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Solution Properties

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Aspects of Polymer Solubility

High polymers with all their complexities somehow appear to be governed by the same basic laws as applicable to simple, small molecules. However, in view of their large molecular size and varied degrees of molecular size distribution, and the fact that they may be caused to undergo drastic changes in shape and dimensions, much of their behaviours significantly differ from those of low molecular weight materials. It is for this reason, manipulation of (high) polymers in melt and solution or emulsion conditions is an altogether different proposition and experience.

In the context of prediction and understanding of solubilities, it is important to keep the following factors into consideration :

(i) 'like dissolves like' is the common experience; the aromatic compound aniline is better soluble in benzene, the simplest aromatic hydrocarbon than in the comparable aliphatic hydrocarbon, n–hexane or its cyclic counterpart, cyclohexane. Likewise, n–hexane is completely miscible with its immediate higher homologue, n–heptane.

(ii) comparable / similar polarity induces miscibility and solubility.

(iii) solubility is usually higher and dissolution takes place more readily at a relatively or moderately high temperature.

(iv) solubility tends to get lowered or retarded as the molecular weight of the solute of a given type is increased.

It is further instructive to note that solubility relations of high polymer systems appear really distinctive and complex in view of their long chain – like complex molecular structure, size and shape, exhibition of high viscosities in solution and odd distribution and variations in crystalline and amorphous regions in them in the fibre form or in glassy and rubbery states, which again depend largely on the thermomechanical history through which the polymer system is made to pass.

Factors that Influence and Control Swelling and Solubility of Polymers

For a solvent to dissolve a mass of solute, the molecules of the former are required to be inherently able to penetrate the solute molecules and must overcome the cohesive forces between the solute molecules significantly and sufficiently to enable the latter to gradually separate out from one another; and in effect, under the influence of the favourable and overpowering solute – solvent interaction, the solvent molecules induce or literally force the solute molecules to diffuse into solution. For the complex high polymer solute molecules and the simple, small solvent molecules, the solvent penetration into the solute system is usually a slow process, often aided by heat application and mechanical agitation or stirring. The final state of uniform dispersion or dissolution follows a primary process of progressive swelling of the mass of the polymer solute as a consequence of extensive solvent penetration. In case, the specific solvent – solute interaction or affinity is high, solvation, associated with progressive swelling followed by complete dispersion of the solute mass in the solvent medium may result, finally yielding a solution of relatively high viscosity. Dissolution preceded by notable to heavy swelling is sure evidence that the solute material is a high polymer.

(a) Effects of Polarity, Branching, Cross Linking and Crystallinity: Polymers bearing polar, hydrophilic groups such as $-SO_3H$, $C=O$, $\diagdown\!\!\diagup CHO$, $-COOH$, $-OH$, $-CONH_2$ etc. may swell and finally dissolve in polar solvents such as water, alcohol – water mixtures, formamide, dimethyl sulfoxide etc. Cross linked or network polymers, polar or non – polar, fail to dissolve in a solvent, even though they may show varied degrees of swelling in different solvents, polar or non – polar. Branched polymers are usually less symmetrical and less crystallizable, and more flexible and soluble; branching imparts a change in shape of polymer molecules along with infusion of higher intermolecular voids resulting in lowering of density, while cross linking imparts notable changes in both shape and size of polymers with enhancement in their hardness, stiffness, rigidity and density. Extensive cross-linking may limit or even prevent swelling. Presence of extensive hydrogen bonding, both intramolecular and intermolecular, causing a high degree of crystallinity in an apparently linear polymer, such as cellulose, renders it insoluble in water and in most common solvents. Non – polar linear and branched polymers are usually soluble in comparable non – polar solvents.

Under a comparable environment, the solution viscosity at a given concentration and at a given temperature is higher for a given polymer having a higher molecular weight. Much like introduction of branching, incorporation of comonomer units in chain polymers through copolymerization of two or more different monomers also results in poorer molecular symmetry and hence higher chain flexibility, rendering the resulting copolymer more readily soluble too. Branching and copolymerization enhance ease of solvent–penetration, swelling and dissolution.

(b) Consideration of Use of Mixed Solvents: Use of mixed solvents seems to be more effective in selected polymer systems. Partly nitrated cellulose may be cited as an important example in this context[4]. Part nitration of cellulose lowers its high order of molecular symmetry or structural regularity as a consequence of part and progressive substitution of the $-OH$ groups by $-ONO_2$ groups at random, and thereby contributes to a notable lowering in degree of crystallinity and in the scope for inter molecular H – bond formation. A mixture of alcohol and ether proves to be a more effective solvent system and swelling agent for partially nitrated cellulose than either solvent alone.

