5. FLORY THEORY APPLIED TO POLYMER SOLUTIONS

5.1. STATISTICAL THERMODYNAMICAL THEORY DUE TO FLORY - METHOD OF EVALUATION OF THEORETICAL EXCESS FUNCTIONS

In the present work an attempt is made to apply the liquid state theory (based on statistical thermodynamical model approximations) as developed by Flory and co-workers [1], to the polymer solutions. The entire discussion is based on theories of liquid state. The solvent solute interaction is identical to interactions in binary liquid mixtures. Flory and school have explained this fact in their publications as cited in this chapter. Without loss of generality we treat the polymer solution as equivalent to a binary liquid mixture. The basis for this assumption is explained in the following sections.

Any theory of liquid or solution state generally deals with two aspects. It derives expressions for the entropy associated with the dispersion of the two molecular species (or their constituents if the molecules dealt are quite complex). For example the lattice model estimates the combinatorial entropy of the mixture which depends on the properties of the molecular species. The other aspect of the theory is estimation of the interaction between the neighbouring molecules. For example Prigogeni’s [2] model concentrates on the evaluation of difference of interactions between “like” and “unlike” molecular species present in the mixture.

The equilibrium properties of a liquid [3] are strongly dependent on the so called ‘local structure’ (expressed as packing density or free volume or free length or a radial distribution function). This local structure strongly depends upon forces between the molecules, volume or size of the molecules and it would change with composition of the two species. The term that is associated with the in forces of the molecules is known as ‘pure interaction term’. The term that predicts the change purely in terms of the size (and
or shape) of the molecular species is called as combinatorial term.

More sophisticated treatments of liquid state theories has been possible in recent times through 1) Cell Model [4] 2) Universal intermolecular potential model [5]. In recent times the complexity is on the increase while more sophisticated concepts have been on the rise. It is likely that within a decade or two theories would become finer & would predict most of the thermodynamic parameters of the liquid mixtures.

5.2. STATISTICAL THERMODYNAMICAL THEORY DUE TO FLORY- METHOD OF EVALUATION OF EXCESS FUNCTIONS OF POLYMER SOLUTIONS:

Flory and co-workers as derived a partition function [1,6] particularly suitable for liquid mixtures of non-polar molecules differing in size and shape. Initially the theory is applied to liquid mixtures. The properties of the mixtures are expressed in terms of the parameters of the pure components and an interaction parameter known as characteristic term. The interaction energy term is characteristic of the pair of molecules and is a function of composition for molecules that differ in size and shape. The excess properties of the liquid mixture can be predicted on evaluation of this parameter. Later the theory was extended to liquids of chained molecules. Recently the theory has been redefined for polymers and polymer solutions [14]. In this chapter the discussion is centred on binary liquid mixtures in general. However this treatment can be extended to ternary mixtures [10] and polymer solutions [11] as investigated by our school. The preliminary study undertaken by the author and Rajasekhar [11] is the first basis for a successful application of Flory theory to polymer solutions. Even though it is possible to deal with studies pertaining to solvents and solutes using the concept of chemical potential, we preferred the general method of Flory theory as this method was successfully adopted by our school [11]. The entire expressions discussed in this chapter hold good as if
component 1 is solvent and component 2 is solute or vice versa. The change is chemical potential is taken care by the interaction term of the mixture. Hence from now on it is presumed that what is true of liquid mixtures is also true of polymer solutions, the solvent and solute molecules replace the two molecular species. The entire discussion is based on the binary liquid mixtures.

Using the Hirschfelder-Eyring cell potential function [7-9] assuming the intermolecular energy to depend on volume and assuming a hard sphere repulsive potential (following the Prigogine’s treatment of r-mer chain molecules) [1,14] Flory and his co-workers [6] formulated the following partition function:

$$Z = Z_{comb}[\gamma(\bar{V}^{1/5} - \nu^*^{1/3})^{3C}] \exp(-E_0/kT) \quad \quad (5.1)$$

Where $Z_{comb}$ is a combinatorial factor which takes into account the number of ways of interspersing $\gamma N$ elements among one another, $3C$ represents the number of external degrees of freedom per element, $\gamma$ is the geometric factor, $E_0$ the intermolecular energy, $\bar{V}$ the volume per segment and $\nu^*$ is the associated molar core volume. The intermolecular energy can be represented as suggested by Frank [12] and in favour of the argument put forward by Hildebrand and Scott [13] by the equation.

