Introduction to Polymer Physics
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Lecture- 09
Determination of Polymer Molar Mass: Osmometry

Hello everyone. So, in the last few lectures we have been talking about the thermodynamics of polymer solutions. In the last lecture we also discussed little bit about the thermodynamics of polymer blends and block o polymers. So, now, in today's lecture and in the few lectures that we will follow we will be talking about the determination of polymer molar mass. So, in the very introductory first lecture we discussed that there can be many different types of average molar mass is defined for a polymer sample because a given polymer sample little consist of chains of different lengths.

In today's class and in the following few classes we will be talking about different methods that are used to determine the different average molar masses that we have discussed in the first lecture. So, in today's lecture the focus will be on techniques that are used to determine the number average molar mass. It would be advisable to go back to lecture 1, so that you get an idea of how this average molar masses are defined.

In lecture 1 we defined 4 kinds of average molar masses a number average molar mass, a weight average molar mass, z average molar mass and viscosity average molar mass. So, out of these 4 we will discuss methods that are used to determine number average molar mass, the weight average molar mass and the viscosity average molar mass we will not be talking about any methods that are used to find out the z average molar mass

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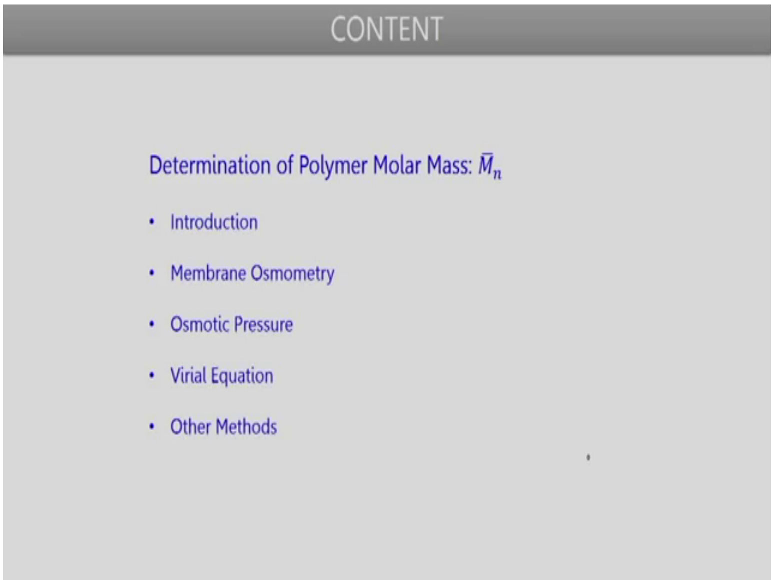

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- Other Methods

In today's lecture we will the content is basically initially an introduction to the topic and then description of the most common method that is employed for determining the number average molar mass and that is Membrane Osmometry. So, we will be talking about this method in more detail and there after we will be discussing the mathematical details of the concept of Osmotic Pressure and how can we can develop equations that can be used to find out the osmotic pressure and from there how one can actually obtain the number average molar mass.

And we will also discuss the concept of Virial Equation as it is defined for osmotic pressure and towards end we will just briefly touch upon some other methods which are also used to calculate the number average molar mass although the detail focus today will be only on membrane osmometry.

So, since we will be discussing some topics which are related to thermodynamics of polymer solutions today it is also advisable that you go back and have a look at lectures 5 and 6 where the Flory Huggins theory as it applies to dilute polymer solutions has been developed and equations for chemical potentials have been derived starting from the Flory Huggins theory. Because these are some of the equations that we will use our in our current in discussion.

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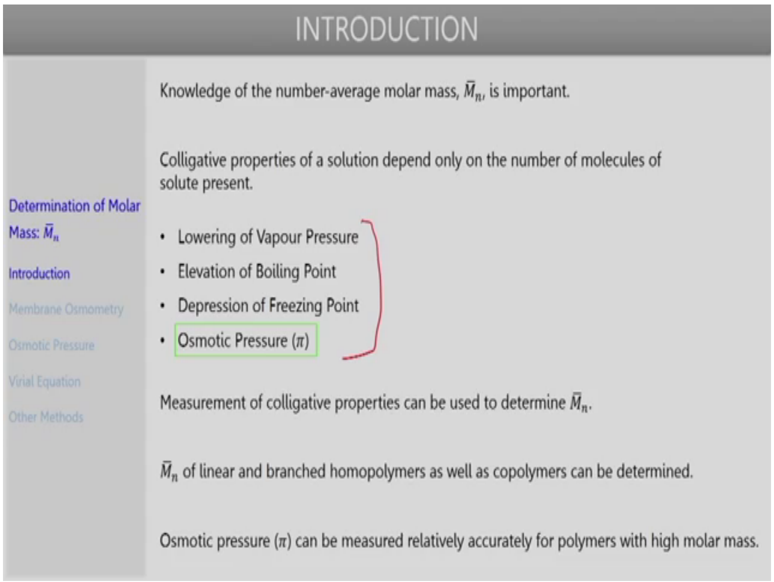

INTRODUCTION

Determination of Molar Mass: $\bar{M}_n$

Introduction

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Knowledge of the number-average molar mass, $\bar{M}_n$, is important.

Colligative properties of a solution depend only on the number of molecules of solute present.

- Lowering of Vapour Pressure
- Elevation of Boiling Point
- Depression of Freezing Point
- Osmotic Pressure (π)

Measurement of colligative properties can be used to determine $\bar{M}_n$.

$\bar{M}_n$ of linear and branched homopolymers as well as copolymers can be determined.

Osmotic pressure (π) can be measured relatively accurately for polymers with high molar mass.

Determination of or knowledge of this number average molar mass is important because it is seen that many macroscopic properties of polymers actually depend on the number average molar mass. So, finding out number average molar mass and knowledge of this quantity is important. So, we will see later on that properties like the glass transition temperature even the melting point these things are dependent on them average molar mass of polymers so, measuring these quantities is average molar masses is of importance.

Let us see what are the properties that can be measured through which number average molar mass can be determined, one class of methods for determining number average molar mass actually uses what is called the measurement of colligative properties. So, colligative properties if you recall it something that should be familiar to most of you, colligative properties are properties of a solution which depend only on the number of solute molecules that are present in the solution.

So, a colligative property will not depend on the nature of the solute or the size of the solute it will simply be proportional to the number of solute molecules present in a given volume of your solution. So, typically the 4 common colligative properties that are there are listed right here. So, first one is the, what is called a lowering of solvent vapour pressure. So, on addition of a non volatile solute to a solvent a lowering of the solvent vapour pressure is observed. So, that is a colligative property and the amount by which the solvent vapour pressure lowers is seen to be proportional to the number of molecules of solute present.

Similarly a elevation in boiling point of a solvent when again a non volatile solute is added to it so, that is also colligative property. Depression in freezing point where addition of a solute leads to lowering of the freezing point of a solvent so, that is the third colligative property. And, what is called the osmotic pressure that is the fourth colligative property and this is the property that we will look at in more detail in today’s lecture because that is the property whose measurement will be studying for determining the number average polymer molar mass.

As we discussed now n the measurement of any of those this 4 colligative properties can be used to determine the M n bar or the number average molar mass and the number average molar mass that we find out it can be determined for linear as well as branch polymers as well as for homo polymers as well as copolymers. So, it is a versatile technique and it does not it is not something that is valid only for linear polymers, it can be used for branched polymers as well. And the reason why it can be used for the different architect polymer architectures is that the properties, the colligative properties depend only on the number of solute molecules present and not on the size or nature of solute as we discussed before.

So, that is why the number average molar mass for all these different types of polymer architectures can be obtained through the measurement of these colligative properties. Out of the 4 that we have listed here it turns out that the measurement of osmotic pressure for a given polymer is actually can be carried out most conveniently and accurately. If we talk about polymers having high molar masses it turns out that the lowering of vapour pressure or the elevation of boiling point or the depression of freeze freezing point. These kind of effects are produced when a polymer of high molar mass is added to a solvent.

