Introduction to Polymer Physics
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Lecture – 06
Thermodynamics of Polymer Solutions

Hello. So, in the last couple of lectures, we have been looking at the Thermodynamics of Polymer Solutions. Specially, we have discussed the lattice model of Flory Huggins and how it can be applied to develop expression for the Gibb's free energy change of mixing of polymer solutions and we saw that this Gibb's free energy change of mixing.

This expression actually contains contributions of 2 different types; one is due to the combinatorial entropy, which is primarily because of the multiple different confirmations that the polymer chain can adopt and the other term in this Gibb's free energy change of mixing appears due to the contact interaction which is primarily the intermolecular effect of intermolecular interactions between the polymer molecules and the solvent molecules.

So, the final expression for the Gibb's an free energy change of mixing that can contain both these terms and from the we also introduced the parameter called the Flory Huggins interaction parameter of the chi parameter which is a measure of the polymer solvent interaction and this parameter also appears in the expression for the Gibb's free energy change of mixing and the parameter the chi parameter itself incorporates the effect of the lattice, type of lattice that is chosen for the development of the Flory Huggins theory as well as the contact Gibb's free energy change.

So, starting from the Gibb's free energy change of mixing, from the Flory Huggins theory, we developed expressions for the chemical potential as well as activity of polymer solutions. So, what will be the chemical potential or activity of the solvent as well as the polymer? In a given polymer solution, we developed that by considering the Flory Huggins equation for the delta g of mixing. So, we will continue that discussion today and in today's lecture, we will focus on dilute solutions.

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CONTENT

Thermodynamics of Polymer Solution:

- Dilute Solution
- Theta Condition
- Solubility Parameter

So, the content for today's lectures will be divided into 3 parts; for the first part, will focus primarily on the behavior of dilute solutions. So, earlier while discussing Flory Huggins theory, we talked about the fact that it contains or it involves a mean field approximation which is not a good assumption for dilute solutions. But, even though that is assumption is not a good one, we will see that applying Flory Huggins theory to dilute solution at least gives some qualitative information that that is predicted by more sophisticated theories as well as that something, which is observed experimentally as well.

So, we will after discussing that the behavior of dilute solutions within the framework of Flory Huggins theory, we will move on to discussing a special condition under which the polymer solutions which are inherently non ideal, but under this special conditions, this polymer solution solutions behave ideally.

So, this condition is called theta condition. So, we will briefly talk about concept of theta conditions and towards the end of this lecture, we will introduce and briefly discuss the concept of solubility parameter, which is useful while trying to get measure of how soluble a given polymer is in a solvent. So, despite it is limitations, the solubility parameter approach is actually useful one.

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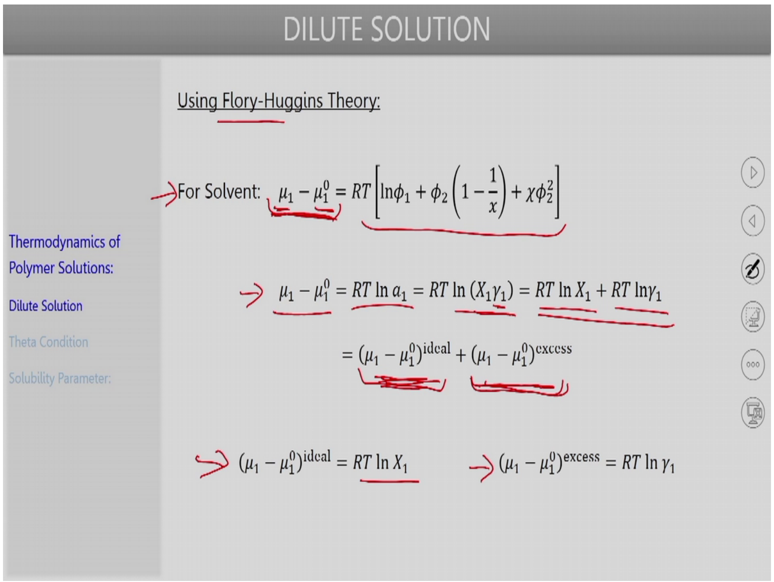

DILUTE SOLUTION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

Using Flory-Huggins Theory:

For Solvent: $\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$

$$\mu_1 - \mu_1^0 = RT\ln a_1 = RT\ln(X_1\gamma_1) = RT\ln X_1 + RT\ln\gamma_1$$

$$= (\mu_1 - \mu_1^0)^{\text{ideal}} + (\mu_1 - \mu_1^0)^{\text{excess}}$$

$$(\mu_1 - \mu_1^0)^{\text{ideal}} = RT\ln X_1 \qquad (\mu_1 - \mu_1^0)^{\text{excess}} = RT\ln\gamma_1$$

So, let us begin by starting off with the application of Flory Huggins theory to your dilute solution. So, again as discussed, the Flory Huggins theory is the assumptions involved are not particularly suited for dilute solutions. But, we will just see we will just try to apply Flory Huggins theory nonetheless and see what results and how good the result is in or how applicable the result is compared to the real situation.

So, in the previous lecture, we developed this equation for the chemical potential of the solvent in a polymer solution. So, this term mu 1 minus mu 1 naught which is the chemical potential of the solvent in the solution minus the chemical potential of the solvent in it is standard set, which can be the pure solvent. So, this quantity based on the Flory Huggins theory is given by this expression here. So, we will refer to this difference in chemical potential; let us say as the relative chemical potential.

So, for the solvent, the relative chemical potential expression was developed in the previous lecture using the Flory Huggins theory.

So, starting off with this expression, now we also discussed in the previous lecture that this relative chemical potential of the solvent mu 1 minus mu 1 naught that is related to the activity of the solvent through this expression. So, the relative chemical potential is equal to R T times ln a 1 and the activity of the solvent itself can be expressed as a product of the mole fraction the solvent and what is called the activity coefficient of the solvent which is represented by gamma 1 here. So, these are some of the things that we developed and discussed in the previous lecture.

So, expanding this log term, we will get these 2 terms here; R T ln X 1 plus R T ln gamma 1. So, now the mu 1 minus mu 1 naught the relative chemical potential for the solvent that we can split into 2 parts on one can be an ideal contribution which will correspond to the chemical potential difference. That we will see in an ideal solution and along with this, since the solution is not a actually ideal. So, along with this another term will be there which is called the excess term.

So, this excess chemical potential difference is basically the excess contribution above the ideal contribution to the chemical potential difference. So, the first term is something that we will see in an ideal solution and in any real solution, we will see non zero second term as well.

So, comparing the expressions this the first term the for an ideal solution it is well known that this chemical potential difference or relative chemical potential is just given by R T times ln X 1. So, based on these observations what we can say is that, for the excess chemical potential that is defined as R T times ln gamma 1.

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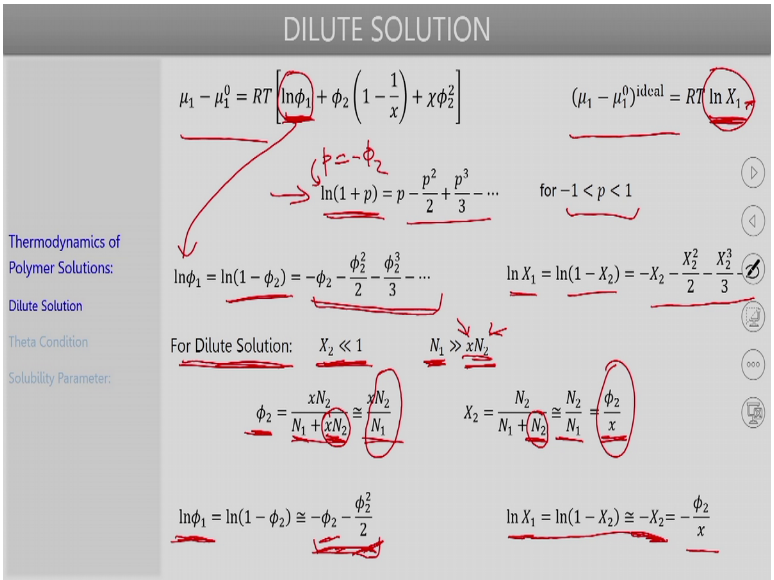

