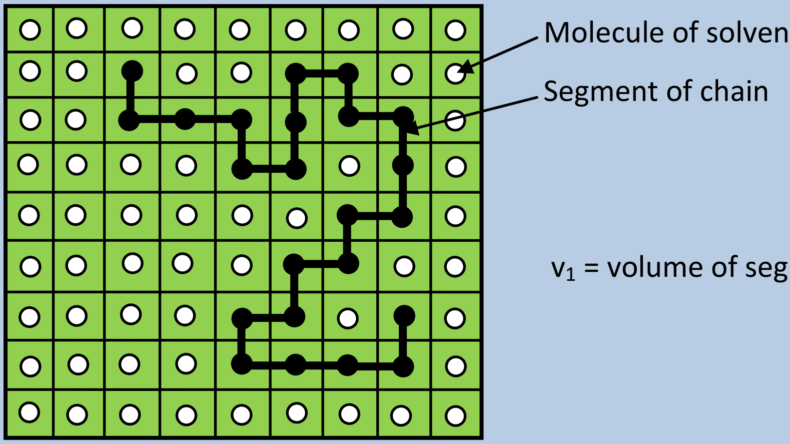
CHEM630 (Selective topics)

Polymers in solution

1- Flory Huggins theory

1.1 Athermal macromolecular solutions

The liquid crystalline network model of Flory and Huggins



v_1 = volume of segment

volume of segment = volume of molecule solvent (v_1)

If v_2 is the volume of polymer and x the number of segment per chain in this condition $v_2 = x.v_1$

If n_1 is the solvent molecule number and n_2 the number of macromolecules, using this model it is possible to calculate the ΔS (configuration) value of a mixture containing a polymer and a solvent.
If the macromolecular solution is athermal (no change the heat with the surrounding, $\Delta H_M = 0$) , ΔS(conf.) ≈ ΔS_M

$$\Delta S_M = -k(n_1 \mathrm{Log}\varphi_1 + n_2 \mathrm{Log}\varphi_2) \qquad (1)$$

with $\varphi_1 = \dfrac{n_1}{n_1 + x \times n_2}$ and $\varphi_2 = \dfrac{x \times n_2}{n_1 + x \times n_2}$

and the macromolecules number = x .n_2

If N_1 and N_2 is respectively the mole numbers of solvent and solute respectively, R = k x A, R = gas constant.

$$\Delta S_M = -R(N_1 \mathrm{Log}\varphi_1 + N_2 \mathrm{Log}\varphi_2) \qquad (2)$$

In case of athermal solution $\Delta S_M^E \neq 0$ and $\Delta H_M = 0$,

ΔS_M^E is the excess enthropy of the mixture

The free enthalpy of the mixture $\Delta G_M = -T\Delta S_M$

ΔG_M value can be also calculated from the following equation:

$$\boxed{\Delta G_M = -RT(N_1 \mathrm{Log}\varphi_1 + N_2 \mathrm{Log}\varphi_2)} \qquad (3)$$

1-2. The regular macromolecular solutions

A regular macromolecular solution is characterized by a small value of the mixture enthalpy (ΔH_M) compared with the thermal agitation energy which is alone responsible of the molecular repartition in the liquid network. So, the entropy of regular solution (polymer -solvent) has the same value that attributed to athermal macromolecular solution. This constitutes the ideal model of the real polymer solutions.

1-2.1. Heat of mixtures, Interaction parameter $\chi_{1,2}$

In the Flory–Huggins theory, the calculation of the heat of mixture (ΔH_M) is exactly the same relationship used for the determination of that used for the regular simple solution. The segment of macromolecular notion lead to the consideration of the elementary interactions solvent-solvent, solvent-segment and segment-segment respectively characterized by the elementary energies ε_{11},ε_{12} and ε_{22}.

$$\Delta H_M = z\left[\left(\frac{N_1\varepsilon_{11}}{2} + \frac{N_2 x\varepsilon_{22}}{2}\right) - \left(\frac{N_1^2\varepsilon_{11}}{2(N_1 + xN_2)} + \frac{N_2^2 x^2\varepsilon_{22}}{2(N_1 + xN_2)} + \frac{xN_1N_2\varepsilon_{12}}{N_1 + xN_2}\right)\right] \qquad (4)$$

z is the cell number adjacent of the segment number in the liquid crystalline network model's Flory.

This expression is usually written as fellow

$$\boldsymbol{\Delta H_M = RT\, \chi_{12} N_1 \varphi_2 \qquad (5)}$$

χ_{12} is a coefficient without dimension, called "interaction parameter" of the polymer-solvent couple or "Flory's parameter" and also determined by the following relationship:

$$\chi_{12} = (z - 2)\frac{\Delta\varepsilon_{12}}{RT} \qquad (6)$$

The energetic quantity ($RT\chi_{12}$) present theoretically the thermal effect accompanied the transfer of one mole of solvent from the solvent to pure polymer.

The free enthalpy (ΔG_M) of the regular macromolecular solution which indicates practically the case of a real solution at weak thermal effect is expressed as follow:

$$\boldsymbol{\Delta G_M = RT(N_1 \mathrm{Log}\varphi_1 + N_2 \mathrm{Log}\varphi_2 + \chi_{12} N_1 \varphi_2) \qquad (7)}$$

1-2.2. Notion of good solvent and mediocre (bad) solvent

The dissolution phenomenon of solute (2) in solvent (1) is effective when the free enthalpy of mixture (ΔG_M) take a negative value. As the entropy of mixture is always positive, the dissolution of a polymer in a solvent is conditioned essentially by the sign and the heat intensity of ΔH_M.
Therefore, the interaction parameter, χ_{12}, measures the quality of a solvent towards a polymer.

By analogy with the theory of the regular simple solutions, the expression of the heat ΔH_M calculated from the Flory –Huggins theory is affected by a positive sign (*endothermic mixture*). This is practically true for the majority of the macromolecular solutions. It was observed some exceptions when the constituents (solvent and polymer) both have polar structure.

Example: the dissolution of the poly(methylmethacrylate) in trichloroethylene give a negative value of ΔH_M.

The endothermic macromolecular solutions which represent the major part of the real cases are, in opposite, characterized by the positive values of the interaction parameters χ_{12}.

