

Connectivity and Spacing Effects in Hydrogen-Bonding Polymer Solutions and Blends

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ABSTRACT: In recent experimental work, it was found that the number of hydrogen bonds in polymer mixtures is strongly influenced by chain-connectivity effects and the spacing of functional groups along the chain. In this article, the relationships between the equilibrium constants used to describe the number of hydrogen bonds in mixtures of various types (blends, solutions, random copolymers, etc.) is elucidated and described. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1273–1281, 1998

Key words: hydrogen bonding; polymer blends; polymer solutions

INTRODUCTION

Most theories of polymer solutions and blends deal with mixtures where the interactions between the molecules involve dispersion and relatively weak polar forces only. Because at ordinary temperatures such forces are much smaller than thermal energy, RT , it has seemed reasonable to assume a random mixing of molecules and, a more subtle point, the segments of polymer chains. In other words, the number of contacts between chain segments in a blend or segment/solvent contacts in a solution is assumed to be the same as in a mixture where these segments are “disconnected” and randomly mixed with solvent molecules or the disconnected segments of another chain. This gives rise to the usual $\phi_A\phi_B\chi$ interaction term in the Flory–Huggins theory,

where the $\phi_A\phi_B$ term is proportional to the number of AB contacts in a random mixture of A/B units.

Deviations from random mixing can occur for various reasons: If the interaction energy favors certain types of contacts over others, then one might expect a higher proportion of such contacts. Such deviations have often been handled using Guggenheim’s quasi-chemical approximation,¹ but calculations by Prigogine et al.² demonstrated that this model only allows small deviations from random contacts. This is because the χ term in systems with weak interactions is positive and unfavorable to mixing. As a result, even though one would expect significant deviations from random mixing as the interaction energy approaches RT , phase separation occurs well before this point. However, in systems where there is an interaction component to the free energy that is “strong” but favorable to mixing, such as those that hydrogen bond, there should indeed be and are non-random contacts; we will return to this point shortly.

A second reason for deviations from random contacts involves correlation or connectivity effects. It was pointed out by de Gennes³ that within the radius of gyration defined by a given chain there is a “correlation hole,” inside which

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the concentration of segments from other chains is depleted. It follows that one would expect more "like" contacts between polymer segments than would be predicted on the basis of segmental random mixing. Such intrachain contacts were included to some degree in the original work of Huggins⁴ and explicitly in complex contemporary treatments, such as those due to Szleifer⁵ and Schweizer and Curro.⁶ These latter approaches do not readily lend themselves to the everyday treatment of data; however, so in the "applied" or "practical" sense, it would be of some value to have a simple treatment that accounted for correlation or connectivity effects. Similarly, to test the validity and utility of this (and other) models, it would be of considerable importance to develop a technique that is capable of counting the number of contacts in blends and solutions. For a particular type of interaction (hydrogen bonds), such a technique is available (infrared spectroscopy). The measurement of contacts is to some degree limited, however, by various spectroscopic factors, and the interpretation of the results is complicated by the fact that we have deviations from random contacts due to favorable energetic factors superimposed upon connectivity or correlation effects. Nevertheless, by carefully comparing the number of hydrogen bonds in systems containing the same types of functional groups, but arranged in a different manner (e.g., blends versus random copolymers of the same units), considerable insight can and has been gained. This systematic experimental work was published in a series of articles.⁷⁻¹⁰ Here, our intention is to describe how these data can be treated using a fairly simple approach. Although our focus is on hydrogen-bonded systems, the ramifications of this work are much broader. Some of these ideas can be adapted to non-hydrogen-bonded polymer solutions in order to explain the observed composition dependence of the measured value of χ , and they also open the possibility of an experimental measurement of the Kuhn segment length for certain types of polymer segments. These ideas will be explored in a separate publication¹¹ and future work.

THEORY

In the model that we developed to describe hydrogen-bonded systems^{12,13} and the treatment described by Veytsman¹⁴ and Panayiotou and Sanchez,¹⁵ it is assumed that weak interactions

can be treated separately from nonspecific interactions, so that the partition function can be written

$$Z = Z_{FH}Z_H \quad (1)$$

where the Z_{FH} term describes the random mixing of *chains* (not necessarily segments) and their "physical" (nonhydrogen-bonded) interactions. As mentioned above, we considered the effect of intrachain contacts on this term in a separate publication.¹¹ The Z_H term imposes the constraints due to hydrogen bonding (including the fact that there are more hydrogen-bonded contacts than would be predicted on the basis of a random mixing of segments). The Z_H term can be written

$$Z_H = \sum_h \Omega_h \exp(-F_h/kT) \quad (2)$$

where h represents a certain distribution of hydrogen bonds and F_h is a free-energy term.

