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Low viscosity ionic liquids based on organic salts of the dicyanamide anion

Douglas R. MacFarlane,* Jake Golding, Stewart Forsyth, Maria Forsyth and Glen B. Deacon

Centre for Green Chemistry, School of Chemistry, PO Box 23, Victoria 3800, Australia.
E-mail: dmacfarlane@sci.monash.edu.au

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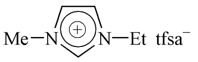
New families of salts *viz.* quaternary ammonium, *N*-alkyl-*N*-methylpyrrolidinium or 1-alkyl-3-methylimidazolium dicyanamides, $\mathrm{Cat^+N(CN)_2^-}$, are low melting compounds, most being liquid at rt, water-miscible and have low (for ionic liquids) viscosity at rt, *e.g.* η = 21 cP for 1-ethyl-3-methylimidazolium dicyanamide.

Currently, many chemically inert ionic liquids, which are of interest as media in Green Chemistry,[1] have viscosities much higher than those of solvents normally used in synthesis. Thus the search for new, more versatile ionic liquids is driven in part by the need for materials of lower viscosity. High viscosities not only lead to handling difficulties *e.g.* in filtration, decantation, and dissolution, but may also lead to reduced reaction rates and competitive unimolecular side reactions. One of the most fluid, inert of families of ionic liquids is that based on the bis(trifluoromethanesulfonyl)amide, $\mathrm{N(Tf)_2^-}$ ion,[2] for example, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (**1**) (η = 34 cP 20 °C;[2a] *cf.* H_2O, 1 cP; toluene 0.59 cP).



1 $\mathrm{N(Tf)_2^-}$ = $\mathrm{N(SO_2CF_3)_2}$

There is also a need for donor solvent characteristics. We now report several new series of salts based on the dicyanamide (dca) anion, *viz.* quaternary ammonium, pyrrolidinium, and imidazolium dicyanamides (**2–4**), most of which are liquids at rt. These have a different solubility profile from the corresponding bis(trifluoromethanesulfonyl)amides, potential donor characteristics as the anion is a powerful ligand,[3] and, in representative cases, lower viscosity.

$\mathrm{[N(C_6H_{13})R_3]^+\ dca^-}$

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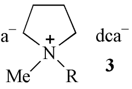

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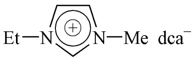

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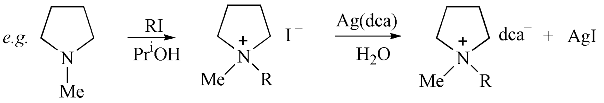
dca = $\mathrm{N(CN)_2}$

Quaternary iodide salts of triethylamine, tributylamine, *N*-methylpyrrolidine, and 1-methylimidazole were prepared by reported methods,[2,4] and were converted into the corresponding dicyanamides by reaction with a slight excess of silver dicyanamide in water or ethanol (Scheme 1).

Filtration to remove AgI and evaporation of water under vacuum gave the ionic liquid. Preparative details for two examples are provided;† more extensive details and discussion of properties will be published elsewhere.[5] Identification was by ^{1}H NMR and positive and negative electrospray MS.† The possible presence of residual $\mathrm{I^-}$ and $\mathrm{Ag^+}$ were examined *via* inspection of the appropriate mass regions of the respective mass spectra. The sensitivity of the MS measurement to trace amounts of $\mathrm{I^-}$ was determined by spiking the ionic liquids with known iodide concentrations; the noise limited detection limit was thereby found to be 0.5% (w/w) $\mathrm{I^-}$. No discernable I mass peaks were found in the dca salts, therefore indicating a residual I content of < 0.5% (w/w). The same considerations and lack of a detectable signal indicate residual Ag < 0.5% (w/w). It is known[6] that impurities such as halides and water can have an effect on properties such as viscosity, though the effect of water in particular is expected to be more dramatic when the viscosity differs greatly from that of pure water (*e.g.* emim $\mathrm{BF_4}$[6]). After rigorous final drying, compounds were handled in a nitrogen drybox during preparation of thermal analysis samples. Viscosity measurements were carried out in a drybox.



