



# Amidinium salts: Towards enabling electrochemistry in non-polar media from alkanes to ionic liquids



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## ABSTRACT

There is little known about electrochemical behavior in non-polar media due to lack of compatible, hydrophobic salts. In this work, this difficult challenge has been overcome by following a strategy based on designing and synthesizing a novel family of organic salts with highly-delocalized cations and anions. The salts are based on the amidinium cation with highly-delocalized positive charge and long alkyl groups that enable good miscibility in heptane, an archetypical, non-polar media, while being hydrophobic, room-temperature ionic liquids. The electrolyte solutions show ionic conductivities that span the range  $10^{-11}$ – $10^{-4}$  S cm<sup>-1</sup> and electrochemical activity which enable their application as antistatic agents and also as new type of hydrophobic electrolytes in various electrochemical devices.

## 1. Introduction

Electrochemistry in non-polar media is a difficult challenge due to the poor ionic conductivity of their electrolyte solutions even if salt solubility is enhanced by the use of surfactants [1,2]. This is because ionic conductivity in fluid, polar media (macroscopic level for liquids and microscopic for polymers above  $T_g$ ) depends on the solvation properties (for solubility) and the dielectric constant (for charge separation) of the medium [3]. Non-polar media such as liquid alkanes (e.g. hexane, heptane ... etc) lack electron pairs for interaction with cations while C and H atoms have similar electronegativity that prevents the formation of hydrogen bonds with anions, and hence their small dielectric constant ( $\epsilon < 2$ ) is solely due to electronic bond polarizability [4].

There are many benefits in making non-polar media ionically conductive: For example, it was shown previously that electrochemical rather than chemical (burning) oxidation of liquid alkanes is a viable path to eliminate CO<sub>2</sub> emissions from transportation or convert them to higher value chemicals [5,6]. Another is to improve their safety during transportation where ions can help disperse the electrostatic surface charge build-up, a serious flammability hazard considering the widespread use of these fuels [7,8]. Also, there is a need for non-polar media as electrolytes for electrochemical devices to replace the polar ones that are sensitive to water and prone to attack by very reactive

intermediates such as radicals and nucleophiles, all detrimental to the performance of the device. For example, they can replace carbonate and ether solvents in Li/S and Li/O<sub>2</sub> batteries as they offer greater chemical stability due to the absence of polar bonds such as C=O carbonyl or C–O–C (ether) [9,10].

As expected, conventional inorganic salts do not dissolve in a non-polar media such as liquid alkanes. However, organic salts can be designed to maximize the interaction with the liquid alkane by attaching long alkyl groups to, for instance, a quaternary ammonium cation. Yet, the saturation solubility of tetrakis(decyl or dodecyl)-ammonium-based salts in cyclohexane is very limited even with the use of very bulky, hydrophobic anions [11].

A successful strategy that we have adopted in this work is to prepare hydrophobic salts of highly-delocalized cations coupled with highly-delocalized anions. In the case of the anion, research on new salts for the relatively non-polar polymer electrolytes have resulted in the design of new families of anions with very low solvation energies. The archetype of this new family is bis(trifluoromethanesulfonyl)imide, [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]<sup>-</sup>, abbreviated as TFSI and will be referred to as imide from herein on. In the gas phase, the corresponding acid requires some of the lowest reported energies for H...X bond breaking [12]. Oxygen in conventional anions is the most demanding in terms of solvation while in TFSI the two trifluoromethyl, electron-withdrawing groups and the participation of a soft center (nitrogen) for charge delocalization concur