The magnitude of the effect produce is actually quite small. So, if the polymer polymerize has a quite high molar mass then the effect produce will be so, small that it will be very difficult to accurately measure that effect. So, for example, let us say if we want to measure the molar mass of a sample where the molar mass is of the order of 10 to the power 5 or 10 to the 6 gram per mole. So, in that case the low lowering of vapour pressure effect or the elevation of boiling point depression of freezing point these effects the magnitude of these effects produce will be very small and using the common measurement techniques available the magnitude the effect cannot be accurately measured.

Whereas, for osmotic pressure even if the polymer molar mass is quite high up to let us say even 1 million gram per mole even then appreciable and measurable effect is seen and the osmotic pressure can be measured relatively accurately. So, that is why we will focus more on the technique where osmotic pressure is measured and from there the number average molar mass is determined in the present lecture.

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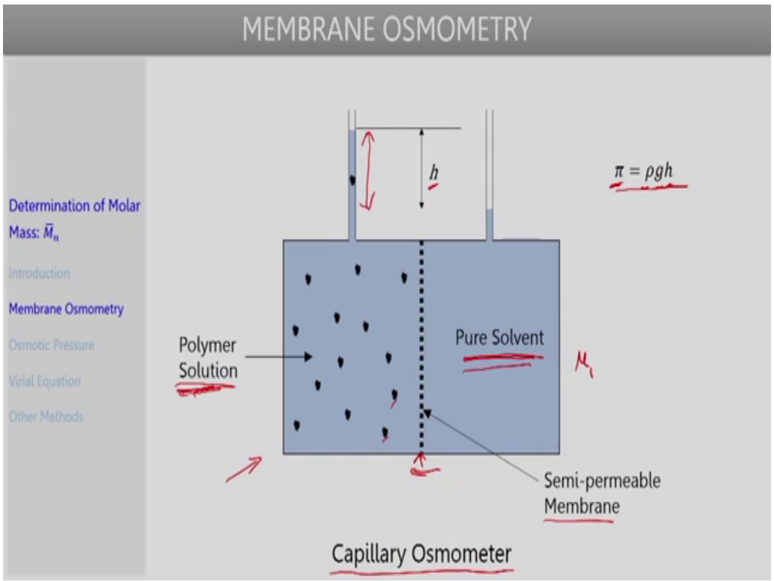

MEMBRANE OSMOMETRY

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Capillary Osmometer

Let us talk about the concept of osmotic pressure first because that is the property colligative property that we will be using for determining the polymer molar mass. Osmosis as most of you might know is a phenomenon where flow of solvent molecules takes place from a pure solvent chamber to a solution chamber across the semi permeable membrane.

So, if we look at the schematic that is drawn here or the diagram that is drawn here this device is referred to as a capillary osmometer and it is something that can be used to measure the osmotic pressure for a given polymer solution. So, what is done is on in one chamber that is the chamber on the right side in this case, pure solvent is placed and on the in the other chamber which is the left chamber here polymer solution is placed.

So, the polymer solution contains the solvent as well as this polymer molecules that are shown here and of course, things are not shown to scale here for ease of representation. So, polymer molecules of course, will be much smaller than what show shown here, but just for the ease of representation we are showing the polymer molecules like this.

Now, we have a semi permeable membrane here this membrane here this is semi permeable and what; that means, is that it only allows the passage of solvent molecules across it, but does not allow the larger size polymer molecules to pass through it. So, that is why flow through this membrane can only take place from right to left because only solvent can pass through and polymer molecules cannot pass through and why the flow will take from right to left only of the solvent molecule is because the initially if we consider just a pure solvent in the polymer solution and initially if they are at the same pressure.

Then what will happen is that, in the pure solvent chamber the chemical potential of the solvent which is let us say is mu 1. So, this mu 1 the chemical potential of the solvent will be higher in higher in this pure solvent chamber and the chemical potential of the solvent in the solution chamber will be lower. So, flow will flow of the solvent molecules will take place down this chemical potential gradient from the right chamber of pure solvent containing pure solvent to the left chamber containing the polymer solution and as the flow takes place what will happen is slowly in the solution chamber there in that is in the left chamber the pressure will start to increase.

So, what we see here is that in the left chamber the pressure is higher than the right chamber and that is why there is this extra height of this column of liquid that is present in the polymer solution chamber. So, as flow take place the pressure in the left and chamber that which contains the polymer solution will increase and ultimately equilibrium will be established where the chemical potential of the solvent in the pure solvent chamber as well as the solution chamber will become equal. And when this condition of chemical equilibrium is established then no further flow will take place across the semi permeable membrane.

So, at that point the left chamber contain the polymer solution will have a higher pressure then the right chamber and this difference in pressure between these 2 chambers that is what is referred to as the osmotic pressure. So, typically osmotic pressure is represented by this symbol pi and in this case it simple to determine this osmotic pressure because if we know that the heights of the liquid columns differ by this quantity h on the 2 sides, then just rho times g times h just from standard fluid, fluid static formula gives us the osmotic pressure.

So, osmotic pressure will be given by the density of the solvent times the accession due to gravity times the height difference between the columns liquid columns on the 2 sides. Now, that we have defined or we have discussed this set of for measuring osmotic pressure let us look into the thermodynamics of it.

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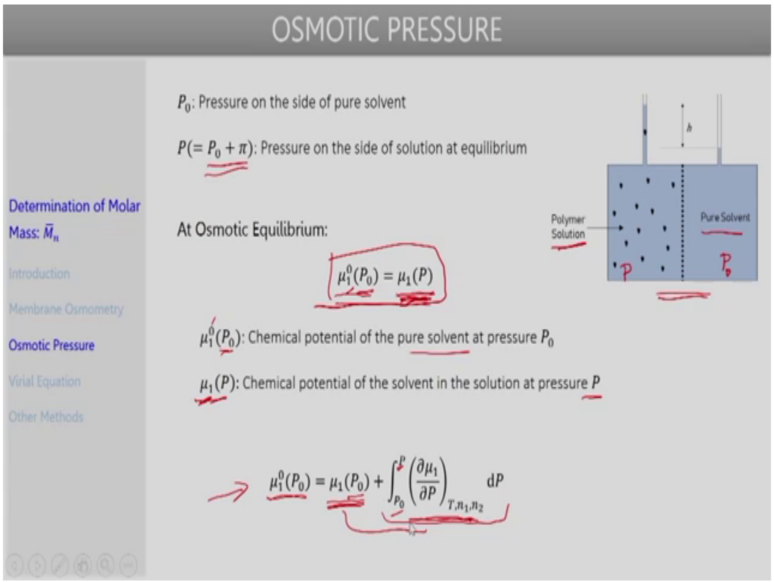

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P_0: Pressure on the side of pure solvent

$P(= P_0 + \pi)$: Pressure on the side of solution at equilibrium

At Osmotic Equilibrium:

$$\boxed{\mu_1^0(P_0) = \mu_1(P)}$$

$\mu_1^0(P_0)$: Chemical potential of the pure solvent at pressure P_0

$\mu_1(P)$: Chemical potential of the solvent in the solution at pressure P

$$\rightarrow \mu_1^0(P_0) = \mu_1(P_0) + \int_{P_0}^{P} \left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} dP$$

Again, we will consider that same set of that we had discussed in the previous slide and here let us say that P naught is a pressure on the side of pure solvent add equilibrium. So, now, do we are talking about case were equilibrium is established on the 2 sides so, that there is no flow taking place now. And when equilibrium is established let us say the pressure on the side of pure solvent is P naught.

So, let us say the pressure here is P naught and let us say the pressure here is just P pressure on the polymer solution side add equilibrium again. So, a that difference between these pressures as we discussed is osmotic pressure. So, this P we can simply write as P naught plus pi this P will be higher than P naught of course, and the it is value will be P naught plus pi where pi is osmotic pressure.

Now, at equilibrium if we talk about the condition of equilibrium we can set it in terms of equality of chemical potentials. So, if we focus on the solvent phase or the solvent species not solvent phase. So, this condition for osmotic equilibrium will be that the chemical potential of the solvent in the pure solvent side becomes equal to the chemical potential of the solvent in the solution side, only then will equilibrium be established and no flow will take place after that.

