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وزارة التعليم العالي والبحث العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

## Electrochemistry

Lecture (8)

Stage 3

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## The Interionic Attraction Theory

The conductivity of the electrolyte solution, as previously mentioned, depends on the number of ions and the number of ions. The charges carried by each ion in addition to the speed of these ions in a solution. If the number The charges of a given electrolyte are constant, so the change is caused by the molar conductivity of the solution It is the change in the number of ions or their speed with concentration, as Arrhenius hypothesized.

It was made clear from the above that Arrhenius' second hypothesis is considered an approximation of my solutions. Dilute and unhealthy weak electrolytes for strong electrolyte solutions for the foregoing considerations. Therefore, the degree of ionization ( $\alpha$ ) deviates from unity when the concentration is increased It cannot be entirely attributed to a deficiency of the electrolyte, where there is a lot of evidence on the The velocity of the ions in the solution depends on the concentration, and the matter will become clearer later. The topic of pregnancy numbers for ions is reviewed in the next parts.

The relationship between molar conduction and the ionic movement of any electrolyte at a given concentration It is given by the following relationship:

$$\Lambda = F(z_+ \mu_+ + z_- \mu_-)$$

From which it can be concluded that the molar conductivity of the electrolyte is unsupported. On the concentration, the ionic motion should not change with the concentration. The mother can be cleared More by looking at the following treatment:

We know that the empirical relationship of the change of molar conduction with concentration is described by an equation Next Kohlrausch:

$$\Lambda = \Lambda^\circ - A\sqrt{c}$$

But ( $\Lambda$ ) for the monovalent electrolyte is given by the following relationship:

$$\Lambda = F(\mu_+ + \mu_-)$$

In the case of infinite dilution, then:

$$\Lambda^\circ = F(\mu_+^\circ + \mu_-^\circ)$$

From the relationship  $\Lambda = F(\mu_+ + \mu_-)$  and the relationship and  $\Lambda^\circ = F(\mu_+^\circ + \mu_-^\circ)$  and their equilibrium The relationship  $\Lambda = \Lambda^\circ - A\sqrt{c}$  we get:

$$\begin{aligned}\Lambda &= \Lambda^\circ - A\sqrt{c} \\ (\mu_+ + \mu_-) &= (\mu_+^\circ + \mu_-^\circ) - A\sqrt{c} \\ (\mu_+ + \mu_-) &= (\mu_+^\circ - A\sqrt{c_+}) + (\mu_-^\circ - A\sqrt{c_-}) \\ \Rightarrow \mu_+ &= \mu_+^\circ - A\sqrt{c_+} \\ \Rightarrow \mu_- &= \mu_-^\circ - A\sqrt{c_-}\end{aligned}$$

And the two equations  $\mu_- = \mu_-^\circ - A\sqrt{c_-}$  and  $\mu_+ = \mu_+^\circ - A\sqrt{c_+}$  It is clear that there is a relationship between The ionic movement and ion concentration, and that the higher the concentration, the lower the movement than the greater value it ( $\mu_-^\circ$ ). It is also important to mention that the movement of ions at concentrations differs from the state of Infinite dilution is independent of each other, and that the greater the number of ions in the The unit of volume and the more the fading from the movement of the ion due to the effect of the other ion is greater And you are right xy. As there is a coupling between the movement of positive and negative ions in The solution, which is not taken into account in Arrhenius' previous hypotheses.

The type of electrolyte is an important factor in determining the behavior of the electrolyte solution. The extent to which it deviates from the ideal behavior, and this can be inferred by looking at the table (13) Which shows the dependence of the degree of ionization on the type of electrolyte in dilute solutions.

Table (13): Dependence of the degree of ionization of electrolytes on the type of electrolyte at different concentrations

Electrolyte type	Molarity ( $\text{mol L}^{-1}$ )		
	0.001	0.01	0.1
uni-uni	0.98	0.93	0.83
uni-uni	0.95	0.87	0.75
bi-uni	0.95	0.87	0.75
bi-bi	0.85	0.65	0.40

It was also noted that the constant (A) in the Kohlrausch equation  $\Lambda = \Lambda^\circ - A\sqrt{c}$  Depends on n and type The electrolyte, i.e. (1:1) or (2:2), etc., is more than depending on the nature of the electrolyte, This can also be clarified by looking at Figure (8).

