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Thermodynamics of Hydrogen Bonding in Polymer Blends. 1. Application of Association Models

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ABSTRACT: The application of association models to the description of the free energy changes related to hydrogen bonding between components of binary polymer blends is discussed for a system where one polymer self-associates while the second does not but is capable of forming a hydrogen bond with the first. A previous model is generalized, and the proper definition of equilibrium constants is considered. It is demonstrated that a definition of these equilibrium constants in terms of chemical repeat units is useful and allows equilibrium constants to be defined and experimentally determined for interactions of a particular generic type (e.g., urethane–urethane, urethane–ether), provided that the polymers considered are structurally similar. The equilibrium constants are simply adjusted by accounting for the difference in molar volume of the chemical repeat units.

Introduction

It is well-known that most hydrocarbon homopolymers do not mix; that is, they form so-called immiscible blends. This follows directly from a simple Flory–Huggins description of the thermodynamics of mixing, which predicts a negligibly small combinatorial entropy and a positive enthalpy term, if simple van der Waals or London dispersion forces are the only intermolecular interactions operating between segments. To obtain miscible homopolymer blends, therefore, it is usually necessary to have some sort of attractive force between unlike segments. If these attractive forces are due to dipole moments that are not localized on the surface of the polymer segment, then it would seem reasonable to treat the system in a conventional manner and simply introduce a negative interaction term. Strictly speaking, the system would not be random, in that unlike segments would have an increased propensity to be adjacent to one another. They are not in the usual sense of the word associated, however, and Flory[1] has argued that for such weak interactions the modification in the calculated entropy of mixing due to nonrandomness is not significant (compared to the effects of other approximations).

Stronger interactions, particularly hydrogen bonds, are different and cannot be dealt with by a simple approximation. Polymer segments that interact in this manner are truly associated, and above the T_g there is a dynamic equilibrium distribution of (hydrogen) bonded species. For example, in ethylene–methacrylic acid copolymers containing only 5% acid units, practically all of the carboxyl groups are present as hydrogen-bonded pairs. This number of contacts could not be predicted on the basis of random mixing.

There are other problems in treating hydrogen-bonding polymer mixtures, apart from formulating a nonrandom arrangement of certain units on a lattice. The forces between interacting functional groups are a complex combination of electrostatic, dispersion, and repulsive terms, and the description of a potential function requires a knowledge of the charge distribution and the specific arrangement of molecules. Furthermore, usual lattice treatments are based on the assumption that the internal degrees of freedom of each molecule (or segment) are not seriously disturbed by the proximity of other molecules in the mixture. The system can then be treated as an assembly whose partition function is the product of a partition function for translations of the molecules and partition functions for the internal degrees of freedom of each single molecule.[2] When molecules or polymer segments become associated by hydrogen bonds, the rotational and vibrational degrees of freedom of each become seriously modified. This effect is clearly observed in the infrared spectrum, where the vibrational modes of the interacting functional groups are strongly perturbed. This is particularly true of –OH and –NH stretching vibrations, which display significant frequency shifts and large changes in intensity as a consequence of intermolecular hydrogen bonding.[3]

A number of theoretical approaches have been developed to account for the difficulties in describing specific directional interactions. For example, Barker[4,5] and Tompa[6] used a treatment in which the surface of a molecule is divided into several contact points and the energy of nearest-neighbor interactions depends upon the relative orientations of the molecules concerned. This approach is (at least to us) mathematically complicated and introduces a number of parameters that cannot be determined independently, but only estimated by a fit to thermodynamic data. As Tompa[6] pointed out, it is uncertain how

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much physical significance could be attached to values so obtained.

An alternative approach is the use of association models. This treats the associated complexes, typically linear chains of hydrogen-bonded small molecules, as new, distinguishable, and independent molecular species. The hydrogen-bonding interaction is treated separately from the forces involved in mixing and essentially defines the number and distribution of species present, typically through equilibrium constants that are related to the free energy change corresponding to the formation (or dissociation) of particular types of hydrogen bonds. The hydrogen-bonded polymers then mix and interact through simple physical forces only, a process that can be readily handled by conventional lattice theories. Because the distribution of hydrogen-bonded polymer species changes upon mixing, however, it is necessary to define reference states with great care. Flory[7] discussed this in some detail, deriving expressions for the thermodynamic properties of solutions of polymers of different molecular weight. These equations are especially suited to a description of chemical equilibria between polymer species, whether covalently linked or hydrogen bonded, as Flory also pointed out.[7,8] Applying this theory, Kretschmer and Wiebe[9] developed an association model describing the mixing of alcohols and hydrocarbons that was later extended and applied by a number of other authors.[9-14] By assuming that the formation of hydrogen bonds in amorphous polymer mixtures is largely unaffected by the covalent linkage of the interacting units into polymer chains, we have adapted this approach to a description of the mixing of a polyurethane with a polyether and demonstrated that the equilibrium constants can be determined by infrared measurements.[15] In effect, we assumed that the covalently linked chains are randomly arranged and there is sufficient segmental flexibility that the interacting functional groups can largely follow their intrinsic proclivities in forming hydrogen bonds. In one sense this assumption is probably unnecessary, in that limitations on the formation and strength of hydrogen bonds will presumably be reflected in the values of the experimentally determined equilibrium constants. To correctly model this latter situation, however, we would have to include a dependence of the equilibrium constants upon the covalent chain stiffness, an unnecessary complication at this stage of our application of association models to the description of hydrogen bonding in polymer blends.

Our interest here is the generalization of the model previously described and the development of equations describing phase behavior. The first paper in this series will consider the proper definition of equilibrium constants for a blend of one polymer that self-associates (i.e., has amide, urethane, or hydroxyl functional groups), while the second does not self-associate but is capable of forming a hydrogen bond with the first (e.g., polymers containing ether, ester, or pyridine groups). In the second and third papers of this series we will consider phase behavior and an experimental test of this theory. In subsequent papers we will consider polymers containing carboxylic acid groups, which can be treated in the same fashion but are distinguishable by their preference for forming strongly hydrogen-bonded pairs rather than chains.

Choice of Association Models

There are a number of thermodynamic models that have been used to describe association in solution, the three most prominent being the attenuated equilibrium constant (AEC) model, the Mecke–Kempter[11,16] association model, and the Kretschmer–Wiebe[9] association model. All assume equal consecutive enthalpies of association in forming a hydrogen-bonded chain of $n + 1$ interacting units, B_{n+1}, from an n-mer, B_n, and a monomer B_1:

$$B_n + B_1 \rightleftharpoons B_{n+1} \tag{1}$$

The entropy change for each step is defined differently in each model, however, resulting in different equilibrium constants. In the AEC model it is assumed that the sequential entropy change decreases monotonically with increasing chain length; the Mecke–Kempter model supposedly assumes equal consecutive entropies of association, ΔS^{MK}, while the Kretschmer–Wiebe model assumes consecutive entropies of association that can be described in the following manner:

$$\Delta S_{n,n+1} = \Delta S^{MK} + R \ln [(n + 1)/n] \tag{2}$$

According to Flory,[7] it is this latter definition that is independent of n. It should be kept in mind that there are two components to the entropy of association, one due to the loss of orientations and one due to the change in the number of "molecules" in the system. A description of all three models can be found in the book by Acree,[17] our concern here is the appropriate choice of model.

The AEC model assumes that the addition of a unit to a chain of hydrogen-bonded molecules depends upon the length of that chain. This is analogous to assuming that reactivity changes with molecular size in a polycondensation reaction. As in these latter reactions, the formation of a dimer may be described by a different constant than the formations of each succeeding n-mer, a point we will deal with later, but the general arguments advanced by Flory[18] concerning the independence of the chemical reactivity of a functional group from the size of the molecule to which it is attached should, in our view, also apply to the formation of linear hydrogen-bonded chains. accordingly, we reject the AEC model for this application.