So, this equality here on the left hand side we have mu 1 naught at P naught. So, this mu 1 naught is a subscript 1 as we whereas, we know stands for the solvent in our discussions. So, this mu 1 naught is the chemical potential of the pure solvent this naught here this one this denotes that we are talking the pure solvent and this chemical potential is defined at this pressure P naught which is the pressure of on the pure solvent side.

This mu 1 is the chemical potential again of the solvent, but in the solution. So, whatever solvent is present in this polymer solution in this is the chemical potential of that solvent and that is at a pressure P so, this mu 1 will be at pressure P. So, these 2 these 2 chemical potential should be equal for equilibrium to be established.

In starting from this condition of osmotic equilibrium what we can do is, the left hand side we will just keep as it is, on the right hand side this mu 1 at pressure P that we can write it as mu 1 at pressure P naught plus this integral of this change in the this chemical potential mu 1 with respect to pressure from P naught to P. Basically we are what we are doing here is, on the solution side we are first considering a term which is the chemical potential at pressure P naught plus we are adding this extra term which accounts for the change in chemical potential as we give go from pressure P naught to P on the solution side. Some of these 2 will basically give us this quantity again, we have just taken this equilibrium condition and restated it in this way. Now, let us see if we can simplify this partial derivative here and proceed further.

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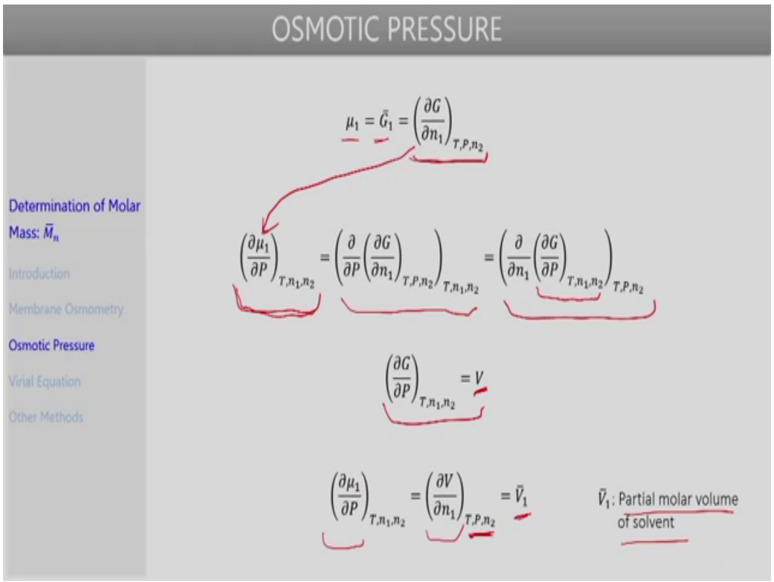

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$$\mu_1 = \bar{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} = \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}\right)_{T,n_1,n_2} = \left(\frac{\partial}{\partial n_1}\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}\right)_{T,P,n_2}$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} = V$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = \bar{V}_1$$

$\bar{V}_1$: Partial molar volume of solvent

For that let us go back to the definition of chemical potential. So, we have again while discussing solution polymer solution thermodynamics, we have introduced to the concept of partial molar properties and we discussed that chemical potential is nothing, but the partial molar Gibbs free energy. So, this mu 1 will be nothing, but the partial molar Gibbs free energy of the solvent and that is defined using this expression.

So, del G del n 1 at constant temperature pressure and the constant number of moles of the solute, once we have this definition then we can what we can do is consider this term which appeared in the previous slide so, this the term that we want to simplify. So, in this term we what we are doing is substituting this expression for mu 1 here. So, upon substitution we get this term here and since we have now 2 partial derivatives, one is with respect to n 1 and the other with respect to P.

What we can do is, just interchange the order of partial derivatives and doing that we will get this term here. So, from here what we see is the, we get this term in here now which is del G del P at constant T, n 1, n 2 which means that the partial derivative of Gibbs free energy with respect to pressure at constant temperature and composition. So, from thermodynamics we know that this partial derivative is nothing, but the total volume of your our solution.

So, now that we have all these equations here we can combine them and what we end up with is this del u del mu and del P is equal to del V del n 1 and at constant T, P, n 2 and this del V del n 1 and at constant T P and n 2 that is the definition of the partial molar volume of the solvent. So, what we finally, get is that this partial derivative of a chemical potential of the solvent with respect to pressure that comes out to be equal to just the partial molar volume of the solvent.

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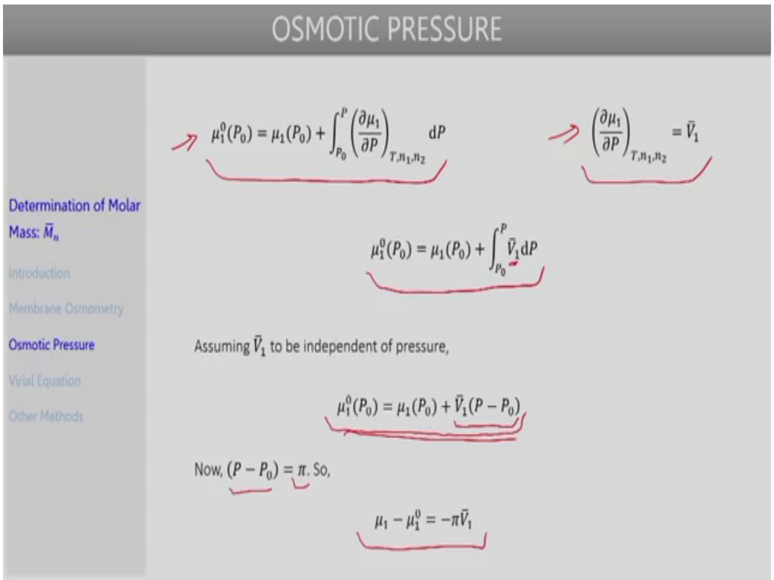

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$$\underbrace{\mu_1^0(P_0) = \mu_1(P_0) + \int_{P_0}^{P} \left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} dP} \qquad \underbrace{\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} = \bar{V}_1}$$

$$\underbrace{\mu_1^0(P_0) = \mu_1(P_0) + \int_{P_0}^{P} \bar{V}_1 dP}$$

Assuming $\bar{V}_1$ to be independent of pressure,

$$\underbrace{\mu_1^0(P_0) = \mu_1(P_0) + \bar{V}_1\underbrace{(P - P_0)}}$$

Now, $\underbrace{(P - P_0)} = \underbrace{\pi}$. So,

$$\underbrace{\mu_1 - \mu_1^0 = -\pi \bar{V}_1}$$

So, now, proceeding from here again we just write down the expression that we had obtained for the osmotic equilibrium couple of slides back. So, that is this equation and this is the equation that we obtain in the previous slide for partial derivative of new 1 with respect to P and we can combine these 2. So, combining these 2 we just get this equation that shown here and of in here in this equation what we can assume is that this partial molar volume of this solvent that is independent of pressure.

So, this is unless the pressure changes are very high such an assumption is a valid assumption because the volume of a liquid is typically is not a very strong function of pressures, unless the pressure difference between P naught and P is quite high we can safely assume that this V 1 bar is independent of pressure. So, if we make that assumption then we can take this V 1 bar just outside this integral sign and upon integration we just get V 1 bar multiplied by P minus P naught.

So, the overall equation or a condition for chemical equilibrium, equilibrium becomes this and now we have already discussed that this difference in the pressure on the solution side and the pure solvent side that difference is what is called the osmotic pressure so, that is the definition of osmotic pressure. So, instead of P minus P naught if we just write pi which is osmotic pressure then we get the condition for equilibrium in this form. So, it is mu 1 minus mu 1 naught is equal to minus pi times V 1 bar.