DILUTE SOLUTION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

$$\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$(\mu_1 - \mu_1^0)^{\text{ideal}} = RT\ln X_1$$

$p = -\phi_2$

$$\ln(1+p) = p - \frac{p^2}{2} + \frac{p^3}{3} - \cdots \quad \text{for } -1 < p < 1$$

$$\ln\phi_1 = \ln(1-\phi_2) = -\phi_2 - \frac{\phi_2^2}{2} - \frac{\phi_2^3}{3} - \cdots$$

$$\ln X_1 = \ln(1-X_2) = -X_2 - \frac{X_2^2}{2} - \frac{X_2^3}{3} - \cdots$$

For Dilute Solution: $X_2 \ll 1$ $\quad N_1 \gg xN_2$

$$\phi_2 = \frac{xN_2}{N_1 + xN_2} \cong \frac{xN_2}{N_1}$$

$$X_2 = \frac{N_2}{N_1 + N_2} \cong \frac{N_2}{N_1} = \frac{\phi_2}{x}$$

$$\ln\phi_1 = \ln(1-\phi_2) \cong -\phi_2 - \frac{\phi_2^2}{2}$$

$$\ln X_1 = \ln(1-X_2) \cong -X_2 = -\frac{\phi_2}{x}$$

So, we have these 2 expressions for the ideal and the excess components of the overall chemical potential difference and let us just look at the expression for the overall actual chemical potential difference and the ideal term in that chemical potential difference. So, let us look at these 2 terms in a bit more detail in both these terms that we have this ln terms appearing so, ln of phi 1 here and ln of X 1 here.

So, before we move on this one expansion or Taylor series kind of expansion, that we will be applying in the next few steps. So, let us just look at that it is mathematically result or expansion. So, what that the expansion or the result states that the natural log of 1 plus p, where p is any variable whose value lies between minus 1 and plus 1.

So, for such a case, expanded form of ln 1 plus p will be p minus p square by 2 plus p cube by 3 minus p to the power 4 by 4 plus p to the power 5 by 5 and so on. So, it is an infinite series and that is how the log of 1 plus p can be represented. So now, let us look at this term here and this term.

So, the the ln phi 1 term in the in the first case and ln X 1 term for the ideal term so, if we consider the ln phi 1 term, this term that is what we are considering here. So, ln phi 1 we can always write at as ln 1 minus phi 2 because phi 1 plus phi 2 will be 1. These are volume fractions and we have binary mixture. So, the sum will be 1.

So, ln phi 1 we can always write as ln 1 minus phi 2 and this ln 1 minus phi 2 we can expand using the formula that we have just discussed. So, upon expanding this ln 1 minus phi 2, we get this infinite series here. So, oh this expansion we have carried out by just substituting p is equal to minus phi 2 here. So, in this equation, if we substitute p equal to minus phi 2, then we get this result here.

Similarly, for this ln X 1 term, for this term again X 1 can be written as 1 minus X 2. So, from there, again by applying this same formula and instead of p, if we replace p by minus X 2 here then, we will get this infinite series representation of this term ln X 1. So now, that we have express these 2 the ln or natural log terms in terms of 2 infinite series. Next, let us consider the case of a dilute solution.

So, everything that we have done till now, all the steps till now apply to any kind of in solution. We have not involved any assumption or we have not invoked any assumption with regards to how dilute or how concentrated the solution is. So, next let us apply the condition that a psi as a solution is very dilute. So, for a very dilute solution, what we can see is that this the mole fraction of the polymer X 2.

So, the mole fraction of the solute or the polymer X 2 that will be much less than one and also the number of molecules N 1 of the solvent that will be much larger than the number of segments of polymer polymers present.

So, here N 2 is the number of molecules of polymers present and x is the number of segments in 1 polymer molecule. So, the dilute solution condition basically means that, the number of solvent molecules is much larger than that the total number of polymer segments present in the solution and also, it of course, also implies as a mole fraction of the polymer is much smaller than 1. So, using these 2 assumptions, we can actually simplify the expression for the volume fraction phi 2 of the polymer in the solution.

So, the volume fraction of phi 2 which is defined like this. So, here since this term X 2 times and x times N 2 which is the number of segments in the solution number of polymer segments. So, since that is much smaller than N 1, so what we can do is, we can neglect this term from the denominator and we approximately get phi 2 as x times N 2 by N 1. Similarly, for the mole fraction X 2 that is defined as N 2 by N 1 plus N 2 and again this since x times N 2 is much smaller than N 1.

So, of course, N 2 itself will also be much smaller than N 1 and so, we can neglect this term N 2 with respect to N 1 and we get X 2 as approximately N 2 by N 1. So now, if we look at the again the expression for phi 2 here, this ratio N 2 by N 1 here that we can just express as phi 2 by x. So, if we do that, then this N 2 by N 1 we can write as phi 2 by x. So, the expression for X 2 becomes just phi 2 by x.

So, we see that the mole fraction X 2 the mole fraction X 2 is much smaller than the volume fraction phi 2 because, for a typical polymer molecule, the number of segments x will be quite high in the order of 100s or even 1000s or even more.

So, X 2 typically will be much smaller than the mole fraction volume fraction phi 2 and based on the fact that we have a dilute solution, here what we can do is the expansion that we had develop for ln phi 1. We can truncate that up to the first 2 terms only because, if since that solution is dilute even the volume fraction of the polymer in the solution will be quite small.

So, let us consider only the first 2 terms in the volume fraction in that expansion. So, only up to the second power and higher order terms, we are neglecting in this case. So, any term containing phi 2 q phi 2 to the power 4 and so, they will be very small because of the dilute nature of the solution and we are neglecting those terms for the case of ln X 1 we are truncating this series only after the first term.

So, we are not even considering the square and the cube and other terms, the reason we are truncating this only after the first term. Whereas, here we are considering 2 terms is that X 2 itself will be much smaller than phi 2. So, one can think of X 2 as being comparable to the term phi 2 square and X 2 square will be comparable to then phi 2 to the power 4 or of that order.

So, that will be negligible in with regards to the terms that we will be considering. So, since X 2 is much smaller than phi 2, we are considering only one term in this expansion and we know that X 2 is equal to phi 2 by x from here. So, this ln X 1 we can express as minus of phi 2 by x. So now, the now that we have developed the expressions for these 2 natural log terms here, let us try to see what happens or what expressions we get once we substitute those expressions.

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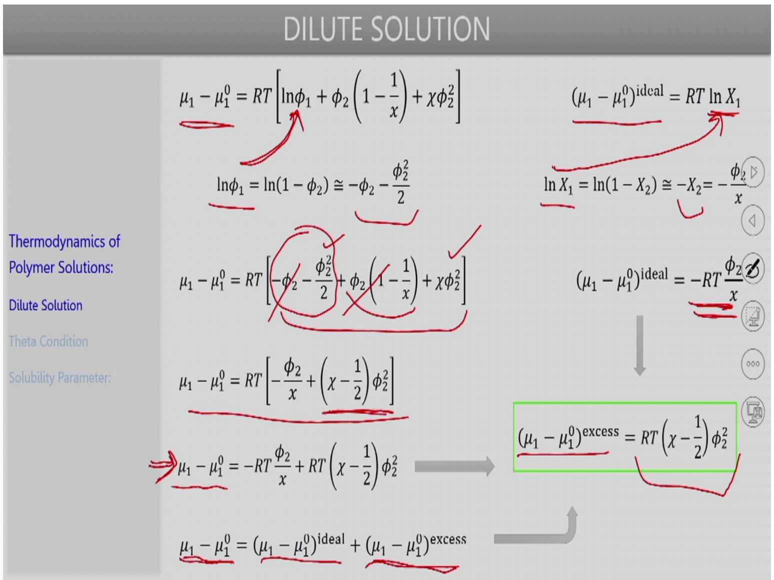

