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Thermochemical Investigations of Hydrogen-Bonded Solutions. Part 7. Extension of Mobile Order Theory to Inert Solutes Dissolved in Binary Alcohol Ether and Other Interactive Cosolvent Mixtures

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THERMOCHEMICAL INVESTIGATIONS OF HYDROGEN-BONDED SOLUTIONS. PART 7. EXTENSION OF MOBILE ORDER THEORY TO INERT SOLUTES DISSOLVED IN BINARY ALCOHOL + ETHER AND OTHER INTERACTIVE COSOLVENT MIXTURES

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For the thermodynamics of Mobile Order and Disorder a molecule B in a liquid does not occupy a given place in a quasi-lattice, but rather occupies a mobile domain whose volume is equal to the total volume V of the liquid divided by the number N_B molecules of the same kind, i.e., $\text{Dom } B = V/N_B$. The center of this domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all part of their domain without preference. Hydrogen-bonded contacts lead to deviations with respect to this "random" visiting. These principles enable new equations to be derived for the entropy of mixing, and for the effect of H-bonds on the chemical potential of dissolved substances. From this point-of-view, addition and insertion H-bonds are essentially different. In the present study general equations are deduced for predicting the solubilities of inert solutes in various noncomplexing and complexing binary solvent mixtures. Nonspecific solute-solvent interactions are eliminated from the final derived predictive expressions in favor of the experimental solute solubilities in the pure solvents. The limitations and application of Mobile Order theory is illustrated using experimental solubility data for anthracene dissolved in seven binary alcohol + dibutyl ether solvent mixtures.

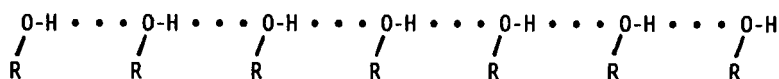
Keywords: Anthracene solubilities; insertion H-bonds; addition H-bonds

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INTRODUCTION

This work continues a systematic search for simple mixing models which will provide reasonable mathematical descriptions for the thermochemical properties of a solute in mixtures containing an alcoholic cosolvent. To date, we have examined both the applications and limitations of Mobile Order Theory to describe the solubility behavior of anthracene in 24 binary properties+alkane [1] and 7 binary alcohol+alcohol [2] solvent mixtures. The basic model [3–9] assumes that all molecular groups perpetually move in the liquid, and that neighbors of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume V of the liquid divided by the number N_A molecules of the same kind, i.e., $\text{Dom } A = V/N_A$. The center of domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential contacts lead to deviations with respect to this “random” visiting. This is especially true in the case of hydrogen-bonding which requires a hydroxylic hydrogen atom to follow most of the time the proton acceptor group of a neighboring molecule in its walk through the liquid, thus originating a kind of “mobile order”.

The success of Mobile Order theory in describing the solubility behavior of anthracene in binary solvent mixtures containing alcohol and/or alkane cosolvents suggests that the basic model might be applicable to other types of complexing systems, such as inert solutes dissolved in binary alcohol (B) + ether (C) solvent mixtures. Such systems are characterized not only by the presence of long H-bonded chains of the type



wherein alcohol molecules are temporarily “inserted” into the chain, but also by shorter chains

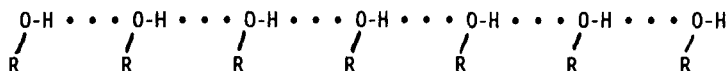


caused by addition bonds formed with an ether molecule. From the point-of-view of Mobile Order theory, addition and insertion bonds are essentially different. The two lone electron pairs on the ether oxygen atom provide acceptor sites for hydrogen-bond fixation. The ether molecule does not have a hydroxylic proton needed to continue the hydrogen-bonded chain. Addition bonds then terminate the chain at the site of the ether molecule, and the total number of hydrogen bonds that can be formed is determined by the number of alcohol molecules present. The hydroxylic proton H-bond donors are in the minority. This was not the case in our earlier studies involving binary alkane + alcohol [1] and alcohol + alcohol [2] mixtures where the number of hydroxylic oxygen and hydrogen atoms were equal. In the present communication an expression is derived for predicting the solubility of an inert crystalline solute in mixtures containing both alcohol and ether cosolvents.