Our general points are most easily made by considering a specific example, representing the class of polymers that we have most often studied. Such mixtures involve one component that self-associates, such as poly(vinyl phenol), by which we mean it hydrogen bonds to itself in the pure state. The second component has only an acceptor group, such as an ester, as in acrylate, methacrylate, and acetate polymers. The types of hydrogen bonds that occur in such mixtures are illustrated in Figure 1. We represent phenol groups by the letter B , and note that these hydrogen bond in the form of chains, $B-B-B$, etc. For these types of mixtures, we can write the hydrogen-bonding partition function as

$$Z_H = \sum_h \Omega_O p_{BB}^{n_{BB}^h} p_{AB}^{n_{AB}^h} \times \exp[-n_{BB}f_{BB} - n_{AB}f_{AB}]/kT \quad (3)$$

The Ω_O term involves the combinatorics of distributing the hydrogen bonds between the functional groups of the system, while p_{BB} and p_{AB} are the probabilities that a B group is adjacent to a chosen B group and the probability that an A group is adjacent to a close B group ($p_{AB} = 1 - p_{BB}$), respectively. These terms account for the fact that segments or molecules must be next to one another to hydrogen bond. Each term enters the partition function n_{BB}^h and n_{AB}^h times,

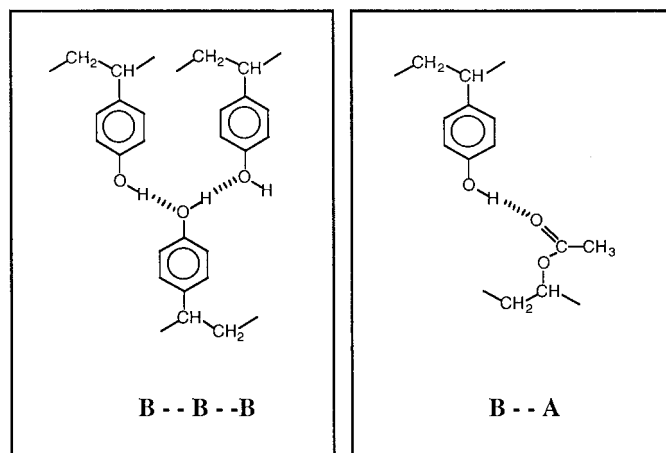


Figure 1 Schematic representation of hydrogen bonding between like units (self-association in poly(vinyl phenol): (left side) $B \cdots B$ -type hydrogen bonds and unlike units [poly(vinyl phenol)/poly(vinyl acetate)-type hydrogen bonds]; (right side) $A \cdots B$ -type hydrogen bonds).

where n_{BB}^h and n_{BA}^h are the number of BB and BA hydrogen bonds.

The formation of hydrogen bonds involves not only the energy of the interaction, but also a loss of rotational and translational degrees of freedom of the segments or molecules involved, so the exponential term must be weighted by a free-energy as opposed to just a simple energy term. However, the energy and entropy changes associated with each type of hydrogen-bond formation can be combined into a single parameter, an equilibrium constant, because from standard thermodynamics we have

$$\Delta g_{BB} = -RT \ln K_B \quad (4)$$

$$\Delta g_{AB} = -RT \ln K_A \quad (5)$$

where g represents the Gibbs free-energy change per hydrogen bond (essentially the same as the Helmholtz free energy under the usual conditions encountered in mixing polymers and solvents) and K_B and K_A are the equilibrium constants describing the formation of BB and AB hydrogen bonds, respectively. The beauty of this approach is that K_B and K_A can, in principle (there are some experimental difficulties), be measured directly by infrared spectroscopy through equations describing the stoichiometry of hydrogen bonding (i.e., the relationships among K_B , K_A , n_{BB}^h , n_{BA}^h , and composition).^{12,13}

The major difficulty is that for various reasons we cannot measure the self-association constant

K_B directly in polymers.¹³ (Actually, for OH groups, we need two equilibrium constants to describe the self-association, but this does not affect the general arguments that we are making here; it simply makes the algebra a little more involved.) In our previous work, we used a value from low molecular weight analogs of the system that we are considering (e.g., phenol), where K_B can be measured, and assume that the polymer has the same value. This assumption is to some degree wrong, but the error introduced is unimportant for most of the simple systems that we have studied in previous work. We will return to this point shortly, but given this assumed value of K_B , we then calculate a value of K_A from the experimentally observed fraction of A groups that are involved in AB hydrogen bonds (this can be readily measured by infrared spectroscopy) using the stoichiometric equations.^{12,13} It is relatively easy to show that it is the ratio K_A/K_B that is most important in determining the number of BB and AB hydrogen bonds, which, in turn, solely determine the contribution of hydrogen bonding to the free energy of mixing.¹²⁻¹⁵ For example, Figure 2 shows the calculated fraction of BB and AB hydrogen bonds for a system where $K_B = 50$ and $K_A = 100$. If both these values are doubled or both halved, such that the ratio is the same, the calculated fraction of bonded groups is changed only a little, certainly within the error of experimentally measuring these quantities.

