Electrochemistry

Lecture (9)

Stage 3

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Debye – Huckel – Onsager Equation

Previously, we explained the effect of disability resulting from the effect of relaxation and the effect of electrophoresis and rhythm on the velocity of the ions, and accordingly on their conductivity. It is possible to find a correlation between These two effects are the properties of the ions and the solvent and the temperature of the solution. It has been possible for you to From Debye and Hawkl who formulated a mathematical equation that was later developed by Onsager showing the relationship between Molar conduction and concentration of fully ionized monovalent electrolytes on their image the following simplified:

$$\Lambda = \Lambda^{\circ} - \left[\frac{82.4}{(DT)^{1/2} \eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda^{\circ} \right] \sqrt{C}$$

Where (η) is the viscosity of the solution. The previous equation is usually known as the Un-Sager equation.

The first term is given within the arc $\left(\frac{82.4}{(DT)^{1/2} \eta} \right)$ In the Unsäger equation, the magnitude of the Electrophoretic effect while crossing the second term $\left(\frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda^{\circ} \right)$ About the effect of relaxation.

And write the equation

$$\Lambda = \Lambda^{\circ} - \left[\underbrace{\frac{82.4}{(DT)^{1/2} \eta}}_{A} + \underbrace{\frac{8.20 \times 10^5}{(DT)^{3/2}}}_{B} \Lambda^{\circ} \right] \sqrt{C}$$

Simply put, as follows:

$$\Lambda = \Lambda^{\circ} - \left(A + B\Lambda^{\circ} \right) \sqrt{C}$$

And the equation $\Lambda = \Lambda^{\circ} - (A + B\Lambda^{\circ})\sqrt{C}$ Equation of a straight line with a slope $(A + B\Lambda^{\circ})$ The secant is equal to (Λ°). the constants (A) and (B). They depend on the nature of the solvent and the temperature, table (14) shows some values of different solutes at a temperature .(25 ℃).

Table (14) Some values of the Onsager equation constants for monoelectrolytes and in different solvents.

Solvent	D	$\eta \times 10^3$	A	B
Water	78.5	8.95	60.20	0.229
Methanol	31.5	5.45	156.1	0.923
Ethanol	24.3	10.8	89.7	1.33
Acetone	21.2	3.16	32.8	1.63
Nitrobenzene	34.8	18.3	44.2	0.776

Substituting for the Onsager constants for water at a temperature of (298 K), the equation is:

$$\Lambda = \Lambda^\circ - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}}\Lambda^\circ \right]\sqrt{C}$$

It leads to the following formulas:

$$\Lambda = \Lambda^\circ - \left(A + B\Lambda^\circ\right)\sqrt{C}$$
$$A = 60.20, \ B = 0.229$$

$$\Rightarrow \Lambda = \Lambda^\circ - \left(60.2 + 0.229\Lambda^\circ\right)\sqrt{C}$$

and the equation $\Lambda = \Lambda^\circ - (60.2 + 0.229\Lambda^\circ)\sqrt{C}$ Similar to the K-Wehlrausch equation $\Lambda = \Lambda^\circ - A\sqrt{C}$. **Thus, it was possible from Debye's ionic atmosphere model, and he developed a relationship It can be considered as the theoretical basis for the empirical Kohlrauch equation.**

The validity of the Onsager equation can be judged to describe the relationship between molar conductivity Emphasis on the accurate experimental results, with the confirmation that the relationship between them is linear as it is. The case in most dilute strong electrolyte solutions is not sufficient for this. BLN the value of mil This linear relationship, which is equal to $(A + B\Lambda^\circ)$ is considered an important measure for determining the extent of Applicability between experimental results and those calculated theoretically.

Figure (11) shows the relationship between (Λ) and ($\sqrt{C}$) for a number of monoelectrolytes - monovalent at (25 ºC), where the circles represent the experimental values, while the line The section represents the calculated values.
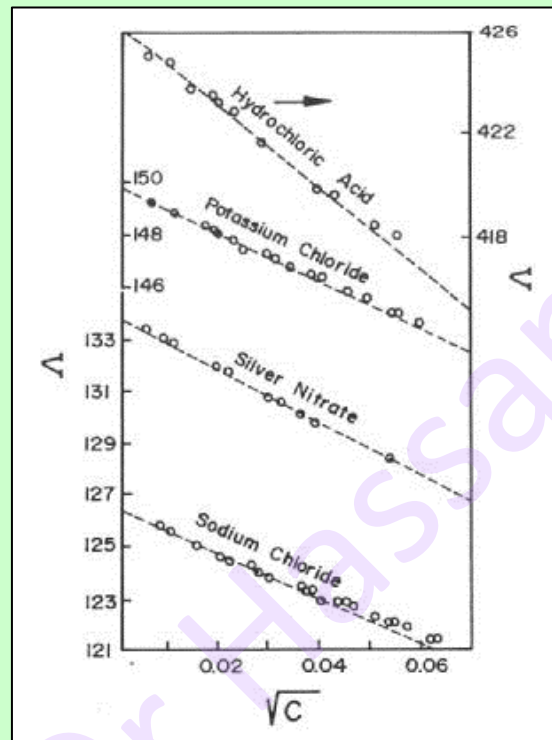

Figure (11): Comparison between On-Sagger and the experimental results of some monovalent monoelectrolytes.