Applicability of the newly-derived equation is illustrated using published experimental solubility data for anthracene dissolved in seven different binary alcohol + dibutyl ether solvent mixtures [10].

MOBILE ORDER THEORY: BASIC CONCEPTS

Essential features of Mobile Order theory, pertaining to solutions containing one and two alcohol cosolvents (with and without a noncomplexing hydrocarbon cosolvent), will be briefly reviewed in order to facilitate the extension of the basic model to more complex alcohol + ether mixtures having both insertion and addition hydrogen-bonds. As demonstrated by dipolar measurements, alcohol molecules form long open H-bonded chains moving in the liquid:



Such a chain is regularly interrupted, however. The spectroscopic results of Luck [11] showed that in ethanol at 25°C for instance, the interruption occurs only on the average every fifty or hundred molecules. Such a rupture corresponds to the loss of the (negative) energy of the one H-bond ($\approx -25 \text{ kJ mol}^{-1}/L$; where L is Avogadro's

number). NMR measurements indicate that the ruptures are not permanent and that in a time interval of about 10^{-7} seconds all molecules of encountered all possible situations of binding. If the ensemble is considered over a very short interval of time, then the resulting four situations are: bonded at both sides $\bullet\bullet\bullet\text{OH}\bullet\bullet\bullet$ (this is the most frequent situation in pure ethanol); bonded at the left but not at the right $\bullet\bullet\bullet\text{OH}$; bonded at the right but not at the left $\text{OH}\bullet\bullet\bullet$; and free at both sides OH (very seldom). Situations involving bonding at only one side are encountered in one or two percent of the cases.

Rupture of the H-bonded chain leads to the loss of a single bond, but there are two alcohol molecules involved in its breaking. Should the "lost" energy be ascribed to the $\bullet\bullet\bullet\text{OH}$ or to the $\text{OH}\bullet\bullet\bullet$? Some people will think that this is not a real problem in that one could decide arbitrarily to attribute the energy of the bond to only the first molecule. Alternatively, the energy $1/2 \Delta H_{\text{H-bond}}/L$ could be attributed to each situation $\bullet\bullet\bullet\text{OH}$ and $\text{OH}\bullet\bullet\bullet$. It is thus possible to manage the energy of the whole system with ensemble fractions using such rules. But it is not possible to preserve then a Boltzmann distribution of the states, because this amount of energy comes in an exponential, i.e., $\exp -0.5 \{\Delta H_{\text{H-bond}}/(LkT)\}$.

The statistics of Boltzmann is thus not applicable to the entities $\bullet\bullet\bullet\text{OH}$ and $\text{OH}\bullet\bullet\bullet$ and, as a consequence, their concentrations are not ruled by a Guldberg and Waage expression. What is the profound difference between the above hydrogen-bonding scheme and the dissociation of a molecular acid, such as acetic acid, is that in the solution neither the acetate nor hydrogen ions are in possession of the association energy. Molecular acetic acid is in possession of the bond energy all of the time that the molecule does not dissociate. In contrast, the entities $\bullet\bullet\bullet\text{OH}$ and $\text{OH}\bullet\bullet\bullet$ are still involved in hydrogen bonding, but the energy of the H-bond is only defined for the state of *complete insertion* at both sides. $\bullet\bullet\bullet\text{OH}$ and $\text{OH}\bullet\bullet\bullet$ are states of *incomplete insertion*. (Note, there are no comparable states of incomplete dissociation for acetic acid). $\bullet\bullet\bullet\text{OH}$ and $\text{OH}\bullet\bullet\bullet$ are thus not unambiguously in possession of the insertion bond. During their life-time (in contrast to the entities $\bullet\bullet\bullet\text{OH}\bullet\bullet\bullet$ and OH) the energy of the insertion bond is passing from the medium to the entity or vice versa. Or if one prefers, another way to describe this situation is to say that these two entities form in the ensemble a *couple* exchanging

permanently in the course of time the insertion energy through the intermediacy of the medium. To such couples, when they are found in the ensemble, we cannot ascribe the insertion energy.