For an endothermic mixture realized at temperature (T), the complete dissolution of the macromolecular solute in the solvent is the best with the weak interaction parameters. The solvent with the weak interaction parameters is designed by a good solvent for the polymer considered. In this way, the natural rubber-carbon tetrachloride, poly(vinyle-tetrahydrofuran chloride) and cellulose nitrate are characterized by a χ_{12} of 0.28, 0.14 and 0.27 respectively. On opposite, the solvent with the χ_{12} near 0.5 is designed by the mediocre solvent for the polymer considered. The polyisobutylene is dissolved easily at ordinary temperature in the cyclohexane (χ_{12}= 0.44) than in benzene (χ_{12} = 0.5). The good solvent and the bad solvent are closely linked to the temperature.

1-3. Real macromolecular solutions

In general, the concept of the regular macromolecular is not applicable in case of the real macromolecular solutions which the heat of mixture (ΔH_M) take a notable value or when the components of the mixture are more polar. In fact, for these types of solution it is impossible to identify the entropy of configuration (ΔS_{conf}) from the entropy of mixture (ΔS_M). Because the dispositions of the macromolecular segments in solution are not only governed by the statistical considerations and ΔH_M can take a positive value. The segments of macromolecules tempt to withdraw into oneself for favorite the segment-segment interactions.

$$\Delta S_M = -R[N_1 \mathrm{Log}\varphi_1 + N_2 \mathrm{Log}\varphi_2 + \frac{d(\chi_{12} T) N_1 \boldsymbol{\varphi}_2}{dT} \qquad (8)$$

$$\Delta H_M = -RT^2 . \frac{d\chi_{12}}{dT} . N_1 \boldsymbol{\varphi}_2 \qquad (9)$$

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad (10)$$

Now, it is possible to resume the definitions of the different categories of macromolecular solutions as follow.

Table Definitions of the different categories of macromolecular solutions

Athermal macromolecular solution	$\Delta S_M^E = 0$	$\Delta H_M = 0$
Regular macromolecular solution	$\Delta S_M^E = 0$	$\Delta H_M = RT\chi_{12} N_1 \boldsymbol{\varphi}_2$
Real macromolecular solution	$\Delta S_M^E = \frac{d}{dT}(\chi_{12} T) N_1 \boldsymbol{\varphi}_2$	$\Delta H_M = -RT^2 \frac{d\chi_{12}}{dT} N_1 \boldsymbol{\varphi}_2$

2- Macromolecular diluted solutions

In general, we admit that the macromolecular chains in solution have practically a homogeny repartition when the volume fraction of solute is superior to 0.04. Before this limit, the effective volumes occupied by the chains can be more or less separated and the Flory-Huggins theory is not experimentally verified. In a particular case, the partial molar entropy of solvent takes clearly the weakest values compared with those deducted by the calculation. For the as diluted solutions, the partial molar entropy of solvent can be expressed as fellow.

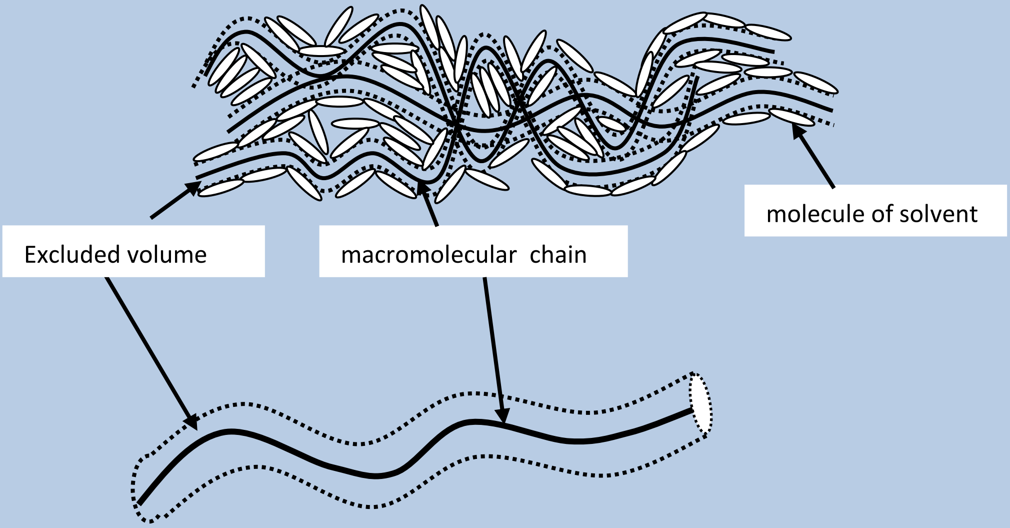
$$\overline{\Delta S_1} = -R\left(\frac{\boldsymbol{\varphi}_2^2}{2} + \frac{\boldsymbol{\varphi}_2^3}{3} + \ldots\right) \qquad (11)$$

The $\overline{\Delta S_1}/R\boldsymbol{\varphi}_2^2$ value goes to 0.5 when the macromolecular solution became more and more diluted.

2.1 Notion of the excluded volume

The excluded volume is the space unoccupied by the macromolecules in solution.

Each macromolecule has an excluded volume (domain delimited by the repulsion of two adjacent macromolecules)



If u is the excluded volume by each macromolecule, V_1^o the molar volume of solvent, $\mathcal{N}$ the Avogadro number and x is the number of segment the ΔS_M take the following equation:

$$\Delta S_M = -RN_2(\mathrm{Log}\,\varphi_2 - \frac{\mathcal{N}u}{2V_1^o x}\varphi_1) \qquad (12)$$

Because the diluted macromolecular solution is practically considered as athermal, the free enthalpy of this solution can be expressed as fellow:

$$\Delta G_M = -T.\Delta S_M = RTN_2(\boldsymbol{Log\,\varphi_2} - \frac{\mathcal{N}u}{2V_1^o x}\varphi_1 - ...) \qquad (13)$$

In this present case the variation of the chemical potential $\overline{\Delta G}_M = \Delta\mu_1$

In which $\Delta\mu_1$ is expressed as follow:

$$\Delta\mu_1 = -RT(\frac{\varphi_2}{x} + \frac{\mathcal{N}u}{2V_1^o x^2}\varphi_2^2 + ...) \qquad (14)$$

In case of an isomolecular sample in which the molecular weight value of the polymer is M_2 and c_2 is the concentration of polymer (g/ml) in solution ϕ_2 can be expressed as follow:

$$\boldsymbol{\varphi}_2 = \frac{c_2 V_1^o x}{M_2} \tag{15}$$

The $\Delta\mu_1$ expression can be also expressed as fellow

$$\Delta\mu_1 = -c_2 RTV_1^o\left(\frac{1}{M_2} + \frac{\mathcal{N}u}{2M_2^2}c_2 + \ldots\right) \tag{16}$$