DILUTE SOLUTION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

$$\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\ln\phi_1 = \ln(1 - \phi_2) \cong -\phi_2 - \frac{\phi_2^2}{2}$$

$$\mu_1 - \mu_1^0 = RT\left[\cancel{-\phi_2} - \frac{\phi_2^2}{2} + \cancel{\phi_2}\left(\cancel{1} - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\mu_1 - \mu_1^0 = RT\left[-\frac{\phi_2}{x} + \left(\chi - \frac{1}{2}\right)\phi_2^2\right]$$

$$\mu_1 - \mu_1^0 = -RT\frac{\phi_2}{x} + RT\left(\chi - \frac{1}{2}\right)\phi_2^2$$

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{\text{ideal}} + (\mu_1 - \mu_1^0)^{\text{excess}}$$

$$(\mu_1 - \mu_1^0)^{\text{ideal}} = RT\ln X_1$$

$$\ln X_1 = \ln(1 - X_2) \cong -X_2 = -\frac{\phi_2}{x}$$

$$(\mu_1 - \mu_1^0)^{\text{ideal}} = -RT\frac{\phi_2}{x}$$

$$\boxed{(\mu_1 - \mu_1^0)^{\text{excess}} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2}$$

So, again we have written down the equations for the chemical potentials of the actual solution and the ideal term contribution. And, let us just substitute the expression for ln phi 1 and ln X 1 that we have developed just now with the assumption of a dilute solution which is why we have truncated these terms these 2 2 N 1 terms respectively.

So, if we substitute these expressions for ln phi 1 here ln X 1, we can substitute here. So, let us see what happens when we substitute the ln X 1 here first. So, this ideal term actually becomes minus R T ln sorry minus R T phi 2 by x this term.

So, the ideal term chemical potential difference becomes minus R T phi 2 by x. Next, if we are considering this substitution of ln phi 1 term in the expression for mu 1 minus mu 1 naught, then we get this expression here and these 2 basically, these 2 terms come from the ln phi 1 expansion and what we see is that, this minus phi 2 here and the plus phi 2. Here, these will get cancelled.

So, 2 terms get cancelled and once simplification this is the expression that we get. So, here this phi 2 by x comes from this term and the phi 2 square. There are 2 phi 2 square terms; one is this one, one is this one. These 2 we can combine in the single term here. So, we get the chemical potential differences R T times minus phi 2 by x plus chi minus half phi 2 square. So, again if we can expand or multiply throughout by R T, so we get the expression that shown here and let us now compare this with the ideal and excess contributions.

So, we already know that this mu minus mu naught will have an ideal and an excess contribution. Already the ideal contribution expression we have developed here for an ideal for a dilute solution and for the actual chemical potential difference the expression shown here. That is what has been developed for a dilute solution.

So, if we combine these 2 and realizing the fact that this chemical potential contains an ideal and an excess contribution. So, combining all these equations, what we get is that the excess contribution to this chemical potential difference that is just equal to R T times chi minus half phi 2 square. So, that is the expression here and this is the expression that is of interest for us with regards in dilute solution. If we are trying to apply the Flory Huggins theory to describe it is behavior.

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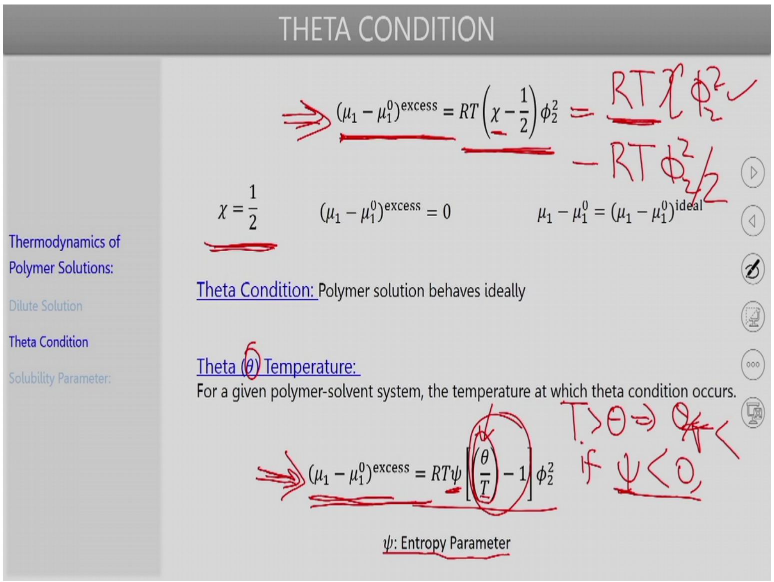

THETA CONDITION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

$$(\mu_1 - \mu_1^0)^{excess} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2 = RT\chi\phi_2^2 - RT\phi_2^2/2$$

$\chi = \frac{1}{2}$ $\quad (\mu_1 - \mu_1^0)^{excess} = 0 \quad \mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{ideal}$

Theta Condition: Polymer solution behaves ideally

Theta (θ) Temperature:

For a given polymer-solvent system, the temperature at which theta condition occurs.

$$(\mu_1 - \mu_1^0)^{excess} = RT\psi\left[\left(\frac{\theta}{T}\right) - 1\right]\phi_2^2$$

$T > \theta \Rightarrow \theta/T <$

if $\psi < 0$,

ψ: Entropy Parameter

So, this is the expression that we have just develop for the excess contribution to chemical potential difference for a dilute polymer solution within the framework of Flory Huggins theory. So, if you look at this equation on the right hand side, we can actually consider 2 different terms. So, this we can write as one term is R T chi phi 2 square minus R T phi 2 square by 2. So, these are the 2 terms that are present here.

So, the term the first term the this term this term containing the chi parameter that basically accounts for if we trace our derivation steps all the way back to the Flory Huggins equation, then this chi parameter the term here that contains the chi parameter that is basically comes about due to the contact interaction terms or the contact terms which arise due to intermolecular interactions and the second term here which is this R T phi 2 square by 2. That term basically appears because of the combinatorial entropy that change that we had calculated earlier.

So, the second term which is always negative this term arises due to entropic effects and this the first term which need not which is mostly positive it can be negative also depending on the sign of the chi parameter. So, the that term basically captures the contact term or the intermolecular effect of intermolecular interactions. So, now under certain special conditions, these 2 terms can actually balance each other in a polymer solution.

So, if for the equation that we have derived if we have a condition there chi parameter is half. So, under this condition, what will happen is that the excess chemical potential difference will become 0 ok. And the chemical potential difference will just be equal to what? The chemical potential difference will have in an ideal solution.

So, the excess part is 0 and the chemical potential difference is just equal to what we get for an ideal solution. So, under these special conditions where the polymer actually the polymer solution although the polymer solution, we know is not truly speaking in ideal solution because of the large difference in the size between the size of the polymer molecule and the solvent molecule.

So, it is not an ideal solution strictly speaking, but under the special conditions where these 2 factors basically cancel each other the effect of entropic contribution and the contact or intermolecular interaction contribution to the chemical (Refer Time: 21:03) when these 2 cancel each other under some special conditions which for the equation, that we have derived corresponds to the value of half or chi parameter.

So, under these conditions, the excess chemical potential becomes 0. The chemical potential difference for this polymer solution becomes equal to that for an ideal solution and the polymer solution tends to behave like an ideal solution in this case.

So, such condition is referred to as a theta condition where the polymer solution behaves ideally and this solution where we observe this theta condition where the polymer solution is behaving ideally. So, such a solution is referred to as a theta solution. So, in our previous discussion of a real polymer chain behavior, when we were discussing the behavior of real polymer chains in solution. So, if you have a good solvent, then the chain expands pure solvent the chain will tend to contract because, it does not like the interacting with the solvent molecules.

So, there we discussed there also we discussed the special case where the excluded volume repulsions of the polymer segments basically get balance by the solvent segment repulsions. So, so that the polymer chains adopt their ideal sizes or unperturbed dimensions so, that was a discussion on the theta condition or theta solution from the point of view of a polymer chain dimensions and the interactions and here the same concept of theta solution is being discussed from the point of view of polymer thermodynamics.

