

Enantioselective voltammetry in chiral ionic liquid media

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Chiral media enabling enantioselective recognition of chiral probes on achiral electrodes (in terms of significantly different peak potentials for the two probe enantiomers) represent an attractive target in voltammetry. Concerning possible *ad hoc* strategies, (a) on one hand, transmission of the chiral information should be more and more efficient with increasing structural order at the chiral medium|charged electrode interphase, and it has been recently shown that ionic liquid|electrode interphases are extremely well organized for many layers [1]; (b) on the other hand, outstanding enantioselective performances have been recently observed on electrode surfaces consisting in "inherently chiral" oligomer films, in which chirality originates from the whole main molecular backbone (also determining the material electroactivity), on account of a tailored torsion with high racemization barrier [2-6].

Combining both approaches, we recently developed two "inherently chiral" ionic liquids, consisting of dialkylated bicolindinium salts, with an atropisomeric bipyridinium cation featuring at least one octyl chain and bistriflimidate counteranions.[7] They show high enantioselectivity in terms of wide potential differences for the enantiomers of a chiral probe when tested even as low concentration additives in commercial achiral ionic liquids. Importantly, similar ability (increasing with additive concentration) was also shown by other selectors of the same family, having shorter alkyl chains and/or different counteranions, and thus solid at room temperature but easier to synthesize [7].

Using such chiral selectors as additives in an achiral ionic liquid rather than as bulk media is even more attractive, since only a small quantity of the enantiopure selector is needed and a low melting point is no more required, but only sufficient solubility in the achiral ionic liquid. For instance, this allowed us to successfully exploit as additives for chiral voltammetry in ionic liquids other inherently chiral selectors based on different stereogenic elements, *i.e.*, a bibenzimidazole atropisomeric scaffold [8,9] and a helicene one.

The study provides further evidence of the general validity of the "inherent chirality" strategy, since large potential differences are observed on achiral electrodes for the enantiomers of chiral probes even of very different structure and electroactivity (like in our parallel research on inherently chiral electrodes), and possibly even in experiments with more than one chiral probe.

Work is also in progress to better elucidate the process, including evaluation of the twisting power of our selectors as well as comparison with a family of ionic liquids and additives having cations derived from the natural pool, in which chirality originates from one or more stereocentres.

References

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