Rheology of Complex Materials
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Lecture - 04
Applications of rheology: some example material systems

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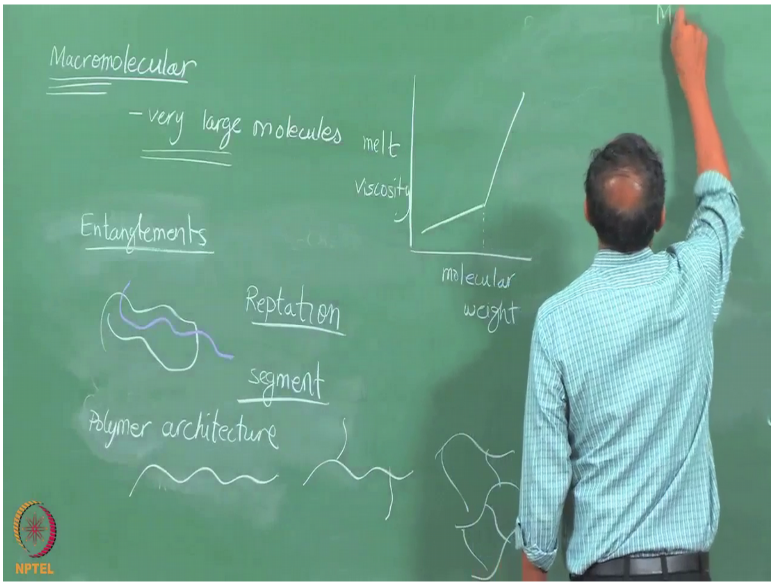

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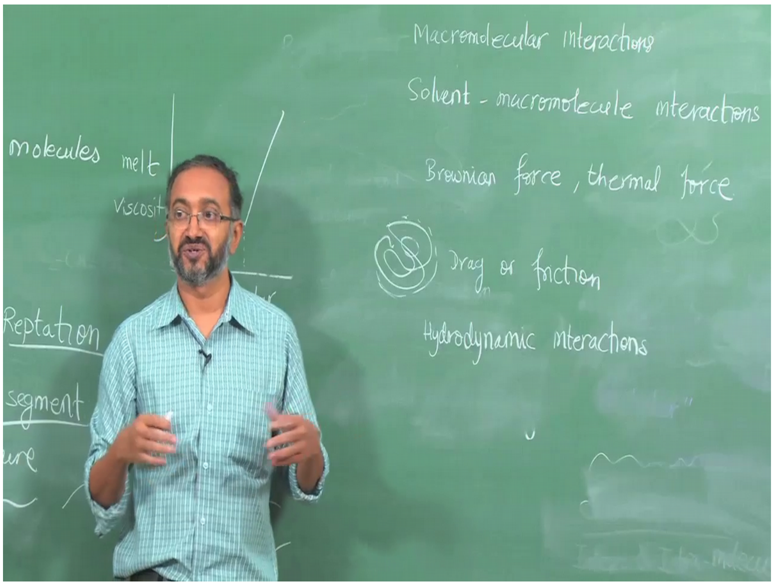

So now continuing on; having seen the macromolecular interactions, we will now see interactions between solvent and macromolecule. So, generally we tend to think here in terms of broadly three types of interactions the fact that solvent molecules are continuously colliding with the macromolecule and solvent molecules themselves are also randomly move moving around is the Brownian force or the thermal force.

So, that is one level and that is the reason why for example, the cc bond rotation energy is possible that there is sufficient thermal energy in the system for bond rotations to take place. So, therefore, in general one force which is present whenever solvent is present is the Brownian force or its also can be called the thermal. So, hypothetically if we look at let us say 0 Kelvin system, then this will not be present right this the thermal energy and Brownian motion will not be there, but most through a polymer solutions when we discuss we will have this.

Then given that we were talking about polymer forming a coil right we can think of the overall polymer as a spherical object right and when this moves around it exchanges friction is like a stokes law like a ball which is moving around or a small marble which falls there is a terminal velocity it attains and so on. So, we can also think of that because there is a relative velocity between the surrounding solvent and the polymer as on a hole there is friction being exchanged between the polymer molecule and the solvent.