The details of the osmotic pressure of a macromolecular solution allow representing the previous equation as fellow

$$\Delta\mu_1 = -c_2 RTV_1^o(A_1 + A_2 c_2 + \ldots) \tag{17}$$

with $A_1 = \frac{1}{M_2}$ and $A_2 = \frac{\mathcal{N}u}{2M_2^2}$

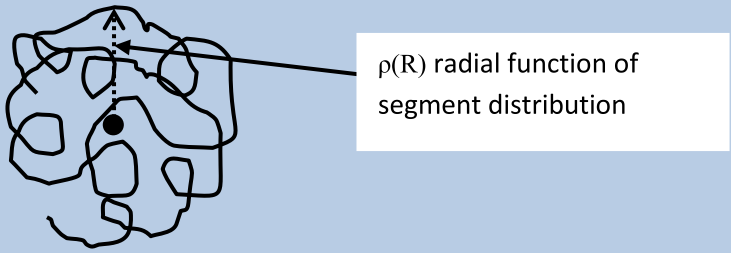
A_1 and A_2 are respectively the first and second Virial coefficients.

This equation constitutes the base of the molecular weight determination. A_1 and A_2 (interaction parameter) can be deducted from the classical physic-chemistry macromolecular techniques.

2.2 Flory and Krigbaum Theory

The spherical and stick forms of macromolecules proposed by Zimm and Huggins in reality are two models very simplified. This proposition constitutes two cases diametrically opposed of macromolecules in solution which depended to the solvatation of the polymer in its solvent.

Flory and Krigbaum have calculated the general expressions of the excluded volume (u) and the second coefficient of Viral (A_2) which characterize the macromolecules gifted by a good flexibility. In case of a much diluted macromolecular solution, each isolated macromolecule can be definite by a radial function of segments distribution from the mass center of the molecule to its surface.



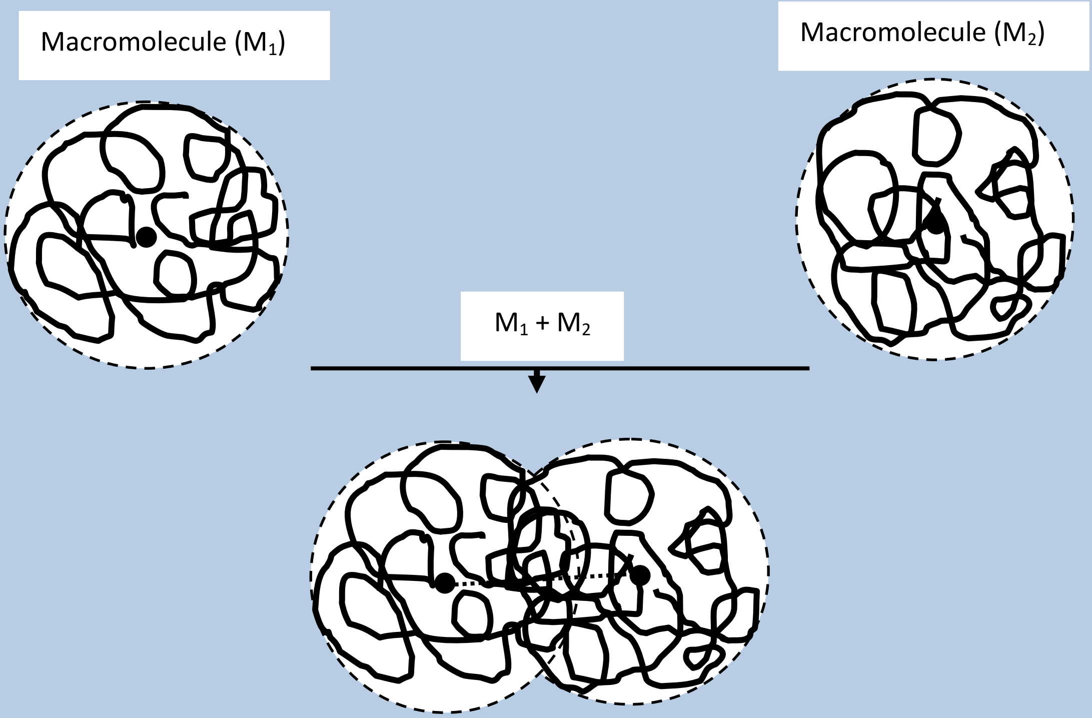
$$\rho(R) = x \times \left(\frac{3}{2\pi \times R_G^2}\right)^{3/2} e^{-3R^2/2R_G^2} \qquad (18)$$

with R_G is the gyration radius

This function presents the density of segments occupied by a macromolecule chain. This representation is usually called “Gaussian ball”. This notion is applicable only in the particular case of the θ-conditions (θ-solvent and θ-temperation).

2.2.1 Volume excluded by a flexible macromolecular chain

Considering that in a solution contained two macromolecules isolated



In these conditions, the second coefficient of Virial (A_2) of the previous general equation which characterizes the flexible macromolecular chain in diluted solution according to the Flory – Krigbaum theory is:

$$A_2 = \frac{\mathcal{N} u}{2M_2^2} = (\frac{1}{2} - \chi_{12}) \frac{\bar{v}_2^2}{V_1^o} F(X) \qquad (19)$$

with

$$\bar{v}_2 = x \times v_1^o \times \mathcal{N} / M_2$$

$\bar{v}_2$ is the specific volume of polymer in solution

The excluded volume (u) can take the fellowed expression

$$u = 2 \times (\frac{1}{2} - \chi_{12}) \times x^2 \times v_1^o \times F(X) \qquad (20)$$

v_1^o is the volume of the molecule of solvent and F(X) is a complex integral that is possible to develop it in series as:

$$F(X) = 1 - \frac{X}{2^{3/2} 2!} + \frac{X^2}{3^{3/2} 3!} - \ldots \qquad (21)$$

with

$$X = 2(\frac{1}{2} - \chi_{12}) \frac{\bar{v}_2^2 M_2^2}{V_1^o \mathcal{N}} (\frac{3}{4\pi \times R_G^2}.)^{3/2} \qquad (22)$$

The variation of the chemical potential ($\Delta\mu_1$) determined previously can be expressed from the following relationship

$$\Delta\mu_1 = -c_2 RT V_1^o [\frac{1}{M_2} + (\frac{1}{2} - \chi_{12}) \frac{\bar{v}_2^2}{V_1^o} c_2 + \ldots] \qquad (23)$$

2.2.2 ϑ-Solvent and ϑ-temperature

One of the principal consequences of the Flory–Krigbaum theory is that the excluded volume (u) and the second coefficient of Virial (A_2) both are the functions of the interaction parameter χ_{12}.