This can however be done on a time schedule. When we find $\text{OH}\bullet\bullet\bullet$ or $\bullet\bullet\bullet\text{OH}$ in the ensemble, we know that for a time schedule both have to be considered as half of the time in possession of the insertion bond and half of the time as free. According to this principle the fraction of the time γ_{Bh} during which a given molecule alcohol B is free from H-bonding (and which governs the thermodynamic equilibrium) is related to the ensemble fractions (which no longer govern the equilibrium) by means of the equations

$$\gamma_{\text{Bh}} = \alpha_{\text{OH}} + 0.5\alpha_{\bullet\bullet\bullet\text{OH}} + 0.5\alpha_{\text{OH}\bullet\bullet\bullet} \quad (1)$$

$$1 - \gamma_{\text{Bh}} = \alpha_{\bullet\bullet\bullet\text{OH}\bullet\bullet\bullet} + 0.5\alpha_{\bullet\bullet\bullet\text{OH}} + 0.5\alpha_{\text{OH}\bullet\bullet\bullet} \quad (2)$$

Equations (1) and (2) clearly deviate from the ergodic rule, which requires that γ_{Bh} should be equal to α_{OH} . Inapplicability of the ergodic rule has dramatic consequences for thermodynamics. For example, the vapor pressure of ethanol is ruled by γ_{Bh} and not by the monomer fraction in the ensemble α_{OH} . The above procedure gives preeminence to time fractions for calculation of thermodynamic probability. Einstein defended this point-of-view in 1911.

The thermodynamics of Mobile Order theory expresses the equilibrium condition in terms of time fractions for the time schedule of a given molecule, and not in concentrations of the various entities *presumed* to be present in the ensemble. Thus, in the case of alcohols one considers the time fraction γ_{Bh} and not the concentrations of the various i-mers in the ensemble. This does not mean that these i-mers do not exist, but rather their concentrations do not govern the thermodynamic probability. γ_{Bh} is the fraction of the time during which a given molecule in the ensemble is free from H-bonding, this means the molecule does not possess the energy of the H-bond. But it is by no means the fraction of the time during which the molecule is free at both sides. As argued above, a molecule bonded at one side is free from H-bonding one-half of the time. This is not so easy to imagine. Fortunately, it is possible to relate the fraction under consideration to another physical concept which is much more

understandable, and which is more directly connected to the molecular motions. The quantity $1-\gamma_{\text{Bh}}$ corresponds also to the fraction of the time during which a given hydroxylic hydrogen atom follows the proton acceptor site of a neighboring molecule in its walk through the liquid, irrespective of whether the oxygen is followed by another OH proton or not. Hydrogen-bonding equilibrium is achieved whenever the ration of time fractions $(1-\gamma_{\text{Bh}})/\gamma_{\text{Bh}}$ reaches a given numerical value.

In the quantitative development of the thermodynamics of Mobile Order theory, the concept of "mobile domain" for a given kind of molecule is essential. Molecules in the pure liquid state do not occupy a fixed position in a kind of deformed lattice, as it is assumed in the quasi-lattice theory of Flory. A given molecule can be found after a sufficiently long time in every part of the whole volume, and contrary to the crystalline state, molecules in the liquid are not restricted to a particular position in the lattice. A given molecule, however, shares the whole volume of the phase, V , with all molecules of the same kind. The domain of a molecule in the liquid phase is therefore a mobile one which constantly moves over the whole space of the liquid phase.

The Mobile Order domain has well-defined characteristics:

- (1) The average volume is the same for all the molecules of the same kind. For example, in the case of alcohol B this domain corresponds to

$$\langle \text{Dom } B \rangle = V/N_B = V/(n_B L) \quad (L = \text{Avogadro's number}) \quad (3)$$

the total volume divided by the number of alcohol molecules. It may be considered as one molecule's share in the volume, which all the molecules of alcohol have at their disposal for their permanent translations in the liquid state.

- (2) The center of gravity of the domain perpetually moves in the solution; and
- (3) The average extent of the domain taken in a given direction over the time is independent of this direction, even for molecules which are anisotropic, i.e., $\text{C}_6\text{H}_5\text{CH}_3$.