It is logical to presume that the alcohol exerts the desired solvating action on the residual $-OH$ groups of partially nitrated cellulose, while the ether exerts the necessary solvating action on the nitrate ($-ONO_2$) groups. Acetone, being an effective solvating agent for the nitrate groups only, it is no wonder that with increase of degree of substation (DS) during the later stages of nitration, the cellulose nitrate being formed becomes more prone to solvation and swelling on use of acetone as the solvent, and that fully nitrated cellulose, viz. cellulose trinitrate (DS ~ 3.0) readily dissolves in acetone, while it acts as a poor solvent for relevant products of low degree of nitration.

Further, it is interesting to note that having comparable polarity and carbon – hydroxyl ratio for cellulose – $(C_6H_{10}O_5)_n$ – and poly (vinyl alcohol) – $(C_2H_4O)_n$ –, the latter is

soluble in water in view of its overtly simple, linear structure and flexibility, while the former, appearing as a polymer of β–glucose rings and having interplay of extensive intermolecular H–bonds through the three – *OH* groups in each of the glucose rings is moderately crystalline and significantly rigid despite the flexibilizing effect of the 1, 4 β – glucosidic (– *O* –) inter-unit linkages, with the net effect that it acts as a good natural fibre that is insoluble and infusible.

In case a chain polymer solute containing polar units of one or some other kind in its structure is put into a solvent, also containing polar groups, then the more polar units of the solvent molecules will be oriented towards the polar groups of the chain molecules; consequently, the non – polar or less polar segments / units of the solvent molecules will get directed outward or away from the chain molecular surface. In effect, then the solvated molecular chain will provide a less strongly polar outer surface than the initial polymer. The addition of a second, less polar solvent then goes to enhance the solubility, as because, the second solvent reduces the polarity of the environment to a level that is more close to that of the surface regions of the initially solvated chain polymer solute, thereby setting the stage right and ready for the chain polymer solute to progressively go into solution. This may also partly explain the observed enhanced solvent action of alcohol – ether mixture on partly nitrated cellulose.

(c) Other Important Points: Studies of the influences of variations of environmental conditions, such as temperature, stirring or agitation, the nature of solvent / solvent – mixture etc. can reveal a range of useful information's about the polymer.

The absence of solubility does not necessarily indicate presence of cross-linking. Chemical nature of the repeat units such as polarity may contribute to sufficiently high intermolecular attractive forces, both intrinsic between two neighbouring chain segments and cumulative over each entire chain molecule, so as to hinder or prevent solubility. The existence of high degree of crystallinity consequent to extensive H – bonding, both intramolecular and intermolecular is a matter of special importance in this context. Crystalline polymers, owing their crystallinity to high order of molecular symmetry, allowing ready fitting into a lattice structure, specially the non – polar ones such as the polyethylenes (LDPE and HDPE), do not readily dissolve, except however, at relatively high temperatures near their crystalline melting temperatures (T_m). The reason is that crystallinity decreases as the T_m is approached and that the melting point is itself lowered by the presence of the solvent of comparable or like polarity. Solubility can thus be variously facilitated and achieved at temperatures close to but below the melting point.

Thus, linear polyethylene, i.e., the well known high density polyethylene (HDPE), having crystalline melting point T_m in the range of 127 – 132^{0}C can be actually dissolved in xylene, toluene or their mixtures at or near 100 – 110^{0}C; likewise, the low density polyethylenes (LDPE), having a lower degree of crystallinity for having a branched structure, and having its crystalline melting point in the range of 110 – 117^{0}C, can be somewhat more readily dissolved in the said non – polar solvents or solvent mixtures at or near 80 – 90^{0}C.

Solubility Parameter

Solubility is expected to occur when the free energy of mixing, ΔG *(= ΔH – TΔS)* is negative. It is commonly recognized that the entropy of mixing, ΔS is always positive, such that, the sign of *ΔG* is determined by the sign and magnitude of the enthalpy (i.e. the heat of mixing) term, *ΔH*. For by and large non-polar solvent and solute – polymer molecules and in the absence of hydrogen bonding, ΔH is said to be positive and is given by the expression,

$$\Delta H = v1\, v_2\, (\delta 1 - \delta_2)^2 \qquad (1)$$

where *v* denotes volume fraction and the subscripts 1 and 2 refer to solvent and solute respectively. The quantity δ^2 is the cohesive energy density, and for small molecules, it stands for energy of vaporization per unit volume. The quantity δ is commonly referred to as solubility parameter. Miscibility or solubility can be expected or believed to be favourable if δ1 and *δ2* values are close and $(\delta 1 - \delta_2) < 1.8$; but solubility is not favoured if the solubility parameter difference is much higher; these features are more or less relevant particularly in systems devoid of strong interactions, such as H-bonding. Existence of extensive intramolecular and intermolecular H-bonding acts as a hindrance to solubility; and in such cases, only solvents, that can favourably engage the solute molecules (or segments of polymer molecules) through solute – solvent H – bonding, can impart or infuse solubility. Typical values of solubility parameters for some monomers solvents and polymers are listed in Table 1.