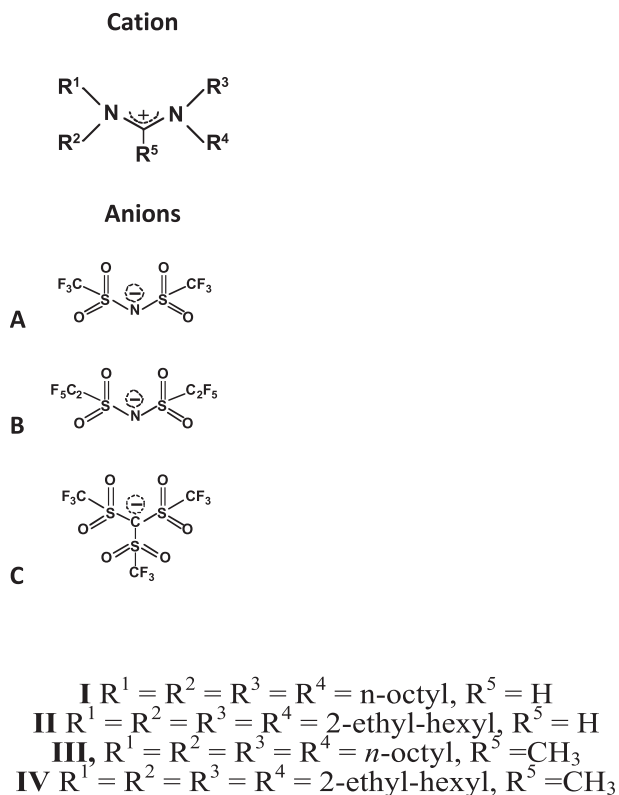
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to the remarkable properties of the salt derived from this anion. In parallel, the interest for room-temperature molten salts, better known as ionic liquids, have been revived with the emergence of covalent anion-based systems [13], far more stable and practical than the previously known chloroaluminates. In particular, the delocalized anions, i.e. TFSI and analogues (for example the  $\text{CF}_3\text{CF}_2$  equivalent, bis(pentafluoroethanesulfonyl)imide,  $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$ , abbreviated as BETI, or other anions with the negative charge on a central carbon atom such as tris(trifluoromethanesulfonyl)methide,  $[(\text{CF}_3\text{SO}_2)_3\text{C}]^-$ , abbreviated as TFSM), are the source of a wealth of new room temperature molten salts with high conductivity and low viscosity [14]. Such materials, like 1-ethyl-3-methyl-imidazolium TFSI are still polar and not appreciably soluble in liquid alkanes. Moreover, in most common ionic liquids that are based on the aliphatic or ringed ammonium cation, the positive charge is localized on the nitrogen atom which keeps the lattice energy slightly high (i.e. solubility low). In this work, we chose the amidinium cation,  $\{[(\text{Alkyl})_4\text{N}]_2\text{-C-R}\}^+$ , whose positive charge can be delocalized onto two nitrogen atoms with identical C–N bond lengths [15]. This, along with the four, long alkyl groups, results in a new family of low lattice energy, highly hydrophobic salts. The salts synthesized in this work are based on amidinium cations with a H atom or  $\text{CH}_3$  group on the central carbon atom and linear or branched octyl groups on the nitrogen atoms and the bulky, highly-delocalized anions with the chemical structures shown in Scheme 1. Most of the salts are liquid at room temperature and can be mixed with liquid alkanes over a wide concentration range. This property allows electrochemical studies with continuity between non-polar medium and ionic liquids at the other end of the concentration range.

## 2. Experimental

The cations were obtained by an hitherto unreported but simple trans-amination reaction from the corresponding amidinium where  $\text{R}^{1-4} = \text{H}$ , as acetate or chloride and dioctylamine or bis(ethylhexylamine) in ethanol (reflux) with elimination of ammonia.



Scheme 1. Chemical structure of the amidinium-based salts.