So, this theta condition we just discussed is a special condition where the polymer tends to behave ideally and for a given polymer solvent system, normally the theta condition will be observed at a particular temperature. So, the temperature which for a given polymer solvent system the temperature which corresponds to theta condition that temp or the temperature at which the theta condition will occur that temperature is referred to as a theta temperature.

So, theta temperature one can actually express this the excess mu 1 minus mu 1 naught in terms of theta temperature the theta temperature we are representing by the symbol theta here. So, in terms of the theta temperature also, one can express the mu 1 minus mu 1 naught excess term and that is what is shown here and here this psi is referred to as what is called the entropy parameter,.

So, if we again look at these 2 equation, this equation where the excess chemical potential difference is being expressed in terms of the chi parameter Flory Huggins interaction parameter and this equation where the excess chemical potential difference is being expressed in terms of the theta temperature.

So, if you look at the these 2 expressions, then for the first expression, this one we can say is that if the value of chi is less than half. So, if the value of chi is less than half, then this excess term will be negative, ok. So, if the value of chi is less than of the excess term will be negative and the as such a condition where the excess chemical potential difference is negative that basically favours mixing, ok. So, the more negative this excess chemical potential value is the more favorable the dissolution of the polymer in the solvent will be.

So, so, that what that implies is the lesser the value of chi with respect to half. This number half is the better will be the mixing. On the other hand, if have we just saw that if chi is half then we get the theta condition where, it behaves the solution behaves ideally if the value of chi is more than half.

Then, in that case the excess chemical potential difference. This term basically becomes positive and the larger the value of chi the more positive. It will become an the less favorable the mixing will be. Similarly, if we look at the other equation in terms of the theta temperature for the excess chemical potential difference, there the value of this theta temperature with respect to T.

So, whatever the temperature we are at and what is the theta temperature of the particular solution or polymer solvent system is. So, that will basically dictate whether the mu 1 minus mu 1 naught excess will be negative or positive. So, let us take a look at that. So, if let us consider the case when T is actually less than theta. So, we are we have our polymer solvent system of the solution at a temperature which is below it is theta temperature. So, if T is below theta, then in that case this ratio theta by T that will of course, be greater than 1.

So, this implies that theta by T will be greater than 1. So, if theta by T is greater than 1, then depending on the sign of this entropy parameter, if this if this psi is positive, if non units also consider as psi. So, if psi is also greater than 0 which means it is positive. So, for this such a case excess chemical potential difference actually will come out to be positive so, that will that is something which will not favor mixing.

So, if this entropic parameter is positive, then under that condition, if we are below the theta temperature the lower the temperature is compared to the theta temperature the less favorable the mixing will be similarly again, let us consider psi is greater than 0, so positive entropy parameter.

Now, if we consider the case where temperature of the solution is above it is theta temperature, ok. So, in that case the ratio theta by T that ratio basically is now less than 1 and this ratio being less than 1. This term the bracketed term becomes negative and since psi is or the entropy parameter that we are considering is also positive.

So, overall this mu 1 minus mu 1 naught excess this term becomes negative in this case. So, if we have a if you have the solution at a temperature above it is theta temperature, then provided the entropy parameter is positive we will basically be favoring mixing will basically be favored because, the excess chemical potential difference will be negative.

But, if we consider the case where psi is negative. So, psi for many polymer solvent systems is actually positive, but for some cases it is also negative.

So, if this entropy parameter psi if this psi is negative. So, if this psi that we have here if it is less than 0, then whatever discussion that we had just now the reverse of that will apply. So, if the psi is negative, then have. If there we are at a temperature above the theta temperature, then that will actually not favor mixing and if we are at a temperature below the theta temperature, for that system mixing will be favored provided entropy parameter is negative.

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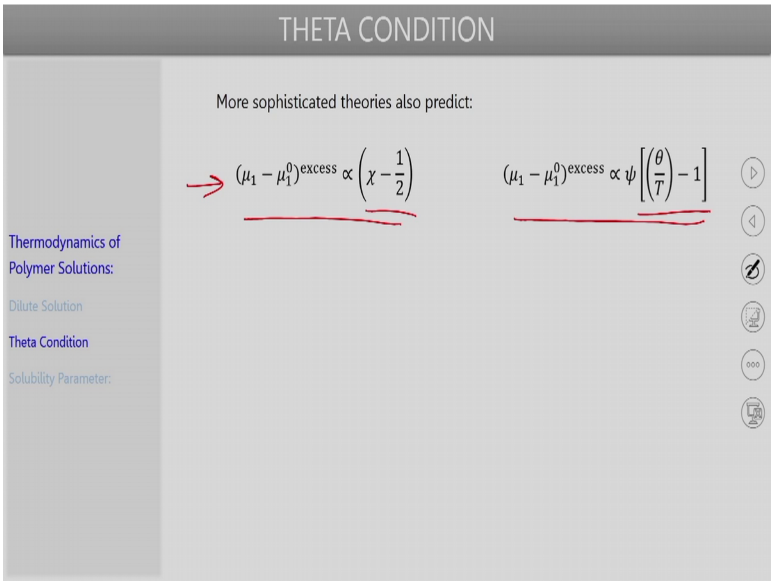

THETA CONDITION

More sophisticated theories also predict:

$$(\mu_1 - \mu_1^0)^{\text{excess}} \propto \left(\chi - \frac{1}{2}\right) \qquad (\mu_1 - \mu_1^0)^{\text{excess}} \propto \psi\left[\left(\frac{\theta}{T}\right) - 1\right]$$

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

So, we till now, we have; what we have done is applied the Flory Huggins theory for the case of a dilute solution and try to develop an expression for the excess chemical potential difference and explore different scenarios. So, what happens when the value of chi is above half or below half or equal to half or what happens when the temperature is above the theta temperature below the theta temperature?.

So, we have explored all these different conditions, but at the beginning, we also discussed that the Flory Huggins theory is not a very good theory for dilute solutions. Because of the one of the assumptions involved is that of mean field approximation, such a mean field approximation can only apply accurately to a system which where the polymer segments are uniformly distributed and that will correspond to a concentrated solution.

So, that does not apply well to a dilute solution and that is why it is said that Flory Huggins theory is not a good theory to describe dilute polymer solutions, but even with that limitation, we have what we have derive the expressions relating the excess chemical potential to the Flory Huggins interaction parameter or the theta temperature.

So, the qualitative form of those expressions, are actually found to be consistent with similar expressions derived using more sophisticated theories. Such as those using excluded volume in interactions or explicitly or those were the fact that the mean field approximation will not work in dilute solutions.

So, theories which incorporate such effects as well, those theories also predict functional forms of this mu 1 minus mu 1 naught so, that functional dependence that they predict that is similar to what is predicted by the Flory Huggins theory.

So, Flory Huggins theory for dilute solution of course, the quantitate prediction will be quite poor, but the qualitative trends or the dependence of chemical potential on the chi parameter or the theta temperatures at the that dependence that the Flory Huggins theory predicts is basically consistent with the predictions of more advanced theories as well.