Therefore, we can think in terms of drag or friction do you see a difference between this and this this is also interaction between solvent molecule and macromolecule this is also interaction between solvent and macromolecule this arises only when average velocity of polymer is different compared to average velocity of solvent. Here even if velocities are 0. In the sense it is a stationary polymer solution Brownian force is being exchanged because solvent molecules are bombarding macromolecule is undergoing motion. So, Brownian force is present.

But if I am doing shear where polymer molecule is moving and solvent molecule is moving and if there is a relative velocity between the 2 that is where we will lead to drag or friction. Therefore, this is a interaction which is based on flow and then if we have multiple such molecules then what we have are called hydrodynamic interactions. So, in this case what we will have is basically, because one molecule moves it will disturb the solvent around it and that disturb solvent will actually go and disturb the other molecule.

So, whenever we have multiple such macromolecules in a system they will disturb each other’s flow and so, what we can say is the 2 molecules are interacting with each other through hydrodynamic interaction. In general let us say if this is a negatively charged macromolecule and we have another negatively charged macromolecule we can say that they will repel each other and so, that is electrostatic interaction, but when we have these two saw molecules separated by solvent when this moves solvent gets disturbed that solvent disturbs this.

So, basically these 2 molecules are interacting by hydrodynamically they are basically disturbing the solvent in between them. So, in dilute systems of course, hydrodynamic interaction will it be important or will it be not important now what about think of the size of the macromolecule and solvent. So, if one part of the chain moves. So, let us say if we look at this and this chain is moving at some velocity and then this chain is moving at some other way. So, the solvent will. Therefore, even if you have dilute solution this chain and this chain may not interact with each other because they are very far Vander Waals interactions may not be present, but hydrodynamic interactions may be present.

So, in dilute system also hydrodynamic interactions may be important because of the size of the polymer macromolecule if you if you think of the overall molecule is only ones sphere; then yes. Then you can say that it is only exchanging, but it is not that right in the end what we will see is this particular macromolecule can be thought of several basically blobs which actually are exchanging friction with the surrounding because each of them is moving with a different velocity, because this overall object is much larger compared to the surrounding solvent.

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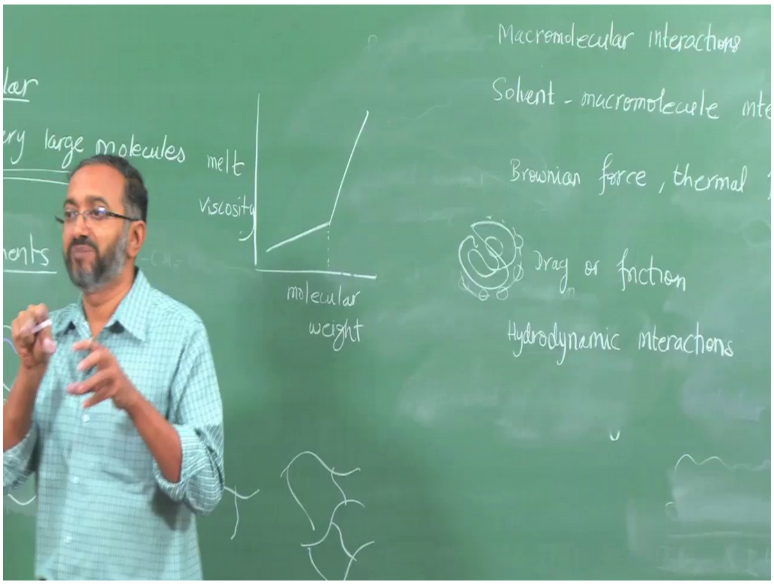

So, therefore, hydrodynamic interaction we have to be careful like that it will be important. In fact, the other extreme hydrodynamic interaction will not be important in melt for example, there is no hydrodynamic interaction because there is no solvent to mediate. So, in concentrated solutions also hydrodynamic interaction will be usually screened out which means it is not very important just the way if you have too many charges if the ionic strength of the medium is very high, then we say that the electrostatic interactions are screened out.

