A Theoretical Study of Free Volume Effect on Phase Stability of Hydrogen Bonded Polymer Mixtures by Lattice Fluid Theory

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ABSTRACT

Strong intermolecular forces such as hydrogen bonds between repeating units of polymer molecules cause association of polymer chains and affect the phase behaviour of polymer-polymer mixtures. In this work, the phase behaviour and miscibility regions of hydrogen bonded polymer mixtures are calculated by a new model based on the lattice fluid theory of mixtures. In this model, the compressibility or free volume effect of the mixture which is originated from empty lattice sites is considered by introducing a new correlation for the number of vacant sites. The spinodal curves are calculated for the mixtures and it is shown that as expected from the theory, higher compressibility causes lower stability and consequently the phase separation.

INTRODUCTION

Polymer mixtures are frequently immiscible . This is because, for the mixing of high molecular weight macromolecules the combinatorial entropy contribution is very small. On the other hand, the enthalpy of mixing is primarily dependent on the energy change associated with changes in nearest neighbour contacts during mixing and is much less dependent on molecular lengths. Hence, the free energy of mixing is dominated by enthalpic term [1]. If the only intermolecular interactions in the mixture are van der Waals or London dispersion forces the enthalpic term will be positive and, therefore, the Gibbs free energy

of mixing will be positive too [2, 3].

To promote miscibility, strong interactions must be introduced among the molecules of the mixture. The most important of these interactions is hydrogen bonding between polymer molecules.

Presence of hydrogen bonding interactions causes exothermic effects in the mixing and makes the Gibbs free energy of mixing negative. Therefore, miscibility occurs and the mixture components are said to be compatible.

Another phenomena which reveals its effect on miscibility or phase stability of polymer mixtures is free volume or mixture compressibility. It is thought that appearance of LCST (lower critical solution

temperature) or thermal induced phase separation in hydrogen bonded polymer mixtures is due to free volume [4].

Prediction of thermodynamic properties of hydrogen bonded polymer mixtures and their phase behaviour is an interesting subject for polymer researchers. One of the most effective methods in statistical thermodynamics for studying the phase behaviour of polymer mixtures is the lattice fluid theory of mixtures. In this field at first, Painter et al. [5] adopted the well known Flory-Huggins model for including the hydrogen bonding contribution in polymer miscibility. To do this they employed an additional term in the Flory-Huggins' Gibbs free energy expression of mixing that takes into account the effect of hydrogen bonding. To predict the distribution of hydrogen bonded chains in the mixture, they used the concept of association and equilibrium constants which have been determined by spectroscopic measurements. In their initial model, they had assumed that the size of a repeating unit of polymer chains was equal to an interacting unit. In the extension of their model Painter et al. [6] showed that this assumption was not necessary any more. Graf et al. [7], presented a new model which utilized the Sanchez and Lacombe [2, 3 and 8] lattice fluid theory of polymer mixtures.

The equilibrium constants for predicting the distribution of hydrogen bonded chains also were used and by deriving a relation for the partition function of the mixture the Gibbs free energy of mixing was calculated.

On the other hand Panayiotou and Sanchez [9] presented a model for hydrogen bonding in fluids, using the equation of state approach. This model divides the intermolecular forces into two contributions which are physical (dispersion) and chemical (hydrogen bonding) forces. The physical forces are calculated based on the lattice theory of fluid mixtures, and the chemical interactions are taken into account with the aid of calculating the number of hydrogen bonds among the molecules.

All of above models for studying phase stability of polymer mixtures can be categorized into two main models, namely "regular lattice model" and "equation of state model". For the case when there is no vacant site in the lattice the model is called "regular lattice model", and when vacant sites are present it is called "equation of state model". Here we have presented a developed approach which covers both of them.