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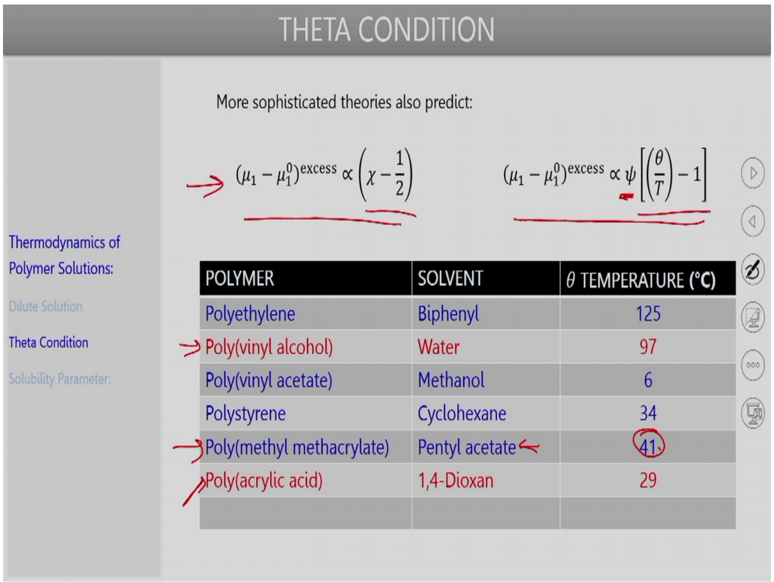

THETA CONDITION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

More sophisticated theories also predict:

$$(\mu_1 - \mu_1^0)^{\text{excess}} \propto \left(\chi - \frac{1}{2}\right) \qquad (\mu_1 - \mu_1^0)^{\text{excess}} \propto \psi\left[\left(\frac{\theta}{T}\right) - 1\right]$$

POLYMER	SOLVENT	θ TEMPERATURE (°C)
Polyethylene	Biphenyl	125
Poly(vinyl alcohol)	Water	97
Poly(vinyl acetate)	Methanol	6
Polystyrene	Cyclohexane	34
Poly(methyl methacrylate)	Pentyl acetate	41
Poly(acrylic acid)	1,4-Dioxan	29

Let us now consider some typical polymer solvent systems and what the theta temperatures are. So, if we consider, let us say polyethylene biphenyl the theta temperature is 125 degree Celsius which means that, at this temperature the solution will tend to behave ideally and for polyvinyl alcohol and water the theta temperature is 97 and so on. So, we have listed a few polymers a few solvents and corresponding theta temperatures for those polymer solvent systems.

So, the theta temperature that we see here, it is specific to the polymer solvent system and for a given polymer, if we change the solvent, then a theta temperature of course, naturally will change as well. Let us say for PMMA that we have shown here. Here, we are considering pentyl acetate as the solvent and the theta temperature that we have is 41.

If instead PMMA polymer in butyl acetate solvent is considered, then for such solutions the theta temperature is actually much lower it is, actually close to minus 20 degree Celsius.

So, different types of solvents I can lead to different values of theta temperature for the same polymer. One more point to be made here is that, if we look at all the entries here, some are in blue color and couple of them are in red color. All the blue color entries basically correspond to the condition where this entropy parameters psi is greater than 0 and the 2 red entries the polyvinyl alcohol in water and the polyacrylic acid in 1 4 Dioxan.

So, these 2 entries basically correspond to solutions where this entropy parameter is actually negative. So, for these 2 particular solutions of Pb in water and polyacrylic acid in 1 4 Dioxan, if we are above the theta temperature, then basically the mixing mixing is not favored.

And, if we are below the lower, we are compared to the theta temperature mixing will be favored. Because, psi is negative for these for all the other systems shown in blue here the psi is positive. So, if we are above the theta temperature, then the mixing polymer solvent mixing will be favored.

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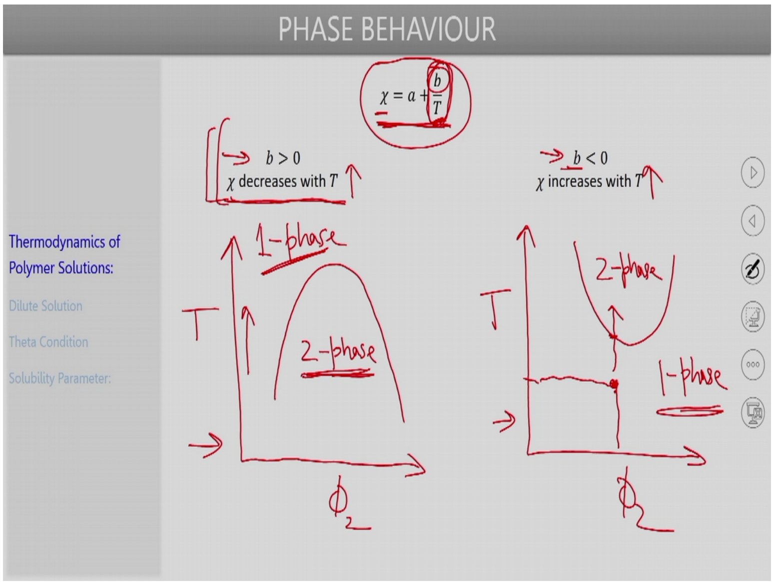

PHASE BEHAVIOUR

$\chi = a + \frac{b}{T}$

$b > 0$

χ decreases with T

$b < 0$

χ increases with T

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

Next, very quickly let us just look at the phase behavior of polymer solutions. So, we will start this discussion by this expression for chi parameter which is which gives a dependence of this chi parameter on temperature. So, the phase behavior the typical phase diagram in for polymer solutions are in general, any liquid solutions it is common to draw a phase diagram where the y axis is the temperature and the x axis is some kind of measure of compositions.

So, in some cases, temperature versus mole fraction graphs, are drawn for polymer solutions. It is more common to draw a temperature versus a volume fraction kind of curve that kind of curve is referred to as a phase, phase diagram for polymer solutions. So now, we start with this chi parameter expression and we consider first this case where let us say, this parameter b is greater than 0.

So, if b is greater than 0, what it means is that, this chi parameter will decrease with temperature right. B is positive, then the larger the value of temperature. We have here the smaller will this ratio become and the smaller this ratio becomes smaller the value of chi will become.

So, chi in this case will decrease as temperature increases. So, if we draw the temperature on the y axis and in the x axis, if we have the polymer volume fraction, then for a case like this where the chi is decreasing with increasing temperature typical phase diagram will a representative phase diagram can look like this. The curve shown here basically marks the boundary between the 2 phase region and the one phase region.

So, this region that we have here this is the 2 phase region and here we have outside this phase boundary, we have one phase really. So, when we say 2 phase region, this is a region where actually the polymers solution is not a single phase. It has split into 2 phases; one rich in the polymer and the other rich in the solvent. So, let us see why for this kind of a condition this kind of a phase diagram is observed.

So, if we consider this phase diagram here, then under this condition we see say that chi is decreasing with as temperature increases. So, as we are going up in temperature, the value of this chi parameter is decreasing. So, the lower the value of the chi parameter becomes the more favorable the mixing will become. So, we saw earlier that the if the chi parameter is below half, then the lower the chi parameter value becomes the more negative. The excess chemical potential difference becomes and more favorable mixing will become.

So, as temperature is increasing chi is decreasing. So, that is basically favoring mixing. So, at some certain low temperature, if we have a 2 phase mixture in this region as the temperature is increased basically that chi parameter will decrease and mixing will be favored and above a certain temperature the polymer solvent will become completely miscible and then we will get a 1 phase region.

So, the one phase region here basically represents a region where the polymer solvent are uniformly mixed and the 2 phase region is a region, where the miscibility has become poor. And ultimately, they have split into 2 different phases; one which is rich in the polymer and the other which is rich in the solvent let us consider the other case where if we have a chi parameter for which this quantity b is less than 0.

So, for certain polymer solvent systems, we may have a case where the this parameter b is less than 0. So, in this case, what will happen is this chi parameter actually will increase as temperature is increased right.

So, if b is negative and if we increase the temperature, then this the b by T term the absolute value b by T term of course, will decrease, but since b is negative the overall value of chi actually will increase in this case.

So, in this case if we again try to draw temperature versus volume faction kind of phase diagram for our polymer solution, then the kind of phase behavior that might be expected main ok. It looks something like this where the again we have 2 phase and one phase regions and the curve that we have that is basically the phase boundary separating the 2 phase region from the one phase region.

So, this curve that separates the 2 regions that is typically referred to a binodal curve. So, in b, both the diagrams the curve that we have that is that is called a binodal curve. So now, in this second case here what is happening is as temperature is. So, let us say we are in at some point here on the phase diagram at some volume fraction of the polymer and at some temperature.

So, we are at this point on the phase diagram and let us say; now we start increasing the temperature. So, as temperature increases, chi also increases in this case. We again saw in the previous slides, that as the value of chi becomes larger than half, then the large more the value of chi increases the more positive the excess chemical potential difference becomes and hence the less favorable of the mixing will be.

