

# Dissecting the mobility of ion pair from cationic clusters in hydroxylated ionic liquids by $^2\text{H}$ NMR

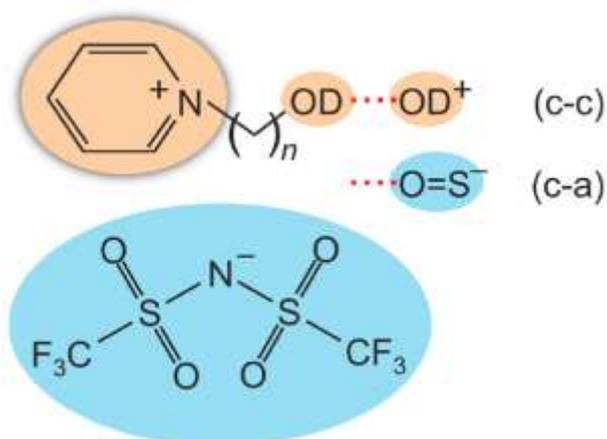
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Ionic liquids (IL) attract major attention as advanced electrolytes, solvents and reaction control agents. However, up to date, their structure-property relationship remains mostly empirical. Despite being essentially a Coulomb-type system, in many aspects their properties are governed by weaker interactions – hydrogen bonding and even dispersion interactions. Although the Coulomb interaction is more than an order of magnitude stronger than the hydrogen bond, the local and directional nature of the hydrogen bond matters and influences characteristically the properties of these fluid salts. Normally, the formation of hydrogen bonds between cation and anion increases the attractive Coulomb interaction and tightens the interaction between the oppositely charged ions, resulting in preformation of ion-pairs, i.e. the (c-a) pairs. Recently, using a combination of IR and solid state  $^2\text{H}$  NMR, we have shown [1-3], that rational desing of hydroxyl functional groups into the alkyl side chains in the pyridinium or piperidinium-based cations creates the possibility of formation of stable positively charged hydrogen bonded cationic (c-c) clusters both in liquid an solid states of the IL.



**Figure 1:** OD Groups of the Hydroxy-Functionalized 1-(n-Hydroxyalkyl)pyridinium Cations with  $n = 2-4$ . These OD groups form hydrogen bonds either with the oxygen of the OD groups of another cation or with the oxygen of the O=S group of the anion bis(trifluoromethylsulfonyl)imide, resulting in (c-c) clusters or (c-a) ion pairs.

In this contribution we discuss, that the presence of these somewhat counteintuitive (c-c) clusters greatly affect the physical properties of the ionic liquids, their molecular scale structure and dynamics. In particular, we show that the presence of (c-c) clusters alters the nature of the phase transition from liquids-solid to liquid-glass type, preventing thus the crystallization process. By means of the  $^2\text{H}$  NMR  $T_1$  and  $T_2$  relaxation analysis we show, that the mechanism of the isotropic diffusion, and consequently of the microscopic viscosity, is greatly affected by the availability of the the (c-c) clusters: for such liquids the isotropic rotational diffusion is driven by two distinct rate constants, one operating in the range of low temperatures and supercooled region and the second one govering the dynamics at high temperatures. Notably, when only the (c-a) pairs are present, the

isotropic diffusion is characterized the a single rate constant in the whole range of temperatures. . We finally discuss the role of the dispersion interactions for the observed phenomena, by inspecting cations with variable alkyl-chain lenght.

This work has been supported by the Russian Science Foundation (grant № 21-13-00047) and the Alexander von Humboldt Foundation.

## REFERENCES

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