Ministry of Higher Education and Scientific Research

Al-Muthanna University

College of Science

وزارة التعليم العالي والبحث العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

Electrochemistry

Lecture (11)

Stage 3

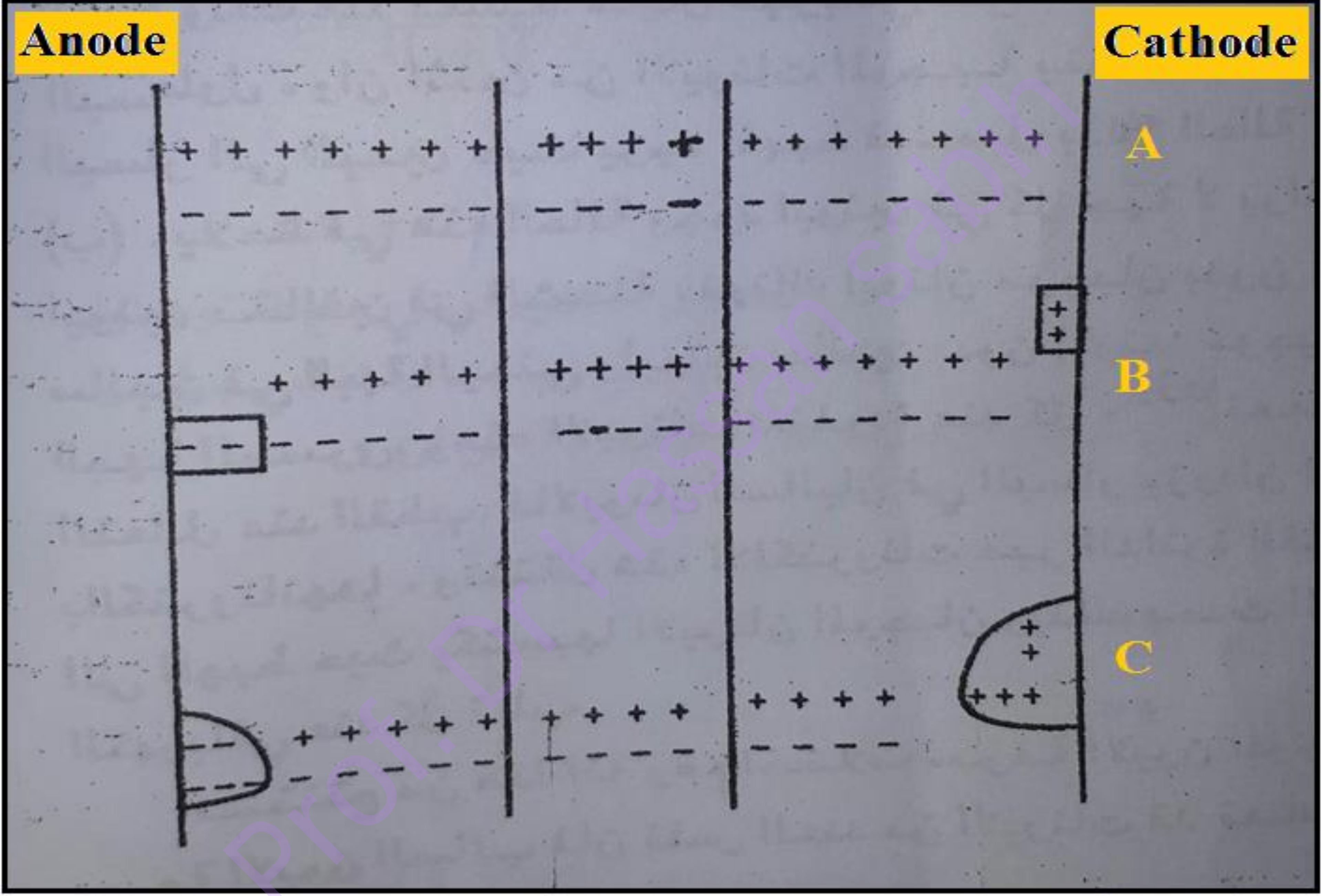
Prof. Hassan Sabih

Experimental of Determination of Transport number

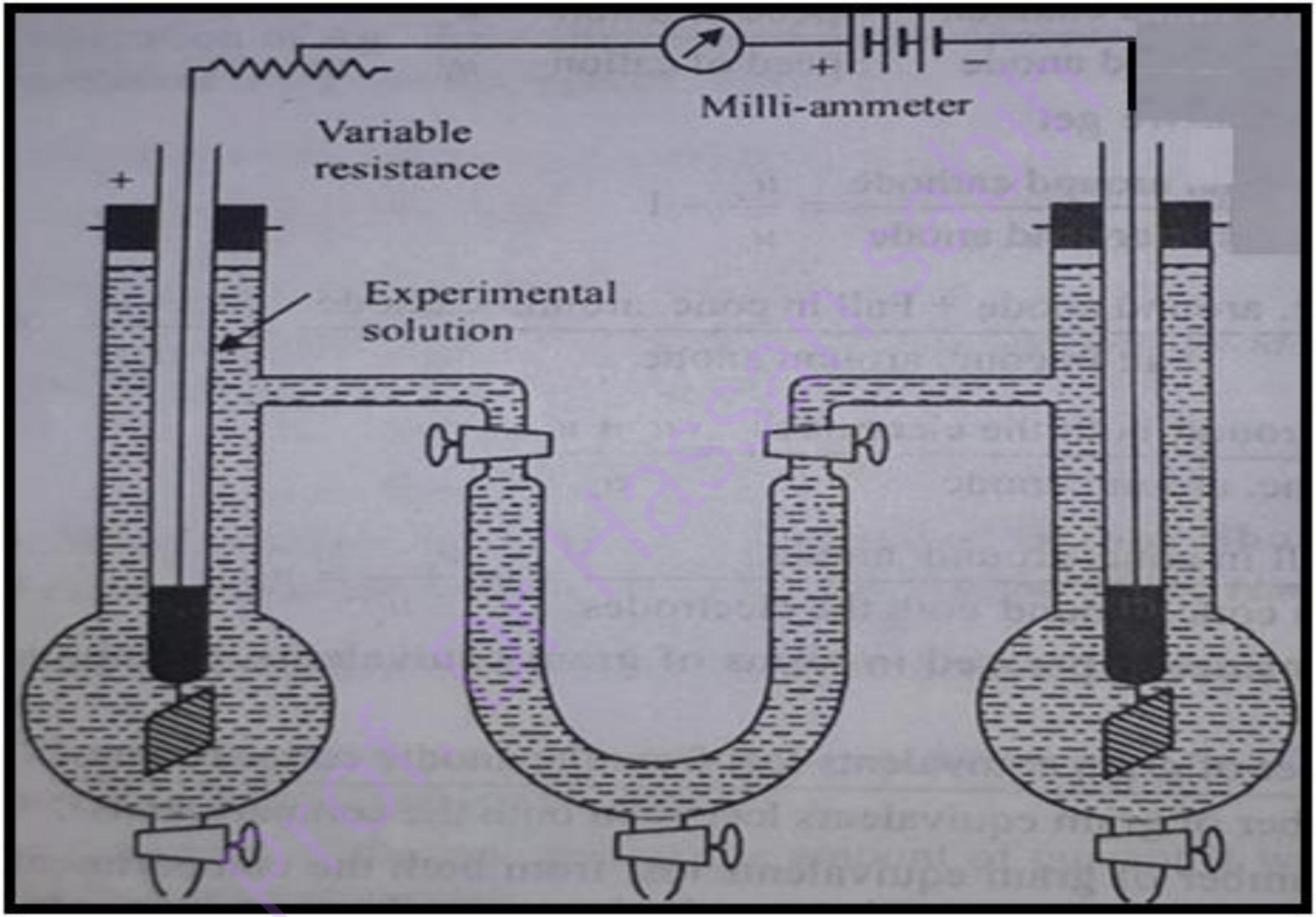
(Hittrof Method)

This method is based on the measurement of changes in the solution concentration near the electrodes. As direct current passes through the solution, the anions are transported to the anode, and the cations, to the cathode. Suppose equivalents of anions are transported from the cathode during the electrolysis. As result the electrolyte near the cathode, called catholyte contains excess equivalents of cations.