The difference between the Mecke–Kempter model and the Kretschmer–Wiebe model can be shown to depend upon the choice of reference states for mixing heterogeneous polymers. In Flory's original paper on this subject[7] and in a subsequent note[8] where he points out the generality of his treatment and therefore its applicability to reversible hydrogen-bonded association (in addition to equilibrium between covalently bonded species), that state where the individual molecules (i.e., the various n-mers) are separate and oriented is indentified as the proper standard reference state. The entropy change upon forming a mixture from n_s molecules of solvent and N_1, N_2, N_3, etc., molecules of monomer, dimer, trimer, etc., each initially separated according to chain length into ordered "crystalline" states, is given by

$$-\Delta S_{\text{mixing}}/R = n_s \ln \Phi_s + \sum(N_n \ln (\Phi_n/n)) - \sum[(n - 1)N_n][\ln (\gamma - 1) - 1] + N \ln \sigma \tag{3}$$

We use the symbol n_s to represent the number of solvent molecules, which should not be confused with n, the length of the hydrogen-bonded chain, to be as consistent as possible with Flory's nomenclature, which we assume is the familiar form to most readers. The terms Φ_s and Φ_n are the volume fractions of solvent and n-mer, respectively, γ is a coordination number for the lattice, and σ is a symmetry number for the polymer molecule. This expression is the sum of three contributions: the entropy of disorientation of the individual (n-mer) pure components; the entropy of mixing these with one another; the entropy of dilution of the mixture. (An enthalpy term describing physical interactions between the n-mers and the solvent can be included, if desired, but cancels from the final expression for the equilibrium constant.) If athermal mixing of the components is assumed, then the partial molar free energy of an n-mer is given by

$$\frac{\Delta\bar{G}_n}{RT} = \ln\,[\Phi_n/n] + n\Phi_p[1 - 1/\bar{n}_n] - [n-1]\ln\,[\gamma - 1] + \ln\,\sigma \quad (4)$$

where Φ_p is the volume fraction of all polymer molecules ($=\sum\Phi_n$). For the equilibrium described in eq 1 Flory[7] demonstrates that

$$\Delta\bar{G}_{n+1} - \Delta\bar{G}_n - \Delta\bar{G}_1 + \Delta G^\circ = 0 \quad (5)$$

where ΔG° is the standard free energy for formation of a linkage and is independent of the length of the chains being joined. Substituting from eq 4 yields

$$\frac{\Delta G^\circ}{RT} = -\ln\left[\frac{\Phi_{n+1}}{\Phi_n\Phi_1}\,\frac{n}{n+1}\right] + \ln\,[\sigma(\gamma - 1)] \quad (6)$$

Because γ is a function of the liquid structure only and σ is a constant, an equilibrium constant K can be defined as

$$\ln K = -\frac{\Delta G^\circ}{RT} + \ln\,[\sigma(\gamma - 1)] \quad (7)$$

where

$$K = \frac{\Phi_{n+1}}{\Phi_n\Phi_1}\,\frac{n}{n+1} \quad (8)$$

This is a dimensionless quantity equal to the definition of an equilibrium constant in terms of molar concentrations (C) divided by the molar volume per structural unit, V_B, i.e.

$$K = \frac{C_{n+1}}{C_nC_1}\,\frac{1}{V_B} = \frac{K'}{V_B} \quad (9)$$

As Flory points out, because V_B is a constant characteristic of the molecule concerned, either K or K' is an acceptable equilibrium constant.

The derivation of the Mecke–Kempter equilibrium constant follows precisely the same procedure but takes the separate but disoriented species as the reference state, rather than the condition where the molecules are separate and oriented. As a result the following expressions for the partial molal free energy is obtained:[7]

$$\Delta\bar{G}_n{}^*/RT = \ln\,\Phi_n - (n-1) + \Phi_p n[1 - 1/\bar{n}_n] \quad (10)$$

and an equilibrium constant can be derived in the same manner as above to give

$$K^{\mathrm{MK}} = \frac{\Phi_{n+1}}{\Phi_n\Phi_1} \quad (11)$$

Both the Kretschmer–Wiebe and Mecke–Kempter model have been successfully applied to the description of the excess properties of alcohols in hydrocarbon solvents.[17] It is not possible to choose between the models on the basis of this work, however, because equilibrium constants have almost invariably been determined from binary data reduction, so that their values are strongly influenced by the criteria adopted to separate the physical from the "chemical" (i.e., hydrogen bonding) contributions. Also, at high degrees of association (large n), the values of the equilibrium constants approach one another in value. Nevertheless, we believe that the Kretschmer–Wiebe model is the proper choice. Flory[7] argues that for the treatment of chemical equilibria between polymer species the most appropriate and least ambiguous reference state is that one in which the individual species are separate and oriented. This allows the assumption of a free energy per linkage, ΔG° in eq 5, that is constant regardless of the length of the chains being joined. Thus, we will define our equilibrium constants according to eq 8.

Equilibrium Constants

Our treatment depends upon three assumptions concerning the equilibrium constants describing association:

(a) The hydrogen-bonded species that can form are unaffected by the covalent linkage of interacting units into polymer chains.

(b) The equilibrium constants are independent of the length of the *hydrogen-bonded* chains (not to be confused with the covalently linked chains in assumption a).

(c) The equilibrium constants can be defined in terms of a chemical repeat unit and can thus be experimentally determined by spectroscopic measurements.

In this paper our principal aim is to demonstrate the validity of assumption c and develop equations in terms of transferable equilibrium constants (i.e., that depend upon the functional group involved and a normalization factor related to the size of the chemical repeat unit). Assumption a was discussed in the Introduction. In effect, as long as the interacting units are linked by flexible units of sufficient length, then the ability of these functional groups to hydrogen bond should be unaffected (except, of course, by the dilution factor resulting from the presence of non-hydrogen-bonding segments). Assumption b is probably not accurate. It can be argued on theoretical grounds[19] that the equilibrium constant describing dimer formation should be different from that describing subsequent n-mer ($n > 2$) formation. This can be dealt with conceptually in a relatively easy fashion by the definition of an additional equilibrium constant. This theoretical precision comes at the expense of more complicated algebra, however, together with the experimental uncertainties and errors that go with fitting two equilibrium constants to spectroscopic data. In initial calculations on the self-association of urethanes we have found little difference in the predicted stoichiometry of a system or in the values of free energy calculated by using the assumption of one equilibrium constant rather than two. In certain systems (particularly those involving hydroxyl groups where there may be an energetic difference between the formation of dimers and n-mers) the use of only one equilibrium constant may be inappropriate, so for completeness we will include a two-equilibrium constant model for self-association in the Appendix.

