Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 08

Lecture 37 | Ion Exchange Adsorbents

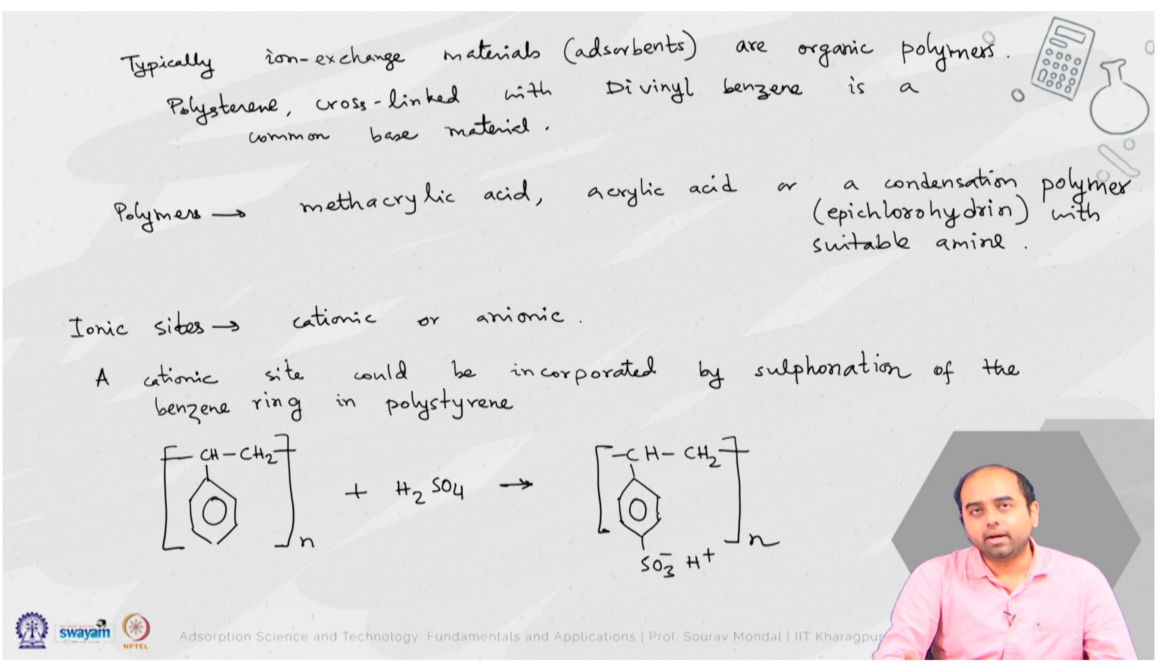
Hello everyone, in this class we are going to talk about in this ion exchange resins mostly what are the different types chemically what does they represents what is water swelling and some typical values of the ion exchange selectivities for these different kinds of cation and anion exchange resins. So, commercially these ion exchange regimes are actually derived from organic polymers. So, the most common organic polymers that are used are polystyrene with some quantity of you know divinyl benzene that is used as a base material. So, a polymer or polystyrene with 10 percent divinyl benzene is a very common you know this resin that is generally used. The polymers are generally so we will just write down. So, this typically ion exchange materials or these adsorbents are organic polymers.

So, polystyrene cross linked with this divinyl benzene is a common base material. There are also other types for example, you know prepared from polymers, prepared from methacrylic. So, polymethamethacrylate PMMA methacrylic acid or normally acrylic acid or a condensation polymer, condensation polymer of epichlorohydrin with suitable amine are also used instead of polystyrene. As you know this major application of this ion exchange process is in water softening that is what something I already discussed in the last class.

