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Preface

The concept of the “self-disproportionation of enantiomers” (SDE) is a new working term that has been introduced to describe the general transformation, under any physical process, of an enantiomerically enriched sample into fractions consisting of more racemic and more enantiomerically pure states (i.e. fractions perturbed from the original optical state, both enantiomerically enriched and depleted). Interestingly, the very manifestation of the phenomenon of SDE for an enantiomerically enriched system actually infers that the physico-chemical behavior of the system can be described more precisely as a mixture consisting of a racemate and the excess enantiomer rather than as a mixture of unevenly proportioned enantiomers. This demarcation can also be evident by various achiral property and spectroscopic measurements whereby samples of racemates, pure enantiomers and states in between these two extremes do not necessarily possess the same achiral properties or exhibit linear responses. For chiral properties, non-linear behaviors can also be observed for such systems.

Potentially, the eventual outcome of a process and system wherein SDE is occurring is the complete separation of the racemate from the excess enantiomer. The most widely known and familiar process for which this occurs is crystallization. Notably though, the SDE phenomenon can, at least in principle, spontaneously occur during any physical process. However, SDE occurrences via other physical processes such as distillation, evaporation, sublimation, extraction or achiral-phase chromatography amongst others seem to be substantially less appreciated by the wider chemical community and indeed it appears that many practitioners are even completely unaware altogether of the occurrence of the SDE phenomenon in these processes.

Of all the elements, fluorine possesses the highest electronegativity, ionization potential and electron affinity and is also the least polarizable. Thus it is unsurprising that the presence of fluorine in an organic compound significantly impacts the compound’s physical properties, a fact that has been well documented. The physical properties that are strongly affected by the presence of fluorine include increased density and viscosity and lowered surface tension, refractive index and dielectric constant. Various chemical properties are also strongly perturbed and include increased stability towards oxidation and intermolecular interactions such as dipole–dipole, hydrogen bonding and electrostatic repulsions. Of considerable interest, and as has been well documented in the recent literature, the altered properties arising from the presence of fluorine in a molecule can strongly accentuate the SDE phenomena. Indeed, there are a number of cases where non-fluorinated analogs do not exhibit noticeable magnitude of the SDE in contrast to their fluorinated counterparts which do so with considerably increased magnitude. Consequently, compounds possessing a fluorine atom and/or fluorine-containing groups may hold great potential in facilitating the study and further practical applications of SDE. Additionally, fluorine has the potential to reveal disparities that may otherwise lie unnoticed, e.g. with a large chemical shift range and high sensitivity to environmental influences (not to mention highly favorable NMR properties for detection), the sharp lines of ^{19}F NMR offer a sometimes unparalled means for enabling system metrics.

The major goal of this Special Issue is to bring the promising potential of SDE to the attention of the general chemical community by providing an overview of the current exciting research that is being conducted on this topic as well as to highlight the strong effects that fluorine imparts to a molecule with respect to exhibiting SDE. Additionally, other chiral phenomena are also covered to a degree since the various phenomena are all intricately linked and share a fundamental underlying basis. In particular, the implications that the SDE phenomenon has for the emergence of prebiotic homochirality (“the chirality of life”, i.e. the predominance of L-amino acids and D-sugars in living matter) is contemplated by various authors. Thus, the reports contained herein draw examples from a number of general processes and states – e.g. solid, liquid, gas, solution → solid (crystallization), solid → liquid (melting), solid → gas (sublimation), liquid → gas (distillation), as well as achiral-phase chromatographic systems – and include chiral-specific spectroscopic examinations as well as theoretical calculations of the systems under study.[1] Finally, it is hoped that this Special Issue will stimulate greater intellectual interest, new ideas and further research into this fascinating and important, though challenging, field of endeavor.

Vadim A. Soloshonok
Karel D. Klika
William R. Dolbier Jr.*
University of Florida, Department of Chemistry, PO Box 117200,
Gainesville 326117200, FL United States

*Corresponding author. Tel.: +1 3523920591;
fax: +1 3528461962
E-mail address: wrd@chem.ufl.edu (W.R. Dolbier Jr.)

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[1] A limited number of systems included are also which do not incorporate fluorine in the molecules to note the generality of the observed behaviors and conclusions that have been drawn.

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