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Hydrogen Bonding in Polymer Blends. 2. Theory

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ABSTRACT: Recent work in this laboratory has focused on FTIR studies of a range of polymer blends. Although various "rules of thumb" have been formulated as a guide to miscibility in these systems, we have not, until now, been able to use our spectroscopic measurement in the framework of the usual thermodynamic theories of mixing. This is because of the well-known inadequacies of the Flory–Huggins theory in handling strong, specific, directional interactions. We present an equilibrium approach based largely on theoretical work described in the chemical engineering literature for the self-association of alcohols in hydrocarbon solutions. The adoption to polymers is straightforward and we consider the potential of the equations for describing the phase behavior of polymers that hydrogen bond.

Introduction

The phase behavior of macromolecular mixtures is a topic of intense interest in polymer science and needs no general introduction from us. For nonpolar polymers, a broad understanding has been achieved by considering the balance between three principal contributions to the Gibbs free energy: a combinatorial entropy of mixing, a van Laar type energy of interaction characterized by a Flory–Huggins interaction parameter, and a free volume term. Because this balance is generally unfavorable to mixing, the presence of relatively strong, specific, intermolecular interactions between the different components in the blend has often been considered a necessary condition for miscibility. Intriguing exceptions to this general rule have been independently described in blend systems containing copolymers[1,2] by using a Flory–Huggins-type theoretical description developed by Kambour et al.[3] This was extended to directional-specific interactions by ten Brinke and Karasz[4] using the approach of Sanchez and Lacombe[5,6]. These latter interactions are not as simply formulated, however, because they involve an entropy loss in addition to an exchange energy term.

We believe there is a fundamental flaw in some of the theoretical models that have attempted to incorporate specific interactions, namely, the assumption of a mean field to describe the number of unlike AB contacts, N_{AB}. This assumption leads to equations that include an $E_{int}\Phi_A\Phi_B$ term, where E_{int} depends upon the specifics of the model and Φ_A and Φ_B are the volume fractions of the components. Energy terms that incorporate such factors are in a particularly convenient form for subsequent differentiation to give expressions for the chemical potentials and critical conditions, thus helping to make the description of phase behavior a tractable problem. If there are specific, directional interactions, however, then the assumption of a mean field is clearly invalid. When unlike AB contacts are favored by the presence of specific interactions, the number of such contacts will exceed that due to random mixing (which is proportional to $\Phi_A\Phi_B$) by an amount that depends upon the free energy of the interaction.

An initial view of the problem of describing specific interactions in polymer blends was developed in this laboratory by Howe and Coleman,[7] who formulated an equilibrium model where the relative probability of an interaction depends upon its energy. This approach echoes views expressed by Prigogine[8] more than 30 years ago that there is no satisfactory theory of strong orientational effects, principally because the rotational partition function is no longer independent of the translational partition function. Prigogine proposed that the formation of a complex be treated by using the assumption of a chemical equilibrium between the monomolecules of the associated species. Such a "chemical" theory of solutions was first proposed by Dolezalek[9] around the turn of the century and in its original form interpreted all deviations from ideality as a consequence of the formation of new chemical species (aggregates). In this view, the problem of solution thermodynamics becomes the identification of the "true" species present. The early history of solution theory is enlivened by the bitter polemics between the "physical" and "chemical" schools of thought,[10,11] but as Hildebrand has pointed out in the 1950 edition of his book,[12] the former view prevailed in the form of regular solution theory, in part because "chemical" treatments were badly misapplied to inappropriate systems. Hildebrand also pointed out, however, that there are systems where "chemical" effects are important, liquids where the molecules associate through hydrogen bonding being one example. As a result there has been a revival in the chemical theory of solutions in recent years, particularly as applied to alcohol/hydrocarbon solutions, with good agreement between the calculated and experimental thermodynamic parameters being obtained.[13]

Specific interactions, particularly hydrogen bonds, are of central importance to a large number of polymer-blend systems.[14-17] To reiterate, most theoretical treatments employ modifications of Flory–Huggins-type parameters to describe the exchange interaction. For the reasons outlined above, we do not believe that this approach can be successful in systems involving strong intermolecular interactions. An additional complication is that in most polymer mixtures of interest at least one of the component polymers self-associates to form chains of hydrogen bonds (for example, polymers that contain aliphatic and/or aromatic hydroxyl, amide, or urethane functional groups). Accordingly, a theoretical framework that simply considers 1:1 complexes between donor and acceptor groups located in different chains, but which are incapable of forming hydrogen bonds between units of their own type, would only be of limited value. We will therefore initially consider polymer mixtures analogous to the blends of polyurethanes with polyethers,[17] where one component self-associates to form chains of hydrogen bonds. The second component is only weakly self-associated and does not hydrogen bond to itself but is capable of forming a complex with the first. As we will see, the balance of this competition is not solely determined by the relative strengths of the interactions but by entropy changes accompanying the formation of the various types of complexes. The approach we have used is based on contemporary extensions of Dolezalek's theory and we have borrowed heavily from the treatment of alcohol mixtures by Kretschmer and Wiebe,[18]

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as described by Renon and Prausnitz,[19] Nagata,[20] and Acree.[13]