So for example: two charges which are far away from each other will not see each other’s presence because there are too many other charges. So, we say there is a screening of electrostatic charges. Similarly, if there are too many macromolecules in a concentrated system the fact that solvent gets disturbed in one point. Basically, we will already die down because of so many other macromolecule present and a macromolecular part which is slightly away I may not see actually the hydrodynamic interaction at all.

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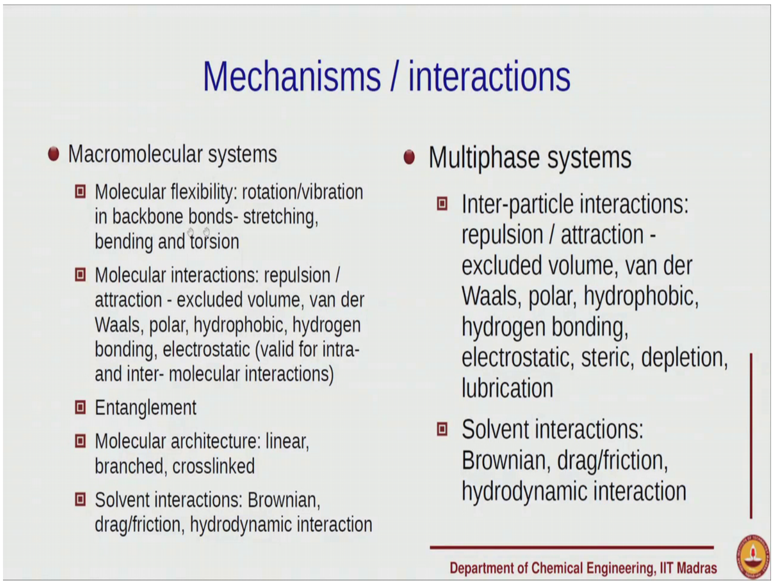

Mechanisms / interactions

- Macromolecular systems
  - Molecular flexibility: rotation/vibration in backbone bonds- stretching, bending and torsion
  - Molecular interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic (valid for intra- and inter- molecular interactions)
  - Entanglement
  - Molecular architecture: linear, branched, crosslinked
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction
- Multiphase systems
  - Inter-particle interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic, steric, depletion, lubrication
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction

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So, each of these mechanisms we will have to see where when they are relevant where they are relevant and then analyze the situation accordingly so that sort of sums up the overall set of interactions. So, we said that initially flexibility which is all related to bond rotation and flexibility at the bond scale or bonded interactions. Then we had molecular interactions which could be intra or inter and which are attractive or repulsive depending on what the specific interactions are then entanglement which is far more important only for melt state and for concentrated solutions.

And then of course, architecture is an important aspect because that determines how some of the other things may play out and finally, the interaction with solvents and so. This is the summary of interactions which are present when we have a macro molecular system now what about a multiphase system.

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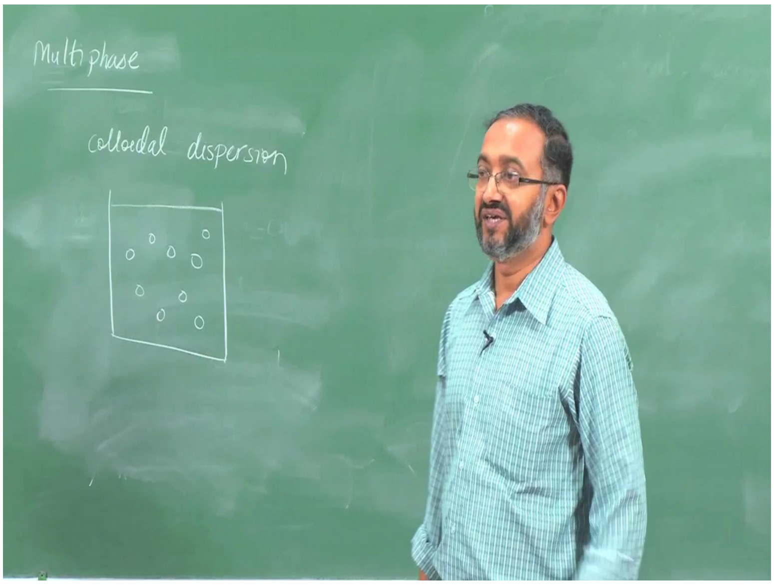

