MSc (Chemistry)
II-Semester
Physical Chemistry-II Unit-2

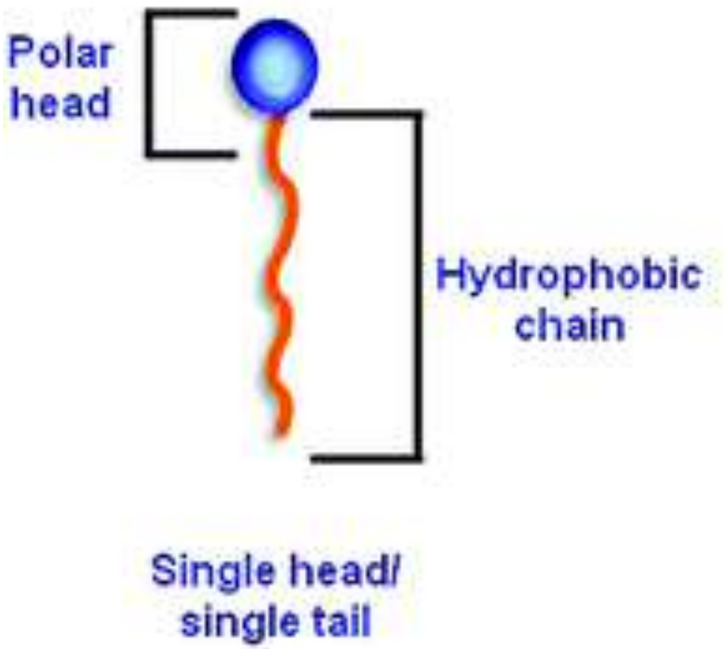
Surfactants, micelles, and macromolecules

Dr. Rakesh Kumar Pandey
Associate Professor, Department of Chemistry
MGCU, Bihar

Surfactants

Surfactants: SURface ACTive AgENT: Surfactants are amphiphilic molecules that have a tendency to lower the surface tension between liquid-liquid, liquid-gas, liquid-solid.

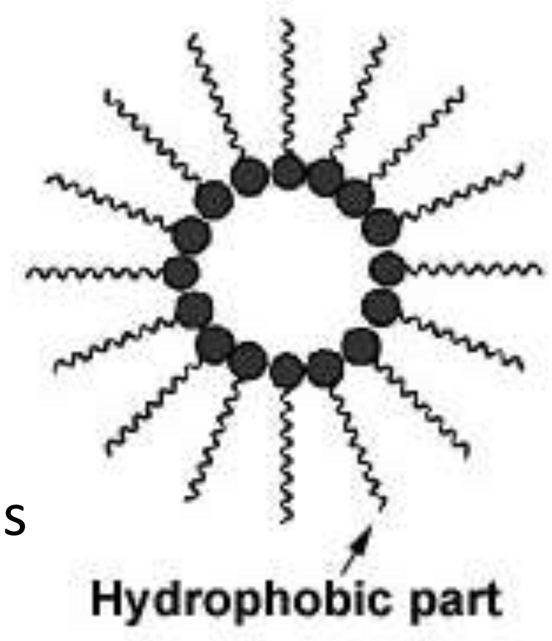
Amphiphilic molecules: Amphiphilic molecules are molecules with a polar or hydrophilic head group and a hydrophobic chain. When present at low concentration, they can adsorb on the surface or interface. The adsorption on the surface lowers the interfacial tension.

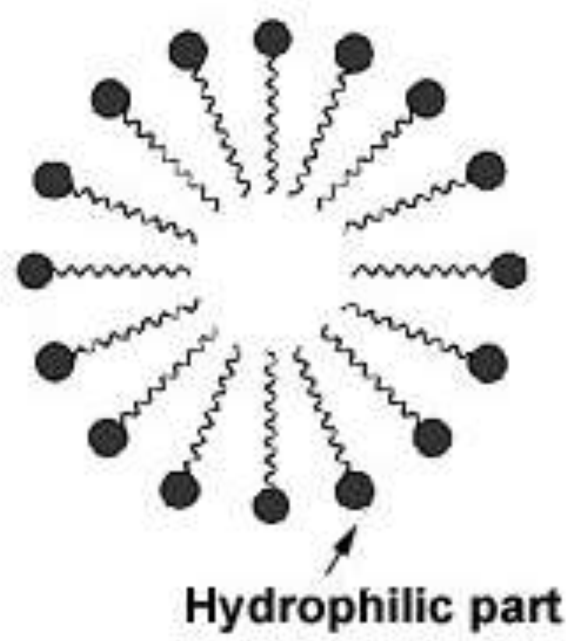


Micelles

Micelles: Micelles are formed in the solution of amphiphilic molecules in order to avoid interaction of water. The hydrophobic chains of amphiphilic molecules want to avoid interacting with water so assemble as aggregate in water solution. Opposite to this is inverse micelles where hydrophilic part form the inner part of the micelles.

