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Statistical Thermodynamics of Associated Polymer Solutions

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ABSTRACT: The lattice-fluid theory for polymer solutions has been modified to account for strong interactions (hydrogen bonding) between the polymer and solvent. The resultant model is an equation-of-state model able to describe thermodynamic properties of these systems over an extended range of external conditions from the ordinary liquid state up to the critical or supercritical state. The general case is treated where the solvent self-associates and cross-associates with the polymer. The model has been tested against consistent sets of experimental data on vapor pressures, heats of mixing, and volumes of mixing of chloroform + polyether solutions. It is shown that the model is able to predict the sigmoidal-shaped isotherms characteristic of these systems.

I. Introduction

Hydrogen bonding in polymer solutions has attracted particular attention in recent years especially in bioapplications.[1-3] Aqueous polymer solutions are the most interesting from the practical viewpoint. From the theoretical viewpoint, hydrogen bonding, even in ordinary liquid solutions, remains a challenge. Two major approaches, approximate in nature, are widely used: the nonrandom molecular or group contribution approach[4-7] and the association or physical–chemical approach.[8-11] Both approaches have been extended to polymer solutions,[11b,12-14] and by their nature (rigid lattice theories) they attribute the occurrence of the lower critical solution temperature (LCST) in these systems exclusively to hydrogen bond forming and breaking. It is, however, well-known that the compressible character of polymer solutions may give rise to LCSTs even in systems of nonpolar substances. Integration of the above approaches to equation-of-state theories such as the Flory–Patterson–Prigogine (FPP)[15-17] theory and the lattice-fluid (LF)[18,19] theory appears particularly attractive. It could give an appropriate frame for studying associated polymer solutions over extended ranges of temperature and pressure.

In a series of recent papers[20] we have presented a lattice-fluid associated solutions (LFAS) model by combining Flory's theory for polydisperse polymer solutions[21] with the lattice-fluid theory of liquid mixtures.[18,19] The LFAS model has been applied to self-associated molecules from ordinary conditions up to their critical state. Only consecutive linear association complexes have been considered so far. In multiassociated polymer solutions, the association complexes are rather branched molecular entities or "graft" copolymers and their enumeration is nontrivial. In this work we will extend the LFAS model to polymer solutions by adopting an enumeration scheme similar to that of Matasuyama and Tanaka.[13a] These authors have not considered compressibility effects and solvent self-association. The formalism presented here is consistent with the previous formalism for nonmultiassociated molecules[20] and reduces to it by the appropriate substitution of the association parameters. Only the basic thermodynamic properties of solutions will be considered in this work. Phase-stability studies will be postponed for a subsequent publication.

II. Theory

The formalism presented in this section is applicable to binary polymer and solvent systems where the solvent self-associates and cross-associates with the polymer. The polymer is considered as having m equivalent sites for cross-association. Polymer/solvent systems where only cross-association is possible constitute a special case of the more general formalism presented here. Developments in this section and the bulk of the nomenclature are based on our previous work.[20] Only the essentials will be given here.

A. Basic Assumptions. Consider a mixture of N_A solvent molecules with N_B polymer molecules at temperature T and external pressure P. The following are assumed:

1. The intermolecular interactions can be separated into chemical (hydrogen bonding) and physical (van der Waals forces). As a consequence, the contributions to the basic thermodynamic quantities are separated into chemical and physical.

2. Chemical interactions lead to the consecutive formation of association complexes. In the present case we consider two types of chemical interactions, namely, one between solvent molecules A (self-association) and one between solvent and polymer molecules (cross-association). The association complexes are then homopolymers of A and "graft" copolymers of A and B (A chains grafted onto B). A schematic presentation of these association complexes is shown in Figure 1. All reactions involved are assumed to be characterized by only two equilibrium constants (K_A and K_{AB})

$$A_i + A_j \overset{K_A}{\leftrightarrow} A_{i+j}$$

for all i, $j \geq 1$ and

$$B + A_i \overset{K_{AB}}{\leftrightarrow} BA_i$$

Formation of cyclic complexes is not considered in this work.

3. The association complexes, when formed, interact with each other only through physical forces. For the description of this real polydisperse (co)polymer mixture, we will use the LF theory of mixtures.[18,19]

According to LF, the molecules are considered to be arranged on a quasilattice of N_r sites, N_0 of which are empty. It is further assumed that the molecules A, either

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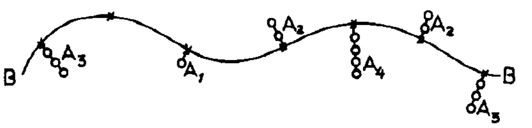

Figure 1. Schematic presentation of a graft copolymer association complex between solvent A and polymer B. Polymer B has seven association sites ($m = 7$). In this example one of its sites is connected to a quadruplet of A (A_4), two to triplets (A_3), two to doublets (A_2), one to a singlet (A_1), and one is empty; i.e., $m_0 = 1$, $m_1 = 1$, $m_2 = 2$, $m_3 = 2$, and $m_4 = 1$.