Commonly, in all above mentioned models, for introducing the effect of free volume in spinodal calculations it is needed to obtain an equation of state for the mixture. Solving the equation of state is accompanied with the problem of obtaining mixture characteristic values such as hard core density (the density of mixture at closed packed state), closed packed lattice cell volume and so on. Unfortunately these values are not available in many cases for polymer mixtures. In present paper, based on the lattice fluid mixtures theory, this problem has been overcome by introducing a relation for the number of vacant sites in the lattice. Using this relation, it is not necessary to solve equation of state and with the aid of a straightforward path for calculating the reduced volume (the ratio of mixture volume to closed packed lattice volume of mixture), miscibility regions and spinodal curves are obtained for hydrogen bonded polymer mixtures.

MODEL DESCRIPTION

Consider a mixture of polymer molecules. The number of "i"th component molecules is N_i and each molecule consists S_i segments (S_i-mer), at temperature T and pressure P. Assume M_i is the degree of polymerization of component "i", thus n_i, the total number of "i"th component repeating unit is equal to $M_i N_i$. In lattice theory it is assumed that all molecules are arranged on a lattice of n_r sites, n_v of which are empty. Total number of lattice sites which occupied with "i"th component segments are $S_i N_i$, and the total number of lattice sites are:

$$n_r = \sum_{i=1}^{i=n} S_i N_i + n_v \qquad (1)$$

The site fraction of component "i", f_i, is defined as:

$$f_i = \frac{S_i N_i}{\sum_{i=1}^{\bar{m}} S_i N_i} \qquad (2)$$

and the vacant site fraction:

$$f_v = \frac{n_v}{\sum_{i=1}^{\bar{m}} S_i N_i} \qquad (3)$$

The volume fraction of "i"th component, on the other hand can be obtained by the following relation:

$$\varphi_i = \frac{S_i N_i}{\sum_{i=1}^{\bar{m}} S_i N_i + n_v} = \frac{S_i N_i}{n_o} \qquad (4)$$

In order to proceed further, the total number of configurations available to our system must be calculated. According to the Flory's [10] combinatorial expression for the number of configurations, the partition function in its maximum term approximation may be written as [2, 8, 11]:

$$Q(T, P) = (\frac{1}{f_v})^{n_v} (\frac{\omega_1}{f_1})^{N_1} \dots (\frac{\omega_a}{f_a})^{N_a} \exp[-\frac{(E+PV)}{kT}] \qquad (5)$$

$$\omega_i = \frac{\xi_i S_i}{\sigma_i e^{S_i - 1}} \qquad (6)$$

where k is the Boltzman constant, E and V are the total energy and volume of mixture, respectively, σ_i is a symmetry number and ξ_i is a flexibility parameter characteristic of component "i", and ω_i may be recognized to be the number of configurations available to an S_i-mer in the closed packed pure state [10].

From statistical thermodynamics Gibbs free energy of the mixture is expressed as [12]:

$$G = -kT \ln Q(T,P) \qquad (7)$$

As it is seen from eqns (6) and (7), the total energy and volume of mixture must be calculated for obtaining the Gibbs free energy of mixture. For calculating E, we assume that only the nearest neighbours

interact. The interaction energy of a mer of type "i" when surrounded by mers of type "j" is equal to $\in_{ij}$. Therefor, total interaction energy of the system is:

$$E = (\sum_{i=1}^{\bar{m}} S_i N_i) (\sum_{i=1}^{\bar{m}} \in_{ij}) \qquad (8)$$

The volume of the mixture can be obtained by multiplying the total number of lattice sites, n_0, into lattice cell volume, v^* (the average closed packed volume per segment in the mixture), thus:

$$V = (\sum_{i=1}^{\bar{m}} S_i N_i)v^* \qquad (9)$$

In this work we have considered binary systems where one of the polymers can self-associate through intermolecular hydrogen bonding. The other polymer is assumed to be unassociated but is capable of association with the first, again, through hydrogen bonding. The unassociative component is represented by the symbol "A" and the self-associative one by "B".