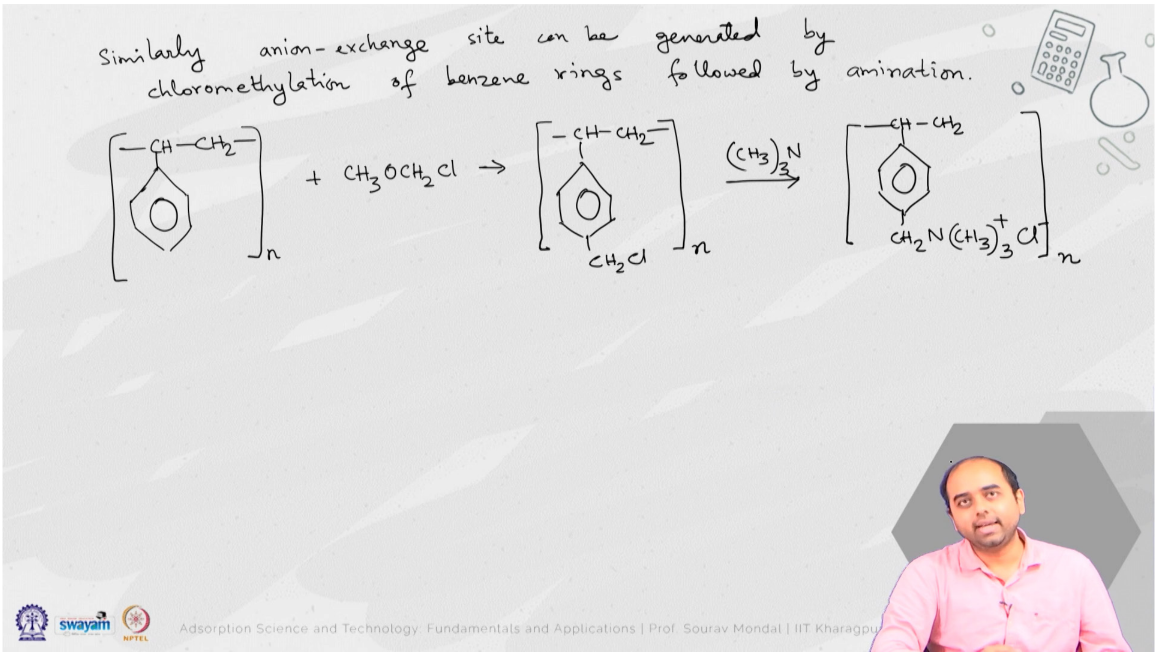
It is also used for demineralization or producing deionized water which have a water resistivity close to 18 you know this, mega ohms per meter. So, this is typically the application to produce extremely high quality of you know water using this process of ion exchange. But they are also used you know you know for water purification for catalysis examples for separation or removal of metal ions for treatment of boiler feed waters, but primarily the application or the application science is based on demineralization or you know this softening of this water. The ionic sites in this regime in this regime could be I mean cationic or anionic in nature even though cationic ions are very more popular than the ionic, but nevertheless ionic ions are also popular. So, these sites are generally incorporated within this polymer base to produce a suitable synthetic ion exchange resin.

So, it could be like so for example, for cationic site could be incorporated by sulfonation sulfonation or you know of the benzene ring in polystyrene. So, for example, polystyrene. So, this is the monomer unit of the polystyrene. So, this is the polymer and if you sulfonate it with sulfuric acid you are going to land up with with a sulfonated which on hydrolysis in water will produce you know this cationic site where this sodium or calcium ions can be exchanged. So, this is a strong acid cationic polymer or a cationic material.

Similarly, the anion exchange site can be generated by chloromethylation of benzene rings followed by amination. So typical example could be once again this polystyrene or the styrene molecule so where it is chloromethylation is performed. So this would give this substitution at the parasites, chlorination at the parasites. This is trimethylamine one would be getting substitution here at the parasite in in the fluorinated part because of this amine and this tetra carbon atom, at which on hydrolysis would produce a strong base anion exchange regime. Now typically the fixed charges for the case of cationic resins which could be produced here as an example I have shown for the case of sulfonation it could be like other groups for example COO⁻ acetic groups or even nitrate groups present there.

