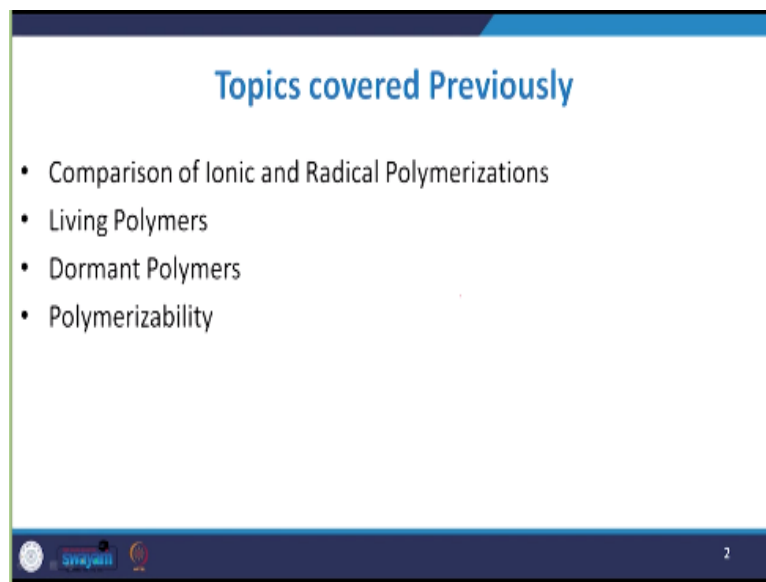


Polymer Reaction Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology – Roorkee

Lecture – 56
Ionic Polymerisation - I

Welcome to the new chapter of ionic polymerization. We have discussed about the radical polymerization and others. if you recall that previously, we discussed about the comparison between ionic and radical polymerization.

(Refer Slide Time: 00:37)



We had a discussion about the living polymers and dormant polymers. We asked about the polymerizability of the polymer process or monomers under the head of thermodynamic discussion.

(Refer Slide Time: 00:56)

Topics to be covered

- Classification of Various Ionic Species
- Effect of Solvent
- Ionophores and Ionogens, Ion Pairs, and Covalent Species
- Equilibria Between Free Ions and Ion-Pairs: Conductance Studies
- Heat and Entropy of Dissociation of Ion-Pairs
- Type of Ions
- Initiation and Propagation in Ionic Polymerization
- Effect of Solvating Agents

in this particular chapter, we will discuss about the classification of various ionic species. We will discuss about the effect of solvents because solvent play a vital role in the polymerization process especially in ionic polymerization. Then we will discuss about the ionophores and ionogens, ionic pairs, then we will discuss about the covalent species, which are again integral part of this ionic polymerization.

We have will we have discussion about the equilibria between the free ions and ionic pairs under the aegis of conductance studies. We will have a look of the heat and entropy dissociation of ionic pairs. Since we were discussing we are discussing about the ionic pairs, we will have a look about the different types of ion. Then, as a core part of ionic polymerization, we will discuss about the initiation and propagation step in ionic polymerization. We will have a discussion about the effect of solvating agents.

(Refer Slide Time: 02:07)

Classification of Various Ionic Species

- Matter in bulk is electrically neutral and each time it incorporates electrically charged species, i.e., ions or their aggregates, their opposite charges have to stabilize each other exactly.
- Conceptually, the easiest procedure converting electrically neutral molecules into electrically charged ions outcomes from electron ejection (ionization) triggered by means of photolysis or radiolysis
- It is triggered by the action of high-energy projectiles, e.g., γ rays, speedy electrons, etc.

So, let us start with the classification of various ionic species. usually the matter in bulk is electrically neutral and each time it incorporates electrically charged species that is ions or their aggregates, sometimes their opposite charges have to stabilize each other exactly. So, the conceptually the easiest procedure converting electrically neutral molecules into electrically charged ion this outcome from electron ejection, this is referred as ionisation.

And this is usually triggered by means of either photolysis or radiolysis. these two things are very much popular nowadays. it is the basic protocol behind it is that it is usually triggered by the action of high energy projectiles, maybe gamma rays, maybe x rays, maybe speedy electrons etcetera. So, these things look into so, the prerequisite is that you must have those high energy projectiles or you may have these high energy particles to carry out these processes.

