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Presumption of innocence and solution chemistry

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When faced with the challenging task of determining thermodynamic parameters for a given system, we oftentimes make meaningful decisions without even realizing it.

One of such decisions is the choice of the working ionic medium. In this context, the use of the so-called innocent anions - among which weakly coordinating nitrate and perchlorate are still among the most common - is widespread. Yet, how do we know for sure that such species are truly innocent? The only meaningful answer is that most of the times we do not, we simply decide to assume so and not to bother any further.

An even more critical parameter is the choice of the solvent: when studying solution equilibria, we generally focus on solute-solute interactions (e.g. binding phenomena), but this does not mean that the implicit presence of solute-solvent interactions is not affecting the position of the equilibrium itself.

Despite this being true for all chemical species, including TCEs, transition metals cations and their gigantic binding constants generally prevent appreciation of these comparatively small effects. On the other hand, anion coordination chemistry, cation's neglected twin, offers unique insights on these across-the-board topics.

Our group recently developed novel s-tetrazine-based ligands which allowed to explore subtle ion-specific effects and thermodynamics of anion complexes formation in aqueous solution [1]. Despite these studies having been proven relevant for core inorganic chemistry (e.g. discriminating between halide anions according to their periodic properties [2]), organic chemistry (e.g. shedding light on the interplay of different supramolecular forces [3]) and the make-up of novel supramolecular materials [4], the amount of accumulated evidence is just a humble memorandum that different ions behave differently in solution, demanding that anyone dealing with solution chemistry is aware of this and remains vigilant concerning his own experimental set-up.

References

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