We mentioned above that association models describing the behavior of alcohols in hydrocarbon solvents have been relatively successful, but that equilibrium (and other) constants are usually obtained by reduction of phase equilibria and enthalpy data. As a result, different values of self-association constants have been obtained, including some that varied with the nature of the diluent. As Brandani[20] points out, this latter result cannot be reconciled with the statistical mechanics of these mixtures (the equilibrium constant should be a property of the associating component). This author demonstrated that these difficulties are largely overcome by assuming that the molecule behaves as a set of segments. In our previous paper,[15] for want of more precise definitions, the size of the "interacting unit" was assumed to be equal to the size of the parent molecule or, since we are largely concerned with polymer–polymer mixtures, the chemical repeat unit. In molecules with large repeat units, however, there is clearly a substantial "inert" portion, by which we mean segments that play no role in hydrogen bonding but affect the free energy of mixing through the usual physical interactions. These segments naturally occupy volume or, in the usual lattice model, sites, and we did not discuss how this factor would affect the equilibrium description of association. In effect, we implicitly assumed that the difference in size of the interacting unit compared to the parent molecule or chemical repeat unit would be absorbed into the value of the equilibrium constant. This relationship can be shown explicitly in two ways; by simple substitution or by returning to first principles and constructing an appropriate lattice model. We will consider both, deferring a discussion of the lattice model until later. We start here as in our previous paper[15] by letting the suffix B (or β) represent molecular parameters characteristic of the self-associating species and use the suffix A (or α) to designate parameters assigned to the molecules competing to form complexes with the B units. We now define the molar volumes of the "true interacting units" to be V_β and V_α. For urethane–ether mixtures we would intuitively expect that V_β would be approximately equal to the volume of the OCONH group; a description of the ether interacting unit is more elusive, perhaps involving atoms adjacent to the oxygen (COC). In any event, we make no initial assumptions concerning the precise molecular identity of these groups, but define a parameter $r_i = V_\alpha/V_\beta$. We now let the molar volume of the *chemical repeat* of the self-associating species be V_B and that of the competing species be V_A. We can now define the following ratios:

$$s_B = V_B/V_\beta \tag{12}$$

$$s_A = V_A/V_\alpha \tag{13}$$

The quantities s are thus the number of segments in each chemical repeat when the segment size is defined equal to the volume of the interacting unit. (In general, $V_B \neq V_A$, so that it might at first seem that we have defined a lattice consisting of cells of different size. As the equations are developed it will be apparent that this is not so; V_B defines the cell size and differences in the size of the segments in the two units, defined by eq 12 and 13, are accounted for by the factor $r = V_A/V_B$.) Following Flory,[7] we can now define equilibrium constants for the competing equilibria

$$\beta_n + \beta_1 \overset{K_\beta}{\leftrightharpoons} \beta_{n+1}$$

$$\beta_n + \alpha \overset{K_\alpha}{\leftrightharpoons} \beta_n\alpha$$

as

$$K_\beta = \frac{\Phi_{\beta_{n+1}}}{\Phi_{\beta_n}\Phi_{\beta_1}}\left(\frac{n}{n+1}\right) \tag{14}$$

$$K_\alpha = \frac{\Phi_{\beta_n\alpha}}{\Phi_{\beta_n}\Phi_{0\alpha}}\left(\frac{nr_i}{n+r_i}\right) \tag{15}$$

where Φ_{β_n} represents the volume fraction of n-mers, Φ_{β_1} and $\Phi_{0\alpha}$ represent the volume fraction of interacting units that are *not* hydrogen bonded to other groups (i.e., totally "free"), and the factor $r_i = V_\alpha/V_\beta$ accounts for the difference in size of the interacting units.

The problem in using these definitions directly is that we presently lack a precise definition of the size of the interacting units. It is a relatively straightforward task to express the equilibrium constants K_β and K_α in terms of the volume fractions of the chemical repeat units (or molecules, in a mixture of low molecular weight materials), however, and as we shall see this leads to some very useful results. We start with the following definitions of volume fractions:

$$\Phi_{\beta_n} = n_{\beta_n}V_{\beta_n}/V \tag{16}$$

$$\Phi_{B_n} = n_{B_n}V_{B_n}/V \tag{17}$$

where Φ_{β_n} is again the volume fraction of self-associating interacting units present as n-mers, Φ_{B_n} is the corresponding volume fraction of chemical repeat units present as these n-mers, n_{β_n} is the number of hydrogen-bonded chains of interacting units of length n, n_{B_n} is the corresponding number of chains of chemical repeat units associated in chains of length n, V is the total volume of the sample, finally, V_{β_n} and V_{B_n} are the molar volumes of a chain of n interacting units or chemical repeat units, respectively. Assuming no change in volume upon association

$$V_{\beta_n} = nV_\beta \tag{18}$$

$$V_{B_n} = nV_B \tag{19}$$

Because we are confining our discussion to the most common situation of one interacting unit per molecule or chemical repeat

$$n_{\beta_n} = n_{B_n} \tag{20}$$

(For certain types of random copolymers the application of this model requires the definition of an average repeat unit, each of which contains, for example, only one urethane (or ether) group.)

Hence

$$\Phi_{\beta_n} = \Phi_{B_n}\frac{V_{\beta_n}}{V_{B_n}} = \Phi_{B_n}\frac{V_\beta}{V_B} = \frac{\Phi_{B_n}}{s_B} \tag{21}$$

Substituting equivalent definitions for $\Phi_{\beta_{n+1}}$ and Φ_{β_1} into eq 14, we obtain

$$\frac{K_\beta}{s_B} = \frac{\Phi_{B_{n+1}}}{\Phi_{B_n}\Phi_{B_1}}\left(\frac{n}{n+1}\right) \tag{22}$$

Our previous definition of the equilibrium constant in terms of chemical repeat units[15] is equal to the constant K_β/s_B defined here. A similar result is obtained for the equilibrium constant K_α describing interactions with the competing species:

$$\Phi_{\beta_n\alpha} = \frac{n_{\beta_n\alpha}(V_{\beta_n} + V_\alpha)}{V} \tag{23}$$

$$\Phi_{B_nA} = \frac{n_{B_nA}(V_{B_n} + V_A)}{V} \tag{24}$$

Using $n_{\beta_n\alpha} = n_{B_nA}$

$$\Phi_{\beta_n\alpha} = \Phi_{B_nA}\left[\frac{n + r_i}{ns_B + V_A/V_\beta}\right] \tag{25}$$

Writing similar expressions for Φ_{β_n} and $\Phi_{0\alpha}$ in terms of Φ_{B_n} and Φ_{0A}, it follows that

$$K_\alpha = \frac{\Phi_{B_nA}}{\Phi_{B_n}\Phi_{0A}}\,\frac{s_Bs_Anr_i}{ns_B + V_A/V_\beta} = \frac{\Phi_{B_nA}}{\Phi_{B_n}\Phi_{0A}}\,\frac{s_Anr_i}{n + V_A/V_B} \tag{26}$$

Noting that

$$\frac{s_Ar_i}{s_B} = \frac{V_A}{V_\alpha}\,\frac{V_\alpha}{V_\beta}\,\frac{V_\beta}{V_B} = \frac{V_A}{V_B} \tag{27}$$

Then

$$\frac{K_\alpha}{s_B} = \frac{\Phi_{B_nA}}{\Phi_{B_n}\Phi_{0A}}\,\frac{n(V_A/V_B)}{n + V_A/V_B} \tag{28}$$

If we let $r = V_A/V_B$ and write the equation for the equilibrium constants side-by-side for comparative purposes, we obtain

$$K_\alpha = \frac{\Phi_{\beta_n\alpha}}{\Phi_{\beta_n}\Phi_{0\alpha}}\left(\frac{nr_i}{n + r_i}\right) \qquad K_A = \frac{K_\alpha}{s_B} = \frac{\Phi_{B_nA}}{\Phi_{B_n}\Phi_{0A}}\left(\frac{nr}{n + r}\right)$$

$$K_\beta = \frac{\Phi_{\beta_{n+1}}}{\Phi_{\beta_n}\Phi_{\beta_1}}\left(\frac{n}{n + 1}\right) \qquad K_B = \frac{K_\beta}{s_B} = \frac{\Phi_{B_{n+1}}}{\Phi_{B_n}\Phi_{B_1}}\left(\frac{n}{n + 1}\right)$$

Clearly, the equilibrium constants determined in our preceding paper, where the chemical repeat units of a polyurethane and a polyether were assumed to be equal to the interacting unit, are the quantities defined above as K_B and K_A and are equal to the constants K_α/s_B and K_β/s_B. A much more important point, however, is the fact that *both* equilibrium constants are adjusted by the *same* quantity, s_B, the number of segments in the urethane chemical repeat. This is because we (implicitly) defined a lattice cell size in terms of the urethane interacting unit. Differences in size of the urethane and ether units are then accounted for by the factors r_i and r in the definition of the equilibrium constants. Furthermore, provided that the interaction strength (or, more precisely, the free energy of formation of a hydrogen bond) is unaltered in a series of molecules that have chemical repeat units of different size, we have effectively defined a "transferable" equilibrium constant, one whose value is simply modified according to a ratio of molar volumes. We will discuss this in more detail when we consider the equations for the free energy of mixing.