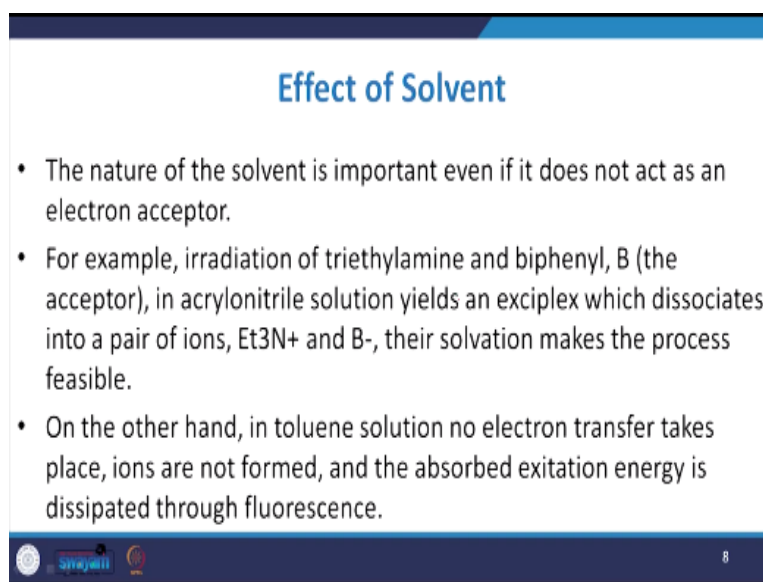
the ejected electrons they are usually captured subsequently, with the aid of some neutral molecules yielding then the negative ions by ionised molecule constitute the positive ions. So, a direct ionisation of a neutral molecule it may require a massive amount of energy and sometimes it is 9 eV/mol or even more. So, such quantities of energy are readily available in radiolysis and in photolysis induced with the aid of radiation of a very short wavelength.

Sometimes the vacuum UV, but no longer in the photolysis is induced by means of a near ultraviolet or visible light. the latter enable the electron transfer provided that some electron acceptors of sufficiently excessive electron affinity is reachable in the neighbourhood of radiation absorbing electron donors. Now let us have a brief look about the effect of solvent.

So, various species may act as electron acceptor. Even some solvent may play these roles. For example, if you are talking about the near UV irradiation of aromatic amines in water, they sometimes yield the respective radical cation and solvated electrons. So, water acts here as an electron acceptor. So, it all depends on the affinity and it all depends on the the the solvent on the solvation ability of the the reactant in question.

So, in the media however, in the media poorly solvating ions such as hydrocarbons of same irradiation of amine, they sometimes produce neutral radicals and not the ions.

(Refer Slide Time: 05:43)



The slide is titled "Effect of Solvent" in blue text. It contains three bullet points:

- The nature of the solvent is important even if it does not act as an electron acceptor.
- For example, irradiation of triethylamine and biphenyl, B (the acceptor), in acrylonitrile solution yields an exciplex which dissociates into a pair of ions, Et₃N⁺ and B⁻, their solvation makes the process feasible.
- On the other hand, in toluene solution no electron transfer takes place, ions are not formed, and the absorbed excitation energy is dissipated through fluorescence.

At the bottom of the slide, there are logos for "swinburn" and "UNSW" on the left, and the number "8" on the right.

the nature of solvent is important even if it does not act as an electron acceptor. So, for example, like irradiation of trimethylamine and biphenyl B is the acceptor in the acrylonitrile solution this yields an exciplex with the dissociation into the pairs of ion and sometimes referred as Et₃N⁺ and B⁻. Their solvation and makes the process feasible.

Sometimes, on the other hand, in the toluene is solution, the there is no electron transfer take place and ions are not formed. And absorbed x excitation energy is dissipated through the fluorescence. So, although mono photonic process resulting from irradiation by near ultraviolet or visible light does not provide enough energy for direct ionisation so, ions may be formed by the biphotonic process.

Let us take the example that the ionisation potential of benzene being 9.2 eV/mol is too high to allow the formation of its radical cation by mono photonic UV irradiation. So, this particular thing need to be addressed or this particular thing need to be keep in mind while selecting the

solvent a proper solvent. this however, the excitation energy of a benzene to the singlet let us say 4.84 eV/mol is followed by the intersystem crossing to the triplet.

And they are having the the energy domain of 3.7 eV/mol, this may lead to two ionisation caused by the consecutive absorption of two photons. So, the first yielding triplet while the second causing its ionisation. So, this is the sequential effect that how you can optimise the things based on the low energy concept. in counter of a species of a very low ionisation potential with another of very high electron affinity might lead to electron transfer.

And the formation of oppositely charged ion even in the absence of radiation, sometimes provided that the electro reaction takes place in a well solvating media. So, indeed the solvation of resulting ions contributes substantially to driving force of the process. So, the reaction of alkali metal with the aromatic hydrocarbons, it provide another example stressing the role of solvents in electron transfer process.

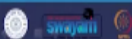
So, in well solvating media, this reaction yields aromatic radical ion anions and alkali cations. So, you may have enough opportunity or enough options to carry out these reactions. Alternatively, ions are formed on transfer of some charged moiety from one neutral molecule to another one and proton transfer from a covalent acid to a covalent base is the most common example of such a process.

