Transport Phenomena in Biological Systems
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Lecture – 54
Charges/Ions in Solution

Welcome back, we are discussing charge flux. And this would most likely be the last class for that chapter. So we are going to look at the charges or ions in solution. Many biological systems are solution based and therefore we need to have a good understanding of as to how to approach charges in the situation. So, that would give us some reasonably complete set of tools to look at manipulation of charges which, we will start doing in the actual context in when we begin the next chapter. So, let us see 3 important concepts of charges or ions in solutions in the context of charge flux.

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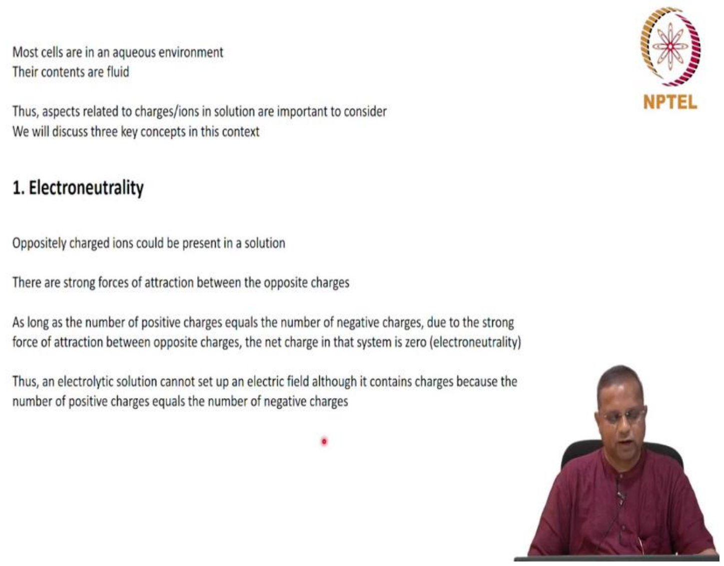

Most cells are in an aqueous environment
Their contents are fluid

Thus, aspects related to charges/ions in solution are important to consider
We will discuss three key concepts in this context

1. Electroneutrality

Oppositely charged ions could be present in a solution

There are strong forces of attraction between the opposite charges

As long as the number of positive charges equals the number of negative charges, due to the strong force of attraction between opposite charges, the net charge in that system is zero (electroneutrality)

Thus, an electrolytic solution cannot set up an electric field although it contains charges because the number of positive charges equals the number of negative charges

So, formally speaking, most cells are in an aqueous environment. The contents themselves are fluid and therefore aspects area related to charges ions in solution are important to consider. And the 3 concepts we going to look at, First one is electroneutrality. It is very simple, but quite often confused. So do not just look at what it is and apply it to wherever it is applicable and do not get confused in out of the box situations.

There are always situations where electroneutrality may not be valid, but given everything else electroneutrality is valid in a solution is what this says. Let us go through it oppositely charged ions could be present in solution of course, you have KCl solution of KCl very typical electrolyte, you have K^+ and Cl^- ions that are present there. So, oppositely charged ions could be present in a solution.

There are strong forces of attraction between these opposite charges and as long as the number of positive charges equals the number of negative charges. Due to the strong force of attraction between the opposite charges, the net charge in that system is 0. So, note every single aspect of this sentence is important to avoid confusion as long as the number of positive charges equals the number of negative charges. Due to the strong force of attraction between opposite charges, the net charge in that system would be 0.

This is the condition of electroneutrality. In other words, electroneutrality is valid when the number of positive charges equals the number of negative charges. You go and introduce another deliberately a positive charge into that, then it is not going to be electro neutral. Relation is no longer going to be electro neutral. So you need to keep that into it keep that clearly in your mind.

Thus an also there other interpretation of this which is very important for us and electrolyte electrolytic solution, which has opposite charges equal number of opposite charges, K^+ Cl^- for that matter, for example, cannot set up an electric field, although it contains charges, because the number of positive charges equals the number of negative charges and they cancel it.