Table 1: Solubility Parameter Values of some Monomers, Solvents and Polymers

Solvent/Monomer	**δ_1 (Cal/cm^3)$^{1/2}$**	**Polymer**	**δ_2 (Cal/cm^3)$^{1/2}$**
Methanol	14.5	Cellulose	15.65
Ethanol	12.7	Benzyl cellulose	12.33
2-Ethyl hexanol	9.5	Poly (vinyl alcohol)	12.60
n-Butyl acetate	8.5	Poly (vinyl acetate)	9.59
Acetonitrile	11.8	Polyacrylonitrile	12.50
Acetone	9.9	Poly (methyl cyanoacrylate)	14.00
Benzene	9.2	Poly (dimethyl siloxane)	7.35
Ammonia	16.3	Polystyrene	8.56
Glycerol	16.5	Polyethylene	7.70
Formamide	19.2	Natural rubber	7.90
Acetic acid	10.1	Epoxy resin	10.91
Acrylic acid	12.0	Polymethacrylonitrile	10.71
Pyridine	10.7	Poly (ethylene terephthalate)	10.70
Water	23.4	Poly (vinyl chloride)	9.42

Thermodynamics of Polymer Solution

Now, we know that the overall response of polymers towards solvents is characteristically different from that of low molecular weight material systems. The size and different possible conformations of dissolved polymer molecules need to be viewed and analyzed somewhat differently to obtain worthy information about their solution

properties. On the other hand, studies of solution properties possibly reveal a lot of information about their size and shape.

(a) Simple Liquid Mixtures: Under conditions of equilibrium at a temperature T, free energy, ΔG of dilution of a solution may be expressed as

$$\Delta G = k T \ln \left(\frac{p}{p^o} \right) \tag{2}$$

where the dilution results from the transfer of one molecule of a liquid (solvent) from its pure liquid state with vapour pressure p^o to a large amount of solution with vapour pressure p, and k is Boltzmann's constant. Just like the vapour pressure lowering relationship as in equation (2), one may write expressions for other colligative properties such as freezing point depression, boiling point elevation and osmotic pressure.

(b) Ideal Solutions: In the most simple type of mixing, the molecules of components 1 (say, solvent) and 2 (say, a simple, small solute) have comparable sizes, shapes and force fields. The solution so formed is said to be ideal, if Raoult's law is obeyed. The law states that the partial vapour pressure of each component in the mixture is proportional to its mole fraction such that

$$p_1 = p_1^{\,o} \cdot \frac{N_1}{N_1 + N_2} = p_1^{\,o}\, n_1 \tag{3}$$

where n signifies mole fraction and N, number of molecules, so that equation (2) may be written in the form

$$\Delta G_1 = k T \ln n_1 \tag{4}$$

The total free energy of mixing may then be expressed as

$$\begin{aligned} \Delta G &= N_1 \Delta G_1 + N_2 \Delta G_2 \\ &= k T \, (N_1 \ln n_1 + N_2 \ln n_2) \end{aligned} \tag{5}$$

Further, the condition for ideal mixing imply zero heat of mixing, ΔH , meaning that the components simply mix and no change in energy is involved. As $\Delta G = \Delta H - T \Delta S$, the entropy of mixing, ΔS reduces to the form

$$\Delta S = -k \, (N_1 \ln n_1 + N_2 \ln n_2) \tag{6}$$

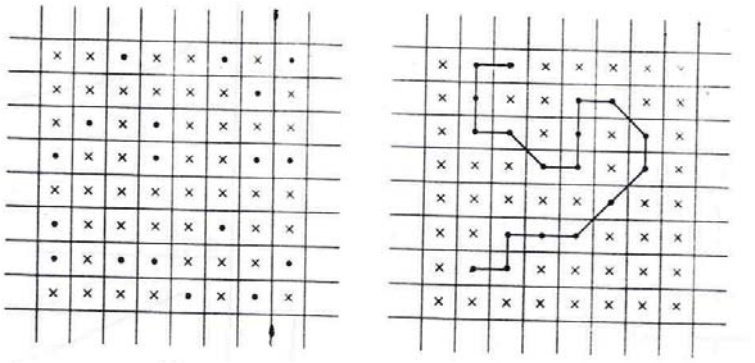
(c) Deviations from Ideality: A polymer molecule with its long chain-like structure is far different in size, shape and force fields from the far too small solvent molecules used to dissolve them to make a solution. They deviate from Raoult's law at finite concentrations (except at extreme dilutions). A non-ideality is not only expected for polymer solutions at finite concentrations, however small, it is also the real experience. A polymer solution is expected to be non-ideal on grounds of entropy considerations alone.