Therefore, the anhydrous perchloric acid sometimes it reacts with the equimolar amount of water yielding the crystalline ionic salt sometimes referred as $\text{H}_3\text{O}^+ \text{ClO}_4^-$ in the non conducting solution of hydrogen bromide in sulphur dioxide.

(Refer Slide Time: 09:23)

Effect of Solvent H_3O^+ , ClO_4^- Br^-

- Alternatively, ions are formed on transfer of some charged moiety from one neutral molecule to another.
- Proton transfer from a covalent acid to a covalent base is the most common example of such a process.
- Thus anhydrous perchloric acid reacts with an equimolar amount of water yielding a crystalline ionic salt, H_3O^+ , ClO_4^- ; the nonconducting solution of HBr in sulfur dioxide becomes conducting on addition of an equimolar amount of water due to the formation of free H_3O^+ and Br^- ions.



12

This may become the conducting on addition of an equimolar amount of water that may be attributed to the formation of free H_3O^+ ions or Br^- ions.

(Refer Slide Time: 09:49)

Ionophores and Ionogens, Ion Pairs, and Covalent Species

- Ionophores can be called as “charge carriers or charge bearers”
- It is also known as ion complexers which was first used as anti-coccidial agents.
- Many solids are built up of neutral molecules cemented together by van der Waals forces, while others, known as ionic crystals, are composed of ions as their building blocks. The latter, referred as ionophores, dissociate quantitatively into free ions in media in which they are soluble.


13

Let us take about the ionophores and ionogens or ionic pairs or a covariant species. So these ionophores in the polymerization system, they can be called as the “charge carriers are charged bearers”. It is also known as ion ion complexes, which was first to use as the anti coccidial agents. So, many solids they are built up of neutral molecules cemented together by the Van der Waal forces and these forces are very weak forces.

So, so, when they are joined together by Van der Waal forces, while other known as ionic crystals, they are composed of ion as they are building blocks. So, these building blocks are later referred as the ionophores dissociate the quantitatively into the free ions in media in which

they are soluble. So, these ionophores are specific molecules that carry specific cations and facilitate their transport to through biological membranes.

So, while taking the application of all those things, we may consider this particular approach in our mind. So, they are the molecules that act as a membrane shuttles for the particular ion across the lipid membrane without the expenditure of energy. Let us have a look about the ionogens. the ionic molecules that react with the solvent, the force the forms are they are forming then the oppositely charged ions, they are classified as ionogens.

Let us take the example of dissociation of acetic acid in water. So, while we discussed about the the basic methodology, basic protocol of this ionophores and ionogens let us discuss about the generalised structure of those ionophores. these ionophores contain hydrophilic centres that binds to specific ions and a hydrophobic protein that interact with the lipid interior to the membrane.

So, most ionophores they adopt a cyclic ring formation by concentrating oxygen nitrogen functional group at the centre of their structure to associate with the cation. with the hydrophobic group in contact with the acyl group of the membrane the ionophore is able to dissolve and diffuse to the opposite side of the membrane so that they may become very selective in this nature.

Ionophores when we talk about the various spectrum of ionophores ionogens, then the things arises related to the the classification of ionophores. So, these can be classified either based on the mechanism of direction. again they are subdivided as mobile carrier ionophores, these bind to a particular ion and shield it charged from the hydrophobic environment of the membrane.

They form the lipid soluble complex with the cation which then diffuse across the membrane. Sometimes, by reversibility binding to the ion to form the lipid soluble complexes, which rapidly diffuses across the membrane. they catalyse the passive transfer of cation across the otherwise impermeable hydrophobic membrane. So, the processes become more and more selective. Usually when we carry out this particular thing, this is a three step process. One is that the complexation of ionophores with the ion. The second is the diffusion of the complex via the membrane interface to the other side of the membrane. And third one is the reverse complexation process.

Another aspect is the **channel forming ionophores**. these ionophores introduce a hydrophilic pore into the membrane around the specific cation to pass through without coming into contact with the hydrophobic initiator of the membrane.

So, this is again a very beautiful approach, so that the polymeric chain may not get into the dead zone. These are the channel forming ionophores that usually are having the larger molecules in nature. another route of classification is based on the chemical structure. So, one is that the poly ether ionophores that is the monensin or meduracin, then peptide ionophores they are some the biological polymers.

Then cyclo desipeptide that is the macrocyclic compound containing that tetrahydrofuran carboxylic acid residues linked together, then cryptates that is the synthetic bi and polycyclic multi dentate linked ligands for a variety of cations, then crown ethers. It create the electrochemical gradient resulting in changes in the the physiological state of cell structure like oxidative phosphophorylation, sometimes osmotic balance, then neurotransmission, then cell signalling, then harmones etcetera.