So field is not set up by an electrolytic solution is one of the key things that is coming out of the principle of electroneutrality, which is certainly very useful for us when we start looking at things in detail to design aspects related on electrical aspects to design, biological systems, biological processes, biological tools based on electrical aspects. So, this is a electroneutrality.

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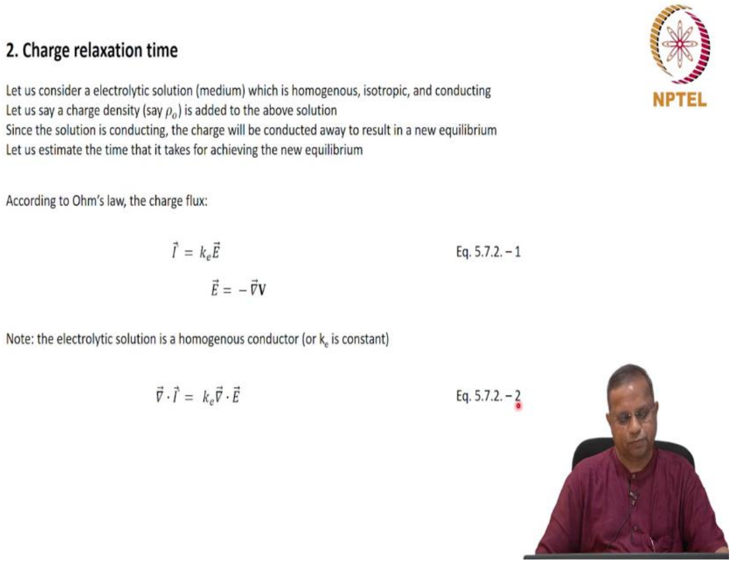

2. Charge relaxation time

Let us consider a electrolytic solution (medium) which is homogenous, isotropic, and conducting
Let us say a charge density (say ρ_o) is added to the above solution
Since the solution is conducting, the charge will be conducted away to result in a new equilibrium
Let us estimate the time that it takes for achieving the new equilibrium

According to Ohm's law, the charge flux:

$$\vec{I} = k_e\vec{E} \qquad \text{Eq. 5.7.2. – 1}$$

$$\vec{E} = -\vec{\nabla}\text{V}$$

Note: the electrolytic solution is a homogenous conductor (or k_e is constant)

$$\vec{\nabla}\cdot\vec{I} = k_e\vec{\nabla}\cdot\vec{E} \qquad \text{Eq. 5.7.2. – 2}$$

The second is a totally different concept is called charge relaxation time. Let us spend some time on this. Let us consider an electrolytic solution which could be a medium which is homogeneous properties are the same; well mixed isotropic it does not change with direction and conducting. So, this is our electrolytic solution the medium which is homogeneous isotropic and conducting.

The charge flux (current density), according to Ohm's law is

$$\vec{I}\,' = k_e\vec{E} \tag{5.7.2-1}$$

where $\vec{E} = -\vec{\nabla}\mathbf{V}$.

Since we are considering the electrolytic solution to be a homogenous conductor (k_e is constant)

$$\vec{\nabla}.\vec{I}\,' = k_e\vec{\nabla}.\vec{E} \tag{5.7.2-2}$$

From Gauss' law, we know that

$$\vec{\nabla}.\epsilon\,\vec{E} = \rho \tag{5.7.2-3}$$

where ρ is charge density at any time t.

Therefore, by substituting Eq. 5.7.2-3 into 5.7.2-2, we get

$$\vec{\nabla}.\vec{I}\,' = \frac{k_e}{\epsilon}\rho \tag{5.7.2-4}$$

If we assume that upon application of ρ_o, the increase in charge density in the solution is uniform, we can use Eq. 5.5-5, the charge conservation (charge continuity) equation here, i.e.

