Transcriber's Name: Prabhavathi

Environmental Soil Chemistry

Prof. Somsubhra Chakraborty

Agricultural and Food Engineering Department

Indian Institute of Technology-Kharagpur

Lecture-20

Soil Solution-Soil phase Equilibria and Sorption in Soils (Contd.)

Welcome friends to this last lecture of week 4 or module 4. And in this module we are we are talking about the soil solid solution equilibria as well as the soil sorption. So, in the last lecture, we started discussing about the Gouy-Chapman theory and Gouy-Chapman model of diffuse double layer. And we have started solving some numerical problems depending on the Gouy-Chapman theory.

And I have shown you how to calculate this, how to solve this problem. Here basically the problem is to plot the relationship between electrical potential at this, you know, electrical potential and distance from the surface x for four different, you know, distances, one is at 0 and then 5 into 10 to the power – 9, 1 into 10 to the power - 8 and 2 into 10 to the power - 8 meter, according to the Gouy-Chapman theory given all these different values of the different parameters.

And I showed you how we can calculate that, remember, first we have to calculate the reciprocal of the thickness that is K reciprocal of the thickness of the diffuse, diffuse double layer that that is K. So, we have first calculated the K and all the values were substituted and we got the value of K. And then for getting the thickness of the diffuse double layer, we we will basically take a reciprocal of K, so 1 by k which was we cal, which we calculated around 9.62 into 10 to the power - 9 meter.

Then to solve for different values of psi as a function of x. We basically use this equation of Gouy-Chapman diffuse double layer equation. And here in the right hand side, you know that Ze psi 0 and 4 kT all e - kx. So, all these values are known to us K is basically the reciprocal of the thickness which you have just calculated that is 1.04 into 10 to the power 8 per meter. So, we have put all these values in the right hand side and then we solve it.

Ultimately by solving these it will come at, you know, we will get this final form that is tan h of Z e psi by 4 kT equal to 0.75. So, if you take the inverse of tan then we get this Z e psi by 4 kT equal to 0.97. Now, from there we solve the psi by putting all the values rest of the values like Ze and K and T. So, all the values are known from there we are getting the value of 9.96 into 10 to the power - 2 joule per coulomb. So, similarly for all the distance of x we can calculate this psi.

And once we calculate this psi or surface put in or the potential then we can plot as a function of the x or distance from the surface. And then we can see that we are getting this in, you know, exponential decrease of potential as, you know, as postulated by Gouy and Chapman in their diffuse double layer model.

Now another problem is to compare the thickness of the double layer which is basically 1 by k, the reciprocal of K for 0.001 molar with that is mole per cubic decimeter. NaCl that is sodium chloride which you have just calculated in the previous example as well as we have to calculate 0.01 molar of sodium chloride and 0.001 molar of calcium chloride.

So, basically the, so basically the 1 by k for 0.001 mole per day cubic decimeter of sodium chloride was earlier found to be 9.62 into 10 to the power - 9 meter in the previous problem. So, we are calculating now for the second molar concentration of sodium chloride that is 0.01 molar. So, basically we have to use only one formula of k, so here we can put all the formulas and then we can all the parameter values.

And basically then from, from there we can get this value of k. Once we get the value of k then the the thickness of the diffuse double layer can be calculated by taking a reciprocal. Similarly for calcium chloride we are also including all the parameter values here. Here only the difference between these is basically the z and from there we can, you know, if we put these 0.001 molar for CaCl2 it will be just equal to that but, you know, when we when we when we use this formula and incorporate all the values only this z values will be changed.

So, basically we will get a value of 1.80 into 10 to the power 8 per meter. So, taking a reciprocal we will get 5.55 into 10 to the power - 9 meter. So, this basically problem basically in this problem we basically have to calculate the k using the formula where all the parameters are already given and it is basically the second part of the problem. So, in the first part of the problem we have already given the values of these Avogadro's number, Boltzmann coefficient, molar gas constant and all these values are given, e’s values are also given.

