Hydrogen-Bond Cooperativity in 1-Alkanol+*n*-Alkane Binary Mixtures

Ram B. Gupta and Ray L. Brinkley
Dept. of Chemical Engineering, Auburn University, Auburn, AL 36849

Hydrogen-bond cooperativity is an effect when hydrogen bonding is influenced by the previously formed hydrogen bond on the molecules. Using Fourier-transform infrared spectroscopy, we have measured the extent of self hydrogen bonding in 1-hexanol and 1-pentanol dissolved in n-hexane. Conventional theories without hydrogen-bond cooperativity, such as the statistical-association-fluid theory, lattice-fluid-hydrogen-bonding theory, and associated perturbed-anisotropic-chain theory, cannot represent the experimental data accurately. The extended lattice-fluid-hydrogen-bonding theory that includes hydrogen-bond cooperativity agrees well with the experimental data. Study suggests that the equilibrium constant for the second hydrogen bond on 1-alkanol molecules is 10 times larger than that for the first hydrogen bond formation. Hence, strong hydrogen bond cooperativity exists in 1-alkanol self association. Equations of state dealing with 1-alkanol mixtures need to be modified to account for this strong hydrogen-bond cooperativity.

Introduction

Hydrogen bonding (*h*-bonding) plays an important role in fundamental sciences and in industrial applications (Lammers, 1991; Ross and Toczylkin, 1992; Ikhlaq, 1992; Hicks and Senules, 1991; Bestani and Shing, 1989; Olson and Cordray, 1992; Bourrel and Schechter, 1988; Missopolinou and Panayiotou, 1995; Green and Yan, 1990; Lee and Parrish, 1989; Gupta et al., 1993; Fulton et al., 1990; Yee et al., 1992; Nickel and Schneider, 1989; Poliakoff et al., 1995). The *h*-bond is a weak attractive interaction. However, it is stronger and has a much longer lifetime than the ordinary van der Waals interaction. In fact, the phase behavior of nonionic polar fluids is usually dominated by *h*-bonding (Prausnitz et al., 1986). The *h*-bond is perhaps the most important interaction to humans after the carbon-carbon bond since life on earth is based on water, a *h*-bonding molecule (Pimentel and McClellan, 1960).

The purpose of this study is to contribute toward our understanding of *h*-bonding interactions in fluid-phase equilibria encountered in an industrially important system, 1-alkanol+*n*-alkane binary mixtures. Accurate quantitative measurements can now be performed with recent advances in spectroscopy and computers. The concentration of non-*h*-bonded (free) and *h*-bonded species can be obtained by Fourier-transform infrared (FTIR) spectroscopy. Free and *h*-bonded species have molecular vibrations at different infrared frequencies. For example, the fundamental vibrational stretching frequency for non-*h*-bonded OH species is observed at 3,600–3,640 cm^{-1}, while the vibrational band for hydrogen-bonded OH species is found in the range 3,000–3,400 cm^{-1} (Martinez, 1986). The corresponding overtone bands are found at approximately 7,100 cm^{-1} and 6,900 cm^{-1} for free and *h*-bonded species, respectively (Luck et al., 1988; Coleman and Painter, 1996; Coleman et al., 1990; Luck, 1980; Walsh et al., 1989; Economou et al., 1991; Koh et al., 1993).

Using FTIR spectroscopy, Gupta et al. (1993) and Kazarian et al. (1993) have observed a large solvent effect on *h*-bonding equilibria. Using fluctuation theory, Veytsman and Gupta (1996) have shown how near-critical fluctuations can enhance this solvent effect. Maes and Smets (1993) have utilized matrix isolation FTIR spectroscopy to study *h*-bond cooperativity in HF, HCl, and H_2O. The presence of cooperativity, which is of primary importance for control and regulation of processes occurring in living organisms, has been supported by several theoretical calculations (Scheiner, 1991).

The main focus of this work is on *h*-bond cooperativity. For molecules having more than one *h*-bonding sites, such as

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Correspondence concerning this article should be addressed to R. B. Gupta.