$$\vec{\nabla}.\vec{I}\,' = -\frac{\partial\rho}{\partial t} \tag{5.5-5}$$

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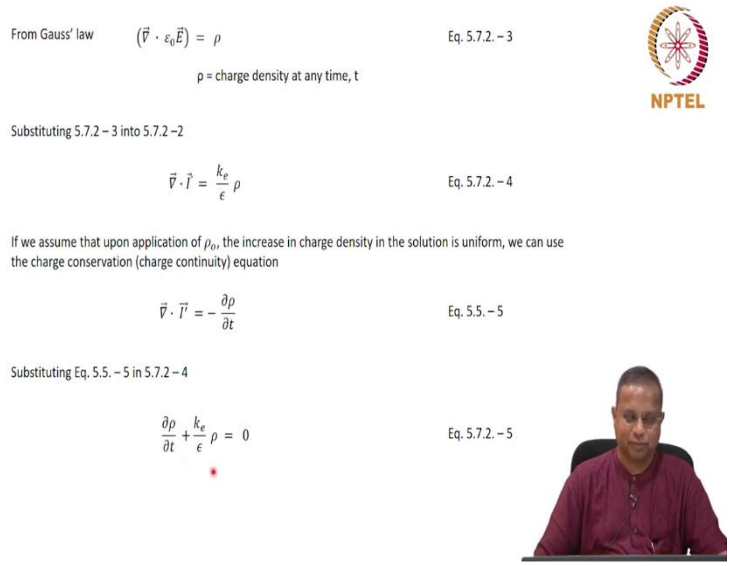

From Gauss' law $(\vec{\nabla} \cdot \varepsilon_0\vec{E}) = \rho$ Eq. 5.7.2. – 3

ρ = charge density at any time, t

Substituting 5.7.2 – 3 into 5.7.2 –2

$\vec{\nabla} \cdot \vec{I} = \frac{k_e}{\epsilon}\rho$ Eq. 5.7.2. – 4

If we assume that upon application of ρ_o, the increase in charge density in the solution is uniform, we can use the charge conservation (charge continuity) equation

$\vec{\nabla} \cdot \vec{I'} = -\frac{\partial \rho}{\partial t}$ Eq. 5.5. – 5

Substituting Eq. 5.5. – 5 in 5.7.2 – 4

$\frac{\partial \rho}{\partial t} + \frac{k_e}{\epsilon}\rho = 0$ Eq. 5.7.2. – 5

Substituting the above equation in 5.7.2-4, we get

$$\frac{\partial \rho}{\partial t} + \frac{k_e}{\epsilon}\rho = 0 \qquad (5.7.2\text{-}5)$$

The solution of the differential equation given in Eq. 5.7.2-5 is

$$\rho = \rho_o \exp\left(\frac{-t}{\tau_r}\right) \qquad (5.7.2\text{-}6)$$

where $\tau_r = \frac{\epsilon}{k_e}$ is the charge relaxation time.

So, therefore, the charge continuity equation is very fundamental widely valid. This is nothing but directly from Maxwell's first equation very fundamental equation, we applied both 2 solutions and we have come up with this equation, which gives us the variation of ρ with time.

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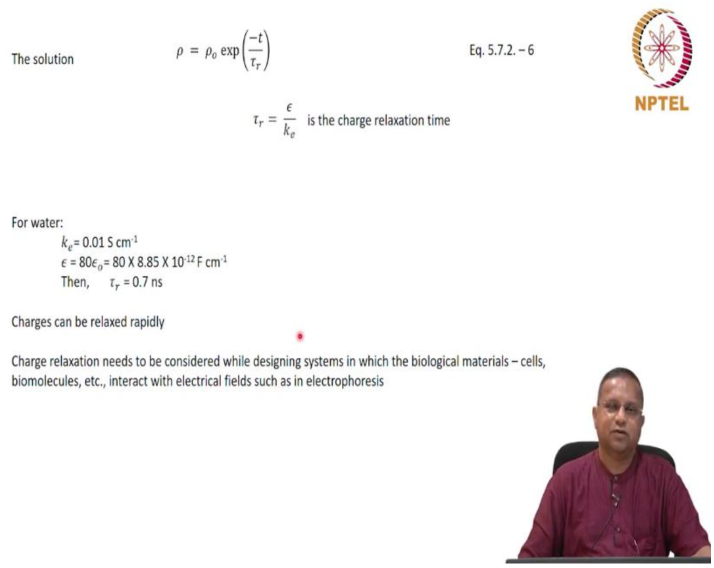