So, basically we have to put all these values and only the, you know, and then we have to calculate this for these 2 concentration of different 2 chemicals, one is NaCl another is CaCl2. So, this is how you solve these two problem. Now, let us discuss the diffuse double layer properties. Now, there are diffuse properties, I mean the type of the colloid that is either it is variable charge or constant charge basically affects the various double layer parameters including surface charge, surface potential and double layer thickness.

So, let us see one example, so in this example this is basically showing the variable charge surface and this example is from the constant charge, you know. So, this is for the permanent charge surface and this is for the variable charge surface. So, let us consider only this variable charge surface. So, we can see with a variable charge surface, the overall diffuse layer charge is increased at higher electrolyte concentration. So, basically when we are increasing the electrolyte concentration earlier it was n, now we are increasing the electrolyte concentration to n dash.

So, that is by diffuse, you know, when we are increasing the concentration of diffuse layer, it basically compress the thickness compress the diffuse layer. In other words what, you know, the diffuse charge is concentrated in a region closer to the surface when electrolyte is added and the total net diffuse charge that is C dash, A dash that is C dash, A dash and D dash which is the new surface charge is greater than the surface charge at the lower electrolyte concentration.

So, initially our electrolyte concentration was basically, you know, the lower the surface charge for lower electrolyte concentration was basically C, A and D. Now, by increasing the electrolyte concentration we are getting a surface charge of C dash, A dash and D dash, obviously this C dash, A dash and D dash is greater than the CAD. And the surface potential remains the same but one thing is clear.

That by increasing the electrolyte concentration, the 1 by k becomes less or the reciprocal of the thickness become less in the second condition. And as a result of that, the psi or surface potential decrease more rapidly with increasing distance. So, you can see in the second condition when you are increasing the electrolyte concentration, there is a steep decrease of potential with the increase in the distance however it is more steeper than that of the previous condition.

So, that basically says when you are increasing the ionic concentration in a diffuse double layer, it compresses the thickness of the diffuse double layer in case a variable sur surface variable charge surface. So, so in a variable charge surface charge system the surface potential is dependent on the activity of the PDI that is PDI basically is a short form of potential determining ions that is H + and OH - in the solution phase.

So, the psi 0 it is not affected by the addition of an indifferent electrolyte solution. For example, sodium chloride which is an indifferent electrolyte. So, you know, that the sodium chloride is the electrolyte, you know, is the electrolyte where the electrolyte ions do not react non-electrostatically with the surface.

So, if the if the electrolyte solution does not contain PDI and if the activity or concentration of the PDI is not affected by the by the indifferent electrolyte, so basically then this psi 0 is also not affected. So, so the idea is for the, the gist of this slide is the psi 0 that is the potential is not affected by the addition of an indifferent electrolyte solution which does not interfere with the potential determining ions in cases variable charge surface just like the first picture.

Now in the variable charge system the surface charge which is basically denoted by this sigma v can be expressed in terms of this equation, ok. That is sigma v equal to 2 in 2 e kT by pi 1/2 multiplied by this multiplied by this sine h into Z e by 2kT into constant psi 0, so where sine h is the hyperbolic sign. So, in the PD if the PDI or potential determining ions which we have already seen in the last slide that is H + and OH - the constant surface potential is related to H + by the Nernst equation.

So by the Nernst equation we can see that psi 0 is related to the H + and H + 0 using this formula. And if we simplify this formula we will get this equation

2, now in this equation 2 and 1 basically z, you know, basically denotes the valence of the PDI potential determining ions, H + is the activity of the H + ion, H0 + is the hydrogen ion activity when psi equal to 0 and pzc is the point of 0 charge.

We have already discussed what is point of zero charge it is basically the pH at which is the summation of both constant charge or the variable charge becomes 0. So, that is called point of zero charge, another name of this point of zero charge is isolative point. Now, if we substitute these value of psi 0 from 2 to equation 1, we will get this equation the this is called equation 3. So, this 3 equals, you know, this is the third equation which you get for the surface charge of a variable charge system.

So, one thing is clear that the surface charge or psi, you know, or sigma v is affected by the valance, dielectric constant, temperature and then electrolyte concentration pH of the bulk solution and the, you know, zero point charge of the surface. There are several ways through which the surface charge can be manipulated in variably charged field soil. For example, CEC could be increased by lowering the, you know, lowering this pzc and by increasing the pH, how?