$$E_0 = \text{Constant} / \nu^m \quad \quad (5.2)$$

Where $m = 1.0$ to 1.5 for non-polar liquids. To restrict the parameters of the partition function, a simple van der walls type of liquid model

$$E_0 = \text{Constant} / \nu \quad \quad (5.2a)$$

was found to be suitable [6,14]. The reduced equation of state

$$\bar{p}\bar{V}/\bar{T} = \nu / (\nu^{1/3} - 1) \quad \quad (5.3)$$

obtained from the partition function is identical with that of Hirschfelder and Eyring [7,8]. Here $\bar{p}$, $\bar{V}$ and $\bar{T}$ represent the reduced pressure, reduced volume and reduced
temperature respectively.

The treatment has been extended to binary mixtures. Assuming random mixing of the two species the mean intermolecular energy of a binary mixture has been derived

$$-E_{\phi}N = p^*v^*/\tilde{\nu} = c k T^*/\nu$$  \hspace{1cm} (5.4)

Where

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 X_{12}$$  \hspace{1cm} (5.4a)

Where $p^*$, $v^*$ are the characteristic pressure & volume of the mixture, $\theta$ site fraction $\phi$ segment fraction defined through

$$\theta_1 = 1 - \theta_1 = \phi_2 / (\phi_2 + \phi_1 (v_{12}^* / v_1^*))^{\phi_1}$$  \hspace{1cm} (5.5)

For nearly spherical molecules $\phi_1$ and $\phi_2$ are the segment fractions given by

$$\phi_2 = 1 - \phi_1 = x_2 v_2^* / (x_1 v_1^* + x_2 v_2^*)$$  \hspace{1cm} (5.6)

$x_1$ and $x_2$ are the mole fractions of the components and $X_{12}$ is the interaction energy parameter characteristic of the system. This energy parameter is the measure of the difference of interaction energy between the unlike pairs and the mean of the like pairs and is a constant independent of composition for a system of non-polar molecules that are spherical and of similar size, at a given temperature [15,16]. The characteristic pressure $p_1^*$, volume $v_1^*$ and temperature $T_1^*$ of the pure liquids can be related to their physical properties through the reduced equation of state [putting $p=0$ in equation (5.3)]

$$p^* = (\alpha/\beta_T) T \tilde{\nu}^2 \hspace{1cm} (5.7a)$$

$$v^* = V/\tilde{\nu} \hspace{1cm} (5.7b)$$

$$T^* = T/\tilde{T} \hspace{1cm} (5.7c)$$

Where reduced temperature $T$ is given by

$$\tilde{T} = (\tilde{\nu}^2 - 1)/\tilde{\nu}^5$$  \hspace{1cm} (5.8)

and
\[ (\tilde{v}^{th} - 1) = \frac{\alpha T / 3}{1 + \alpha T} \]  

(5.9)

Where \( \alpha \) is the thermal expansion coefficient, \( \beta_T \) is the isothermal compressibility. The reduced volume \( \tilde{v} \) and reduced temperature \( \tilde{T} \) can be obtained through equations (5.7) and (5.8). The characteristic temperature of the system is given by

\[ \frac{1}{T^*} = \left[ \left( \frac{\phi_1 p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*} \right) / p^* \right] \]  

(5.10)

5.2.1 Excess volume \( V^E \):

Let \( \tilde{v} \) represent the reduced volume per segment if no volume change occurred on mixing. For an ideal binary mixture the reduced volume is equal to the ideal term

\[ v = \tilde{v}_0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \]  

(5.11)

Where \( \tilde{v}_1 \) and \( \tilde{v}_2 \) are the reduced volumes of the pure components at the same temperature and pressure. But in practice many binary solutions deviate from ideality. The reduced excess volume per segment given by

\[ \tilde{V}^E = \tilde{v} - \tilde{v}_0 - \frac{v^E}{\tilde{v}_0 \phi_1 \phi_2 \tilde{x}_1 \tilde{x}_2} \]  

(5.12a)

and the excess volume hence turns out to be

\[ V^E = \tilde{V} - (\phi_1 \tilde{v}_1^* + \phi_2 \tilde{v}_2^*) v_0 \]  

(5.12b)

