



Physico-chemical properties and nanoscale morphology in N-alkyl-N-methylmorpholinium dicyanamide room temperature ionic liquids



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ABSTRACT

A series of new room temperature ionic liquids based on N-alkyl-N-methylmorpholinium cations (the alkyl chain ranging from ethyl to nonyl) and a hydrophilic anion (dicyanamide), a mostly unexplored class of room temperature ionic liquids (RTILs), has been synthesized and characterized. Selected physico-chemical properties (density, viscosity and ionic conductivity) have been measured and the salts' propensity to organize into ionic clusters has been explored. The inspection of their Walden plots and electrospray ionization spectra strongly prompts for the occurrence of clustering phenomena, especially for salts bearing long alkyl chains. This structural organization has been confirmed using X-ray scattering techniques and the existence of a high degree of intermediate range order has been detected, as fingerprinted by distinct diffraction features at low Q. These evidences are rationalized in terms of a structural model where, similarly to other RTILs, the alkyl chains tend to segregate from the charged moieties.

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1. Introduction

Over the past ten years, as a consequence of their physico-chemical properties [1], ionic liquids (ILs) have been the object of an increasing interest, being proposed as environmental friendly solvents for chemical synthesis, [2–4] (bio)catalysis, [5–7] separation technologies [8,9] and as solvents/templates for nanomaterial preparations [10,11]. Moreover, owing to their unique electrochemical properties [12] a large number of ILs have been investigated to promote the safety and performance of solar cells, fuel cells, capacitors and lithium batteries. The most commonly studied ILs are based on imidazolium cations, combined with different anions, such as hexafluorophosphate $[\text{PF}_6]^-$, tetrafluoroborate $[\text{BF}_4]^-$ or bistriflimide $[\text{Tf}_2\text{N}]^-$. Imidazolium-based ILs have been extensively investigated in the last decade; on the other hand very few studies exist on other classes of ILs, such as morpholinium-based ones: these are peculiar salts as they bear a cyclic cation with a significant dipolar moment and can also bear a side alkyl chain that can affect several physico-chemical properties: recently, some long chain salts of this class have attracted attention because of their structural properties for the design of IL crystals

[13–15]. Earlier this year, N-alkyl-N-methylmorpholinium bistriflamide (alkyl = even chains from ethyl to octyl) has been thoroughly investigated probing the fluorescence response of Coumarin-153 and rotational dynamics of dipolar probes when dissolved in these liquids [16,17]. The authors highlighted that morpholinium-based RTILs are characterized by a high level of structural heterogeneity. Morpholinium-based ILs have been considered also of interest as catalysts for organic synthesis, [18] heat stabilizers, or antioxidants for lubricating oils [19] and for electrochemical applications [20–24]. Protic morpholinium-based ILs have been proposed as electrolytes for fuel cell devices and thermal transfer fluids [25].

Melting points in these ILs are often above or close to room temperature; for example, N-ethyl-N-methylmorpholinium bromide is a solid with a high melting ($\text{mp} = 188^\circ\text{C}$) and the association with common anions, such as $[\text{BF}_4]^-$, $[\text{Tf}_2\text{N}]^-$, $[\text{PF}_6]^-$, gives ILs that are solid at room temperature, characterized by higher viscosities and lower conductivities than the analogous pyrrolidinium- or piperidinium-based ILs due to the presence of an oxygen atom in the cyclic ring [26].

Significantly, sporadic data of toxicity reported for some N-dialkylmorpholinium based ILs have evidenced [27–29] lower environmental impact of these salts with respect to other commonly used ILs. A recent study on bromides salts has shown that low toxicity to *Vibrio fischeri* is a peculiarity of morpholinium salts bearing short alkyl chains [30]. Moreover, in the case of the ethyl derivative this low toxicity is

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associated to a significant biodegradability (around 40%), comparable to that characterizing the more biodegradable functionalized imidazolium-based ILs. Recent studies have however shown that dicyanamide ($[\text{N}(\text{CN})_2]^-$) anion is able to give highly fluid and conductive ILs, [31–33] which are generally characterized by toxicity levels at least to aquatic species (algae and crustaceans) lower than analogous salts bearing other common anions, such as tetrafluoroborate and trifluoromethanesulfonate [34].

In this framework of sporadic studies on this class of ILs, we conducted a systematic characterization of the physico-chemical and solvent properties of *N*-alkyl-*N*-methylmorpholinium dicyanamide (alkyl = ethyl-nonyl), exploring the effect of the alkyl chain length on several properties (including density, viscosity and conductivity) and on the degree of association between the ions. The mesoscopic order in these ionic liquids has also been explored using X-ray scattering techniques, in order to extract information on their propensity to structurally organize via alkyl tail segregation, a phenomenon that is ubiquitous in ionic liquids (see e.g. [35–41]), but was not so far observed in ILs bearing cyclic ether functionalized cations (we mention that the Samanta's study [16,17] provides preliminary indication of such a behavior also in morpholinium-based salts).

2. Experimental part

2.1. Synthesis and characterization

The investigated *N*-alkyl-*N*-methylmorpholinium dicyanamides have been synthesized as reported in Scheme 1. In the first step, the corresponding alkyl bromide and *N*-methylmorpholine were reacted in acetonitrile at 70 °C to produce *N*-alkyl-*N*-methylmorpholinium bromides, $[\text{Mor}_{1,n}]\text{Br}$, **1**. In the case of short chain bromides, an excess of the alkyl halide was used to prevent problems arising from evaporation due to the reaction temperature. Subsequent metathesis of **1** with silver dicyanamide ($\text{Ag}[\text{N}(\text{CN})_2]$), freshly prepared by reacting AgNO_3 and $\text{Na}[\text{N}(\text{CN})_2]$ in equimolar quantities, resulted in the corresponding dicyanamide salts **2**, i.e. $[\text{Mor}_{1,n}][\text{N}(\text{CN})_2]$.

