Supramolecular Chemistry-I

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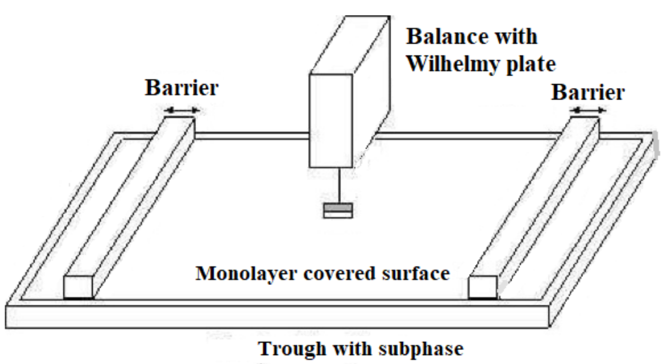
Lecture - 39

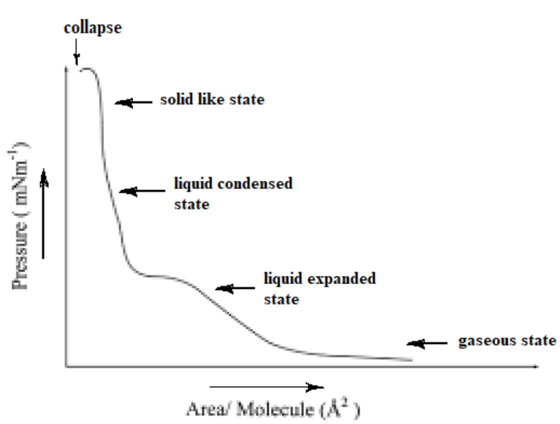
Good morning and welcome back. So, today I will talk about the LB technique. A wealth of useful information starting from molecular sizes to intermolecular forces can be obtained from studies of monolayers at the air–water interface. Great resurgence of interest in this area of science has been largely due to the fact that films can be transferred from the water surface onto a solid substrate using what has become universally known as the Langmuir–Blodgett (LB) technique. LB technique is the most effective way of depositing thin films onto solid surfaces and with precise molecular dimensions because we deposit molecules as layers. So, one layer then another layer of molecules. So, it has precise molecular dimension which is very important in many technical applications. This technique has assumed greater importance in recent times with the demand for materials with tailored interfacial properties. Besides, organized molecular layers provide unique environments for molecular interactions and consequently for molecular recognition. Using monolayer assemblies that may possess characteristics uniquely different from those in homogeneous media can develop new molecular recognition systems. These supramolecular systems should be important in applications such as chemical sensors, in understanding molecular interactions on biological cell surfaces, and in developing novel 2D molecular assemblies composed of multiple chemical species. Cryptand-based amphiphiles are attractive because they have a closed cavity with donor atoms whose topology can be tailored via ligand design to recognize a specific metal ion / molecular guest. Before I talk about LB technique, let me show you how the LB trough looks like.



It consists of two barriers: one fixed while the other is moveable. One balance is also attached that measures surface pressure. The entire thing is made up of Teflon. The whole thing is thermostated in a dust free environment. Now suppose we put double distilled deionized water in the trough. We put a concentrated solution (concentration empirically determined) of an amphiphile in methylene chloride and add this to the water drop-wise over the entire water surface. Methylene chloride is lighter than water. So it will float. Not only it will float, it will spread all over the water surface. Upon complete evaporation of the methylene chloride we are left with pure water and amphiphiles. These amphiphiles will have their hydrophilic part inside or at the water surface and hydrophobic part in air. The amphiphiles will be away from one another and will not exert any type of interactions amongst them. So this condition is regarded as a two dimensional gas (2D gas). We can bring them closer by moving the barrier towards the fixed barrier. When the distance between the barriers are close enough that the hydrophilic headgroups almost touch one another, overcoming the repulsive interactions between any two. So these amphiphiles are now near to each other, and they will exert a repulsive force on each other. So this 2D analog of pressure is called surface pressure π. So we know what is 2D gas and now I am talking about surface pressure, π. Surface pressure π is when they come close to each other and exert a repulsive interaction and it is liquid like okay.

$$\pi = \gamma_0 - \gamma$$

where γ_0 surface tension of pure subphase (here, water) and γ surface tension with monolayer present. A pressure-area isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure. A pressure-area isotherm obtained in the LB experiment is shown in the figure below. If we push the barrier further when these headgroups are touching each other, they have nowhere to go. Then what will happen? They will all be forced inside the bulk water. That is called collapse. It will form micellar aggregates because of high dipole moment of water.



I am sliding slowly moving or sliding the barrier towards that other part. So this is the part. Here they were very widely so now they are coming closer closer closer but still they do not have any interaction amongst them. So pressure is not increasing that much even though area per molecule means the molecule how much have area to its disposal. So when I close this close the gap between two units one is fixed another is movable then area available to per molecule is less and less. So area per molecule is less and less from here okay some area was there in angstrom whatever the value now area per molecule is less and less. So slowly it is coming but still pressure is not that much because still they are very far when they come close to each other they are coming close almost touching each other then little bit area if I this decrease that means further decrease of the area then the pressure will be high. It will increase repulsive pressure it will increase like this then it can have something like this. So from here this is a gaseous state this we call gaseous state okay and this is liquid state. Liquid state means still there is some gap but the gap is so small that is almost ordered and a solid is perfectly ordered. So it is going slowly it is increasing the pressure now if I further do it do it what I further reducing this distance between two if I come very close then what will happen pressure will increase very much with little bit movement pressure will be increasing very much because when it is solid then nothing moves. So I still I am moving so pressure will be tremendously increasing and after certain point pressure can no longer take it the molecules can no longer take it the pressure take it then it will collapse. So this point is solid like state and this is collapse. As I told you earlier collapse means now if I put further if I push it further molecule has nowhere to go but inside the bulk water. They will be forced to go inside the water and that is called collapse which will somewhat release the pressure. They will form a micellar structure in the bulk water also called sub-phase. So at the point where the headgroups touch each other, we can get the monolayer out on a substrate like a quartz plate. This is all done by a computer and human intervention will not be necessary. The quartz plate containing a monolayer of the amphiphile should be used again for another layer of the amphiphiles. This way hundreds of layers may be deposited on the plate.