Theory

Our concern in this work is to account for the effect of hydrogen bonding on the free energy of mixing of polymer chains. We will not deal explicitly with the dissolution of polymers in hydrogen-bonding solvents, but the equations can be modified in obvious ways to handle this situation. We will start with a simple Flory–Huggins expression for the free energy of mixing two polymers to which we add a term accounting for the free energy of hydrogen-bond formation:

$$\frac{\Delta G^{\mathrm{M}}}{RT} = \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_1}{N_2} \ln \Phi_2 + \Phi_1\Phi_2\chi_{\mathrm{blend}} + \frac{\Delta G_{\mathrm{H}}}{RT} \qquad \text{(I)}$$

where the symbol Φ represents volume fraction, N is the number of segments in the chain, χ is the Flory interaction parameter, and the subscripts 1 and 2 refer to the different polymers. Although at first glance this formulation of the free energy of mixing apparently contradicts the arguments concerning nonrandomness made above, things are not as inconsistent as they appear. Our principal point is that an enthalpy of hydrogen-bonding interaction cannot be formulated in a mean-field form ($E_{\mathrm{int}}\phi_{\mathrm{A}}\phi_{\mathrm{B}}$) and cannot (in most cases) be separated from the entropy of forming such strong directional bonds. Both these contributions reside in ΔG_{H}, which will be considered in greater detail below. We retain a term describing physical interactions between the different components together with the usual combinatorial entropy of mixing. For the mean-field enthalpy term we assume that the coordination number of the hydrogen-bonding group is reduced by either one or two, depending upon whether we have a one-to-one complex or form chains of hydrogen bonds, as in the case of strongly self-associated polymers. In effect, although the units bound by hydrogen bonds are not randomly arranged relative to one another, the other units surrounding the hydrogen-bonded pair are randomly arranged and their interactions can be described by a χ-parameter. Naturally, specific nonrandom interactions will also affect the combinatorial entropy term, but as Flory[21] points out, citing the work of Orr[22] and Guggenheim,[23] the modification in the calculated combinatorial entropy of mixing caused by nonrandomness is, to a first approximation, not significant compared to the effect of other approximations. At this stage we will ignore so-called free volume and other complications, since our aim is to determine an expression for ΔG_{H} in terms of experimentally measurable quantities.

Initially, we will consider the balance between interacting units A and B that are competing to form complexes. (A and B need not necessarily correspond to chemical repeat units but could represent a specific functional group that is part of a larger segment.) B self-associates to form chains of hydrogen bonds that can be described by the following equilibrium:

$$\mathrm{B}_n + \mathrm{B}_1 \overset{K}{\rightleftharpoons} \mathrm{B}_{n+1} \qquad \text{(II)}$$

or

$$n\mathrm{B}_1 \overset{K_n}{\rightleftharpoons} \mathrm{B}_n \qquad \text{(III)}$$

The A segments can form hydrogen bonds with any of the n-mers of B units according to the equilibrium

$$\mathrm{B}_n + \mathrm{A} \overset{K_{\mathrm{A}}}{\rightleftharpoons} \mathrm{B}_n\mathrm{A} \qquad \text{(IV)}$$

The statistics of self-association are the same as those for linear condensation polymerization, providing that the equilibrium constant K is independent of hydrogen bond chain length. It is entirely possible to formulate some of the equations described below in terms of an "extent of reaction" term p, which can be determined experimentally from FTIR measurements of the fraction of hydrogen-bonded species (see preceding paper[17]). The competing species A can then be considered a "chain stopper". To us, this is a pleasing analogy and one that we pursued (in terms of mathematical development) for a short time. Although it works well in describing the pure self-associating component, the inclusion of a "chain stopper" upon blending complicates the situation beyond the simple treatment given in most polymer texts, where the reactivity of the competing monofunctional species is assumed to be equal to that of the bifunctional component. Obviously, this is far too restrictive and we are much more interested in the effect of varying K_{A} relative to K or (equivalently) of different free energies of interaction. In one respect, however, this comparison is not just an aside but provides a result that is fundamental to the proper development of a model for specific association. Flory[24] discussed chemical equilibria in these types of polymer systems and made the seminal observation that, in general, the use of mole fractions in expressing the equilibrium constant is irreconcilable with the statistical mechanics of these mixtures. Instead, molar concentrations or molar volumes have to be used. Accordingly,

$$K = \frac{\Phi_{\mathrm{B}_{n+1}}}{\Phi_{\mathrm{B}_n}\Phi_{\mathrm{B}_1}} \frac{n}{n+1} \qquad \text{(V)}$$

and

$$K_n = \Phi_{\mathrm{B}_n}/n{\Phi_{\mathrm{B}_1}}^n \qquad \text{(VI)}$$

We assume that K is independent of n, so that

$$K_n = K^{n-1} \qquad \text{(VII)}$$

and

$$\Phi_{\mathrm{B}_n} = nK^{n-1}{\Phi_{\mathrm{B}_1}}^n \qquad \text{(VIII)}$$

This is equivalent to assuming that reactivity is independent of chain length in a condensation polymerization. Just as in these reactions, however, this assumption is probably good for large n, but there are deviations for the addition of the first one or two units. This is certainly true for phenolic hydroxyl groups where the formation of hydrogen-bonded dimers is characterized by a different equilibrium constant than the formation of higher n-mers. This can be accommodated,[13] but at the expense of somewhat more complicated algebra and the necessity of fitting an additional parameter to the experimental data. At present we are more concerned with a general approach to determine the relative importance of factors that affect the mixing of polymers involving strong intermolecular interactions. Furthermore, urethane and amide groups do not associate in the form of cyclic complexes that are thought to be present in alcohols and phenols, so our assumption (eq VII and VIII) should be reasonably valid for polymers containing such functional groups. We will consider more complicated systems in future work when we examine the specifics of individual systems.

