Trialkylsulfonium dicyanamides - a new family of ionic liquids with very low viscosities†

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Trialkylsulfonium dicyanamides show surprisingly low viscosities down to −20 °C and are therefore highly interesting liquid materials for separation processes and electrolyte applications at low temperatures.

Ionic liquids (ILs) have gained wide popularity in recent years because of their unique properties.[1] They have been used in a broad variety of catalytic,[2] engineering[3] and electrochemical applications (like dye-sensitized-solar-cells[4] or lithium-ion batteries[5]). However, one of the strongest barriers to many applications of ionic liquids is their relatively high viscosity compared to organic solvents.[6] High viscosity results in low diffusion coefficients and thus leads to slow mass transfer in ionic liquid/fluid multiphase systems. Furthermore, electric conductivities and viscosities are linked in a proportional fashion in many systems with high viscosities leading to low conductivities.

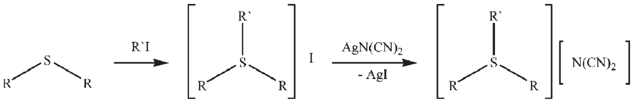
Therefore, considerable research effort has been dedicated to the development of new, low viscous ionic liquids in recent years. So far most of this research has been focussed on the use of imidazolium based ionic liquids. Namely systems including the 1-ethyl-3-methylimidazolium (EMIM) ions proved to be of high interest. Combinations of this cation with tetrachloroaluminate (18 mPa*s/23.0 mS*cm^{-1} at 25 °C),[7] tricyanomethanide (18 mPa*s/18 mS*cm^{-1} at 25 °C),[8] dicyanamide (21 mPa*s/27 mS*cm^{-1} at 25 °C)[9] and thiocyanate (21 mPa*s/21 mS*cm^{-1} at 25 °C)[10] ions were amongst the lowest viscous ionic liquids reported so far. To the best of our knowledge the combination of the [EMIM] cation and fluoride/hydrofluoric acid (4.85 mPa*s/100 mS*cm^{-1} at 25 °C)[11] results in the lowest viscous ionic liquid systems known to date. However, this system is not well defined and extremely difficult to handle: Therefore, it is very unlikely that this system will find practical applications.

Furthermore, *N*,*N*-dialkylpyrolidinium dicyanamide salts have been reported to form low viscous ionic liquids as dicyanamide salts (*e.g.* for methylpropyl pyrrolinium dicynamide a viscosity of 45 mPa*s at 25 °C has been published).[9]

So far only a few trialkylsulfonium based ionic liquids have been described in the literature. The list of salts that have been synthesized and characterized includes some bis(trifluoromethylsulfonyl)imide,[12] bromide[13] and haloaluminate[13] salts. A particularly low viscosity and high conductivity has been reported for trimethylsulfonium bromide/hydrobromic mixtures (8.3 mPa*s/56 mS*cm^{-1} at 25 °C),[14] but again the system is very difficult to handle due to its high corrosiveness.

In the present publication we present for the first time a new family of ionic liquids with surprisingly low viscosities and high conductivities based on trialkylsulfonium dicyanamides.

These ionic liquids are easily obtained in high quality by metathesis of the corresponding trialkylsulfonium iodides and silver dicyanamide (see Scheme 1). The precursors were prepared following the synthetic approach of Paulsson *et al.*[15] by a reaction of equimolar amounts of dialkylsulfide and alkyl iodide in dry acetone at ambient conditions.



Scheme 1 Synthesis of trialkylsulfonium dicyanamides.

Silver dicyanamide was precipitated by mixing aqueous solutions of silver nitrate and sodium dicyanamide (1 : 1 molar ratio). All ionic liquids were obtained as colourless or faint yellow liquids. Details of the synthesis are given in the ESI†.

All new ionic liquids described in this paper were characterized by ^{1}H and ^{13}C-NMR as well as by ESI-MS. The water content was determined by Karl–Fischer titration (for more details see ESI†).

The viscosities of all ionic liquids were measured in the range from −20 °C to 80 °C. The conductivities were recorded at 20 °C.