When χ_{12} is negative, the case of certain exceptional couples polymer-solvent, the quantity ($1/2 - \chi_{12}$) is always positive and the excluded volume (u) and the second coefficient of Virial (A_2) increased with the absolute value of χ_{12}. In this fact, the intermolecular interactions between the segments and solvent molecules are energetically more favored than the segment-segment intramolecular interactions, this fact induces a strong deployment of each macromolecular ball.

We know that, in opposite, almost of the macromolecular solutions are characterized by a positive interaction parameter (χ_{12}). In so far as this parameter is inferior to 0.50, the equation (20) shows that the excluded volume (u) and the second coefficient of virial (A_2) are always positives and very weak in case of a mediocre solvent ($\chi_{12} \approx 0.40$ to 0.50) than the good solvent toward the polymer considered ($\chi_{12} \approx 0$ to 0.30).

When the interaction parameter is exactly 0.5, the relation (20) shows a nil excluded volume. The absolute temperature in which the interaction parameter value (χ_{12}) is 0.5 is called θ-temperature or Flory temperature. Such as solvent necessary a mediocre solvent for this polymer taking in the same conditions of temperature is designed as θ-solvent. θ-solvent can be a pure liquid or a liquid mixture.

Other definition, the θ-temperature can be defined more rigorously as the temperature of the macromolecular solution in which the second coefficient of Virial A_2 is nil.

2.3 The coefficient of molecular expansion

We know that the conformations adopted by the primary structure of the linear and flexible macromolecules in solution are characterized by two dimensions:

- The average square distance $\overline{L^2}$ between the two extremities of each chain
- The gyration radius R_G in which its average square performs the average weight of the square distances R_i^2 taking at the mass center.

$$R_G = (\overline{R^2})^{1/2} = \Big(\overline{\frac{\sum_i m_i R_i^2}{\sum_i m_i}} \Big) \qquad (24)$$

The conformational statistic allows knowing the two parameter values. The general expression of the average square distance is:

$$\overline{L_o^2} = Na^2 \qquad (25)$$

where N is the bond number which is identify, in the case of the simple synthetic polymers, as the number of segments (x) we can write

$$\overline{L_o^2} = \mathrm{x}a^2 \qquad (26)$$

where "a" is a parameter which depends to the nature of the considered model.

For example, if the macromolecule chain is considered as analogue to that used for the distance measurement, in which the existence of valence angles are ignored, ɑ can be take the length of the bond.

If the calculation concerns the chains which the rotations around the valence angles are completely free, the value of (ɑ) take the followed expression:

$$\boldsymbol{a} = \frac{\boldsymbol{l}(1+\boldsymbol{\mu})}{1-\boldsymbol{\mu}} \qquad (27)$$

With µ is the cosinus value of the principal valence angle and l the length of the bond.

The gyration radius is linked to average precedent by the followed equation

$$(\boldsymbol{R_G})_{\boldsymbol{o}}^2 = \frac{\overline{\boldsymbol{L_o^2}}}{6} \qquad (28)$$

The zero index used in the $\overline{\boldsymbol{L}^2}$ and $\boldsymbol{R_G^2}$ formalisms symbolizes the dimensions of chains in solution using the θ-solvent. The dimensions $\overline{\boldsymbol{L_o^2}}$ and $(\boldsymbol{R_G})_{\boldsymbol{o}}^2$ are, in this way, called dimensions *"none disrupted".*

Outside of the θ-conditions, the average square distance ($\overline{\boldsymbol{L}^2}$) and the gyration radius ($\boldsymbol{R_G^2}$) values are highest compared with those of the corresponding non disrupted dimensions. It was signaled previously that this dilatation is more important in case of a good solvent compared with that of the mediocre solvent.

For considering the combined effects of the solvent nature and exclusion volume, Flory and Fox are introduced a empiric parameter called "α" which define the real dimensions " *disrupted*"

$$\overline{\mathrm{L}^2} = \boldsymbol{\alpha}^2 \overline{\mathrm{L}_{\mathrm{o}}^2} \qquad (29) \qquad \text{and} \qquad \boldsymbol{R_G^2} = \boldsymbol{\alpha}^2 (\boldsymbol{R_G})_{\boldsymbol{o}}^2 \qquad (30)$$

In these conditions "α" is called, coefficient of molecular expansion. This parameter takes a positive value superior to one for the good and the mediocre solvents, in opposite, for the θ-solvent, this parameter is characterized by α = 1.

The experimental determination of "α" is possible by using the light scattering or the viscosimetry methods. This viscosimetric technique is a usual physic-chemistry method used in the laboratories. This technique consists to measure the intrinsic viscosity ([η]) of the macromolecular sample dissolved in any solvent and another dissolved in a θ-solvent ($[\eta]_\theta$). The coefficient "α" is deduced by the following relationship

$$\alpha^3 = \frac{[\eta]}{[\eta]_\theta} \qquad (31)$$

Exercises

1) What does mean by the athermic macromolecular solution?

2) What is the difference between an athermic macromolecular solution and an ideal solution?

3) A poly(vinylalcohol) solution contains 0.25 mol of polymer and 523 g of water, if this solution is considered as athermic and the average number of molecular weight of PVA is 4.10^4 g/mol, calculate:
   a) The enthalpy of this solution
   b) The free enthalpy of this solution
   c) The entropy of this solution

4) 10^{-3} molar solution of poly(acrylamide) in water is considered as regular and the polymer is isomolecular and its average number molecular weight is $2.3\ 10^5$ g/mol. Determine:
   a) The interaction parameter at the equilibrium
   b) The enthalpy of the mixture
   c) What is the character of water toward the poly(acrylamide)

5) 10^{-2} molar solution of an unknown polymer in water, the polymer is isomolecular and its average number molecular weight is equal to 5.10^6 g/mol. If the interaction parameter vary with the temperature according the following relationship $\chi_{1,2} = 1.6 - 0.0036T - 2.10^{-2}/T^2$ determine:
   a) the heat of this solution
   b) the excess entropy of this solution
   c) What is the character of this solution? (athermic, regular or real)
      Indicate if the water constitutes a good solvent at ambient(room) temperature for this unknown polymer

6) Calculate the average molecular weight of poly(methylvinylketone) if this polymer dissolved in toluene is considered as linear and flexible. The excluded volume and the coefficient of Virial are 2.9×10^{-14} and 0.874 respectively.