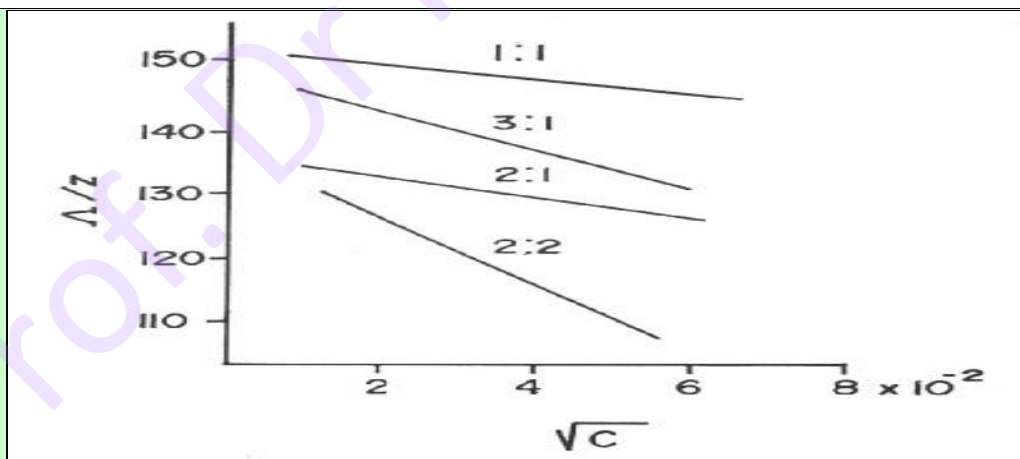


Figure (8): Dependence on the relationship between  $\left(\frac{\Lambda}{Z}\right)$  and  $\sqrt{c}$  on the type of electrolyte.

Which shows the type of relationship between molar conductivity and the square root for various types of electrolytes.

From the two previous observations, it can be said that the higher the ion charge, the greater the decrease in molar conductivity, which calls for the interactions between The ions and their expected effect on their velocity should be taken into consideration.

Dissolving an ionic substance (sodium chloride, for example) in a polar solvent such as water results in two types. Of the mutual influences are:

- a) ion–solvent interaction.
- b) ion-ion interactions.

The extent to which the properties of the solution are affected by the second type of mutual influence depends on the amount of The distance between those ions - and this is affected by the number of ions in the solution -, because: The electric field of the ion depends on this distance in addition to its dependence on the nature of Electrolyte and its ionization in solution.

When the ions are separated by large distances compared to their sizes (the dilution state infinite) these mutual effects are very weak, but with increasing concentration, the Reducing the distances between ions creates an attractive force between ions of different charges. According to Coulomb's law, which states that **the force of attraction or repulsion is Between two charges, such as (ze) and (-ze), are proportional to the sum of multiplying the magnitude of the two charges. and reflectively with the square of the space between them (r) in the median and permeability) ( $\epsilon_r$ )** It is given by the following relationship:

$$F = \frac{z^2 e^2}{4 \pi \epsilon_0 \epsilon_r r^2}$$

Where ( $\epsilon_0$ ) is the permeability of vacuum and when the charges differ The force between charges is an attractive force. When the charges are similar, the force between the two charges is be repulsive force.

Q) The number of types of interactions between ions in the solution.

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## Debye and Hückel theory of the ionic atmosphere

The quantitative treatment of the effect of ionic attraction on electrolyte conduction was a field of study by a number of researchers and the most famous and successful of those studies was the one carried out by Debye and Hückel (Debye and Huckel) in the year 1923 AD. We will present this following (in the following) theory without going into the mathematical equations in this part.

It contains (1 cm<sup>3</sup>) of monovalent electrolyte solution, for example, its concentration. (0.001 mol L<sup>-1</sup>) or (2 x 6.02 x 10<sup>17</sup>) cations and anions and an approximate number of solvent molecules, and because this large number of ions is difficult to treat mathematically, it is that Debye and Hückel proposed a simplified model by choosing one ion called the reference ion. (reference ion) has a specific charge and is not positive, so it will be around this ion. The reference is the sum of more negative charge than positive charge. In other words, the possibility of presence and presence of ions of opposite charge around an ion will be more than the probability of having ions of the same charge, which is what is known as the ionic atmosphere, and indicates the relationship of the charges. In the ionic atmosphere it is equal in value and opposite in sign of the charge of the ion. Reference, while the charge density is the highest possible near of the reference ion and decreases as we move away from it, see Fig (9).