Writing eqns (5), (8) and (9) for these binary mixtures and substituting in eqn (7) gives the Gibbs free energy of mixture:

$$G_{mixture} = kT[n_A \ln(\frac{\varphi_A}{\omega_A}) + n_B \ln(\frac{\varphi_B}{\omega_B}) + n_v \ln(1 - \bar{\rho}) +$$

$$(n_A + n_B)\ln\bar{\rho}] + n_v v^*(-\bar{\rho}P^* + \frac{P}{\rho}) + kT[n_A \ln(\varphi_A \frac{\bar{\rho}}{S_A}) +$$

$$\sum n_{B_i} \ln(\varphi_B \frac{\bar{\rho}}{S_B}) + \sum n_{B_i} \ln(\varphi_B \frac{\bar{\rho}}{S_B + S_A}) -$$

$$kT[n_A \ln(\varphi_A \frac{\bar{\rho}}{S_A}) + n_B \ln(\varphi_B \frac{\bar{\rho}}{S_B})] + kT[(n_B - \sum n_{B_i})[1 -$$

$$\ln(z - 1)] + \sum n_{B_i} \ln\sigma] \qquad (10)$$

where $\bar{\rho}$ is the reduced density of mixture and n_{B_i} is the number average length of a polymer chain and z is the co-ordination number of the lattice.

In a binary polymer mixture the stability condition may be defined by the following eqn [13]:

$$d^2 \Delta G^{mix}/d\varphi_i^2 > 0 \qquad (11)$$

where ΔG_{mix} is the Gibbs free energy of mixing of two polymers . This inequality define the spinodal in the

phase diagram. The spinodal separates the metastable region from the two phase unstable region.

If eqn (11) is written for self-associating component "B" and variation of ΔG_{mix} with density is taken into account it can be shown that the following equation will hold [14]:

$$\frac{d^2\Delta G^{mix}}{d\varphi_B^2} = \frac{\partial^2\Delta G^{mix}}{\partial\varphi_B^2} + \frac{\partial^2\Delta G^{mix}}{\partial\varphi_B\partial\rho}\frac{d\rho}{d\varphi_B} = \frac{\partial^2\Delta G^{mix}}{\partial\varphi_B^2} -$$

$$[\frac{\partial^2\Delta G^{mix}}{\partial\varphi_B\partial\rho}]^2[\frac{\partial^2\Delta G^{mix}}{\partial\rho^2}]^{-1} \qquad (12)$$

At low pressures the following equation is also true [15]:

$$[\frac{\partial^2\Delta G^{mix}}{\partial\rho^2}]^{-1} \equiv \kappa_r\rho^3 > 0 \qquad (13)$$

where κ_r is the isothermal compressibility.

Thus it is seen from eqns (11), (12), and (13) that the mixture's isothermal compressibility κ_r should have the reverse effect on the phase stability. This is because the higher compressibility of mixture causes the second term in the right hand side of eqn (12) to be larger (with minus sign) and consequently causes a more decrease in the left hand side of eqn (12).

In phase stability studies eqn (12) must be used. In this equation the second derivative of the Gibbs free energy of mixing is needed. The Gibbs free energy of mixing is obtained as:

$$\Delta G_{mix} = G_{mixture} - G_{pure\ A} - G_{pure\ B} \qquad (14)$$

The values of $G_{pure\ A}$ and $G_{pure\ B}$ can be obtained from eqn (11) for $\phi_A = 1$ and $\phi_B = 1$, respectively. The resulted equations have been derived by Graf et al. [7] and presented in the Appendix.

As it is seen from eqns A(1) to A(3) in the Appendix, for phase stability calculations the reduced density, $\bar{\rho}$, or reduced volume, $\bar{v}$, of mixture is needed.

Obtaining reduced volume or reduced density of mixture requires an appropriate equation of state for the mixture, and some experimental data such as hard core density and closed packed volume of mix-

ture as a function of volume fraction of components. Unfortunately, these values are not available for polymer mixtures. To overcome this problem in this work we present a new approach in calculating the Gibbs free energy of mixture which does not need application of an equation of state.