7) From the data of the precedent exercise, determine the interaction parameter χ12 that exist between the methyvinylketone units and the solvent molecules if X = 0.45 and $(\overline{v}_2)^2 = 1.5V_1^o$. What do you think about this value?

8) Determine the molecular expansion parameter of poly(methyl methacrylate) in THF if the viscosimetry study allows the intrinsic viscosity of THF 1.22 dl/g and 0.46 dl/g in an unknown θ-solvent. What do you think about the "α" value?

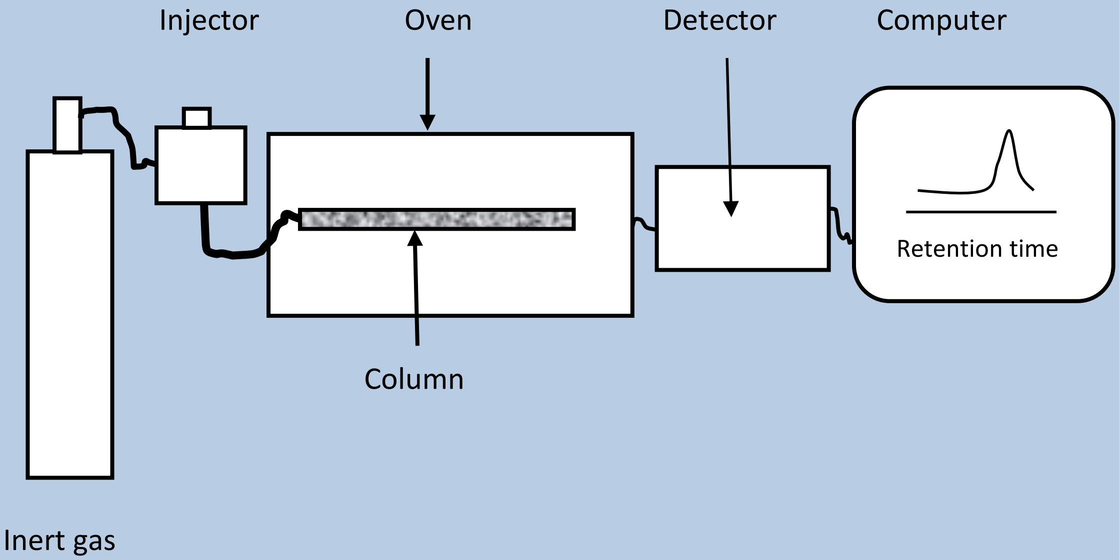
3 Technique using for determinate the interaction parameter polymer

3.1 Inverse gas chromatography

Employed in it inverse state, this technique leads to obtain several parameters as ΔHa (heat of absorption), ΔHd(heat of dissolution), Tg (glass transition temperature) and the solvent–polymer, non solvent polymer and polymer-polymer interaction parameters of Flory.

Inverse state means the injection of a known substance called probe and study indirectly the stationary phase (polymer).

Scheme



- The principal element in the inverse gas chromatography is the column
- The column is treated and loaded by a inert support impregnate by the polymer.

- The infinite quantity (some µl) of molecule probe (solute) is injected in the column loaded.
- The retention time of the solvent is taking at the summit of the peak.

The retention volume Vg is calculate according to the following equation

$$Vg = \frac{t_r}{m_f} \times \frac{273}{T_a} \times D \times \frac{P_1^o - P_{H2O}}{P_1^o} \times J$$

Where t_r is the retention time of the molecule probe injected, mf, the mass of the stationary phase (polymer), Ta, the ambient temperature.

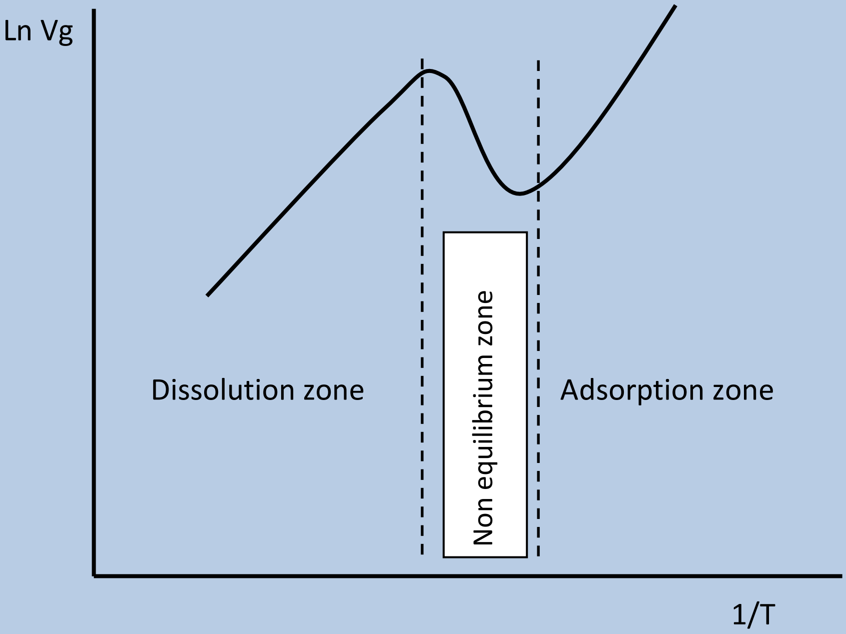
P_1^o and P_{H2O} are respectively the atmospheric pressure and the vapor pressure of water at T_a. D is the flow rate of the vector gas in outlet of the column.

J is the James Martin correlation factor

$$J = \frac{3}{2} \times \frac{[(P_{in} / P_{out})^2 - 1}{[(P_{in} / P_{out})^3 - 1]}$$

Where P_{in} and P_{out} are respectively the input and output pressure of the column.

The resulting chromatogram of ln Vg versus 1/T leads to the following curvature



The study of the polymeric stationary phase by this technique permit to determine the Tg (glass transition temperature).

a- Zone of absorption

This zone corresponds to the temperatures inferior to Tg where the polymeric phase is in its glass state. In this case, the mechanism is principally governed by the adsorption phenomena.

The heat of adsorption ΔHa of the solute (molecule probe) by the polymer (stationary phase) is determined from the following relationship.

$$\frac{\partial \mathrm{LnVg}}{\partial(1/T)} = -\frac{\Delta H_a}{R}$$

where R is the constant of gas

b- Zone of none equilibrium

In this zone the retention mechanism is generally complex, the stationary polymeric phase is in the chromatographic non equilibrium state due to the physical state transition of this phase.

c- Zone of dissolution

The stationary phase is in its liquid state, this zone correspond to the temperatures superior to Tg (mobility of the polymeric chains). In this zone the thermodynamic analysis of interaction is possible. The phenomenon of the retention is governed by the partition between the gas phase and the polymeric stationary phase.