Let us talk about the ion pairs. some molecules which are basically not associated ions, when they present in a solution along with other molecule, they start acting as an ionic molecule.

(Refer Slide Time: 16:18)

The slide is titled "Ion Pairs" in blue text. In the top right corner, there is a handwritten chemical structure: $BF_3O(C_2H_5)_2$ with a red arrow pointing to $BF_3OC_2H_5^-$ and $C_2H_5^+$. The slide contains two bullet points:

- Some molecules which are basically not associated ions, when present in a solution along with other molecule, start acting as an ionic molecule.
- For example, the adduct $BF_3O(C_2H_5)_2$ is not an ion pair. It does not dissociate into $BF_3OC_2H_5^-$ anions and $C_2H_5^+$ cations, although it acts as if it were an ion-pair, e.g., it transfers the positively charged $C_2H_5^+$ moiety to vinyl ethers, and thus initiates their cationic polymerization.

At the bottom left of the slide, there are logos for "Sri Jayachandran" and "Sri Jayachandran". At the bottom right, the number "23" is visible.

So, let us take the example that adductor $BF_3O(C_2H_5)_2$ is not an ionic pair. It does not dissociate into $BF_3OC_2H_5^-$ anions and minus and $C_2H_5^+$ cations, although it acts as if it were on the ionic pair. e.g., it transfers the positively charged $C_2H_5^+$ moiety to vinyl ethers, and thus initiates their cationic polymerization.

Now in chemistry the tight ion pair concept usually introduced by Saul Winstein described that the interaction between a cation, anion and surrounding solvent molecules. Now in ordinary aqueous solution of inorganic salt and ion is completely solvated and shielded from the counter ion. In less polar solvent two ions can still be connected in some extent. Let us have a look about those tight or intimate contact ion pair.

There are no solvent molecules between their two ions. So, when we talk about the solvation so, if the solvation increases the ionic bonding decreases and a loose or a solvent shared ion pair results. The ion pair concept explains the stereochemistry in solvolysis.

(Refer Slide Time: 17:59)

Type of Ion Pairs

- In a tight or intimate or contact ion pair there are no solvent molecules between the two ions.
- When solvation increases, ionic bonding decreases and a loose or solvent-shared ion pair results. The ion pair concept explains stereochemistry in solvolysis.

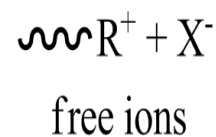
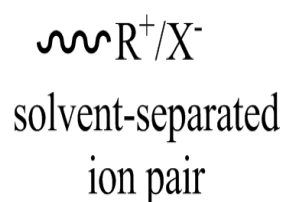
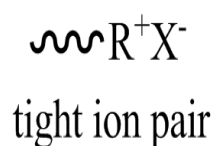
$\sim\text{RX}$
covalent

$\sim\text{R}^+\text{X}^-$
tight ion pair

$\sim\text{R}^+/\text{X}^-$
solvent-separated ion pair

$\sim\text{R}^+ + \text{X}^-$
free ions

25



And you see here we have this is the tight ion pair R plus X and then this is you see that the solvent separated ion pair and when this the solvent X is thrown, then it may become the free ions like R⁺ and X⁻ charged.

(Refer Slide Time: 18:18)

Type of Ion Pairs

- An ion in solution may approach its partner, surrounded by a tightly attached solvation shell, with no hindrance until it contacts the shell.
- Thereafter, the resulting associate may retain its structure of a loose, solvent-separated pair, or it may collapse, squeezing out the solvent molecule (or molecules) separating the ions.

So an ion in a solution may approach its partner surrounded by a tightly attached solvation shell with no hindrance until it contacts the shell. So, thereafter, the resulting associate may retain its structure of loose solvent separated pair or it may collapse, squeezing out the solvent molecule or molecules by separating the ions. Now in latter case a tight contact pair is formed.

And the essence of this is that these 2 alternative outcome of the association are equivalent to the establishment of an equilibrium between the loose and the tight ion pairs. So, the 2 type of ion pairs from thermodynamically distinct species, each characterised by its own specific properties. let us have a look about this concept that is equilibrium equilibria between free ions and ion pairs.