The solution $\rho = \rho_0 \exp\left(\frac{-t}{\tau_r}\right)$ Eq. 5.7.2. – 6

$\tau_r = \frac{\epsilon}{k_e}$ is the charge relaxation time

For water:

k_e = 0.01 S cm^{-1}
$\epsilon = 80\epsilon_0 = 80 \times 8.85 \times 10^{-12}$ F cm^{-1}
Then, τ_r = 0.7 ns

Charges can be relaxed rapidly

Charge relaxation needs to be considered while designing systems in which the biological materials – cells, biomolecules, etc., interact with electrical fields such as in electrophoresis

For water k_e happens to be about 0.01 Siemens per centimetre. Recall the units of conductivity Siemens per centimetre ϵ is about 80 times the permittivity of free space for water this you may recall from your working out of problems from your high school pre engineering levels therefore, and you know that ϵ_0 is $8.85*10^{-12}$ Farad per centimetres therefore, its 80 times that.

Therefore, τ_r is ϵ / k_e and that turns out to be 0.7 nanoseconds. So, you add the charge density uniform charge density of ρ not into a conducting solution in fine 7 seconds whole equilibrium is achieved a whole new equilibrium is achieved that is a great insight. So if you keep adding charges and expect some effects to remain there, it is all gone and 0.7 nanoseconds push to a new equilibrium, but it is all gone.

And now the flip side, you do not have to wait long for the new equilibrium to be achieved done at 0.7 nanoseconds. So, these are the kind of insights that you can get. So, charges can be relaxed rapidly and charge relaxation needs to be considered while designing systems in which biological materials such as cells, biomolecules and so on and so forth. Interact with electrical fields such as electrophoresis.

So an electrophoresis design, these principles are all embedded there. So, electron neutrality, so no field is set up by the solution that is a very essential thing and charge relaxation. You cannot keep on adding charges to expect some manipulations in the dynamic aspects because charges are relaxed very rapidly.

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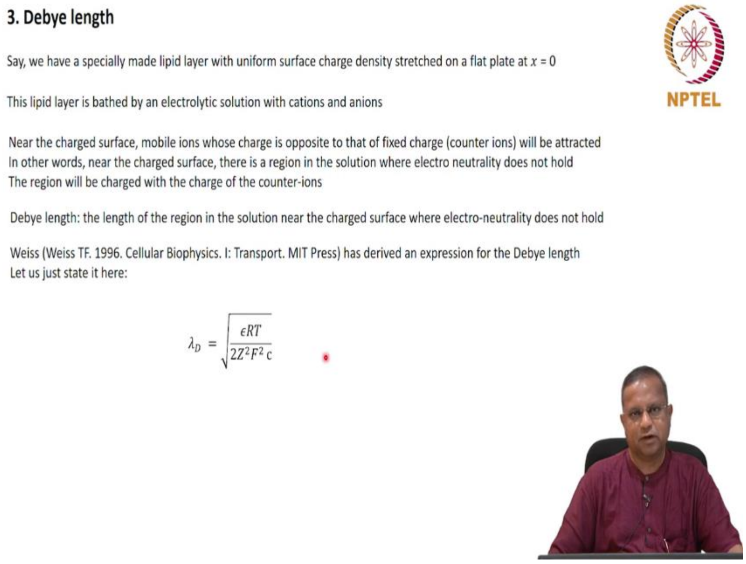


3. Debye length

Say, we have a specially made lipid layer with uniform surface charge density stretched on a flat plate at $x = 0$

This lipid layer is bathed by an electrolytic solution with cations and anions

Near the charged surface, mobile ions whose charge is opposite to that of fixed charge (counter ions) will be attracted
In other words, near the charged surface, there is a region in the solution where electro neutrality does not hold
The region will be charged with the charge of the counter-ions