The equilibrium constant for the addition of species A is written in an equivalent form to eq V and VI,[13,20] although now the difference in the molar volumes of segments A and B have to be accounted for

$$K_{\mathrm{A}} = \frac{\Phi_{\mathrm{B}_n\mathrm{A}}}{\Phi_{\mathrm{B}_n}\Phi_{0\mathrm{A}}} \frac{nr}{n+r} \qquad \text{(IX)}$$

where $r = V_A/V_B$, V_A and V_B are the respective molar volumes, and Φ_{0A} is the volume fraction of A units in the mixture that remain *unassociated*. We can now proceed to obtain an expression for ΔG_H in terms of K, K_A, and the concentration of unassociated species present. At this stage we will ignore the fact that the A and B units are segments or portions of segments of different polymer chains and consider them to be individual low molecular weight species. The restrictions imposed by the incorporation of these units into macromolecular chains will be imposed later.

Flory[24] pointed out that for the treatment of chemical equilibria between polymeric species (in this case the polymers formed by linking n groups to form a hydrogen-bonded chain), the proper standard state is where the individual species are separate and oriented. In outline, our approach is to derive an expression for the ideal free energy of mixing such already formed associated species, ΔG_{ch}. The subscript ch denotes that this free energy term is determined on the basis of Dolezalek's chemical theory. This free energy term includes the combinatorial entropy of mixing the species in addition to the changes in the free energy due to the changes in the distribution of hydrogen-bonded species present. To obtain ΔG_H we therefore have to subtract the entropy of mixing the units of the hydrogen-bonded chains. Physical interactions and the combinatorial entropy of mixing the covalently bonded polymer species can then be introduced to give the overall free energy of mixing described in eq I.

The ideal free energy of mixing the hydrogen-bonded polymer species is simply given by the Flory–Huggins expression:

$$\Delta G_{ch}/RT = \sum_{n=1} n_{B_n} \ln \Phi_{B_n} + \sum_{n=0} n_{B_nA} \ln \Phi_{B_nA} \quad \text{(X)}$$

This is the approach used by Nagata[20] and it does treat the polymer molecules as separate and distinguishable, partly in accord with Flory's standard state for describing a system where there are chemical equilibria between polymer species. The entropy of disorientation of the individual molecules is omitted, however, but it is relatively easy to show that these terms cancel in the final equations. We therefore proceed in the same manner as in the literature and obtain the chemical potentials of the hydrogen-bonded n-mers B_n and the complexes B_nA by differentiation,

$$\frac{\mu_{B_n} - \mu^*_{B_n}}{RT} = \ln \Phi_{B_n} + 1 - \frac{V_{B_n}}{V} \quad \text{(XI)}$$

$$\frac{\mu_{B_nA} - \mu^*_{B_nA}}{RT} = \ln \Phi_{B_nA} + 1 - \frac{V_{B_nA}}{V} \quad \text{(XII)}$$

where the asterisk refers to Flory's standard state and V, the molar volume, is given by

$$\frac{1}{V} = \sum_{n=1} \frac{\Phi_{B_n}}{V_{B_n}} + \sum_{n=0} \frac{\Phi_{B_nA}}{V_{B_nA}} \quad \text{(XIII)}$$

We now use Prigogine's[8] result that the chemical potential of a stoichiometric component is equal to the chemical potential of the monomer, i.e.:

$$\mu_B = \mu_{B_1} \quad \text{(XIV)}$$

$$\mu_A = \mu_{0A} \quad \text{(XV)}$$

As we will see, this not only simplifies the equations but expresses them in terms of the concentration of species that can (in principle) be measured by infrared spectroscopy. We thus obtain

$$\frac{\mu_B - \mu^*_B}{RT} = \ln \Phi_{B_1} + 1 - \frac{V_B}{V} \quad \text{(XVI)}$$

and

$$\frac{\mu_A - \mu^*_A}{RT} = \ln \Phi_{0A} + 1 - \frac{V_A}{V} \quad \text{(XVII)}$$

At this point it should be recalled that we are using Flory's definition of the standard state, where individual species B_n are separate (and oriented). We now wish to transform to a standard state defined as pure solutions of the individual components. Accordingly, we first write

$$\frac{\mu_B{}^0 - \mu^*_B}{RT} = \ln \Phi_{B_1}{}^0 + 1 - \frac{V_B}{V^0} \quad \text{(XVIII)}$$

where the superscript^0 refers to solutions of pure B. Subtraction gives

$$\frac{\mu_B - \mu_B{}^0}{RT} = \ln \left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0} \right] - \frac{V_B}{V} + \frac{V_B}{V^0} \quad \text{(XIX)}$$

Similarly

$$\frac{\mu_A - \mu_A{}^0}{RT} = \ln \Phi_{0A} + 1 - \frac{V_A}{V} \quad \text{(XX)}$$