We consider that the mixture contains N_1 solvent molecules each of which separately occupies a single site in the lattice we propose to fill. The system further contains N_2 polymer molecules, each of which having a degree of polymerization n, occupies n lattice sites. A polymer molecule is thus defined to occupy a volume n times bigger than the volume of each solvent molecule with the assumption that each repeat unit of the polymer molecule is comparable in size with a solvent molecule, fig. 1. It can then be easily appreciated qualitatively as to why the entropy of mixing of polymer solutions is measurably small relative to that for small, simple solutes. There are fewer ways in which the same number of lattice sites can be occupied by polymer segments, as because, fixing one segment at a lattice site severely limits the number of sites available for the adjacent segment. The entropy of mixing for simple liquids as given by equation (6) requires to be modified to equation (7) for polymer solutions:

$$\Delta S = -k\,(N_1 \ln v_1 + N_2 \ln v_2) \qquad (7)$$

where *1* and *2* stand to signify the solvent and the polymer respectively and v_1 *and* v_2 refer to their volume fractions as defined by

$$v_1 = \frac{N_1}{N_1 + nN_2} \quad \textit{and} \quad v_2 = \frac{nN_2}{N_1 + nN_2} \qquad (8)$$



(a) (b)

Fig. 1: Two-dimensional representation showing occupation of lattice sites by a mixture of small molecules indicated by cross and dot marks (a), and by small solvent molecules indicated by cross marks and by segment / repeat units of a polymer molecule, indicated by jointed dots (b)

Freely Jointed Chain

A simple conceivable model of a polymer chain consists of a series of *n* links successively joining the repeat units of length *l* in a linear sequence putting little restrictions on the angle between successive bonds. The probability that such an array of chain molecule has a given *end – to – end distance* r, can be calculated employing the classical random flight method of Rayleigh (1919). The most consequential outcome of the calculation leads to a simple expression showing the root mean square random flight end – to – end distance, $(r_f^2)^{1/2}$ as proportional to the square root of the number of links or repeat units, i.e.,

$$(\overline{r_f}^2)^{1/2} = l\, n^{1/2} \qquad (9)$$

This again shows that $(\overline{r_f}^2)^{1/2}$ is proportional of $M^{1/2}$, M being the molecular weight of the polymer chain is directly proportional to n. It may be further concluded that $(\overline{r_f}^2)^{1/2}/M)$ is a characteristic property parameter of the polymer chain, independent of chain length or molecular weight.

(a) Short – Range Interaction: Flory (1969) calculated completely and accurately the effect of short – range interactions on the dimensions of random coil polymers. Restricted rotation for whatever reason is real and it contributes to increase in chain expansion, contrary to the effects of the freely jointed chain concept. The net result of short – range interactions can be expressed as a characteristic ratio of the square of the actual chain dimensions $(\overline{r_o}^2)$ (called the *unperturbed dimensions* in the absence of long – range interactions) and the square of the random flight end – to – end distance, $(l^2 n)$. The characteristic ratio $(\overline{r_o}^2 / l^2 n)$ for some high chain length polymers as evaluated by Flory (1969) are shown in Table 2.

Table 2: Data for the Characteristic Ratio $(\overline{r_o}^2 / l^2 n)$ for some Polymers

Polymer	$(\overline{r_o}^2 / l^2 n)$
Poly (ethylene oxide)	4.0
Polypropylene (isotactic)	5.7
Nylon 66	5.9
Polyethylene	6.7
Poly (methyl methacrylate)	6.9
Polystyrene	10.0

(b) Long-Range Interactions and the Excluded Volume: Corrections of dimensions of chain polymers for short – range interactions are still unable to eliminate conformations where two widely separated chain segments occupy the same space. In fact, each segment of a real chain finds place within a volume from which all other segments are excluded. Theoretical calculation of the excluded volume and in turn, its effect on polymer chain dimensions remained a challenge for many years. In the final analysis, it has come to be recognized that over sufficiently extended chain length, proportionality between end – to - end distance and square root of the number of chain segment is a general reality.

In practice, the direct consequence of long – range interactions is a measurable expansion of the polymer chain over its unperturbed dimensions, in view of the fact that more of the compact conformations, giving small values of r^2, must be excluded. The actual dimensions of the real chain $(\overline{r^2})^{1/2}$ apparently exceed the unperturbed dimensions $(\overline{r_o}^2)^{1/2}$ by an expansion factor signified by the term α, such that $(\overline{r^2})^{1/2} = \alpha (\overline{r_o}^2)^{1/2}$. The exact value of α very much depends on the solvent used; for a thermodynamically 'good' solvent, α is large, and for a thermodynamically 'poor' solvent, the value of α is low.

In a very poor solvent or at a sufficiently low temperature, it is likely that a condition given by $\alpha = 1$ is reached and the real chain attains its unperturbed dimensions. This special, characteristic feature for a given polymer – solvent system is attained at a temperature called the *Flory temperature* or θ *temperature*; a solvent used at $T = \theta$, is referred to as the θ – solvent.

