Colloids and Surfaces
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Lecture - 43
Relationship between Electrophoretic Mobility and Zeta Potential - II

So far we have developed what are called as Huckel equation and Helmholtz-Smoluchowski equation for relating electrophoretic mobility to zeta potential. Now, we will look at what is called as a Henry's solution for the same before we do that a quick recap of the 2 equations.

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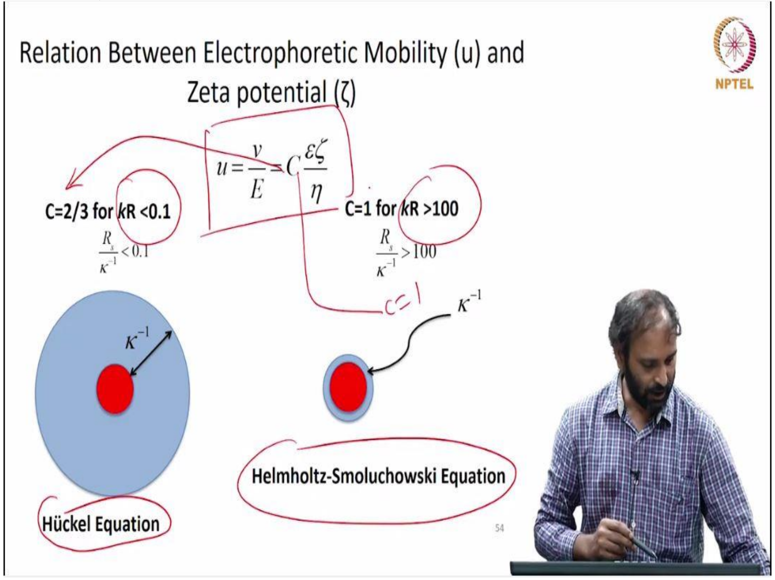

Relation Between Electrophoretic Mobility (u) and Zeta potential (ζ)

$$u = \frac{v}{E} = C\frac{\varepsilon\zeta}{\eta}$$

C=2/3 for κR <0.1

$$\frac{R_s}{\kappa^{-1}} < 0.1$$

C=1 for κR >100

$$\frac{R_s}{\kappa^{-1}} > 100$$

Hückel Equation

Helmholtz-Smoluchowski Equation

So, one is what is called the Huckel equation, and other one is Helmholtz-Smoluchowski. So, that is a general expression with C taking a value of 2/3, for Huckel’s limit and C taking a value of 1 for Helmholtz-Smoluchowski equation. So, and as we have discussed, so, these solutions are applicable only for certain condition that is when k times R is less than 0.1 or k times R is greater than 100.

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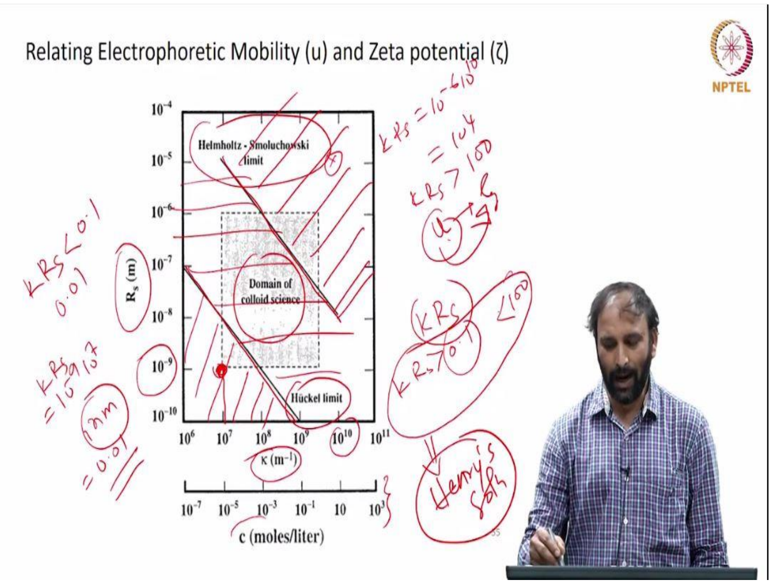

Relating Electrophoretic Mobility (u) and Zeta potential (ζ)

So, just to talk about the need for developing Henry's equation, what you have is a plot of Rs that is the radius of the spherical particle. And on the x axis you have the concentration of the particle expressed in moles per liter. And for the concentration that I know, that are given, I can calculate what is kappa because we know that there is an expression that relates kappa to the concentration of colloids. So, therefore, I could calculate what is kappa times Rs value?

So, let us take, so, what you see is there are 2 lines, this line is what is called as a that is the Huckel limit, and this line is what is called as represents the Helmholts-Smoluchowski limit. So, what I mean by that is, let us take some particular value of kappa. So, if I take kappa value of 10 power 10 and if I take some dimension of the particle to be 10 power - 5 that means, if I go to a region there, so, therefore, kappa times Rs is going to be 10 power - 6 times 10 power 10 therefore, you are going to have 10 power 4.

So, therefore, kappa times Rs in this case is larger than 100 therefore, one could use the Smoluchowski limit for you know converting the mobility value that have been measured to obtain the zeta potential. However, if I take like say a typical value for example, 10 power - 9 is the particle dimension that is, now we are talking about in this case we are talking about 10 power - 9 meter is the dimension that means, we are talking about nanoparticles the particles are 1 nanometer in size.