1-alkanols, *h*-bonds can be cooperative. After formation of the first *h*-bond, the second *h*-bond may be easier or more difficult to form, depending upon the rearrangement of the electronic charges on the molecule. Thus, when a chain is formed, two molecules first bond to form a dimer, and then another molecule bonds to one of the two molecules of the dimer but due to cooperativity this bond is either stronger or weaker than the bond in the dimer (Sear and Jackson, 1996).

Our first objective is to measure *h*-bonding data using FTIR spectroscopy and then to analyze to see if bond cooperativity existed in 1-alkanol self *h*-bonding. The second objective is to examine current thermodynamic theories of *h*-bonding to see if they could accurately correlate/predict the spectroscopic behavior.

Experimental Studies

Apparatus and material

The experimental apparatus (Figure 1) consists of a mixing chamber, a pump (Fluid Metering Inc., model QG 400), a six-port injection valve (Rheodyne Model 7012 loop filler port), a temperature controller (Cole-Palmer Digi-Sense model 2186-20) and an IR cell (constructed in-house). The mixing chamber is initially charged with a known amount of *n*-hexane. The six-port injector allows the addition of fixed volumes of the *h*-bonding compound without risk of the loss of solution or contamination by atmospheric moisture. A temperature controller maintains the solution temperature passing through the IR cell within 0.1°C.

N-hexane (Fisher cat. no. H303-4, Optima grade) was used as received. *N*-pentanol (Aldrich cat. no. 39,826-8) and *n*-hexanol (Aldrich cat. no. H1,330-3) were dried with 4 Å molecular sieves (Fisher, cat. no. M514-500) to remove any trace amounts of water prior to use.

The IR cell, built at Auburn University, consists of two sapphire windows separated by a 0.5 mm thick stainless steel spacer and sealed with Teflon rings in an aluminum body. The cell is placed in the sample compartment of the FTIR spectrophotometer (Perkin-Elmer FTIR Spectrum 2000). Background moisture is removed by purging the compartment with nitrogen (BOC grade 5.0) for one hour. The cell and all tubing are insulated to aid in temperature control.

Spectral analysis

A background spectrum is recorded after the sample compartment has been purged and the solution has reached its set point temperature. The background consists of 50 spectra averaged over a two-and-a-half minute interval. Multiple scans reduce the amount of noise in the spectrum. The sample scan is performed by the same method after the injection of the *h*-bonding compound. FTIR spectra (Figure 2) are recorded with increasing 1-alkanol concentration.

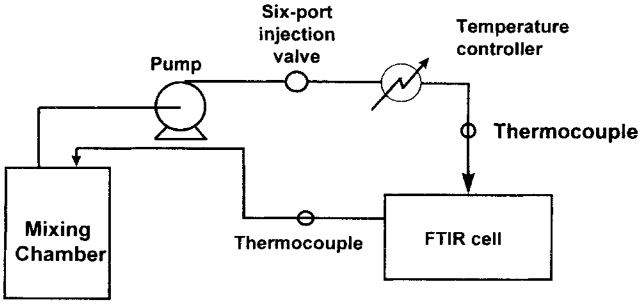

Figure 1. Apparatus for *h*-bonding measurements using FTIR spectroscopy.

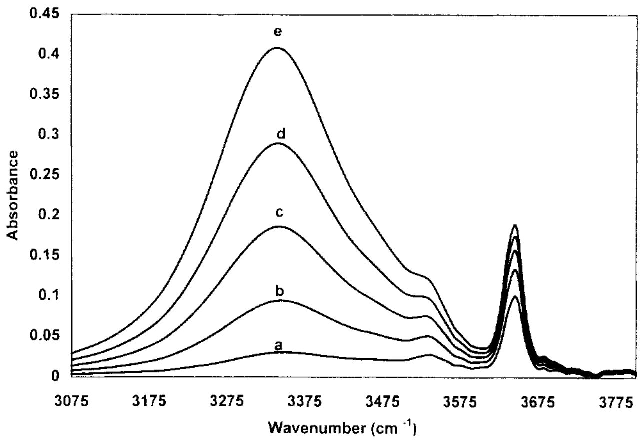

Figure 2. FTIR spectra for 1-hexanol + *n*-hexane mixtures with varying 1-hexanol mole fraction at 25°C.