All synthesized *N*-alkyl-*N*-methylmorpholinium bromides are colorless solids at room temperatures whereas the corresponding dicyanamides are colorless liquids. The structures and compositions of all ILs were confirmed by electrospray ionization mass spectrometry (ESI-MS), IR, ^1H and ^{13}C NMR spectroscopy. ^1H NMR and head space GC-MS analyses were used to check for residues of unreacted reagents or solvents. On the other hand, ESI-MS spectra showed that species such as Ag^+ or Br^- , arising from not completely conducted metathesis reactions, were not detectable in the samples used for physico-chemical property determination. Finally, to ensure that the amount of water and other volatile compounds in ILs was reduced as much as possible, each IL was kept under vacuum (pressure around 10^{-3} mbar) with a stirring at 80–90 °C for 24 h before each test. On the other hand, measurements conducted in not completely closed systems (for example, IR spectra) were performed within 1–2 min to reduce the measurement errors arising from the slight increase in water content.

^1H NMR and ^{13}C NMR measurements were conducted on a Bruker Advance II 250 spectrometer operating at 250 MHz. Electrospray

ionization spectra were recorded on a Finnigan LCQ Advantage (Thermo Finnigan, San Jose, CA, USA) ion trap instrument equipped with an Excalibur software. Solid samples were dissolved in proper volume of acetonitrile (HPLC grade) and injected directly (20 ppm) by a pump syringe (5 $\mu\text{l}/\text{min}$) in the ESI-MS system. The MS spectra were performed in the 50–2000 m/z range by the following ESI-MS parameters: positive mode–sheath gas flow 20 arb., spray voltage 4.5 kV, capillary temperature 280 °C, capillary voltage 24 V, tube Lens Offset 45 V; negative mode–sheath gas flow 20 arb., spray voltage 4.5 kV, capillary temperature 280 °C, capillary voltage –16 V, and tube Lens Offset –25 V.

Density was determined using the vibrating tube method with a Mettler Toledo DM45 instrument at 25 °C. Conductance measurements were performed using a CON 510 bench meter supplied with conductivity/TDS electrode. This electrode has a stainless steel ring and a cell constant of $K = 1.0 \text{ cm}^{-1}$. It also has an inbuilt temperature sensor for automatic temperature compensation. Viscosity and rheological measurements were conducted using a Brookfield DV-II + Pro concentric cylinder viscometer and a rotational rheometer (Rheostress RS150, Haake). Data were determined at shear rate ranging from 0 to 200 s^{-1} .

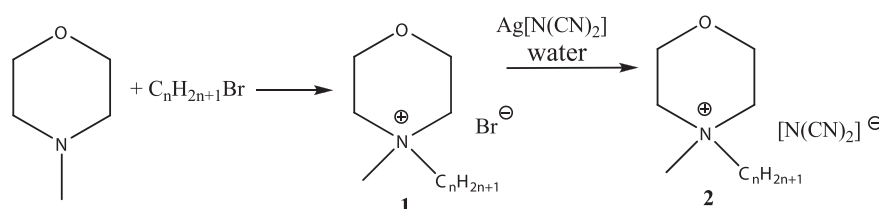
X-ray scattering experiments were conducted at the high brilliance beam line ID02 and at the high energy diffraction beamline ID15b of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The first beamline makes use of an instrumental setup that covers the momentum range $Q = 0.1\text{--}2 \text{ \AA}^{-1}$. Measurements were performed at 25 °C using a thermostated bath. The samples were kept inside a temperature controlled flow-through cell with an internal diameter of 1.9 mm. The corresponding empty cell contribution was subtracted. Calibration in absolute units (mm^{-1}) was performed with a neat water sample in a 2-mm capillary. Measurements conducted at ID15b allowed covering a much larger Q range (up to 20 \AA^{-1}), given the higher incoming X-ray energy ($E_{\text{incoming}} = 55.60 \text{ keV}$). The instrumental setup was based on a LINKAM TMS-600 thermostat that allows measurements to be conducted as a function of temperature, using a 1 mm outer diameter capillary. The corresponding empty cell contribution was subtracted.

3. Results and discussion

For all synthesized *N*-alkyl-*N*-methylmorpholinium dicyanamides, fundamental properties including density (ρ), viscosity (η) and conductivity (σ) have been measured after accurate drying (see above) and the corresponding data are shown in Table 1. Data for density and viscosity are plotted as a function of the alkyl chain length in Fig. 1.

The density values of the eight investigated morpholinium salts lie in the range 1.17 to 1.03 g/cm^3 . Thus, a moderate effect of cation structure on density can be evidenced: density decreases as the alkyl chain on the cation gets longer; moreover indications of an odd–even effect can be observed, the odd members showing a significantly higher density trend than the one followed by the even members of the homologous series.

Dicyanamide-based ILs are known to be characterized by small viscosity [31,32]; however, the inclusion of the ether oxygen in the



Scheme 1. Synthetic route to prepare *N*-alkyl-*N*-methylmorpholinium dicyanamide ILs.

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