Stoichiometry of Association

We have seen that defining the equilibrium constants in terms of the volumes of individual molecules (for mixtures of low molecular weight materials) or chemical repeat units (for polymers) rather than the volumes of the interacting units changes their value by the simple factor s_B. Clearly, either definition can be used, but the equations describing the stoichiometry of the system have to be adjusted accordingly. An equation relating the volume fraction of all of the self-associating interacting units present in a mixture to the volume fractions of non-hydrogen-bonded species and the equilibrium constants is simply derived from materials balance considerations:[9-15]

$$\Phi_\beta = \frac{\Phi_{\beta_1}}{(1 - K_\beta\Phi_{\beta_1})^2}\left(1 + \frac{K_\alpha\Phi_{0\alpha}}{r_i}\right) \tag{29}$$

This derivation will not be reproduced here, but the same methodology is applied to the determination of the stoichiometric relationships when self-association is described in terms of two equilibrium constants, and this is given in the Appendix together with a derivation of the corresponding free energy expressions.

As long as there is only one self-associated unit per chemical repeat (for a random copolymer an average chemical repeat can be defined, each containing one such interacting unit), then, as above, the number of interacting units is equal to the number of chemical repeat units and

$$\Phi_\beta = \frac{\Phi_B}{s_B}; \quad \Phi_\alpha = \frac{\Phi_A}{s_A}; \quad \Phi_{\beta_1} = \frac{\Phi_{B_1}}{s_B}; \quad \Phi_{0\alpha} = \frac{\Phi_{0A}}{s_A} \tag{30}$$

In terms of the volume fraction of interacting units we therefore obtain by substitution

$$\frac{\Phi_B}{s_B} = \frac{\Phi_{B_1}/s_B}{(1 - K_\beta\Phi_{B_1}/s_B)^2}\left(1 + \frac{K_\alpha\Phi_{0A}}{r_is_A}\right) \tag{31}$$

Using

$$r_is_A = \frac{V_A}{V_B}s_B \tag{32}$$

and recalling that $r = V_A/V_B$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2}\left(1 + \frac{K_A\Phi_{0A}}{r}\right) \tag{33}$$

Similarly, for the volume fraction of ether units present in the mixture

$$\Phi_A = \Phi_{0A}\left[1 + \frac{K_A\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] \tag{34}$$

Consequently, the equations used previously to describe the stoichiometry of associating species are equally valid when expressed in terms of "interacting units" or chemical repeat units. The equilibrium constants absorb a term $s_B = V_B/V_\beta$ to account for the difference in size or number of segments. If the quantity V_β could be determined, then an absolute value of the equilibrium constant would be defined. Unfortunately, the quantity s_B cannot be determined from stoichiometric equations alone. A set of similar urethanes can be studied and values of $K_B = K_\beta/s_B$ determined from infrared spectroscopic measurements, but this quantity will simply vary directly with the ratio of the size of the molecules, and we have insufficient information to calculate s_B. As we will see, however, a knowledge of s_B is not necessary for the calculation of phase behavior.

Free Energy of Mixing

In a review of the thermodynamics of polymer solutions Flory[21] wrote "Instead of seeking a theory which is accurate in detail as well as comprehensive in scope, it may be more fruitful to adopt a simpler treatment of reasonable generality at sacrifice of accuracy of representation of individual cases".

Our initial aim in this work is just that; obtain a simple treatment that qualitatively predicts observed behavior but that can be later modified, where necessary, to obtain better quantitative agreements with experiment. Accordingly, we choose a simple Flory–Huggins expression for the free energy of mixing to which we simply add a term ΔG_H accounting for the free energy associated with the changing pattern of hydrogen bonding that occurs as a function of blend composition. This assumption is not as extreme as might appear at first sight. For small molecules associated in the form of hydrogen-bonded chains it is a valid statistical mechanical[2] approach to treat mixing of the equilibrium distribution of "polymers" with solvent according to the Flory–Huggins theory. The only problem is that the equilibrium distribution of "polymers" changes with dilution, sometimes drastically if the solvent can also form hydrogen bonds with the solute. Flory[7,8] demonstrated that this situation can be handled through the correct choice of reference state, which he identified as one where the molecules are separate and oriented. An expression for the free energy of mixing the equilibrium distribution of polymers found in initially pure solute with solvent, relative to this reference state, is thus obtained. A similar expression for the free energy of mixing the (different) equilibrium distribution of hydrogen-bonded polymers found subsequent to dilution with the defined amount of solvent, again relative to Flory's reference state, is also determined. The difference between these two expressions then gives the free energy change of mixing relative to the initial, separate species. Clearly, this treatment involves no additional assumptions to those implicit in lattice models. The physical forces representing non-hydrogen-bonding interactions are equivalent to those between covalently linked polymers of the same chain length and solvent molecules and can thus be defined by the usual χ parameter.

The equation obtained in this manner contains expressions for the combinatorial entropy of mixing together with terms that define a free energy change resulting from the change in the number of molecules in the mixture that is a consequence of the changing pattern of hydrogen bonding as a function of dilution. If we now obtain the usual entropy of mixing the initial (pure solute) distribution of polymer molecules with solvent, i.e., assume these hydrogen bonds are now converted to covalent bonds so that there is no change in the number of molecules upon dilution, we then obtain a term we define as ΔG_H by subtracting this entropy of mixing from the free energy expression described above (without the "physical" interaction contribution). The resulting expression gives the free energy change associated only with the changing pattern of hydrogen bonding. As mentioned above, its derivation involves no more assumptions than those usually encountered in polymer lattice models and implicitly includes the changes in combinatorial entropy, entropy of disorientation, entropy of localization, and the enthalpy of hydrogen-bond formation through equilibrium constants that define the change in such quantities per hydrogen bond. It is a natural consequence of this model that the forces of association are treated separately from the weaker physical forces between the molecules.