So, in the at low temperatures in this case, we have a 1 phase region which means at the polymer solvent are very well mixed and they form a single phase system and as the temperature is increased, we will reach a point where the value of chi has increased so much that the polymer solvent that one phase system basically splits into 2 phases because, the miscibility of the polymer in the solvent has decreased due to the increase in the value of chi.

So, this reduction miscibility ultimately will result in the splitting of the single uniform polymer solution into 2 different phases where again one phase will contain the polymer in higher high concentration and the other phase will primarily consist of the solvent molecules with the only few polymer molecules.

So, that this is the just a very preliminary kind of description of phase behavior of polymer solution and how it relates to the chi parameter. In the one of the next lectures, we will look at the phase behavior and specially phase separation of polymer solutions in a bit more detail. But today, what we will do is next, we will focus on another important concept in related to the miscibility or solubility of polymers in solvents and that is called the solubility parameter.

So, this solubility parameter basically is parameter that was proposed originally by Hildebrand for a liquid solutions or liquid mixtures. So, initially it was not proposed for polymer solutions, but just for solutions of simple liquids (Refer Time: 41:48). It is found to apply well for polymer solutions as well. So, a it is a useful kind of solubility parameter approach as we will see is a useful approach to get a feel of how soluble a given polymer is in a certain solvent, ok.

So, if we have a polymer, anyway if we are trying to figure out, which solvent will dissolve at the best, then we can calculate the solubility parameters and based on that, we can comment on which solvent will be the best for dissolving this particular polymer.

And, this can essentially be used to screen out certain solvents which this approach predicts to be not good for the particular polymer. Another application of solubility parameter approach can be to figure out for a given network polymer what kind of solvents will lead to the maximum amount of swelling and what kind of solvent will actually lead to minimal swelling.

So, in applications where an network polymer like an elastomeric rubber. If that is exposed to a certain solvent, then if we have some knowledge of how much swelling will occur in the presence of a certain solvent, that basically will help in from the application perspective.

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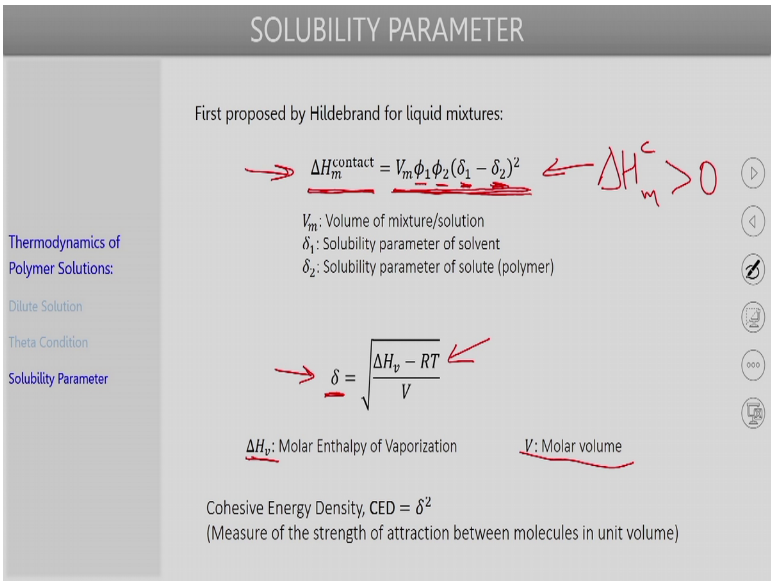

SOLUBILITY PARAMETER

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter

First proposed by Hildebrand for liquid mixtures:

$$\Delta H_m^{contact} = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

$\Delta H_m^c > 0$

V_m: Volume of mixture/solution
δ_1: Solubility parameter of solvent
δ_2: Solubility parameter of solute (polymer)

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V}}$$

ΔH_v: Molar Enthalpy of Vaporization

V: Molar volume

Cohesive Energy Density, CED = δ^2
(Measure of the strength of attraction between molecules in unit volume)

So, the solubility parameter approach or the solubility parameter was first proposed as (Refer Time: 43:14) just discussed by Hildebrand. It was introduced to define the enthalpy change of mixing of liquid solutions or liquid mixtures.

So, for our case, the kind of terminology that we are using that would correspond to that delta H of mixing the contact delta H of mixing or the contact enthalpy of mixing. So, the delta H of mixing the contact term resulting for intermolecular interactions Hildebrand proposed that it is given by an expression like this.

So, this contact enthalpy of mixing Hildebrand proposed that, this contact enthalpy of mixing basically can be expressed in terms of the volume of the mixture solution formed as well as the respective volume fractions phi 1 phi 2 of the 2 components and the square of the difference of these 2 parameters which are referred to as a solubility parameter of the 2 components.

So, again, as we have been the convention that we have been using is that subscript one denotes the solvent substitute denotes the solute or the polymer. So, here also delta 1 is the solubility parameter of the solvent and delta 2 is the solubility parameter of the solute. So, one thing to note here is that this delta H m contact that this Hildebrand's approach gives it will always be positive because, everything on the right hand side here every term is positive.

So, it can only describe systems where the delta H of mixing or enthalpy change of mixing is positive and that is fine for a lot of systems. But, there are many systems where the enthalpy change of mixing actually is negative. Especially, for systems where hydrogen bonding and such directional effects are interactions are prevalent.

So, that the delta H of mixing actually can be negative so, this approach actually does not describe such solutions properly. So, the solubility parameter that appears in the delta H term here delta H term in the Hildebrand expression that solubility parameter is basically define as shown here. So, it is defined as the square root of the ratio of the, what is called the energy of change of vaporization divided by the molar volume of the mixture or the solution that is formed.

So, this energy change of vaporization, if the vapor is assumed to be ideal, the energy change of vaporization that can be expressed in terms of the molar enthalpy of vaporization delta H v minus R T. So, this corresponds to the numerator corresponds to the energy change of vaporization or energy change associated with the vaporization process and the denominator V is just the molar volume.

So, square root of this ratio gives the, is how the solubility parameter is defined by Hildebrand and the square of this. So, the square of the solubility parameter delta square that is referred to as what is called the Cohesive Energy Density or CED. So, this cohesive energy density again as a name suggests, it is measure of the strength of interaction in our solution a per unit volume. So, it is a measure of the interaction strength density ok. That is why, it is refer to as cohesive energy density and it is just square of the solubility parameter.

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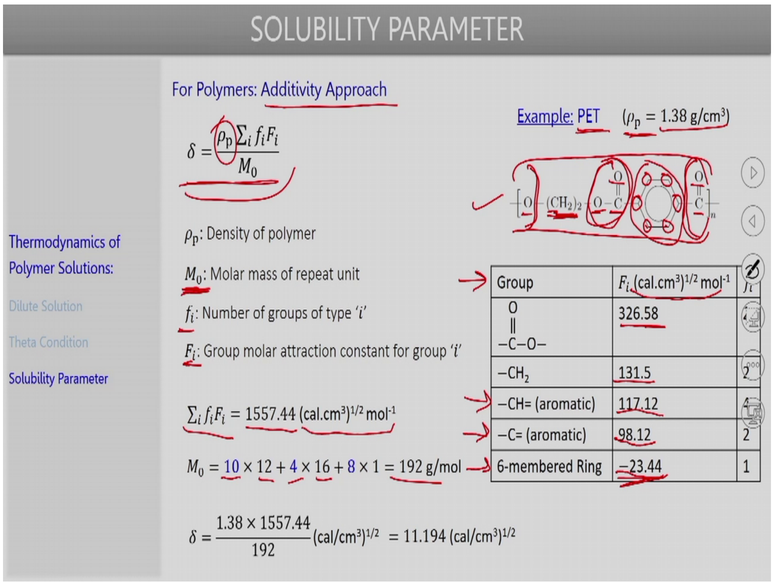