The heat of dissolution ΔHd of the solute by the polymeric stationary phase is giving by the following equation:

$$\frac{\partial \mathrm{LnVg}}{\partial(1/T)} = -\frac{\Delta H_d}{R}$$

3.1.1 The interactions polymer-solvent

The Flory-Huggins theory applied to the real binary system constituted of polymer and solvent permit the determination of the interaction parameters ($\chi_{1,2}$) from the following equation:

$$\chi_{1,2} = \ln(\frac{273.15\times R\times v_2}{V_g \times P_1^o \times V_1}) - 1 - \frac{P_1^o}{R\times T}(B_{11} - V_1)$$

v_2 is the specific volume of polymer, V_1 molar volume of the molecule probe (solute).
B_{11} is the second coefficient of Virial linked to the solute in the gaseous phase at T .
Vg is the retention volume.

3.1.2 The interaction solvent/Polymer-Polymer

The Flory-Huggins theory applied to the real ternary system constituted of two polymers and solvent permit the determination of the interaction parameters ($\chi_1(_{2,3})$) from the following relationship:

$$\chi_{1(2,3)} = \frac{V_o}{V_1}(\ln\frac{273.15\times R(w_2\times v_2 + w_3\times v_3}{V_{g_{blend}}\times V_1\times P_1^o}) - 1 + \frac{V_1}{M_2\times v_2} + \frac{V_1}{M_3\times v_3} - \frac{(B_{11} - V_1)}{R\times T}\times P_1^o)$$

V_o is the reference volume and M_2 , M_3 are respectively the average number molecular weight of polymer(2) and polymer(3).
v_1 , v_2, v_3 are the specific volume of the solvent, polymer (2) and polymer (3) respectively.
w_2 and w_3 are the weight fraction of Polymer (2) and polymer (3) in the blend respectively.

Here, $\chi_{1(2,3)}$ is related to other binary interaction parameters as shown in the following expression:

$$\chi_{1(2,3)} = \varphi_2 \times \chi_{12} + \varphi_3 \times \chi_{13} + \varphi_2 \times \varphi_3 \times \chi_{13}$$

3.1.3 The interaction Polymer-Polymer

The Flory-Huggins theory applied to the real ternary system constituted of two polymers and solvent also permit the determination of the interaction parameters polymer- polymer $\chi_{2,3}$. The polymer-polymer interaction parameter related to the solvent volume, $\chi'_{2,3}$ is introduced as:

$$\chi'_{23} = \frac{[\ln(V_{g,blend}/v_b) - \varphi_2\times\ln(V_{g,2}/v_2) - \varphi_3\times\ln(V_{g,3}/v_3)]}{\varphi_2\times\varphi_3}$$

$$v_b = w_2 \mathrm{x} v_2 + w_3 \mathrm{x} v_3$$

$Vg_{,blend}$, $Vg,_{\ 2}$ and $Vg_{,3}$ are respectively the retention volume of the blend, polymer (2) and polymer (3).

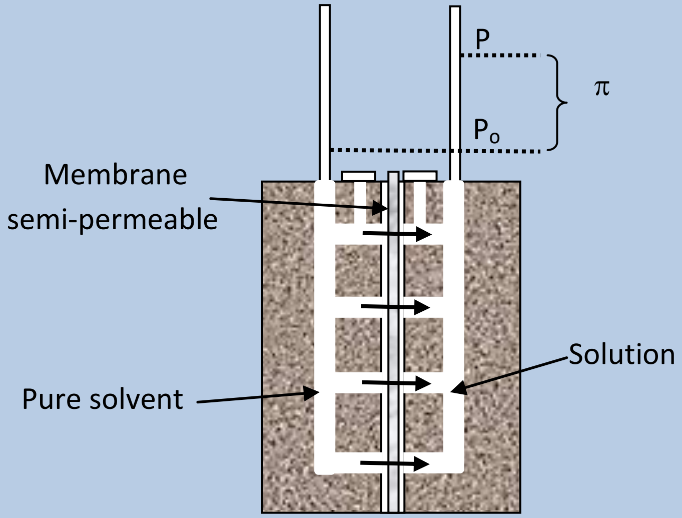
The polymer-polymer interaction parameter related to the solvent volume, $\chi'_{2,3}$ is also introduced as:

$$\chi'_{23} = \chi_{23} \times \frac{V_1}{V_2}$$

$$\chi_{23} = \frac{V_2}{V_1} \times \{ \frac{[\ln(V_{g,blend} / v_b) - \varphi_2 \times \ln(V_{g,2} / v_2) - \varphi_3 \times \ln(V_{g,3} / v_3)]}{\varphi_2 \times \varphi_3} \}$$

3.2 Osmotic pressure of diluted macromolecular in solution

The osmotic phenomenon through a membrane " semi-permeable" is widely employed in the macromolecular physical chemistry.



Scheme of osmometric apparatus

Membrane : cellophan, poly(vinylalcohol), poly(vinylacetate) …

The difference between P and P_o is called osmometric pressure (π)

$$\pi = P - P_o$$

3.2.1 Thermodynamic expression of the osmotic pressure

$$\mu_1^o = \mu_1 + \int_{p_o}^{P} \overline{V_1} dP$$

μ_1 and μ_1^o are the chemical potential of the solvent and the standard respectively and $\overline{V}_1$ represent the partial molar volume of the solvent in the solution. For the liquid solution not very compressible

$$\mu_1^o - \mu_1 = -\overline{V}_1 (P - P_o)$$

$$\pi = -\frac{\Delta\mu_1}{\overline{V_1}}$$

For the macromolecules, the solutions must be infinitely diluted

The $\Delta\mu_1$ can be substituted by

$$\Delta\mu_1 = -c_2 RTV_1^o (A_1 + A_2 c_2 + ...) \text{ with } A_1 = \frac{1}{M_2} \quad \text{and} \quad A_2 = \frac{N \times u}{2M_2^2}$$