These equations for the chemical potentials can be combined to give an expresson for the free energy of mixing species A and B. This contains a combinatorial entropy of mixing component that needs to be subtracted to give the required "excess" function, ΔG_H, the change in free energy associated with just the change in the distribution of hydrogen-bonded polymer species. The appropriate reference state for our purposes is therefore the entropy of mixing the pure liquids with no change in polymer species present ($\sum N_{B_n}{}^0 \ln \Phi_B + N_A \ln \Phi_A$, where $N_{B_n}{}^0$ and N_A are the number of molecules of each species). In order to be consistent with this form of the free energy of mixing described in equation 1, we also convert from a molar to unit volume basis and define a reference volume V_r equal to the molar volume of species B, V_B (see below). Thus we obtain

$$\frac{\Delta G_H}{RT} = \Phi_B \ln \left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0} \right] + \frac{\Phi_A}{r} \ln \Phi_{0A} - [\Phi_A V_B + \Phi_B V_B]\frac{1}{V} + \frac{\Phi_A}{r} + \frac{\Phi_B V_B}{V^0} - \left[\frac{\Phi_B}{\bar{n}_H{}^0} \ln \Phi_B + \frac{\Phi_A}{r} \ln \Phi_A \right] \quad \text{(XXI)}$$

where $\bar{n}_H{}^0$ is the number-average length of the hydrogen-bonded chains in a solution of pure B.

With some manipulation, this can be rearranged (by using eq XIII) to give

$$\frac{\Delta G_H}{RT} = \Phi_B \ln \left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0} \right] + \frac{\Phi_A}{r} \ln \Phi_{0A} + K\Phi_B[\Phi_{B_1} - \Phi_{B_1}{}^0] + \Phi_B[1 - K\Phi_{B_1}]\left[\frac{x}{1 + x} \right] - \left[\frac{\Phi_B}{\bar{n}_H{}^0} \ln \Phi_B + \frac{\Phi_A}{r} \ln \Phi_A \right] \quad \text{where } x = \frac{K_A \Phi_{0A}}{r} \quad \text{(XXII)}$$

In order to obtain values of the free energy as a function of composition, we now need to obtain expressions relating

Φ_{B_1} and Φ_{0A} to the other parameters. The volume fraction of B units is given by

$$\Phi_B = \sum_n \Phi_{B_n} + \sum_n \Phi_{B_nA}\left(\frac{n}{n+r}\right) \qquad \text{(XXIII)}$$

Using eq V–VIII gives

$$\Phi_B = \Phi_{B_1}\sum_n n[K\Phi_{B_1}]^{n-1} + \sum_n \frac{1}{r}K_A\Phi_{0A}\Phi_{B_1}[K\Phi_{B_1}]^{n-1} \qquad \text{(XXIV)}$$

For $K\Phi_{B_1} < 1$ the summation term converges and we obtain

$$\Phi_B = \frac{\Phi_{B_1}}{(1-K\Phi_{B_1})^2}(1+x) \qquad \text{(XXV)}$$

Similarly,

$$\Phi_{0A} = \Phi_A\left[1 + \frac{K_A\Phi_{B_1}}{(1-K\Phi_{B_1})}\right]^{-1} \qquad \text{(XXVI)}$$

Kehiaian[25] has given a proof that $K\Phi_{B_1}$ is indeed less than 1.

Free Energy of Mixing Hydrogen-Bonding Polymers. We can now obtain an expression for the mixing of two polymers, one that has both donor and acceptor groups and can therefore form hydrogen-bonded chains, while the second polymer has acceptor groups only; we simply substitute eq XXII in eq I. What is less obvious, however, is the relationship between the polymer segments, defined relative to a reference volume, V_r, as Φ_1/N_1 and Φ_2/N_2 in eq I and the volume fractions of the interacting units Φ_B, Φ_A. Here, these latter segments will be defined to be equal to the individual polymer chemical repeat units. K and K_A will then have values that are relative to these reference volumes. Alternatively, in a polyurethane with a large number of methylene groups separating the self-associating urethane units, for example, we could define Φ_B in terms of the interacting segment alone and treat the remainder of the chemical repeat unit as an inert diluent. It can be readily shown that a term, $\Phi_I \ln (\Phi_I/\Phi_I) = 0$, where the subscript I refers to inert diluent, is the only additional term introduced into the expressions for self-association in pure B. As a result, this definition merely serves to reduce the values of Φ_B and Φ_{B_1} and change the calculated value of K in proportion. The distribution of hydrogen-bonded species remains unaltered. Where problems start to occur is when we mix B with component A, where the latter also has an interacting segment that is a (different) fraction of the molar volume of its repeat unit. The stoichiometry of the system, relating Φ_A and Φ_B to Φ_{B_1} and Φ_{0A}, then changes in a complicated fashion. This problem could be readily handled if the segment fractions comprising the interacting units were easily defined. Unfortunately, they are not. In an ether, for example, is the interacting unit just the oxygen atom or does it comprise, perhaps for steric reasons, the adjacent chemically bonded groups? At this stage in the development of the theory we choose to neglect the errors introduced by defining the interacting segment to be equal to the chemical repeat unit of the polymer. In studies of the mixing of alcohols with hydrocarbons, reasonable agreement has been obtained between calculated and observed excess functions by using this assumption. A consequence, however, is that equilibrium constants determined for one system cannot be transferred to a chemically similar mixture.