SOLUBILITY PARAMETER

For Polymers: Additivity Approach

$$\delta = \frac{\rho_p \sum_i f_i F_i}{M_0}$$

ρ_p: Density of polymer

M_0: Molar mass of repeat unit

f_i: Number of groups of type 'i'

F_i: Group molar attraction constant for group 'i'

$\sum_i f_i F_i = 1557.44\ (\text{cal.cm}^3)^{1/2}\ \text{mol}^{-1}$

$M_0 = 10 \times 12 + 4 \times 16 + 8 \times 1 = 192\ \text{g/mol}$

$$\delta = \frac{1.38 \times 1557.44}{192} (\text{cal/cm}^3)^{1/2} = 11.194\ (\text{cal/cm}^3)^{1/2}$$

Example: PET ($\rho_p = 1.38\ \text{g/cm}^3$)

Group	F_i (cal.cm^3)$^{1/2}$ mol^{-1}	f_i
$-\overset{O}{\overset{\Vert}{C}}-O-$	326.58	[illegible]
$-CH_2$	131.5	2
$-CH=$ (aromatic)	117.12	4
$-C=$ (aromatic)	98.12	2
6-membered Ring	−23.44	1

So, the definition that we just discussed for solubility parameter it involves the molar volume as well as the enthalpy of vaporization, right.

So, the enthalpy of vaporization for liquids consisting of simple molecules, the enthalpy vaporization is something that is readily measurable. So, for simple solvents like let us say acetone or ethanol or toluene, the enthalpy of vaporization can be measured and it is well known and widely reported in various handbooks. But, if we try to apply that same formula to determine the solubility parameter of a polymer, then we run into problems because polymers will typically be non-volatile materials.

So, measuring or estimating enthalpy of vaporization is normally not possible. So, in general, for any non-volatile material the previous formula, which is a definition of the solubility parameter does not apply very well. So, for the polymers, a an approach that is commonly adopted to get a measure of the solubility parameter is what is called the additivity approach in this approach the solubility parameter is defined using the expression that shown here.

So, delta is given by the density of the polymer multiplied by summation of number of groups of a certain time multiplied by what is called the group molar attraction constants F i and whole thing divided by the molar mass of a repeat unit. So, this additivity approach basically assumes that the overall behavior of these molecules can be described by considering the contributions from the individual sub groups are small; smaller groups of molecules that constitute the bigger molecule.

So, these smaller groups they took their contribution can be added together to get the effect for the entire molecule. So, that is the philosophy behind this additivity approach and for a polymer molecules determining that delta of using additivity approaches seem to give reasonably good results for a many polymers although, further refinements to this approach have been done by others especially by Van Krevelen.

So, this additivity approach in many cases gives good estimates, but more refined and more sophisticated approaches starting from this kind of an approach are also available. If we consider this additivity approach, this F here which refers to as the group molar which is referred to as the group molar attraction constant F is these the values of these group molar attraction constants are listed for a wide range of groups. These are available in standard handbooks and such values can be used from such sources and through the use of such value the delta or the solubility parameter for polymers can be obtained.

The small f i here is the as we just discuss a number of groups of a particular type present in a given repeat unit.

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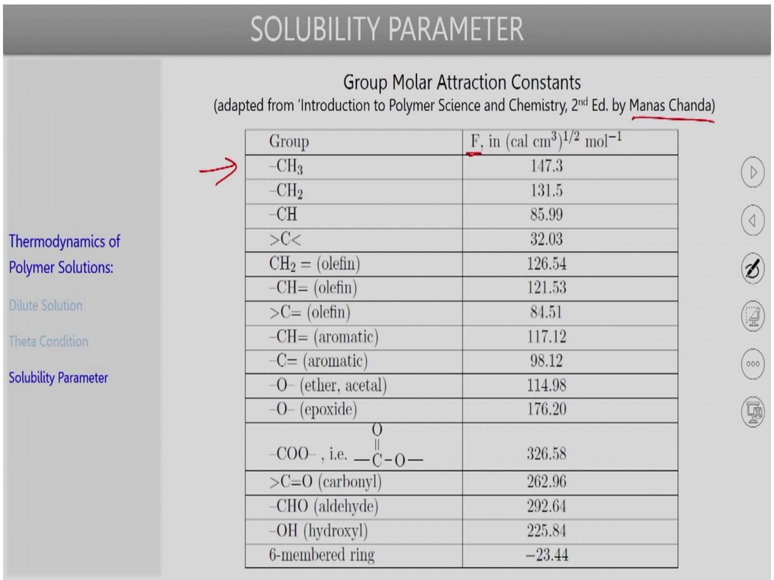

SOLUBILITY PARAMETER

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter

Group Molar Attraction Constants

(adapted from 'Introduction to Polymer Science and Chemistry, 2nd Ed. by Manas Chanda)

Group	F, in $(\text{cal cm}^3)^{1/2}\ \text{mol}^{-1}$
$-CH_3$	147.3
$-CH_2$	131.5
$-CH$	85.99
$>C<$	32.03
$CH_2 =$ (olefin)	126.54
$-CH=$ (olefin)	121.53
$>C=$ (olefin)	84.51
$-CH=$ (aromatic)	117.12
$-C=$ (aromatic)	98.12
$-O-$ (ether, acetal)	114.98
$-O-$ (epoxide)	176.20
$-COO-$, i.e. $-\overset{O}{\overset{\parallel}{C}}-O-$	326.58
$>C=O$ (carbonyl)	262.96
$-CHO$ (aldehyde)	292.64
$-OH$ (hydroxyl)	225.84
6-membered ring	−23.44

So, the group molar attraction constants the listings are available here representative table for some typical groups that are found in many polymer systems. A polymer molecules that listing is provided here. It is adapted from a book by Manas Chanda and that book itself also takes these values from the work of a high and small and other researchers.

So, here we see that for different kinds of groups the value of this F the molar group molar attraction constant these are there and this is just a representative list for some common groups for many other groups such the values of f are actually listed in literature. So, these f values are readily available and next, what we can do is just try to work an example and see how this approach can be applied to calculate the solubility parameter of a typical polymer molecule.

So, let us consider the example of P E T which is polyethylene terephthalate, which is a very common aromatic polyester. It is has wide range of application in textile industry in packaging. So, bottles for many soda, soft drinks. They are made up of P E T many fabrics are made up of polyester fibers. So, P E T is a widely used polyester and the density of amorphous P E T is around 1.38 gram per centimeter cube.

So, that is what that that is a value that will take for rho p in this formula. So, we also want to find out the molar mass of a repeat unit of our polymers. So, for that let us draw the chemical structure of P E T. So, the P E T basically consists of this repeating shown here and this repeating it is repeated many times along the length of the chain to get the entire polymer molecules.

So, the m naught the parameter m naught here that will just be the molar mass of this repeat unit. Next, the group molar attraction constants F i and the corresponding numbers of such groups small f i those we have tried to list in this table here for this particular repeat unit. So, we see that there are 2 COO groups and the COO groups from the table that we just saw the COO group. The F i value is 326.58 and in our repeat unit they are 2 actually to such COO groups.

So, apart from the one that is here we have, another one which is this part here. So, 2 COO groups are here. So, we have 2 small f i is 2 and Ch 2 group also there are 2 Ch 2 groups.

So, that is what we have here. If you consider this aromatic 6 membered ring here, it contains 4 1 2 3 4 Ch groups which are incorporated here and these 2 are actually just C groups. So, C in an aromatic ring that is what these 2 are and finally, because we have a 6 membered ring, an additional term actually comes in when we have 6 membered rings and that value is also taken in here.

So now that we have all these values of F i and small f i we can what we can do is carry out this summation. So, in each case, multiply the number of groups present times the group molar attraction constant for that group and sum take the sum for all the groups present. So, we will get 2 multiplied by 326.58 plus 2 multiplied by 131.5 plus 4 multiplied by 117.12 plus 2 multiplied by 98.92 plus 1 multiplied by this 23.44.