The major assumption in this work is thus not the separate treatment of hydrogen-bonding interactions (ΔG_H) from the other forces involved in mixing (χ), which seems eminently reasonable for small molecules. For polymer molecules, however, the interacting functional groups are covalently linked to form polymer chains. If these chains are flexible and the hydrogen-bonding functional groups are sufficiently separated by other species, we can assume that there are no restrictions on the ability of such groups to form hydrogen bonds. We therefore write

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \Phi_A \Phi_B \chi + \frac{\Delta G_H}{RT} \quad (35)$$

where χ accounts for the "physical" interactions between segments (but may have an entropic as well as enthalpic component, as in Flory's early treatments of interactions; more sophisticated treatments, such as those involving free volume, will be ignoted until the imperatives of quantitative experimental data make them a necessity). The ΔG_H term was shown previously[15] to be

$$\frac{\Delta G_H}{RT} = \Phi_\beta \ln \left[\frac{\Phi_{\beta_1}}{\Phi_{\beta_1}{}^0 \Phi_\beta{}^{1/\bar{n}_H{}^0}} \right] + \frac{\Phi_\alpha}{r_i} \ln \left[\frac{\Phi_{0\alpha}}{\Phi_\alpha} \right] + \Phi_\beta K_\beta [\Phi_{\beta_1} - \Phi_{\beta_1}{}^0] + \Phi_\beta [1 - K_\beta \Phi_{\beta_1}] \left[\frac{X}{1 + X} \right] \quad (36)$$

where $X = K_\alpha \Phi_{0\alpha}/r_i$ and $\bar{n}_H{}^0$ is the number average length of the hydrogen-bonded chains in pure β. The derivation of this equation has been given previously in some detail,[15] but it is useful to briefly discuss its form and the meaning of the terms before considering the transformation to a description in terms of chemical repeat units. As described above, it is derived by considering the free energy of athermally mixing the hydrogen-bonded n-mers present in the mixture (using Flory's reference state, where they are initially separate and ordered) and subtracting a similar expression for mixing the n-mers present in the pure liquids. As a result, the first two terms have the form of a combinational entropy of mixing. The logarithm terms involve $\Phi_{0\alpha}$, Φ_{β_1}, and $\Phi_{\beta_1}{}^0$, the volume fractions of non-hydrogen-bonded units ($\Phi_{\beta_1}{}^0$ being the volume fraction of "monomers" in pure β), because in the derivation of this expression the chemical potentials of the stoichiometric components (μ_β, μ_α) are put equal to the chemical potentials of the monomer molecules (μ_{β_1}, μ_{α_1}), a relationship demonstrated by Prigogine[22] that depends only upon the complexes being in chemical equilibrium with one another. The derivation initially assumes that the β and α interacting units are not linked covalently into polymer chains, so the free energy of mixing term includes a combinational entropy of mixing component that has to be separated from the free energy changes associated solely with the change in hydrogen-bonded species. This term is equal to $(\Phi_\beta/\bar{n}_H{}^0) \ln \Phi_\beta + (\Phi_\alpha/r_i) \ln \Phi_\alpha$, the free energy of athermally mixing the two liquids with no change in hydrogen bonding. Finally, the last two terms in eq 36 are related to the decrease in the number of β–β hydrogen bonds and the increase in the number of α–β hydrogen bonds, respectively.

Given the initial assumptions of the association model, eq 36 is valid for the mixture, providing that the parameters Φ_β and Φ_α refer to the corresponding interacting units. Our task is to now substitute for these parameters those defined in terms of chemical repeat units, as this allows a calculation of their values from infrared spectroscopic measurements.[15] This might at first seem totally straightforward; simply replace all the terms in Φ_{β_1}, K_β, etc., by terms in Φ_{B_1}, K_B, etc. Obviously, ΔG_H decreases as the proportion of non-hydrogen-bonding material in each chemical repeat increases, but this results in a proportional decrease in the values of the equilibrium constant ($K_B = K_\beta/s_B$) and thus corresponding changes in the calculated stoichiometry and free energy of hydrogen-bond formation. By adjusting in this manner, however, we implicity assume that all of the inert segments in the chemical repeats associate in the same way as the interacting units; i.e., the whole chemical repeat unit occupies a single lattice site. This may be appropriate for small, stiff molecules, but even for low molecular weight materials a more appropriate model is one where the inert portion dangles from each segment giving a "hairy chain" structure of the type depicted in the Figure 1. We will return to this when we consider a lattice model.

For small molecules, we can model this situation in two ways. First, we can treat the inert segments as being simple diluent molecules that are not confined to particular sites on a lattice (i.e., each side arm is severed from the trunk of the chain and takes up random positions). Alternatively, we can apply a Flory lattice treatment and derive explicit equations for the model. Extending this latter treatment to a polymer, where all the interacting units are linked by inert segments into a covalently bonded chain is presently beyond our talents, however. Nevertheless, we can demonstrate that the two treatments outlined above give the *same* result, and it would therefore seem reasonable to assume that the treatment should also apply by extension to *flexible* polymer molecules.

Assuming that the inert portion of small molecules acts as a simple diluent, we now obtain an equation for ΔG_H using eq 30. In making these substitutions, we note that in the derivation of eq 36 we subtract a quantity $(\Phi_\beta/\bar{n}_H{}^0) \ln \Phi_\beta + (\Phi_\alpha/r_i) \ln \Phi_\alpha$ to obtain an excess function, one that solely reflects changes in free energy that are a result of changes in the pattern of hydrogen bonding. Substituting $\Phi_B = \Phi_\beta/s_B$ in this equation results in an extraneous ln

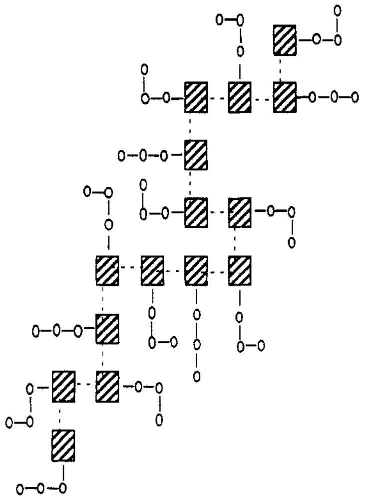

Figure 1. Chain of hydrogen bonded units with dangling "inert" segments.

$(1/s_B)^{1/\bar{n}_H^0}$ term, i.e., there is a nonzero entropy of mixing when $\Phi_B = 1$. This extraneous factor is simply due to the fact that in the pure urethane there are both interacting (Φ_B/s_B) and noninteracting $(\Phi_B(s_B - 1)/s_B)$ units, and in this simple treatment we have artificially made these distinguishable. Removing this factor we obtain

$$\frac{\Delta G_H}{RT} = \frac{\Phi_B}{s_B} \ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0}\left(\frac{1}{\Phi_B}\right)^{1/\bar{n}_H^0}\right] + \frac{\Phi_A}{r_i s_A} \ln\left[\frac{\Phi_{0a}}{\Phi_A}\right] + \frac{\Phi_B K_\beta}{s_B{}^2}[\Phi_{B_1} - \Phi_{B_1}{}^0] + \frac{\Phi_B}{s_B}\left[1 - \frac{K_\beta \Phi_{B_1}}{s_B}\right]\frac{\left(\dfrac{K_\alpha \Phi_{0A}}{r_i s_A}\right)}{\left(1 + \dfrac{K_\alpha \Phi_{0A}}{r_i s_A}\right)} \tag{37}$$

Using

$$s_A r_i = r s_B$$

$$K_A = \frac{K_\alpha}{s_B}$$

$$K_B = \frac{K_\beta}{s_B}$$

then

$$\frac{\Delta G_H}{RT} = \frac{1}{s_B}\left(\left[\Phi_B \ln\left\{\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0}\left(\frac{1}{\Phi_B}\right)^{1/\bar{n}_H{}^0}\right\} + \frac{\Phi_A}{r}\ln\left\{\frac{\Phi_{0A}}{\Phi_A}\right\}\right] + \Phi_B K_B(\Phi_{B_1} - \Phi_{B_1}{}^0) + \Phi_B(1 - K_B\Phi_{B_1})\left\{\frac{\dfrac{K_A\Phi_{0A}}{r}}{1 + \dfrac{K_A\Phi_{0A}}{r}}\right\}\right) \tag{38}$$

Note that in this treatment the lattice cell size is defined by the "interacting unit". To obtain the free energy per molecule or segment defined by a chemical repeat unit we remove the factor s_B.