(Refer Slide Time: 19:21)

Equilibrium between free ions and ion pairs

Conductance Studies

$$A^- + B^+ \xrightleftharpoons[k_{diss}]{k_{ass}} A^- \cdot B^+$$


Dissociation Constant $K_{diss} \rightarrow$ Dependence of Equival Conductance of the solution Λ

$C \rightarrow$ Concentration of the salt

$\Lambda_0 \rightarrow$ Limiting Conductance

$$\Lambda_0 = \lim_{C \rightarrow 0} \Lambda(C)$$

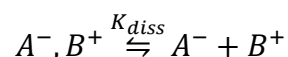
Kohlrausch



This is a very important thing, while discussing about this ionic polymerization that how we can establish the the equilibria between the free ions and ion pairs. So we discussed about this free ion, we discussed about these ionic pairs. So the foremost thing which we need to address that is called the conductance studies. Now in solutions of partially dissociated salt for conducting free ions, sometimes they are in equilibrium with the non conducting ionic pairs.

Equilibria Between Free Ions and Ion-Pairs: Conductance Studies

In solutions of partially dissociated salts the conducting free ions are in equilibrium with the nonconducting ion-pairs, e.g.,



The dissociation constant K_{diss} is derived commonly from the dependence of the equivalent conductance of the studied solution Λ , on the concentration of the salt denoted by c , in conjunction with the value of the limiting conductance Λ_0 ,

$$\Lambda_0 = \lim_{c \rightarrow 0} \Lambda(c)$$

The latter is needed in the calculation of K_{diss} . The simplest procedure, due to Ostwald, leads to the values of both constants, K_{diss} and Λ_0 , derived from a linear plot:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \Lambda c / K_{diss} \Lambda_0^2$$

Thus Λ_0 is given by the reciprocal of the intercept, whereas the reciprocal of the slope provides the value of $K_{diss} \Lambda_0^2$ from which K_{diss} is computed.

(Refer Slide Time: 21:52)

Ostwald Λ_0 K_{diss}

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda c}{K_{diss} \Lambda_0^2}$$

Λ_0 is given by the reciprocal of the intercept

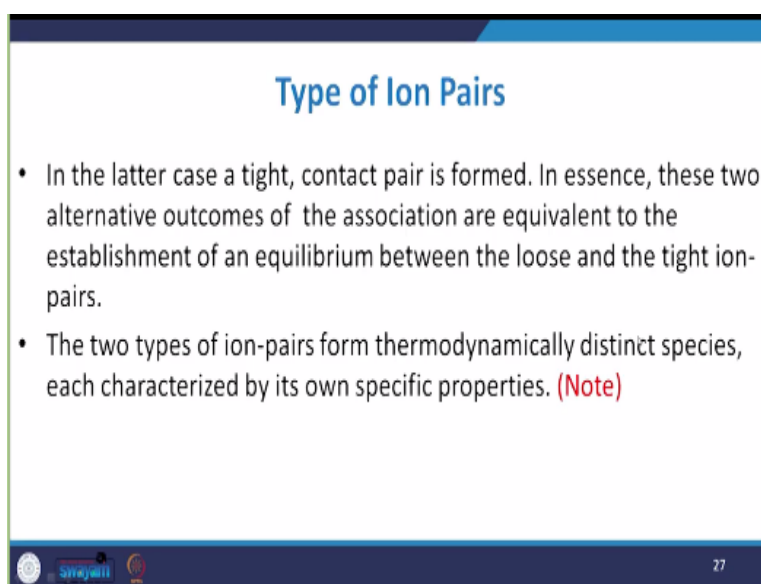
Reciprocal of the slope provides the value of $K_{diss} \Lambda_0^2$ from which K_{diss} may be computed

This lead to the values of both constant that is this conductance limiting conductance and K dissociation. So, if we try to formulate the things, then it experimentally, then it may give you

the linear plot and we can calculate or we can represent this in this particular mathematical equation, upon K dissociation squared. Now this that is this, the limiting conductance is given by the reciprocal of the intercept.

Here the reciprocal of of the slope provides the value of K dissociation limiting factor squared from which the K dissociation maybe computed. So, by this way, we can calculate the K dissociation as well as the limiting conductance.

(Refer Slide Time: 23:24)