So, if you look at colloidal dispersion for example. So, if we say colloidal dispersion which of these is already present I have already written there. So, for example, for a multiphase system and let us say we have a colloidal dispersion.

So, we have small micron size particles in a continuous liquid. So, we have let us say spherical particles this could be silica or any other particles maybe a polymer like polystyrene particles in water or in some other liquid medium ink. For example, is a common right the solid particles of the pigment and then in a liquid. Now, what are the interactions that are possible, here we do not have any intra right inter particle interactions is only what we have, but the inter particle interactions are exactly the same as what are there in case of a molecular interactions.

So, they will be exactly the same depending on the surface chemistry of the particle here and particle here we may have electrostatic interactions maybe we may have Vander Waals interactions and so on; what I could possibly do is hydrophobically modify this surface and some surface if I do hydrophilic modification. Then I might see that hydrophilic hydrophilic particles get together while hydrophobic hydrophobic particles get together its possible.

So, many such interactions can again be played around with, but the set of interactions are all similar and these are inter particle interactions or inter droplet interactions if it is an emulsion. So, basically the interactions between the dispersed phase particles or dispersed phase entities and the other set of interactions which are with solvent are again similar also. So, a Brownian force way which will basically even if this is stagnant the particles will undergo a Brownian motion, because solvent is on random bombarding these particles and that is the Brownian interaction if we put this in shear. And therefore, force these particles to move then there will be drag exchange between the particles and the surrounding fluid.

And then finally, if there are too many particles then disturbed flow and they will interact with hydrodynamic interactions. So, clearly let us say if in some application I am interested in not the bulk response. So, for example, for ink or. So, something maybe I am interested only in the overall viscosity of this or some other rheological response, but let us say if I am going to have a monolayer of these particles right then usually the particle and liquid and air interface may be very close.

So, in that case, I am interested in knowing the let us say the rheological response of a very thin film of these systems. So, in that case interfacial interactions may be important. And it is known that when you have let us say a particle at interface like this in addition to these interactions there will be additional interactions. So, for example, this particle will induce a curvature the surface tension of this air water interface is also there. So, there will be additional interactions because of the particles being at the interface.

So, those are over and above what we see what we have listed here though again the molecular origin of them again relates to hydrogen bonding or any other molecular interaction the fact is.

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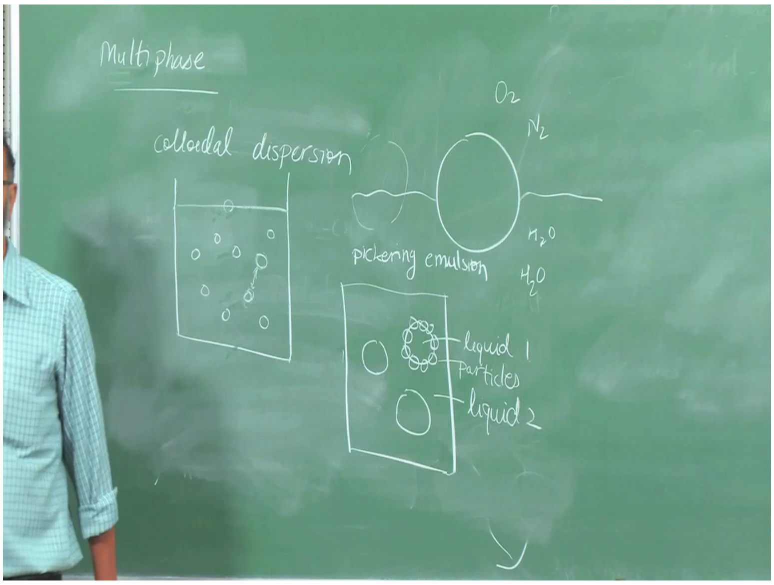