So, if we increase the pH obviously then in the variable charge surface there will be different, there will be generation of negative charge as we have already seen previously. So, if we increase the pH there will be generation of the negative charge which in turn increase the cation exchange capacity. So, cation exchange capacity can be increased by increasing the pH and that in turns lowers the pzc.

Because when we are increasing the pH the negative charges increasing to sub to neutralize that negative charge the z pzc has to be decreased. So, that that that, you know, you know, a total electro neutrality can be achieved. So, this could be done by adding an anion that would be adsorbed into the surface and impart more negative charge. For example, if we add if for example phosphate ion which basically adsorb to the surface and phosphate is negatively charge.

So, when the negatively charge phosphate ion gets adsorbed into the surface that will increase the total negative charge and as a result the cation will be more attracted, so cation exchange capacity will be increased. And so, this is how we can manipulate the, you know, the surface charge in a variable charge surface.

Now, adding phosphate to an oxisol results in the pzc decreasing with a concomitant increase in net negative charge. Obviously, as I have told you that in this condition, you know, you know, when, you know, here one example is given. When when we increase the phosphate concentration in an oxisol, oxisol is basically composed of either kaolinite as well as iron and aluminum oxide which has huge amount of variable charge.

So, this variable charge surface will attract these negatively charge phosphate in the and these basically increase the cation exchange capacity. So, the CEC of a soil containing variably charge soil components increases pH increases as we have seen. Now, lining the soil would increase the pH and the CEC if we if we increase the lime, you know, if if if we put lime that is calcium carbonate that would increase the soil pH and the CEC.

However it is difficult to raise the pH of a variable charge soil above 6.5. So, generally in case of any type of soil when we apply lime it basically increase the pH and CEC because calcium because of the presence of the calcium carbonate. However, in a variable charge surface when you are adding the lime and, you know, when the when the pH of the variable charge surface is above 6.5 particularly, you know, if the soil has a high buffering capacity along with the high surface, you know, high surface area.

So, it is difficult to raise the pH in that condition why, because the hydroxyl ion which is produced from the hydrolysis of carbonate when calcium carbonate dehydrated. So, basically when we add the calcium carbonate or lime into the soil, that get hydrolyzed and this hydroxyl ion which is produced from the hydrolysis of the carbonates basically it is the pH. However in a variably charged system containing hydroxylated surface, these H + ion which neutralize the OH + ion is released.

So, basically although the production of OH - ion can increase the pH, the H + ion or proton which are present in the variable charge surface can neutralize this hydroxyl ions. And as a result of that, there is a significant resistant to pH change or buffering. In other words, let me tell you again when we add the calcium carbonate in a particular soil it basically increases the pH as well as the cation exchange as well as the cation exchange capacity.

Because when you add this calcium carbonate it basically, you know, it produces the hydroxyl ion as a result of calc, you know, hydrolysis of the carbonates. However these hydro hydroxyl ion get neutralized by the protons which are present in the variable charge surface. So, as a result there is a development of a buffering capacity and as a result the increase in the pH is very slow in this variable charge surface.

Now with a constant surface charge mineral like vermiculite, you know, in the vermiculite, the total net surface charge or CED is not affected by higher electrolyte concentration or n dash. But 1 by k that is basically the reciprocal of the or, you know, reciprocal of k or in other words 1 by k is basically the the thickness of the DC diffuse double layer is lower and that psi 0 decreases.

So, you can see in this picture, right picture which is basically showing a constant, you know, surface charge mineral like vermiculite. It, this is the first condition and in the second condition when we are applying more electrolyte there is no significant change in the total surface charge. So, you can see this is the CAD which was previously surface charge and the neck and after adding after adding the more electrolyte, we are getting C dash, A dash and D dash however we do not see any significant changes between these two.

