# Peter Debye and Electrochemistry

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**Debye won the 1936 Nobel Prize in Chemistry for his contributions to molecular structure, dipole moment relationship and for diffraction of X-rays and electrons. Electrochemists, however, remember him for the Debye–Hückel limiting law that describes the behavior of strong electrolytes. In explaining the non-ideal behavior of strong electrolytes, his mathematical treatment assumes that each ion is surrounded by an ionic cloud of oppositely charged ions, which retards the movement of ions in the medium. The theory not only provides a method for calculation of activity coefficients, but has also helped, among other things, in our understanding of diffusion in ionic media, change in the rate of ionic reactions upon addition of salts, and biochemical reactions.**

In his article [1] on the founding of the International Society of Electrochemistry, J O'M Bockris recalls the status of electrochemistry of that time: *"Electrochemistry in 1949 was an old and breaking science. In Europe it was dominated by industry and thoughts, e.g. of aluminium. In England and America, the textbook and reading was dominated by solution theory. ... Who were the leading names in 1949? The most mentioned was that of Nernst. Wagner and Traud were, of course, often mentioned by Pourbaix's presence because of his interest in corrosion. Debye and Hückel were names mentioned much in universities when one talked about electrochemistry. The most frequent exam question related to activity coefficients... ."* The importance and relevance of the theory of electrolyte solutions are amply clear from this account. In fact, even though Peter Debye [2] was awarded the 1936 Chemistry Nobel Prize for his work on dipole moments and the diffraction of X-rays and electrons in gases, he is best known to electrochemists for the Debye–Hückel theory of electrolytes.

Debye is often called the 'Master of the Molecules' for his pioneering work in molecular structure. His basic training was in physics, mathematics and electrical engineering. His entry into chemistry was rather late, but he was a dominant figure in physical chemistry and chemical physics during the first half of the 20th century. Debye, along with Erich Hückel, one of his assistants at the Eidgenossische Technische Hochschule (ETH) in Zurich, developed a theory on the inter-ionic attraction in electrolytes. In 1923, they published two fundamental treatises on electrolytic solutions. They suggested that solutions of electrolytes differ from ideal behavior due to inter-ionic attractions. The treatises propelled enormous progress in the field of electrochemistry. The Debye–Hückel theory of electrolytes (1923) marked a great advance in the theories of the time that were limited to very dilute solutions. It accounts for the fact that ions in solution are attracted to ions of the opposite charge. Two years later, in 1925, Lars Onsager, a Norwegian-born American physical chemist and winner of the 1968 Chemistry Nobel Prize made a correction to the theory propounded by Debye and Hückel. The correction related to Brownian movement of ions in solution. In fact, Onsager travelled to Zürich to discuss the flaws of the theory of Debye and Hückel with Debye. A much impressed Debye took Onsager as his assistant at the ETH.

In the early 1900s, one could apply the simple laws of Arrhenius[1] and van't Hoff [2] to describe the equilibrium and transport properties of weak electrolytes such as organic acids and bases, but these laws failed to account for similar data on solutions of strong electrolytes such as inorganic acids, bases and salts. Several physical chemists, including Niels J Bjerrum and William Sutherland, assumed that strong electrolytes are completely dissociated in solution. Based on this assumption, Milner calculated osmotic coefficients, a quantity related to the activity coefficient. However, the behavior of strong electrolytes could not be explained in mathematical terms. Debye and Hückel developed a mathematical route to treat equilibrium properties of strong electrolytes. They based their treatment on the assumption that

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[1] Swedish physical chemist who won the 1903 Nobel Prize in Chemistry.
[2] Dutch physical and organic chemist and the first winner of the Nobel Prize in Chemistry. See *Resonance*, Vol.12, No.5, 2007.

electrostatic forces between ions led to the non-ideal behavior of strong electrolyte solutions. To lessen the mathematical rigor, they restricted their analysis to dilute solutions of electrolytes. According to them, ions were similar-sized spheres with charges distributed symmetrically around them. The solvent was considered as a medium of uniform dielectric constant, which did not change upon addition of solute ions. The ions were supposed to be in random thermal motion in the medium. However, ions of one sign tended to cluster around ions of the opposite sign. This resulted in time-averaged ionic clusters, which were neither completely regular nor completely random in character. Thus, each ion experienced an average net electrostatic attraction by all the other ions, whose magnitude is related to the product of the charges of the ions and the mean distance between them, which is a function of the concentration of the solution.

The electrostatic attraction and repulsion between ions were calculated by Coulomb's law, which led to a square root relationship with the concentration. First, the most probable distribution of an ionic atmosphere about a central ion was determined. The average electrical potential of a given ion in the presence of the surrounding ions was then calculated invoking a combination of the Poisson differential equation and the Boltzmann distribution function. Based on this potential, the excess free energy resulting from the electrostatic interactions was computed. The excess free energy was then attributed to non-ideal behavior.