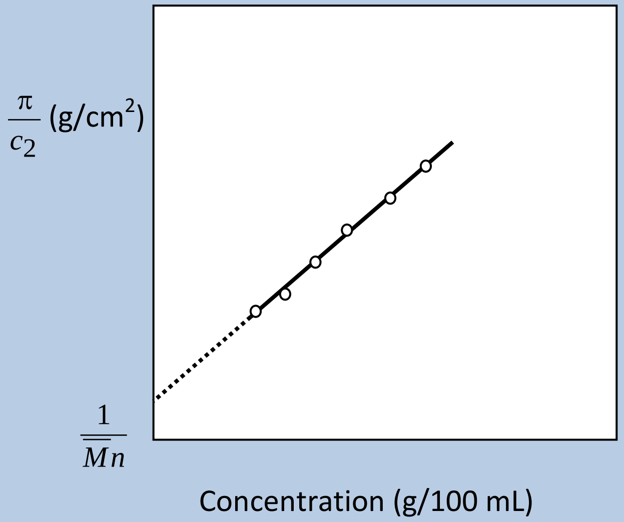
$$\frac{\pi}{c_2} = RT\left(\frac{1}{M_2} + A_2 c_2 + ...\right)$$

This equation constitutes the base for the determination of the molecular weights and the interaction parameters A_2.

3.2.2 Determination of average number molecular weights

The previous relationship shows that the extrapolation to infinitely dilution of the experimental curves $\pi / c_2 = f(c_2)$ and leads to the depermination of the average number molecular weights of the macromolecular sample. We have

$$\frac{1}{\overline{M}_n} = \frac{1}{RT} \lim_{c_2 \to 0} \left[\frac{\pi}{c_2}\right]$$



3.2.3 Determination of the interaction parameters

The osmometry technique is also a method used for the determination of the interaction parameters through the Virial coefficient (A_2) for the polymer-solvent system.

In general $$\frac{\pi}{c} = RT\left(\frac{1}{\overline{M}_n} + A_2 c_2 + \ldots\right)$$

It is easy to note that $$A_2 = \frac{1}{RT} \lim_{c \to 0} \left[\frac{d(\pi / c)}{dc} \right]$$

The A_2 corresponds in reality to the slope of the $\frac{\pi}{c}$ = f(c)

3.2.4 Thermodynamic methods study based on the Raoult's laws

It is possible to determinate the molecular weights of polymer in much diluted solution using the Raoult' laws.

$$\lim_{c_2 \to 0} \left[\frac{\Delta\theta_F}{c_2} \right] = \left(\frac{\Delta\theta_F}{c_2} \right)_0 = \frac{RT^2}{\rho_1 \Delta H_1^F} \times \frac{1}{M_2}$$

$\Delta\theta_F$ is the decrease in the freezing-point , ΔH_1^F and ρ_1 are the heat of fusion and the density of the pure solvent respectively.

$$\lim_{c_2 \to 0} \left[\frac{\Delta\theta_E}{c_2} \right] = \left(\frac{\Delta\theta_E}{c_2} \right)_0 = \frac{RT^2}{\rho_1 \Delta H_1^v} \times \frac{1}{M_2}$$

$\Delta\theta_E$ is the decrease in the boiling-point , ΔH_1^E and ρ_1 are the heat of fusion and the density of the pure solvent respectively.

The second technique based on the Raoult's laws is the "**tonometry"** this technique is more delicate in its manipulation. This method consist to measuring the decrease of the vapor pressure of pure solvent in diluted solution Δp_1 and by the application of the Raoult's equation

$$x_2 = \frac{\Delta p_1}{p_1^o} \quad \text{and} \quad \lim_{c_2 \to 0} \left[\frac{\Delta p_1}{c_2} \right] = \left(\frac{\Delta p_1}{c_2} \right)_0 = \frac{M_1 p_1^o}{\rho_1} \times \frac{1}{M_2}$$

where x_2 is the molar fraction of solute (polymer).

4. Solubility of polymers

4.1 Hildebrand Solubility parameters

Hidebrand has defined a solubility parameter (δ_i) characterizing each molecule of the same type as $\delta_i = \left(\frac{\varepsilon_{ii} \times z}{2\overline{V}_i} \right)$

where ε_{ii} is the associated energy of the same type of molecule and z, the coordination number of the liquid network (the number of the immediate molecules neighbor), $\overline{V}_i$ the partial molar volume of the solvent.

This parameter can be obtained experimentally from the vaporization energy of the liquids. The enthalpy of mixture takes definitively the following form:

$$\Delta H_M = V\varphi_1\varphi_2(\delta_1 - \delta_2)^2$$

It well know that the solubility of a solute in a solvent is possible when

$\Delta G_M = \Delta H_M - T\Delta S_M < 0$ ΔS_M is always positive

For a good solubility ΔH_M take the weak positive value

The necessary condition for obtain a solution is $\Delta H_M \approx 0$ or $\delta_1 \approx \delta_2$

5. The phases separation in the systems at weak interactions

5.1 The binary systems

5.1.1 Systems containing a polymer and a solvent

A) Athermic solutions

According to the hypotheses that the dissolution of the flexible macromolecular chain is occurs neither variation of volume and nor energy transfer during the mixing. The variation of energy takes the following equation:

$$\frac{\Delta G_m}{RT} = N_1 \ln \varphi_1 + N_2 \ln \varphi_2 \qquad (1)$$

N_1 and N_2 are the mole number of the compound 1 and 2 respectively, φ_1 and φ_2 are their volume fraction. It was noted that:

$$\frac{\Delta\mu_1}{RT} = \frac{\overline{\Delta G_1}}{RT} = \ln \varphi_1 + (1 - \frac{1}{x})\varphi_2 \qquad (2)$$

x is the ratio of the molar volume of solute /molar volume of solvent. x is proportional to the polymerirization degree.

B) Regular solutions

In the regular solutions model, Flory supposes that: if the mixture occurs with the energy transfer, the enthalpy effect is very weak. In this case, the enthalpy of mixture takes the following form:

$$\frac{\Delta H_m}{RT} = \chi N_1 \varphi_1 = \chi \varphi_1 \varphi_2 (N_1 + xN_2) \qquad (3)$$

where χ is the interaction parameter between the solute and the solvent.