Where \( v \) is the reduced volume of the real system, which can be obtained through the relation:

\[ p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 x_{12} = \left[ T \tilde{V}^{th} / (\tilde{v}^{th} - 1) \right] \left[ \phi_1 p_1^* / T_1^* + \phi_2 p_2^* / T_2^* \right] \]  

(5.13)

The evaluation of \( v \) enables one to determine the excess volume \( V^E \) through equation (5.12a). Instead of following the above mentioned procedure, \( V \) can also be obtained directly adopting Flory's procedure [14]

\[ V^E = (\tilde{T} - \tilde{T}_0) \tilde{v}_0^{\gamma/3} / (4/3 - \tilde{v}_0^{1.3}) \]  

(5.14)

Where \( \tilde{T}_0 = (\tilde{v}_0^{1.3} - 1) / \tilde{v}_0^{4.3} \),

(5.15)

where \( \tilde{T}_0 \) is the reduced ideal temperature.
5.2.2 Excess Enthalpy $H^e$:

Ignoring the small difference between enthalpy and energy for a condensed system, the excess enthalpy per mole of the system is given by

$$H^e = E - (x_1 E_1 + x_2 E_2) \quad \ldots \quad (5.16)$$

Which in the light of equation (5.4) can be written as

$$H^e = x_1 v_1^* p_1^* \left(1/v_1 - 1/v\right) + x_2 v_2^* p_2^* \left(1/v_2 - 1/v\right) + x_1 v_1^* \theta_2 X_{12} / \bar{v} \quad (5.17)$$

The last term in equation represents the contribution from contact interaction terms—the difference between 1,2 pairs and the mean of 1,1 and 2,2 pairs. This term is designated as the contact interaction term contribution due to other terms is referred to as ‘equation of state’ term.

5.2.3 Excess Isothermal compressibility $\beta_T^E$:

The excess isothermal compressibility of the system is defined as

$$\beta_T^E = \beta_T - \beta_T^e \quad \ldots \quad (5.18)$$

Using equations (5.11) and (5.12a) we can rewrite for the excess compressibility

$$\beta_T^e = 3 \bar{v}^2 \left(\bar{v}^{\frac{1}{3}} - 1\right) / \{p^* [1 - 3 (\bar{v}^{\frac{1}{3}} - 1)] - (\phi_1 v_1 \beta_{T1} + \phi_2 v_2 \beta_{T2}) / \bar{v}\} \quad (5.19)$$

where $\beta_T^e$ is the ideal compressibility.

5.2.4 Excess Internal pressure $\pi^e$:

The internal pressure $\pi$, of a system can be related to the thermal pressure coefficient ($\delta P/\delta T$)$_V$ by the following equation.

$$\pi = T \left(\delta P/\delta T\right)_V - P = T \alpha/\beta_T - P \quad \ldots \quad (5.20)$$

This equation is often called the thermodynamic equation of state. For most of the liquids and systems $T \alpha/\beta_T$ is very much larger than the external pressure, $P$. The value of $P$ is neglected compared to $T \alpha/\beta_T$. Using equation (5.7) the internal pressure of the binary system is
The excess internal pressures are evaluated from the following equation:

\[ \pi - \pi_0 = \frac{p^*}{v^2} - T \alpha / \beta \]

where \( \pi_0 \) is the ideal internal pressure of the system.

5.2.5 EXCESS COHESIVE ENERGY DENSITY \((\Delta U_V/V)^E\):

The energy of the vapourization of a real mixture \( \Delta U_V \) to the perfect gas state can be calculated using the relation:

\[ \Delta U_V = \sum_x \Delta H_{V,x} \cdot x - H^f - RT \]

where \( \Delta H_{V,1} \) and \( \Delta H_{V,2} \) are the enthalpies of vaporization of components 1 and 2 respectively. Ideal mixing occurs with no change in the enthalpy of the system. The energy of vaporization for ideal system is given by

\[ \Delta U_{V,\text{id}} = \sum_x \Delta H_{V,x} \cdot x - RT \]

On dividing this term by ideal volume the cohesive energy density of ideal system is resulted. Substituting the value of \( H \) obtained from equation (5.17) into equation (5.23), enthalpy of vaporization of the system can be evaluated. Using \( V \) of equation (5.12b) and the ideal volume, the molar volume of the system is resulted. The cohesive energy density of the system can be evaluated theoretically. The excess cohesive energy density is therefore expressed:

\[ (\Delta U_{V,\text{id}}/V)^E = (\Delta U_V/V) - (\Delta U_{V,\text{id}}/V) \]

5.2.6 INTERACTION PARAMETER:

The evaluation of the characteristic parameters of the pure liquids and the interaction energy parameter \( X_{12} \) of the system enables one to calculate the excess functions of the binary systems.