Scheme 1

Thermal properties of the salts were investigated by differential scanning calorimetry. All of the dca salts, except the *N*,*N*-dimethylpyrrolidinium compound, are liquids at rt with well defined mps below 0 °C (Table 1), providing a large liquid range. Notably, the mps are 20–30 °C or even more below those of the corresponding salts,[2a] perhaps an unexpected result since charge delocalisation could be expected to be greater for dca, producing weaker ion–ion interactions. Many of the dca salts are glass forming, with very low glass transition temperatures, T_g (Table 1), and only very sluggish crystallization kinetics at any temperature. The dimethylpyrrolidinium compound shows evidence of multiple solid phases, with a solid–solid thermal transition around −6 °C (Table 1) which consumes a large fraction of the total entropy of melting. This behaviour is indicative of plastic crystal phase formation and in the case of these ionic compounds, the plastic phases are often highly conductive.[7]

The viscosities of representative compounds at 25 °C (Table 1) are lower than those of the corresponding salts, *e.g.* 1-ethyl-3-methylimidazolium dca (η = 21 cP) and (η = 34 cP); *N*-butyl-*N*-methylpyrrolidinium dca (η = 50 cP) and (η = 85 cP).[2c] This rather useful trend is possibly related to the smaller size of the anion and parallels the lower mps of the dca compounds. In practical terms, it is possible to filter at rt a precipitate from a suspension in the lower viscosity dca salt with a sintered glass frit under vacuum.

Table 1 Thermal properties of dicyanamide salts[a]

Compound[b]	T_g/ °C ±2	$T_{s\text{–}s}$/ °C ±2	Mp/ °C ± 2	ρ/gcm^{-3} ±5% (25 °C)	Viscosity/ cP ±5% (25 °C)
$\mathrm{P_{11}(dca)}$		−6	115	—	
$\mathrm{P_{12}(dca)}$			−10	—	
$\mathrm{P_{13}(dca)}$			−35	0.92	45
$\mathrm{P_{14}(dca)}$	−106		−55[c]	0.95	50
$\mathrm{P_{16}(dca)}$	−100		−11	0.92	45
$\mathrm{N_{6222}(dca)}$	−82				
$\mathrm{N_{6444}(dca)}$			−43[c]		
emim(dca)	−104		−21	1.06	21

[a] T_g = glass transition temperature, $T_{s\text{–}s}$ = solid–solid transition temperature. [b] P = *N*,*N*-dialkylpyrrolidinium, N = tetraalkylammonium, subscripts refer to the number of carbons in the alkyl chains. [c] In these cases the melting transition is weak and the reported value only approximate.

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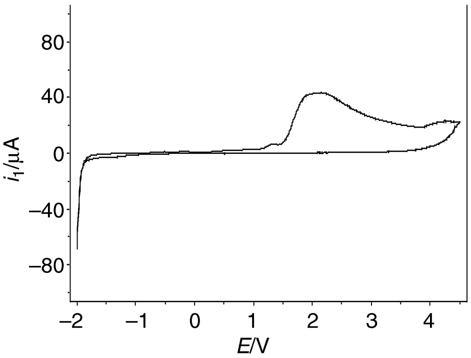

Fig. 1 Cyclic voltammetry of neat 1-ethyl-3-methylimidazolium dicyanamide (emim(dca)) carried out at 100 °C under a nitrogen atmosphere (dry box), on a glassy carbon microelectrode, with a platinum counter electrode and Ag/Ag$^+$ pseudo reference electrode.

The dca compounds which are liquid at rt are hygroscopic and are completely miscible with water, by contrast with the water-immiscible analogues.[2] The compounds also appear to absorb carbon dioxide readily. Extended periods at temperatures in excess of 100 °C have produced no evidence of breakdown. Qualitative tests showed that a number of hydrated cobalt(II), and copper(II) salts are appreciably soluble in 1-ethyl-3-methylimidazolium dca at rt with enhanced solubility on heating to 75 °C, whereas little dissolution of nickel salts and CuCl occurs. By contrast, the dca-soluble $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ are insoluble in the corresponding liquid at rt and only dissolved slightly at 75 °C. The solubility of the salts in the dca solvent may be due to its donor ligand properties, consistent with the rich coordination chemistry that is known of the anion,[3] though the inert behaviour of nickel salts is surprising. Of further interest is that glucose is soluble in the dca ionic liquid but not in the salt. Thus, the corresponding dca and salts show complementary solvent properties.