The reduced volume of the mixture is defined as the ratio of mixture volume to closed packed lattice volume. Using eqn (9) the reduced volume of mixture for a two component system can be written as follows:

$$\bar{v} = \frac{1}{\bar{\rho}} = \frac{V}{V^*} = \frac{n_A S_A + n_B S_B + n_v}{n_A S_A + n_B S_B} \qquad (15)$$

For calculating reduced volume, $\bar{v}$, we need the total number of vacant sites, n_v, and the number of segments for repeating units of polymer chains, S_i, in the mixture. It is impossible to calculate directly S_i because the hard core density and closed packed lattice cell volume for the mixture are not available. Thus, at first we calculate the number of segments for a repeating unit of each polymer component in pure state, S_i^*, by using the following equation:

$$S_i^* = \frac{M_{wi}}{v_i^*\rho_i^*} \qquad (16)$$

where M_{wi} is the molecular weight, and ρ_i^* is the hard core density of component "i" in pure state. Then we can calculate the number of segments for repeating units of each polymer component, S_i, in a mixture by assuming that the number of segments per lattice cell volume in pure state S_i^*/v_i^* and in mixture S_i/v^* remain the same i.e:

$$\frac{S_i}{v^*} = \frac{S_i^*}{v_i^*} \qquad (17)$$

In the above equation we define the lattice cell volume v^* as follows:

$$v^* = \varphi_A v_A^* + \varphi_B v_B^* \qquad (18)$$

For a two component system we propose the following equation for calculating, n_v, the number of vacant sites:

$$n_v = (1 - K_{ab})(n_{vA} + n_{vB}) \qquad (19)$$

where K_{ab} is an adjustable parameter and n_{vA}, n_{vB} are the number of vacant sites of the polymers in the pure state. The number of vacant sites in the mixture n_v is proportional to the sum of vacant sites in pure components. When $K_{ab} = 0$ this number is equal to the sum of pure component vacant sites. This equation is general enough to cover all the possible cases of variation of the number of polymer mixture vacant sites due to mixing. From eqn (14) for the pure components "A" and "B" we have:

$$\bar{v}_A = \frac{1}{\bar{\rho}_A} = \frac{n_A S_A^\bullet + n_{vA}}{n_A S_A^\bullet} \quad \tilde{v}_B = \frac{1}{\bar{\rho}_B} = \frac{n_B S_B^\bullet + n_{vB}}{n_B S_B^\bullet} \qquad (20)$$

Then by substituting for n_{vA}, n_{vB} in eqn (19) the following equation is obtained:

$$n_v = (1 - K_{ab})(n_B \frac{S_B^\bullet}{\bar{\rho}_B} + n_A \frac{S_A^\circ}{\bar{\rho}_A} - n_B S_B^\bullet - n_A S_A^\bullet) \qquad (21)$$

where $\tilde{\rho}_B = 1/\tilde{v}_B$ and $\rho_A = 1/\tilde{v}_A$ are the pure component reduced densities.

CALCULATIONS

For phase stability calculations we proceed according to the following steps:

(1) Hard core densities for pure components are calculated from the following relation:

$$\rho_i^\bullet = \frac{M_{w_i}}{V_i^{\bullet}} \qquad (22)$$

where M_{w_i} is the "i"th component molecular weight and $V_i^\bullet$ is the molar volume at absolute zero temperature. Values of $V_i^\bullet$ are obtained from reference 16.

(2) Characteristic pressure values, $P_i^\bullet$, are obtained from solubility parameter according to eqn A(4) in the Appendix. All of required values for $P_i^\bullet$ are given in reference 7.

(3) The number of segments of each molecule in pure state, S_i°, and in the mixture, S_i, are calculated from eqns (16), (17), respectively. Values of lattice cell

volume for pure components, $v_i^\bullet$, are given in reference [8].