There are mainly three methods [6] to evaluate the energy term \( X_{12} \). First method is to assume that the reduced temperature \( T \) of the system is a linear function...
of the segment fraction

\[ T = \phi_1 T_1 + \phi_2 T_2 \]  

(5.26)

This method is strictly valid for \( P_1^* = P_2^* \) and \( X_{12} = 0 \). This assumption is approximately valid for spherical or chain molecules of nearly equal characteristic pressures and whose interactions are weak (\( X_{12} \) is small or negligible). The reduced temperature of the system can be related to the interaction energy parameter \( X_{12} \) through equation (5.10).

The second method (also approximate) of evaluating the energy parameter is through the familiar Berthelot geometric mean rule [6,13]. The characteristic parameters of the pure liquids can be related to the interaction energy \( X_{12} \) through the relation [6]

\[ X_{12} = p_1^* \left\{ 1 - \left[ \left( \frac{v_1^*}{v_2^*} \right)^{1/3} \left( \frac{p_1^*}{p_2^*} \right)^{1/2} \right]^2 \right\} \]  

(5.27)

The excess properties can be evaluated using the value of \( x \) so obtained.

The third and more general method of evaluation of \( X_{12} \) requires the knowledge of one of the excess parameters of the liquid system. Flory and co-workers [6,14], Benson and co-workers [15-17] and several others have used equation (5.17) to evaluate \( x \) by fitting the \( H^E \) data (using adjustment method since \( X_{12} \) is a function of \( H^E \) as well as \( H^F \)). Rastogi and his co-workers [18,19] and Nigam and Singh [20] have used equations (5.12) and (5.13) to evaluate \( X_{12} \). Benson and Singh [16] have discussed relative merits of the two methods.

In the present work excess volumes are measured using density measurements as described in chapter 4. In view of the fact that experimental \( H^E \) are not available in literature, \( X_{12} \) is derived using equations (5.12) to (5.14). Other excess parameters are
predicted using the respective equations. In order to compare this procedure with the Flory's procedure (evaluating $X_{12}$ using $H^f$ data and predicting the other excess functions) literature values of heats of mixing are utilised. A third excess property like $\beta_T^k$ evaluated by the two procedures gives an idea of the difference, if any, of the two procedures [16,19].

It may be mentioned that the agreement between the experimental and the predicted excess functions is a test for the internal consistency of the theory. The agreement of excess internal pressures [20-24] and cohesive energy densities is a further test of the theory. The relevant discussion is presented in chapter 6.

5.3 Application of Flory Theory to Polymer Solutions and Binary Liquid Mixtures

5.3.1 Polymer Solutions - Application of Flory Theory

As already indicated the Flory theory has been applied to polymer solutions [11]. Preliminary results on several polymer solutions in toluene [11] indicate that the general Flory theory has been quite successful in predicting excess thermodynamic parameters. The study of polymer solutions is visualised through the study of binary mixtures. The solute is treated as one component and the solvent is treated as the other. The volume change on solution is equivalent to the volume of mixing of binary mixtures while the heat on solution is equivalent to the enthalpy on mixing that results in binary mixtures. Issac Sanchez [24A] has applied the improved Flory of corresponging-states to polymer solutions. It would be appropriate to adopt the Flory theory for polymer solutions as cited by Flory [25] and Huggins [26] independently. Flory theory has been recent. Recent publications on diversified topics of polymer solutions is presented in Sec 5.3.3.
5.3.2 Binary Mixtures - Application of Flory Theory