So, therefore, and if I take a corresponding kappa value to be 10 power 7 therefore, kappa times Rs takes the value of 10 power - 9 times 10 power 7, so, which is 10 power 0.01. So, therefore, or 10 power - 2. So, therefore, again what we have considered now, it again falls into the regime of k times Rs less than 0.1 because, the value of k times R is that we got is 0.01. So, therefore, so, if I take for any value of Rs and kappa in this range, so, we can use the Huckel limit and for when you value of R and kappa, which fall into this regime.

So, we could use Helmholtz-Smoluchowski limit and then we can convert the mobility values to zeta potential. However, there is a large region of particle sizes and the concentration of electrolyte range where there is a lot of work that occurs both in terms of formulations both in terms of you know, tuning the stability and causing the destabilization of colloids. So, it so happens that in the colloidal in the domain of colloidal science, which is of practical relevance.

You will have always have a range of kappa times Rs which is more than 0.1 and less than 100. So therefore, so we do not have any expression that relates mobility to zeta potential in that range, and to this end, Henry's solution would develop. So, Henry solution is a general solution that is, that relates mobility to zeta potential for any value of kappa Rs that is both, it combines the Huckel limit at one end, and Helmholtz-Solumochowski limit at the other end. And, of course, it is also applicable for any range of kappa times Rs between 0.1 and 100 as well.

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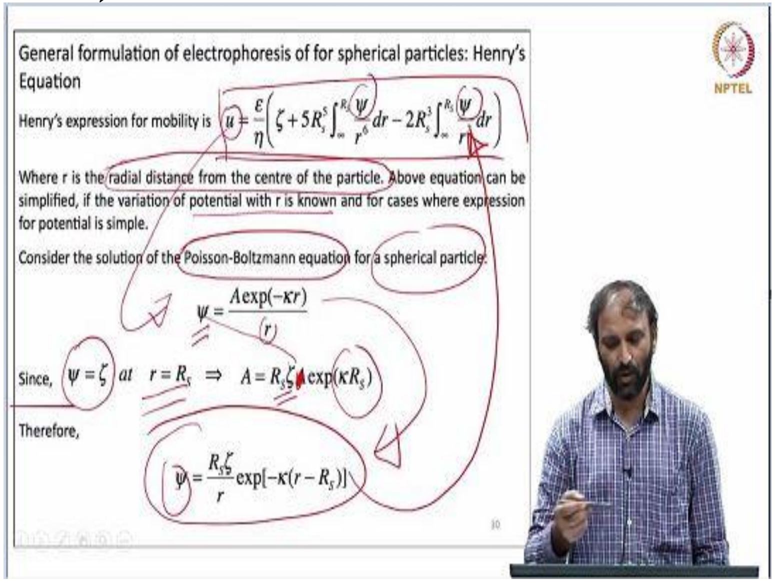

General formulation of electrophoresis of for spherical particles: Henry's Equation

Henry's expression for mobility is $u = \frac{\varepsilon}{\eta}\left(\zeta + 5R_s^5\int_\infty^{R_s}\frac{\psi}{r^6}dr - 2R_s^3\int_\infty^{R_s}\frac{\psi}{r}dr\right)$

Where r is the radial distance from the centre of the particle. Above equation can be simplified, if the variation of potential with r is known and for cases where expression for potential is simple.

Consider the solution of the Poisson-Boltzmann equation for a spherical particle:

$$\psi = \frac{A\exp(-\kappa r)}{r}$$

Since, $\psi = \zeta$ at $r = R_s \Rightarrow A = R_s\zeta\exp(\kappa R_s)$

Therefore,

$$\psi = \frac{R_s\zeta}{r}\exp[-\kappa(r - R_s)]$$

So, the general expression that Henry's developed for the mobility is given by this. And so if you want to obtain mobility, all you need to know is how does the potential psi varies as a function of R. And so therefore, this R in this case is the radial distance from the center the particle. And so, one could simplify this expression to obtain the expression for mobility, if we know how the potential varies with R, so what we will do is we will take a simple case of Poisson Boltzmann equation.

And that for a spherical particle, we have derived that psi goes as A times exponent of minus kappa r divided by r, therefore, now, if I substitute for the fact that the potential becomes zeta potential add r going to Rs, therefore, I would have there is a mistake here, so, this A should not be there. Therefore, this A becomes zeta potential, that is here times Rs, that is here multiplied by exponent of minus is going to be divided by exponent of minus kr or exponent of plus k times Rs.

So, therefore, if I substitute the value of A back into this expression, we will end up with psi = Rs into zeta divided by r exponent of - k times r - Rs. So, therefore, now, I know that how the potential varies with R, therefore, one could substitute the equation back here.