Lattice Model

A lattice model for a "hairy chain" is obtained by following Flory.[1,7,8] The number of sets of contiguous sites available to a chain of n interacting units, each with $(s_B - 1)$ side-arm segments, after j such chains have been added to the lattice is given by

$$\nu_{j+1} = (n_0 - ns_{B_j})\left(\frac{n_0 - ns_{B_j}}{n_0}\right)^{n-1}(\gamma - 1) \times (\gamma - 2)^{n-2}\left(\frac{n_0 - ns_{B_j}}{n_0}\right)^{n(s_B-1)}(\gamma - 1)(\gamma - 2)^{n-1}(\gamma - 1)^{n(s_B-2)} \tag{39}$$

The first term in parentheses is the number of sites available to the first interacting unit of the chain; the second is the volume fraction of sites that are empty and in the Flory treatment is assumed equal to the expectancy that a cell adjacent to one just occupied is also vacant. There are $(n - 1)$ such terms for the hydrogen-bonded chain. An equivalent term raised to the power $n(s_B - 1)$ represents the number of permissible segments available to the inert "side chains". The $(\gamma - 1)$ and $(\gamma - 2)$ terms, where γ is the coordination number of the lattice, are somewhat arbitrarily defined, depending on the order in which the main chain and side chains on the lattice are placed. These terms cancel from the final equations for the free energy, however, and for simple convenience and to a first approximation we replace all $(\gamma - 2)$ terms by $(\gamma - 1)$. The equation for the entropy of mixing a heterogeneous distribution of such chains is then

$$-\frac{\Delta S_M}{R} = n_S \ln \Phi_s + \sum N_n \ln(\Phi_n/ns_B) - \sum[N_n(ns_B - 1)][\ln(\gamma - 1) - 1] + N \ln \sigma \tag{40}$$

and the partial molar free energy of an n-mer in an athermal solution is thus

$$\frac{\Delta \bar{G}_n}{RT} = \ln(\Phi_n/ns_B) + ns_B\Phi_p\left(1 - \frac{1}{\bar{n}_n}\right) - (ns_B - 1)\ln(\gamma - 1) + \ln \sigma \tag{41}$$

Comparing this with eq 4 and the subsequent derivation of the equilibrium constants (eq 5–8) it can be seen that an expression relating the equilibrium constants

$$\frac{K_\beta}{s_B} = K_B = \frac{\Phi_{B_{n+1}}}{\Phi_{B_n}\Phi_{B_1}}\,\frac{n}{n+1} \tag{42}$$

is obtained directly. Similarly, an expression for the free energy change associated with the hydrogen-bonding interactions can be obtained from eq 41 by using the methods applied previously[15] to obtain eq 38. The factor $1/s_B$ simply arises from a conversion of the free energy equation from a description in terms of number of molecules to one where the reference volume is defined equal to V_β, the volume of the interacting unit. Note that a free energy of mixing for small molecules that includes a component identified above as ΔG_H can thus be directly obtained from a lattice model without further assumptions.

Discussion

Equation 38 for ΔG_H is a very pleasing result. It shows that the hydrogen-bonding contribution to the free energy of mixing not only can be equated to parameters defined in terms of the chemical repeat units and thus determined experimentally by infrared spectroscopy but also varies linearly with the factor $1/s_B$. This is entirely reasonable. As s_B gets larger or we include more "inert" (non-hydrogen-bonding groups) in the chemical repeat unit, then the predicted free energy contribution from hydrogen-bonding interactions should decline in direct proportion to the ratio of molar volumes. And it does.

To a first approximation we can calculate a value for s_B by assuming that the volume of the interacting unit is equal to the molar volume of the functional group involved, but this is unnecessary. In most situations of interest we calculate a free energy change with respect to a reference volume that is defined by an interacting molecule or the volume of a chemical repeat in a polymer (V_B). The change from a definition in terms of the volume of the interacting unit (V_β) results in the removal of the factor s_B from eq 38. The value of ΔG_H changes with the amount of "inert" material in the molecule through variation in the values of K_B and K_A (equal to K_β/s_B and K_α/s_B).

A second crucial and even more pleasing result of this treatment arises from the definitions of the equilibrium constants and the way they are used in the free energy equation. If the equilibrium constants K_β and K_α are characteristic of particular types of "interacting *units*" (e.g., urethane and ether functional groups) and assumed to be independent of the rest of the molecule or chemical repeat, a reasonable assumption for materials that are chemically similar (i.e., where we do not change things drastically by introducing groups that affect electronic structure or result in steric hindrance), then equilibrium constants determined in one system can be applied to structurally similar polymers by simply accounting for differences in their size. In effect the *strength* of the hydrogen bonds that do form (or more precisely, the free energy change associated with the formation of each bond) remains the same, but the *number* of interactions changes as a result of the different proportions of interacting and noninteracting units. This follows in a simple way from the definition of equilibrium constants in terms of chemical repeat units:

$$K_B = K_\beta/s_B \qquad K_A = K_\alpha/s_B \tag{43}$$

Both equilibrium constants are adjusted by the *same parameter* s_B (as they should for a consistent definition of lattice cell size). Consequently, the *same* equilibrium constants can be applied to a description of the phase behavior of, for example, a specific polyurethane with a whole range of polyethers. The differences in size of the polyether units are accounted for in the stoichiometric and free energy equations solely by the known factor $r = V_A/V_B$, the ratio of the molar volumes of the ether and urethane repeat units.

Conversely, the equilibrium constants for a range of polyurethanes will vary but can also be simply determined given that a value for one is known, as follows:

For polyurethane (a)

$$K_B{}^{(a)} = \frac{K_\beta}{s_B{}^{(a)}} = \frac{K_\beta}{V_B{}^{(a)}} V_\beta \tag{44}$$

For polyurethane (b)

$$K_B{}^{(b)} = \frac{K_\beta}{s_B{}^{(b)}} = \frac{K_\beta}{V_B{}^{(b)}} V_\beta \tag{45}$$

So

$$K_B{}^{(b)} = \frac{K_B{}^{(a)}}{V_B{}^{(b)}} V_B{}^{(a)} \tag{46}$$

In fact, this simple equation should allow a test of the validity of our assumption that a "true interacting unit" can be defined for a particular functional group in a range of different but structurally similar molecules or polymers. Values of K_B can be calculated from infrared measurements and plotted against $1/V_B$. The result should be a straight line of slope $K_\beta V_\beta$.

Acknowledgment. The theoretical work described here is aimed at providing a general framework for a range of problems involving the description of hydrogen bonding. Accordingly, we gratefully acknowledge the support of the National Science Foundation, Polymers Program, the Office of Basic Energy Sciences, Department of Energy, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. In addition, we are grateful for the support of the E. I. du Pont de Nemours and Shell Companies and to Dr. Stephen Howe for many intense and illuminating discussions.

Appendix: Two Equilibrium Constant Model for Self-Association

Stoichiometry. The equations describing the stoichiometry of binary mixtures when dimer formation in the self-associating component is described by a different equilibrium constant than the addition of each succeeding unit is straightforward and has been used by a number of authors to describe the self-association of alcohols in various solvents (see ref 17 and citations therein). The derivations are reproduced here under the assumption that the volume of the interacting unit is equal to the volume of the chemical repeat. The situation where these differ follows in a straightforward manner from the treatment given in the main body of this paper through the introduction of the factor s_B in the equations for the free energy.