The Onn-Sager equation is perfectly applicable to the experimental results at concentrations smaller than (0.001 mol L^{-1}) , while the diffraction starts at d concentrations higher than this value. The state of polyvalent electrolytes diffraction appears at concentrations lower than these for monoelectrolytes so that the relationship between (Λ) and ($\sqrt{C}$) is not linear, but takes curved shape.

From the above, it can be said that the Un-Sager equation in its present form is a range-bound equation While the concentration and that this range depends on the type of electrolyte, as referred to The basis and the simplified assumptions on which the equation is built. But in spite of that, the The hypothesis of the complete dissociation of strong electrolytes and the existence of mutual effects between ions It is sufficient at these concentrations to explain the connection relationship to the focus.

Equations appeared more sophisticated and complex than the On-Sager equation that could describe The relationship between conduction and concentration to concentrations) (5.0 mol L^{-1}), and we will not discuss it here. The behavior of some electrolytes deviates from the On-Sagger equation when the relationship is inclined. Between (Λ) and ($\sqrt{C}$) is greater than that calculated theoretically, that is, the observed connection for those The solutions are lower than what would be expected by the Un-Sager equation. This can be returned to you until you unpack it The electrolyte is not complete, thus increasing the number of ions that can transfer the current. The electronegativity of the solution is less than that resulting from the complete ionization of the electrolyte. Well the mouth n It is necessary to enter a new quantity **called**:

(degree of dissociation) (g)

It is defined as the part of the electrolyte that will dissociate in solution to give Free ions that transfer current. Therefore, the Onsager equation can be written in the form following:

$$\Lambda = g\left[\Lambda^{\circ} - \left(A + B\Lambda^{\circ}\right)\sqrt{gC}\right]$$

or in short:

$$\Lambda = g\Lambda'$$

where:

$$\Lambda' = \Lambda^{\circ} - \left(A + B\Lambda^{\circ}\right)\sqrt{gC}$$

Where ($\Lambda`$) is the molar conductivity of a mole of free ions in solution at a concentration worth (gC).

and the equation $\Lambda = g[\Lambda° − (A + B\Lambda°)\sqrt{gC}\,]$ Correct ionic electrolytes Especially polyvalent or monovalent ones in solvents with dielectric constants low. And Table (15) shows the slope of the On-Sager equation, the scenes and the theory of the solution. (KI) in a number of solvents. The difference in tendencies is noted in the case of solvents such as Acetone, for example.

Table: (15) Observed Onsager miles and calculated for (KI) at (25 °C)

solvent	D	Onsager slope	
		observed	calculated
Water	78.5	73	80
Methanol	31.5	260	268
Ethanol	25.2	209	153
Benzonitrile	25.2	263	142
Acetone	20.9	1000	638

Weak electrolytes represent a special case of the equation $\Lambda = g[\Lambda° − (A + B\Lambda°)\sqrt{gC}\,]$ Where the degree of disintegration can be equal to the degree of Ionization, because the concentration of ions in this case is very low, and consequently, the ($\Lambda`$) is not It is very different from Λ_o, so the equation $\Lambda = g\Lambda'$ comes down to the formula:

$$\Lambda = \alpha\, \Lambda°$$

It is the same equation that Arrhenius put in the previous electrolytic ionization theory. The fact that the degree of dissociation (g) for a number of electrolytes is not equal to unity can be traced back There are two reasons for strong and weak electrolytes. Most of the mother will not be in a condition Ionized even when it is in the solid state, and it can be said that it is completely ionized at any concentration.

However, the ions in the solution do not have an absolute freedom of movement and independent of each other, as it is a result of the presence of electrostatic forces of attraction between the charged ions The different types may form what is known as ion-pairs. To clarify the concept of Ion pair the solution to be (A^-) and (B^+) ions, the solution will certainly not contain a molecule Like (BA), but an ion pair can be formed on the image (B^+A^-) as a result of attraction. The electronegativity between the two ions, when the distance between them is less than a certain value. Depends on the ionic charge (z), the dielectric constant of the solvent (D), and the temperature. Absolute (T). This distance (q) is given by the following relationship:

$$q = \frac{z_i \ z_j \ e^2}{2 \ D \ k \ T}$$

According to the requirements of the previous relationship and from the empirical evidence, it was noted that the possibility of The ionic pairs are higher the higher the ion has a small volume in the solution and the higher the charge. In addition, the smaller the dielectric constant, the greater the extent of these pairs ionic, but rather it goes beyond that to form another state of gathering ions called the tripartite Ionic (ion-triplets) are in the form of ($A^-B^+A^-$) or ($B^+A^-B^+$). The case for the case of the ionic pair in that the latter has a related charge equal to zero. While the ionic triple state will have a charge and thus can conduct current Electrophoresis. Based on the above, the degree of dissociation will be less than unity despite the The electrolyte is fully ionized.

