Aggregating anions or cations? H-bonding found to trump electrostatics in ionic liquids

Two of the most persistent and vexing conceptual problems of modern physical chemistry concern (i) the fundamental nature of the hydrogen bond and (ii) the molecular-level structure and dynamics of condensed liquids, which H-bonding often dominates. In recent years, the theory of liquids has been further challenged by the remarkable new class of “ionic liquids” (low-melting salts), whose strong ionic forces and low volatility suggest a wide range of novel “green solvent” applications as well as unique atomistic-level forces compared to those of ordinary molecular liquids such as water or alcohols. Recently, our research team employed IR spectroscopic techniques and quantum chemical calculations to investigate a prototype ionic liquid that casts light on both these issues, providing the first observational evidence for a theoretically speculated “anti-electrostatic” (like-charge) form of H-bonding that seemingly defies widely-held assumptions concerning the nature of H-bonding and the dominant forces of liquid structure and dynamics in both normal and ionic fluids.

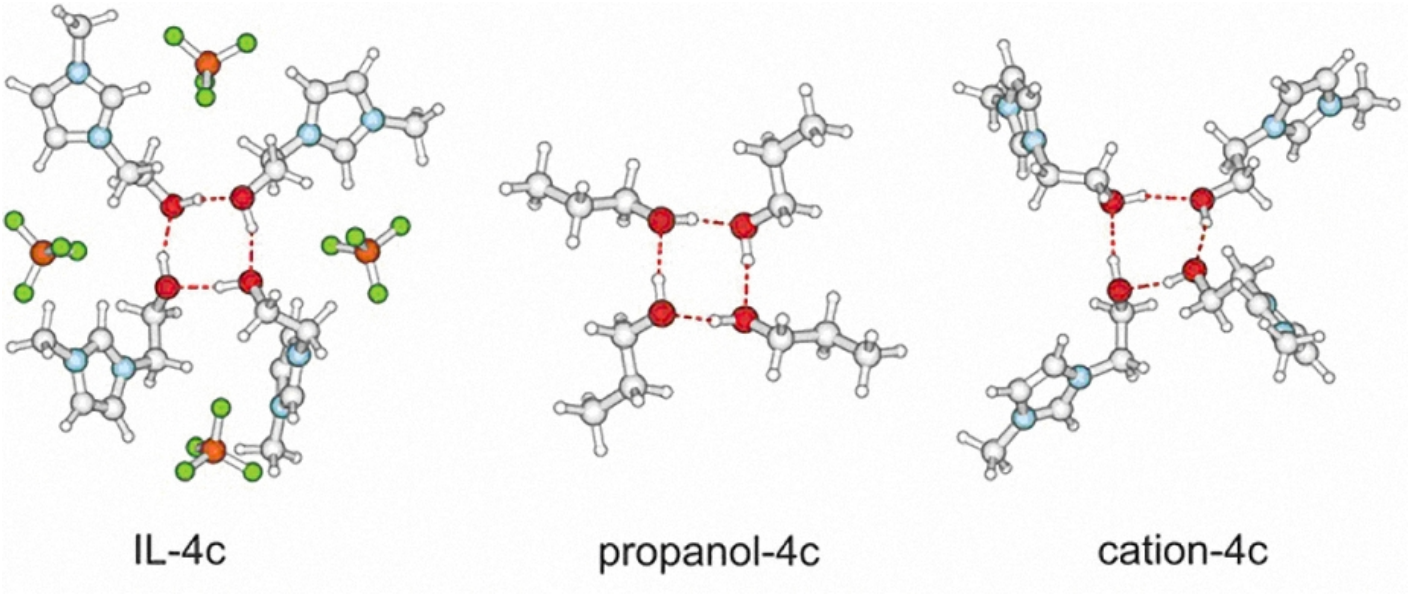

Fig. 1. B3LYP-6-31G*-D3 calculated structures of cyclic tetramers for ionic liquid IL-4c (including BF4– counterions), propanol and pure cationic clusters, showing isostructural analogies in H-bonding motifs despite vastly different electrostatic environments.

Our results serve to emphasize the ubiquity and adaptability of the H-bonding phenomenon to control clustering and rearrangements in a wide variety of liquid phases, whether of ionic or molecular composition. More importantly, experimental confirmation of like-charge H-bonding casts further doubt on the common textbook assumptions that H-bonding is merely a type of “dipole-dipole” attraction, related to the familiar classical electrostatic conceptions of like-charge repulsions

and unlike-charge attractions. Indeed, H-bond formation is found to *oppose and transcend* ("trump") classical electrostatic expectations, manifesting instead the profoundly "spooky" hallmarks of quantum superposition and chemical bonding interactions that are expected to become dominant in the short-range regime of condensed liquid-phase phenomena. Ominously for current understanding of liquid theory, the relevant quantum-level forces differ appreciably from those that have been assumed in popular molecular dynamics force-fields and numerical simulations of liquids throughout the past half-century.

Our group had previously found spectroscopic evidence for the surprising persistence of directional H-bonding, rather than close-packing, between constituent ions of common ionic liquids (composed, e.g., from imidazolium derivatives as cations and common triflates, sulfonates and the like as anions). More recent theoretical evidence had suggested a still more surprising possibility, namely, that H-bonding could actually lead to counterintuitive *like*-charge (cation-cation or anion-anion) dimers that are kinetically stable at the short-range separations characteristic of liquid densities. Related lines of theoretical and experimental evidence have also inspired recent efforts by the *International Union of Pure and Applied Chemistry* (IUPAC) to revise the formal definition of hydrogen bonding to emphasize its essential quantum-mechanical character (in more technical terms, 3-center, 4-electron "resonance"-type covalency), in contrast to the electrostatic rationalizations of earlier IUPAC definitions.

To address these questions, we fashioned a simple hydroxyimidazolium-based ionic liquid whose only possible O×××HO hydrogen bonds are of cation-cation type, but could in other respects be compared with well-known counterparts in simple alcohols. In accordance with quantum chemical calculations on both neutral and like-ion clusters, the subtle tell-tale signatures of like-ion H-bonding are redshifted in the mid IR spectra. Rather surprisingly, we found experimental evidence not only for doubly-charged dimers, but also for higher-charged trimers (3+) and cyclic tetramers (4+; Fig. 1.) as detectable polyion components of the equilibrium cluster distribution. Future work is expected to employ NMR techniques for additional characterization of this strikingly novel form of like-charge H-bond complex, which has now achieved promotion from "theoretically predicted" to "experimentally confirmed" status.

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