as free monomers or as repeating units in the (co)polymers, are characterized by the same LF scaling parameters, namely, r_A subsegments per molecule, v^*_A close-packed volume per subsegment, and an average interaction energy per subsegment ϵ^*_A. The corresponding quantities for molecules B are r_B, v^*_B, and ϵ^*_B, respectively. The LF scaling temperature and pressure are defined by

$$\epsilon^*_A \equiv \frac{s_A}{2}\epsilon_A \equiv RT^*_A \equiv P^*_A v^*_A \qquad (1)$$

and similarly for molecule B. The s_A in eq 1 is the average number of external contacts per subsegment A and ϵ_A the interaction energy per contact A–A. For simplicity in this work we will assume $s_A = s_B$. The formalism can easily be extended to cover the general case $s_A \neq s_B$ as shown previously.[19,20] Besides mole fractions x_A and x_B, segment fractions ϕ_A and ϕ_B will be used throughout. They are defined as follows:

$$x_A \equiv \frac{N_A}{N_A + N_B} \equiv \frac{N_A}{N} \equiv 1 - x_B \qquad (2)$$

$$\phi_A \equiv \frac{r_A N_A}{r_A N_A + r_B N_B} \equiv \frac{r_A N_A}{rN} \equiv 1 \equiv \phi_B \qquad (3)$$

Mixing and combining rules shall now be defined. The one-fluid approach will be used here for the description of our mixture. For the sake of simplicity, it is assumed that the average volume per lattice site is given by the linear relation

$$v^* = \phi_A v^*_A + \phi_B v^*_B \qquad (4)$$

This neutral choice guarantees that, as the temperature approaches absolute zero, the volume of the mixture is additive for the pure lattice fluid. That is, the volume of mixing at absolute zero is zero. At finite temperatures the physical or lattice-fluid contribution to the total volume is

$$V_{LF} = N_r v^* \equiv (r_A N_A + r_B N_B)\tilde{v}v^* \equiv rNv^*/\tilde{\rho} \qquad (5)$$

where $\tilde{v} \equiv 1/\tilde{\rho}$ is the reduced volume of the system and $\tilde{\rho}$ the reduced density. The physical or lattice-fluid contribution to the total potential energy of our mixture is[18,19]

$$-E_{LF} = rN\tilde{\rho}(\phi_A\epsilon^*_A + \phi_B\epsilon^*_B - \phi_A\phi_B RTX) \equiv rN\tilde{\rho}\epsilon^* \qquad (6)$$

where the dimensionless binary interaction parameter X is given by

$$RTX \equiv \epsilon^*_A + \epsilon^*_B - 2\epsilon^*_{AB} \qquad (7)$$

and

$$\epsilon^*_{AB} = \xi(\epsilon^*_A\epsilon^*_B)^{1/2} \qquad (8)$$

The dimensionless binary parameter ξ is expected to have values close to unity ($\xi = 1$ is Berthelot's rule). In this work we set $\xi = 1$.

B. Equilibrium Constants. A proper definition of the equilibrium constants for the above association reactions is essential. According to our previous work,[20] the following scheme may be conceived for the formation of our (co)polymer mixture: (a) formation of association complexes in their reference state of perfect orientation from perfectly oriented monomers (subsegmental orientation) at T and P; (b) disorientation of complexes; (c) mixing of disoriented complexes and empty sites until the reduced volume of the system is equal to the final value $\tilde{v}$ of our mixture. This scheme, as described in detail in ref 20a, leads to the following equations for the equilibrium constants K_A and K_{AB}:

$$K_A = \tilde{v}\frac{\phi_{A_{i+j}}}{\phi_{A_i}\phi_{A_j}}\frac{ijr_A}{i+j} = \tilde{v}r_A K^F_A = \exp(-\Delta F^0_A/RT) \qquad (9)$$

$$K_{AB} = \tilde{v}\frac{\phi_{BA_i}}{\phi_{A_i}\phi_{B_1}}\frac{ir_A r_B}{(ir_A + r_B)} = \tilde{v}r_A K^F_{AB} = \exp(-\Delta F^0_{AB}/RT) \qquad (10)$$

where K^F_A and K^F_{AB} are the classical Flory equilibrium constants[21] and ΔF^0_A and ΔF^0_{AB} are the free energy changes upon hydrogen-bond formation during the above self-association and cross-association reactions, respectively. They are given by

$$\Delta F^0_A = \Delta E^0_A + P\Delta V^0_A - T\Delta S^0_A \qquad (11)$$

$$\Delta F^0_{AB} = \Delta E^0_{AB} + P\Delta V^0_{AB} - T\Delta S^0_{AB} \qquad (12)$$

where ΔE^0, ΔV^0, and ΔS^0 are the energy, volume, and entropy changes, respectively, upon hydrogen-bond formation. As stressed repeatedly in previous works,[20] the quantities K^F widely used in the literature as equilibrium constants, depend on both the solution density and the molecular size of the solvent monomer units:

$$K^F_A = \frac{\tilde{\rho}}{r_A}K_A \quad \text{and} \quad K^F_{AB} = \frac{\tilde{\rho}}{r_A}K_{AB} \qquad (13)$$

On the basis of these relations, we must now evaluate the number of the associated complexes N_{A_i} and N_{BA_i} in the mixture. Repeated use of eq 9 for the consecutive formation of the complex A_i gives

$$N_{A_i} = N_{A_1}(K^F_A\phi_{A_1})^{i-1} \qquad (14)$$

Since the numbers N_{A_i} are bounded, eq 14 requires $K^F_A\phi_{A_1} < 1$. Before proceeding further we must specify the various graft copolymers in the real mixture according to the number and type of their side chains A_i.