The effect of the formation of ionic pairs on some properties of electrolyte solutions, such as Electrical conduction Looking at Figure (12) where it is noted the large deviation from Onn-Sager's law even at these dilute concentrations, which indicates a decrease in the number of ions The conductor of the electric current in the solution as a result of the formation of ion pairs.
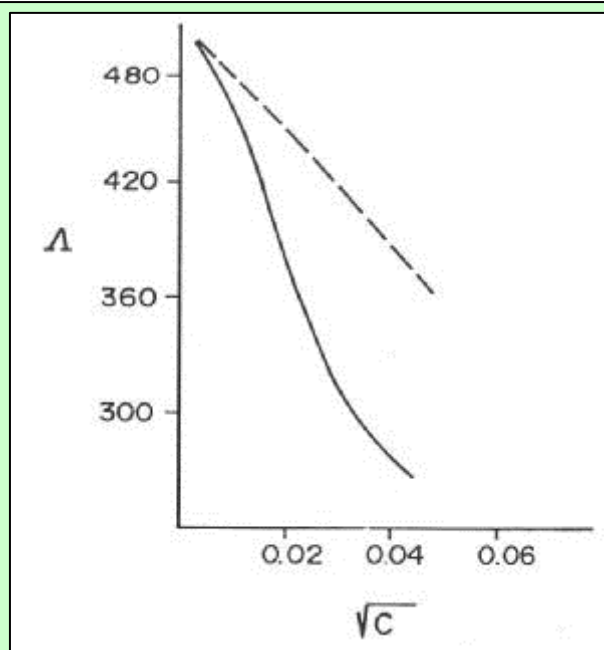
Figure (12): Comparison of the molar conductivity calculated from the Onsager equation (---) and that measured in practice for (LaFe(CN)$_6$) solution.

Weak electrolytes represent the other state in which their solutions do not equal the degree of dissociation as unit, in addition to the possibility of the formation of some ionic pairs, there is an amount of The electrolyte is in molecular form, for example, an acetic acid solution will contain molecules of The de-ionized acid (CH$_3$COOH) in addition to the ions (H$^+$) and (CH3COO$^-$). Which ion pairs can be in the form (CH3COOH), so the degree of dissociation is as Represents the portion of acetic acid capable of transmitting electric current.

Q) What does the slope $(A + B\Lambda_o)$ express in the Onsager equation?

Q) What is the difference between the degree of ionization and the degree of dissociation, and when are they equal?

Example//

If the molar conductivity of a solution (10^{-3} mol L^{-1}) of acetic acid is equal to $\left(\Lambda_{CH_3COOH} = 48.63\,\Omega^{-1}cm^2mol^{-1}\right)$ at (25 ºC) Calculate the degree of ionization (α) and degree of disintegration (g) knowing that $\left(\Lambda^0_{CH_2COOH} = 390.7\,\Omega^{-1}cm^2mol^{-1}\right)$ and (A = 60.2, B = 0.229)

Solution//

The degree of ionization can be calculated from the equation:

$$\alpha = \frac{\Lambda}{\Lambda^\circ}$$

$$\alpha = \frac{48.63}{390.7} = 0.124$$

That is, acetic acid is ionized at this concentration (12.4 %).

By substituting into the equation $\Lambda = g\left[\Lambda^\circ - (A + B\Lambda^\circ)\sqrt{gC}\,\right]$, Assuming that α, g:

$$\Lambda = g\left[\Lambda^\circ - \left(A + B\Lambda^\circ\right)\sqrt{gC}\,\right]$$

$$48.63 = g\left[390.7 - \left(60.2 + 0.229 \times 390.7\right)\sqrt{0.124 \times 10^{-3}}\,\right]$$

$$48.63 = g\,(389.03)$$

$$g = \frac{48.63}{389.03} = 0.125$$

It is noted that the degree of dissociation is approximately equal to the degree of ionization. This is expected in a local case Weak Electrolytes.

That is, the degree of dissolution of sodium chloride at this concentration is approximately (100%).

Example//

The following results show the change of molar reach with (sodium lactate) concentration. : at (298 K)

$C \times 100^{-3}(\text{mol L}^{-1})$	0.1539	0.3472	0.6302	1.622	2.829	4.762
$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	87.89	87.44	86.91	85.80	84.87	83.78

Draw the relationship between (Λ) and ($\sqrt{C}$) and find the slope of the straight line, read (Λ°) Graph and compare the experimental slope with that calculated from the Onsager equation.