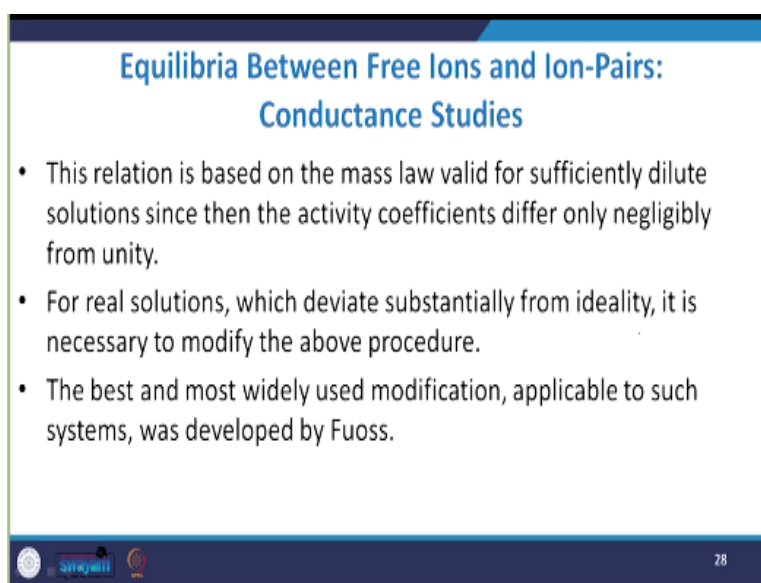


Type of Ion Pairs

- In the latter case a tight, contact pair is formed. In essence, these two alternative outcomes of the association are equivalent to the establishment of an equilibrium between the loose and the tight ion-pairs.
- The two types of ion-pairs form thermodynamically distinct species, each characterized by its own specific properties. (Note)

swayam 27

(Refer Slide Time: 23:29)



**Equilibria Between Free Ions and Ion-Pairs:
Conductance Studies**

- This relation is based on the mass law valid for sufficiently dilute solutions since then the activity coefficients differ only negligibly from unity.
- For real solutions, which deviate substantially from ideality, it is necessary to modify the above procedure.
- The best and most widely used modification, applicable to such systems, was developed by Fuoss.

swayam 28

So, by this way, we can establish the equilibria between free ion and ionic pairs. this relation is the purely based on the mass law that is valid for sufficiently dilute solution, since then the activity coefficient differ only negligibly from the unity. for real solution, these this particular

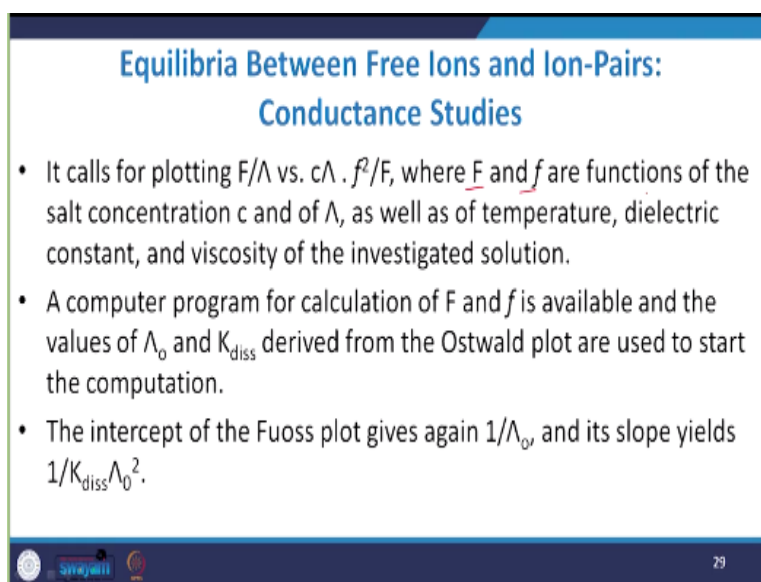
thing deviates substantially from ideality and it is necessary to modify these this procedure or which the mathematical procedure which we discussed priori.

It calls for plotting F/Λ vs. $c\Lambda \cdot f^2/F$, where F and f are functions of the salt concentration c and of Λ , as well as of temperature, dielectric constant, and viscosity of the investigated solution.

A computer program for calculation of F and f is available and the values of Λ_0 and K_{diss} derived from the Ostwald plot are used to start the computation.

The intercept of the Fuoss plot gives again $1/\Lambda_0$, and its slope yields $1/K_{\text{diss}}\Lambda_0^2$.

(Refer Slide Time: 24:37)



**Equilibria Between Free Ions and Ion-Pairs:
Conductance Studies**

- It calls for plotting F/Λ vs. $c\Lambda \cdot f^2/F$, where F and f are functions of the salt concentration c and of Λ , as well as of temperature, dielectric constant, and viscosity of the investigated solution.
- A computer program for calculation of F and f is available and the values of Λ_0 and K_{diss} derived from the Ostwald plot are used to start the computation.
- The intercept of the Fuoss plot gives again $1/\Lambda_0$, and its slope yields $1/K_{\text{diss}}\Lambda_0^2$.

swayam 29

So, usually, when we talk about the values, the intercept of these first plot gives again 1 upon limiting conductance and its slope yields the value of $1/K$ dissociation and the square of limiting conductance. So, in the course of the studies of ionic polymerization, dissociation constant is usually kept low and that is around 10^{-12} M.