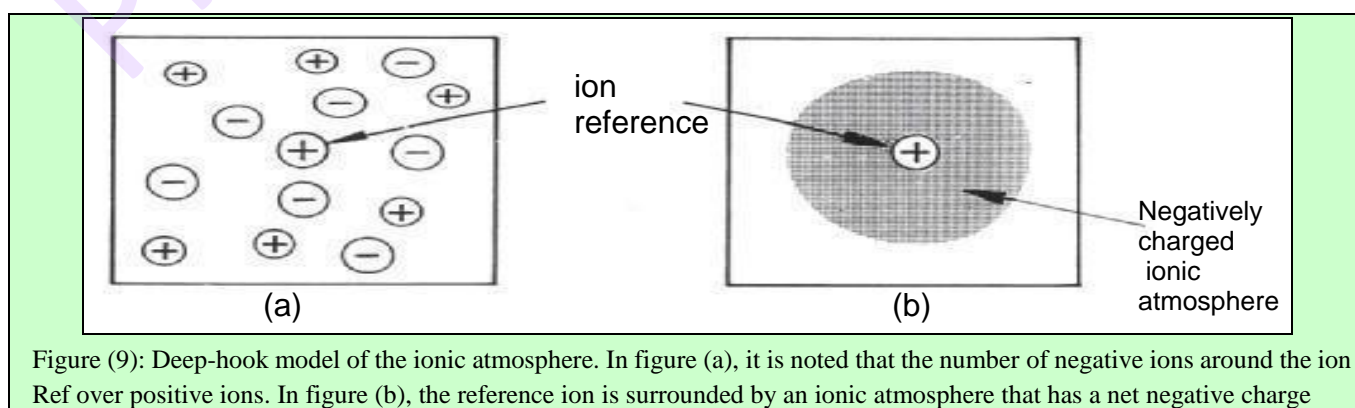


Figure (9): Debye-Hückel model of the ionic atmosphere. In figure (a), it is noted that the number of negative ions around the reference ion is greater than positive ions. In figure (b), the reference ion is surrounded by an ionic atmosphere that has a net negative charge.

But how do these mutual effects between the ions - represented by the ionic atmosphere model - affect What is the speed of movement of ions in the solution?

A reference ion image has a positive charge, in the absence of a driving force any external electric field - the ionic atmosphere will be similar Spherical the shape around the reference ion and the probability of the presence of the negative ion at a distance from The reference ion will be equal in all directions, likewise if the charge relative For the reference ion, its ionic face is zero. How does it affect the reference ion? With an external electric field, it will move a certain distance, distorting the symmetrical distribution. For charging via the reference ion. The ionic atmosphere can re-symmetry around the ion The reference if its contents can immediately change its position to the new position of the ion Ref. This is possible if the transformation is instantaneous and if the reference ion does not follow its movement. Accordingly, sufficient time is required to restore the regular shape, and this time is called the relaxation time. The electric field is far from the ionic face, which cannot catch up with it. So that's the part The back of the ionic atmosphere appears to be fixed in place because the effect of the electric field of the ion The central ion has been transformed, while the area in front of the central ion will It is formed continuously, so the ionic atmosphere will not be spherical, but will have a brittle shape oval (egg-shaped) and the charge density behind the reference ion will be greater than it greater than it in front of it, and this will not be the net electric charge equal to zero as in the case The reference ion will be an ionic face, but this will create an attractive force. Electricity between the atmosphere and the ionic and the reference ion working in the direction with the X to the direction of the field External electrolyte, which results in a retardation of the movement of the reference ion.



Consequently, its speed will decrease. This effect is called the relaxation effect. or the asymmetry effect see figure (10).

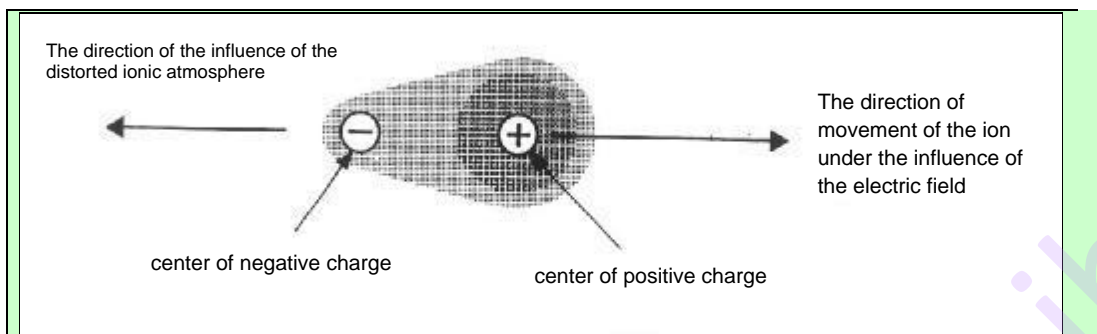


Figure (10): Illustration showing the effect of relaxation after deformation of the ionic atmosphere and the formation of an attractive force between the charge of the ion and charge of the ionic atmosphere.

The effect of the external electric field is not limited to the ion, but extends to the atmosphere. An ion with an opposite charge, which will move in a direction with the X of the ion's movement Marg p. During this movement the ionic atmosphere tries to keep the contents of the Include ions and solvent molecules in addition to the ion returned by a force called by the electrophoretic effect that will add a factor to another impairment on ion velocity reference.

**Q) The number of factors on which both the relaxation effect and the electrophoretic effect depend.**