(a) 0.0094; (b) 0.0115; (c) 0.0118; (d) 0.0139; (e) 0.0160.

At the low concentrations ($x_{1\text{-alkanol}} < 0.0007$), only one peak at 3,650 cm^{-1} is observed which corresponds to all of the 1-alkanol being in the free, that is, non-*h*-bonded form. The area of the peak is used to calculate the absorption coefficient for calibration. This absorption coefficient is assumed to be constant for the given 1-alkanol in the range of concentration studied here. In the exact sense, the free OH absorption coefficient at fundamental vibration is sensitive to its electronic environment. However, as long as the concentration of the *h*-bonding solute is kept relatively low, solvent effects should be negligible. This approach has been used previously by many researchers (Walsh et al., 1989; Economou et al., 1991; Fulton et al., 1990).

At mole fractions greater than 0.0007, intermolecular bonding peaks begin to appear. These peaks overlap the free peak and a spectral curve fitting process is required to isolate them to obtain the free peak area. A commercial software package, PeakSolve (Galactic Industries Corporation), is used which separates the desired peaks, as shown in Figure 3. In the curve fitting procedure, Voigt peak shape is used for all peaks. The Voigt shape is a combination of the Guassian and Lorentzian peak shapes and accounts for the broadening present in the FTIR spectrum (Economou et al., 1991). The peak center, height, Gaussian width, and Lorentzian width for each peak are optimized to fit the FTIR spectrum. The curve fitting, in addition to the free OH peak, produced up to six different *h*-bonded peaks as the concentration is increased in small steps. The bonded peaks represent the multiple bonding forms of a self-associating alcohol, that is, dimers, trimers, and so on. However, the exact configurations of these bonded forms are not the focus of this article and are therefore not explored further.

Once the free peak area has been calculated, the amount of free 1-alkanol is found by using the calibration curve. The

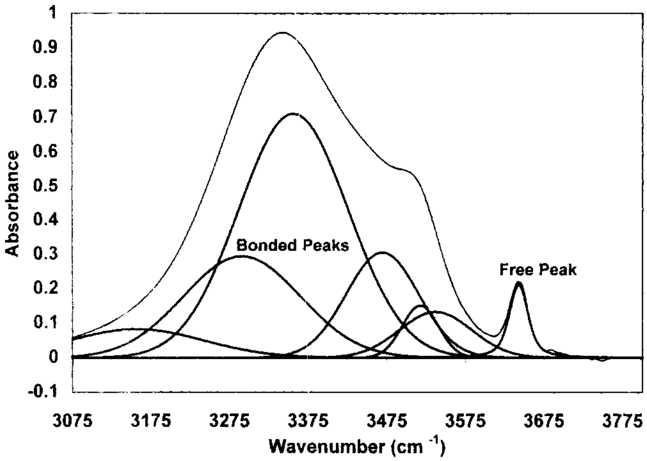

Figure 3. Deconvolution of a FTIR spectra for 1-pentanol + n-hexane mixture.

Peak at 3,645 cm^{-1} is due to free OH vibration and other peaks are due to h-bonded vibration. Top curve is experimental spectrum and others are deconvoluted spectra.

extent of h-bonding is calculated by subtracting free 1-alkanol from the total 1-alkanol present in the mixture. H-bonded peaks were not used to calculate the extent of h-bonding, due to the difficulty in knowing the absorption coefficient of these peaks.

New experimental data

Experiments were carried out at ambient pressure and at 25 and 35°C. For 1-pentanol + n-hexane mixtures, data are shown in Table 1. For 1-hexanol + n-hexane mixtures, data are shown in Table 2. As the alkanol concentration is increased, more h-bonding is observed due to higher probability of donor-acceptor encounters. This is also evident from the FTIR spectra of 1-hexanol + n-hexane in Figure 2 where bonded peak (in the range 3,200–3,600 cm^{-1}) increases with the increasing 1-hexanol content. Increasing temperature from 25°C to 35°C, h-bonding decreases due to higher thermal energy at the higher temperature.