So, that this if I do a more magnified version what we will have let us say in a one case there are all water molecules interacting with this particle while on the other side we may have let us say if we have air these nitrogen and oxygen interacting. So, because of the differences of these interactions we have the surface tension and all the other features and there may be curvature induced in this surface tension. And therefore, there may be a force because of this curvature two particles if they are nearby they may because of the curvature of the interface they may feel attraction or repulsion.

So, this will be called capillary attractions a capillary repulsion and so on because they are related to surface tension in the bulk case there is no interfacial interactions that we have to really consider, but let us say if they reserve. We look at a more advance system of where we have let us say a liquid system which is stabilized by particles and these are called Pickering emulsions. So, if we have one liquid in another liquid. So, this is a liquid one and this is liquid 2 and instead of surfactant we can have particles which are stabilizing.

So, then again interfaces are important this is also example of multiphase, but now it is liquid in liquid and on the interface there are solid particles. In general in the complex fluids or complex materials that we are going to study in the course. Now, what we can do is we can start looking at example systems. And this is just a small survey to talk about what kind of application may be there what kind of material system may be there and then we can say- because of this application because of this material system this is the rheological question that we might have to answer.

And then our interest in the course will be whether we are learning all the tools to answer those questions or not.

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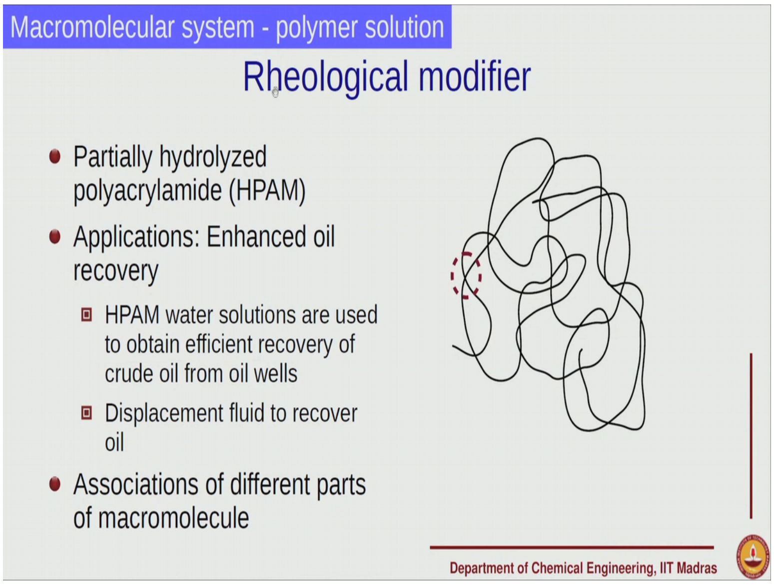

Macromolecular system - polymer solution

Rheological modifier

- Partially hydrolyzed polyacrylamide (HPAM)
- Applications: Enhanced oil recovery
  - HPAM water solutions are used to obtain efficient recovery of crude oil from oil wells
  - Displacement fluid to recover oil
- Associations of different parts of macromolecule

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So, just to go through the first example that I have taken is that of a rheological modifier by definition needs modifies the rheological response of a solution or of a liquid and this is an example of a macromolecular system which is a polymer solution and the example that I have taken is partially hydrolyzed polyacrylamide. So, polyacrylamide is a polymer which is used in from bio in bio technological applications in for example, gel electrophoresis the gels are made out of polyacrylamide.

It is a water soluble polymer and it is quite commonly used is as a rheological modifier so.