Micelles





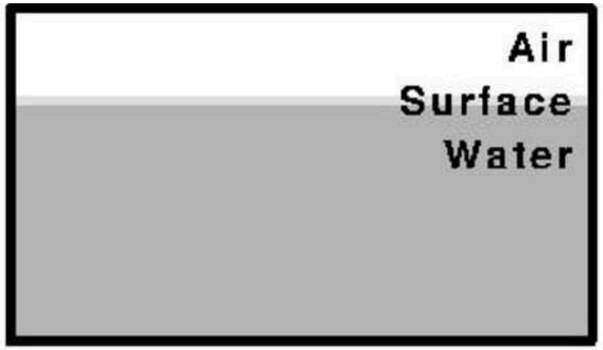
Inverse-Micelles

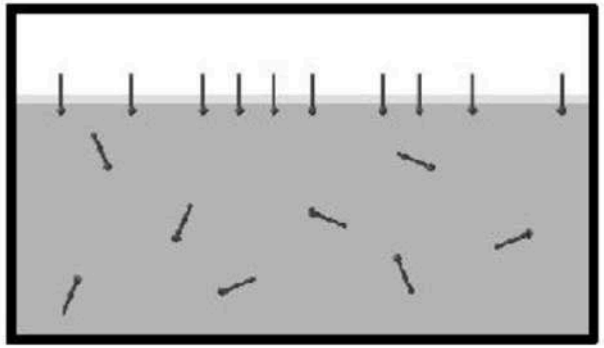
Micelles (CMC)

Upon the addition of surfactants in the solution the following things happen;

(1) Lowering the energy of the interface

(2) Avoiding the interaction of hydrophobic part to that of water and formation of a monolayer on the surface





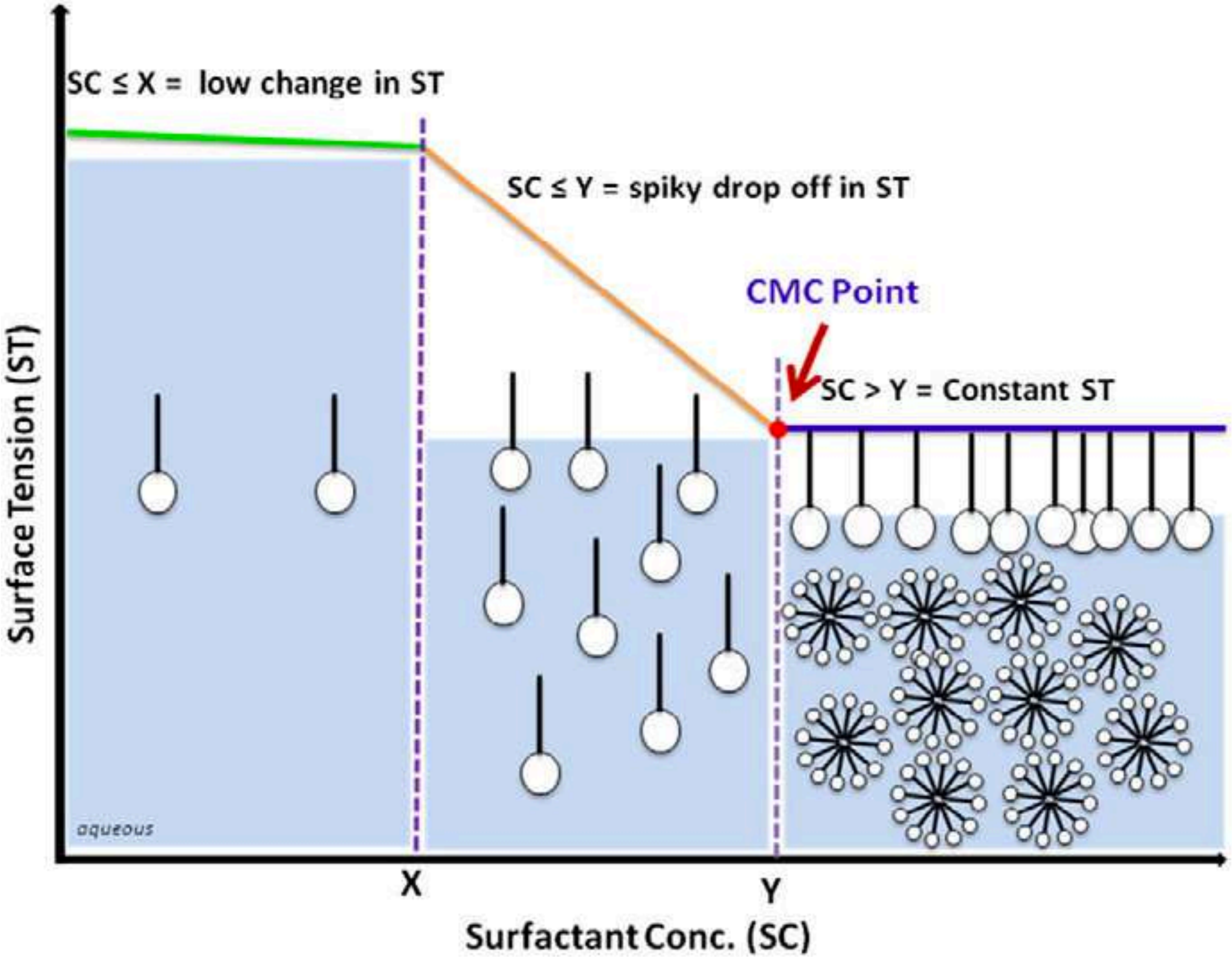
(3) Upon reaching a concentration (CMC), micelles form in the solution.