(Refer Slide Time: 25:43)

Equilibria Between Free Ions and Ion-Pairs: Conductance Studies

10^{-12}

- In the course of studies of ionic polymerizations, dissociation constants as low as 10^{-12} M have to be determined.
- To get reliable values for the slope and intercept of the Fuoss plot, it is imperative to extend the measurements to very low concentrations of the salt, often lower than 10^{-6} M; otherwise the slope is too low and the intercept too high.

30

This need to be determined. to get the reliable values for the slope and intercept of this plot, it is imperative to extend the measurement of to very low concentration of the salt, sometimes often lower than 10^{-6} M. Otherwise, the slope is too low and the intercept too high. let us see which this is the plot which we are talking about.

(Refer Slide Time: 26:13)

Equilibria Between Free Ions and Ion-Pairs: Conductance Studies

- This is clearly shown by Figure. Since both errors reinforce each other, the error in the such computed K_{diss} could be very large.

Figure 2.7. The Fuoss plot of F/A vs. Pc/VF for the conductance of sodium polystyryl in tetrahydropyran at 25°C. Note the curvature of the plot and the error caused by failure to extend the measurements to very low salt concentration.

31

you see here in the figure the both error reinforce each other. So, the error in such a case computed the K_{diss} and this could be a very large. So, you can have a look up this plot.

(Refer Slide Time: 26:30)

Heat and Entropy of Dissociation of Ion-Pairs

- The equation deduced in the preceding section for K_{diss} leads to:

$$\Delta H_{diss}^0 = \left\{ \frac{N_A e^2}{\epsilon(r_1+r_2)} \right\} \cdot \left(1 - \frac{d \ln \epsilon}{d \ln T} \right)$$

- Since $d \ln \epsilon / d \ln T$ is usually smaller than -1 (e.g., -1.16 for tetrahydrofuran, -1.33 for diethyl ether, and so on), the dissociation of bulky ion pairs is expected to be slightly exothermic.
- The values of ΔH_0 calculated from the above equation agree fairly well with the experimental ones for bulky ions in poorly solvating media

Heat and Entropy of Dissociation of Ion-Pairs

Let us have a discussion about the heat and entropy of dissociation of ionic pairs.

The equation deduced in the preceding section for K_{diss} leads to:

$$\Delta H_{diss}^0 = \left\{ \frac{N_A e^2}{\epsilon(r_1+r_2)} \right\} \cdot \left(1 - \frac{d \ln \epsilon}{d \ln T} \right)$$

Since $d \ln \epsilon / d \ln T$ is usually smaller than -1 , (e.g., -1.16 for tetrahydrofuran, -1.33 for diethyl ether, and so on), the dissociation of bulky ion pairs is expected to be slightly exothermic.

The values of ΔH_0 calculated from the above equation agree fairly well with the experimental ones for bulky ions in poorly solvating media.

So, the values of enthalpy under the initial start that may be calculated from this equation agree fairly well with the experimental ones for bulky ion in the poorly solvating media.

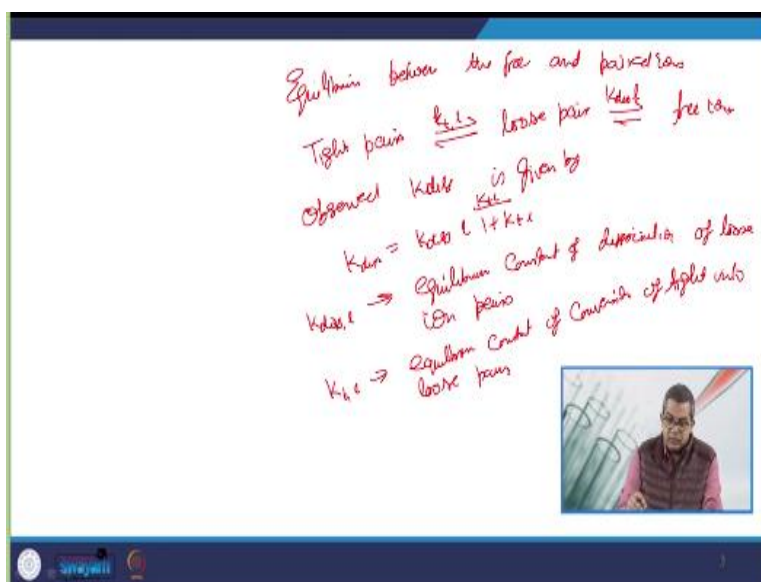
(Refer Slide Time: 27:40)

Heat and Entropy of Dissociation of Ion-Pairs

- However, for small ions in well solvating media the exothermicity is substantially larger.
- Its increase arises from the more extensive degree of solvation of free ions than of the associated ion-pairs.
- Consequently, the dissociation of such pairs decreases the entropy of the system since it immobilizes the solvent molecules that become incorporated into solvation shells of the free ions. **(Note)**

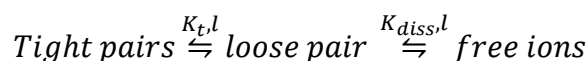
When we talk about the heat and entropy dissociation that is for a small ion in a well solvating media the exothermic city is substantially larger. It increase or its increase arises from more extensive degree of solvation of free ions than of the associated ion pairs. Consequently, the dissociation of such pair decreases the entropy of the system, sometimes it immobilises the solvent molecule that becomes incorporated into the solvation shell of free ions.