We write the equilibria describing dimer and subsequent n-mer ($n > 2$) formation in the self-associating species as

$$B_1 + B_1 \overset{K_2}{\rightleftharpoons} B_2 \tag{A1}$$

$$B_n + B_1 \overset{K_B}{\rightleftharpoons} B_n \qquad (n \geq 2) \tag{A2}$$

where K_2 and K_B are defined according to Flory:

$$K_2 = \Phi_{B_2}/2\Phi_{B_1}{}^2 \tag{A3}$$

$$K_B = \frac{\Phi_{B_{n+1}}}{\Phi_{B_n}\Phi_{B_1}}\left(\frac{n}{n+1}\right) \tag{A4}$$

For the competing equilibrium

$$B_i + A_1 \overset{K_A}{\rightleftharpoons} B_iA \tag{A5}$$

where the A unit makes no distinction between forming a hydrogen bond to a dimer or an n-mer, we have

$$K_A = \frac{\Phi_{B_iA}}{\Phi_{B_i}\Phi_{0A}}\left(\frac{ir}{i+r}\right) \tag{A6}$$

where $r = V_A/V_B$ as in the main body of the text.

The stoichiometric relationships are simply obtained from materials balance considerations. The total volume fraction of all B units present in the mixture is give by

$$\Phi_B = \Phi_{B_1} + \sum_{n=2}^{\infty}\Phi_{B_n} + \sum_{i=1}^{\infty}\Phi_{B_iA}\left(\frac{i}{i+r}\right) \tag{A7}$$

We note that for formation of dimer, trimer, ..., n-mer, according to eq A1 and A2 we have

$$\Phi_{B_2} = 2K_2\Phi_{B_1}{}^2$$

$$\Phi_{B_3} = {}^3\!/_2 K_B\Phi_{B_2}\Phi_{B_1}$$

$$\vdots$$

$$\Phi_{B_{n-1}} = \frac{n-1}{n-2}K_B\Phi_{B_{n-2}}\Phi_{B_1}$$

$$\Phi_{B_n} = \frac{n}{n-1}K_B\Phi_{B_{n-1}}\Phi_{B_1}$$

By successive substitution of $\Phi_{B_{n-1}}$, $\Phi_{B_{n-2}}$, ..., Φ_{B_2}, we obtain

$$\Phi_{B_n} = nK_B{}^{n-2}\Phi_{B_1}{}^{n-2}K_2\Phi_{B_1}{}^2 \tag{A8}$$

hence

$$\Phi_{B_n} = \frac{K_2}{{K_B}^2} n(\Phi_{B_1} K_B)^n \tag{A9}$$

and

$$\sum_{n=2}^{\infty} \Phi_{B_n} = \frac{K_2}{{K_B}^2} \sum_{n=2}^{\infty} n(\Phi_{B_1} K_B)^n \tag{A10}$$

However, for $K_B \Phi_{B_1} < 1$

$$\sum_{n=1}^{\infty} n(\Phi_{B_1} K_B)^{n-1} = \frac{1}{(1 - K_B \Phi_{B_1})^2} \tag{A11}$$

So we rewrite eq A10 as

$$\sum_{n=2}^{\infty} \Phi_{B_n} = \frac{K_2}{{K_B}^2} \Phi_{B_1} K_B \sum_{n=1}^{\infty} n(\Phi_{B_1} K_B)^{n-1} - \frac{K_2}{{K_B}^2} 1(\Phi_{B_1} K_B)^1 \tag{A12}$$

Hence

$$\sum_{n=2}^{\infty} \Phi_{B_n} = -\frac{K_2}{K_B} \Phi_{B_1} + \frac{K_2}{K_B} \Phi_{B_1} \left[\frac{1}{(1 - K_B \Phi_{B_1})^2} \right] \tag{A13}$$

Similarly

$$\sum_{i=1}^{\infty} \Phi_{B_i A} \left(\frac{i}{i + r} \right) = \sum_{i=1}^{\infty} K_A \Phi_{B_i} \Phi_{0A} \left(\frac{n + r}{nr} \right) \left(\frac{n}{n + r} \right) = \frac{K_A \Phi_{0A}}{r} \sum_{i=1}^{\infty} \Phi_{B_i} = \frac{K_A \Phi_{0A}}{r} [\Phi_{B_1} + \sum_{n=2}^{\infty} \Phi_{B_n}] \tag{A14}$$

Substituting

$$\Phi_B = \Phi_{B_1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K\Phi_{B_1})^2} \right) \right] \left[1 + \frac{K_A \Phi_{0A}}{r} \right] \tag{A15}$$

Similarly, from

$$\Phi_A = \Phi_{0A} + \sum_{i=1}^{\infty} \Phi_{B_i A} \left(\frac{r}{i + r} \right) \tag{A16}$$

and using

$$\sum (\Phi_{B_1} K_B)^{n-1} = \frac{1}{1 - K_B \Phi_{B_1}} \tag{A17}$$

we obtain

$$\Phi_A = \Phi_{0A} + K_A \Phi_{0A} \Phi_{B_1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{1 - K_B \Phi_{B_1}} \right) \right] \tag{A18}$$

We note that for $K_2 = K_B$, eq A15 and A18 reduce to eq 25 and 26 in our preceding paper,[15] as they must.

Free Energy Equations. As before,[15] the free energy of athermally mixing the hydrogen-bonded n-mers is given by the Flory–Huggins expression

$$\frac{\Delta G_{ch}}{RT} = \sum n_{B_n} \ln \Phi_{B_n} + \sum_{n=0} n_{B_n A} \ln \Phi_{B_n A} \tag{A19}$$

Although this free energy expression should be relative to Flory's standard state for describing a system where there are chemical equilibria between polymer species, the entropy of disorientation term is omitted for simplicity of presentation. It cancels from the final expression. The next step is to obtain the chemical potentials:

$$\frac{\mu_{B_n} - {\mu_{B_n}}^*}{RT} = \ln \Phi_{B_n} + 1 - \frac{V_{B_n}}{V} \tag{A20}$$

$$\frac{\mu_{B_n A} - {\mu_{B_n A}}^*}{RT} = \ln \Phi_{B_n A} + 1 - \frac{V_{B_n A}}{V} \tag{A21}$$

where V, the molar volume is given by

$$\frac{1}{V} = \sum_{n=1}^{\infty} \frac{\Phi_{B_n}}{V_{B_n}} + \sum_{n=0}^{\infty} \frac{\Phi_{B_n A}}{V_{B_n A}} \tag{A22}$$

Equations A20 and A21 are defined relative to Flory's standard state (asterisk). The next step is to consider the chemical potentials of the monomers, $n = 1$ in eq A20 and $n = 0$ in eq A21, so that we can use Prigogine's[22] demonstration that the chemical potential of a stoichiometric component (e.g. μ_B) is equal to the chemical potential of the monomer (μ_{B_1}) for a set of complexes in chemical equilibrium. Equivalent equations are written for pure solutions of the individual components, ${\mu_B}^0$ and ${\mu_A}^0$, which are then subtracted from eq A20 and A21 to transform to a standard state defined as these pure solutions. Hence

$$\frac{\mu_B - {\mu_B}^0}{RT} = \ln (\Phi_{B_1}/{\Phi_{B_1}}^0) + \frac{V_{B_1}}{V^0} - \frac{V_{B_1}}{V} \tag{A23}$$

$$\frac{\mu_A - {\mu_A}^0}{RT} = \ln \Phi_{0A} + 1 - \frac{V_{0A}}{V} \tag{A24}$$

For a stoichiometric mixture of x_A and x_B moles we can then obtain a "chemical" free energy of mixing:

$$\frac{\Delta G_{ch}}{RT} = x_B \ln (\Phi_{B_1}/{\Phi_{B_1}}^0) + x_A \ln \Phi_{0A} - \frac{V_M}{V} + x_A + x_B \frac{V_{B_1}}{V^0} \tag{A25}$$

where

$$V_M = x_A V_A + x_B V_B \tag{A26}$$

These equations are precisely the same as those obtained previously.[15] Of course the relationship of Φ_{B_1} and Φ_{0A} to Φ_B and Φ_A follows the more complicated dependence on K_2, K_B, and K_A given in the preceding section. Similarly, expressions for V and V^0 are also more complicated, and it is these substitutions that we need to consider next.