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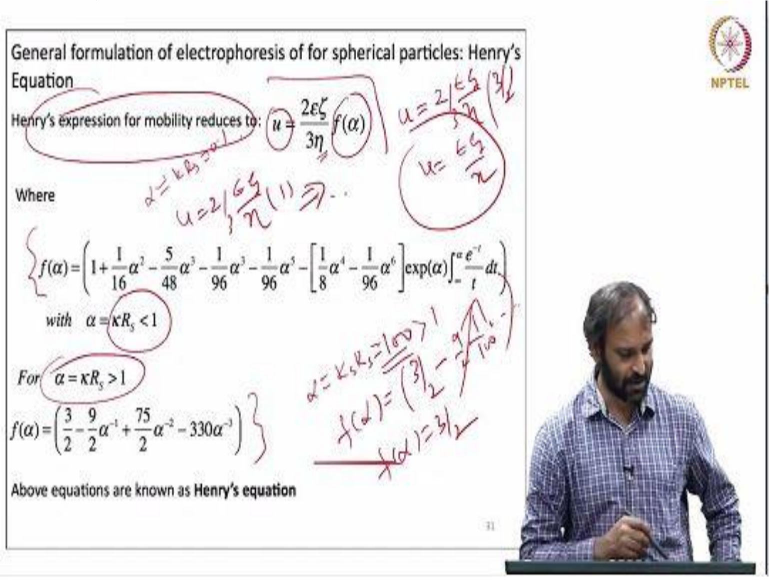

General formulation of electrophoresis of for spherical particles: Henry's Equation

Henry's expression for mobility reduces to: $u = \frac{2\varepsilon\zeta}{3\eta} f(\alpha)$

Where

$$f(\alpha) = \left(1 + \frac{1}{16}\alpha^2 - \frac{5}{48}\alpha^3 - \frac{1}{96}\alpha^3 - \frac{1}{96}\alpha^5 - \left[\frac{1}{8}\alpha^4 - \frac{1}{96}\alpha^6\right]\exp(\alpha)\int_{\infty}^{\alpha}\frac{e^{-t}}{t}dt\right)$$

with $\alpha = \kappa R_s < 1$

For $\alpha = \kappa R_s > 1$

$$f(\alpha) = \left(\frac{3}{2} - \frac{9}{2}\alpha^{-1} + \frac{75}{2}\alpha^{-2} - 330\alpha^{-3}\right)$$

Above equations are known as **Henry's equation**

$\alpha = \kappa R_s \to 0$

$u = \frac{2}{3}\frac{\varepsilon\zeta}{\eta}(1) \Rightarrow \cdots$

$u = \frac{2}{3}\frac{\varepsilon\zeta}{\eta}\left(\frac{3}{2}\right)$

$u = \frac{\varepsilon\zeta}{\eta}$

$\alpha = \kappa_s R_s = 100 > 1$

$f(\alpha) = \left(\frac{3}{2} - \frac{9}{100} \cdots\right)$

$f(\alpha) = 3/2$

And then if you do a simple integration, so, you will end up with Henry’s expression for mobility, which is given by u times 2/3 epsilon zeta divided by n, where eta is the viscosity of the fluid in which the particles are dispersed and a term f of alpha and f of alpha depends on what is the kappa times Rs value. So, if for kappa times Rs less than 1, it takes this functional form and for alpha greater than 1, it takes this function form. So, we could quickly cross check that if I take alpha = k times Rs of the order of 100, that is much larger than 1.

So, therefore, f of alpha becomes 3/2 minus and because we are talking about alpha to be 100, therefore, you have 9/2 times 1 over 100 time and so, therefore, the all the terms can be neglected. So, you will end up with f of alpha = 3/2. Therefore, expression u = 2/3 epsilon zeta divided by eta times 3/2 for kappa times r about 100. Therefore, u becomes epsilon into zeta by eta. Therefore, we essentially recover the Helmholtz-Smoluchowski limit.

And similarly, if you take the expression that corresponds to alpha less than 1 therefore, if I take alpha to be very small for example, k times Rs is of the order of say 0.1 then again what will have is f of alpha will become 1 plus again I can neglect the higher order term. Therefore, in such a case u becomes 2/3 into epsilon zeta by eta times 1 again we recover back the Huckel limit. So, therefore, the Henry's expression for mobility is a general solution that is applicable for obtaining you know, the zeta potential measurements zeta potential values from the mobility measurements for any given value of kappa times Rs.

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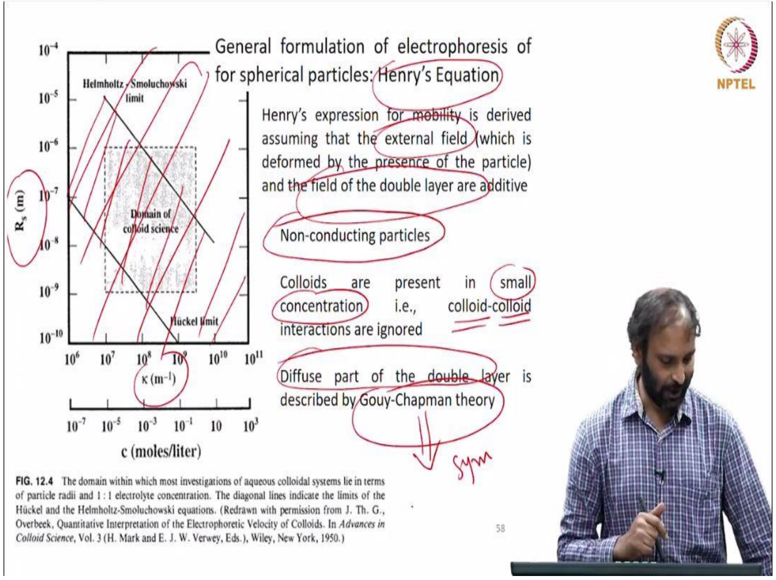