$$\Delta G = RT \ln(CMC)$$

Micelles (CMC)

Critical Micelle Concentration: There is a critical concentration above which micelles start forming. This concentration of amphiphilic molecules is called the critical micelle concentration (CMC).

Kraft Temperature: This is the temperature at which the solubility of the surfactant is equal to the CMC



L.P. Singh et al. / Advances in Colloid and Interface Science 214 (2014) 17–37

Micelles (CMC)

Factors affecting the Critical Micelle Concentration: After the formation of micelles in the solution, the properties of the solution significantly change and therefore it is critical to study the factors that can affect the CMC.

(1) **Structure of the amphiphiles:** In general CMC decrease as the hydrophobic character of the surfactant increases.

(2) **Ionic surfactants:** in general surfactants with ionic headgroups have a higher CMC in aqueous solution than surfactants with non-ionic headgroups.

(3) **Bulky hydrophobic/hydrophilic groups:** Due to the difficulty in incorporating bulky groups in the interior of the micelle, the bulkiness of the surfactants increases the CMC.

Micelles (CMC)

(4) Presence of Additives:

(1) Electrolyte: High ionic strength solution lowers the repulsion between the head groups due to the presence of counter ions surrounding the groups, therefore the CMC decreases

(2) Organic: Organic compounds (impurities) can either penetrate the micellar regions or modify the interaction between solvent-micelles. For example Urea, formaldehyde are believed to increase the CMC by disrupting the H-bonding network.

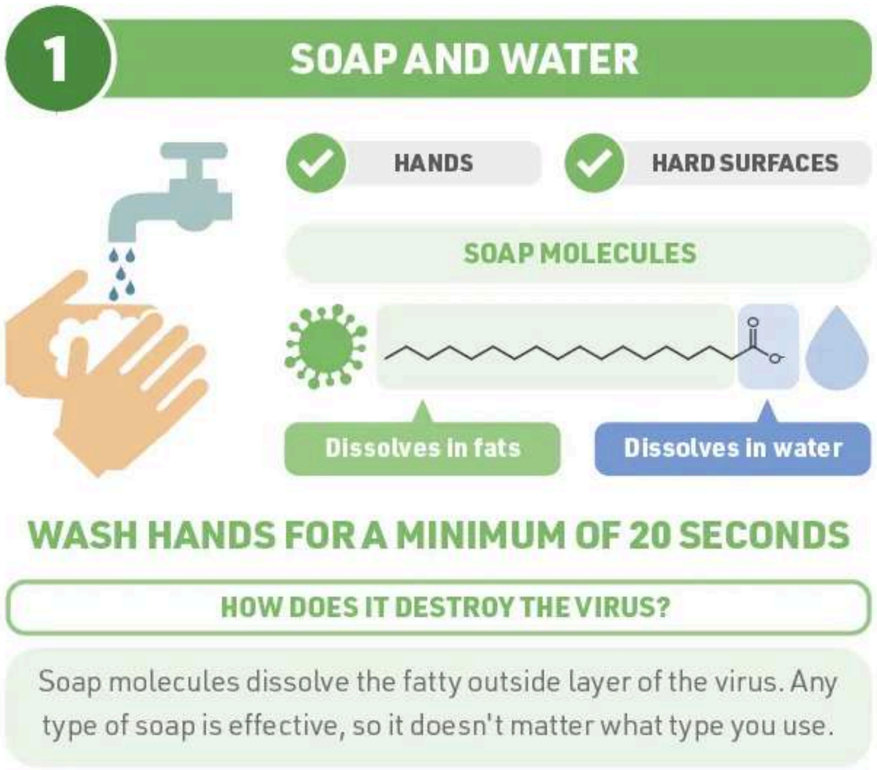
(5) Experimental conditions:

(1) Temperature: High temperature causes a decrease in hydration of the hydrophilic groups and thus it favors micellization (low CMC). High temperature may cause disruption in structured water around head groups and CMC increases.

Micelles (CMC)

(2) pH: CMC will be high at a pH value where head group is charged for example:

Low pH for –COOH head group and high pH for –NH2 group will increase the CMC for both cases.



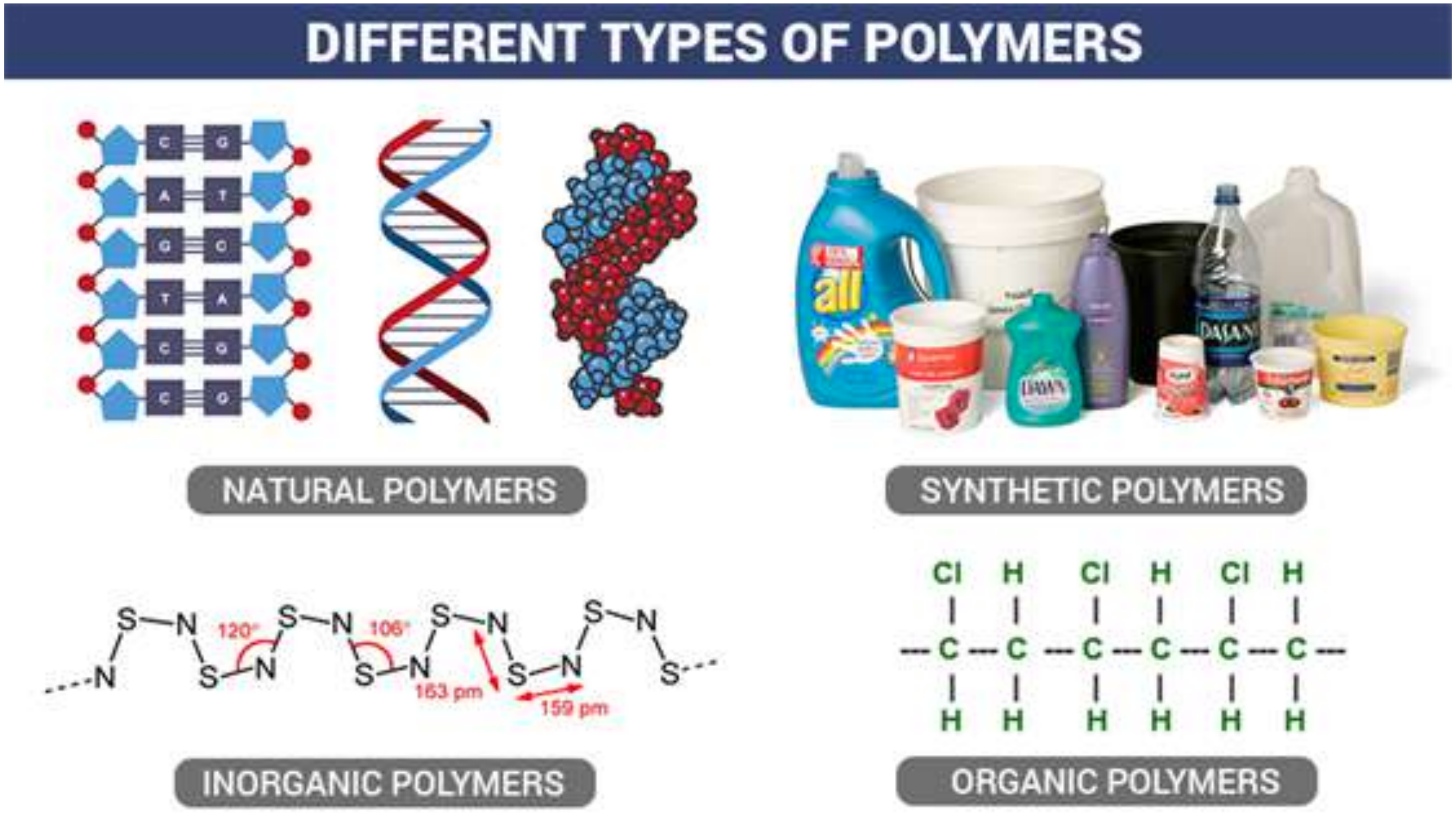
Soap molecules dissolve the fatty outside layer of the virus. Any type of soap is effective, so it doesn't matter what type you use.