Let m_i be the number of A_i side chains on the graft copolymer of length i (i.e., m_1 A_1 chains, m_2 A_2 chains, ..., m_n A_n chains). This copolymer could be specified as $BA_{m_1m_2...m_n}$ or, in an abbreviated notation, as $BA_{\{m_i\}}$. In the example of Figure 1 we have $m = 7$, $m_1 = 1$, $m_2 = 2$, $m_3 = 2$, and $m_4 = 1$. Since there are only m possible grafting sites, the number of grafts or AB bonds (m_{ab}) is given by

$$m_{ab} = \sum_{i=1} m_i = m - m_0 \qquad (15)$$

where m_0 is the number of empty grafting sites. The number of AA bonds within the grafts is

$$\sum_{i=1}(i-1)m_i = m_a - m_{ab} \qquad (16)$$

where m_a is the total number of A monomers associated with polymer B. The set $\{m_i\}$ specifies completely the graft copolymer from the energetic viewpoint (excluding cyclical associations between side chains). The detailed sequence of the side chains A_i along the main chain B is not needed, although a combinatorial factor, equal to the number of ways of connecting a given set of side chains to the main-chain polymer, is required.[13] Taking this factor into account and combining eqs 10 and 14, we obtain for the number of $BA_{\{m_i\}}$ complexes for a specified set $\{m_i\}$ (also derived in the appendix)

$$N_{BA_{\{mi\}}} = N_{B_1}\frac{m!}{m_0!m_1!...m_n!}\left(\frac{K^F_{AB}}{K^F_A}\right)^{m_{AB}} \times (K^F_A\phi_{A_1})^{m_1}(K^F_A\phi_{A_1})^{2m_2}...(K^F_A\phi_{A_1})^{nm_n} \quad (17)$$

Summation of $N_{BA_{\{m_i\}}}$'s over all sets $\{m_i\}$ yields the total number N_B of the polymer molecules or

$$N_B = \sum_{\{m_i\}} N_{BA_{\{m_i\}}} = N_{B_1}\sum_{\{m_i\}}\frac{m!}{\prod_{i=0} m_i!}\prod_i\left[\frac{K^F_{AB}}{K^F_A}(K^F_A\phi_{A_1})^i\right]^{m_i} = N_{B_1}\left[1 + \sum_i\frac{K^F_{AB}}{K^F_A}(K^F_A\phi_{A_1})^i\right]^m = N_{B_1}\left[1 + \frac{K^F_{AB}\phi_{A_1}}{1 - K^F_A\phi_{A_1}}\right]^m \quad (18)$$

In terms of segment fractions eq 18 can be rewritten as

$$\phi_B = \phi_{B_1}(1 + \Psi)^m; \quad \Psi = \frac{K^F_{AB}\phi_{A_1}}{1 - K^F_A\phi_{A_1}} \quad (19)$$

The corresponding conservation equation for A molecules is

$$N_A = \sum_{i=1}^{\infty} iN_{A_i} + \sum_{\{m_i\}} m_a N_{BA_{\{m_i\}}} \quad (20)$$

The first sum in eq 20 is

$$\sum_{i=1}^{\infty} iN_{A_i} = \frac{\partial[\sum_{i=1}^{\infty} N_{A_i}]}{\partial[K^F_A\phi_{A_1}]} = N_{A_1}\frac{\partial[1 - K^F_A\phi_{A_1}]^{-1}}{\partial[K^F_A\phi_{A_1}]} = \frac{N_{A_1}}{[1 - K^F_A\phi_{A_1}]^2} \quad (21)$$

Similarly for the second term in eq 20

$$\sum_{\{m_i\}} m_a N_{BA_{\{m_i\}}} = \phi_{A_1}\frac{\partial N_B}{\partial\phi_{A_1}} = \frac{m\Psi(1 + \Psi)^{m-1}N_{B_1}}{(1 - K^F_A\phi_{A_1})} = \frac{m\Psi N_B}{(1 + \Psi)(1 - K^F_A\phi_{A_1})} \quad (22)$$

and thus eq 20 becomes

$$\phi_A = \frac{\phi_{A_1}}{(1 - K^F_A\phi_{A_1})^2} + \frac{m(r_A/r_B)\Psi\phi_B}{(1 + \Psi)(1 - K^F_A\phi_{A_1})} \quad (23)$$

Equations 19 and 23 reduce to the corresponding eqs 21 and 22 of ref 20d, as they should, by setting $m = 1$ and neglecting self-association of B. Note that eq 23 is a cubic equation in ϕ_{A_1}. The physically relevant solution for ϕ_{A_1} is positive, and $K^F_A\phi_{A_1} < 1$ as noted after eq 14. The other relevant concentration is ϕ_{B_1}. It is obtained from eq 19 and ϕ_{A_1} is determined from eq 23.

C. Basic Thermodynamic Quantities. The form of the equation of state of our mixture is the same as that in the original LF equation,[18a] namely

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/\bar{r})\tilde{\rho}] = 0 \quad (24)$$

where $\bar{r}$ is the *number average* of segments per molecule

$$\bar{r} = \frac{\sum_{\{m_i\}}(r_B + r_A m_A)N_{BA_{\{m_i\}}} + \sum_{i=1}^{\infty}(ir_A)N_{A_i}}{\sum_{\{m_i\}} N_{BA_{\{m_i\}}} + \sum_{i=1}^{\infty} N_{A_i}} \quad (25a)$$

or by using eqs 14, 18, and 20

$$\frac{1}{\bar{r}} = \frac{\sum_{\{m_i\}} N_{BA_{\{m_i\}}} + \sum_{i=1}^{\infty} N_{A_i}}{r_A N_A + r_B N_B} = \frac{\phi_B}{r_B} + \phi_{A_1} r_A(1 - K^F_A\phi_{A_1}) \quad (25b)$$

The reduced temperature, $\tilde{T}$, and pressure, $\tilde{P}$, are given by

$$\tilde{T} = \frac{T}{T^*} = \frac{RT}{\epsilon^*}; \quad \tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{\epsilon^*} \quad (26)$$