Given a certain ratio of K_A/K_B , the contribution of hydrogen bonds to the free energy of mix-

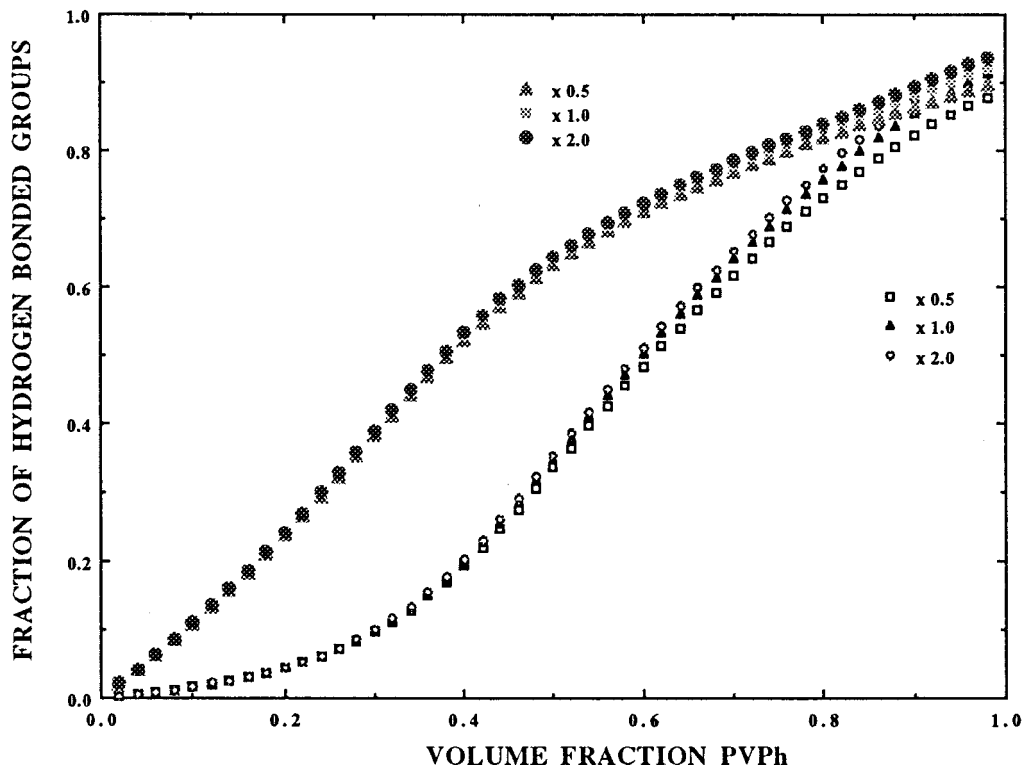


Figure 2 Calculation of the number of *BB* and *AB* hydrogen bonds in a system where $K_B = 50$, $K_A = 100$, and the ratio $K_A/K_B = 2$. The figure shows calculations for $K_A/K_B = 1$; $K_A/K_B \times 0.5$ (i.e., $K_B = 25$, $K_A = 50$) and $K_A/K_B \times 2$.

ing can be calculated for a wide range of homopolymer and copolymer blends. By assuming that “physical” interactions can be determined from solubility parameters, a wide range of phase behaviors has been successfully predicted^{12,13} for certain types of homopolymer and copolymer blends, principally those involving copolymers with “inert” or nonhydrogen-bonding units (i.e., vinyl phenol/styrene copolymers). However, the model starts to break down when we consider copolymers containing different types of hydrogen-bonding functional groups. Furthermore, it is unsatisfactory to leave the theory with what are to some degree empirical parameters. It would be far more satisfactory to have available “intrinsic” equilibrium constants, characteristic of certain types of functional groups, and then modify these to account for connectivity or other effects. Even more intriguing would be the possibility of experimentally measuring such effects, because this would allow us to “count” interchain and intrachain contacts in polymer systems (see below). Accordingly, we need to develop a suitable model to account for connectivity or intramolecular screening effects in a simple and practical man-

ner. Unfortunately, there is an additional complication. In recent experimental work, we discovered that there are also “spacing” effects, associated with changes in the degrees of freedom of hydrogen-bonding functional groups relative to one another when separated by “inert” (nonhydrogen bonding) copolymer units.¹⁰ However, these two effects enter the partition function in different ways: the first through the probability of units being adjacent [the p_{BB} and p_{AB} terms in eq. (3)] and the second through the free-energy weighting terms (f_{BB} and f_{AB} ; hence, the entropy change upon hydrogen bonding). We will discuss both and start by considering connectivity effects.