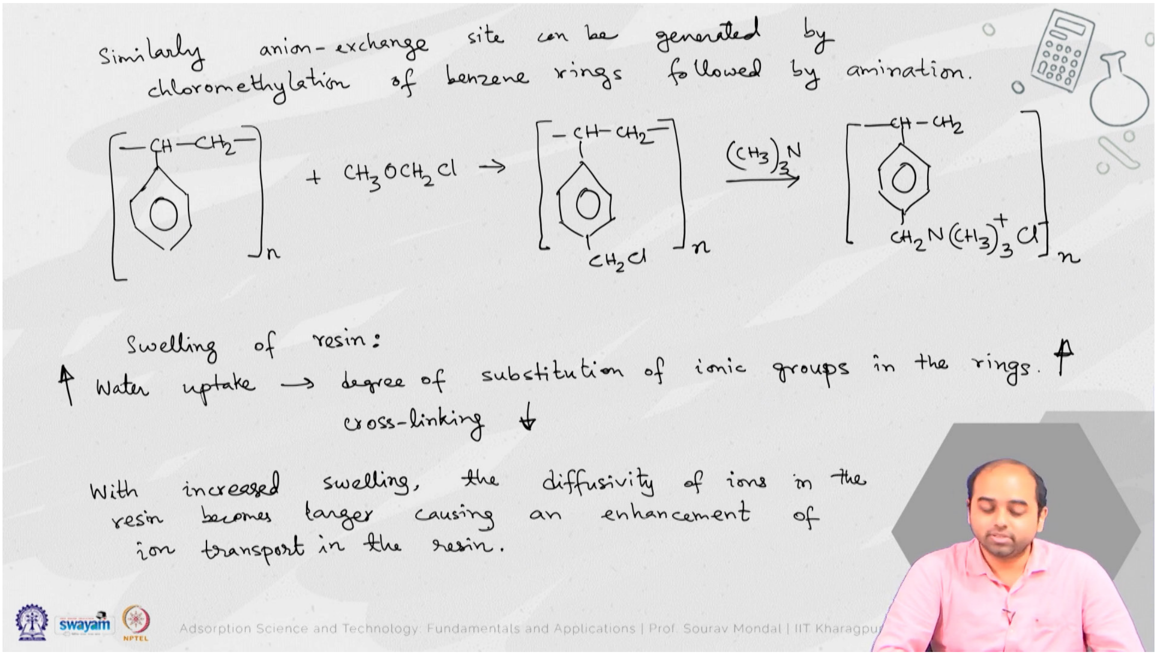


Similarly in the case of the cationic. So, in the case of the anionic sites this would be one of these instead of amination. So, amine is the most popular one any other such you know anionic sites is generally not so very popular. Now, this coming to the aspect of swelling of the ion exchange I want to you know focus on this aspect of swelling of this resins this is very important. So, the swelling is the amount this water which is up taken by this resins during the process of ion exchange.