As already mentioned, the basic assumption underlying this model is that there is a physical (lattice-fluid) and a chemical contribution to the basic mixing properties of our system. Thus, the chemical contribution to the potential energy of the system is

$$E_{chem} = \Delta E^0_A\sum_i(i - 1)N_{A_i} + \Delta E^0_A\sum_{\{m_i\}}(m_a - m_{ab})N_{BA_{\{m_i\}}} + \Delta E^0_{AB}\sum_{\{m_i\}} m_{ab}N_{BA_{\{m_i\}}} \quad (27)$$

By using

$$\sum_{\{m_i\}} m_{ab}N_{AB_{\{m_i\}}} = K^F_{AB}\frac{\partial N_B}{\partial K^F_{AB}} = N_{B_1}m\psi(1 + \Psi)^{m-1} = N_B\frac{m\Psi}{(1 + \Psi)} \quad (28)$$

and eqs 18, 21, and 22, E_{chem} becomes

$$E_{chem}/N = x_A K^F_A\phi_{A_1}\Delta E^0_A + x_B\frac{m\Psi}{1 + \Psi}\Delta E^0_{AB} \quad (29)$$

The two factors in the above equation have a simple interpretation: $K^F_A\phi_{A_1}$ is the fraction of A monomer that is bound in pure A sequences (A_j) or in side chains on polymer B (BA_j); $m\Psi/(1 + \Psi)$ is the average number of AB graft or side chains on polymer B. Entirely analogous to E_{chem} is an expression for the volume chemical contribution to the system:

$$V_{chem}/N = x_A K^F_A\phi_{A_1}\Delta V^0_A + x_B\frac{m\Psi}{1 + \Psi}\Delta V^0_{AB} \quad (30)$$

The heat and volume of mixing are then

$$H^E/N = r(\phi_A\tilde{\rho}_A\epsilon^*_A + \phi_B\tilde{\rho}_B\epsilon^*_B - \tilde{\rho}\epsilon^*) + E_{chem}/N - x_A K^F_A\phi^0_{A_1}\Delta E^0_A \quad (31)$$

and

$$V^E/N = r(\tilde{v}v^* - \phi_A\tilde{v}_A v^*_A + \phi_B\tilde{v}_B v^*_B) + V_{chem}/N - x_A K^F_A\phi^0_{A_1}\Delta V^0_A \quad (32)$$

where $\phi^0_{A_1}$ is the free monomer segment fraction in pure solvent A.[19a]

Table I
Lattice-Fluid Scaling Parameters for Pure Components

fluid	T^*, K	P^*, MPa	ρ^*, kg/m^3
chloroform	499	476	1709
poly(ethylene oxide)	541	605	1172
poly(propylene oxide)	529	421	1093

The form of the equations for the chemical potential is the same as that in our previous work.[19] For component A it is (derived in the appendix)

$$\mu_A/RT = \mu_{A_1}/RT = \ln \phi_{A_1} + 1 - r_A/\bar{r} + r_A\tilde{\rho}\phi_B^2 X + r_A[-\tilde{\rho}/\tilde{T}_A + \tilde{P}_A\tilde{v}/\tilde{T}_A + \tilde{v}(1-\tilde{\rho})\ln(1-\tilde{\rho}) + \ln(\tilde{\rho}/\omega_{A_1})/r_A] \quad (33)$$

and similarly for component B. ω_{A_1} in eq 33 is a constant characteristic of component A that can be ignored in all applications of interest. The pressure term is also ignorable under the usual conditions of atmospheric pressure. The free monomer concentration ϕ_{A_1} is determined from eq 23. The Gibbs free energy of the associated solution is given by the usual

$$G = N_A\mu_{A_1} + N_B\mu_{B_1} = N_A\mu_A + N_B\mu_B \quad (34)$$

or more explicitly by

$$G/kT = rN\left[\frac{\phi_A}{r_A}\ln \phi_{A_1} + \frac{\phi_B}{r_B}\ln \phi_{B_1} + \frac{1}{r} - \frac{1}{\bar{r}}\right] + rN\left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{\tilde{P}\tilde{v}}{\tilde{T}} + (\tilde{v}-1)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho}\right] \quad (35)$$

where r, as before, is the number-average value of the r_i prior to any association reactions; i.e.

$$r = x_Ar_A + x_Br_B \quad \text{or} \quad \frac{1}{r} = \frac{\phi_A}{r_A} + \frac{\phi_B}{r_B} \quad (36)$$

Using eqs 23 and 21b, it can be easily verified that

$$\frac{1}{r} - \frac{1}{\bar{r}} = \frac{K_A^F\phi_{A_1}}{r_A} + \frac{m\Psi\phi_B}{r_B(1+\Psi)} \quad (37)$$

III. Applications

In this section we apply the formalism to chloroform + polyether systems. In these systems hydrogen bonding occurs, primarily, through cross-association of the polyether and chloroform. This is a special case and the appropriate formalism may be obtained by setting $K_A^F = 0$ in the above formalism (self-association of chloroform is neglected). For two such systems [chloroform + poly(ethylene oxide) (PEO), chloroform + poly(propylene oxide) (PPO)] Malcolm et al.[22,23] have provided excellent experimental data on vapor pressures, heats of mixing, volumes of mixing, and volumetric properties of pure components appropriate for testing the model. The volumetric properties of pure components along with data on thermal expansion coefficients provided by Allen et al.[24] have been used to obtain the lattice-fluid scaling parameters of the polymers presented in Table I.