General formulation of electrophoresis of for spherical particles: Henry's Equation

Henry's expression for mobility is derived assuming that the external field (which is deformed by the presence of the particle) and the field of the double layer are additive

Non-conducting particles

Colloids are present in small concentration i.e., colloid-colloid interactions are ignored

Diffuse part of the double layer is described by Gouy-Chapman theory

FIG. 12.4 The domain within which most investigations of aqueous colloidal systems lie in terms of particle radii and 1 : 1 electrolyte concentration. The diagonal lines indicate the limits of the Hückel and the Helmholtz-Smoluchowski equations. (Redrawn with permission from J. Th. G., Overbeek, Quantitative Interpretation of the Electrophoretic Velocity of Colloids. In *Advances in Colloid Science*, Vol. 3 (H. Mark and E. J. W. Verwey, Eds.), Wiley, New York, 1950.)

58

And Henry's expression for mobility is derived by assuming that and as I said that so, it is applicable for Henry's in a solution is applicable for the entire range of the Rs times kappa value Rs and values of Rs and kappa that are important from a practical point of view and Henry's expression from mobility is derived by assuming that the external field we know that the external field that is applied to the colloidal particle in a fluid.

It will also be disturbed by the presence of the particle and of course, this field is also going to influence the electrical double layer as well and Henry solution is derived by assuming that the external field is and the field that is developed because of the electrical double layer are additive and it is applicable for a non conducting particles therefore, if one for inert particles like such as polystyrene or PMMA or you know particles of that sort in once you know there are particles that are conducting like gold or any metallic particle.

One has to be careful in using these equations and it is also applicable to cases where the colloids are present in small concentration that is, so, that the colloid-colloid interactions can be ignored and in obtaining Henry's solution the diffuse double layer is described by the Gouy Chapman theory therefore, it is that means, the Henry solution is applicable for symmetric electrolyte. So, therefore, one has to make sure that appropriate expression for the mobility and appropriate mobility zeta potential relation is used in order to obtain the correct values of zeta potential.

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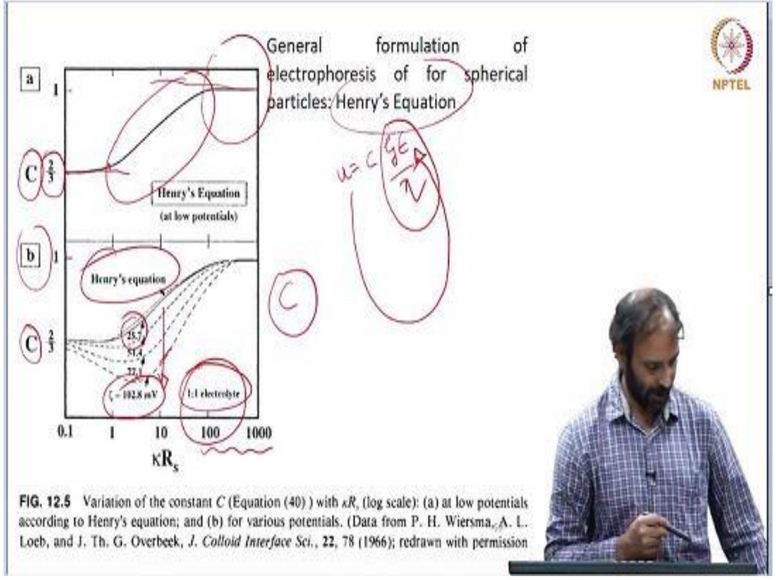

General formulation of electrophoresis of for spherical particles: Henry's Equation

$u = C \frac{\zeta \varepsilon}{\eta}$

FIG. 12.5 Variation of the constant C (Equation (40)) with κR, (log scale): (a) at low potentials according to Henry's equation; and (b) for various potentials. (Data from P. H. Wiersma, A. L. Loeb, and J. Th. G. Overbeek, *J. Colloid Interface Sci.*, 22, 78 (1966); redrawn with permission

And so, what you seeing is a plot where the constant C that is, so, we wrote that mobility u goes as some constant C times zeta epsilon divided by eta that is what we had developed that is somewhere here. So, therefore, and we know that C takes a value of 2/3 for the Huckel limit and it plateaus and then takes a value is equal to 1 when the k times Rs values are large. And however, if you take you can already see that when the k times Rs becomes of the order of 1.

That somewhere here you already see that you know the constant C deviates from this terminal values. Therefore, that means, the value of constant in the intermediate range deviates from the values that correspond to the terminal state that is you know of the order of 0.1 and more than 100 and it varies the nature of variation is actually captured by Henry's equation and you will see that so, what you see in the plot is that the variation of the constant C is plotted for different zeta potentials.

That is going from very low potential to of the order of 100 millivolts which is a case of a highly charged particle and this is plotted for 1 is to 1 type of electrolyte and you will see that when the charge of the particle becomes really large that is when the zeta potential becomes considerably large you will see that the value of the C that is obtained it deviates significantly from what is predicted by Henry's equations.

So, therefore, one has to exercise caution as to what is the typical value of the constant that one should use and that depends on several factors including the zeta potential of the particle or the surface charge in the particle and the electrolyte that we are considering and other factors as well.