(4) For calculating reduced volume or reduced density of mixture, we use our proposed relation for the number of vacant sites, n_v, eqn (22) joined with eqn (15).

Using the above algorithm, and substituting eqns A(1) to A(3) in eqn (12), we calculate spinodal curves for the mixture of poly vinylphenol (PVPh) as the self-associative component and poly hexylmethacrylate (PHM), in temperature range of 220– 670 K and for the molecular weights varying from 50 to 20.0×10^3 for both components.

RESULTS AND DISCUSSION

The results of calculations for the degree of polymerization equal to 500 and $K_{ab} = 0$ and 1 for the mixture of PVPh and PHM are shown in Figure 1. As it is seen from Figure 1 the addition of vacant sites (K_{ab} going from 1 to 0) will expand the instability region. This behaviour is consistent with the understanding that the mixture compressibility destabilizes the mixture and promotes phase separation [14]. This is indicative of the fact that our proposed approach shows a significant quantitative advantage in predicting the phase behaviour of hydrogen bonding polymer blends relative to regular lattice model. It should be noted that for the spinodal calculation of regular lattice model there is no vacant sites in the mixture($n_v = 0$ or $K_{ab} = 1$) and thus $\tilde{\rho} = 1$ and:

$$\frac{\partial^2 \Delta G^{mix}}{\partial \varphi_B \partial \bar{\rho}} = \frac{\partial^2 \Delta G^{mix}}{\partial \bar{\rho}^2} = 0 \qquad (23)$$

The results of calculations for various cases of K_{ab} (1, 0.5, 0, –1) are represented in Figure 2. It is seen that LCST (lower critical solution temperature), UCST (upper critical solution temperature) and immiscibility loops are calculated successfully. According to the basic relations of thermodynamics (eqns. (12) and (13) of this paper) it has been proved that considering the compressibility must destabilize the mixture and lead to phase separation. In Figure 2 the curves assigned by $K_{ab} = 1$ present the results of regular
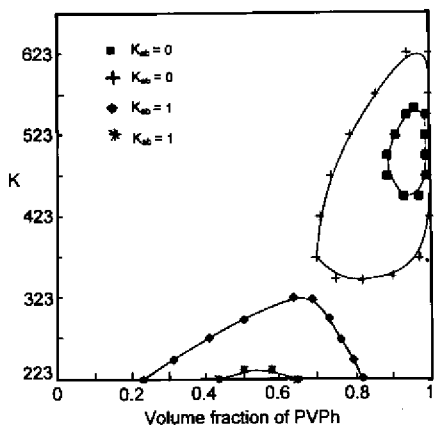
Figure 1. Spinodal curves for poly hexylmethacrylate (PHM) and poly vinylphenol (PVPh) with degree of polymerization equal to 500.

lattice model, where the reduced density is constant and equal to unity. When $K_{ab} \neq 1$ it means that there are some vacant sites in the mixture and the resulting curves belong to the equation of state model.

Decreasing K_{ab} (or increasing free volume) causes further and further phase separation. As it is expected, the new approach presented in this paper
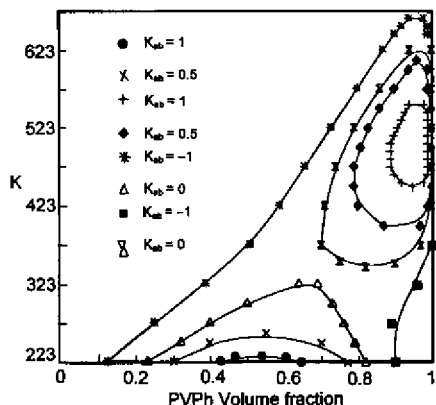