Because ionic solutions do not behave ideally, many chemical calculations require activities rather than concentrations. The activity of a solution is related to its concentration by a proportionality constant called the activity coefficient $\gamma$. It must be noted that the activity coefficient of individual ions cannot be measured independently; in fact, all ions change energy together. The activity coefficient takes into account the interaction energy of ions in solution. Thus, recognizing that electrochemists normally seek values of the activity coefficient, Debye in 1924 reformulated his original paper with Hückel (1923), which dealt with osmotic coefficient. It is this second derivation that one

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studies in modern physical chemistry textbooks. The Debye–Hückel equation or Debye–Hückel limiting law relates the mean activity coefficients of ions in a dilute solution of known ionic strength by the equation:

$$\ln(\gamma_i) = -\frac{z_i^2 q^2 \kappa}{8\pi\varepsilon_r\varepsilon_0 k_{\mathrm{B}}T} = -\frac{z_i^2 q^3 N_{\mathrm{A}}^{1/2}}{4\pi(\varepsilon_{r\delta}\varepsilon_0 k_{\mathrm{B}}T)^{3/2}}\sqrt{\frac{I}{2}} = -\mathrm{A}z_i^2\sqrt{I} \,,$$

where $z_i$ is the charge on the ion $i$; $q$ is the elementary charge; $\kappa$ is the inverse of the Debye screening length; $\varepsilon_r$ is the relative permittivity of the solvent; $\varepsilon_0$ is the permittivity of free space; $k_{\mathrm{B}}$ is Boltzmann constant; $T$ is the temperature of the solution; $N_{\mathrm{A}}$ is Avogadro's number; $I$ is the ionic strength of the solution; and $A$ is a constant that depends on the solvent. The theory assumes that ions in an electrolyte collectively exert a screening effect on the electric field from individual ions. The screening length is called the Debye length and varies as the inverse square root of the ionic strength.

A more difficult problem sought to be tackled by the Debye–Hückel theory was electrical conductance. According to the Arrhenius theory, the equivalent electrical conductance is a function of the number of ions, which varies with concentration – a law of mass action effect. While this theory held good for weak electrolytes, it was found wanting in explaining conductance behavior of strong electrolytes. For example, Kohlrausch had experimentally established a square root of concentration decrease in equivalent conductance with increasing concentration. It was immediately seen that because the number of carriers (ions) remained essentially constant per unit volume in dilute solutions, the conductance behavior should be attributed to a decrease in the ionic mobilities, which decreased with increasing electrolyte concentration. This, therefore, takes us back to inter-ionic interactions that are the basis of the Debye–Hückel formulation. To explain this, Debye and Hückel introduced two key properties of the ionic atmosphere, namely relaxation time and electrophoretic effect. However, their treatment largely ignored

*Peter Debye (1884–1966)*
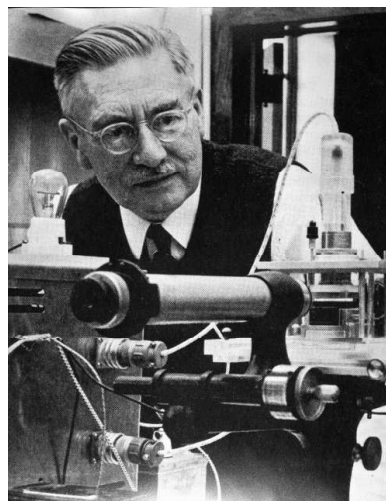
the effect of the Brownian movement of the ions during displacement in an electrical field. As mentioned earlier, it was Onsager who modified the theory to today's Debye–Hückel–Onsager theory.

The seminal contributions from Debye initiated a sea change in the study of electrolyte systems. For example, it led to an explanation for the change in solubility of a sparingly soluble salt caused by the addition to the solution of a salt without a common ion. Debye described the separation of organic solutes from saturated aqueous systems upon salt addition as due to an inhomogeneous electrical field produced by localized charges carried by the ions. In 1928, Debye and Falkenhagen presented a frequency dependence of the electrical conductivity of strong electrolyte solutions as a result of the finite time of relaxation of the ionic atmosphere. The frequency dependence could also explain deviations from Ohm's law at high field strengths. Debye's contributions to electrolyte solutions also come in handy in understanding a variety of seemingly unrelated areas, for example, change in the rate of ionic reactions with addition of a salt to the system; and the protein chemists' three-component system of water, protein and salt. Indeed, the scope of the theory extends to areas that even Debye would not have imagined.

## Suggested Reading

[1]    J O M Bockris, *Electrochim. Acta*, Vol.36, p.1, 1991.
[2]    J W Williams, *Peter Joseph Wilhelm Debye (1884–1966)*, *A Biographical Memoir*, National Academy of Sciences, Washington DC, 1975.
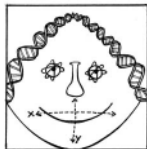
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