So, now the equation that we have derived till now we have not invoked any assumptions which restricted it is application only to polymer solutions. So, this equation is actually quite valid for any kind of solution whether it is ideal or non ideal need not be a polymer solution also. So, it is a general thermodynamic condition because till now we have only used general thermodynamics relations to arrive at this relation.

Now what we will do is, try to apply a expressions derived using the Flory Huggins equations earlier to this condition to the condition that we have here and the we will try to see how this equation osmotic equilibrium condition gets reduced for the case of polymer solution and most specifically for the case of dilute polymer solutions.

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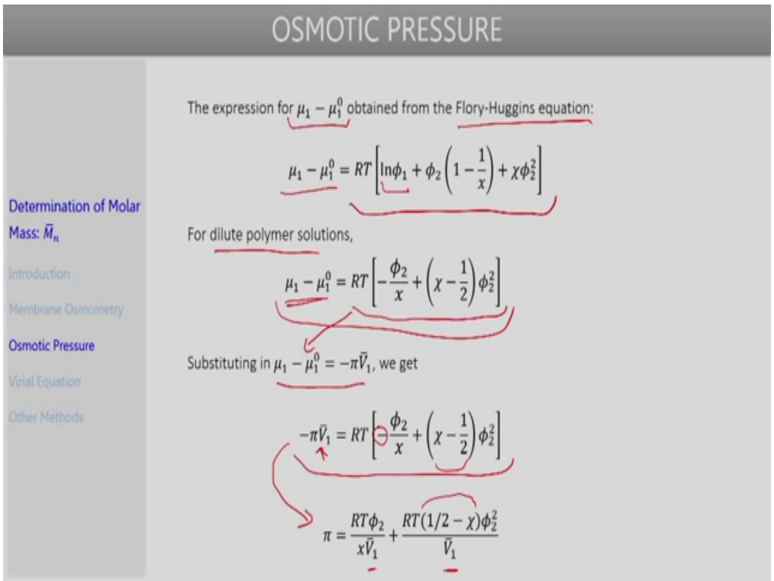

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The expression for $\mu_1 - \mu_1^0$ obtained from the Flory-Huggins equation:

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

For dilute polymer solutions,

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

Substituting in $\mu_1 - \mu_1^0 = -\pi\bar{V}_1$, we get

$$-\pi\bar{V}_1 = RT\left[-\frac{\phi_2}{x} + \left(\chi - \frac{1}{2}\right)\phi_2^2\right]$$

$$\pi = \frac{RT\phi_2}{x\bar{V}_1} + \frac{RT(1/2 - \chi)\phi_2^2}{\bar{V}_1}$$

So, if you recall again from believe lecture 5, the expression that we derive for mu 1 minus mu 1 naught for a polymer solution using the Flory Huggins equation. So, this was for a any polymer solution need not be dilute so, far any polymer solution where Flory Huggins theory equation applies the equation for mu 1 minus mu 1 naught that was derived to be this.

And then what we have done in lecture 6 is, simplified this equation for the case of dilute polymer solution. So, in the case of dilute polymer solution where the polymer concentration is quite low we can basically simplify the terms by doing an expansion of this l n phi 1 and so on. So, all this things we have already done and the expression for dilute polymer solutions that we obtain is what is given here. So, this is something that was discussed in lecture 6 and this is also derived starting from the Flory Huggins equation and read considering very dilute solution case.

So, now that we have this expression for mu 1 minus mu 1 naught and in the previous slide we saw that the condition for osmotic equilibrium is that mu 1 minus mu 1 naught is equal to minus pi times V 1 bar. So, if we combine these equations then we get the condition for osmotic equilibrium for a dilute polymer solution. So, if we substitute this whole expression here in the osmotic equilibrium condition, then we get this equation here which is a the osmotic equilibrium condition for our dilute polymer solution assuming Flory Huggins theory applies.

So, we have discussed previously that Flory Huggins theory actually is not a very good theory for dilute polymer solutions primarily because of the mean field approximation. But here what we are doing is just we will try to develop an expression for the osmotic pressure of polymer solutions using this Flory Huggins theory for dilute polymer solution with the knowledge that it is not very accurate description. And the expression that we get at the end might be qualitatively correct might show trends that are correct, but quantitatively it will not give a good prediction, but in any case we have been using Flory Huggins theory till now. So, we will continue our use of that and try to develop an expression for the osmotic pressure using this Flory Huggins approach.

So, now we from here to here all we have done is taken the minus sign and this V 1 bar on the other side. So, this V 1 bar appears in the denominator here in these 2 terms and because the minus sign also has been taken on the other side so, this minus sign disappears and instead of chi minus half we get a half minus chi here. So, this is the expression for our osmotic pressure that we have derived using Flory Huggins equation for dilute polymer solutions.

Now, let us see if we can further simplify it so, what we have right now does not contain any number average molar mass term right and our aim is to basically develop an expression where the osmotic pressure is related to this number average molar mass so, that the measurement of the osmotic pressure can be used to determine the number average molar mass. So, let us further simplify the equation that we have developed here so, as to obtain a relation between the osmotic pressure and the number average molar mass.

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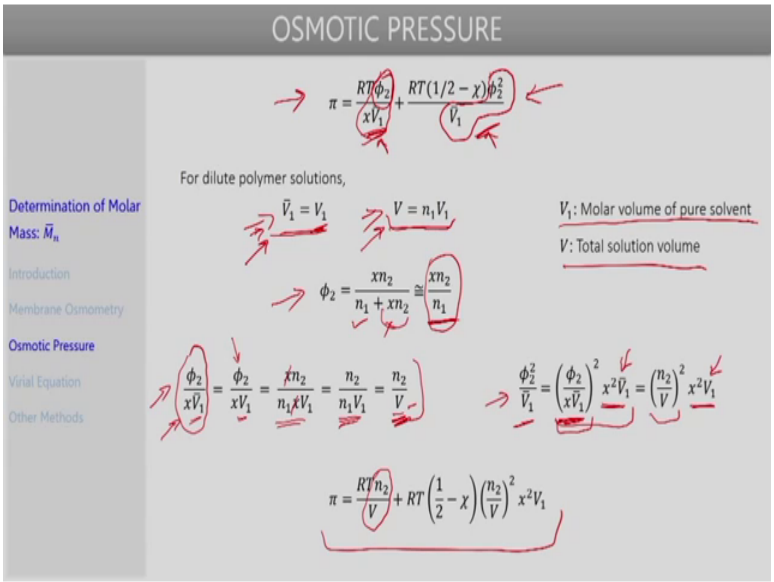

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$$\pi = \frac{RT\phi_2}{x\bar{V}_1} + \frac{RT(1/2-\chi)\phi_2^2}{\bar{V}_1}$$

For dilute polymer solutions,

$$\bar{V}_1 = V_1 \qquad V = n_1 V_1$$

V_1: Molar volume of pure solvent

V: Total solution volume

$$\phi_2 = \frac{xn_2}{n_1 + xn_2} \cong \frac{xn_2}{n_1}$$

$$\frac{\phi_2}{x\bar{V}_1} = \frac{\phi_2}{xV_1} = \frac{\cancel{x}n_2}{n_1\cancel{x}V_1} = \frac{n_2}{n_1V_1} = \frac{n_2}{V} \qquad \frac{\phi_2^2}{\bar{V}_1} = \left(\frac{\phi_2}{x\bar{V}_1}\right)^2 x^2\bar{V}_1 = \left(\frac{n_2}{V}\right)^2 x^2V_1$$

$$\pi = \frac{RTn_2}{V} + RT\left(\frac{1}{2}-\chi\right)\left(\frac{n_2}{V}\right)^2 x^2V_1$$

So, again this is the equation last equation on the previous slide and here what we can do to start with is first try to develop an expression for this ratio phi 2 by x V 1 bar. So, to do that we will invoke again the assumption of dilute solution that we have already done previously and using that we will make some simplifications and from there we will try to obtain an expression for this ratio as well as this quantity here. So, we will try replace this with quantities that are more easily measurable.