Table 1. 1-Pentanol Self Hydrogen Bonding in 1-Pentanol + n-Hexane Binary Mixture

$T = 25$°C		$T = 35$°C	
1-Pentanol Mole Fraction	%H-Bonding $(M/N) \times 100$	1-Pentanol Mole Fraction	%H-Bonding $(M/N) \times 100$
0.01022	54.5	0.01142	42.1
0.01269	58.1	0.01389	46.3
0.01515	62.9	0.01634	50.9
0.01760	66.2	0.01879	54.5
0.02005	68.0	0.02124	58.0
0.02249	70.8	0.02367	60.9
0.02493	72.1	0.02611	63.4
0.02735	74.5	0.02853	66.3
0.02977	76.5	0.03095	67.1
0.03219	77.0	0.03336	68.5
0.03459	78.2	0.03576	69.9
		0.03816	71.4
		0.04055	72.6
		0.04293	73.9
		0.04530	74.8
		0.04767	76.1
		0.05004	76.2

Table 2. 1-Hexanol Self Hydrogen Bonding in 1-Hexanol + n-Hexane Binary Mixture

$T = 25$°C		$T = 35$°C	
1-Hexanol Mole Fraction	%H-Bonding $(M/N) \times 100$	1-Hexanol Mole Fraction	%H-Bonding $(M/N) \times 100$
0.01306	43.0	0.01392	37.6
0.01519	48.5	0.01603	41.8
0.01732	52.2	0.01814	45.0
0.01945	55.7	0.02025	48.1
0.02157	58.6	0.02236	50.5
0.02369	60.9	0.02444	52.6
0.02580	63.5	0.02653	54.9
0.02790	65.4	0.03070	58.3
0.03001	67.3	0.03277	60.5
0.03210	69.1	0.03485	62.5
0.03420	70.6	0.03691	63.4
0.03628	71.9	0.03898	65.2
0.03837	73.2	0.04104	67.0
		0.04309	68.3

Theory

Recent theories without H-bonded cooperativity

Recent theories of h-bonding are based on the chemical equilibria approach (Heidemann and Prausnitz, 1976), perturbed-hard-chain theory (Walsh and Donohue, 1989), statistical association (Huang and Radosz, 1990, 1991, 1993), and lattice-fluid-hydrogen-bonding (Veytsman, 1990; Panayiotou and Sanchez, 1991; Gupta et al., 1992; Gupta and Johnston, 1994; Gupta and Prausnitz, 1996). Even after a relatively long history of theoretical developments, an accurate equation of state for h-bonding fluids is not available.

Economou and Donohue (1991) reviewed and compared recent h-bonding models including associated-perturbed-anisotropic-chain theory (Ikonomou and Donohue, 1986, 1988), statistical-association-fluid theory (Chapman et al., 1988; Huang and Radosz, 1990, 1991, 1993), and lattice-fluid-hydrogen bonding theory (Panayiotou and Sanchez, 1991; Gupta et al., 1992). All these models provide following expression for the number of h-bonds, M, in 1-alkanol + n-alkane binary mixtures

$$M = \frac{\left(2N + \frac{N_T}{K}\right) - \sqrt{\frac{N_T}{K}\left(4N + \frac{N_T}{K}\right)}}{2} \tag{1}$$

where N is the number of 1-alkanol molecules, and N_T is the total number of molecules in the mixture, and K is the equilibrium constant. Here each 1-alkanol molecule is considered to have one proton donor and one proton acceptor site as suggested by Missopolinou and Panayiotou (1995) and Gupta et al. (1992). Alternatively, 1-alkanol can also be considered to have one proton donor and two proton acceptor sites (due to two lone pair of unbound p-orbital electrons of the 1-alkanol oxygen). We have chosen the former due to steric hindrance. Nonetheless, both cases provide same final conclusion about h-bonding in this article.