Surfactants (amphiphiles) action on novel corona virus fat layer by dissolving it

c.f., https://www.compoundchem.com/

Macromolecules

Macromolecules (polymers) give rise to the structures that are absent in small molecules. This makes them to show a mass variation. The variation in mass is critical for the polymer properties.



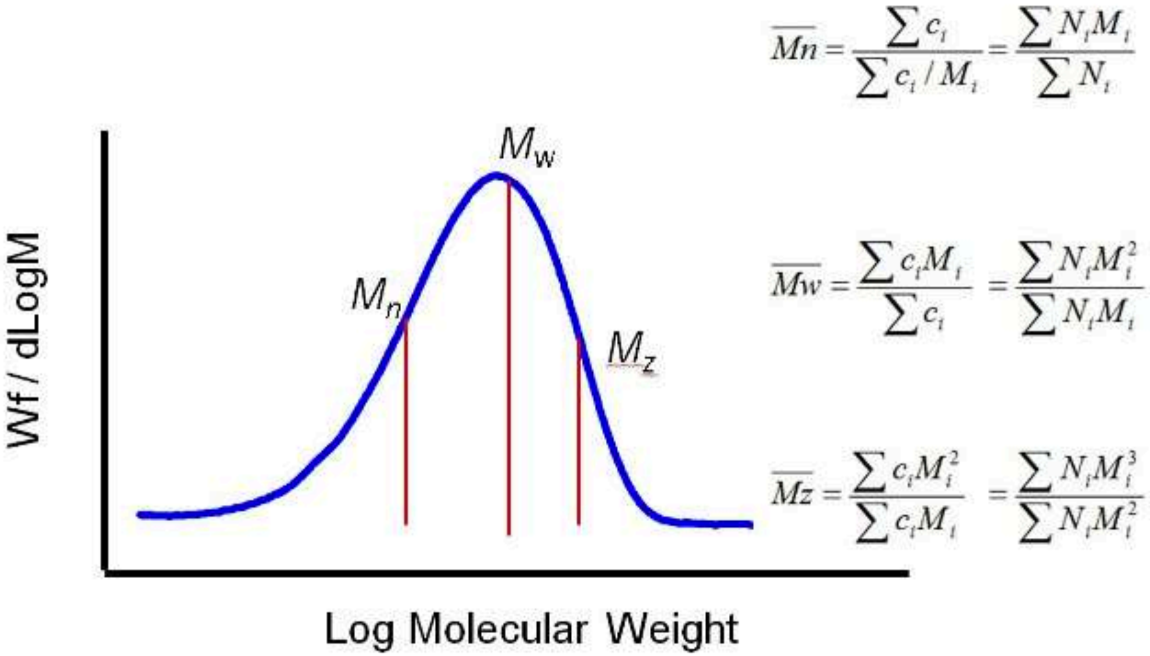
Macromolecules

Number-average molecular weight: This is a simple arithmetic mean of all the molar masses.

$$\overline{Mn} = \sum niMi/\sum ni$$
$$\overline{Mn} = n1M1+n2M2+n3M3+......../n1+n2+n3+...$$

Weight-average molecular weight: This is the sum of fractional masses that each molecule in a given sample contribute to the average according to the ratio of its mass to that of whole compound..

$$\overline{Mw} = \sum niMi^2/\sum niMi$$
$$\overline{Mw} = n1M1^2+n2M2^2+n3M3^2+......../n1M1+n2M2+n3M3+...$$



$$\overline{Mn} = \frac{\sum c_i}{\sum c_i / M_i} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{Mw} = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\overline{Mz} = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