For non – linear, branched chains, in view of multiplicity of (chain / branch) ends, the chain dimension is expressed in terms of radius of gyration $(s^2)^{1/2}$. A branched molecule occupies a smaller volume than one that is linear, with the same number of segments, i.e., the same molecular weight, and the size diminution factor $g = s^2$ (branched) / s^2 (linear), calculable statistically for different degrees and types of branching, is conveniently used.

Even at the theta temperature and for solvents giving nearly the same or closeby θ temperatures, it is noted that some polymers do not have the same or similar unperturbed dimensions in different solvents. Consequent to this fact and other evidences, it may be inferred that portions of dissolved polymer chains may tend to exist in preferred specific (non-random) conformations, viz. helices.

The lattice modal treatment of dilute polymer solution, commonly known as the Flory – Huggins treatment, however, neglects the feature obtaining in a very dilute polymer solution; Unlike regular solutions of small molecules, such a solution must be discontinuous in structure, showing domains or clusters of polymer chain segments that are separated on the average by zones of polymer – free solvent (free – volume theory). A modification assuming the cloud or cluster of segments as approximately spherical is characterized by a density gradient with a maximum at the center and decreasing in an approximately Gaussian function with distance from the center; this concept later developed and detailed by Flory and Krigbaum, has also been found to be not free from shortcomings.

Powerful new theories recognize the dissimilarity in the free volumes of the polymer and the solvent consequent to the great differences in their size; the solvent is believed to be much more expanded than the polymer. The total volume change on mixing is usually negative and is accompanied with a negative ΔH with a negative contribution to ΔS.

Phase Separation in Polymer Solutions

When the temperature of solution of a polymer is raised or lowered, the solvent eventually turns thermodynamically poorer. A temperature is ultimately reached beyond which polymer and solvent are no more miscible in all proportions. Flory – Huggins theory predicts that a dominant role is played by polymer – solvent interaction in determining the parameter χ_1 as described by the expression for the heat of mixing of polymer solutions (analogous to that of ordinary solutions), viz.,

$$\Delta H = \chi_1 \, k \, T \, N_1 \, v_2 \qquad (10)$$

where χ_1 is used to characterize the interaction energy per solvent molecule divided by kT. Combining equations (7) and (10) gives the Flory – Huggins expression for the free energy of mixing of a polymer solution having normal heat of mixing:

$$\Delta G = kT (N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \quad (11)$$

The Flory – Huggins theory predicts χ_1 to increase monotonically as the temperature goes down, curve 1, fig. 2 So, phase separation is predicted to occur on lowering the temperature, and the system would be characterized by an upper critical solution temperature as in fig. 3. One also encounters cases where phase separation occurs invariably when the temperature is raised until one reaches a lower critical temperature as in fig. 3. This feature is explicable by free – volume concept of polymer solutions. The influencing of χ_1 by the free – volume dissimilarity between solvent and polymer is recognized to be an increasing function of the temperature, curve 2, fig. 2. The resultant interaction parameter apparently passes through a minimum (curve 3, fig. 2).

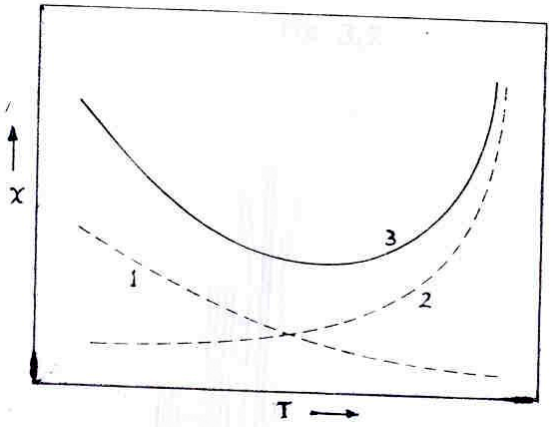


Fig 2: Dependence of the value of χ with change in temperature T (Schematic) and 2.3

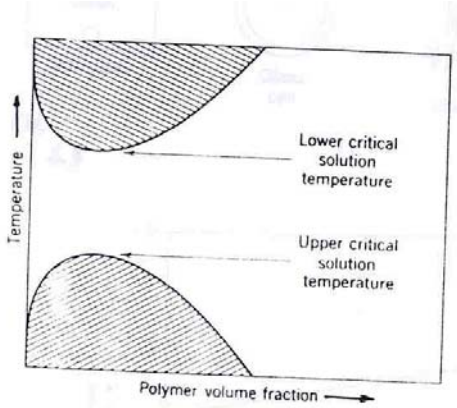


Fig. 3: Schematic phase diagram (plot of temperature vs. polymer volume fraction)

Solvent Power

Having gone through the thermodynamics of dissolution of polymers and having some exceptions in the form of both ΔH and ΔS being negative for selected systems, the applicability of the solubility parameter concept may occasionally appear inappropriate or inadequate. Despite this shortcoming, the said concept is still by and large very helpful, even making allowances for the mismatch for the handful of unusual cases.