They should discharge on the cathode so that the solution remains electrically neutral. In this case, the decrease in the amount of the salt in the catholyte in similar way, the decrease in the amount of the salt near the anode will be equivalents of cations which have moved away from the anode. The charge of equivalent of ions is equal to the faraday constant.



migration of ions



Apparatus for the determination of transport number by Hittorf 's method.

Theory of electrolytic conductance

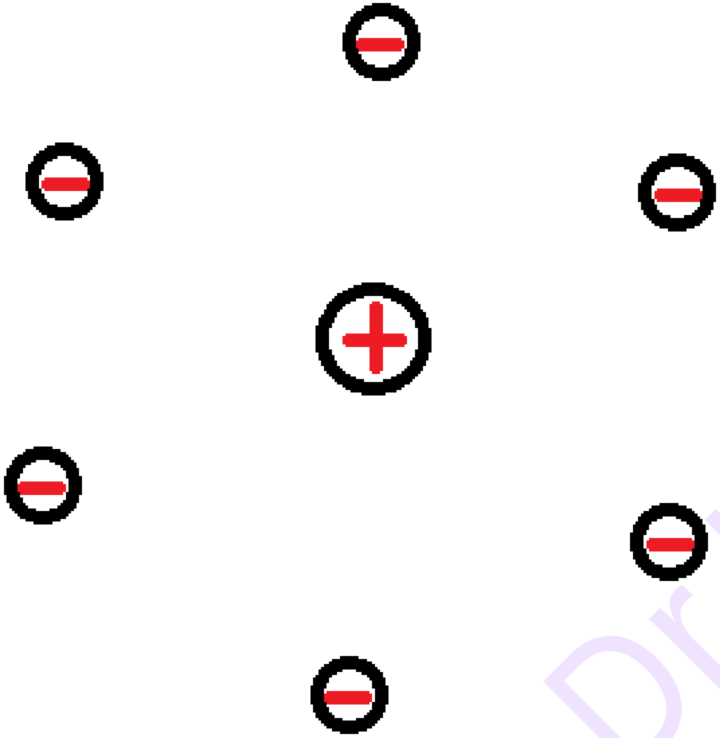
- **Debye-Huckel theory**

it explains the increase in conductance of strong electrolyte on dilution based upon following two effects:

1- Relaxation effect or Asymmetry effect:

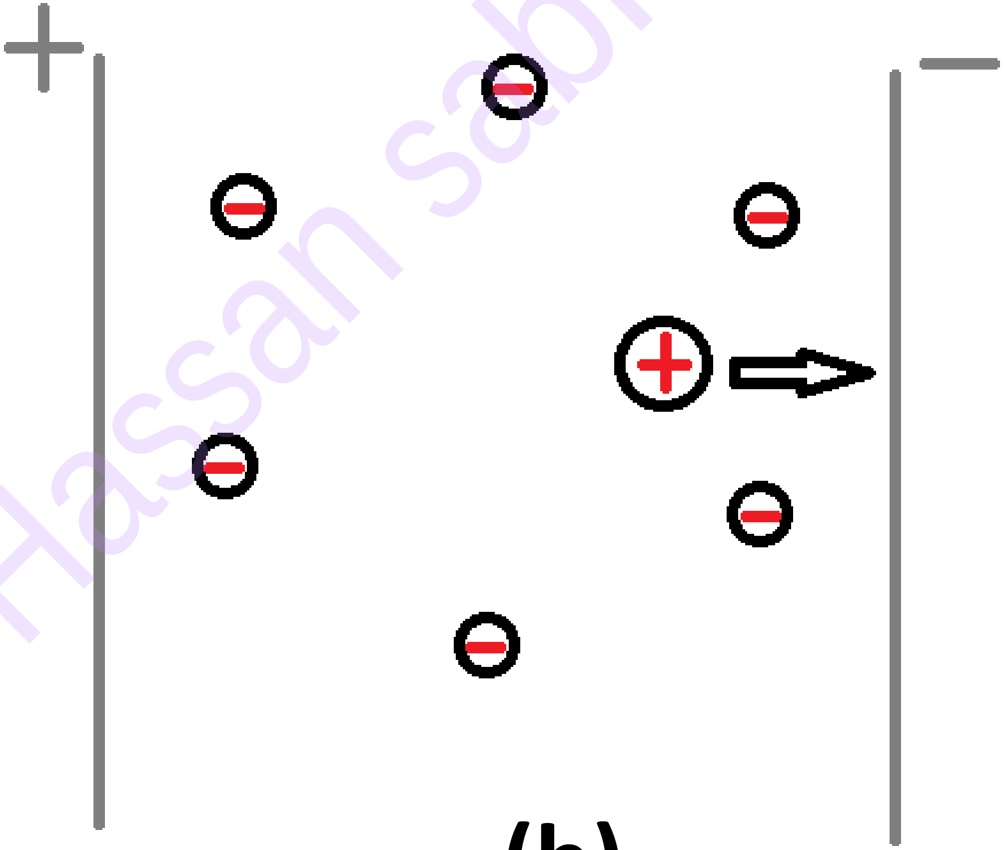
In the solution, each ion is surrounded by an ionic atmosphere of opposite charge. So long as no electric field is applied, the ionic atmosphere remains symmetrical around the central ion as shown in figure (a). However, when a current is passed through the solution, the central ion moves towards the oppositely charged electrode. As it is moving out of the ionic atmosphere, it has to rebuild an ionic atmosphere of opposite charged around it and the old ionic atmosphere dies out. However, the destruction of the old ionic atmosphere and the formation of the new ionic atmosphere do not take place at the same time. There is some time lag called time of relaxation between the destruction of the old and the formation of new ionic atmosphere. During this time, the old ionic atmosphere pulls the moving ion backward and hence retards its motion

(figure b). Hence this effect is called relaxation effect. Alternatively, it may be argued that as the central ion moves, the symmetry of the ionic atmosphere is lost; more ions of the ionic atmosphere are left behind than are present in the front (figure b). The excess ions of the ionic atmosphere present behind the moving ion drag the ion backward and retard its motion. Thus, the effect arises because of the asymmetry of the ionic atmosphere of the moving ion and hence is also called asymmetry effect.



(a)

