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One Century of the Debye-Hückel Equation: A Simple Explanation of its Thermodynamical Background

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In 1923, Peter Debye and Erich Hückel published a paper in which they derived a simple equation that could be used to quantitatively predict mean activity coefficients of electrolytes in dilute aqueous solutions.[1] The equation soon became one of the most widely used equations in analytical and physical chemistry and was soon adapted also for calculation of many other thermodynamical and transport properties in electrolyte solutions.

Despite its widespread use, the Debye-Hückel equation is still not well understood, as evidenced not only by physically incorrect derivations of the Debye-Hückel equation in numerous respected textbooks of physical chemistry and electrochemistry,[2] but also in the classic treatise on the thermodynamics of polyelectrolyte solutions.[3]

Here we show that the activity coefficient of a single ion in the Debye-Hückel equation can be easily determined from the electric potential in the solution, while the energy involved in attractive and repulsive interactions within the model ionic solution can be determined simultaneously. The change in Gibbs free energy can be evaluated by summing up the attractive and repulsive electrostatic interactions in the solution determined through the two-step process. With this new insight into the Debye-Hückel equation, it is possible to better understand the thermodynamics of electrolyte solutions.

Keywords: activity coefficient, electric potential, Debye length

References

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