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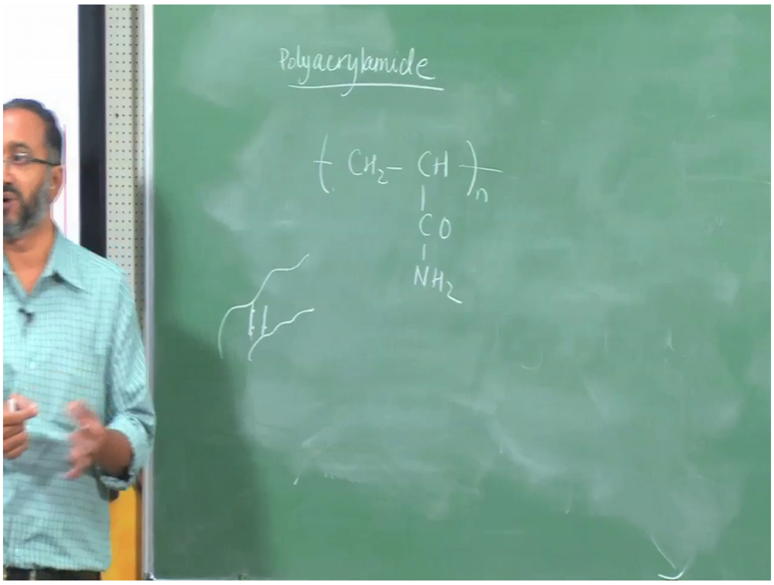

Polyacrylamide and so, it is CH 2 this is the polymer when we write usually and just to indicate that it is a very long chain. So, what you can see in this polymer is this hydrogen bonding centers CO and NH 2 are strong hydrogen bonding centers. So, when you have a one part of this molecule is so CO of A. So, these can be basically you can have interaction between one molecule with the other molecule, because there is strong hydrogen bonding possible between 1 CO NH 2 and another CO NH 2.

Therefore, intermolecular interactions and intramolecular interactions are very strong in case of this polymer because of the presence of hydrogen bonding, if you have let us say a polymer which is like the CH 2; CH 2.

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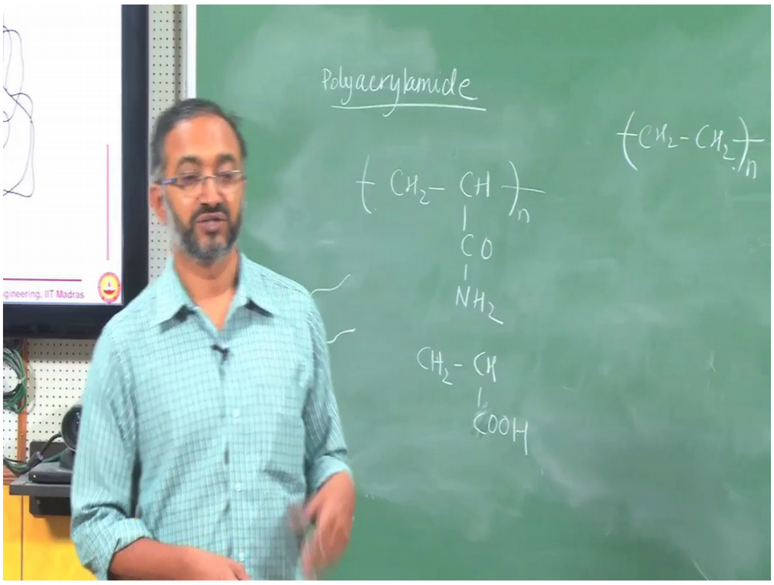

Which is this polyethylene in some solution then the only interactions are just Vander Waals interactions or basically what are called dispersive interactions. So, in this case strong hydrogen bonding is present. So, in general polyacrylamide can change the viscosity of water, let us say quite significantly because the intra and intermolecular hydrogen bonding present.

So, now what is used in enhanced oil recovery is a partially hydrolyzed polyacrylamide. So, enhanced oil recovery is a process in which oil is basically trapped in rocks right porous rocks. So, what we do is we pump water from above some water solution basically and then push the oil out. So, basically we use water as a pushing liquid and we push oil out and then in this process of course, many of the pores oil will not come out because water will itself get pushed out and some oil will remain there.