Unsymmetrical salts  $\text{R}^1 = \text{R}^2 = \text{methyl}$  and  $\text{R}^3 = \text{R}^4 = n\text{-octyl}$  results from the reaction of di-octylamine hydrochloride with dimethylformamide di-methyl acetal. The metathesis reaction in water with a Li or K salt of the corresponding anion gave the ionic liquid as liquid precipitate. All reagents and solvents were commercially available and used without further purification. Ionic conductivity measurements were performed using the AC impedance spectroscopy technique by varying the frequency between 1 MHz and 5 Hz using a conductivity cell with a cell constant of  $1 \text{ cm}^{-1}$ . The temperature was varied between  $-20$  and  $100^\circ\text{C}$  at intervals of  $2^\circ\text{C}$  allowing 20 min for thermal equilibration at each set point. Differential scanning calorimetric analysis was performed using a Perkin-Elmer Pyris 1. All the samples were sealed in aluminum DSC pans in an argon filled glove box and then scanned from  $-150$  to  $150^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ . Cyclic voltammetry measurements were made at a scan rate of  $50 \text{ mV/s}^{-1}$  on a VMP multichannel potentiostat (Bio-Logic Science Instrument). Pt micro-electrode (radius =  $25 \mu\text{m}$ ) was used as working electrode while a Ag wire was used as a counter and pseudo reference electrode.

## 3. Results and discussion

The salts are room temperature ionic liquids and the DSC scans, not shown here, show no thermal events except for a glass transition at low temperature. As a typical example, the **IIA** salt showed a glass transition temperature below  $-70^\circ\text{C}$ . This behavior is expected due to the very large size of the ions, especially the long alkyl chains that make molecular packing unfavorable [13].

The synthesized salts were first tested for solubility in heptane as a model alkane solvent and hydrocarbon fuel. The synthesized salts showed either complete solubility throughout the tested concentration range ( $> 0.4 \text{ M}$ ) (examples are **I** and **II** cations of **A** and **B** anions) or limited (**III** and **IV** cations of **A**, **B**) or no miscibility at all even at very low concentrations (salts of **C** anion). The solutions of **IA** and **IB** showed higher solubility reaching over  $0.4 \text{ M}$  compared to solutions of **IIA** and **IIB**, but the solutions are not stable over a very long period of time as we have noticed a minor precipitate that was not quantified after few months of storage. This might be due to the presence of impurities originating from the reactants such as excess protons and halides. We have also synthesized salts, not shown here, with less delocalized anions or cations  $\text{R}_1 = \text{R}_2 = \text{octyl}$ ,  $\text{R}_3 = \text{R}_4 = \text{methyl}$  and effectively had limited solubility. In summary, this can be considered as a significant increase in miscibility and pushes the limit to higher values compared to the limit observed by ammonium-based cations currently at slightly above  $0.25 \text{ M}$  [11].

Fig. 1a shows the dependence of conductivity of all the miscible salts (**IA**, **IB**, **IIA**, and **IIB**) on concentration in heptane. All have shown a general behavior: at low concentrations, all the solutions have shown low but applicable conductivities that lie in the range between  $10^{-9}$  and  $10^{-11} \text{ S cm}^{-1}$ . This range is high enough to enable these salts to work as an antistatic agent in transportation fuels. At higher concentration, the conductivity increased rapidly to reach values above  $10^{-4} \text{ S cm}^{-1}$  at  $1 \text{ M}$ .

The amidinium imide salt **IIB** showed the highest conductivity among all the salts in the concentration range from  $1 \text{ mM}$  to  $0.4 \text{ M}$ . This can be attributed to its high delocalization of the negative charge and the enhanced hydrophobicity of the BETI anion due to the two extra  $\text{CF}_2$  groups compared to other anions like TFSI (**IIA**). This results in a higher degree of dissociation and hence higher number of charge carriers and ionic conductivity. The solutions of BETI-based salts showed higher conductivities than those of the TFSI imide-based salts. At the highest concentration region of the figure, it can be clearly seen that the conductivity curves merge to values closer to  $10^{-4} \text{ S cm}^{-1}$ . This value is high enough to enable electrochemical activity in devices similar to batteries, electrolyzers and fuel cells. Fig. 1b shows the dependence of molar conductivity on concentration for all the miscible salts. It is clear that the molar conductivity increases significantly, in a logarithmic

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