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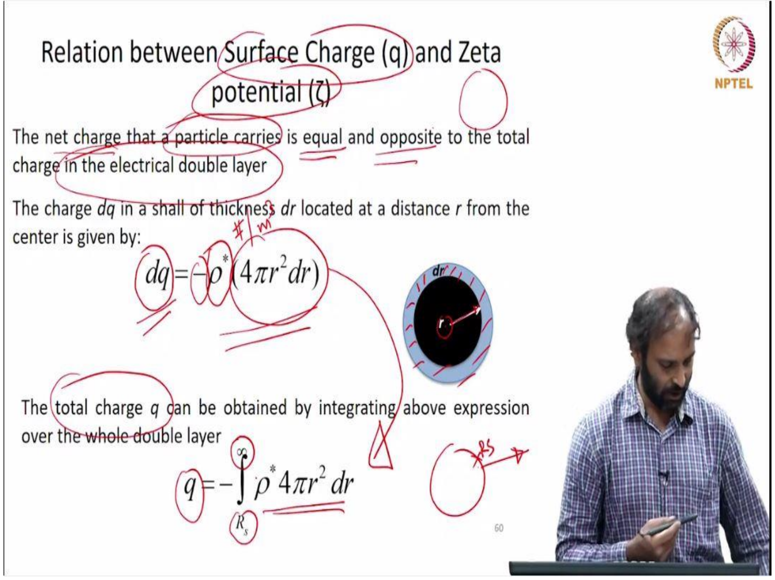

Relation between Surface Charge (q) and Zeta potential (ζ)

The net charge that a particle carries is equal and opposite to the total charge in the electrical double layer

The charge dq in a shall of thickness dr located at a distance r from the center is given by:

$$dq = -\rho^{*}(4\pi r^{2}dr)$$

The total charge q can be obtained by integrating above expression over the whole double layer

$$q = -\int_{R_s}^{\infty}\rho^{*}4\pi r^{2}\,dr$$

With that in mind, so, now, we would like to develop an expression for relating the surface charge q and the zeta potential and, the reason why an expression for q could be useful is that there are several techniques which are available, where the charge of the particle can be measured directly by certain technique such example or a couple of example could be conductometric methods and potentiometric methods and these are titration based method in which what you do is you consider a colloidal dispersion containing particles.

And you add some additive and monitor, for example, the change in the conductivity and at certain condition there is there will be an abrupt change in the conductivity and from that you can back calculate what is the charge. So, now, if there are techniques that are available, which enable us to get the charge directly, and if there are technicals, there are techniques where zeta potential can be measured, in order to compare the 2 different techniques you know the applicability of different techniques.

There should be a relation which will from which I should be able to back calculate one from other. So, in that context, so, what we will do is, we will try and develop an expression for our relation between the surface charge q and the zeta potential and for that we will consider the case of a charged particle charged spherical particle to be more precise, and what we are going to do is we are going to invoke the condition that the net charge that the particle carries is equal and opposite to the total charge in the electrical double layer.

And this condition is kind of met when in one works with particles dispersed in like say salt free solutions, for example. And what we will do is we will consider a thin shell of dimension dr which is located in distance r. And so, the total charge q or the charge in this thin strip is given by the charge density that is the number of charges per unit volume multiplied by the volume of this you know thin shell.

And if you want to calculate the total charge q, you can integrate this expression or the whole double layer that means, q is given by and you have a negative sign, because the charge on the particle and the charge in the double layer they are equal and opposite in sign. And therefore, q can be obtained by integrating this expression for the limits going from Rs to infinity wherein Rs corresponds to the surface of the charged particle and we are accounting for all the ions all the way up to infinity. So, infinity what we essentially mean is that, we are considering distances which are larger than double layer thickness.

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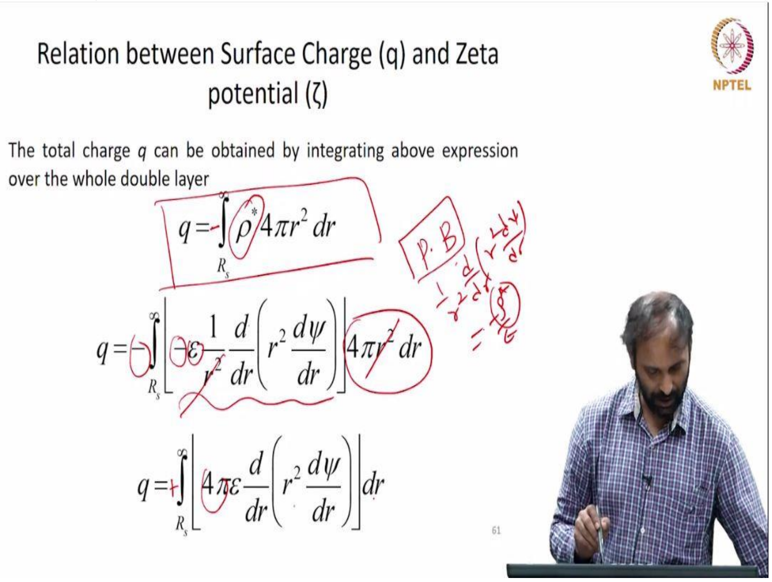

Relation between Surface Charge (q) and Zeta potential (ζ)

The total charge q can be obtained by integrating above expression over the whole double layer

$$\boxed{q = -\int_{R_s}^{\infty} \rho^* 4\pi r^2 \, dr}$$

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$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{\rho^*}{\varepsilon}$$

$$q = -\int_{R_s}^{\infty}\left[-\varepsilon \frac{1}{\cancel{r^2}}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)\right]4\pi \cancel{r^2} \, dr$$

$$q = +\int_{R_s}^{\infty}\left[4\pi\varepsilon \frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)\right]dr$$

So therefore, one could obtain q from this and if I want to integrate this, I should know what is rho star that is the charge density. And for that we are going to again invoke the Poisson Boltzmann equation. And we know that for a spherical coordinate system, and if you are considering the variation of the potential only in the r direction, 1 over r square into d/dr of r square d psi / dr should be equal to minus rho star times epsilon, I can replace for rho star from this expression.