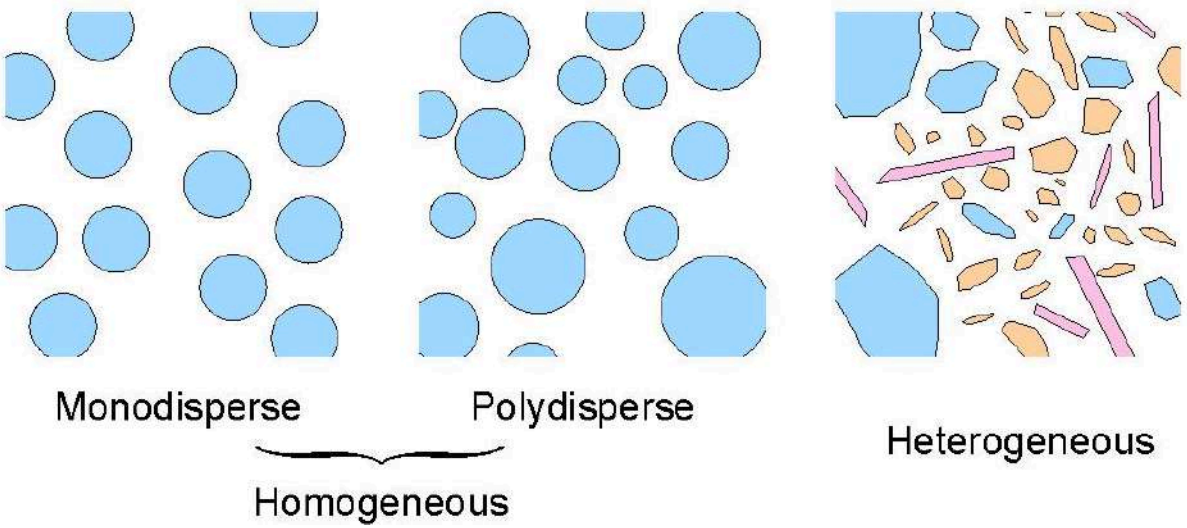
Macromolecules

Z-average molecular weight: This is the third power average molecular mass.

$$\overline{Mz} = \sum niMi^3 / \sum niMi^2$$

$$\overline{Mz} = n1M1^3 + n2M2^3 + n3M3^3 + \ldots\ldots\ldots / n1M1^2 + n2M2^2 + n3M3^2 + \ldots$$

Dispersity: It is the measure of the heterogeneity in the sizes of molecules in the mixture. It is considered to be one for a perfectly dispersed uniform sample. $\overline{Mn} = \overline{Mw}$



Allen T. (1975) Particle size measurement, Chapman and Hall

Macromolecules

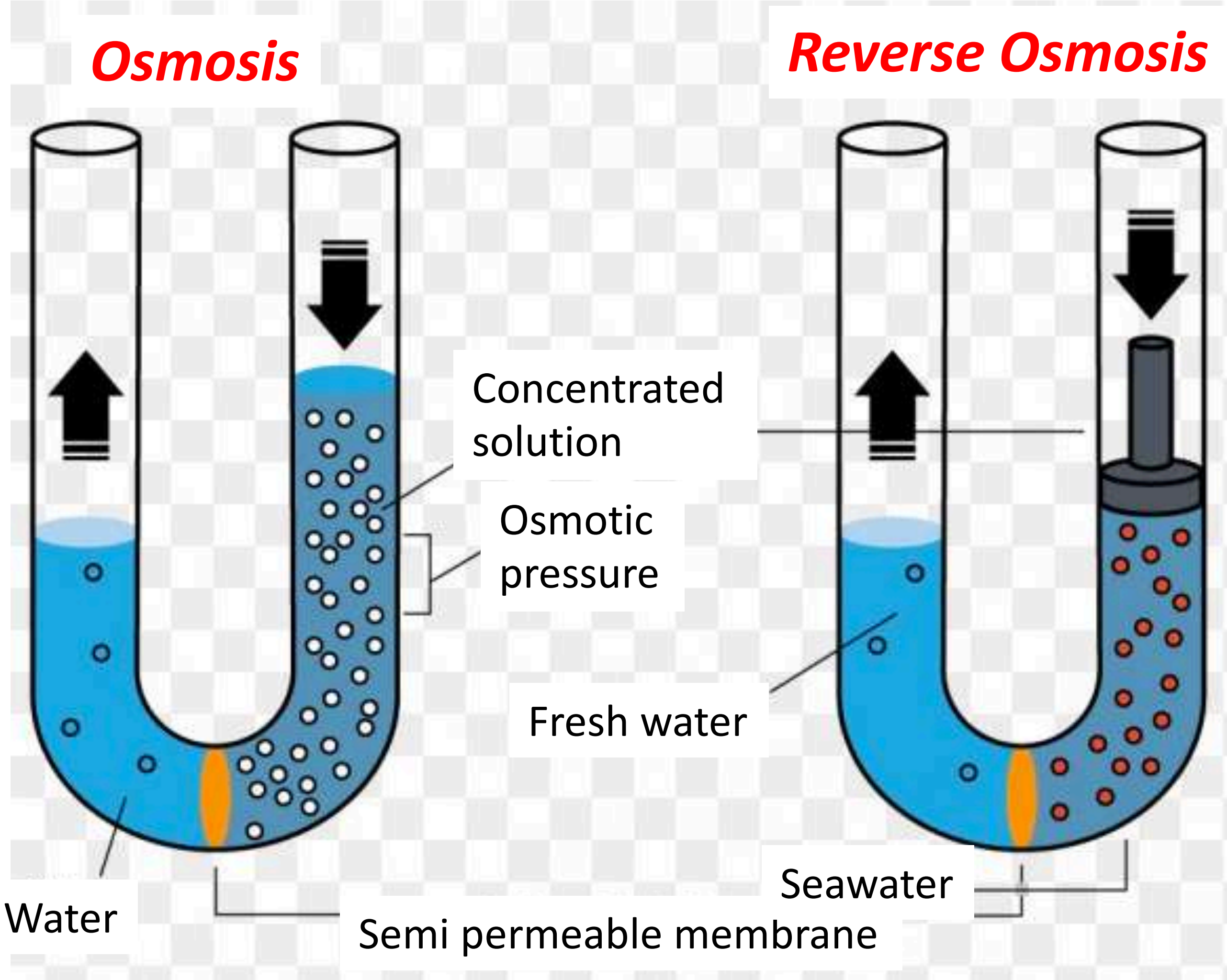
Methods for determining molecular weights of macromolecules