Debye length: the length of the region in the solution near the charged surface where electro-neutrality does not hold

Weiss (Weiss TF. 1996. Cellular Biophysics. I: Transport. MIT Press) has derived an expression for the Debye length
Let us just state it here:

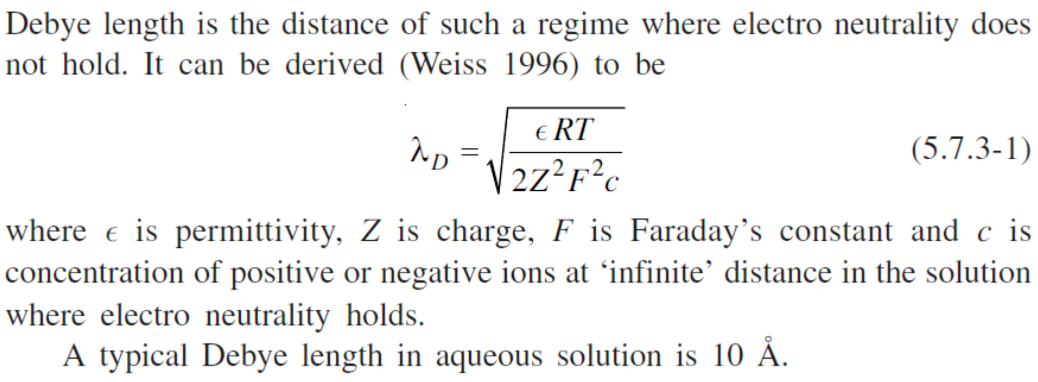
$$\lambda_D = \sqrt{\frac{\epsilon RT}{2Z^2F^2\,c}}$$

So, those were 2 principles we said 3, the third one is called Debye length. Say, to understand the balance that is considered this, say we have a specially made lipid layer with uniform surface charge density stretched on a flat plate at x = 0. So, somewhere here you have the plate, you have the lipid specially made liquid layer with uniform surface charge density and we are stretched it out on a flat plate which stands something like this.

The liquid layer let us say is bathed by an electrolytic solution with cations, anions, so there are charges on lipid by layer and the charges around. Near the charged surface, because it is uniformly charged mobile ions, whose charge is opposite to that of the fixed charge will be attracted. So, that is nature oppositely attracted oppositely charged ions are practical. So, if you have a negative charge here it is going to attract only positive charges close to the surface.
In other words near the charge surface, there is a region in the solution where electroneutrality does not hold because of this charge, it is going to attract the oppositely charged ions close to it. Therefore, there is a region where electro neutrality is not going to be valid in the solution. You take the plate and the solution together yes, but in the solution itself, electro neutrality is not going to be valid.

The region will be charged with the charge of the counter-ions and the Debye length is nothing but the length of this region in the solution near the charge surface, where electro neutrality does not hold that is it. There is a very thin region. There is a region it turns out to be very thin layer. There is region close to a charge surface where electro neutrality does not hold in solution, that length or which that region exists is called a Debye length. And if you look at Weiss we have already seen this book earlier.

This is cylinder by physics 1 transport MIT Press published in 1996. He has derived an expression for Debye length. I am not going to get into the derivation in this course. You can look at it up and look, look it up. Here



Debye length is the distance of such a regime where electro neutrality does not hold. It can be derived (Weiss 1996) to be

$$\lambda_D = \sqrt{\frac{\epsilon RT}{2Z^2F^2c}} \qquad (5.7.3\text{-}1)$$

where ϵ is permittivity, Z is charge, F is Faraday's constant and c is concentration of positive or negative ions at 'infinite' distance in the solution where electro neutrality holds.

A typical Debye length in aqueous solution is 10 Å.

So, in this chapter, we have looked at 3 important concepts related to ions in solution charges in solution. First one was the concept of electroneutrality second was the concept of what did we do? First we looked at Debye length the third concept, charge relaxation, then Debye length, we will stop here. And we have completed this chapter. When we begin the next class, we will or the next class will be a review class of the concepts that we have seen in the chapter.