So, if we add all the terms of we get 1557.44 and this is the unit that we are working with because, that that is the unit in which this F i is reported next, the molar mass of the repeat unit. So, we see that there are actually if you consider carbon atoms first, there are 2 carbon atoms here one here one here. So, 4 plus 6 carbon atoms in the 6 membered ring present. So, we have 10 carbon atoms and if we approximate the molar mass of carbon to be 12 gram per mole.

So, you get 10 times 12 plus we have a 4 oxygen atoms. We have one oxygen atom; here is one here one here one here. So, 4 oxygen atoms are present and each if we consider the molar mass to be 16, then that is 6 4 times 16 and we have 8 hydrogen atoms. So, 4 hydrogen atoms are present here and 4 molar present at the 4 positions in the 6 membered ring. So, 8 hydrogen atoms.

So, total molar mass comes out to be 192 gram per mole and the delta solubility parameter by substituting all the values in the formula for solubility parameter using the additive approach finally comes out to be around 11 calorie per centimeter cube to the power half.

So, this value is actually comparable to what is reported for P E T. It is slightly higher, but it is still in reasonable agreement. So, this additivity approaches something that can be used to estimate the solubility parameter of polymers.

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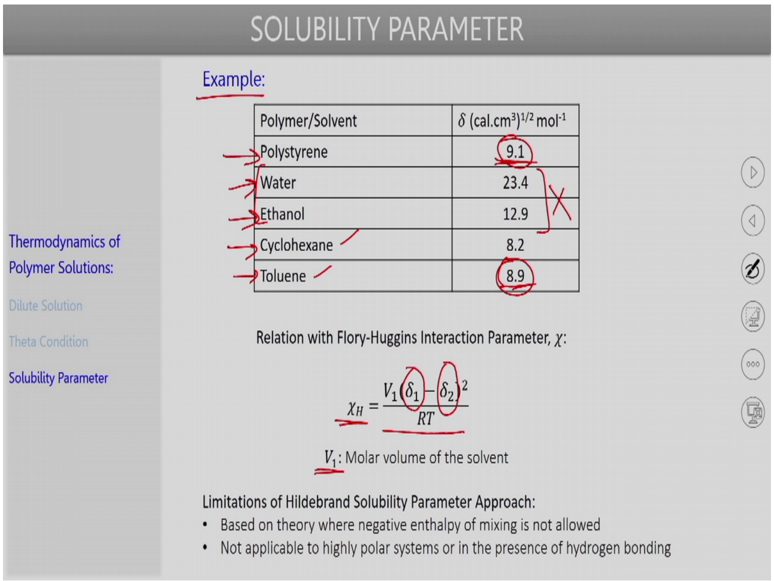

SOLUBILITY PARAMETER

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter

Example:

Polymer/Solvent	δ (cal.cm^3)$^{1/2}$ mol^{-1}
Polystyrene	9.1
Water	23.4
Ethanol	12.9
Cyclohexane	8.2
Toluene	8.9

Relation with Flory-Huggins Interaction Parameter, χ:

$$\chi_H = \frac{V_1(\delta_1 - \delta_2)^2}{RT}$$

V_1: Molar volume of the solvent

Limitations of Hildebrand Solubility Parameter Approach:

- Based on theory where negative enthalpy of mixing is not allowed
- Not applicable to highly polar systems or in the presence of hydrogen bonding

Now, let us see how this solubility parameter is useful in predicting the predicting the solubility of a polymer in a solvent. So, if we recall the expression for the delta H of mixing, the Hildebrand expression which was V m multiplied by phi 1 phi 2 multiplied by delta 1 minus delta 2 square.

So, the minimum value that that expression can have is 0. It cannot be negative and if and that minimum value will be attained when delta 1 is equal to delta 2. So, normally a polymer and solvent are said to be highly miscible or a polymer said to be readily dissolve in a solvent if the solubility parameter values are comparable or close.

So, larger the difference between the solubility parameter of the polymer and the solvent the correspondingly the larger will be the enthalpy change of mixing larger positive value will then enthalpy change of mixing have and that will basically not favor mixing.

So, if you consider an example where we have consider poly styrene as a polymer. It is solubility parameter is around 9.1. If you consider 4 solvents water ethanol cyclohexane toluene. So, based on a comparison, what we can say is see is that toluene has a solubility parameter which is closest to this 9.1 value for polystyrene. So, this solubility parameter approach will suggest that toluene is the best solution for polystyrene amongst the ones that are listed here.

So, if we if we just were trying to compare the solubility behavior of polystyrene in cyclohexane and toluene and if we use the solubility parameter approach of Hildebrand, then would have we would have in fine and since toluene is closer to polystyrene in terms of the delta value, we can say that toluene is better solvent for polystyrene. But, this Hildebrand solidity parameter approach is actually not applicable to these 2 solvents because, these 2 solvents are quite polar and so, presence of hydrogen bonding as well.

So, for these 2 solvents, one can one should basically avoid the direct use of solubility parameter approach of Hildebrand to predict solubility apart from that the fact that hydrogen bonding and those things can also happen that also has to be taken into account. So, for this case, since polystyrene is pretty much a kind of hydrophobic polymeric materials so, anyways these 2 will not be very good solvents, but in general, solubility parameter approach we should not use indiscriminately for cases where polar interactions or hydrogen hydrogen bonding is dominant, ok.

Now, this solubility parameter that we have discussed just now it can also be related to the Flory Huggins interaction parameter. So, solubility parameter is we just saw is it can describe the solubility of a polymer in a solvent and Flory Huggins interaction parameter. We earlier saw that it describes a polymer solvent interaction as well.

So, it is natural that the 2 should be connected and the relation between the enthalpy component of the Flory Huggins interaction parameter and the solubility parameter is this expression here. Here, V 1 is the molar volume of the solvent delta 1 is the molar or the solubility parameter of the solvent delta 2 is the solubility parameter of the polymer.

So, again to reiterate a polymer will be highly soluble in a given solvent if it is solubility parameter is close to the solubility parameter of that solvent and if the delta 1 minus delta 2, this difference is large. Then the solubility will become relatively poorer. Finally, just to conclude, just we will discuss a couple of limitations of this Hildebrand solubility parameter approach for estimating the solubility of polymers in solvents.

So, we saw that the delta H of mixing expression that that is a foundation of this theory or this approach that basically does not predict a negative delta H of mixing. It can only predict positive delta H of mixing or 0 delta H of mixing.

So, for solutions where the enthalpy change of mixing is negative, specially where hydrogen bonding in such or such interactions are present. For such cases, this approach is not advisable and for the same reason, any in any system where either the polymer or the solvent or both have a strong polar interactions or hydrogen bonding kind of interactions. Then, Hildebrand Hildebrand solubility parameter approach should not; should be avoided because of the limit inherent limitations there.

So, for systems where we have polar interactions or hydrogen bonding actually, other more complex solubility parameters have been proposed; one such parameter is that by Hansen. So, Hansen has proposed at not one, but 3 solubility parameters for any given solvent or polymer and the solubility parameter basically contains a dispersion term a polar interaction term and hydrogen bonding term.

So, all those are explicitly accounted for in this course, we will not go into further detail of the Hansen solubility parameter approach. But, it is something which one can employ if one is dealing with polar systems.

So, we will conclude today’s lecture and in summary what we discussed today is how the Flory Huggins theory if applied to a dilute polymer solution, how it quantitatively of course, is not expected to give any good results because it is not a good theory for dilute solutions. But, how qualitatively it actually predicts certain trends which is consistent with an in agreement with the predictions of more sophisticated theories as well. And in particular, we found that at certain special conditions.

So, for a given polymers solvent system at certain special temperatures, the polymer solution can start behaving ideally such conditions referred to as theta condition and the corresponding temperature is referred to as a theta temperature. And finally, we also discussed the solubility parameter approach which is useful to get an estimate of how soluble a given polymer will be in set of solvents or in a particular solvent.

So, we will continued the discussion on polymer thermodynamics in 1 or 2 more lectures and they will look at the phase behavior in more detail. Especially, from the point of view of a phase separation and we will also after that briefly discuss the thermodynamics of polymer blends and copolymers.