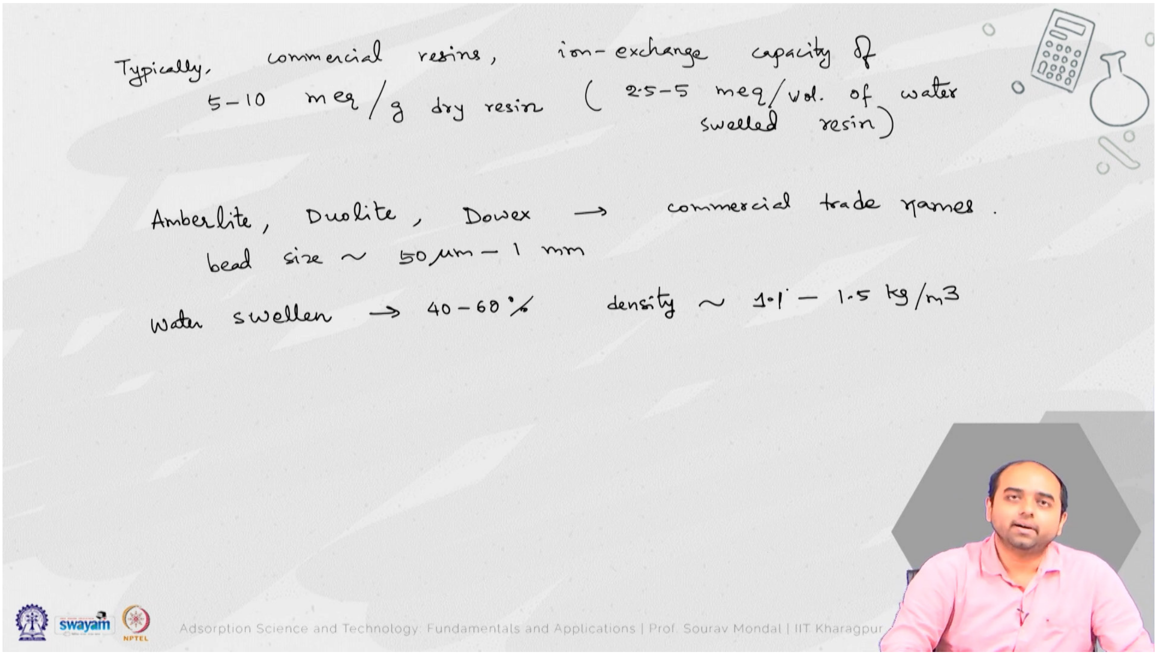
So, depending on the degree of substitution of the ionic rings or the ionic groups in the rings, the degree of you know increase or decrease of cross linking affects the amount of the water uptake. So, the water uptake amount by the resin is affected by the degree of substitution of ionic groups in the rings. So, the water uptake increases with increase in the degree of substitution, but decreases with increase in the cross linking. So, the water uptake actually is inversely related to the degree of cross linking, but directly related to the degree of substitution. So, more is the substitution more would be the water uptake, but if the cross linking is more then in that case water uptake would be reducing.

So, thus generally the water uptake because you cannot you know control the degree of substitution because that will reduce the efficiency of the you know ion exchange capacity of the resin. So, naturally what is done is that the degree of you know cross linking is actually you know controlled so as to reduce the water uptake capacity as much as possible. So, the more the this cross linking is the more is the force to prevent this swelling or this water uptake. So, what happens with this water uptake is that so with increased swelling. So with increased swelling the diffusivity of ions in the resin becomes larger or increases I would say causing an enhancement of ion transport in the resin.



So, this is something which is not very desirable because then diffusion or mass transfer effects starts to dominate the reaction equilibrium. So, swelling is something which is not something very desirable and that is what something one needs to reduce. Moreover increase in the swelling increase reduces the volume concentration of the total you know capacity of the resin which again reduces the capacity. So, the ion exchange resin capacity given. So, this generally or typically I would say that most ion exchange typically commercial resins has an ion exchange capacity capacity of 5 to 10 you know milli-equivalents per gram of dry resin.

So, which is equivalent to almost 2.5 to 5 milli-equivalent per volume of water swelled water swelled resins assuming that the resin has increased its volume to double of its size or the density of the you know this resin has reduced from the dry basis to the wet basis. In that case the volume capacity or the milliequivalent capacity in terms of volume becomes a very significant instead of the mass concentration. Generally the you know the common commercial you know trade names are this very important to also you know be aware of these names Amberlite then you have Duolite all these are polymers regimes DOWEX. So, these are commercial trade names they are generally present in the form of tiny beads ranging from almost 50 micron to 1 millimeter and size.

