Effects of ether-functionalized ionic liquids on membrane fusion related to their aggregation properties.

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Ionic liquids (ILs) are salts with relatively low melting points (below 100 °C). ILs are based on tuneable huge combinations of cations and anions whose combination strictly determines the physical-chemical properties and toxicological behaviour of the ILs themselves.

Since now the attention towards this promising class of alternative solvents and materials has been focused on the synthesis of ILs with unique physical properties (1st ILs generation), on the design of ILs with targeted chemical behaviour combined with specific physical features (2nd ILs generation), up to the recent exploitation as reaction media for small scale applications, in various industrial fields [1]. The environmental impact of ILs and their effective "greenness" have been analyzed in a series of interdisciplinary fundamental studies [2], underlying the importance of a preventive evaluation in the ILs' design, from technological, toxicological and eco-toxicological points of view.

The ether-functionalized imidazolium-based ILs are a class of solvents with some interesting applicatory properties, such as high solubility for polar substrates (e.g. carbohydrates), suitable features as reaction media for some biocatalytic processes and for catalytic asymmetric reaction, capability to be exploited in dye-sensitized photoelectrochemical solar cells, and nanoparticles stabilizing properties.

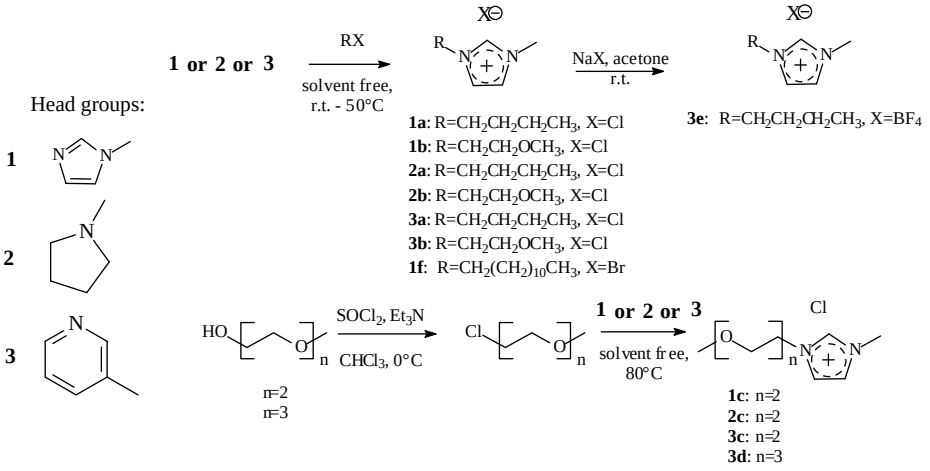

Figure 1 – Synthesis of ILs and intermediates.

Three series of ether-functionalized ILs have been synthesized (Figure 1) starting from different cationic head groups (imidazolinium, pyridinium, pyrrolidinium) and then they were tested in membrane fusion with the aid of the fluorescent molecule pyrene [3].

Plasma membrane is the first structure of cell protection and communication with external environment. Membrane fusion is a crucial event in the biological function of living organisms. However, spontaneous membrane fusion reactions are not achieved because of large energetic barriers in biological membranes.

Membrane fusion induced by ILs has been expressed in relation to a common surfactant and a "model" IL, with long alkyl chain in the cation (1-dodecyl-3-methyl imidazolium bromide), having properties similar to a surfactant. Critical micellar concentrations (cmc) of ILs have been measured based on the emission of vibronic bands of pyrene, and related to the extent of membrane fusion [4]. Pyridinium ILs gave the higher extent of membrane fusion when compared with imidazolinium and pyrrolidinium ILs. An increase of fusion is in relation with the elongation of the cationic later chains (Figure 2).

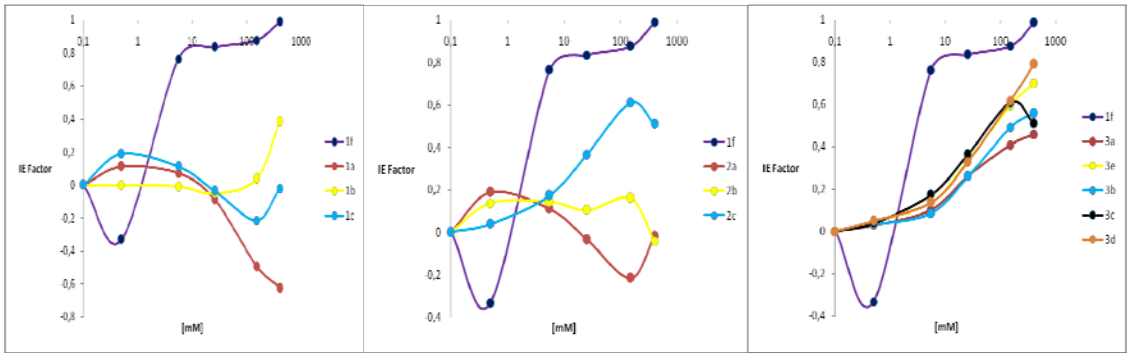

Fig. 2 – IE factors in presence of different ILs.

An increase of pyrene excimer population is observed at low IL concentrations, and it has been related with the insertion of IL cationic side chains and head groups in the double layer.

References

[1] Plechkova N.V.; Seddon K.R.; *Chem. Soc. Rev.* **2008,** 37, 123–150.

[2] Ranke J.; Stolte S.; Sto¨rmann R.; Arning J.; Jastorff B.; *Chem. Rev.* **2007,** 107, 2183-2206.
Stolte S.; Matzke M.; Arning J.; Böschen A.; Pitner W.R.; Welz-Biermann U.; Jastorff B.; Ranke J.; *Green Chem.* **2007,** 9, 1170 – 1179.

[3] Kashiwada A. et al; *Chem. Eur. J.* **2008**, 14, 7343 –7350.

[4] Ananthapadmanabhan K.P.; Goddard E.D.; Turro N.J.; Kuo P.L.; *Langmuir* **1985**, 1, 352-355.
Kalyanasundaram K.; Thomas J.K.; *J.a.c.s.* **1977**, 99, 7, 2039-2044.