So, for dilute polymer solutions what we can say is that, the partial molar volume of the solvent is approximately equal to the molar volume of pure solvent. So, since a solution is dilute and the number of polymer molecules is very small in the solution so, the partial molar volume of the solvent in the solution is approximately equal to it is molar volume in this pure state. So, here the V 1 as we have discussed the V 1 is the molar volume of the pure solvent then what we are saying is for dilute solution it is approximately equal to the partial molar volume of the solvent in the solution.

Similarly, another assumption that can be made for dilute polymer solution is that this V is just n 1 V 1. So, this V is a total solution volume and what we are saying is that this total solution volume is primarily accounted for by the volume of the solvent and the polymer or the solute volume is negligible.

So, strictly speaking the total solution volume is actually given by n 1 V 1 bar plus n 2 V 2 bar, but here what we are assuming is that that n 2 V 2 bar that solute term is negligible because the solution is dilute and n 1 V 1 bar we can replace by n 1 V 1 because we have assumed that V 1 bar is also equal to V 1. So, that gives us V equal to n 1 V 1 and also for the phi 2 the volume fraction of the solute or the polymer we that of that expression can also be simplified.

So, phi 2 we know that it is defined as x times n 2 divided by n 1 plus xn 2, but since a polymer solution is we are that we are considering is dilute. So, this xn 2 term can be neglected compared to this n 1 term. So, we get phi 2 as approximately xn 2 by n 1. So, with these 3 assumptions this, this and this let just see how this term and this term these 2 terms can be simplified.

First focus on this phi 2 by x V 1 bar term so, we see that upon several steps we end up with fact that phi 2 by x V 1 bar is equal to n 2 by V and let us just go through this step by step to see how we are arrive at this final condition. This phi 2 x V 1 bar in the next step what we can do is replace this V 1 bar by V 1 because the solution is dilute using this equation or this condition.

And in the next step we will replace phi 2 by it is approximate definition here for a dilute solution so, that leads us to this expression and here the x's these 2 x will get cancelled. So, we end up with n 2 by n 1 V 1 and finally, using this condition for the dilute solution we replace n 1 V 1 by V and that gives us n 2 by V as phi 2 over x 2 V 1 bar. So, we have the simplified the this first term here this second term also can be simplified quite easily so, this phi 2 square by V 1 bar.

So, phi 2 square by V 1 bar what we can do is write it, this phi 2 square by V 1 bar we can just rewrite it in this form so, we have multiplied and divided by x square V 1 bar. So, we get this term which is phi 2 by x V 1 bar whole square and this which is multiplied by x square V 1 bar and this term we already see that from here this term is n 2 by V. So, this term here becomes n 2 by V whole square and the that is multiplied by x square V 1 we had V 1 bar earlier, but here it is V 1 only because we have again used this condition where we have assumed that V 1 bar equal to V 1.

So, now that we have simplified these 2 terms we can substitute both this term as well as this term back in this equation and upon that substitution we get the equation that shown here. So, we get pi equal to RT times n 2 by V plus the second term RT half minus chi n 2 by V square times x square V 1. So, we have eliminated the that partial molar volume from our expression, but we can actually further simplify this and we will see that upon some further simplification that term m n bar which is the number average molar mass that will appear in this equation.

So, next what we will do is focus on this term n 2 by V and see how we can further simplify that this term here as well.

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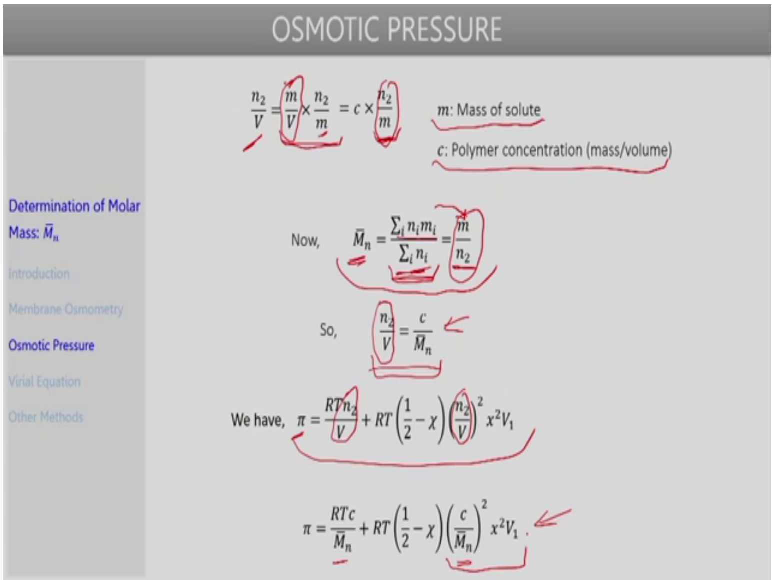

OSMOTIC PRESSURE

Determination of Molar Mass: $\bar{M}_n$

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$$\frac{n_2}{V} = \frac{m}{V} \times \frac{n_2}{m} = c \times \frac{n_2}{m}$$

m: Mass of solute

c: Polymer concentration (mass/volume)

Now, $\bar{M}_n = \frac{\sum_i n_i m_i}{\sum_i n_i} = \frac{m}{n_2}$

So, $\frac{n_2}{V} = \frac{c}{\bar{M}_n}$

We have, $\pi = \frac{RTn_2}{V} + RT\left(\frac{1}{2} - \chi\right)\left(\frac{n_2}{V}\right)^2 x^2 V_1$

$$\pi = \frac{RTc}{\bar{M}_n} + RT\left(\frac{1}{2} - \chi\right)\left(\frac{c}{\bar{M}_n}\right)^2 x^2 V_1 .$$

So, now let us look at this quantity n 2 by V so, n 2 by V we can rewrite in this form we have where we have divided and multiplied by this quantity m. So, m here is nothing, but the total mass of the solute present in the solutions. So, it is a total mass of the polymer that is present in the solution what this leads us to is this equation which is expression where we have c times n 2 by m. So, this m by V if we look at this quantity that m is the mass of the solute or mass of the a polymer in the solution and V is the total volume of the solution.

So, that m by V is nothing, but the concentration of the polymer or the concentration of the solute in the solution and it is a mass concentration. So, m as we just discuss is the mass of solute or mass of the polymer present in the solution and c which is defined as m by V that is the polymer concentration that is the mass per unit volume of polymer present in the solution. Now, that be a have n 2 by V is equal to c times n 2 by n, let us just see whether we can further simplify this term n 2 by m.

So, to do that let us go back to the basic definition of the number average molar mass. So, in the very first lecture we had defined the number average molar mass as a summation of n i m i divided by summation n i, where this n i is the number of moles of polymer chains having mass m i. So, if we consider this summation of over n i so, that is the summation of over all the numbers of all the different types of or the different lengths or chains that are present in the our polymer sample. So, in this case the polymer that we are considering is the polymer that is present in the solution.

So, this sigma n i the summation number of moles of all the chain lengths that are present. So, that summation will simply be equal to n 2 which is that total number of moles of this polymer that is present in the solution and this sigma n i m i this is nothing, but the total mass of the polymer sample. So, in this case that polymer sample is the polymer that is dissolved in the solvent. So, this sigma n i m i is nothing, but the total mass of the polymer present in the solution so, that is just m. So, we see that this M n bar in this case can written as simply the ratio m by n 2. Where m is the mass of the polymer present in the solvent n 2 is the number of moles of polymer that is present in the solution.

Now, that we have m n bar express like this. So, this n 2 by V now we can simply write as c over M n bar. So, this n 2 by V that this n 2 by m from here will be 1 by M n bar. So, this n 2 by V will be c by M n bar. So, now, let us substitute this n 2 by V term back in the expression that we have in had in the previous slide for the osmotic pressure. So, that expression I have just rewritten again here.

So, this was expression that we had in the previous slide for pi and if we instead of n 2 by V in these 2 places if we substitute c by M n bar so, the expression that we get is written here and here we see that the osmotic pressure is actually now related to the number average molar mass of the polymer. So, we have M n bar appearing here as well as here in the final few steps what we will do is try to further simplify this second term that we have here. So, we will try to further simplify this particular term and that will lead us to the final expression for osmotic pressure which is related to the number average molar mass.