It is quite essential to investigate the success of the Flory theory for binary liquid mixtures. We wish to briefly review the contemporary works of binary solutions that support to the extension to polymer solutions. We select a few of the several published data as cited by Ahmed [27]. All the publications as cited by Ahmed on binary mixtures and ternary mixtures are confined to certain broad classification. The classification is rather broad and of diversified approaches. Van der Waals simple or refined expressions are used by certain workers [28] later extending the model to Flory theory [29]. Using the so called ideal terms from Prigogine’s model with the help of Flory theory as suggested by Patterson certain workers [30, 31] have determined the excess functions. This refined model has met with a reasonable success as applied to binary mixtures. Certain workers [32, 33, 34] have adopted the Jacobson’s free length model to investigate the binary mixtures. The so called free length of the component molecules are first evaluated using ultrasonic (or compressibility) data. The free lengths of the mixtures are determined to evaluate the other thermodynamic properties. Sometimes the free length is correlated to the collision factor proposed by Schaffs [34]. On a almost similar ground the so called free volume is evaluated using semi-emperical relations [33, 35, 36, 37, 38]. Different approaches (such as Rao’s constant approach) have been used for the evaluations [39, 40]. In reference 35, the Glasstone’s partition function is evaluated using such a approach.

Flory theory has been tested on several binary mixtures [15-24, 41, 42-44, 45] by various investigators by determining the so called interaction term, usually by using one of the (experimentally measured) excess parameters. Flory theory has also been derived for
polymers using cumulant expansion [46]. This demonstrated that the statistical thermodynamic approximations as derived by Flory can also be derived using some what different methods. Some investigators [27] indirectly used Flory theory by assuming ideal behaviour of characteristic pressure or reduced temperature as suggested by Flory [6]. The scaled particle theory, hard sphere like treatment, significant structure theory and such others cited [27]. Certain others [47, 48] Special theories similar to the cell model, Balescu's theory is applied [49], Eyrings (priliminary model) [50] or deriving excess parameters assuming ideal values [51]. Phase equilibria methods have been used to evaluate the excess parameters [52, 53]. The application of Flory theory or similar fundamental theories are on the increasing trend [27].

5.3.3 Diversified Studies on Polymer Solutions:

Thermodynamic studies in polymers and polymer solutions is a quite diversified field of study. Several studies of all varieties have been undertaken and it is beyond the scope of this work to cite all references. However selected references that are related to the present study are cited here [54-76]. Dudowics et al [54] have studied the role of molecular structure on the thermodynamic properties polymer blends and concentrated polymer solutions. Using the Monte Carlo methods, thermodynamic properties of dilute polymer solutions have been studied by by Pavatov, Khaltur and Eskin [55]. Structural studies have been made on polystyrene in toluene by Chatani et al [56]. Floudas studied solvent and polymer dynamics in concentrated polystyrene + toluene solutions [57]. Konak and Brown studied the coupling of density to concentration fluctuations in concentrated solutions of polystyrene in toluene [58]. The influence of concentration on the activation energy for diffusion in polymer-solvent systems has been undertaken by
Zielinski and Duda [59]. Raman and Varada Rajulu studied the acoustical parameters of polystyrene in binary mixture of certain organic liquids [60]. Ultrasonic properties of some polyvinyl chloride solutions have been studied by Narasimhan et al [61]. Nakajima and Goto studied the spatial distribution and configuration entropy of mixing of polymer solutions [62]. Volume fluctuation thermodynamics of polymer solutions by Issac Sanchez [63], behaviour of thermodynamic interaction parameter in dilute polymer solutions by Van Dijk and Wakker [64], thermodynamics of polymer solutions by Haegen et al [65] are some of the general studies. Theories of polymer solutions - a review by Avinabhavi et al [66], thermodynamics of polymer solutions and mixtures Yoshiyuki [67], thermodynamics of polymer solutions and blends by Hach [68], thermodynamic interaction parameters in polymer solutions and gels by Ferent [69], review of experimental methods and applications for measurement of thermodynamic by Modarress and Eliass [70], sound velocities in polymer blends and the compatibility by Yamado et al [71], acoustic properties of polymer mixtures by Bardyuk [72], comparison of polymer solution data from various measurements by Broniarz [73] and acoustic studies in solvent solute interactions in non aqueous polymer solutions by Senthil & Rakappan [74] are some of the general studies required for reference. Many other studies pertaining to synthetic polymer solutions exist in literature and it is not useful to cite these as do not have much bearing to the present studies [75, 76]. Several publications by RP Singh et al as cited in Ref 11 and particular studies in polystyrene, polymethylmethacrylate, polyvinyl acetate and polyvinyl chloride by YP Singh & RP Singh [77-92] and Lewis & Johnson [93, 94] have been used as reference papers to discuss various aspects of subsequent chapters.
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