With this source of error noted, we will now define the reference volume V_r implicit in eq I equal to the volume of the chemical repeat unit of the self-associating species V_B. Hence,

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B + \Phi_A\Phi_B\chi_{\text{blend}} + \Phi_B \ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0\Phi_B{}^{(1/\bar{n}_H{}^0)}}\right] + \frac{\Phi_A}{r}\ln\left[\frac{\Phi_{0A}}{\Phi_A}\right] + K\Phi_B[\Phi_{B_1} - \Phi_{B_1}{}^0] + \Phi_B[1 - K\Phi_{B_1}]\left[\frac{x}{1+x}\right] \qquad \text{(XXVII)}$$

where N_A and N_B are the degrees of polymerization of the polymer defined relative to the reference volume V_B and the volume fractions of polymers 1 and 2 in the blend are put equal to the volume fractions of their respective monomer units, A and B, present in the blend.

Before considering calculations of ΔG as a function of composition, some comments on the "chemical" component of eq XXVII, represented by the last four terms and previously given symbol ΔG_H (eq XXII), are in order.

Examined closely, it can be seen that ΔG_H has the *form* of an equation typical of regular solutions, with the first two terms being similar to a combinatorial entropy of mixing expression. *If* these terms represented the entropy change corresponding to changes in the distribution of hydrogen-bonded species, the final two terms would represent an exchange energy. In fact, ΔH_H can be determined and contains these two terms. Using

$$\Delta H_H = R\left[\frac{\partial(G_H/RT)}{\partial(1/T)}\right] = R\left[\frac{\partial(G_H/RT)}{\partial K}\right]\left[\frac{\partial K}{\partial(1/T)}\right] \qquad \text{(XXVIII)}$$

and $\partial K/\partial(1/T) = (-h_BK)/R$, where h_B is the enthalpy of formation of a single hydrogen bond between the self-associating B species, we can obtain (with some manipulation; for the general methodology see Acree[13])

$$\Delta H_H = h_B\Phi_BK[\Phi_{B_1} - \Phi_{B_1}{}^0] + h_{BA}\Phi_B[1 - K\Phi_{B_1}]\left[\frac{x}{1+x}\right] \qquad \text{(XXIX)}$$

where h_{BA} is the enthalpy of formation of a single hydrogen bond between self-associating B and competing A units. This is because these terms are related to the number of B–B hydrogen bonds broken and the number of A–B bonds formed (and therefore also related to the number-average length of the hydrogen-bonded chains; see following section). The entropy associated with the change in hydrogen-bonded species can then be written as

$$\Delta S_H = -R\left[\Phi_B \ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0\Phi_B{}^{(1/\bar{n}_H{}^0)}}\right] + \frac{\Phi_A}{r}\ln\left[\frac{\Phi_{0A}}{\Phi_A}\right]\right] + \left[\frac{\Delta H_H}{T} - R\left[K\Phi_B[\Phi_{B_1} - \Phi_{B_1}{}^0] + \Phi_B[1 - K\Phi_{B_1}]\left[\frac{x}{1+x}\right]\right]\right] \qquad \text{(XXX)}$$

This equation demonstrates that in spite of the similarity of the first two logarithm terms of eq XXII to entropy of mixing expressions and the relationship in the form of the final two terms to the expression for ΔH_H, they cannot be separately equated to entropy and enthalpy of hydrogen bond formation. These latter quantities remain

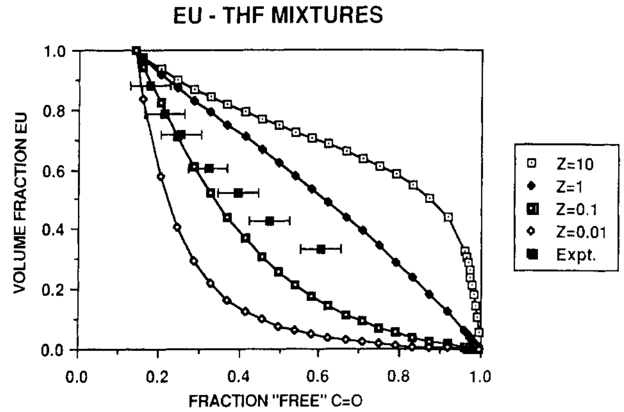

Figure 1. Plot of the volume fraction of ethyl urethane versus the fraction of "free" carbonyl groups in ethyl urethane–tetrahydrofuran mixtures.

inseparably combined, except in one circumstance, namely, when the overall change in enthalpy due to the changing pattern of hydrogen bond formation is given by

$$\Delta H_{\rm H} = RT\left[K\Phi_{\rm B}[\Phi_{{\rm B}_1} - \Phi_{{\rm B}_1}{}^0] + \Phi_{\rm B}[1 - K\Phi_{{\rm B}_1}]\left[\frac{x}{1 + x}\right]\right] \qquad \text{(XXXI)}$$