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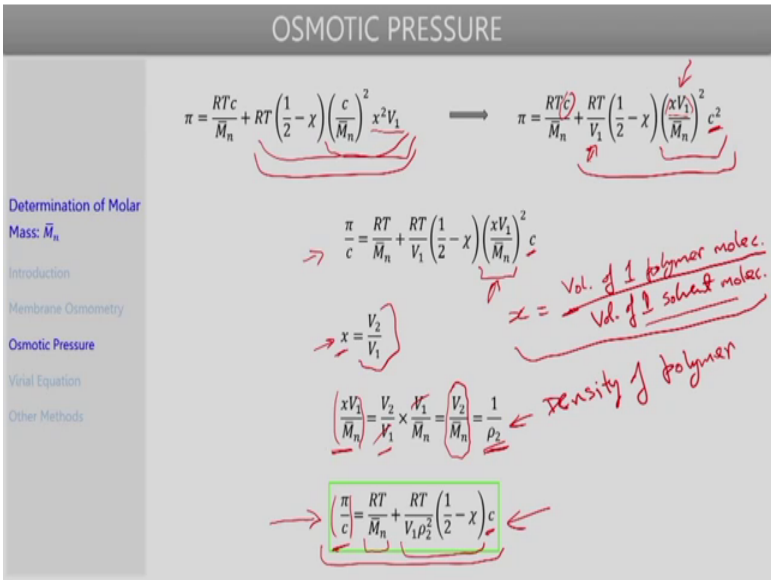

OSMOTIC PRESSURE

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$$\pi = \frac{RTc}{\bar{M}_n} + RT\left(\frac{1}{2}-\chi\right)\left(\frac{c}{\bar{M}_n}\right)^2 x^2 V_1 \longrightarrow \pi = \frac{RTc}{\bar{M}_n} + \frac{RT}{V_1}\left(\frac{1}{2}-\chi\right)\left(\frac{xV_1}{\bar{M}_n}\right)^2 c^2$$

$$\frac{\pi}{c} = \frac{RT}{\bar{M}_n} + \frac{RT}{V_1}\left(\frac{1}{2}-\chi\right)\left(\frac{xV_1}{\bar{M}_n}\right)^2 c$$

$$x = \frac{V_2}{V_1}$$

$x =$ Vol. of 1 polymer molec. / Vol. of 1 solvent molec.

$$\left(\frac{xV_1}{\bar{M}_n}\right) = \frac{V_2}{\cancel{V_1}} \times \frac{\cancel{V_1}}{\bar{M}_n} = \frac{V_2}{\bar{M}_n} = \frac{1}{\rho_2}$$

Density of polymer

$$\boxed{\frac{\pi}{c} = \frac{RT}{\bar{M}_n} + \frac{RT}{V_1\rho_2^2}\left(\frac{1}{2}-\chi\right)c}$$

So, now let us again start from the equation that we had in the previous slide and let us look at the second term and specially this part of the second term. This part we can rewrite in this way, here what we have done is taken this c outside so, that becomes c square, c we have taken outside the bracket, this x times V 1 we have taken inside the bracket here. So, we basically have this term when it is brought out of the bracket it will be x square V 1 square. So, here we had x square V 1 only so, to account for that we have also divided by this V 1 here. So, that when we when we expand and simplify this term we will get this term back.

So, now again let us look at the quantity that we have here inside the bracket x V 1 over M n bar. So, before doing that what we have done is just taken this quantity c in denominator here on the left hand side. So, what we get is pi by c equal to RT over M n bar plus this second term and where we still have a c because we had a c square here. So, we will still have c here.

So, now, let us look at this term x V 1 by M n bar, x let us focus on this quantity x first. So, we know from our discussion of Flory Huggins theory is that x is a number of segments that is present in a given polymer molecule. So, and in the Flory Huggins theory we also discuss the fact that one of the assumption is that the say volume of a polymer segment is equal to the volume of a solvent molecule.

So, with that assumption what we can say is that x is nothing, but the volume of a polymer molecule divided by the volume of a solvent molecule ok, because 1 segment of the polymer actually has a same volume as 1 solvent molecule and we have x segments in a given polymer molecule. So, x can be just thought of as a ratio of the volume occupied by 1 polymer molecule and the volume occupied by 1 solvent molecule. So, here what you have done is written x as the ratio of molar volume of the polymer and the solvent, what we just discussed according to that x is the volume of 1 polymer molecule divided by volume of 1 solvent molecule.

So, now in this directly comes on the Flory Huggins theory and if we in the what we have written here if we multiply and divide by the Avogadro number then this volume instead of volume 1 polymer molecule where that give us the volume of 1 mole of polymer molecules similarly this will become the volume of 1 mole of solvent molecule.

So, that ratio volume of 1 mole of polymer molecules by volume of 1 mole of solvent molecule that is what this ratio is because V 2 being the molar volume of the polymer that just the volume of 1 mole of polymer and similarly V 1 being the molar volume of the solvent that is the volume of 1 mole of solvent. So, we see that Flory Huggins theory we can directly see that the number of segment x is the ratio of the molar volumes of the polymer and the solvent.

Now, if we consider this term x V 1 by M n which appears here instead of x we can write V 2 by V 1 now. So, this V 1 will cancel this V 1 so, we get V 2 by M n bar here. So, V 2 if you look V 2 is the molar volume of polymer and M n bar is the number average molar mass of the polymer. So, V 2 is the molar volume of the pure polymer ok. So, this ratio of M n bar by V 2 so, M n bar is the molar mass of mass of 1 mole of polymer and V 2 is the volume of 1 mole of polymers. So, that ratio is simply the density of the polymer so, we can write M n bar by V 2 as rho 2.

So, this V 2 by M n bar we can simply write as 1 over rho 2 where this rho 2 is the density of polymer. So, we see now that we have simplified our terms into terms which contain quantities which are either readily available or measurable. So, upon substituting this expression that is 1 over rho 2 for x V 1 by M n bar the final expression that we get for the osmotic pressure or the what is called reduce osmotic pressure, which is pi by c that is equal to RT by M n bar plus RT divided by V 1 rho 2 square multiplied by half minus chi times c.

So, this is the mean equation that we have developed from the Flory Huggins theory of polymer solution dilute polymer solutions and we will see that using this equation. And using appropriate experimentation one can actually obtain measurement of the polymer number average polymer molar mass.

So, now what we can do is, if we go back to the previous slide and this equation here we see that left hand side contains this term pi by c which is the osmotic pressure by concentration of polymer. So, if we plot this pi by c against pi against c then we see that the equation that we have is that of a straight line ok, where the intercept will be RT over M n bar and the slope will be this whole term. So, let us see using that plot of pi by c against c how we can calculate M n bar or obtain M n bar.

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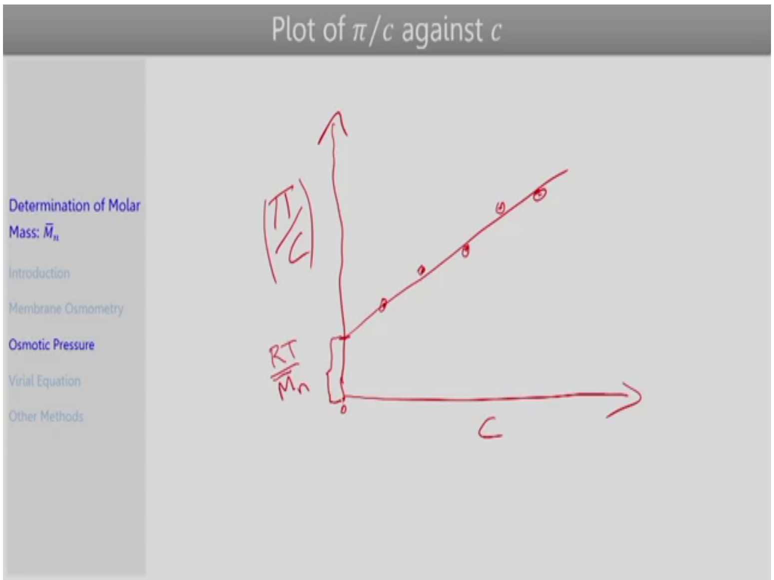

Plot of π/c against c

Determination of Molar Mass: $\bar{M}_n$

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Just consider a plot where the y axis on the y axis we are plotting this quantity pi by c on the x axis we are plotting c. So, this pi by c obtaining this pi by c experimentally is quite straight forward. So, initially we discuss the capillary osmometer set up and there we set that for a given polymer solution the osmotic pressure can be measured as a difference between the height on the 2 sides of the of that apparatus.