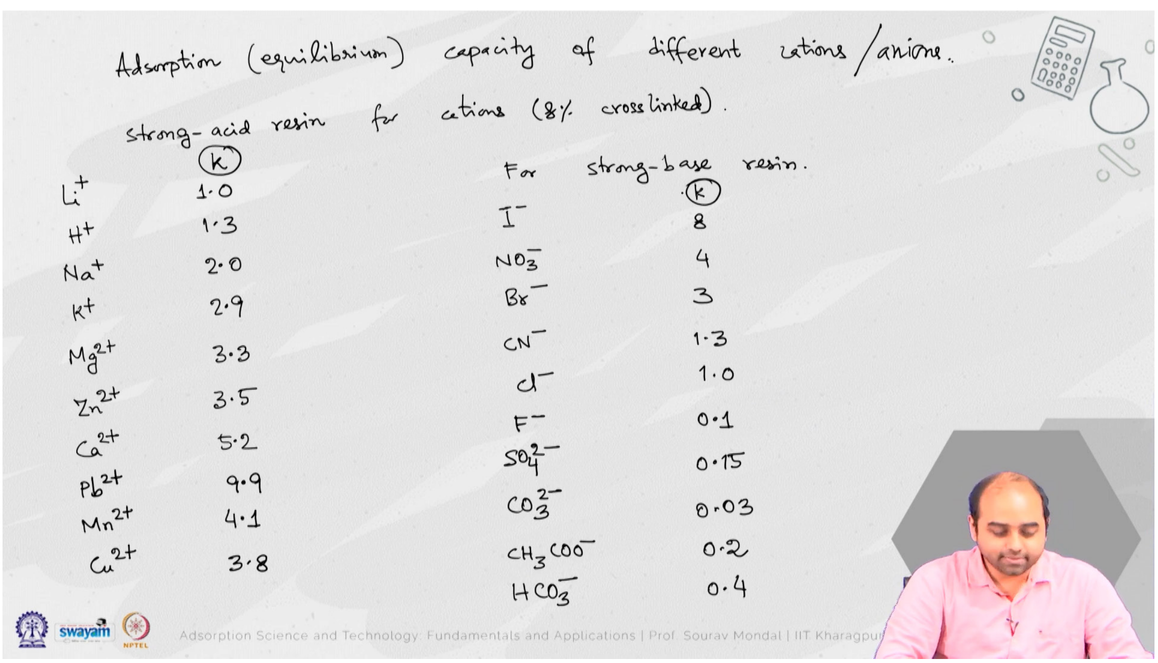


So, this bead size of this resin is generally in the range of 50 micrometer to all the way up to 1 millimeter and this water swollen beads or this water swelling is around 40 to 60 percent and its density change is in the range of 1.1 to 1.5 kg per Now also swelling depends on the type of the counter ions, but it is mostly the degree of cross linking and the nature of the substitution or the amount of the substitution that affects it. I will just list down few of the you know adsorption sorry or this capacity of different of classical you know these ion exchange regimes is capacity adsorption or this equilibrium Capacity of different cations and anions. So this considering a strong acid regime for cations which is like 8% cross-linked.

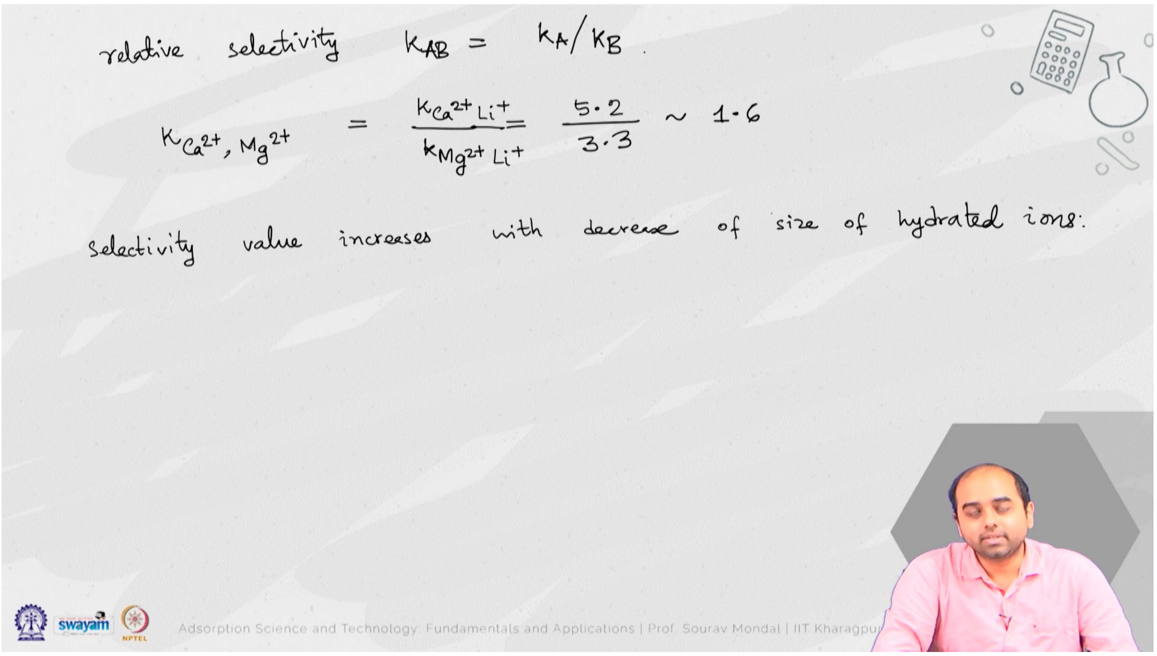
So this selectivity constants k for different ions as you can see here. I mean this information for different ions is actually given by the manufacturer and for different types of ion one can find out you know from the database or from the manufacturer specification that what is the typical values of these k higher is the value larger is the selectivity or the capacity of that ion towards that particular cation or the anion. I will write down some of the popular ones. Generally, divalent ions have larger constants.