However you can see there is a slight decrease in the distance from the surface and as a result of that the slope is the slope of decrease of surf potential along with the distance from the surface is higher in case of second condition than that of first condition. So, this is the this is the this is the scenario which we can see in case of constant surf surface charge like vermiculite where most of the surface charge are due to the permanent charge or isomorphous substitution

So, let us consider the diffuse double layer properties, now Gouy-Chapman model of the electrical double layer can be used to predict the effect of electrolytes valence on the colloidal stability. So, here you can see 2 different solution the right solution is basically the stable suspension. However when the soil get, you know, soil shows flocculation we will see this type of condition where the soil will settle down or the all the particles will settle down, so this is called a flocculating flocculation this is called the flocculation.

And the right one is the stable suspension where all the all the soil particles are dispersed. So the valence of the electrolytes significantly affects the stability of the flocculation status of the suspension. For example, if we add AlCl3 which is more effective in flocculation than sodium chloride, then the flocculation will be happen. So, if this is a sodium chloride solution if we add AlCl3 in this solution, we will see the flocculation of the soil particles.

At this can be governed by Schulze-Hardy rule, what Schulze-Hardy rule basically says. The Schulze-Hardy rule basically says the coagulative power of a salt is determined by the very valency of one of the ions and the prepotent ion ion either the negative or the positive ion according to whether the colloidal particles move down or up the potential gradient and the coagulating ion is always, you know, coagulating ion is always of the opposite electrical sign to the particles.

So, basically if we simplify this statement we will see that in other words flocculation is mainly determined by the valency of the ion in the electrolyte that is, you know, that is of opposite charge to the surface. So, obviously the flocculating ion will be always the opposite sign to the charge surface, so it is a charge. If the charge is negative in the surface, the flocculating ion has to be positive.

So, with a negatively charged surface the valency of a cation in the electrolyte is important. Thus the higher the valency the greater is the flocculating power of the electrolyte and hence lower the electrolyte concentration needed to Claus cause this flocculation. So, more valency of the cation then lower amount of cation needed to flocculate the soil particles.

So, following concentration ranges are needed to cause the flocculation of the suspension. In case monovalent ion, we can get the flocculation from a concentration of the monovalent ion varying from 250 25 to 150 millimole per cubic decimeter. In case of divalent ion, it is varies from 0.5 to 2, in case of trivalent ion it is 0.01 to 0.1 millimole per cubic decimeter.

And the flocculating power of the group 1 cation in the periodic table of the negative suspension decreases slightly in the order where cesium shows the highest flocculating power and lithium shows the lowest flocculating power. Now, the third one is called the Stern theory, Stern 1924 modified the Gouy-Chapman model as follows. So, basically in the Stern theory they say that the first layer of the ion that is called a Stern layer if you can see in this picture the the first layer of the ion is called the Stern layer, so this is called the Stern layer.

And it is not immediately at the surface but a distance away from it just like the Helmholtz layer. And the counter ion charge is separated from the surface charge by a layer of thickness, delta. So, this is this is the, this is the this is the this is the separation distance between the counter ion. So, for example positive cat cations are are separated from the negatively charge surface with a distance of delta. In which there is no charge exists and model assumes that the charge that exists at the surface, that is sigma, is balanced by the charge in the solution which is distributed between the Stern layer, so this is called the Stern layer.

And this is the and at the junction of the Stern layer thus the surface potential is sigma and rest of the cations are diffused into the diffuse or Gouy layer, so here the the the the the charge is sigma 2. So, basically we can see the total surface charge can be can be balanced by the summation of the sigma 1 and sigma 2, where sigma 1 is the charge at the Stern layer and sigma 2 is the charge at the diffuse Gouy layer.

So, basically the total surface charge sigma in Coulomb per square meter is basically summation of these two sigma 1 and sigma 2 where sigma 1 is the Stern layer charge in Coulomb per square meter and sigma 2 is the diffuse layer charge in Coulomb per square meter. So, the charge in the Stern layer then can be expressed within using this equation where these N i is basically the number of available sites per square meter for adsorption.

M is basically the molecular weight of the solvent in gram per gram per mole, W is basically solvent density, this n is basically the electrolyte concentration in in ions. And this psi delta is basically the Stern potential and the psi is is is is the specific adsorption potential in the Stern layer in joule.