The extent of hydrogen bonding and its contribution to the thermodynamic properties of the systems are completely determined by specifying the hydrogen-bonding energy ΔE_{AB}^0, entropy ΔS_{AB}^0, and volume ΔV_{AB}^0. Unfortunately there are no a priori estimations of these three parameters. They must, however, be nearly the same for the two systems studied. In order to test this hypothesis, we have used the available experimental data for the system $CHCl_3$–PEO for determining the above three unknown parameters. These parameters have then been used to predict the behavior of the second system $CHCl_3$–PPO. The values of the parameters are $\Delta E_{AB}^0 = -11.44$ kJ/mol, $\Delta S_{AB}^0 = -9.74$ J/mol·K, and $\Delta V_{AB}^0 = -0.85$ cm^3/mol that yields a $K_{AB} = 31.4$ at 25 °C. These parameters are within the range of expected values for comparable systems.[9,25] In the system $CHCl_3$–PEO the number of cross-association sites, m, was set equal to 7, which is the number of $-CH_2CH_2O-$ repeating units in PEO. Experimental and calculated heats of mixing, volumes of mixing, and vapor pressures for the system $CHCl_3$–PEO are presented in Figures 2–4, respectively. As observed in Figure 2 the chemical contribution is the overwhelming contribution to the heat of mixing. The physical contribution to the volume of mixing is not, however, negligible

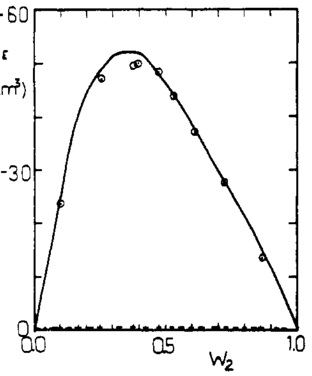

Figure 2. Experimental and calculated heats of mixing for the system $CHCl_3$–PEO at 5.53 °C. Experimental data[23] are denoted by dotted open circles: (—) calculated with the present association model; (- - -) calculated by the LF model without association ($\xi = 1$). See Table I for the equation of state parameters.

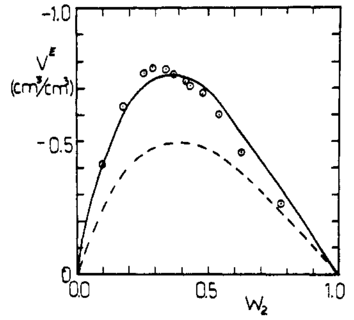

Figure 3. Experimental[23] and calculated volumes of mixing for the system $CHCl_3$–PEO at 5.53 °C. Symbols are as in Figure 2.

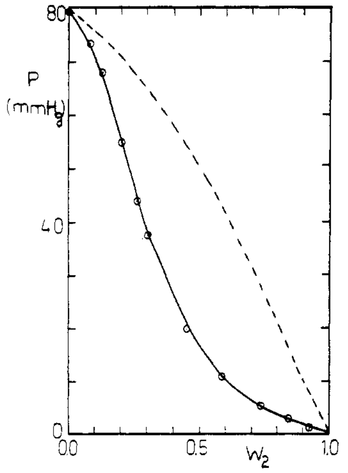

Figure 4. Experimental[23] and calculated vapor pressures for the system $CHCl_3$–PEO at 5.53 °C. Symbols are as in Figure 2.

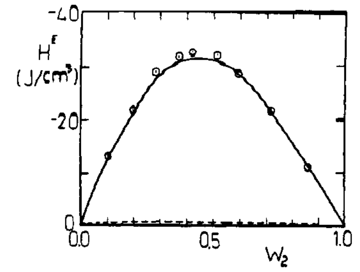

Figure 5. Experimental[22] and calculated heats of mixing for the system $CHCl_3$–PPO at 5.53 °C. Symbols are as in Figure 2.

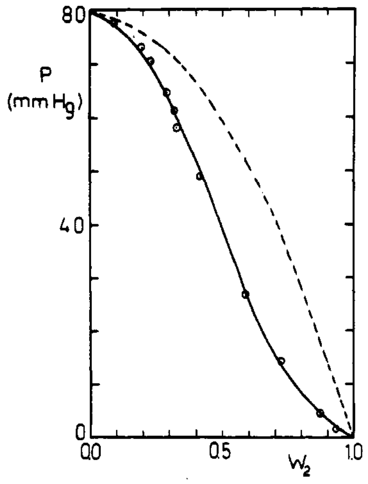

Figure 6. Experimental[22] and calculated vapor pressures for the system $CHCl_3$–PPO at 5.53 °C. Symbols are as in Figure 2.

as observed in Figure 3. The most peculiar behavior of this system is its sigmoidal-shaped vapor pressure isotherm shown in Figure 4. Similar isotherms have been observed in aqueous solutions of agar–agar[26] and nitrocellulose + ketones[27] where cross-association reactions are also of primary importance. As shown in Figure 4, the present association model is able to reproduce quantitatively this sigmoidal-shaped isotherm by adjusting only the hydrogen-bonding parameters (ΔE^0_{AB} and ΔS^0_{AB}). In the same figure is shown the calculated isotherm of the lattice-fluid model neglecting association ($\xi = 1$).