So, from that height difference we can get the osmotic pressure, pressure as rho g h. So, we the osmotic pressure for a given polymer solution having a given concentration can be obtained from the height that height difference and what we can do is in that same osmometer we can place polymer solutions having different concentrations or different values of c and then we can measure the value of the different h that we get and from that we can get the different values of pi or the corresponding osmotic pressures that generated.

So, for range of concentration or c values we can obtain the corresponding osmotic pressure or pi values and then if we have the pi and c values then for each point we can just divide pi by c to get this quantity pi by c and then. So, that we can construct in the form of a table and then we can plot that pi by c against c for each of the different polymer concentrations that we have that we have done the measurement on.

If we have the data any plotted pi by c against c then from this plot what we can say is that let us say the plot that we get contains some different points. So, to obtain the number average molar mass what we can do is fit a straight line through all the data points that we. So, these are the data points we can do a best fit kind of linear regression best fit using a straight line and the intercept of the that line. So, if this is 0 then the intercept of that line that this quantity according to the previous equation is nothing, but RT over M n bar.

So, from lot of pi by c against c we can try to fit a straight line and the intercept of that straight line can be directly read off and that intercept is nothing, but RT over M n bar and from there we know that we will know the temperature of our experiments and R is the universal gas constant. So, from that the value of M n bar can be readily calculated. So, that is a typical approach for calculating the number average molar mass from osmometry experiments.

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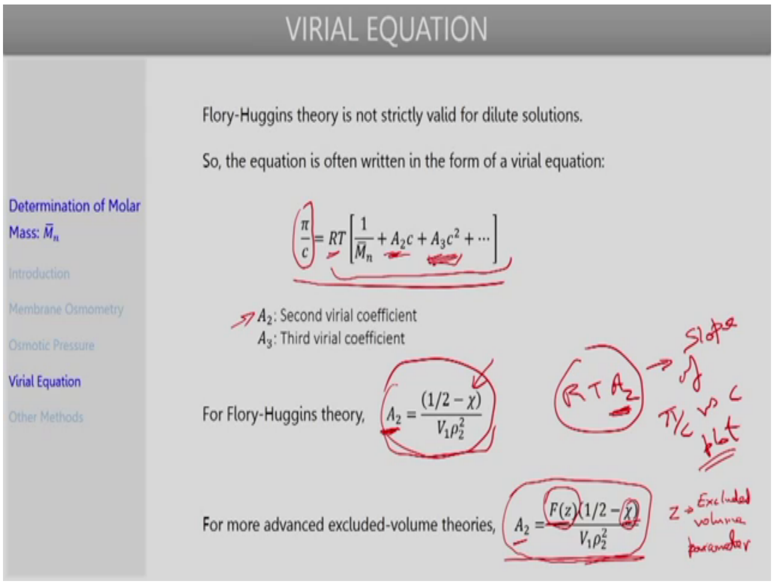

VIRIAL EQUATION

Determination of Molar Mass: $\bar{M}_n$

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Flory-Huggins theory is not strictly valid for dilute solutions.

So, the equation is often written in the form of a virial equation:

$$\frac{\pi}{c} = RT\left[\frac{1}{\bar{M}_n} + A_2c + A_3c^2 + \cdots\right]$$

A_2: Second virial coefficient
A_3: Third virial coefficient

For Flory-Huggins theory, $A_2 = \dfrac{(1/2 - \chi)}{V_1\rho_2^2}$

$RTA_2 \rightarrow$ Slope of π/c vs c plot

For more advanced excluded-volume theories, $A_2 = \dfrac{F(z)(1/2 - \chi)}{V_1\rho_2^2}$

$z \rightarrow$ Excluded volume parameter

Next let us talk about the fact that Flory Huggins as we know is not very good description of dilute polymer solutions. So, it is not strictly valid for dilute solutions it would not be very accurate. So, instead what is usually done is this relation between pi by c and M n bar is written in kind of a virial equation form. So, at typical virial equation for the osmotic pressure or the reduced osmotic pressure because it we have pi by c here which is the reduced osmotic pressure.

So, virial equation in the virial equation form pi by c is written as RT multiplied by 1 over M n bar plus A 2 c plus A 3 square c square plus so on; so, plus higher order terms A 4 c q and so, on. So, this is a typical virial equation form and you might have encountered this kind of virial equations when in when discussing real gas behaviour in thermodynamics. So, for real gas behaviour description also virial equation equations of the virial form are used.

So, for this osmotic pressure also we are using a similar kind of virial equation and the coefficients that we have here A 2 and A 3 these are refer to as the second virial coefficient and the third virial coefficient. And if we have higher order terms and you will have higher order virial coefficients as well, but typically is in normal circumstances second virial coefficient is the most important and sometimes the third virial coefficient also has value. So, that the third term might not be non negligible, but our focus will be on this second virial coefficient.

So, if we compare the Flory Huggins equation that we had for pi by c that we had developed couple of slides back then based on comparison of terms what happens is that this quantity A 2 the second virial coefficient for Flory Huggins theory comes out to be half minus chi divided V 1 rho 2 square. So, from the plot that we had done in the previous slide that was pi by c against c so, we saw that the intercept gives us the number average molar mass.

It turns out that if we measure the slope of the straight line which we are fitting to that data then that slope actually gives us the second virial coefficient, RT times A 2 this corresponds to the slope of pi by c versus c plot. So, this quantity RT times A 2 if we look at again this equation RT multiplied by A 2 that basically corresponds to the pi slope of pi by c versus c plot at low concentrations. At high concentrations the higher order term might become important and the fitting with the straight line might not be the best way to fit the data, but at low concentrations the curve will still be linear and the straight line fit at low concentrations will give us the second virial coefficient from the slope of that fit.

So, Flory Huggins theory says that A 2 is equal to half minus chi by V 1 rho 2 square. So, if we get A 2 from the slope of that fit then from this equation here we can get a measure of chi also. So, the Flory Huggins interaction parameter also can be calculated, but we saw that Flory Huggins theory is not a very good theory for dilute solutions and whatever estimates that we get will not be quantitatively accurate qualitatively it is fine, but if we want quantitative information then with the using the Flory Huggins theory directly is not a good idea.

So, they have been more advanced theories absorbed based on the excluded volume approach and such theories actually predict a similar dependence of this second virial coefficient on chi, but there is an extra term here this F z as is actually a function of this quantity z, where z is what is called the excluded volume parameter. So, this is a parameter defined in excluded volume theories which is known as excluded volume parameter and this incorporation of function of that excluded volume parameter, actually makes this expression or the relation between A 2 and chi more accurate and the if we can obtain A 2 from pi by c versus c plot the low concentration the linear region of that plot. Then using this equation the chi can also be obtained that basically concludes our discussion of this membrane osmometry method for calculating the number average molar mass.

And we have a discussed how what is osmotic pressure, how osmotic equilibrium develops and then the what are the thermodynamic equations that that are used to describe the osmotic equilibrium and from there we have derived an expression for the osmotic pressure in terms of the number average molar mass. And we saw that a plot of pi by c against c can be used to obtain the non number average molar mass, from the intercept of the plot if we fit a straight line to the data.

The slope of the straight line also gives us useful information which is the second virial coefficient and from the knowledge of second virial coefficient even the Flory Huggins interaction parameter can be estimated. So, before my finishing this lecture let us just look at some of the other methods in very brief some of the other methods that are available for measuring the number average molar mass.