So, the charge in the diffuse layer layer is given by the Gouy-Chapman theory except the reference is now the Stern potential instead of the surface potential.

So, we can get this the Gouy- chap according to the Gouy-Chapman theory using the Gouy-Chapman theory in the diffuse layer this charge can be expressed using this equation. So, this equation 2 and 3 basically denotes sigma 1 and sigma 2 are valid for both variable charge surface as well as constant charge surface.

So, Stern model basically considered the distance closest to the, you know, distance of closest approach of a counter ion to the charge surface is is limited by the size of the ions. So, with the with this model the addition of electrolyte results in the comp, you know, is the compression of the diffuse part of the double layer and in a shift of the counter ions from the diffuse layer to the Stern layer hence leads to decrease of the Stern potential.

You know, when we add more electrolyte concentration obviously there will be further decrease of the diffuse layer thickness. And the counter ions will basically, you know, the counter ions will compress the diffuse part of the double layer and as a result there will be shift of the counter ions from the diffuse layer to the stern layer ultimately to decrease the Stern layer potential.

So, this is basically Stern double layer model, one thing is clear it is basically combination of Helmholtz layer as well as the Gouy-Chapman layer. In case of Helmholtz layer it was a basically a, you know, the counter ones are are basically arrange themselves in a specific distance from the surface. However, in the diffuse layer it was diffusing away with an increase in the distance. So, basically Stern double layer model shows the combination of both Helmholtz layer as well as Gouy-Chapman layer.

So, basically Stern model can be considered as a combination of Helmholtz layer as well as Gouy-Chapman layer. Now, this is again this Stern, you know, this is a Stern double layer where there is a linear decrease in the potential in the first layer or the stern layer and then there is a diffuse, you know, there is a there is an exponential decrease in the diffuse double layer. So, this is the graphical representation of the Stern layer and this shows basically the difference between the Stern layer, Helmholtz layer and the Gouy-Chapman layer.

Now thickness of the diffuse double layer with increase in the distance ion diffuses away and we know when it is another thumb rule is then equivalent electrolyte concentration the monovalent cations in exchange positions is thicker diffuse double layer than that of divalent ions. So, monovalent ions will produce the thicker diffuse double layer than the divalent ion then the trivalent ion because monovalent ions the hydrated so, you know, that the size of the hydrated monovalent ions is higher than that of divalent ions which is further higher than that of trivalent ion.

So, obviously depends on the radius of the hydrated or in other words it depends on the hydrated radius of the ions or counter ions. So, obviously the thickness of the diffuse double layer is more in case of monovalent ions. So, electrical double layer and clay particles we know that a large, you know, the clays are negatively charged. So, when these negatively charged clay particles comes very close to each other approach to each other there is a repulsion between the particle occur because of the outer parts of the double layers have the same type of charge which is positive.

So, basically we know in case of in case of negatively charged colloid, in case of negatively charged clay surface there is a predominance of positively charged counter ions in the, just adjacent to the surface. So, when two clay particles come together there will be a repulsion between there because of the positive charge of the counter ion. Now because of this approach there will be a rep, you know, in a diffusion counter ion atmosphere of the two particles interfere with each other.

Now, amount of work to bring the changes is called the repulsive energy. One thing is clear from this figure that as we are increasing the inter particle distance obviously the double layer repulsive forces decreases exponentially. So, more close these two particles there will be more repulsion when they are further apart from each other, then the repulsive force we will further go down. The range and effectiveness of the repulsive potential depends on the thickness of the double layer. The repulsive force decreases usually exponentially with increasing distance between the particles.

Now, opposite to the repulsive force there is also inter particle attractive force we call it Vander Waal force. So, this is basically opposite to the repulsive force as you can see at these inter when the inter particle distance is greater than 20 angstroms, these repulsive forces are dominant. However the when the inter particle distance are less than 20 angstrom this, you know, this inter particle attractive force or Vander waal forces are dominant.