Osmometry method:

Osmosis: Osmosis is defined as the spontaneous net movement of solvent molecules through a semipermeable membrane into a region of higher solute concentration. The minimum pressure that is required to prevent the flow of solvent via the osmosis process. The reverse of this process is termed as ***reverse osmosis*** wherein solvent molecules move towards a region of lower solute concentration.

(Osmotic pressure) $\Pi = iCRT$

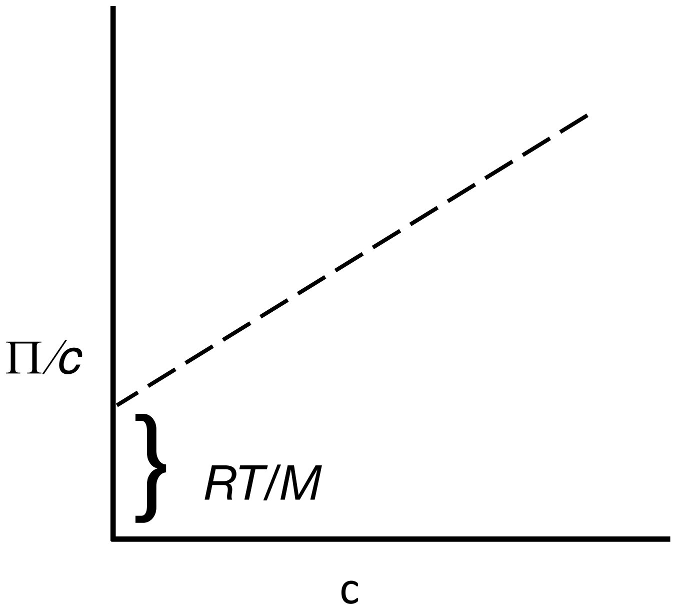
i = van't Hoff factor



Macromolecules

Osmometry method: Since macromolecules are very sensitive to the colligative properties, one can use osmometry method to determine the molecular weight of the polymers. In particular osmotic pressure changes are large and easily detectable as the molecular weight changes.

$$\lim_{c=0} \Pi/c = RT/M$$



Macromolecules

Viscosity method: It is defined as a quantity that expresses the internal friction in a fluid.

