BEYOND POINT-LIKE CHARGE MODEL: A SELF-CONSISTENT THEORY FOR ELECTROLYTE CONDUCTIVITY

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In this plenary talk, we will discuss the Self-Consistent Debye-Hückel-Onsager (SCDHO) theory [1], a major theoretical advancement in understanding electrolyte conductivity. This theory incorporates the non-local charge distribution of solvated ions, going beyond the point-charge approximation used in classical theories for almost a century. We model ions with Slater-type charge form factors to regularize the Coulomb potential at short distances. This captures the fact that an ion's charge is distributed over a finite volume due to its electronic structure and solvation shell. Our theoretical framework is based on a solid foundation in statistical mechanics, combining classical density functional theory (cDFT) with the Ornstein-Zernike formalism. This approach provides analytical expressions for three key factors contributing to ionic conductivity: the mean-field effect, the correlation (aka relaxation) effect arising from the distortion of the ionic atmosphere, and the electrophoretic effect resulting from hydrodynamic drag. Importantly, we find that the electrophoretic effect predominates at high concentrations, while the correlation effect becomes negligible. This result clarifies long-standing questions about the relative significance of these effects and provides a more accurate understanding of ionic conductivity. The predictive power of the SCDHO theory has been demonstrated through extensive validation against experimental data. We have successfully reproduced molar conductivities for a wide range of electrolytes, including 1:1, 2:1, and 3:1 salts, over a concentration range from dilute to highly concentrated solutions. The model accurately captures the temperature dependence using only known solvent properties, without the need for additional fitting parameters. It also extends seamlessly to non-aqueous solvents, such as methanol, ethanol, and dimethyl sulfoxide.

A particularly interesting outcome is the determination of ion-specific charge smearing lengths. These parameters can be transferred across different electrolyte systems and have a clear chemical meaning. For halides, the smearing length increases as we move from fluoride to iodide, reflecting trends in electronic polarizability and the solvation shell structure. The framework we have developed is general and can be applied to multi-electrolyte solutions. Furthermore, by reducing the empirical component by calculating smearing lengths from first principles, we can transform the SCDHO theory into a fully predictive tool. This work provides a robust and physically grounded framework for predicting electrolyte conductivity over a wide range of conditions, with significant implications for areas such as electrochemistry, energy storage, and biophysics.

1. Budkov Y.A., Kalikin N.N. Conductivity of electrolyte solutions: self-consistent Debye-Hückel-Onsager theory // Physical Chemistry Chemical Physics. 2026. Vol. 28, Nr 12. P. 1–13. https://doi.org/10.1039/d5cp04521e