Therefore, I have minus epsilon times 1 over r square into d/dr of r square d psi by dr times, this is the volume term. And with that, this and this get cancelled. So, therefore, I have 4 pi epsilon, that is the, the constant. And because of the fact that I have one negative sign that was coming from the, fact that the charges are in the solution are opposite to that of the particles that have one negative sign there, and there is one negative sign comes from the Poisson Boltzmann equation therefore, they both get cancelled. So, therefore, I have a positive sign here and times d/dr of r square d psi by dr at times dr.

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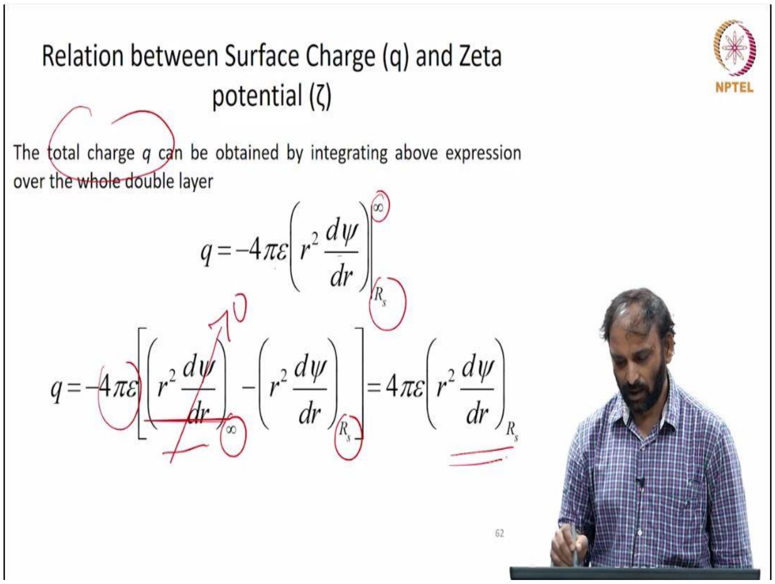

Relation between Surface Charge (q) and Zeta potential (ζ)

The total charge q can be obtained by integrating above expression over the whole double layer

$$q = -4\pi\varepsilon\left(r^2\frac{d\psi}{dr}\right)\Bigg|_{R_s}^{\infty}$$

$$q = -4\pi\varepsilon\left[\cancel{\left(r^2\frac{d\psi}{dr}\right)_{\infty}}^{\to 0} - \left(r^2\frac{d\psi}{dr}\right)_{R_s}\right] = 4\pi\varepsilon\left(r^2\frac{d\psi}{dr}\right)_{R_s}$$

So, therefore, now, to obtain the total charge q, I can integrate the expression therefore, q would be minus I have again so, there is a negative sign here. That is positive. And so, we will just come back to that. So q essentially goes as 4 pi epsilon r square into d psi / dr at and of course, I have these 2 limits, therefore, q becomes the constant term multiplied by this term at infinity and this term at 0 and we know that the potential is 0 at a distance much larger than kappa inverse that is at infinity. Therefore, this term becomes 0. Therefore, q becomes 4 pi epsilon into r square d psi / dr at Rs.

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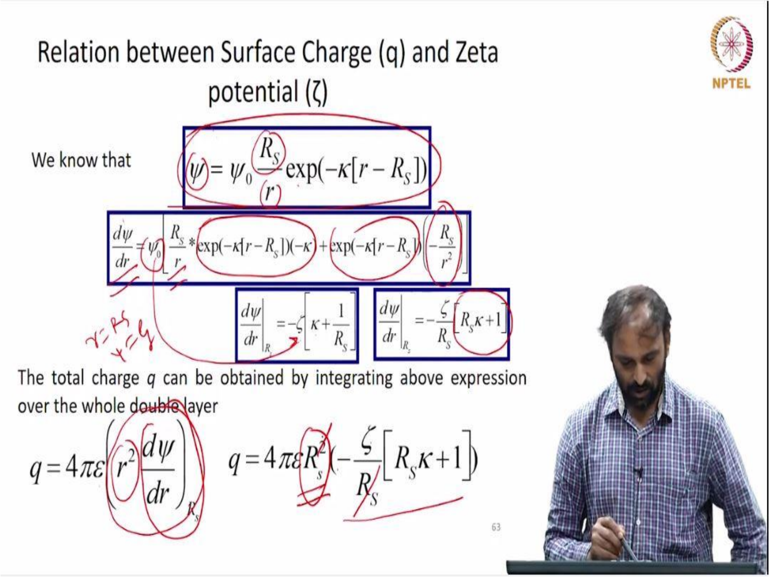