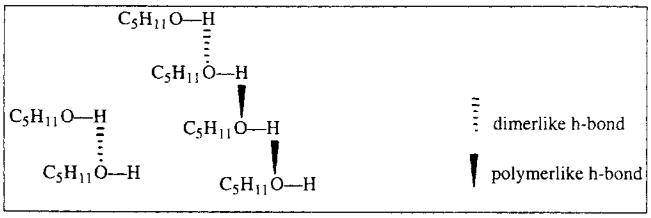

Figure 4. 1-Pentanol self-association with dimerlike and polymerlike *h*-bonds.

Calculation of %*h*-bonding (M/N) 100, from Eq. 1 are compared with the experimental data for 1-pentanol (Figures 5–6) and 1-hexanol (Figures 7–8). In each data set, the value of K is estimated by fitting the theory to all the data points. The difference between theory and experiment is as high as 10% hence, the above theories are not able to correlate *h*-bonding accurately. Experiments show that at higher 1-alkanol concentration more *h*-bonding is observed than that predicted by Eq. 1. This suggests that *h*-bond cooperativity is present, that is, once one *h*-bond is formed on the molecule, the second *h*-bond formation is less difficult to form.

In above theories, all *h*-bonds of the same kind have the same equilibrium constant. In other words, the formation of an *h*-bond is independent of whether other donor or acceptor groups of the molecules are *h*-bonded. This is true for some systems (such as containing carboxylic groups (Coleman et al., 1992)), but does not hold for 1-alkanol molecules as seen here and as shown previously by Karachewski et al. (1991).

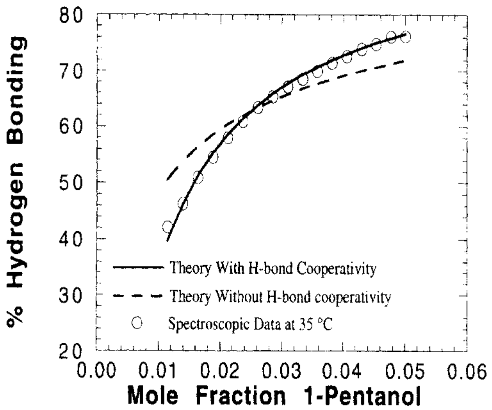

Figure 6. Hydrogen bonding in 1-pentanol + *n*-hexane mixtures at 35°C.

For theory with cooperativity, $K_p = 127$ and $\tau = 0.1$. For theory without cooperativity, $K = 181$.

Theory with H-bond cooperativity

A few theories that consider *h*-bond cooperativity include that of Karachewski et al. (1991), Veytsman (1993), and Sear and Jackson (1996). In this work, theoretical treatment is based on Veytsman's theory due to its simple and elegant derivation with a clear physical meaning for each term based on statistics. In addition, this theory is easily extended to multicomponent systems of molecules having any number of *h*-bond donor and acceptor groups. Veytsman (1993) developed a lattice theory that includes *h*-bond cooperativity for pure substances. We have extended it for *h*-bonding in 1-alkanol + *n*-alkane binary mixtures containing N 1-alkanol molecules and $(N_T - N)$ *n*-alkane molecules and having M_2 dimer-like *h*-bonds and $(M - M_2)$ polymer-like *h*-bonds (see Appendix). Free molecules first form a dimer-like *h*-bond and then, upon addition of more 1-alkanol, form polymerlike *h*-bonds (Figure 4). All polymerlike *h*-bonds are considered identical, but they have different equilibrium constant than dimerlike *h*-bonds, due to the *h*-bond cooperativity. The excess free energy due to *h*-bond formation F_H is given as

$$\frac{F_H}{kT} = M + N \ln\left(1 - \frac{M + M_2}{N}\right) \tag{2}$$

where T is absolute temperature and k is Boltzman's constant. The number of *h*-bonds are calculated from two simultaneous equations

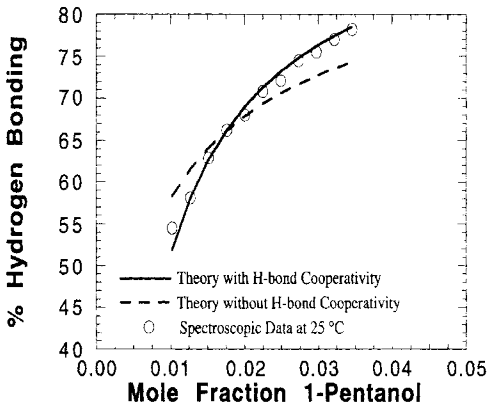

Figure 5. Hydrogen bonding in 1-pentanol + *n*-hexane mixtures at 25°C.