The electrochemical behaviour of these salts is illustrated by the example of the cyclic voltammogram in Fig. 1. The liquid is stable to quite low potentials, around −2 V *vs.* Ag/Ag$^+$, in common with other salts of this cation; the reductive limit presumably reflecting a reduction reaction of the cation. The stability in the oxidative range is reduced as compared to the analogue[2] but still leaves a large (>3.5 V) window for electrochemical use. The irreversible oxidation observed at *ca.* 1.5 V *vs.* Ag/Ag$^+$ may be indicative of the formation of a neutral dimer, $[N(CN)_2]_2$, a compound of theoretical interest but which has not been characterized.[8]

Thus new low melting, water-miscible, ionic liquids of relatively low viscosity which have considerable potential as a reaction medium and with a coordinating anion have been produced.

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Notes and references

† *Representative syntheses: 1-ethyl-3-methylimidazolium dicyanamide*: [emim(dca)]. Ag(dca)[9] (2.0 g, 11 mmol) was added to a solution of emimI (2.60 g, 11 mmol) in water (30 ml), and the resulting suspension was stirred overnight. Filtration and evaporation under vacuum gave the crude title compound, which was then dissolved in DCM and the solution dried over anhydrous $MgSO_4$. Evaporation under vacuum gave emim(dca) which was finally dried under vacuum over SiO_2 (yield, 1.51 g, 96%). Anal. Calcd for $C_8H_{11}N_5$: C, 54.2; H, 6.3; N, 39.5%. Found C, 52.7; H, 6.3; N, 38.6%. IR (liquid film): 3489 (w), 3150 (s), 3106 (s), 2988 (s), 2365 (w), 2232 (v.s), 2195 (v.s), 2132 (v.s), 1637 (w), 1573 (s), 1466 (m), 1427 (w), 1388 (w), 1131 (s), 1170 (s), 1088 (w), 1030 (w), 959 (w), 905 (w), 844 (w), 802 (w), 753 (m), 701 (w), 648 (m), 622 (s) cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO): δ 1.42 (t, CH_3), 3.84 (s, n-CH_3), 4.19 (q, N-CH_2), 7.67 (s, CH), 7.76 (s, CH), 9.10 (s, N-CH-N) ppm. ^{13}C NMR (JMOD) (75 MHz, d_6-DMSO): δ 14.5 (s, CH_3), 35.2 (s, CH_3), 35.2 (s, CH_3), 43.6 (s, CH_2), 121.4 (s, CH), 123.0 (s, CH) ppm, $N(CN)_2^-$ and N–CH–N not cited. Electrospray MS(+ve): *m*/*z* 111 (100% − emim$^+$) MS (−ve) *m*/*z* 66 (100% dca$^-$), 243 (5% [emim-$(dca)_2]^-$.

N-butyl-N-methylpyrrolidinium dicyanamide: [P_{14}(dca)] Ag(dca) (2.10g, 12 mmol) and P_{14}I (2.70g, 10 mmol) gave [P_{14}(dca)] (yield 1.73g, 83%). IR (liquid film): 3488 (m), 2964 (m), 2876 (w), 2227 (s), 2191 (m), 2131 (v.s), 1466 (m), 1340 (m), 1306 (m), 1004 (v.w), 929 (w), 902 (v.w), 830 (v.w) cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO): δ 0.92 (t, CH_3), 1.31 (m, CH_2), 1.67 (m, CH_2), 2.06 (br-t, 2 × CH_2), 2.96 (s, CH_3), 3.24 (q, CH_2), 3.43 (br-m, 2 × CH_2) ppm. ^{13}C NMR (75 MHz d_6-DMSO): δ 13.8 (s, CH_3), 19.6 (s, 2 × CH_2), 21.5 (s, CH_2), 25.3 (s, CH_2), 47.9 (t, CH_3), 63.3 (s, CH_2), 63.8 (t, 2 × CH_2) ppm, $N(CN)_2$- not observed. Electrospray MS (+ve): *m*/*z* 142 (100%, P_{14}^+); MS (−ve) *m*/*z* 66 (100%, dca$^-$).

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