The partial molar enthalpy of solvent takes the following expression:

$$\frac{\Delta H_1}{RT} = \chi \varphi_2^2 \qquad (4)$$

The variation of the free enthalpy of mixture can be expressed as follow:

$$\frac{\Delta Gm}{RT} = N_1 \, ln\, \varphi_1 + N_2 \, ln\, \varphi_2 + \chi \varphi_1 \varphi_2 (N_1 + xN_2) \qquad (5)$$

and the variation of the chemical potential of solvent and solute can be expressed as:

$$\frac{\Delta \mu_1}{RT} = \frac{\overline{\Delta G_1}}{RT} = ln\, \varphi_1 + (1 - \frac{1}{x})\varphi_2 + \chi \varphi_2^2 \qquad (6)$$

and

$$\frac{\Delta \mu_2}{RT} = \frac{\overline{\Delta G_2}}{RT} = ln\, \varphi_2 + (1 - x)\varphi_1 + \chi x \varphi_1^2 \qquad (7)$$

C) The separation of phases

The equation (6) can be rewrite only with the volume fraction of solute φ_2 :

$$\frac{\Delta \mu_2}{RT} == ln(1 - \varphi_2) + (1 - \frac{1}{x})\varphi_2 + \chi x \varphi_2^2 \qquad (8)$$

5.2 The ternary systems

5.2.1 Ternary systems with a macromolecular component

The general problem was treated by Scott. Scott proposes two different approximations for simplified the calculation:

a) In case of the single liquid approximation (the composition of the solvent in is the same in the two phases). The mixture is equivalent to a binary system which the Flory interaction parameter is:

$$\chi = \frac{\chi_{12}\varphi_1 + \chi_{23}\varphi_2}{\varphi_1 + \varphi_2} - \frac{\chi_{12}\varphi_1\varphi_2}{(\varphi_1 + \varphi_2)^2} \qquad (9)$$

The variation of the chemical potential of the polymer is

$$\frac{\Delta\mu_3}{RT} = ln\,\varphi_3 - (x-1)(1-\varphi_3) + x\chi(1-\varphi_3)^2 \qquad (10)$$

with $x_1 = x_2 = 1$ and $x_3 = x$

b) The second approximation is the case of the complete immiscibility, the polymer and solvent are supposed to be completely immiscible (one phase containing the two solvents and other phase containing the swelled polymer).

A) Polymer – solvent – non solvent systems

The more simple case is those of Tompa. Tompa considers that the interaction constant that exist between the polymer and one of the liquids is equal to the relative constant of the two liquids

$$\chi_{12} = \chi_{13} = \chi \qquad (11)$$

The solvent is designed by (2), the non solvent by (1) and the polymer by (3)

Tompa considers also that the interaction parameters of the solvent and polymer are nil: $\chi_{23} = 0$ where $\chi_2 = \chi_3 = 0$ and $\chi_1 = \chi$ and from the supposition of Scott $x_1 = x_2 = 1$ and $x_3 = x$

With the negligence of the entropic term of χ, the variation of the chemical potentials is:

$$\frac{\Delta\mu_1}{RT} == ln\,\varphi_1 + (1-\frac{1}{x})\varphi_3 + \chi(1-\varphi_1)^2 \qquad (12)$$

$$\frac{\Delta\mu_2}{RT} == ln\,\varphi_2 + (1-\frac{1}{x})\varphi_3 + \chi x\varphi_1^2 \qquad (13)$$

$$\frac{\Delta\mu_3}{RT} == ln\,\varphi_3 + (x-1)(1-\varphi_3) + \chi x\varphi_1^2 \qquad (14)$$

B) Polymer –Solvent (1) – Solvent (2) systems (Scott)

The conditions $x_1 = x_2$ and $x = x_3$ are always applicable and χ_{13} and χ_{23} are inferior to 0.5 while χ_{12} is inferior to 2. The three components are supposed miscible in all proportions.

According to Peterson et al if the binary mixture of the two solvents is assimilated to a unique solvent, the interaction between the polymer (A) and the solvent (S) is according to Scott takes the following equation:

$$\chi_{AS} = x_1\chi_{A1} + x_2\chi_{A2} - x_1x_2\chi_{12} \qquad (15)$$

where x_1 and x_2 are the molar fraction of the solvent 1 and solvent 2 and χ_{A1} and χ_{A2} are the interaction parameters between the polymer and each solvent.

4.2.1.3 Polymer – non solvent (1) – non solvent (2) Systems

A polymer insoluble in the solvent (1) and insoluble in solvent (2) separately but it can be soluble in their mixture.

5.3 The polydispersed macromolecular systems

5.3.1. The average molecular seizes

a) The average number molecular weight $\overline{M}n$

$$\overline{M}n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

N_i : number of molecules *and* M_i is the molecule weight of molecule *i*

b) The average weight molecular weight $\overline{M}w$

$$\overline{M}w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

c) The average molecular weight “Z”

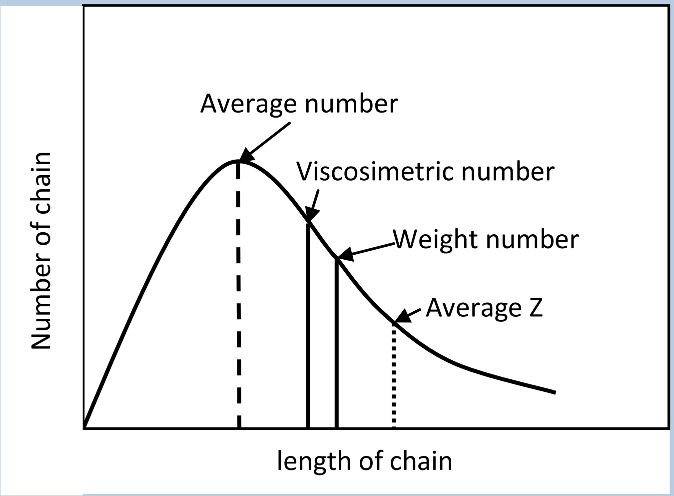
$$\overline{M}z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

d) The average viscosimetric molecular weight $\overline{M}v$

$$\overline{M}v = \left(\frac{\sum_i N_i M_i^{a+1}}{\sum_i N_i M_i}\right)^{1/a}$$

a is the coefficient of viscosimetri equation: $[\eta] = KM^a$

The relative disposition of the different averages for a same distribution is presented as follows:



6. Experimental realization of fractionally

6.1 The fractioned precipitation

This operation is realized by three different ways

- The addition of a non solvent (precipitant) into the solution
- The evaporation of solvent
- The variation of temperature

6.1.1 Method by addition of a non solvent

The polymer dissolved in an adequate solvent then is added progressively to a non solvent and the polymer precipitates immediately. The polymer is then recuperates by filtration.

6.1.2 Method by evaporation of solvent

The Principe of this operation is based on the concentration of the polymeric solution. This solvent is evaporated by air up to the total evaporation of solvent.

6.1.3 Method by variation of the temperature

Some solvents are mediocre or bad, the cooling operation can be used for recuperate the polymer by decantation.