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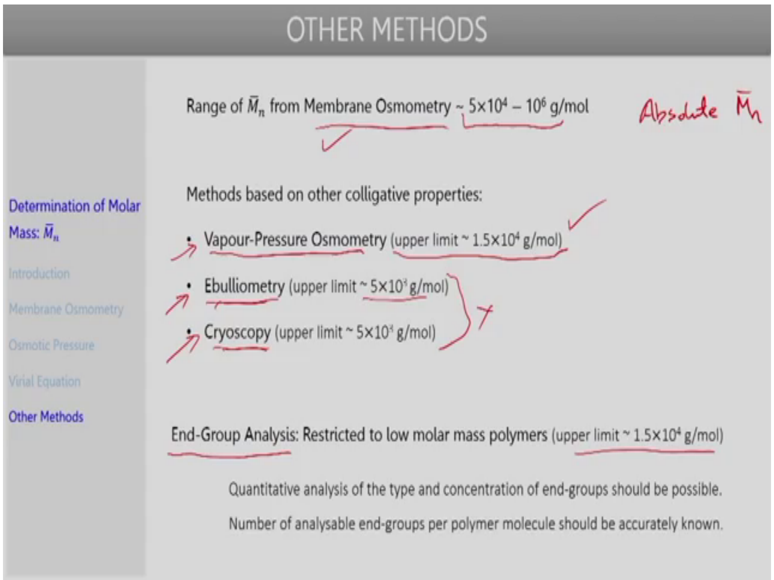

OTHER METHODS

Determination of Molar Mass: $\bar{M}_n$

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Virial Equation

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Range of $\bar{M}_n$ from Membrane Osmometry ~ $5\times10^4 - 10^6$ g/mol

Absolute $\bar{M}_n$

Methods based on other colligative properties:

- Vapour-Pressure Osmometry (upper limit ~ 1.5×10^4 g/mol)
- Ebulliometry (upper limit ~ 5×10^3 g/mol)
- Cryoscopy (upper limit ~ 5×10^3 g/mol)

End-Group Analysis: Restricted to low molar mass polymers (upper limit ~ 1.5×10^4 g/mol)

Quantitative analysis of the type and concentration of end-groups should be possible.

Number of analysable end-groups per polymer molecule should be accurately known.

So, before that at just like to make a mention of the range of molar mass is rather typically measurable using membrane osmometry. So, membrane osmometry is a good technique for measuring molar masses of polymers having high molar masses and buts it also has it is limitations. So, if the molar mass become of the polymer is too high, then the resulting osmotic pressure that develops will be quite small. So, if the molar mass goes beyond let us say a few million grams per mole then the osmotic pressure measurement or the height difference that we get from which we get the osmotic pressure that measurement becomes problematic. So, that imposes an upper limit on the molar mass that highest molar mass that we can measure using membrane osmometry.

Similarly, there is a lower limit also. So, if the polymer molecules are too small they have a very small low molar mass and small size then what can happen is for typical semi permeable membranes that are employed in the osmometers, the small polymer molecules can actually also pass through the membrane. So, membrane does not just allow the solvent to pass the even the smaller polymer molecules can pass and that actually will introduce errors in the measurements, because all the theory that we have developed is based on assumption that only the solvent molecules passed and we have osmotic equilibrium due to that, but if small polymer molecules also can pass through then that will introduce errors.

So, that is why there is a lower limit on the measurement also and typically for membrane osmometry the range of molar mass is number average molar mass is that can be measured is between 5 into 10 to the power 4 into 10 to the power 6. So, from 50000 to around a million grams per mole, another thing to note was membrane osmometry is the molar mass number average molar mass that we get is an absolute quantity there is no calibration involved. So, we get the absolute number average molar mass from membrane as osmometry. So, we get absolute value of the M n bar of the polymer.

Now let us just briefly mention few other techniques which can be employed for calculating the number average molar mass of polymers. So, based on the other 3 colligative properties that we have discussed the vapour pressure osmometry ebulliometry and cryoscopy these are 3 techniques that can be used to estimate the number average molar mass. So, this vapour pressure osmometry is based on the colligative property which is the lowering of the solvent vapour pressure upon the add addition of a non volatile solute.

We will not go into the details of the equipment the set up as an or the mathematical details of the thermodynamic equations, but we will just state that the upper limit for this is around 1.5 into 10 to the power 4. So, around 15000 grams per mole and upper limit here again is because of the fact that if the polymer molecules are even larger and have higher molar mass then the corresponding signal or that we get the effect produced by the presence of the solute is so, small that it is difficult to measure and that is why there is an upper limit.

So, we typically vapour pressure osmometry is also employed as a complimentary technique to membrane osmometry. So, membrane osmometry is good for high larger polymers whereas, for small chain polymers having lower molar mass, the vapour pressure osmometry is more useful. So, it is complementary technique to your membrane osmometry.

Ebulliometry is based on the boiling point elevation it is upper limit is quite small around 5000 grams per mole, similarly cryoscopy is based on the freezing point depression and there were also upper limit is quite small and for both these cases the upper limit is dictated by the effect that is being produced. So, whether it is the elevation freezing boiling point or the depression freezing point the magnitude of that effect which is produced becomes so small at higher molar mass polymers the for higher molar mass polymer that it is measurement becomes very problematic and error prone.

So, that is why these 2 have very limited application and there these are in general not commonly employed for obtaining number average molar masses. So, membrane osmometry is used, vapour pressure osmometry is used, these 2 are not commonly employed. And apart from colligative properties there is another kind of another way in which number average molar mass can be obtained, but that this technique also suffers from some limitations.

So, this technique is referred to as end group analysis slide and it is different from any estimation based on any colligative properties. So, here as a name suggests the number of end groups present is in a given polymer sample that is estimated using some experimental techniques like titration or spectroscopy like enamel spectroscopy.

So, the number of end groups present is estimated and if it is known how many end groups are present on a given polymer molecule if that shown accurately then the number average molar mass of polymer can actually be estimated. Limitation here is that it is restricted again to low molar mass polymer so, again for polymers that have that are quite long chain and have high molar mass is this is not very applicable.

So, again the upper limit is around 15-20000 grams per mole and some of the requirements for this technique to work is that whatever end groups are present. So, end groups means the groups that might be present at the ends of the polymer chains. So, whatever ends groups are present on another the polymer molecules or polymer chains those end groups should be readily measurable using experimental techniques like titration or spectroscopy.

And not just the type of end group that is present the concentration of end groups present should also be enough so, that a quantitative measure is possible. And the second condition is that for a polymer molecule the exact number of end groups that is being measured by the experimental techniques that should be known. So, the number of end groups per polymer molecules should be accurately known only then this technique will work. So, it has some limitation, but it is useful for low molar masses polymers which have a well defined and distinguishable end groups.

So, typically polymers that have prepared by step polymerisation in many cases the molar masses are not that high so, for such low molar polymers this method can be used. And first step polymerisation typically the functional groups also are distinguishable and in most of the cases are regular functional groups like hydroxyl or carboxyl or I mean these kind of functional groups can also be readily measured using experimental techniques. So, that is why low molar masses or mass polymer prepared by step polymerisation there M n bar can be estimated using this method and which is the end group analysis

So, with that we will finish this lecture and just to summarise we have talked about primarily membrane osmometry as the method for determining the M n bar as or the number average molar mass. And we have developed an expression for relating the osmotic pressure to the M n bar using the Flory Huggins equation and we have also noted that Flory Huggins equation itself is not very accurate for dilute solutions. So, we have also discussed a virial form of this osmotic pressure and just briefly mention how more accurate estimates of let us say the Flory Huggins interaction parameter can be obtained if we use employ more advanced excluded volume theories.

We also talked about the other alternatives which are present for calculating or measuring M n bar and we have also discussed the limitations in terms of the range of molar masses that are measurable using the different techniques. So, with that we will end this lecture and in the next lecture what we will do is start discussing how the weight average molar mass can be determined. So, there will see that light scattering is a method of choice for determination of the weight average molar mass.