The Debye-Hückel theory and its importance in modeling electrolyte solutions

A colleague at the Technical University of Denmark has often stated: "Life is too short for electrolytes". Another well-known scientist in the field of molecular simulation has recently said during an international Thermodynamics conference: "All my life I have tried to keep myself away from water and electrolytes". Sadly, what these statements correctly imply is that there are far too many unclear questions and concepts in electrolyte thermodynamics, and associated difficulties in modeling electrolyte solutions. In this work, we attempt to shed some light on some important concepts and misconceptions in electrolyte thermodynamics associated with the development of electrolyte equations of state, with emphasis on those based on the Debye-Hückel theory. Detailed mathematics is needed for some of the derivations but for brevity and in order to emphasize the principles rather than the derivations, the latter are omitted. We first discuss the peculiarities of electrolyte thermodynamics and associated modeling and continue with the derivation of the Debye-Hückel theory. The assumptions and limits of application of Debye-Hückel are discussed in particular. Next, the Born term and its significance and implications are presented in more detail. A discussion and outlook section conclude this review. Several of the statements in this work challenge “accepted beliefs” in electrolyte thermodynamics and, while we believe that this challenge is justified, we hope that a useful debate can result in improved and predictive thermodynamic models for electrolyte solutions.

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