For theory with cooperativity, $K_p = 208$ and $\tau = 0.1$. For theory without cooperativity, $K = 328$.

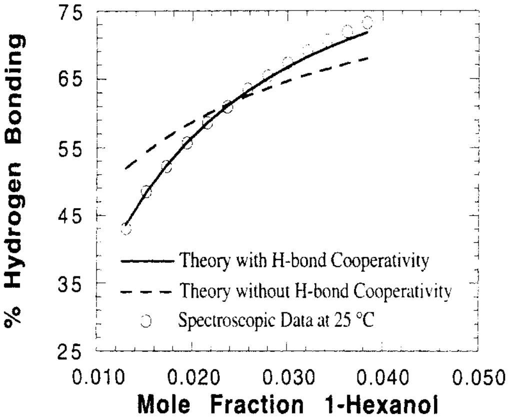

Figure 7. Hydrogen bonding in 1-hexanol + *n*-hexane mixtures at 25°C.

For theory with cooperativity, $K_p = 126$ and $\tau = 0.1$. For theory without cooperativity, $K = 172$.

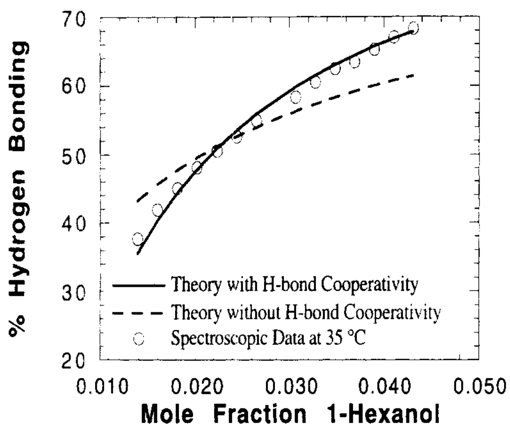

Figure 8. Hydrogen bonding in 1-hexanol + n-hexane mixtures at 35°C.

For theory with cooperativity, $K_p = 92$ and $\tau = 0.1$. For theory without cooperativity, $K = 96$.

$$M = \frac{\left(N - M_2 - \frac{N_T}{K_p}\right) + \sqrt{\left(N - M_2 - \frac{N_T}{K_p}\right)^2 + 4\frac{N_T M_2}{K_p}}}{2} \tag{3}$$

and

$$M_2 = \frac{N_T - \sqrt{(N_T)^2 - 4(\tau - 1)\tau M(N - M)}}{2(\tau - 1)} \tag{4}$$

where K_p is the equilibrium constant for polymerlike h-bonding and τ is the ratio of dimerlike to polymerlike equilibrium constant. For $\tau = 1$, there is no bond cooperativity and Eq. 3 reverts back to Eq. 1.

The values of K_p and τ are calculated from the optimized fit of the data points in Figures 5–8. A constant value of $\tau = 0.1$ for all four data sets is obtained; hence, the only other adjustable parameter that remained is K_p. For higher 1-alkanol concentrations, %h-bonding is predicted and compared with the experimental data in the dame figures. An excellent agreement is observed between theory and experiment, within the experimental errors, less than 1%. It is remarkable that with essentially one adjustable parameter in both theories, calculations from theory with h-bond cooperativity are in much better agreement with the experimental data than the theory without h-bond cooperativity.

A value of $\tau = 0.1$ represents that the equilibrium constant for polymerlike h-bonding is 10 times that of dimerlike h-bonding.

Conclusion

We have measured new data for h-bonding 1-alkanol + n-alkane mixtures using Fourier-transform-infrared spectroscopy. The observed data suggest that h-bond cooperativity plays an important role in 1-alkanol self association. The extended lattice-fluid-hydrogen-bonding theory that includes h-bond cooperativity can accurately predict the degree of h-bonding. Calculations suggest that the polymerlike h-bonds are 10 times easier to form than the dimerlike h-bonds.