Relationship to Experimentally Determinable Quantities. The theoretical development presented here is of little value unless the parameters can be experimentally determined. In principle they are, but the ease of determination depends upon the system. Infrared spectroscopy is very sensitive to, and in fact considered diagnostic for, hydrogen bonding. From measurements of band intensities and a knowledge of extinction coefficients it is possible to determine the proportion of free and bonded groups. As we have pointed out in previous publications, however, there are particular difficulties associated with the measurements of N—H and O—H stretching modes;[26-29] bands attributed to "free" or non-hydrogen-bonded groups can be weak and difficult to measure accurately, while the broad bands characteristic of the hydrogen-bonded species represent a distribution of states that shifts and whose extinction coefficients change, with changes in the average hydrogen bond strength. This is because the A–H stretching displacement is fast compared to A---B displacements in the A—H---B hydrogen-bonded system, so that this mode experiences (and is probably anharmonically coupled to) a slow alternating field that varies with the average A---B distance (and hence temperature). In systems where the B atom is the oxygen of a carbonyl group, however, we observe bands that can be separately assigned to "free" and bonded C=O vibrations, which are relatively unaffected by the anharmonic factors associated with proton displacements. The ratio of the extinction coefficients of the two modes may be determined, in some cases even for polymer films of unknown thickness,[27,29] so that the fraction of "free" carbonyl groups, which we have given the symbol $f_{\rm F}$, is readily determined. We emphasize that this quantity is *not* equal to $\Phi_{{\rm B}_1}$, which represents the amount of an isolated ("monomer") unit or repeat units in, for example, a polyamide where neither the N—H or C=O parts of a *particular* amide group are hydrogen bonded. Rather, $f_{\rm F}$ is a count of the number of "end groups" on hydrogen-bonded chains, as illustrated in Figure 1 in the preceding paper.[17] Accordingly, this must be equal to the number of hydrogen-bonded chains of length n, summed over all n, divided by the total number of interacting units present. If we consider the homopolymer containing self-associating units first,

$$f_{\rm F}{}^0 = \frac{\sum_n N_{{\rm B}_n}}{\sum_n nN_{{\rm B}_n}} \qquad \text{(XXXII)}$$

Using

$$\Phi_{{\rm B}_n} = \frac{N_{{\rm B}_n}V_{{\rm B}_n}}{V} = \frac{N_{{\rm B}_n}nV_{\rm B}}{V} \qquad \text{(XXXIII)}$$

gives

$$f_{\rm F}{}^0 = \frac{\sum \Phi_{{\rm B}_n}/n}{\sum \Phi_{{\rm B}_n}} \qquad \text{(XXXIV)}$$

From eq II, III, VII, and VIII and the sum of the geometric progression as in eq XXIV and XXV,

$$f_{\rm F}{}^0 = 1 - K\Phi_{{\rm B}_1}{}^0 \qquad \text{(XXXV)}$$

It is obvious that the definition of $f_{\rm F}$ stated above is equivalent to the reciprocal of the number-average length of the hydrogen-bonded chains, so that

$$\bar{n}_{\rm H}{}^0 = \frac{1}{f_{\rm F}{}^0} = \frac{1}{1 - K\Phi_{{\rm B}_1}{}^0} \qquad \text{(XXXVI)}$$

We can now employ eq XXV, which relates $\Phi_{\rm B}$ and $\Phi_{{\rm B}_1}$. For the homopolymer $\Phi_{\rm B} = 1$ and $x = 0$, so that

$$\Phi_{{\rm B}_1}{}^0 = [f_{\rm F}{}^0]^2 \qquad \text{(XXXVII)}$$

and

$$K = \frac{1 - f_{\rm F}{}^0}{[f_{\rm F}{}^0]^2} \qquad \text{(XXXVIII)}$$

Of course, these are the simplest expressions obtained by defining our reference volume or interacting unit to be the chemical repeat of the self-associated species. The equations are a little more complicated if the interacting unit is instead defined equal to a segment of the repeat unit, but the process is identical. We use eq XXXVI, which relates the experimentally measurable quantity $f_{\rm F}$ to K and $\Phi_{{\rm B}_1}$, and solve for the two unknowns K and $\Phi_{{\rm B}_1}$ using the known stoichiometry of the system, eq XXV. This assumes, of course, that the interacting segment can be separately defined.

Turning now to measurements of the fraction of "free" carbonyls in the blend, we obtain

$$f_{\rm F} = \frac{\sum N_{{\rm B}_n} + \sum N_{{\rm B}_n{\rm A}}}{\sum nN_{{\rm B}_n} + \sum nN_{{\rm B}_n{\rm A}}} \qquad \text{(XXXIX)}$$

and upon substituting and summing the resulting geometric series we find

$$f_{\rm F} = 1 - K\Phi_{{\rm B}_1} \qquad \text{(XL)}$$

This is identical in form with eq XXXV for the pure homopolymer, but $\Phi_{{\rm B}_1}$ now depends upon $K_{\rm A}$ as well as K, after eq XXV. The equilibrium constant K is, naturally, assumed to be the same in the blend as in the homopolymer, while eq XXV and XXVI can be used in conjunction with eq XL to determine the remaining unknown quantities $\Phi_{{\rm B}_1}$, $\Phi_{0{\rm A}}$, and $K_{\rm A}$.

Comparison to Experimental Data. In the preceding paper,[17] we described FTIR studies of a model low molecular weight mixture, ethyl urethane (EU) and tetrahydrofuran (THF), and a miscible polymer blend consisting of an amorphous polyurethane (APU) with poly[(ethylene oxide)-*co*-(propylene oxide)] (EPO). A quantitative measure of the fraction of "free" C=O groups was obtained as a function of the volume fraction of EU or

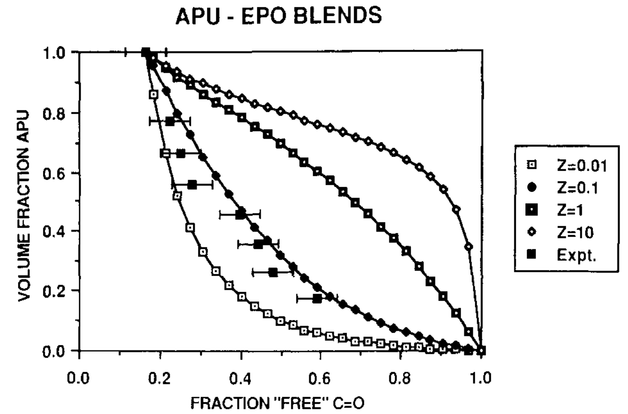

Figure 2. Plot of the volume fraction of amorphous polyurethane versus the fraction of "free" carbonyl groups in polyurethane–poly[(ethylene)-*co*-(propylene oxide)] blends.