Intramolecular Screening or Connectivity Effects

There are two factors that need to be considered here: First, apart from the end groups, each segment of a polymer chain is covalently bonded to two neighbors. This is handled in the surface site fraction approach of Huggins⁴ and Guggenheim,¹ where the number of contacts allowed to a chain of (say) A units is defined by a factor q_A , where

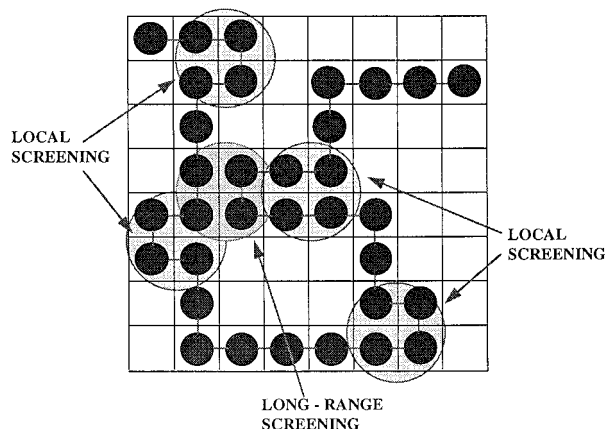


Figure 3 Illustration of intramolecular screening effects.

$$q_A z = z(M_A - 2) + 2 \quad (6)$$

where z is the lattice coordination number and M_A is the number of segments in the chain. Neglecting other effects, the factors p_{BB} and p_{AB} would then simply be given by

$$p_{AB} = \theta_A = \frac{N_A q_A z}{N_A q_A z + N_B q_B z} \quad (7)$$

$$p_{BB} = \theta_B = \frac{N_B q_B z}{N_A q_A z + N_B q_B z} \quad (8)$$

If M_A and M_B are both large, then $\theta_A \approx \phi_A$ and $\theta_B \approx \phi_B$. This is not so when there is a large mismatch in the size of the molecules, as in polymer solutions, unless the Flory approximation is made ($z \rightarrow \infty$). We will return to this point shortly.

We will now introduce intramolecular screening in a simple way. Essentially, we assume that a chain bends back on itself, both through local and long-range effects, as illustrated in Figure 3, so that there is a far higher proportion of same chain contacts than would be predicted on the basis of a random mixing of segments. Simulations of a polymer chain on a cubic lattice⁸ indicate that for a melt the fraction of same chain contacts, γ_s , is surprisingly large, of the order of 0.38 at high molecular weight, and has a molecular weight dependence of the form

$$\gamma_s = a - \frac{b}{M^{0.5}} \quad (9)$$

where a and b are constants. We would expect this fraction to be smaller, but still significant, for real systems (where presumably $z > 6$). Strong experimental evidence supporting the proposition that this effect is significant comes from a comparison of the number of "AB"-type hydrogen bonds found in blends of poly(vinyl phenol) with poly(ethyl methacrylate) relative to random copolymers of the same units.^{7,8} There are far more AB (i.e., OH to carbonyl) hydrogen bonds in the latter, where there is no distinction between the probabilities of same-chain and interchain contacts. In the blends, however, the phenolic OH and methacrylate carbonyls "see" more units of their own type because intramolecular screening and, hence, γ_s are significant.

If we assume that in the concentrated regime, where our experimental work is focused, there is essentially no chain expansion (or collapse) upon mixing, so that γ_s is an average that can be treated as a constant over most of the composition range, then the probability p_{BB} of a B chain segment being adjacent to another B segment is given by;

$$p_{BB} = \gamma_s^B + (1 - \gamma_s^B) \left[\frac{(1 - \gamma_s^B) \theta_B}{(1 - \gamma_s^B) \theta_B + (1 - \gamma_s^A) \theta_A} \right] \quad (10)$$

where the first term is simply the fraction of same chain B — B contacts. There are then $(1 - \gamma_s)$ interchain contacts, and this is multiplied by the factor in square brackets, which gives the fraction of all interchain contacts that are also BB . Other probabilities ($p_{AB} = 1 - p_{BB}$) follow from this in a simple manner.