Results of this study may have significant impact on the thermodynamics of h-bonding mixtures. All modern equation of states for associating mixtures needs to be reevaluated to assure that h-bond cooperativity is accounted for if it is present in the system.

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Appendix

The derivation here follows from the work of Veytsman (1993, 1990). Let us consider N_T total number of molecules in the binary mixture. This has N 1-alkanol molecules and the rest $(N_T - N)$ n-alkane molecules. The 1-alkanol molecules, upon self-association, form total M h-bonds; out of them M_2 are dimerlike and the rest $(M - M_2)$ are polymerlike. The excess free energy due to h-bonds in the mean field approximation is

$$F_H = \Delta F_p(M - M_2) + \Delta F_2 M_2 - kT \ln \Xi \qquad \text{(A1)}$$

where ΔF_P is the change of free energy upon a polymerlike h-bond formation, ΔF_2 is the change of free energy upon a dimerlike h-bond formation, and Ξ is the number of ways of distributing M h-bonds between neighboring donor/acceptor groups with a constraint that M_2 of them should be dimerlike.

The mean field approximation for Ξ is (Marsh and Kohler, 1986)

$$\Xi = \Xi_0 p^M \qquad \text{(A2)}$$

where Ξ_0 is the number of ways of distributing h-bonds disregarding that acceptor and donor must be neighbors, and p is the probability that the given donor/acceptor pair are neighbors. The probability is given as (Panayiotou and Sanchez, 1991)

$$p = \frac{c\tilde{\rho}}{N_T} \qquad \text{(A3)}$$

where c is a constant depending upon the geometry of the molecule, and $\tilde{\rho}$ is reduced density (for conditions in this article $\tilde{\rho}$ is also taken to be a constant) as in the lattice-fluid equation of state (Sanchez and Lacombe, 1976).

Now the expression for Ξ_0 is evaluated for the formation of first dimerlike M_2 h-bonds and then the polymerlike $(M - M_2)$ h-bonds. Donors can be chosen in $N!/(N-M)!$ ways, M_2 dimerlike acceptors can be chosen in $(N-M)!/(N-M-M_2)!$ ways, and polymerlike acceptors can be chosen in $M!/M_2!$ ways. However, M_2 dimerlike h-bonds are indistinguishable and $(M - M_2)$ polymerlike h-bonds are indistinguishable; hence, the result must be divided by $M_2!(M - M_2)!$ to avoid over counting. Thus

$$\Xi_0 = \frac{N!M!}{(N-M-M_2)![M_2!]^2(M-M_2)!} \qquad \text{(A4)}$$

Now, one may note here that only one acceptor has been designated for the oxygen atom. In reality, the oxygen has two lone electron pairs available to accept h-bonding donors.

In order to simplify the math, only one pair is modeled. We believe this to be justifiable since the steric hindrance of the alkyl group should reduce the ability of the oxygen to form a second bond. Using Stirling's approximation, Eqs. A1–A4 yield

$$\frac{F_H}{kT} = -M \ln K_p - M_2 \ln \tau + N \ln\left(1 - \frac{M + M_2}{N}\right) + M \ln\left(\frac{eN_T(M - M_2)}{M(N - M - M_2)}\right) + M_2 \ln\left(\frac{M_2^2}{(N - M - M_2)(M - M_2)}\right) \quad \text{(A5)}$$

where

$$K_p = c\tilde{p} \exp\left(\frac{-\Delta F_p}{kT}\right); \quad K_2 = c\tilde{p} \exp\left(\frac{-\Delta F_2}{kT}\right); \quad \tau = \frac{K_2}{K_p} \quad \text{(A6)}$$

Minimization of F_H with respect to M and M_2 yields

$$(M - M_2)N_T = K_p M(N - M - M_2) \quad \text{(A7)}$$

$$M_2^2 = \tau(M - M_2)(N - M - M_2) \quad \text{(A8)}$$

Excess free energy at this minimum is

$$\frac{F_H}{kT} = M + N \ln\left(1 - \frac{M + M_2}{N}\right) \quad \text{(A9)}$$

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