Relation between Surface Charge (q) and Zeta potential (ζ)

We know that

$$\boxed{\psi = \psi_0\frac{R_S}{r}\exp(-\kappa[r - R_S])}$$

$$\boxed{\frac{d\psi}{dr} = \psi_0\left[\frac{R_S}{r} * \exp(-\kappa[r - R_S])(-\kappa) + \exp(-\kappa[r - R_S])\left(-\frac{R_S}{r^2}\right)\right]}$$

$r = R_S$

$\psi = \zeta$

$$\boxed{\left.\frac{d\psi}{dr}\right|_{R_s} = -\zeta\left[\kappa + \frac{1}{R_S}\right]} \quad \boxed{\left.\frac{d\psi}{dr}\right|_{R_s} = -\frac{\zeta}{R_S}\left[R_S\kappa + 1\right]}$$

The total charge q can be obtained by integrating above expression over the whole double layer

$$q = 4\pi\varepsilon\left(r^2\frac{d\psi}{dr}\right)_{R_s} \qquad q = 4\pi\varepsilon \cancel{R_s^2}\left(-\frac{\zeta}{\cancel{R_S}}\left[R_S\kappa + 1\right]\right)$$

And we know how the potential varies with R for a spherical particle system. So, therefore, I know that psi is equal to psi naught Rs divided by r exponent of minus kappa times r minus Rs, I can differentiate this with respect to dr. Therefore, I have the constant term the first term multiplied by the differential of the second term plus the second term multiplied by the differentiated the first term. So, therefore, d psi / dr at Rs essentially becomes minus zeta that is because at r is equal to Rs psi becomes zeta.

Therefore, I have a zeta there and times a kappa r + 1 divided by Rs and I can take Rs common essentially if I take one over Rs common therefore, I end up with my d psi / dr at Rs = minus zeta divided by Rs times kappa times Rs + 1. So therefore, q becomes 4 pi eta times Rs d psi / dr I can substitute for r square into d psi / dr. Now, therefore, this is so, d psi / dr you know at Rs so, therefore, Rs r square at Rs is Rs square capital Rs square and instead of d psi / dr at Rs I have minus zeta divided by Rs into k kappa times Rs + 1 this and one term gets cancelled.

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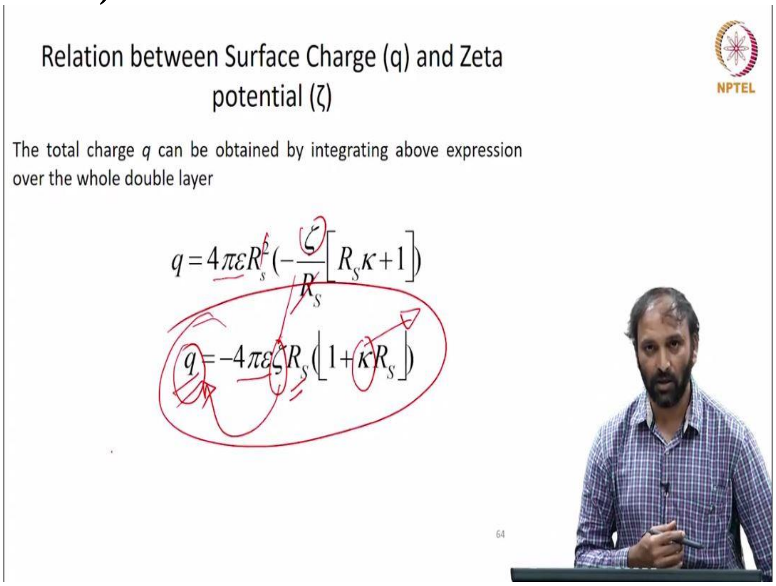

Relation between Surface Charge (q) and Zeta potential (ζ)

The total charge q can be obtained by integrating above expression over the whole double layer

$$q = 4\pi\varepsilon R_s^2 \left(-\frac{\zeta}{R_S}\left[R_S\kappa+1\right]\right)$$

$$q = -4\pi\varepsilon\zeta R_S\left(\left[1+\kappa R_S\right]\right)$$

So, therefore, what we have is this and this gets cancelled therefore, there is 4 pi epsilon into zeta times Rs times 1 plus kappa times Rs therefore, so there this is the relation between the charge q on the particle surface and the zeta potential the size of the particle and the concentration of the electrolyte that you have in the solution which is which determines what does the kappa values. So now, once we have a way to relate zeta potential to q one can compare the q that is obtained by other methods.

And see what is the one to one correlation is it a one to one correlation or other effects that are neglected in one method or the other, you know can be inferred from such a treatment.