So, how do we improve the efficiency of that oil recovery? So, that is what is meant by enhanced oil recovery can we do it in such a way that whatever water solution we are using it effectively displaces pretty much all oil which is down there. And so, for that these rheological modifiers are added to water. So, that they appropriately change the rheological response and then get the oil out. And so commercially available polymers have this and then some of the groups are basically this. So, this is the hydrolyzed part of the polyacrylamide.

So, some groups will have this units some groups will have this unit. So, that is called partially hydrolyzed and you can see now that the interactions between this group and this group are different. Therefore, partially hydrolyzed polymer solution will behave differently compared to completely un-hydrolyzed polymer. And so it has been found that partially hydrolyzed polymer is more effective in terms of removing the oil. And now from a fundamental understanding point of view we would need to answer as to first of all how is the rheological response different when I hydrolyze the polymer.

In order for me to answer that I may also have to see what is the nature of interaction in pure just polyacrylamide and what is the nature of interactions once I hydrolyze it partially the what is the kind of network that gets formed when partial hydrolysis is done does that change. And therefore, the other rheological properties change. And so, there are the associations of a different part of macromolecules are the key in determining what the overall rheological response of this polymer solution will be.

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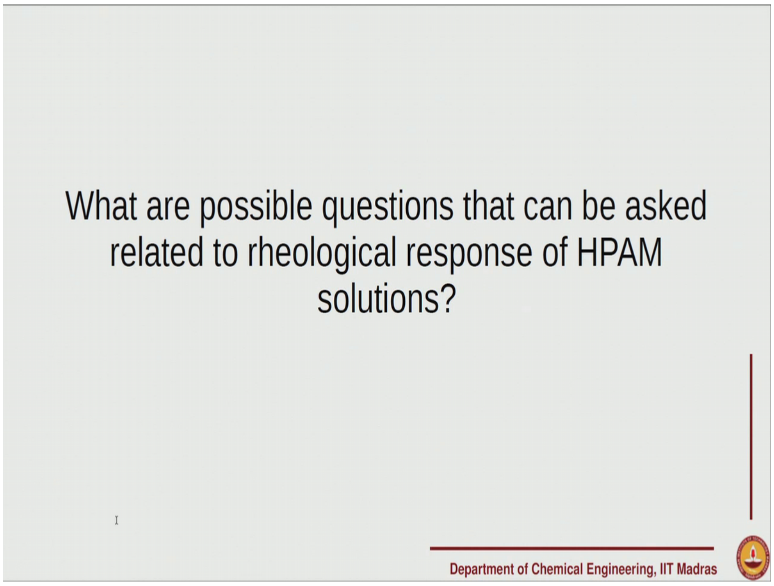

What are possible questions that can be asked related to rheological response of HPAM solutions?

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So, given that I have sort of shown and talked about a an example right a application and I have given you some description of what the application is; can you now think of what are different possible questions that might be there for me to formulate a project or around saying that I am interested in rheology of rheological modifier such as a hydrolyzed polyacrylamide; what are the general questions that come to your mind when we are interested in studying about. Basically I want in the end what would I want as an application I would want a polymer which is cheaper or want a polymer which is better in giving oil and also, hopefully if it is biodegradable then its better, because when it whatever gets left behind will bio.

So, all those are there right. So, that is the context in which we are trying to ask the question which are related to rheology. So, in the presence of salts because remember that we are talking about partial charges hydrogen bonding and if you put salt clearly that will modify the interactions between. Therefore, in all of these what we have seen is there is always an interaction between molecular mechanisms my microscopic mechanisms the overall application and in between our attempt at rheology saying that I should understand the mechanisms appropriately, I should know the application conditions appropriately so I will design my rheological questions appropriately.

So, with that now in the next segment, what we will do is look at quickly those eight applications. And we will also look at combinations of macromolecular and multiphase systems.