All substances show the typical decrease of viscosity with increasing temperature, with $[Et_3S][N(CN)_2]$ showing at 80 °C the lowest viscosity of all systems under investigation (5.7 mPa*s). All results of the viscosity measurements are summarized in Table 1.

All trialkylsulfonium dicyanamides prepared show low viscosities at room temperature, ranging from 20.9 mPa*s for $[Et_3S][N(CN)_2]$ to 60.0 mPa*s for $[MeBu_2S][N(CN)_2]$. Remarkably, the viscosities decrease in the order $[R'Bu_2S] > [R'Pr_2S] > [R'Me_2S] > [R'Et_2S]$ for the methylated ($R' = Me$) and the ethylated ($R' = Et$) species. Furthermore the viscosities of ionic liquids with $R' = Et$ are always slightly lower than those of the corresponding methyl-substituted compounds. To the best of our knowledge some of the new ionic liquids show the lowest viscosities at −20 °C that have been reported so far for binary ionic liquid systems. In order to do a proper comparison at this

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Table 1 Properties of trialkylsulfonium dicyanamide ionic liquids

$[R_2R'S]$ $[N(CN)_2]$	H_2O /ppm	$\eta^{-20\ ^\circ C}$ / mPa*s	$\eta^{0\ ^\circ C}$ / mPa*s	$\eta^{20\ ^\circ C}$ / mPa*s	$\eta^{40\ ^\circ C}$ / mPa*s	$\eta^{60\ ^\circ C}$/ mPa*s	$\eta^{80\ ^\circ C}$ / mPa*s	$\chi^{20\ ^\circ C}$ / mS*cm^{-1}	T_{dec}/ °C[b]
Me_3S	250.7	[a]	76.2	27.2	17.1	10.5	7.2	20.8	183
$MeEt_2S$	582.4	102.0	47.9	22.9	13.2	8.7	6.2	26.8	176
$MePr_2S$	388.4	185.0	70.7	29.5	15.7	9.7	6.6	15.0	178
$MeBu_2S$	139.2	509.0	169.0	60.0	27.8	15.4	9.7	5.9	178
$EtMe_2S$	484.7	120.0	55.7	25.3	14.1	9.1	6.4	22.1	182
Et_3S	271.3	94.9	43.3	20.9	12.1	7.9	5.7	22.4	180
$EtPr_2S$	161.4	173.0	68.6	29.4	15.6	9.6	6.5	14.7	176
$EtBu_2S$	136.8	494.0	143.0	51.7	24.8	14.0	8.8	6.9	179

[a] Solid at −20 °C. [b] TGA-onset.

temperature we also determined the viscosity data of the well known [EMIM] systems [EMIM]$[N(CN)_2]$ (122mPa*s at 355 ppm water content), [EMIM][SCN] (110 mPa*s at 131 ppm water content) and [EMIM]$[(CF_3SO_2)_2N]$ (231 mPa*s at 21 ppm water content). The comparison of these values with the low temperature viscosity data of the trialkylsulfonium dicyanmides clearly reveals the high attractiveness of the new ionic liquids for low temperature applications.

The new ILs show moderate to high conductivities up to 26.8 mS*cm^{-1} for $[MeEt_2S][N(CN)_2]$ at 25 °C. The conductivity depends on the chain length of the alkyl groups attached to the sulfur. For $R' = Me$ and $R' = Et$ the conductivity also follows the order $[R'Bu_2S] > [R'Pr_2S] > [R'Me_2S] > [R'Et_2S]$, indicating the expected correlation between viscosity and conductivity. Therefore the highest conductivities are obtained for $[MeEt_2S][N(CN)_2]$ (26.8 mS*cm1^{-1}) and $[Et_3S][N(CN)_2]$ (22.4 mS*cm^{-1}). It is noteworthy that the ionic liquid with the lowest viscosity in this study did not show the highest conductivity. This effect cannot be attributed to impurities as water or traces of halides should change both the conductivity and the viscosity.[16]

All new ionic liquids were also studied by DSC and TGA analysis. However, using DSC only the melting points of three of the substances were obtained. The melting point of trimethylsulfonium dicyanamide was determined to be at −1 °C, whereas ethyldimethylsulfonium dicyanamide melts at −28 °C and ethyldipropylsulfonium dicyanamide melts at −34 °C. All other systems did not show a proper melting point down to −140 °C. Moreover, all systems except $[Me_3S][N(CN_2)]$ were liquids at −20 °C.