In some preliminary work⁸ we have demonstrated how this approach can be applied to a blend of a copolymer with a homopolymer in the approximation that $\gamma_s^A \approx \gamma_s^B$ (i.e., the fraction of same chain contacts is the same for the two different types of chains). This allowed a fit to the measured fraction of hydrogen bonded groups in certain copolymer blends that could not be obtained under the old assumption of $p_{BB} \sim \phi_B$.⁸

In mixing two high molecular weight polymers of approximately the same chain stiffness (i.e., $\gamma_s^A = \gamma_s^B = \gamma$, $\theta_A \approx \phi_A$ and $\theta_B \approx \phi_B$), equation 10 is reduced to a particularly simple form

$$p_{BB} = \gamma + (1 - \gamma) \phi_B \quad (11)$$

However, things are not as simple in polymer solutions. If we first assume that component B is

a polymer while component A is a low molecular weight analogue (as in mixtures of poly(vinyl phenol) with ethyl isobutyrate, characterized in recent experimental work,⁷ then equation 10 takes the form;

$$p_{BB} = \gamma_s + (1 - \gamma_s) \left[\frac{(1 - \gamma_s)\theta_B}{(1 - \gamma_s)\theta_B + \theta_A} \right] \quad (12)$$

where $\gamma_s^B = \gamma_s$ and $\gamma_s^A = 0$, because there is no intramolecular screening effect in a "small" (non-polymeric) molecule. If we note that, in general,

$$\theta_B = \frac{N_B q_B}{N_A q_A + N_B q_B} = \frac{\frac{\phi_B}{M_B} q_B}{\frac{\phi_A}{M_A} q_A + \frac{\phi_B}{M_B} q_B} \quad (13)$$

and we define

$$\frac{q_B}{M_B} = 1 - \frac{2}{Z} \left(1 - \frac{1}{M_B} \right) = 1 - \gamma_i^B \quad (14)$$

$$\frac{q_A}{M_A} = 1 - \frac{2}{Z} \left(1 - \frac{1}{M_A} \right) = 1 - \gamma_i^A \quad (15)$$

then we obtain for polymer B/solvent A solutions

$$P_{BB} = \gamma_s + (1 - \gamma_s) \left[\frac{1 - \gamma}{(1 - \gamma\phi_B)} \right] \quad (16)$$

where

$$\gamma = \gamma_i^B + (1 - \gamma_i^B) \gamma_s^B \quad (17)$$

This latter definition gives only a minor simplification here, but becomes more significant in treating "physical" interactions in polymer solutions.¹¹

The second probability required in the partition function, p_{AB} , is then

$$p_{AB} = (1 - p_{BB}) = (1 - \gamma_s) \left[\frac{\gamma\phi_A}{(1 - \gamma\phi_B)} \right] \quad (18)$$

When B is the low molecular weight unit and the non-self-associating segments A are part of a polymer chain, we have

$$p_{BB} = \frac{\phi_B}{(1 - \gamma\phi_A)} \quad (19)$$

where γ is now

$$\gamma = \gamma_i^A + (1 - \gamma_i^A) \gamma_s^A \quad (20)$$

It is important to note the distinction in the two cases, because we always use the segment size of the self-associating B unit to define the lattice cell size in the partition function, rather than the size of the solvent molecule, as in the usual Flory-Huggins treatment.

The quantities p_{BB} and p_{AB} can now be introduced into the partition function and used to define the equilibrium constants K_A and K_B that serve to describe the stoichiometry of hydrogen bonding. In our original work,¹² we actually obtained the stoichiometric equations using simple mass balance considerations, where for the type of system being considered here we can write

$$\phi_B = \frac{\phi_{B_1}}{(1 - K_B \phi_{B_1})} \left[1 + \frac{K_A \phi_{A_1}}{r} \right] \quad (21)$$

$$\phi_A = \phi_{A_1} \left[1 + \frac{K_A \phi_{B_1}}{(1 - K_B \phi_{B_1})} \right] \quad (22)$$

where r is the ratio of molar volumes, V_A/V_B , while the quantities ϕ_{A_1} and ϕ_{B_1} are the volume fractions of A and B segments that are "free" (i.e., have no hydrogen-bonded partners whatsoever). The fraction of free carbonyl groups that are measured by infrared spectroscopy is simply ϕ_{A_1}/ϕ_A .