Relative viscosity $\eta_{rel} = \eta_{solution} / \eta_{solvent}$

Specific viscosity $\eta_{sp} = \eta_{rel} - 1$

Intrinsic viscosity $[\eta] =$

$$\underset{c\,=\,0}{Lim}\ \eta_{red}$$

$$\underset{c\,=\,0}{Lim}\ \eta_{sp}/c$$

Viscosity increase

$$[\eta] = \underset{c\,=\,0}{Lim}\ 2.5\,\phi/c$$

$\phi =$ volume fraction of solute

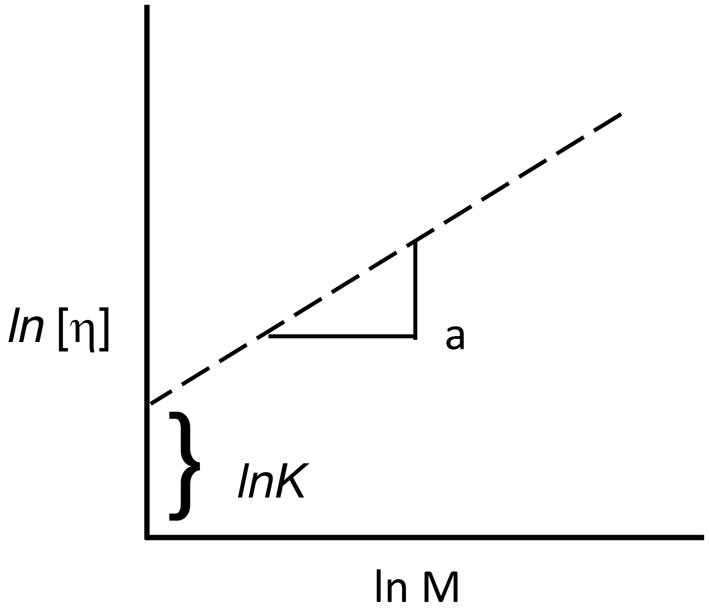
Macromolecules

Staudinger's method:

$$[\eta] = K M^a$$

$$\ln [\eta] = \ln K + a \ln M \text{ (equation of a straight line)}$$

K and a are constants that can be determined using osmometry or light scattering methods



Macromolecules

Glass transition: This is defined as the transition from a brittle glassy state to a viscous state as the temperature is increased. Generally the solids that exhibit this transition are called glass.

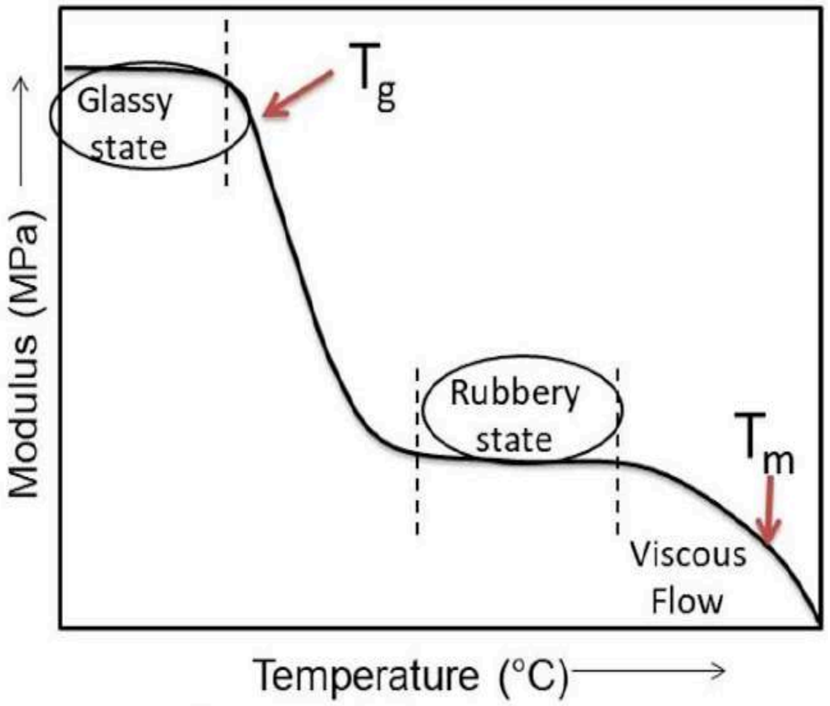
The range of temperatures above which the glass transition occurs. This value is always lower than the melting point of the material.

$$T_g < T_m$$

Below T_g : Polymers are hard and brittle like glass due to the lack of mobility

Above T_g : Polymers are soft and flexible due to the mobility e.g., rubber

Polymers such as PMMA, PS are always used below their glass transition temperature so they are generally brittle and in solid state.



References

1) Atkins' physical chemistry

2) L.P. Singh et al. / Advances in Colloid and Interface Science 2014, 214, 17–37

3) *Allen T. (1975) Particle size measurement, Chapman and Hall*

4) https://chem.libretexts.org/