Since ionic liquids have no apparent vapour pressure, their upper temperature limit is determined by their thermal decomposition temperature. For the new trialkylsufonium dicyanamides these values are given as TGA onset data in Table 1. In comparison to typical imidazolium based ionic liquids the trialkylsulfonium dicyanamides show significant lower temperatures of decomposition (for comparison: the temperature of decomposition for $[EMIM][N(CN)_2]$ has been found to be 240 °C[9]). All ionic liquids studied here decompose in a very narrow range between 176 to 183 °C. From this fact, we conclude that the process of thermal degradation is influenced very little by the alkyl substitution pattern at the ionic liquid's cation. Furthermore, long-term thermal stability of trimethylsulfonium dicyanamide was determined by isothermal TGA experiments in an argon purged system over 12 h. As expected, it was found that the long-term stability in the open system is significantly lower than the TGA onset data. Of course, purging the TGA chamber with a constant argon flow influences the thermal stability, because volatile decomposition products are constantly removed from the equilibrium. As shown in Fig. 1, trimethylsulfonium dicyanamide showed good thermal stability over 12 h at 50 °C, but lost about 5% of its weight in the 12 h experiment at 100 °C. At more elevated temperature the decomposition process was much faster. Remarkably, the TGA measurements at 150 °C indicate a maximum weight loss of *ca.* 43%. For the trialkylsulfonium dicyanamides under investigation this finding correlates to the formation of volatile dimethylsulfide and a non-volatile methyldicyanamide species over time with the latter remaining in the sample chamber.

The absence of the imidazolium moiety in the new ionic liquids prompted us to study the UV/Vis spectra of these new melts. Ionic liquids with no absorbance of light down to the UV range may be of interest for some optical applications. Indeed, trimethylsulfonium dicyanamide dissolved in water shows the same absorbance spectra than an aqueous solution of sodium dicyanamide, indicating that the cation itself is UV/Vis inactive. However, for the same ionic liquid in neat form (measured in a 2 mm cuvette) a significant absorbance occurred at 350 nm with a fairly long absorption tail even beyond 400 nm. The spectra are given in the ESI†. Trimethylsulfonium dicyanamide is soluble in water, acetonitrile and acetone. Miscibility gaps are found with toluene, diethylether and—very remarkably—also with dichloromethane and chloroform.

In conclusion, our results provide strong evidence that trialkylsulfonium dicyanamides are a very promising family of new ionic liquid materials especially for low temperature

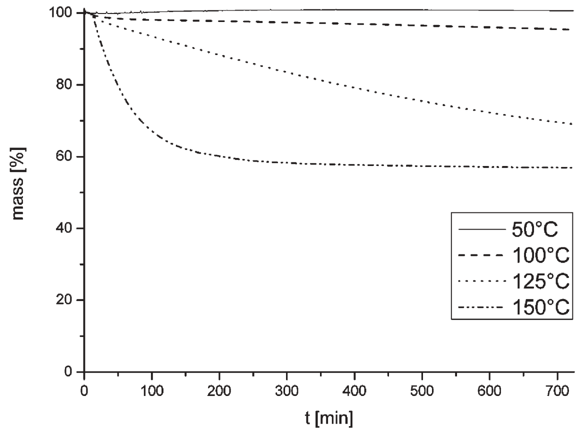

Fig. 1 Long-term stability of trimethylsulfonium dicyanamide.

applications down to −20 °C. This is due to their particularly low viscosity which may help to overcome traditional problems of slow mass transport and low electrical conductivity found in the traditional, more viscous ionic liquids at these low temperatures. We could further show that the thermal stability for applications at temperatures below 50 °C is excellent and an operating temperature range of up to 100 °C may be realistic in closed systems. We anticipate that these new ionic liquids will find applications in the area of low temperature separation technologies (*e.g.*, gas separation) and electrochemical devices such as dye-sensitized-solar-cells.

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