(Refer Slide Time: 28:29)



let us have a look about this dissociation aspect.

Tight and loose ion-pairs are present in these systems. Hence, the equilibrium between the free and paired ions is given by the scheme:




and the observed K_{diss} is given by the relation:

$$K_{diss} = K_{diss,l} \cdot \frac{K_{t,l}}{1 + K_{t,l}}$$

where $K_{diss,l}$ denotes the equilibrium constant of dissociation of loose ion pairs, and $K_{t,l}$ is the equilibrium constant of conversion of the tight into loose pairs.

(Refer Slide Time: 30:26)

A useful approximation when $K_{t,l} \ll 1$
 Slope of van't Hoff line
 $\frac{\Delta H_{t,l}^0 + \Delta H_{diss,l}^0}{R}$
 $\Delta H_{t,l}^0$ and $\Delta H_{diss,l}^0$ \Rightarrow the heat of conversion
 of tight into loose ion-pairs
 and heat of dissociation of loose
 pairs respectively



At high temperatures when $K_{t,l} \ll 1$, the slope of the van't Hoff line is equal then to:

$$\frac{\Delta H_{t,l}^0 + \Delta H_{diss,l}^0}{R}$$

where $\Delta H_{t,l}^0$ and $\Delta H_{diss,l}^0$ denote the heat of conversion of tight into loose ion-pairs and the heat of dissociation of loose pairs, respectively.

(Refer Slide Time: 31:49)

Heat and Entropy of Dissociation of Ion-Pairs

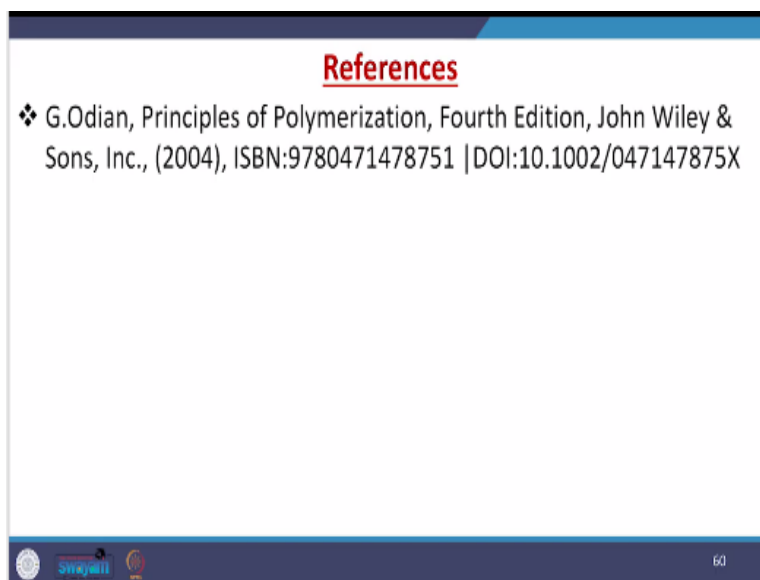
- On the other hand, at very low temperatures when $K_{t,l} \gg 1$ the slope is lower being equal to ΔH_1^0 only.
- The curvature of the Van't Hoff plots deal with the propagation of living polymers.
- The equation for ΔH_{diss}^0 , shown at the beginning of this section, applies to $\Delta H_{diss,1}^0$, since the bulky well-solvated ions are not further solvated on their dissociation.

On the other hand, at very low temperatures when $K_{t,l} \gg 1$ the slope is lower being equal to ΔH_1^0 only.

The curvature of the Van't Hoff plots deal with the propagation of living polymers.

The equation for ΔH_{diss}^0 , shown at the beginning of this section, applies to $\Delta H_{diss,1}^0$, since the bulky well-solvated ions are not further solvated on their dissociation.

(Refer Slide Time: 32:33)



So, in this particular chapter, we discussed about the ionogens, ionophores etcetera, their equilibrium concepts. We discussed about the heat and entropy of various dissociation pairs. We discussed about the efficacy of those ion pairs in the polymerization process.

And we will continue this particular approach in the next lecture and you may look into the various references which we have been listed in the, in this particular slide. Thank you very much.