Figure 2. The effect of number of lattice vacant sites on phase stability of PHM and PVPh mixture.
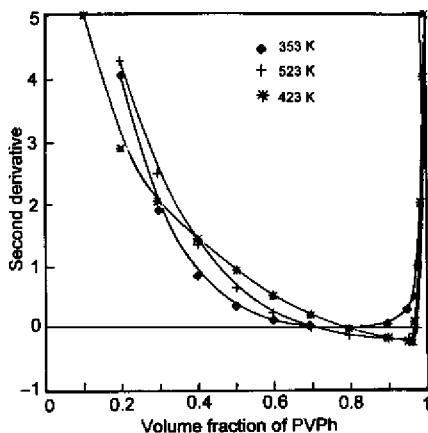

Figure 3. The contact point of zero axis and T=353 K is one point of spinodal curve.

can give a quantitative criterion for the tendency of components to create a homogeneous phase.

The Effect of Temperature

In Figure 3 we present the variation of the second derivative of the Gibbs free energy of mixing for various temperatures. As it is seen from Figure 3 when the second derivative of the Gibbs free energy
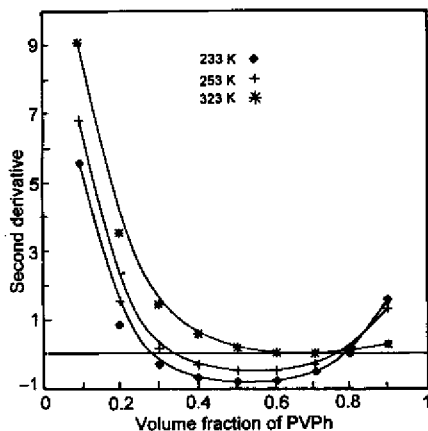

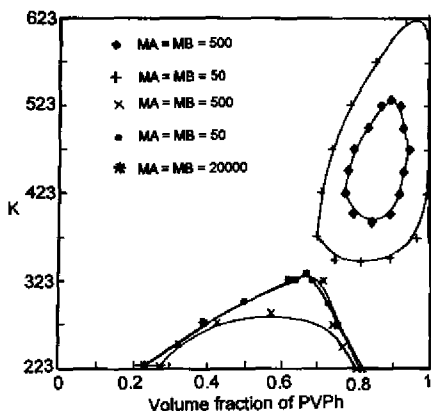**Figure 4.** UCST of PHM and PVPh mixture.

Figure 5. The effect of degree of polymerization on phase stability of PHM and PVPh mixture.

versus volume fraction at a given temperature is equal to zero, we obtain one point of spinodal phase diagram. For the particular temperature of T=353 K on Figure 3 the second derivative of the Gibbs free energy curve is tangent to zero line. This temperature is the LCST of mixture because above this temperature phase separation begines. In order to demonstrate the UCST of the PVPh and PHM mixture by the new presented approach we report Figure 4 for various other temperatures. According to this figure the UCST of PVPh and PHM mixture is 323 K.

The Effect of Degree of Polymerization
For the mixture of PVPh and PHM we calculate the spinodal phase diagrams for various degrees of polymerization, M_i, equal to 50, 500, 20.0×10^3. The results of this calculation are presented in Figure 5. Increasing the degree of polymerization means longer polymer chain lengths. This reduces the molecular motions and promotes entanglement of the long chains. Thus it is expected that increasing the degree of polymerization, causes less compatibility of components and increases two phase region area. The resulted spinodal curves confirm this phenomenon although it is seen that higher degrees of polymerization, ($M_i > 500$), have little effect on phase stability region change.

CONCLUSION

The new theoretical model which has been presented and used in this paper, can clearly answer the question of "how the compressibility and association phenomena dominate the hydrogen bonded polymer mixtures phase behaviour".

Introducing the adjustable parameter in eqn (8) enable the model to predict successfully the lower and upper critical solution temperature (LCST and UCST) and closed loop curves in spinodal diagrams. The approach used in calculating reduced volume and density of mixture made the spinodal calculations independent of the application of equation of state. Considering untractable behaviour of polymer-polymer mixtures reveals the surprising ability of this model for formulating the spinodal calculations and therefore, predicting phase behaviour of hydrogen bonded polymer mixtures.