These equations implicitly assume that $p_{BB} = \phi_B$ and $p_{AB} = \phi_A$. When these assumptions no longer hold, because of connectivity (or other) effects, it can be shown⁸ that we can still use the same equations providing that we replace K_A and K_B with parameters \tilde{K}_A and \tilde{K}_B , defined as

$$\tilde{K}_A = K_A \frac{p_{AB}}{\phi_A} \quad (23)$$

$$\tilde{K}_B = K_B \frac{p_{BB}}{\phi_B} \quad (24)$$

K_A and K_B can then be thought of as "intrinsic" equilibrium constants, values that would be obtained in the absence of connectivity effects (i.e., when $p_{BB} \rightarrow \phi_B$ and $p_{AB} = 1 - p_{BB} \rightarrow \phi_A$).

This finally brings us to the value of K_A that we actually measure and its relationship to such inherent or intrinsic equilibrium constants. As mentioned above, we first assume a value of K_B

from measurements made on low molecular weight compounds [for poly(vinyl phenol), we have used phenol and ethyl phenol]. Let this value be K_B^L . We then calculate a value of K_A , say K_A^{calc} , by fitting the stoichiometric eq. (21) and (22) to (most often) data obtained over a range of compositions (taking care to be in a range where experimental errors are a minimum). Because it is the ratio K_A/K_B that is important in defining this data over a very wide range, we have then

$$\frac{K_A^{\text{calc}}}{K_B^L} = \frac{\tilde{K}_A}{\tilde{K}_B} = \frac{K_A}{K_B} \left[\frac{\phi_B (1 - p_{BB})}{\phi_A p_{BB}} \right] \quad (25)$$

This equation serves to establish the relationship between “measured” and “actual” equilibrium constants. We can now substitute the values of p_{AB} and p_{BB} obtained above for various situations (polymer blends, polymer solutions) and calculate K_A and K_B . Our aim was to obtain such “inherent” equilibrium constants. We will apply these equations to interpret the results of experimental solution work that is now in progress.

Spacing Effects

In recent experimental work,¹⁰ we found that the equilibrium constant K_A^{calc} describing the number of “AB”-type hydrogen bonds (e.g., phenolic OH to carbonyl) hydrogen bonds in poly(vinyl phenol)/poly(vinyl acetate) blends is less than the value found in copolymer blends where the vinyl phenol and vinyl acetate units are “spaced” (i.e., separated along the chain) with nonhydrogen-bonding units (dimethylbutadiene and ethylene, respectively). The incorporation of such units should not affect the intramolecular screening factor described in the preceding section, unless there is chain expansion in the concentrated region where our experimental studies were conducted, which seems unlikely. We believe that there is a separate effect at work here, related to the degrees of freedom that are lost when a hydrogen bond is formed. If we consider two small molecules *A* and *B* that form a hydrogen bond, as illustrated schematically in Figure 4, then clearly there are certain rotational and translational degrees of freedom that are lost, relative to the nonhydrogen-bonded case. If these *A* and *B* units are now incorporated into a polymer chain, there are now internal degrees of freedom associated with bond rotations that are lost, and these will be different from those in nonpolymeric molecules of the same

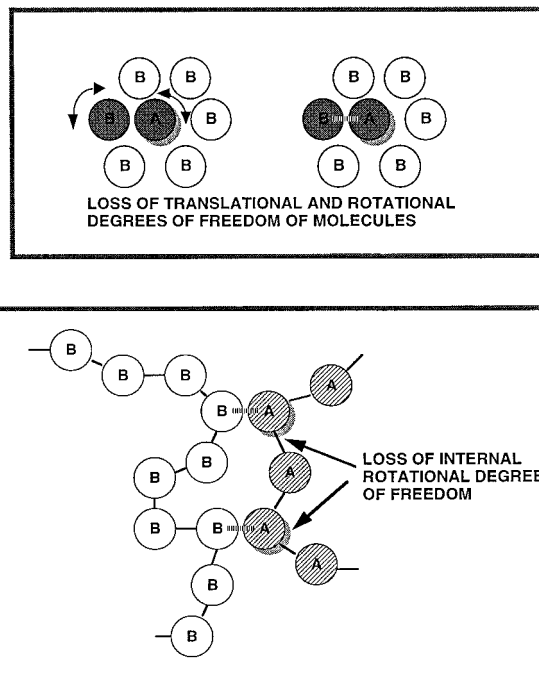


Figure 4 Schematic illustration of loss of degrees of freedom upon hydrogen bonding in (top) small molecules and (bottom) polymers.