Before using the above hydrogen-bonding parameters to the $CHCl_3$–PPO mixture, we must recognize that the presence of the pendant $-CH_3$ group near -O- in PPO limits significantly the available space for the association with $CHCl_3$. This fact, in conjunction with the bulkiness of the $CHCl_3$ molecule itself, makes unlikely the possibility that every oxygen atom in the PPO molecule is associated with a $CHCl_3$ molecule. There should not be, however, significant steric hindrance for the association with every second oxygen atom along the PEO chain. On this basis, the number of association sites, m, in the PPO was set equal to 18, i.e., equal to half the number of $-CHCH_3-CH_2O-$ repeat units. In Figures 5 and 6 are shown the experimental and predicted heats of mixing and vapor pressures, respectively, of the system $CHCl_3$–PPO. As observed, the agreement is almost quantitative. Once again the vapor pressure isotherm of this system is sigmoidal-shaped. In the same figures are shown the predictions of the LF model without association. The volumes of mixing are not reproduced as quantitatively as the other mixing properties. Geometrical packing is more important in this system, implying a more significant physical contribution to the excess volume. The minimum (maximum in absolute value) excess volume predicted by the present model is -0.0037 cm^3/cm^3. The corresponding experimental value is -0.0104 cm^3/cm^3.

IV. Discussion

In testing the predictive character of the model, we have argued about the availability of oxygen atoms in PPO for hydrogen bonding and fixed m equal to 18. An alternative approach would be the consideration of all 36 oxygen atoms in the PPO molecule as equivalent. In this case the cross-association entropy is expected to be different from that calculated for PEO. Since, however, there is not available a tractable scheme for calculation of this entropy from first principles, we have preferred the first alternative in order to avoid further adjustment of parameters. The validity could further be tested if similar experimental data were available for solutions in $CHCl_3$ of other molecular weight PPO. It is hoped that the present work will motivate such experimental work.

The model presented in this paper has been tested only against data on excess thermodynamic properties. One significant component, however, of the model is its ability to predict both an upper and a lower critical solution temperature (UCST and LCST) for these associated polymer solutions. One particular class of polymer solutions that is both of theoretical and practical interest is aqueous polymer solutions. The formalism presented in this work is valid for solvents forming linear association complexes such as alcohols or amines. Proper application of the model to aqueous solutions requires recognition of the network-forming character of water. This is postponed for a forthcoming publication along with the development of a model for self-associated polymers and polymer mixtures.

Appendix

Formally, the constant pressure–temperature partition function for this system is

$$Z = \sum_{\{N_{A_j};N_{BA_j}\}} \exp(-\beta\Delta\mu^0_{chem}) \sum_{N_0=0}^{\infty} \Omega_{LF} \exp[-\beta(E_{LF} + PV_{LF})] \tag{A.1}$$

where $\Delta\mu^0_{chem}$ is the net change in the free energy during hydrogen-bond formation. It is given by

$$\Delta\mu^0_{chem} = \Delta\mu^0_A \sum_i (i-1)N_{A_i} + \Delta\mu^0_A \sum_{\{m_i\}} (m_a - m_{ab}) N_{BA_{\{m_i\}}} + \Delta\mu^0_{AB} \sum_{\{m_i\}} m_{ab} N_{BA_{\{m_i\}}} \tag{A.2}$$

where as before $m_{ab} = \sum_{i=1} m_i$ is the number of AB bonds in the $BA_{\{m_i\}}$ complex with the set of side chains $\{m_i\} = \{m_0, m_1, m_2, ..., m_n\}$; $m_a = \sum_{i=1}(i-1)m_i$ is the total number of A units incorporated into the side chains $m_1, m_2, ..., m_n$. The partition function must be summed over all allowable values of N_{A_j} and N_{BA_j} consistent with the constraints on the system, eqs 18 and 20. E_{LF} and V_{LF} are the lattice-fluid energy and volume given by eqs 6 and 5. The number of ways that the various molecular species can be placed on a lattice of $N_0 + r_A N_A + r_B N_B = rN\tilde{v}$ sites is given in the Flory approximation by[18a]

$$\Omega_{LF} = \left(\frac{1}{f_0}\right)^{N_0} \prod_{j=1} \left(\frac{\omega_{A_j}}{f_{A_j}}\right)^{N_{A_j}} \prod_{\{BA_j\}} \left(\frac{\omega_{BA_j}}{f_{BA_j}}\right)^{N_{BA_j}} \tag{A.3}$$

where N_0 is the number of empty sites, f_0 is the fraction of empty sites

$$f_0 = \frac{N_0}{N_0 + r_A N_A + r_B N_B} = \frac{N_0}{rN\tilde{v}} = \frac{\tilde{v} - 1}{\tilde{v}} = 1 - \tilde{\rho} \tag{A.4}$$

and similarly

$$f_{A_j} = \frac{jr_A}{rN\tilde{v}} = \phi_{A_j}\tilde{\rho} \quad \text{and} \quad f_{BA_j} = \frac{(r_B + jr_A)}{rN\tilde{v}} = \phi_{BA_j}\tilde{\rho} \qquad \text{(A.5)}$$

The ω's are the number of molecular configurations available to a molecule on a filled lattice. In the simplest approximation and for a flexible molecule of size r, it is given by[18a]

$$\omega_r = r\left(\frac{z-1}{e}\right)^{r-1} \qquad \text{(A.6)}$$

where z is coordination number of the lattice. The product over $\{BA_j\}$ means that this is a product over all distinguishable BA_j complexes. Specification of the set $\{m_i\}$ is not sufficient to distinguish a BA_j complex. For a given set $\{m_i\}$ there are $m!/(m_0!m_1!...m_n!)$ distinguishable species. Let $BA_{\{m_i\}_k}$ be the kth distinguishable species from the set $\{m_i\}$. Then the product over $\{BA_j\}$ can be written formally as a double product over all possible sets $\{m_i\}$ and all distinguishable members of these sets:

$$\prod_{\{BA_j\}}\left(\frac{\omega_{BA_j}}{f_{BA_j}}\right)^{N_{BA_j}} = \prod_{\{m_i\}}\prod_{\{k\}}\left(\frac{\omega_{BA_{m_a}}}{f_{BA_{m_a}}}\right)^{N_{BA_{\{m_i\}_k}}} \qquad \text{(A.7)}$$