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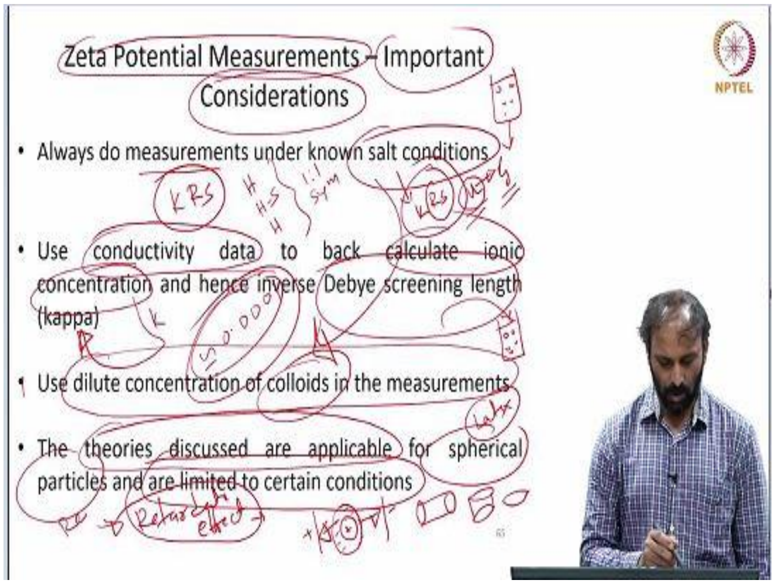

Zeta Potential Measurements – Important Considerations

- Always do measurements under known salt conditions
- Use conductivity data to back calculate ionic concentration and hence inverse Debye screening length (kappa)
- Use dilute concentration of colloids in the measurements
- The theories discussed are applicable for spherical particles and are limited to certain conditions

So I would like to talk a little bit about zeta potential measurements and some important considerations that one should worry about what we should always do zeta potential measurements under a known salt conditions that is because, you can prepare a colloidal dispersion and then you know just plug the sample into one of the instrument that measures that are used for measuring mobility.

So, you may be able to get the value of mobility from the instrument however, to choose an appropriate method to convert the electrophoretic mobility to zeta potential, we know that kappa times Rs is a important factor. So, whether you use a Huckel limit or Helmholtz-Smoluchowski or Henry solution or we are working with 1 is to 1 electrolyte or symmetric electrolyte in general or asymmetrical electrolyte.

So, depending upon you know the conditions that are being used or the solution conditions under which the mobility measurements have been made, one should be able to choose an appropriate relation between the mobility and zeta potential. So, therefore, knowing the salt concentration is of utmost importance, because, once you know that I can get kappa and of course, I should have an idea about what is the size of the dimension of the particle.

And therefore, a combination of that is what should be used or what should be calculated in order to use an appropriate expression for converting mobility to zeta potential. Suppose, if there are if you do not know the salt concentration, so, one of the method could be that you could measure the conductivity of the dispersion and, because we know that the conductivity can be related to the ionic concentration of the particle and again from the ionic concentration I can calculate what is kappa.

So, therefore, if the salt concentrations are not known, one of the nice method could be you measure the conductivity of the solution and then appropriately convert the conductivity data to any concentration and then use ionic concentration data to back calculate what is the inverse Debye screening length that has kappa value and the third consideration is that always use a dilute concentration of colloids and rule of thumb would be that if you take the dispersion of particles in a fluid.

For example, if one is working with say latex particles that is say polystyrene particles we know that they these dispersions appear turbid so, therefore, you use such a low concentration that if you put a finger on the other side of the turbid that contains the solutions, you know your finger should be you know visible clearly. So, typical concentration that one uses would be of the order of you know 0.001 volume percentage or some concentration of that order.

So, therefore, and the reason why this is important is because at higher concentration, the collateral interactions would become important. So, because whatever theories that have been developed, they are applicable for conditions where the colloidal particle is assumed to move in isolation. Therefore, the presence of any other particle in the vicinity is going to affect the measurements therefore, carry out measurements at as dilute a concentration as possible.

And the last point is the theory that have been discussed how are applicable for spherical particles so far whatever we discussed and they are also applicable under certain limiting conditions. So, therefore, if one is interested look at particles of other shapes such as like say rod like particles or disk shaped particles or elliptical particles one has to look for appropriate theory there are there have been some developments in the field.

So, one should refer to the latest literature and then use an appropriate solution to calculate zeta potential from these measurements on also there are several issues that have been omitted in the development that we have discussed one is what is called as a retardation effect. So, what happens is that, when you have a charged particle that is set into motion by an electric field and we know that depending upon the charge of the particle is either going to move towards a negatively charged electrode or a positively charged electrode.

So, however, we should also know that there is going to be the counter ions in solution. So, when the particle moves in a particular direction, the ions that are present in the electrical double layer and therefore, the fluid around it will try and move in a opposite direction therefore, the motion of the particle is hindered that is, there is a retardation force that comes into picture because of these effects. And one has to be careful about incorporating those things, which have not been done in the present developments.

So, there are also what are called as relaxation effects and also the surface conductance effects which also become important under certain conditions. So, therefore, general theory that should be used should consist should contain all these important features inbuilt in those models however, for under specific conditions, so, whatever theory that we have developed, it can still be used to for a meaningful in a measurement of zeta potentials.

So just to conclude, so, what we have done in this particular module is that, we defined zeta potential and we talked about the important implications of zeta potential in different applications. Then, we discussed electro kinetic methods and more discussions have been centered around electrophoresis because it is one of the widely used technique for measuring zeta potential, then, we discussed the relationship between the mobility and zeta potential.

So, we started with talking about mobility of an isolated ion followed by the mobility of charged particles assuming that the charged particles can be treated as macro ions. And then, we developed a relation between the electrophoretic mobility and zeta potential in several cases, Huckel limit and Helmholtz-Smoluchowski limit as well as Henry's equation which is valid for the entire range of kappa times Rs value. And, we finally discussed about what are the important considerations one should think about when measuring zeta potential from any given technique.