The rate of dissolution primarily depends on how rapidly the polymer – solvent system would diffuse into one another. Kinetically good solvents are not necessarily good thermodynamically too. Mixtures of a kinetically good and a thermodynamically good liquid often appear to be powerful and quick dissolving solvents for polymers.

It is a common feature of high polymers that at concentrations of 0.5 to 5.0% their solutions may appear viscous to very viscous and may even form thick non – flowable gels. Particles that are spherical commonly impart lower resistance to flow than those that are oblong or elongated. A particle with an elongated contour rotates in solution and

covers an effective volume greater than its actual volume; particles that are spherical are characterized by equal or comparable actual and effective volumes.

It follows therefore, that in a good solvent, the chain molecules would be in a more elongated condition than in a poor solvent. The intrinsic viscosity (giving a measure of hydrodynamic volume of a unit mass of the polymer solute) in a good solvent is higher than in a poor solvent. At progressively high concentrations, however, the polymer chain molecules will tend to cluster or associate into larger aggregates. This associating trend with rise in concentration will be more severe in the poor solvent than in the good solvent, more so, beyond a low threshold concentration in each case. One may arrive at a balanced effect by using a mixture of a good solvent and a poor solvent in advantageous volume proportions so as to provide a lower viscosity at a higher polymer concentration. Technology of solvent–based surface coatings, viz. lacquers, paints and enamels, utilizes this approach with great advantage for obtaining desired film thickness with (single or) fewer coating applications by trouble – free brushing or spraying.

Viscosity measurements of solutions of lacquer – grade cellulose nitrate (degree of substitution, DS = 1.9 – 2.1) in some ester (ethyl acetate or butyl acetate) – ethyl alcohol mixed solvents indicate that progressive additions of alcohol up to 50 – 60% by volume to its initial high viscous solution in ethyl acetate contribute to enhance the solubility of the polymer and progressively and substantially lower the solution viscosity; still further addition of alcohol causes the solubility to go down and viscosity to go up again.

Solvent power may also be assessed by what is known and described as the dilution ratio approach. The high polymer is dissolved to a specified concentration in each of a number of solvents. It is then required to determine the amount of a specific non – solvent to be added to each solution to cause appearance of light, permanent turbidity or initial precipitation. The solvent, to which the highest amount of the non–solvent is needed under comparable conditions, is viewed as the most powerful.

This dilution – ratio approach apparently suffers from the weakness that the initial addition of the non – solvent or the diluent may, in effect, enhance the solvent power of the (mixed) solvent system, though to different degrees, much in tune with the effects outlined above. Even then, the dilution ratio approach is of immense practical relevance in respect of solvent balance and striking a better economy through replacement of costly solvents by less expensive or most readily available diluents or *latent solvents*.

Thixotropy

Development of primary – valence cross linkages in an initial linear or branched polymer remaining in solution invariably turns it into an irreversible gel as a consequence of ultimate formation of a giant macromolecular network, thus causing virtual immobilization of the solvated and swollen polymer mass. Once formed, the network gel – mass can seldom be redissolved or it opposes all subsequent attempts to make it get back to solution – form on application of thermal and mechanical energy, i.e., by heating and stirring. The gel so formed mostly in a swollen form, may be broken down by stirring to smaller, swollen pieces of gel, or degraded and thermally decomposed on

drastic thermomechanical treatments, but can seldom be redissolved to uniformity. This stands as a case of gelation that is irreversible.

In many other instances, however, a high polymer flowable solution of a somewhat low viscosity may set to a thick gel if left undisturbed at a given temperature. The gel so formed may, however, be readily broken turned to a flowable solution again simply by agitation or stirring; however, the gel form readily appears again on standing. This unique reversible isothermal sol-gel transformation phenomenon as commonly referred to as *thixotropy*.

It may be further mentioned that many such gels exhibit a slow trend of densification on prolonged standing with associated squeezing out of portions of the solvent as a separate phase, recognized as sweating. This odd phenomenon is known as *syneresis*. A thixotropic gel can very well be broken merely by adding a controlled proportion of a second solvent of appropriate nature. Again a significant portion of a thixotropic gel mass can possibly be leached out in special cases, without actually breaking the gel structure.

A thixotropic gel is viewed as a weak, continuous dendritic kind of structure held in place by massive interplay of secondary valence bridging, and it is all the way different from a space polymerized network gel. The process of gel formation on standing and break – down of the gel to a flowing liquid (solution) mass on mechanical agitation at the same specified temperature may be repeated many times. Thixotropic effect may not necessarily or invariably cause gel formation, which, however, may be said to be an extreme manifestation; it may in fact involve simply a physical change from a less viscous solution / liquid mass under stirring to a relatively high viscous mass of solution or a thick mass of restricted mobility on standing.