With $V_{B_n} = nV_B$, the first term of eq A22 is given by

$$\sum_{n=1}^{\infty} \frac{\Phi_{B_n}}{V_{B_n}} = \frac{1}{V_B} \left[\sum_{n=1}^{\infty} \frac{\Phi_{B_n}}{n} \right] = \frac{1}{V_B} \left[\Phi_{B_1} + \sum_{n=2}^{\infty} \frac{\Phi_{B_n}}{n} \right] = \frac{1}{V_B} \left[\Phi_{B_1} + \frac{K_2}{{K_B}^2} \sum_{n=1}^{\infty} (\Phi_{B_1} K_B)^n - \frac{K_2}{{K_B}^2} (\Phi_{B_1} K_B) \right] \tag{A27}$$

For $K_B \Phi_{B_1} < 1$

$$\sum_{n=1}^{\infty} (\Phi_{B_1} K_B)^{n-1} = \frac{1}{1 - K_B \Phi_{B_1}} \tag{A28}$$

$$\sum \frac{\Phi_{B_n}}{V_{B_n}} = \frac{\Phi_{B_1}}{V_B} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{1 - K_B \Phi_{B_1}} \right) \right] \tag{A29}$$

Similarly

$$\sum_{n=0}^{\infty} \frac{\Phi_{B_n A}}{V_{B_n A}} = \frac{1}{V_B} \left[\frac{\Phi_{0A}}{r} + \frac{K_A \Phi_{0A}}{r} \left(\Phi_{B_1} \left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{1 - K_B \Phi_{B_1}} \right) \right) \right] \tag{A30}$$

We now let

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 - K_B\Phi_{B_1}}\right) \qquad (A31)$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\Phi_{B_1})^2}\right) \qquad (A32)$$

and substituting eq A29 and A30 obtain

$$-\frac{V_M}{V} = -V_M\left[\frac{\Phi_{B_1}}{V_B}(\Gamma_1) + \frac{\Phi_{0A}}{rV_B}[1 + K_A\Phi_{B_1}](\Gamma_1)\right] \qquad (A33)$$

But

$$V_M = x_B V_B/\Phi_B = x_A V_A/\Phi_A \qquad (A34)$$

Hence

$$-\frac{V_M}{V} = -\left[\frac{x_B\Phi_{B_1}}{\Phi_B}(\Gamma_1) + \frac{x_A\Phi_{0A}}{\Phi_A}[1 + K_A\Phi_{B_1}](\Gamma_1)\right] \qquad (A35)$$

Substituting for Φ_A and Φ_B from eq A15 and A18

$$-\frac{V_M}{V} = -\frac{x_B}{1 + X}\left[\frac{\Gamma_1}{\Gamma_2}\right] - x_A \qquad (A36)$$

where $X = K_A\Phi_{0A}/r$, as in the body of the text. Similarly for pure B

$$x_B V_B/V^0 = x_B\Phi_{B_1}{}^0\Gamma_1{}^0 \qquad (A37)$$

Noting that

$$\Phi_B{}^0 = \Phi_{B_1}{}^0\Gamma_2{}^0 = 1 \qquad (A38)$$

the last three terms in the free energy expression, eq A25, are given by

$$-\frac{V_M}{V} + x_A + x_B\frac{V_B}{V^0} = -\frac{x_B}{1 + X}\left(\frac{\Gamma_1}{\Gamma_2}\right) + x_B\left(\frac{\Gamma_1{}^0}{\Gamma_2{}^0}\right) = x_B\left[\left(\frac{\Gamma_1{}^0}{\Gamma_2{}^0}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + x_B\left(\frac{X}{1 + X}\right)\left(\frac{\Gamma_1}{\Gamma_2}\right) \qquad (A39)$$

a result obtained by using

$$\frac{1}{1 + X} = 1 - \frac{X}{1 + X} \qquad (A40)$$

This gives an equation in the same form as eq 36 upon conversion to a unit volume basis, multiplication by a reference volume V_B, and subtraction of the combinational entropy term for mixing components A and B with no change in hydrogen bonding:

$$\frac{\Delta G_h}{RT} = \Phi_B \ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0\Phi_B{}^{1/\bar{n}_H{}^0}}\right] + \frac{\Phi_A}{r}\ln\left[\frac{\Phi_{0A}}{\Phi_A}\right] + \Phi_B\left[\left(\frac{\Gamma_1{}^0}{\Gamma_2{}^0}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + \Phi_B\left(\frac{\Gamma_1}{\Gamma_2}\right)\left[\frac{X}{1 + X}\right] \qquad (A41)$$

Because $\Gamma_1{}^0/\Gamma_2{}^0$ reduces to $(1 - K\Phi_{B_1}{}^0)$ and Γ_1/Γ_2 to $(1 - K\Phi_{B_1})$ when $K_2 = K_B$, this equation is consistent with that derived by using a single equilibrium constant to describe self-association.

Relationship of Parameters to Experimental Data. To be useful, the parameters defining ΔG_H have to be experimentally determinable. As before,[15] we relate our infrared measurements to the fraction of nonbonded groups. For urethanes (and amides) the most convenient band for this is the carbonyl. The number of free groups is, of course, a count of the number of hydrogen bonded chains in the system. Accordingly, the fraction free carbonyls in the pure polyurethane, $f_F{}^0$, is also related to the number-average length of the hydrogen bonded chains:

$$f_F{}^0 = \sum_{n=1}^{\infty} N_{B_n} \Big/ \sum_{n=1}^{\infty} nN_{B_n} = \sum_{n=1}^{\infty} (\Phi_{B_n}/n) \Big/ \sum_{n=1}^{\infty} \Phi_{B_n} \qquad (A42)$$

Hence, substituting as above

$$f_F{}^0 = \Gamma_1{}^0/\Gamma_2{}^0 \qquad (A43)$$

$$\bar{n}_H{}^0 = 1/f_F{}^0 = \Gamma_2{}^0/\Gamma_1{}^0 \qquad (A44)$$

Similarly, in the blend

$$f_F = \Gamma_1/\Gamma_2 \qquad (A45)$$

Note that when $K_2 = K_B$, the above two equations for $f_F{}^0$ and f_F together with the stoichiometric relationships for Φ_A, Φ_B, and $\Phi_B{}^0$ (=1) are sufficient to calculate $\Phi_{B_1}{}^0$, Φ_{B_1}, Φ_{0A}, K_A, and K_B, given data from the pure self-associating polymer and one blend. This serves to fix the relationship between f_F and Φ_B that must be followed by all other blend compositions. In practice, of course, data over a range of concentrations are used to define the parameters and minimize the effect of errors. Introduction of a second equilibrium constant for self-association enormously magnifies the effect of these inevitable experimental errors and makes the determination of equilibrium constants a more complicated problem, not least because K_2 and K_B can no longer be fixed by data from the pure self-associating polymer alone. This is discussed in detail in the third paper of this series.

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