I can write. Similarly, for you know strong base resins, you can write down the coefficients or the molar selectivity constants or the equilibrium constants cyanide, chloride, then fluoride it is very low sulfate, carbonate, so for divalent ions this acetate point two bicarbonate. So, for divalent ions we see that this equilibrium coefficient or the constant is very small in that case whereas in the case of this resin sorry in the case of cations as the valency increases the valency as well as molecular weight increases atomic weight increases for the cations. The capacity increases, but in the case of anions as the divalency increases the capacity parameter k decreases. So, typically the selectivity or this so this is for the case of for particular you know anion or cation. Now if one wants to work out what would be the you know this relative selectivity, which is actually important this relative for example, this K of B, AB.

So, that is like K A by K B the coefficient of for the case of you know these relative ion exchange capacities. So, for example, in the case of this calcium to magnesium that is. So you can work out that this is the ratio of is, divided by I mean I have written down for magnesium 3.3 so 5.2 sorry 5.2 by 3.3 gives. So, it may be understood that all of these coefficients are actually scaled with respect to the value of lithium because for the case of lithium as you see here the the coefficient or this selectivity parameter is 1. So, all of these values this potassium, magnesium, zinc that have listed down is scaled with respect to lithium. Similarly, in the case of anion it is scaled with respect to the chloride. Of course, this scaling can be done with respect to H plus here it can be done with respect to OH minus, but this is generally the standard convention in the industry to scale this with lithium and there with chloride.



So, the value of this calcium that we see here is actually based or scaled with respect to lithium. And for magnesium also this scaled with respect to lithium and those two values are used here to find out the relative capacity of this adsorbent or this equilibrium capacity of this adsorbent to remove calcium over magnesium is given as 1.6. So, this means it will preferentially remove calcium over magnesium in the ion exchange process. So, the selectivity value selectivity value actually increases with decrease of the size of hydrated ions since it requires less space to be accommodated in the resin matrix and also the stretching forces exerted on the polymer network could be less.



So, in this, this you know this analogy or this explanation also helps us to reason why the selectivity is different for different you know size of different ions even though their atomic weights are closely related. So, for example, between calcium and magnesium the difference in the atomic weight is not much. But it is the size of the hydrated ions or the hydrated sphere that actually determines the selectivity value in this case. So, I hope I could give a fair you know glimpse of the different types of you know adsorbents which are generally essentially the resins which are generally used in this ion exchange process. And in the next class and in the next few classes in this week we will talk about some problems and design of you know cyclic ion exchange phenomena.

Thank you. I hope all of you found this lecture useful.