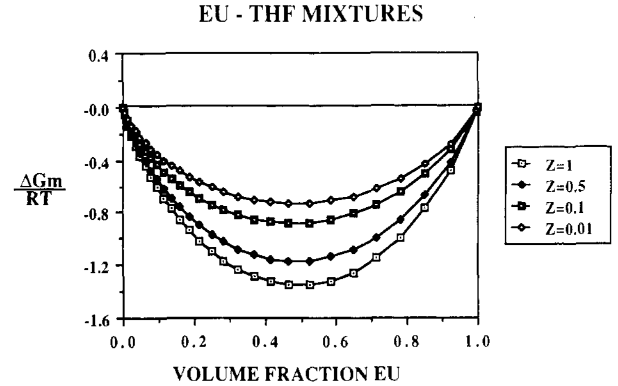

Figure 3. Plot of $\Delta G_m/RT$ versus the volume fraction of ethyl urethane in ethyl urethane–tetrahydrofuran mixtures.

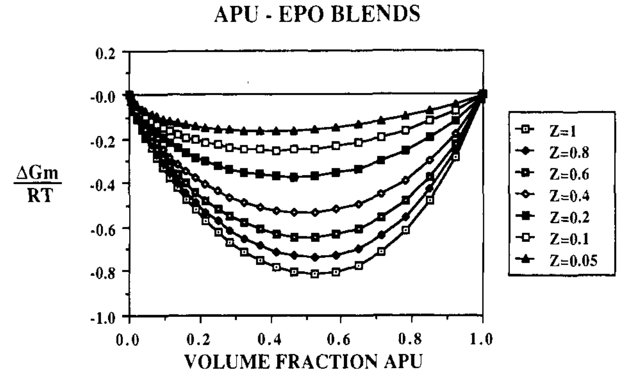

Figure 4. Plot of $\Delta G_m/RT$ versus the volume fraction of amorphous polyurethane in polyurethane–poly[(ethylene oxide)-*co*-(propylene oxide)] blends.

APU in the mixtures (see Tables I and II, ref 17). These data can now be compared to theoretical calculations.

The ratio of the molar volumes of the interacting units, r, was calculated from group contributions in accordance with the procedures discussed in van Krevelen's book.[30] The molar volumes for EU, THF, and an average repeat unit of APU and EPO were estimated at 112, 74.3, 108.3, and 46.7 cm^3 mol^{-1}, respectively. The equilibrium constant K was determined (eq XXXVIII) from the experimental value of the fraction of "free" C=O groups in the pure self-associated EU (0.14) or APU (0.16).[17] For convenience, we have introduced a parameter, Z, defined by the relationship $K_A = ZK$. By varying Z we can vary the magnitude of the equilibrium constant describing the hydrogen bonding between the self-associating component B and the "competing" component A relative to the magnitude of the equilibrium constant describing self-association.

By use of eq XXV and XXVI, together with those developed above for f_F, theoretical curves of the fraction of "free" C=O groups as a function of the volume fraction, Φ_B, were obtained for values of Z between 0.01 and 10. These are shown in Figure 1 and 2. Also included in these figures are the experimentally determined values of the fraction of "free" carbonyl groups in the two mixtures.[17] The experimental data appear to follow the same trends as predicted by the theoretical curves for a Z value of between 0.1 and 1 in the case of the EU–THF mixtures and about 0.1 for the APU–EPO blend. Thus, according to the theory described in this paper, K is approximately 5 and 10 times that of K_A, for the low molecular weight mixture and the polymer blend, respectively.

We should note in passing that even if the strengths (enthalpies) of the primary interactions (hydrogen bonds) involved in urethane–urethane (self-association) and urethane–ether interactions are practically the same—as they are for the APU-EPO blend system[17]—the entropy change per hydrogen bond, and consequently the equilibrium constants, can be very different. For the sake of argument, let us assume that these two intermolecular interactions are indeed equal; i.e., $h_B = h_{BA}$ in eq XXIX. Now

$$\ln K = -\Delta H_B/RT + \Delta S_B/R$$

$$\ln K_A = -\Delta H_{AB}/RT + \Delta S_{AB}/R$$

where the subscripts B and AB represent self-association and association, respectively. Therefore

$$\ln K - \ln K_A = \ln \frac{K}{K_A} = \frac{1}{R}[\Delta S_B - \Delta S_{AB}] \quad \text{(XLI)}$$

For a $K/K_A = 10$, the difference in the entropic contribution, $[\Delta S_B - \Delta S_{AB}]$, is approximately 5 eu. This follows the well-known sensitivity of equilibrium constants to even small changes in free energy (which in this specific case resides largely in the difference in the entropy component of hydrogen bond formation).

