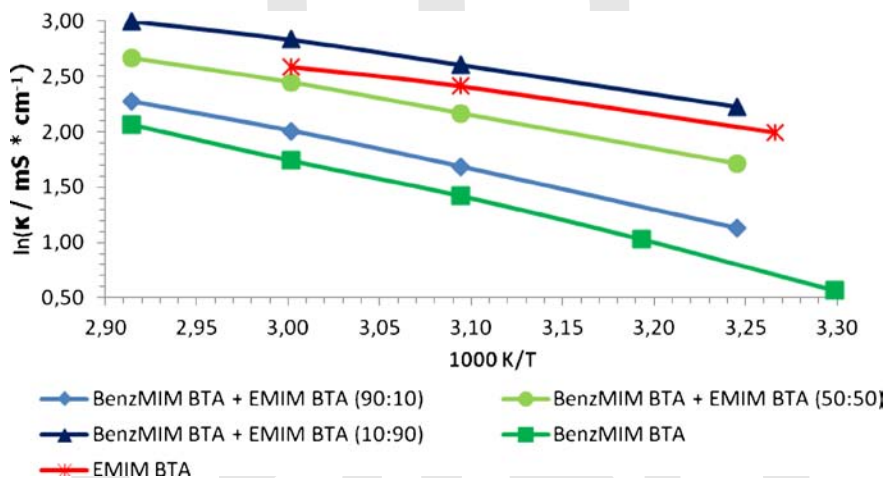


Fig. 9. Arrhenius plot for BenzMIM BTA, EMIM BTA, and the mixtures of BenzMIM BTA and EMIM BTA temperature dependent conductivity.

Figure 10 shows the Walden plot of the investigated ionic liquids and the mixtures thereof. The molar conductivities of the ionic liquids were calculated according to Eq. ((1)).

$$\Lambda_m^0 = \kappa \cdot V_m = \kappa \cdot \frac{M}{\rho} \quad (1)$$

As can be seen, the correlation between the ionic conductivity and the viscosity of the investigated ionic liquids and their selected mixtures are linear. Therefore, the conduc-

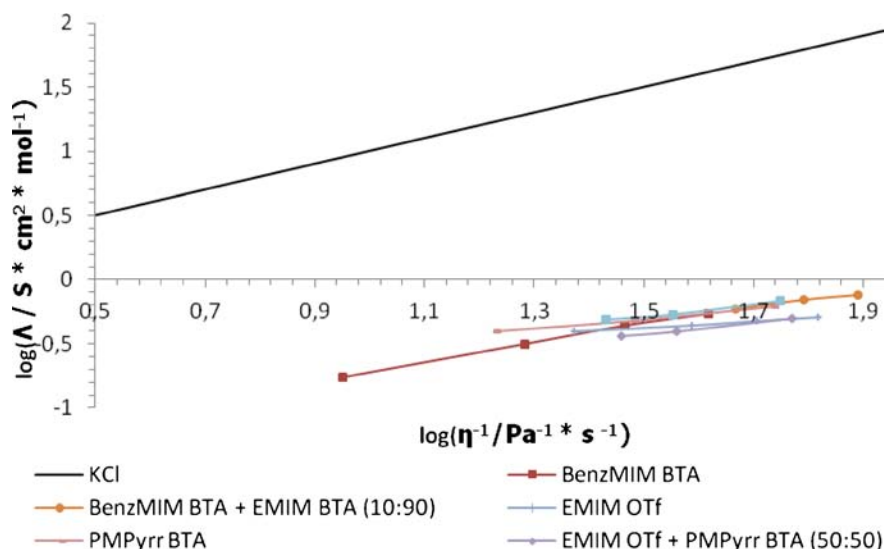


Fig. 10. Walden plot for BenzMIM BTA, EMIM OTf, PMPyrr BTA and selected mixtures thereof in comparison to the ideal KCl line.

tivity is mainly controlled by ion migration. The Walden plots of the selected ionic liquids and of the selected mixtures lie below the so called ideal KCl line which corresponds to a 0.01 M aqueous KCl solution. Therefore the ions of the investigated ionic liquids and their mixtures are not completely dissociated.

3. Conclusion

In this preliminary study we were able to demonstrate that viscosities can be reduced and conductivities can be increased by using binary mixtures of ionic liquids. In upcoming investigations this important principle will be extended to ternary mixtures. The use of mixtures of ionic liquids has a large potential for electrochemical applications in general and for lithium ion batteries in particular. In addition, further investigations are necessary to understand the influence of the bulk structure of the ionic liquids on the viscosity and the conductivity of the mixtures of different ionic liquids and to identify mixtures of ionic liquids which have even higher conductivities. Another approach to decrease the viscosity and to increase the conductivity of electrolytes based on ionic liquids is the addition of molecular solvents which could be shown by Lopes *et al.* [24].

4. Experimental

All ionic liquids used were synthesized by IOLITEC GmbH. The ratio of the mixtures of ionic liquids is given in mol %. The purity of the ionic liquids was determined by

NMR, ionchromatography and Karl-Fischer-titration. We used ionic liquids with the following quality:

ionic liquids with bis(trifluoromethylsulfonyl)amide anions:

purity > 99%, water content < 100 ppm, halides < 100 ppm, lithium ions < 200 ppm, 1-methylimidazole < 1%, 1-bromoethane < 1%,

1-ethyl-3-methylimidazolium trifluoromethylsulfonate:

purity > 99%, water content < 500 ppm, halides < 100 ppm, lithium ions < 10 ppm, 1-methylimidazole < 1%, 1-bromoethane < 1%.

The viscosity measurements were carried out using a Brookfield DV-E viscometer. The measurements were done under air. Conductivities were determined using a Metrohm 712 conductometer with a double platinum-shield electrode. The measuring cell was sealed with a cap during the measurements. The densities were measured with a pycnometer.

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