Rubber, ordinarily a lowly polar natural hydrocarbon polymer (1, 4 cispolyisoprene) is masticated for mechanical / oxidative breakdown of its chains to generate enhanced tackiness in the primary stage of its processing during which more oxygenated polar groups are generated on the degraded rubber chains through oxidation. Rubber adhesives or cements are made by dissolving the masticated and duly compounded rubber mass in a non – polar hydrocarbon solvent system, such as solvent naphtha. Even after optimum mastication, it is difficult to obtain a workable (spreadable / brushable) rubber solution of concentration of more than a few percent. A higher concentration leads to an undesirable formation of a gel – like mass or a solution of problematic high viscosity. To dissolve more rubber mass and at the same time keep the viscosity down for easy, trouble – free manipulation and application, one finds it advantageous to add adequate amount of a polar solvent (or better, non-solvent), such as alcohol whose presence restricts or lowers the trend of expansion of the rubber hydrocarbon chains in solution and thereby restricts the swelling, gelling or the thixotropic effect.

Importance and Advantages of Thixotropy: Thixotropic behaviour is exhibited by a long array of colloidal and high polymeric systems formulated and marketed as lacquers,

varnishes and paints; greases and gums; solutions of starch, gelatin and many proteins; printing inks; clay suspension, plant juices and other biological fluids; emulsions of different kinds; bitumens and lubricating oils at low temperatures etc. Thixotropy is in fact highly desirable or even absolutely necessary for storage, manipulation and application of liquid surface coatings, adhesives and inks etc.

In a good paint optimally formulated, the consistency or viscosity must of necessity be high enough to restrict or prevent settling of pigments on long standing. As a result of what is known as 'caking', the settled mass of pigment forms a compact hard cake on long standing and the cake may turn out to be far too difficult to be stirred back to homogeneity. However, at the same time, consistency of the formulation should be just optimally low so that brushing to a coating of uniform thickness is devoid of any problem and concomitantly, allowing the brush marks to quickly disappear or flatten out by flow of the spread – out paint film before it would have chance to dry up. A fine balance of rheological properties is necessary to infuse into the paint mass all these conflicting requirements. Caking troubles can be avoided or faced to a minimum only if the paint is thixotropic.

Mechanism of Thixotropy : The high consistency of polymer dispersions, emulsions or solutions gets drastically reduced on application of high rates of shear and regained on standing thereafter, thereby indicating thixotropic character for them. The effect may be understood by considering that the surface forces cause and induce the particles at rest to turn into filament–like clustered structu-res or chains which then turn into a mesh–like network structure by continuous scaffolding, thus ultimately giving rise to a physically immobilized gel of high consistency. Sustained mechanical agitation or stirring supplies enough energy to disturb the gel, causing breakdown of the scaffolding or gel network build-up by interplay of secondary valence bridging; the consistency of the system then drops to the normally expected low level. Set at rest again, the scaffolding of the growing filamentous chains of the dissolved or dispersed particles is reformed to full potential and the viscosity rises again and the thixotropic gel is reformed.

Dilute Polymer Solution

A selected single polymer molecule in a dilute solution finds itself under the osmotic action of the surrounding solvent, which tends to swell it to a larger average size than otherwise expected. There is a close parallelism between this expansion and the swelling of a macroscopic three-dimensional network. The single molecule may, in fact, be considered as a submicroscopic prototype of the latter. The single polymer molecule has a rather large number of segments all linked together in a unit structure, though not in the form of a cross linked network, and it gets expanded to a bigger configuration in dilute solution much like the extended swelling of a chain in a network. The segment density within the encompassment of the single molecule is certainly lower than that of a swollen network, and hence, the osmotic forces acting on it are relatively small, even though the two cases are materially similar.

With swelling of the molecule by the osmotic action, an elastic reaction develops into the system, much like that generated on a stretched test piece of rubber. At equilibrium, the

elastic force balances the osmotic forces that cause the swelling. The single molecule in solution is viewed as a tiny thermodynamic system having the characteristic of a cluster of segments confined or encompassed within an outer elastic membrane permeable to the solvent present.

In dealing with solutions of high polymers, it is often difficult to use mole fractions because of uncertainty or lack of exact knowledge of the molecular weight of the material. Moreover, in evaluating entropy effects, the volume occupied by a molecule is more important than its weight (see equation (7)). As a consequence, concentrations of high polymer solutions are better expressed in terms of volume fraction.

Ideal Solutions

The simplest case of an ideal solution is represented by a mixture of two gases at low pressures. The molecules are separated to remote distances from each other and consequently, the intermolecular attractive forces, which fall off rapidly with distance have little measurable effect; the fraction of the total volume occupied by the molecules themselves is then negligible. Each molecule behaves as if others were absent, and for all practical purposes, both Dalton's additive pressure law and Amagat's additive volume law for ideal gas mixtures hold exactly.