type, as also illustrated in Figure 4. These factors influence the equilibrium constants describing hydrogen-bond formation directly, through the entropy component of the free-energy change upon hydrogen bonding (in contrast to “screening”, where the factors p_{BB} and p_{AB} are involved). For the illustrative example that we are using here, we can write (per mole)

$$K_B = e^{-\Delta h_{BB}/RT} e^{\Delta s_{BB}/R} \quad (26)$$

$$K_A = e^{-\Delta h_{AB}/RT} e^{\Delta s_{AB}/R} \quad (27)$$

where Δh_{BB} and Δs_{BB} are the enthalpy and entropy changes, respectively, that occur upon forming a BB hydrogen bond, etc. The frequency shifts that occur in certain infrared absorption bands are proportional to the enthalpy change, Δh , and in the systems we have studied these shifts are identical in polymer blends, random copolymers, polymer solutions, and mixtures of small molecule analogs.^{7–10} Accordingly, it is the entropy change, Δs (negative because of the loss of degrees of freedom), that is important.

Now consider the case of homopolymers such as poly(vinyl acetate) relative to a copolymer such as ethylene-*co*-vinyl acetate, as illustrated in Figure 5.

In the homopolymer, one can envisage a situation where a certain fraction of the vinyl acetate groups are hydrogen-bonded. Because of the steric restrictions on backbone bond rotations, the ability of the remaining nonbonded groups to form a hydrogen bond will be limited, even if adjacent to (say) a vinyl phenol segment, because they may not be able to orient themselves appropriately relative to their neighbors. The same argument holds for the vinyl phenol segments. If we now "space" the hydrogen-bonding functional groups with nonhydrogen-bonding and relatively flexible units, such as ethylene or dimethylbutadiene, then the ability of an acetate group to rotate, *relative to a neighboring acetate group along the same chain*, is increased. One can envisage a limit where the acetate groups are separated by a Kuhn segment length of, for example, ethylene units, such that they then become, in effect, freely hinged and rotating relative to their acetate neighbors in the same chain. Clearly, in such a chain of "spaced" units, the ability of groups to hydrogen bond will be greater than in a chain where there are greater restrictions on the rotational freedom of functional groups relative to one another.

In our initial experimental work,¹⁰ we found that the measured equilibrium constant for *AB* hydrogen bond formation, which we called K_A^{std} , and which again was calculated using the assumed value K_B^L defined above, varied with the "spacing" in both vinyl phenol/dimethylbutadiene and ethylene/vinyl acetate copolymer blends according to an empirical equation of the form

$$K_A^{\text{std}} = 112 - \left[\frac{1630}{V_A + R_A} + \frac{4100}{V_B + R_B} \right] \quad (28)$$

where the value of 112 is the limiting value for mixtures of "fully spaced" groups (i.e., low concentrations of hydrogen-bonding functional groups in each of the copolymer chains), while R_A and R_B are the molar volumes of the ethylene and dimethylbutadiene spacer groups, respectively. The quantities V_A ($= 70$) and V_B ($= 100$) are the molar volumes of the vinyl acetate and vinyl phenol segments. We previously advanced some preliminary ideas, based on effective contacts, but based on the rotational freedom factors described above we can now propose a more detailed and physically interesting model.

Consider the entropic contribution Δs_{AB} to the equilibrium constant K_A in eq. (27). This must have two components, related to loss of degrees of freedom of *A* units when hydrogen-bonded to *B* units and also loss of degrees of freedom of *B* units when hydrogen-bonded to *A*'s. These quantities will vary with the "spacing" or rotational freedom of *A* units relative to one another in the same chain and, similarly, the spacing of the *B* units (in their chains). If we let the spacing of the *A* and *B* units in the *homopolymers* [poly(vinyl acetate) and poly(vinyl phenol) in the example used here] be l_a and l_b , while the corresponding spacing in the *copolymers* is L_a and L_b , as illustrated in Figure 5, then we can assume a relationship of the form

$$\Delta s_{AB} = s_{AB}^{\infty} + \frac{l_a}{L_a} \Delta s_{ab} + \frac{l_b}{L_b} \Delta s_{ba} \quad (29)$$

where Δs_{AB}^{∞} is the value of the entropy change (from both *A* and *B* units) when the hydrogen-bonding functional groups are spaced such that they are effectively "freely hinged" with respect to one another. As the spacing is *reduced*, there are additional restrictions placed on the groups upon hydrogen bonding, because their rotational freedom is limited by the orientation of their neighboring groups. We assume that as we remove spacing groups there is an additional loss of entropy per unit length upon hydrogen bonding: Δs_{ab} for the *A* units (when hydrogen-bonded to a *B*) and Δs_{ba} for the *B* units (when hydrogen-bonded to an *A*). Note that all the Δs quantities in this equation are negative and we have assumed linear increases in entropy per spacer group removed. As Δs_{AB} gets larger (more negative, i.e., as spacing is decreased), the value of the equilib-