Free Energy Change Associated with Mixing Hydrogen-Bonded Species. $\Delta G_M/RT$ can be readily calculated from eq XXVII. First, let us consider the low molecular weight EU–THF system, where combinatorial entropy plays a major role. By use of the value of $r = V_A/V_B$ given above and the assumption $N_A = N_B = 1$ and $\chi = 0$, $\Delta G^M/RT$ may be calculated as a function of Φ_B, the volume fraction of EU. Figure 3 shows the result of such calculations for various values of the parameter Z (recall $K_A = ZK$). Not surprisingly, for all cases, in the range of interest where $Z = 1–10^{-2}$, $\Delta G^M/RT$ is negative throughout the whole composition range. In fact, a close examination of the equations describing ΔG_H shows that $\Delta G_H \leq 0$. The value of zero is, of course, obtained for the reference state of mixing the components with no change in hydrogen bond chain length.

A similar exercise performed for the APU–EPO polymer blend system yields results displayed in Figure 4. Here we employed the appropriate value of r together with values of $N_A = N_B = 100$ (corresponding to modest molecular weights of about 10^4) and $\chi = 0$. Now the combinatorial entropy terms plays a minor role and the free energy, $\Delta G^M/RT$, is dominated by the hydrogen-bonding contributions (last four terms in eq XXVII) and is naturally always negative throughout the entire composition range. The calculated free energy of mixing can only become positive through the contribution of a χ physical interaction term. For the APU–EPO blend system, where the experimental data (see Figure 2) suggest a Z value of the order of 0.1, such a condition is only obtained for unreasonably large values of χ. This is where we believe

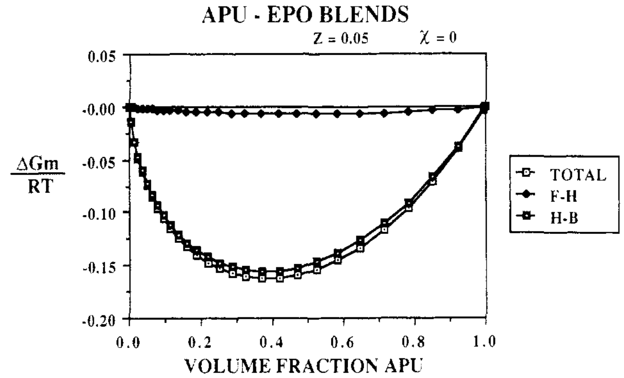

Figure 5. Plot of $\Delta G_m/RT$ versus the volume fraction of amorphous polyurethane in polyurethane–poly[(ethylene oxide)-*co*-(propylene oxide)] blends showing the Flory–Huggins and hydrogen-bonding contributions.

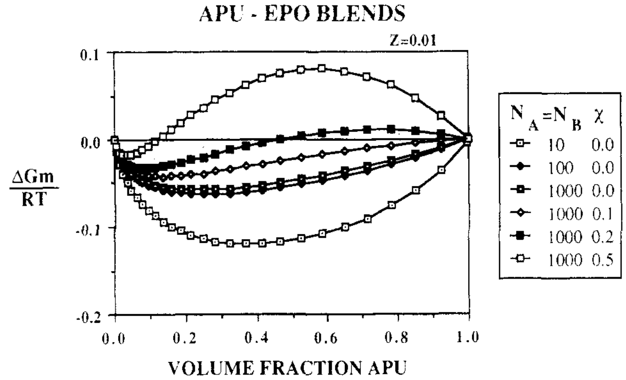

Figure 6. Plot of $\Delta G_m/RT$ versus the volume fraction of amorphous polyurethane in polyurethane–poly[(ethylene oxide)-*co*-(propylene oxide)] blends showing the effect of varying polymer molecular weight and χ.

association theories will prove most useful; predicting situations where the large negative free energy that is responsible for hydrogen bond formation dominates any contribution from physical interactions and free volume effects. It is important to keep in mind what miscibility means in this context, however. It does *not* mean a truly random arrangement of B and A units, but rather a dispersion of a distribution of various lengths of hydrogen-bonded B chains among a number of A units, a portion of which are bound to one end of these chains.

Finally, it is interesting to explore the effect of physical interactions on $\Delta G^M/RT$. To illustrate this, we have employed the constants used above for the APU–EPO blend system and have selected a value for Z of 0.05 (chosen deliberately as the curve of $\Delta G^M/RT$ vs. Φ_B is negative but only slightly so—Figure 4). Again, we initially assume $\chi = 0$ and $N_A = N_B = 100$. Figure 5 shows the individual contributions to $\Delta G^M/RT$ from Flory–Huggins considerations (first three terms of eq XXVII) and hydrogen bonding (last four terms). Not surprisingly, the hydrogen-bonding contribution dominates. Figure 6 illustrates the effect of changing the degree of polymerization and values of χ. The former follows the well-known adage that after a fairly moderate molecular weight the combinatorial entropy is essentially negligible. The contribution from the physical interaction term, $\chi\Phi_A\Phi_B$, is more complex. For a $Z = 0.01$, where it does not take much to render $\Delta G^M/RT$ positive, a reasonable value of χ could tip the balance. Obviously, in systems characterized by such equilibrium constants experimental errors will play a major role. What this approach is capable of predicting, however, are the polymer pairs that will be on such an edge of miscibility.

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Registry No. EU, 51-79-6; THF, 109-99-9; EPO, 9003-11-6; (1,4-butanediol)(tolyl diisocyanate) (copolymer), 37338-53-7; (1,4-butanediol)(tolyl diisocyanate) (SRU), 54633-10-2.

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