APPENDIX

For calculation of second derivative of Gibbs free energy of mixing with respect to volume fraction of self-associative component the following equations is used [7]:

$$\frac{\partial^2[\frac{\Delta G^{mix}}{RT}]}{\partial \varphi_{b}^2} = \frac{1}{r^* M_A \varphi_A} + \frac{1}{M_u \varphi_u} - 2\rho S_u^* \frac{v_u^*}{RT} \Delta p^* +$$

$$2[\frac{-1}{r^* M_A} + \frac{1}{M_u}][\frac{S_A^*}{S_A} - \frac{S_u^*}{S_b}] + \frac{S_u}{s}[\frac{S_A^*}{S_A} - \frac{S_u^*}{S_u}]^2 +$$

$$[-\frac{1}{r^*\varphi_{AI}}(\frac{\partial\varphi_{AI}}{\partial\varphi_B}) + \frac{1}{\varphi_{uu}}(\frac{\partial\varphi_{uu}}{\partial\varphi_u}) - [\frac{1}{r^*\varphi_A} + \frac{1}{n_{Bk}\varphi_u}] +$$

$$2[1 - \frac{1}{n_{B_k}}][\frac{S_A^*}{S_A} - \frac{S_u^*}{S_u}] + \varphi_u[1 - \frac{1}{n_{B_k}}][\frac{S_A^*}{S_A} - \frac{S_u^*}{S_u}]^2$$

$$(A1)$$

$$\frac{\partial^2[\frac{\Delta G^{mix}}{RT}]}{\partial\tilde{\rho}^2} = \frac{S_B}{\tilde{\rho}}[\frac{1}{1-\tilde{\rho}} + \frac{1}{\tilde{\rho}S} - 2\frac{p\tilde{v}^*}{RT}] +$$

$$\frac{1}{\bar{\rho}^2}(\varphi_{B1}\Gamma_2 - \varphi_B\frac{\Gamma_1^\circ}{\Gamma_2}) + \frac{\Gamma_2}{\bar{\rho}}[\frac{\partial\varphi_{B1}}{\partial\bar{\rho}}] \qquad A(2)$$

$$\frac{\partial^2[\frac{\Delta G^m}{RT}]}{\partial\varphi_B\partial\bar{\rho}} = S_B^\bullet\frac{v_B^\bullet}{RT}[p_A^\bullet - p_B^\bullet + \bar{\rho}(\varphi_A - \varphi_B)\Delta p^\bullet] +$$

$$\frac{S_B}{\bar{\rho}}[\frac{S_A^\circ}{S_A} - \frac{S_B^\circ}{S_B}][\frac{\ln(1 - \bar{\rho})}{\bar{\rho}} + 1] + \frac{1}{\rho}[\frac{1}{r^\bullet M_A} +$$

$$\frac{1}{M_B}] + [-\frac{1}{r^\bullet\varphi_{A1}}[\frac{\partial\varphi_{A1}}{\partial\rho}] + \frac{1}{\varphi_{B1}}[\frac{\partial\varphi_{B1}}{\partial\rho}] + \frac{1}{\rho}[1 -$$

$$\frac{1}{n_{B_n}}] \qquad A(3)$$

where $\Gamma_1^\bullet$ and Γ_2 are the fraction of self-associative component repeating units which have not hydrogen bond in pure state and in the mixture respectively, $r^\bullet$ is equal to S_A / S_B, and $P_i^\bullet$ is the "i"th component characteristic pressure defined by the following equation:

$$p_i^\bullet = (\delta_i\frac{\rho_i^\bullet}{\rho_i})^2 \qquad A(4)$$

where δ_i is the solubility parameter of component i and n_{B_n} is the number average length of a polymer chain.

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