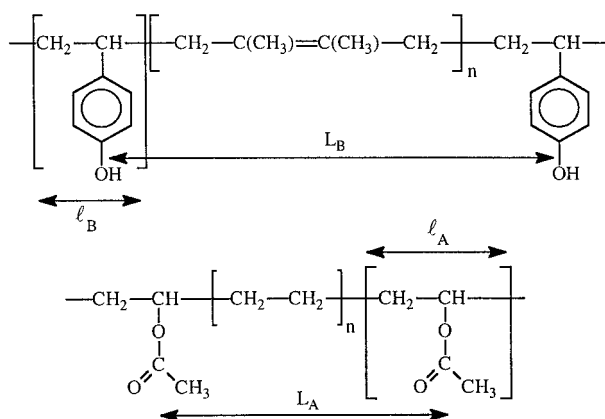


Figure 5 Definition of "spacing" distances in copolymers. The quantities l_a and l_b correspond to the distance (along the chain contour) between hydrogen-bonding functional groups in the homopolymers, while L_a and L_b are the corresponding distances between groups in the copolymers.

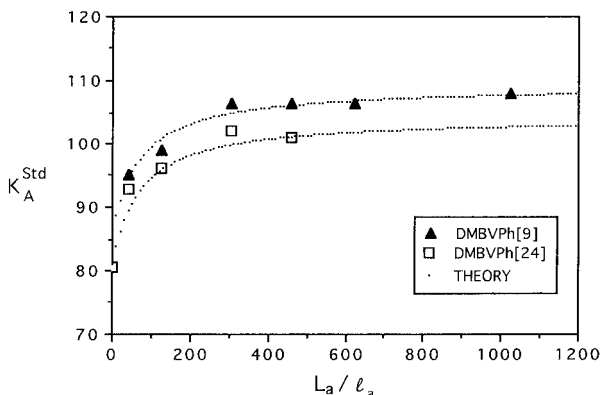


Figure 6 A plot of experimentally measured values of K_A^{std} versus the spacing parameter L_a/l_a for two different vinyl phenol-co-dimethylbutadiene polymers mixed with various ethylene-co-vinyl acetate polymers. Data were reported in ref. 10 and the dotted line is the fit obtained using eq. (32).

rium constant will get smaller, as experimentally observed. The limit in eq. (29) (Δs_{AB}^∞) should actually be reached as L_a and L_b approach the Kuhn segment lengths, but as long as these values are large relative to l_a and l_b (the spacing in the homopolymers), then this equation is a reasonable approximation. It is now possible to obtain an equation of the same form as that obtained by an empirical fit to experimental data [eq. (28)]. We first rewrite eq. (29):

$$\Delta s_{AB} = \Delta s_{AB}^\infty - \frac{l_a}{L_a} |\Delta s_{ab}^\dagger| - \frac{l_b}{L_b} |\Delta s_{ba}^\dagger| \quad (30)$$

then

$$K_A^{\text{std}} = e^{-\Delta h_{AB}/RT} e^{\Delta s_{AB}^\infty/R} e^{-l_a/L_a |\Delta s_{ab}^\dagger|/R} e^{-l_b/L_b |\Delta s_{ba}^\dagger|/R} \\ = K_A^\infty [e^{-l_a/L_a |\Delta s_{ab}^\dagger|/R} e^{-l_b/L_b |\Delta s_{ba}^\dagger|/R}] \quad (31)$$

Expanding the exponentials in a series and truncating after the first terms, we have

$$K_A^{\text{std}} = K_A^\infty \left[1 - \frac{l_a}{L_a} \frac{|\Delta s_{ab}^\dagger|}{R} - \frac{l_b}{L_b} \frac{|\Delta s_{ba}^\dagger|}{R} \right] \quad (32)$$

This equation is of exactly the same form as that found empirically in experimental work [eq. (28), see ref. 10], the only difference being the replacement of a ratio of molar volumes of the repeat units with a ratio of length parameters (l_a/L_a and l_b/L_b). Furthermore, using eq. (28), it

can be shown that the last two terms in brackets are of the order of $0.2 \rightarrow 0.4$, so that to a first approximation it would seem reasonable to neglect higher-order and cross-terms in the expansion of terms in eq. (31). Equation (32) provides a good fit to the experimental data as shown in Figure 6, where we have made the assumption that the ratio of length parameters L_a/l_a can be approximated by the corresponding ratio of molar volumes of the units. The apparent relationship of the spacing parameter to the Kuhn segment length of the spacing units is an intriguing one that we will explore in future work.

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