Symmetrical ionic atmosphere around a positive ion

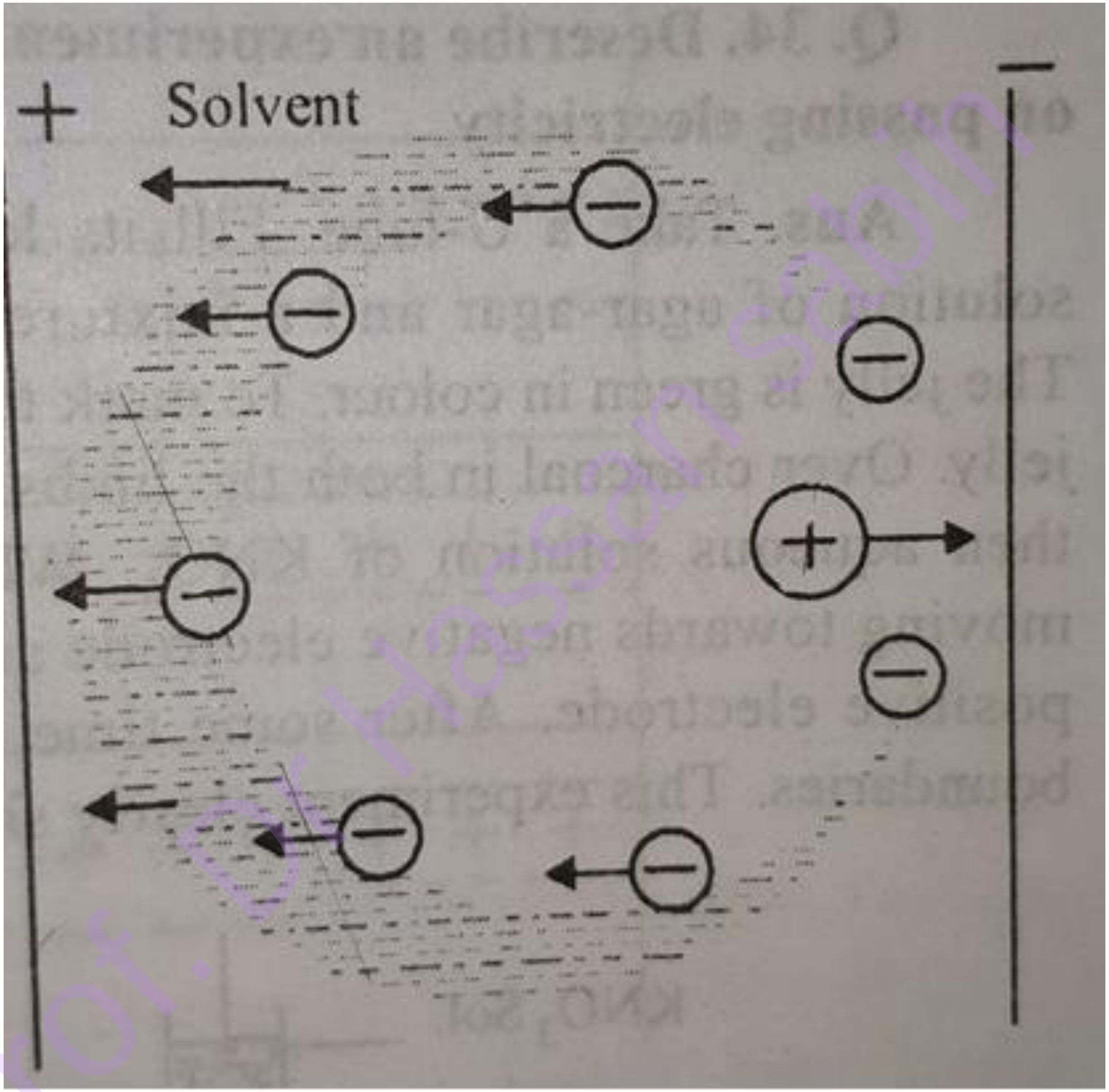


(b)

Ionic atmosphere becoming asymmetric when central ion move

2- Electrophoretic effect:

When Electromotive force (EMF) is applied, the central ion moves in one direction and the oppositely charged ionic atmosphere moves in the opposite direction. As this ionic atmosphere moves, the solvent molecules associated with it also move. Thus the flow of the ionic atmosphere and that of the solvent molecules attached to it takes place in a direction opposite to that of the movement of the central ion. In other words, the central ion is moving against the stream. Hence motion of the ions is retarded. This effect is called electrophoretic effect (Figure c).



(c)

Besides the above two effects, the third retarding force is the normal frictional resistance offered by the medium which depends on the viscosity of the medium, its dielectric constant etc.

Based upon the above ideas, Debye and Huckel (1923) derived a mathematical expression for the variation of equivalent conductance with concentration. This equation was further improved by Onsagar and now the equation is known as Debye-Huckel-Onsagar equation or simply Onsagar equation. it is written in the form.

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

Where

λ_c = equivalent conductance at concentration C

λ_o = equivalent conductance at infinity dilution

D = Dielectric constant of the medium

η = Viscosity of the medium

T = Temperature of the solution in degrees absolute

C = concentration of the solution in moles/litre

As D and η are constant for a particular solvent, therefore, at constant temperature, the above equation can be written in the form

$$\lambda_C = \lambda_o - (A + B\lambda_o)\sqrt{c}$$

Where A and B are constant for a particular solvent at a particular temperature.