SINGLE-ION SOLVATION -
Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities
By P. Hunenberger and M. Reif, of ETH ; 664 + xxvi pages
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A tremendous amount of study has gone into this monograph, with detailed consideration of probably ALL the theoretical approaches to the subject. These include continuum-electrostatics "CE", atom-based simulations "AT" [e.g. Lennard-Jones's, extended], and quantum-mechanics, "QM". These would present a neophyte with a substantial study obligation. Lengthy attention is drawn to intrinsic versus real solvation energies, further considered below.

CE basically elaborate the Born approach, with many amendments including a "surface tension" allowance for the "cavity" in which an ion resides – qualitatively illuminating, but scarcely realistic for calculations. AT ("atomistics") seem more promising , but the parameters required are incomplete, and indeed primitive: who uses Lennard-Jones's C_6 and C_{12} parameters today, which lack higher-order [say quadrupolar] concomitants and more realistic repulsion formulations than C_{12} implies? Even so, copious lists of such parameters, as used by different authors, are faithfully listed.

Not surprisingly the conclusion is that QM will provide the best approach when sufficiently developed, but at present does not outdo alternative models in illustrating basic solvation factors, owing to the high cost of complete multi-electron QM computations. Chapter 5 introduces experimentally based hydration values, but so comprehensively that all have to be entered in small-script tables, one of 5 pages; similarly proton-value estimates.

Thus one must view the work as presenting tools for future use as much as an introduction to and history of the theories of ionic solvation; introductorily there is a ten-line list of what the book does NOT encompass. Very useful for theoreticians' libraries, it should be available to experimentalists researching the solution phase. Regarding the title, however, some mention is needed of the almost total focus on aqueous alkali halide ions. In principle the approach is applicable to other ions and solvents, but multiply charged ions prove difficult, and transition-metal ions are summarily excluded. [So the nice mid-century ligand-field linearization of hydration energies through the first transition series is absent ….]

Much is made of the difference between "real" and "intrinsic" solvation energies, the latter from e.g. MX lattice energies plus MX dissolution energies, subsequently

divided into M^+ and X^- individual values by one or other theory. But so-called real values are for individual-ion (say M^+ alone) immersion into solvent, involving solvent surface potentials difficult to establish, of interest but to some few physicists sending single-ion beams into condensed phases say at CERN or SLAC. Electro-chemists surely need only the former, in rationalising solution-phase phenomena.

Furthermore, the sub-title should rather have been "with special consideration of the alkali halides in water", as other ions or solvents get only incidental mention, though some of their properties are occasionally tabulated.

My advice is to read the first chapter briefly, photocopy the 10 pages of symbols used, skate through the rest to the final chapter, which read, then get down to a proper study of the whole content, perhaps with the above criticisms in mind. The RSC series editor would have done well to get several volumes from the authors, as really a library's-worth of records is presented here. A basic criticism is that few critical recommendations are suggested as to which appear to be the most promising approaches; the reader must judge. But the subject is of huge importance and wide applicability, and the authors deserve enormous commendation for taking on a mammoth task.