The numbers $N_{BA_{\{m_i\}_k}}$ and $N_{BA_{\{m_i\}}}$ are related by

$$N_{BA_{\{m_i\}}} = \sum_{\{k\}} N_{BA_{\{m_i\}_k}} \qquad \text{(A.7)}$$

where there are $m!/(m_0!m_1!...m_n!)$ terms in the sum and

$$N_B = \sum_{\{m_i\}}\sum_{\{k\}} N_{BA_{\{m_i\}_k}} \qquad \text{(A.8)}$$

Notice that the ω's only depend on the size, $r_B + m_a r_A$, of the association complex and not the details of its connectivity. In the Flory approximation linear chains and branched chains have the same ω's if they contain the same number of monomer units. The unassociated or free polymer B (designated as B_1) is included in the above when $m_0 = m$.

The partition function (eq A.1) must be summed over all possible values of the occupation numbers N_{A_j} and $N_{BA_{\{m_i\}_k}}$. However, at equilibrium these numbers will take on values that make the generic term in the partition function a maximum. To determine the equilibrium values, we impose the conditions of equilibrium to all possible equilibrium associations. For example, the association reactions

$$B_1 + m_1A_1 + m_2A_2 + ... + m_nA_n \leftrightarrow$$
$$B_1 + A_{\sum_{i=1} im_i = m_a} \leftrightarrow BA_{m_a}$$

must hold for every distinguishable species $BA_{\{m_i\}_k}$; i.e.

$$B_1 + \sum_{i=1} m_iA_i \leftrightarrow B_1 + A_{m_a} \leftrightarrow BA_{\{m_i\}_k}$$

At equilibrium the corresponding equality among the chemical potentials is

$$\mu_{B_1} + \sum_{i=1} m_i\mu_{A_i} = \mu_{B_1} + \mu_{A_{m_a}} = \mu_{BA_{\{m_i\}_k}} \qquad \text{(A.9)}$$

Formally, these chemical potentials are obtained from the partition function by

$$\mu_i = -kT\left(\frac{\partial \ln Z}{\partial N_i}\right)_{T,P,N_{i\neq j},\tilde{v}} \qquad \text{(A.10)}$$

where N_i is the number of species i. From the conservation relation

$$N_A = \sum_{j=1}^{\infty} jN_{A_j} + \sum_{\{m_i\}}\sum_{\{k\}} m_a N_{BA_{\{m_i\}_k}} \qquad \text{(A.11)}$$

and the corresponding relation for N_B given in eq A.8, we have

$$\frac{\partial N_A}{\partial N_{A_{m_a}}} = m_a \quad \text{and} \quad \frac{\partial N_B}{\partial N_{A_{m_a}}} = 0 \qquad \text{(A.12)}$$

$$\frac{\partial N_A}{\partial N_{B_1}} = 0 \quad \text{and} \quad \frac{\partial N_B}{\partial N_{B_1}} = 1 \qquad \text{(A.13)}$$

$$\frac{\partial N_A}{\partial N_{BA_{\{m_i\}_k}}} = m_a \quad \text{and} \quad \frac{\partial N_B}{\partial N_{BA_{\{m_i\}_k}}} = 1 \qquad \text{(A.14)}$$

Using these results, we obtain for the chemical potentials

$$\mu_{A_{m_a}} = RT[\ln \tilde{\rho}\phi_{A_{m_a}} - \ln \omega_{A_{m_a}} + 1 - r_A m_a/\bar{r}] + r_A m_a\tilde{\rho}[-\epsilon^*{}_A + \phi_B{}^2RTX] + r_A m_a[P\tilde{v}v^*{}_A + RT(\tilde{v}-1)\ln(1-\tilde{\rho})] + (m_a - 1)\Delta\mu_A^0 \qquad \text{(A.15)}$$

$$\mu_{B_1} = RT[\ln \tilde{\rho}\phi_{B_1} - \ln \omega_{B_1} + 1 - r_B/\bar{r}] + r_B\tilde{\rho}[-\epsilon^*{}_B + \phi_A{}^2RTX] + r_B\{P\tilde{v}v^*{}_B + RT(\tilde{v}-1)\ln(1-\tilde{\rho})\} \qquad \text{(A.16)}$$

$$\mu_{BA_{\{m_i\}_k}} = RT[\ln \tilde{\rho}\phi_{BA_{\{m_i\}_k}} - \ln \omega_{BA_{m_a}} + 1 - (r_A m_a + r_B)/\bar{r}] + \tilde{\rho}[-r_A m_a\epsilon^*{}_A - r_B\epsilon^*{}_B + (r_A m_a\phi_B{}^2 + r_B\phi_A{}^2)RTX] + P\tilde{v}(r_A m_a v^*{}_A + r_B v^*{}_B) + (r_A m_a + r_B)RT(\tilde{v}-1)\ln(1-\tilde{\rho}) + (m_a - m_{ab})\Delta\mu_A^0 + m_{ab}\Delta\mu_{AB}^0 \qquad \text{(A.17)}$$

Notice that in the special case of $m_a = 1$, eq A.15 reduces to eq 33 in the text.

