

A Simultaneous Discrimination of Two Different Probes on Achiral Electrodes

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In literature few studies have dealt with electrochemistry or electroanalysis on achiral electrodes, the selector being provided by the medium, either having a chiral selector dissolved into it or being itself endowed with chirality. More recently, we have decided to implement the “inherent chirality” concept for the development of media to combine the powerful strategy of inherent chirality with the physico-chemical properties of the ionic liquids.

Ionic liquids, organic salts with low melting points, are increasingly popular media on account of many peculiar advantageous properties respect to volatile organic solvents (low vapor pressure, chemical and thermal stability, high solvating ability, non-flammability ...). They are even more attractive for electrochemical processes, acting as both solvent and supporting electrolyte, and especially featuring an extremely well-ordered structure at the interface with a charged electrode, expanding for many layers, like a semisolid crystal, even in the presence of significant water traces, and modulated by other species possibly present at the interface. Sometimes, they even border with liquid crystals. A high degree of supramolecular organization can induce significant chirality transfer from the medium to the dissolved species. And, analogously to the electrode case, this attitude could be maximized by the “inherent chirality” strategy, that is, working in inherently chiral ionic liquids, ICILs.

To implement inherent chirality in ionic liquids, that are usually based on a heteroaromatic cation with at least one long alkyl chain (to lower the melting point), Sannicolò *et al.* proposed to start from biheteroaromatic scaffolds, like bipyridine or bibenzimidazole ones. [1] By dialkylation such inherently chiral scaffolds can be converted into the corresponding double salts. With at least one long alkyl chain and a suitable anion, the melting point can be lowered below room temperature; thus, two ICILs have been very recently obtained as enantiopure antipodes, starting from bicollidine, a very convenient scaffold on account of its low-cost synthesis and possibility to be separated into enantiomers by fractional crystallization, without expensive chiral HPLC. Their enantioselectivity was tested as low-concentration additives in achiral commercial ionic liquids on screen-printed electrodes, with chiral probes already used in tests with electrodes modified with inherently chiral surfaces [2]; large, specular enantiomer peak potential differences were observed. Attractively, the same behavior, as chiral additives, was also shown by family terms solid at room temperature, of faster and easier synthesis.

In this context we are studying the effect of the chiral additives on two simultaneously present chiral probes, the first of them giving a chemically reversible ET process. We have to assess the experiments on all possible binary and ternary combinations but evidence of simultaneous discrimination apparently emerges.

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