Ideal liquid and solid mixtures are required to behave exactly the same way. However, it is difficult to imagine or comprehend such a simple state of affairs in real liquid or solid systems. In such real systems, the molecules are close to one another and affect or influence the behaviour of the neighbouring molecules to a significant or measurable extent.

The proximity of the molecules in uniform mixtures / solutions of solids and liquids precludes the ideal situation of no environmental effects such as exists in the ideal gas mixtures. An ideal or perfect liquid or solid solution must, therefore, be defined as one in which a finite but constant environmental effect would prevail through the full range of composition. This constancy of environment, even though somewhat hypothetical, may possibly be realized by following two different approaches:

(i) By diluting the minor component, i.e. the solute with a large quantity of the major comp-onent, i.e., the solvent such that the solute molecule no more exerts any measurable attractive or repulsive forces upon the other solute molecules, and as such, the constant environment of the solvent system prevails. This is the basis of Van't Hoff's *theory of the solution of infinite dilution.* This type of solution is commonly referred to as the *ideal dilute solution.*

(ii) By choosing the binary components so similar in properties that a molecule of either component will experience no change in the fields of force surrounding it even if the composition is varied. This is the ideal or perfect concentrated solution. To achieve this, attractive forces between the like and unlike molecules should be identical, the experiment criteria for these are identified as : (a) complete miscibility, (b) no thermal change on mixing, (c) no volume change on mixing and (d) similar molar volumes.

Since most mixtures do not form ideal concentrated solution, it becomes necessary to fall back to dilute solutions to attain the desired constant environment conditions.

Departure from ideal – solution behavioural pattern is a consequence of a lack of balance in the forces of attraction between like and unlike molecules in the system which are manifested in volume changes, heat effects, viscosity effects, surface tension irregularities and various other departures from the mixture rules, of which the most important is the departure from Raoult's law.

Thus, the entire theory of ideal solutions of low molecular weight substances is based on the substitution of a solvent molecule by a solute molecule without change of environment. This replacement necessarily requires similar, equal or comparable molar volumes, which is a requirement that can not be met in solutions of high polymers. This in itself gives rise to non – ideal behaviour or deviations from ideality, even at an extremely low finite concentration for high polymer solution.

Molecular weights of polymers may be ascertained from appropriate physical measurements on very dilute solutions. The various physical methods and measurements involved in this context are respectively osmotic pressure, light scattering, sedimentation and diffusion properties and solution viscosity. These physical methods fundamentally depend on evaluation of the thermodynamic properties of the solution, viz., the free energy change due to the presence of polymer molecules dissolved in the solvent used, or of the change in the kinetic pressure pattern, viz., the enhancement of solution viscosity, assessed separately or in combination. It is the common experience that polymer solutions even at remarkably low, concentrations generally show significant deviations from their limiting behaviour under infinite dilution condition. It is imperative then to not only conduct the experiments at low concentrations, but also to extrapolate the observed effects to infinite dilution condition for having a reliable measure of the size or molecular weight of the polymer molecules.

References

1. Ghosh, P., Polymer Science and Technology – Plastics, Rubbers, Blends and Composites, 2nd Ed., Tata McGraw – Hill, New Delhi, 2002.
2. Ghosh, P., Adhesives and Coatings Technology, Tata McGraw – Hill, New Delhi (under Publication, to appear in 2007).
3. Flory, P.J., Principles of Polymer Chemistry, Cornell Univ. Press. Ithaca, New York, 1953.
4. Schmidt, A.X. and C.A. Marlies, Principles of High Polymer Theory and Practice, McGraw – Hill, New York, 1948.
5. Billmeyer Jr., F.W., Textbook of Polymer Science, 3rd Ed., Wiley – Interscience, New York, 1984.
6. Brandrup, J., and E.H. Immergut, Polymer Handbook, 3rd Ed., Wiley – Interscience, New York, 1989.
7. Rayleigh, Lord, Phil. Mag. *37* (1919), 321 – 347.
8. Flory, P. J., Statistical Mechanics of Chain Molecules, John Wiley – Inter Science, New York, 1969.
9. Flory, P. J., J. Chem., Phys., *10*, (1942), 51 – 61.

10. Huggins, M.L., J. Phys. Chem., *46*, (1942) 151 – 158; Ann. N.Y. Acad. Sci., *43* (1942), 1 – 32; J. Am. Chem. Soc., *64* (1942), 1712 – 1719.

Selected Readings

1. Morawetz, H., Macromolecules in Selection, Interscience, New York, 1965.
2. Huggins, M.L., Physical Chemistry of High Polymers, Wiley-Interscience, New York, 1958.
3. Lambourne, R., Paint and Surface Coatings, Theory and Practice, Ellis Horwood, Chikester, 1987.