Using these chemical potentials in the equilibrium equation (eq A.9) yields

$$\ln\left[\tilde{v}\frac{\phi_{BA_{\{m_i\}_k}}}{\phi_{A_{m_a}}\phi_{B_1}}\frac{\omega_{B_1}\omega_{A_{m_a}}}{\omega_{BA_{m_a}}}\right] - 1 = \beta[-\Delta\mu_A^0 + m_{ab}(\Delta\mu_A^0 - \Delta\mu_{AB}^0)] \qquad \text{(A.18a)}$$

or by using eq A.6, we have

$$\tilde{v}\frac{N_{BA_{\{m_i\}_k}}}{N_{A_{m_a}}N_{B_1}}rN = (z-1)\exp\{-\beta[\Delta\mu_A^0 + m_{ab}(\Delta\mu_A^0 - \Delta\mu_{AB}^0)]\} \qquad \text{(A.18b)}$$

Defining the equilibrium constants (cf. eqs 10–13)

$$K_A = (z-1)\exp(-\beta\Delta\mu_A^0) = \exp(-\beta\Delta F_A^0) \qquad \text{(A.19)}$$

$$K_{AB} = (z-1)\exp(-\beta\Delta\mu_{AB}^0) = \exp(-\beta\Delta F_{AB}^0) \qquad \text{(A.20)}$$

Equation A.18b can be written as

$$N_{BA_{\{m_i\}_k}} = N_{B_1}\frac{N_{A_{m_a}}}{rN}\tilde{\rho}K_A\left(\frac{K_{AB}}{K_A}\right)^{m_{ab}} = N_{B_1}(K_A^F\phi_{A_1})^{m_a}\left(\frac{K_{AB}^F}{K_A^F}\right)^{m_{ab}} \qquad \text{(A.18c)}$$

where eqs 13 and 14 have been used. Summing over all distinguishable members of the set $\{m_i\}$ yields eq 17.

The equation of state eq 24 is obtained by finding the value of N_0 that yields a maximum in the partition function A.1.[18a] The appropriate derivative is taken, holding all occupation numbers N_{A_j} and N_{BA_j} constant.

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References and Notes

(1) Walter, H., Brooks, D., Fisher, D., Eds. *Partitioning in Aqueous Two-Phase Systems*; Academic Press: New York, 1985.
(2) Kramer, O., Ed. *Biological and Synthetic Polymer Networks*; Elsevier Applied Science Publishers: London, 1988.
(3) Glass, J. E., Ed. *Polymers in Aqueous Media*; Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989.
(4) Guggenheim, E. A. *Mixtures*; Clarendon Press: Oxford, 1952.
(5) Barker, J. A. *J. Chem. Phys.* **1952**, *20*, 1526; **1954**, *22*, 375.
(6) Nitta, T.; Turek, E. A.; Greenkorn, R. A.; Chao, K. C. *AIChE J.* **1977**, *23*, 144.
(7) Kehiaian, H. V.; Grolier, J. P. E.; Benson, G. C. *J. Chim. Phys.* **1978**, *75*, 1031.
(8) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice-Hall: New York, 1986.
(9) Acree, W. E. *Thermodynamic Properties of Nonelectrolyte Solutions*; Academic Press: New York, 1984.
(10) Marsh, K.; Kohler, J. *J. Mol. Liq.* **1985**, *30*, 13.
(11) (a) Heintz, A. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 172. (b) Pouchly, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 1236.
(12) Prange, M. M.; Hooper, H. H.; Prausnitz, J. M. *AIChE J.* **1989**, *35*, 803.
(13) (a) Matasuyama, A.; Tanaka, F. *Phys. Rev. Lett.* **1990**, *65*, 341. (b) Tanaka, F. *Macromolecules* **1990**, *23*, 3784.
(14) Painter, P. C.; Graf, J.; Coleman, M. M. *J. Chem. Phys.* **1990**, *92*, 6166.
(15) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(16) Prigogine, I. (with the collaboration of Bellemans, A.; Mathot, V.) *The Molecular Theory of Solutions*; North-Holland: Amsterdam, The Netherlands, 1954.
(17) Delmas, G.; Patterson, D.; Somcynsky, T. *J. Polym. Sci.* **1962**, *57*, 79.
(18) (a) Sanchez, I. C.; Lacombe, R. *J. Phys. Chem.* **1976**, *80*, 2352. (b) Lacombe, R.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568. (c) Sanchez, I. C.; Lacombe, R. *Macromolecules* **1978**, *11*, 1145.
(19) Panayiotou, C. *Macromolecules* **1987**, *20*, 861.
(20) Panayiotou, C. (a) *J. Phys. Chem.* **1988**, *92*, 2960; (b) *Pure Appl. Chem.* **1989**, *61*, 1453; (c) *Fluid Phase Equilib.* **1990**, *56*, 171; (d) *J. Solution Chem.*, in press.
(21) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425.
(22) Kershaw, R. W.; Malcolm, G. N. *Trans. Faraday Soc.* **1968**, *64*, 323.
(23) Malcolm, G. N.; Baird, C. E.; Bruce, G. R.; Cheyne, K. G.; Kershaw, R. W.; Pratt, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1495.
(24) Allen, G.; Gee, G.; Mangaraj, D.; Sims, D.; Wilson, G. J. *Polymer* **1960**, *1*, 467.
(25) Vinogradov, S.; Linnell, R. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971.
(26) Gee, G. *Quart. Rev.* **1947**, *1*, 282.
(27) Baughan, E. C.; Jones, A. L.; Stewart, K. *Proc. R. Soc. A* **1954**, *225*, 478.

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