You can see also when the inter particle distances are going down, the Vander waal force is also going in going to increase. So, basically this repulsion will dominate at low electrolyte concentration, the clay particles are shielded by relatively thick double layer and decreasing the possibility of mutual approach at high electrolyte concentration. The chance of close approach of the, you know, approach are made possible by compression of the double layer.

In this condition Vander Waal's attraction may overcome the repulsive force and coagulation of the flocculation or colloid colloidal particles rapidly. So, Vander waal inter particle, you know, app inter particle attractive force is responsible for coagulation of the particle.

Another part another another important aspect is called the zeta potential. Now, if we consider this is a negatively charged colloid surface and this is the stern layer which is just adjacent to the just adjacent to the negatively charged colloids. And after that we will see some more positively charged counter ions and a water hull surrounding these positively charge counter ions.

After that you will see the diffuse layer where these ions are positive charge ions are diffused. Now this junction between these water hull surrounding the stern layer and others adjacent positively charged counter ions is called the slipping plane. And the potential, electrical potential one diff which is generated at this slipping plane is known as zeta potential, it is very very important.

Now zeta potential also decreases with high electrolyte concentration and the valency of ions. If you are increasing if we if we if we apply the trivalent cations, then the thickness of the diffuse double layer will decrease and as a result the zeta potential also will decrease. Lower the zeta potential remember if the zeta potential is below a certain critical limit, that will increase the flocculation. And if the zeta potential is increased then the solid, you know, the particles will be in suspension and creating a stable solution and prohibiting the natural tendency to aggregate aggregate. And prohibiting the natural tendency of aggregation is a very problematic for soil because that would not help in soil aggregation which is required for the plant growth.

So, another important aspect is sorption of metal ions, pH dependent sorption of metal ions. As you can see in this graph, it is pH dependent and characterized by narrow pH range where the sorption increases to nearly 100%. It is dependent on different aspects like sorptive concentration, pH, surface coverage and type of adsorbent. And general order of selectivity is again cesium is the lowest and lithium is the highest. Because lithium has the lowest size of the hydrated radius whereas the lithium has the highest size of the hydrated radius.

So, these are different selectivity sequence for the alkali metal cations and various hydro for various hydrous oxide hydrous metal oxides. These are the some selectivity sequences. Sorption of anions also occur, for example the anions nitrate and chloride and then ClO4 are sorbed as outer sphere complexes and sorbed on the surface that exhibit the positive charge. And sorption is very much sensitive to ionic strength in case of sorption of anions.

Now surface precip precipitation as the amount of metal cations or anions at sorbed on the surface increases, sorption can proceed from molecular adsorption to surface precipitation which is a 3 dimensional phase. And so in this next slide you can see in the first it is basically illustration of the metal ion sorption reaction on a particular hydroxide. So, here you can see at low surface coverage isolated side bonding adsorption is the dominant sorption mechanism and the second is the increased metal loading metal hydroxide nucleation begins. So, basically the nucleation begins, so the phase formation starts here.

And with the further increase of metal loadings, further loadings it basically results in the surface precipitation, you can see here and the surface clusters. So, this is how the basically the surface precipitation of different metals occur on different hydroxides.

So, this is the last slide that is called the speciation of metal contaminated soil. So, the ability to speciate metal contaminated soil is critical in developing viable and cost effective remediation strategies and in predicting mobility and bioavailability of the metals. Now remember that metals in contaminated soils can be found in mineral and sorbed phases. And generally we use different types of advanced techniques like x ray diffraction, thermo gravimetric analysis or thermal gravimetric analysis or TGA, X ray photoelectron, spectroscopy or XPS.

For to characterize to characterize these metals in the contaminated soil which is very important. So, guys these are the references of this chapter, I hope that you have gathered some, you know, some info, you know, some useful knowledges which will be useful for your research purpose as well as for understanding several critical soil chemical processes. I know it is not possible to cover all the aspects in details within the timeframe but if you find, you know, at least you have seen the logical flow of different aspects.

And, you know, there there and you have a brief idea of these terms which are related to these soil solution sorption as well as adsorption properties. I hope that you have gathered some knowledge and if you have further any question just feel free to email me I will be more than happy to answer your queries, thank you very much.