

Answer on Question #71467 - Chemistry - Physical Chemistry

Question:

Debye Huckel theory on sagar eqn for non aqueous soln

Solution:

1. The Debye-Hückel theory considers ions as point charges. According to this theory, all the ions of the same valence are identical. In reality, the ion radius reflects its individuality, and the radius of the ion determines the characteristic of the electrolyte.

It should be noted that according to the equations of the Debye-Hückel theory of the second approximation, if the radius of the ion is much smaller than the radius of the ionic atmosphere, its account very little changes the basic formulas of the theory, and therefore replacement of ions by point charges can be considered legitimate from the point of view of this theory. This condition is always observed in dilute electrolytes, for which the Debye-Hückel theory is deemed applicable. Consequently, the refined theory asserts that the ion radius should not affect the characteristics of electrolytes. However, according to experimental data, the radius of an ion basically determines the characteristics of electrolytes.

2. It is known that as a result of the interaction of the energy of the ion, determined by its radius r_i , with the dipole water molecules, the h of the water molecule is added to the ion, forming a hydrated ion of radius r_{ih} . The smaller the ion radius, the greater its energy, and the more water molecules h will join it. Therefore, the smallest ions, as a result of hydration, are converted into large hydrated ions. Consequently, hydration fundamentally changes the parameters of the ion and therefore strongly affects the characteristics of electrolytes. It can not be ignored in determining the parameters of electrolytes, and the Debye-Hückel theory does not take into account the effects of hydration.

To date, a system that is not subject to an external electric field is used. When measuring conductivity, the system is exposed to the oscillating external field due to the application of alternating current voltage to the electrodes immersed in the solution. Debye and Huckle changed their theory in 1926, and their theory was further modified by Lars Onsager in 1927. All the postulates of the original theory were preserved. In addition, it was assumed that the electric field causes deformation of the charge cloud from spherical symmetry. After this is taken into account, along with the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to obtain the theoretical expression for accounting for an empirical bond, known as the Kohlrausch law, for molar conductivity λ_m :

$$\lambda_m = \lambda_m^0 - K\sqrt{C};$$

λ_m^0 known as limiting molar conductivity, K is an empirical constant, and c is the concentration of electrolyte. The limitation here means "on the boundary of infinite dilution"). The statement Onsager is

$$\lambda_m = \lambda_m^0 - (A + B\lambda_m^0)\sqrt{C};$$

where A and B are constants that depend only on known values such as temperature, ion charge, dielectric permittivity and solvent viscosity. This is known as the Debye-Hückel-Onsager equation.

However, this equation only applies to very dilute solutions and was largely replaced by other equations by Fous and Onzager, 1932 and 1957, and later.

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