The domain of a given molecule in the liquid does not only perpetually move with respect to an external observer; but also the

molecular groups belonging to the molecule do not have a fixed place in the domain. In a pictorial way one can say that the CH_3 group of toluene, for instance, constantly visits all parts of $\langle \text{Dom Toluene} \rangle$ in the course of time. These parts are distinguishable by the nature of the groups of neighboring molecules which are in contact with the domain at this place. In toluene, these groups may be the aromatic rings, the CH_3 methyl groups, or the hydrogen atoms of the neighboring molecules. The situation of maximal disorder and highest entropy is achieved whenever absolutely no preference exists for a given situation, and when all the equal parts of $\langle \text{Dom Toluene} \rangle$ are equally occupied by the given CH_3 group. Hydrogen-bonding affects the occupation of the domain. In the absence of hydrogen bonding, the OH hydrogen atom moves everywhere in its mobile domain $\langle \text{Dom } B \rangle$. This is no longer the case when this hydrogen atom is involved in hydrogen bonding. During the time that the OH hydrogen is bonded, it cannot "freely visit" its entire mobile domain, but rather has to be located in a small part v^0 of it, where it has the opportunity to be bonded to the proton acceptor site of the neighbor.

MOBILE ORDER THEORY: FUNDAMENTAL EQUATIONS

The ratio $v^0/\langle \text{Dom } B \rangle$ is clearly a quantitative factor related to the reduction of the choices in the occupation imposed by H-bonding on the hydroxylic hydrogen atom, and this ratio will therefore influence the two fractions $(1-\gamma_{\text{Bh}})$ and γ_{Bh} in the time schedule of the hydroxylic proton. $\langle \text{Dom } B \rangle$ increases upon addition of an inert solvent to the alcohol whereas v^0 remains constant. At a given temperature the ratio of the time fractions is then expected to be

$$(1 - \gamma_{\text{Bh}})/\gamma_{\text{Bh}} = K v^0 / \langle \text{Dom } B \rangle \quad (4)$$

When an inert solvent is added, and its volume fraction is ϕ_A , the last equation can be written as

$$1/\gamma_{\text{Bh}} = 1 + K_B C_B = 1 + (K_B/V_B)(1 - \phi_A) \quad (5)$$

where C_B is the analytical molar concentration (moles/liter) of the alcohol and K_B is the insertion constant of the alcohol in the chain.

The meaning of this equation is that for the OH proton the fraction in time that it can move freely from H-bonding increases when Domain B becomes larger. In a series of homologous alcohols Kv^0 is expected to remain approximately constant at a given temperature.

This equilibrium expression replaces the classical Guldberg and Waage equation, from which it fundamentally differs, because as explained above, it relates time fractions instead of concentrations. However, like a Guldberg and Waage equation, Eq. (5) is related to the Gibbs free energy of the system. In fact, the equation gives the condition for which the derivative of the free energy of the system with respect to the time fraction passes through zero. The corresponding value of the free energy G of the system is given by

$$\begin{aligned} G = & n_B RT [(1 - \gamma_{Bh}) \ln(1 - \gamma_{Bh}) + \gamma_{Bh} \ln \gamma_{Bh}] \\ & - n_B RT (1 - \gamma_{Bh}) \ln[v^0 / \langle \text{Dom } B \rangle] \\ & - n_B (1 - \gamma_{Bh}) RT \ln K + n_B G^{0, \text{free}} \end{aligned} \quad (6)$$

where $G^{0, \text{free}}$ is the molar free energy of B when no hydrogen bonds are formed. Differentiating G with respect to γ_{Bh} , and setting this derivative equal to zero, yields Eq. (4).

It can be shown that the change in the Gibbs free energy of the system brought about by the hydrogen bonds is given by

$$G^h = n_B RT \ln \gamma_{Bh} \quad (7)$$

The above equation is quite general for hydrogen-bonded liquids, and holds also for water. In this case, however, one has to take into account the presence of two proton donor sites in one water molecule. The effect of the hydrogen bonds on the Gibbs free energy of liquid water is

$$G^h = n_{\text{water}} RT \ln \gamma_{\text{OH}_2} \quad (8)$$

related to the fraction of time γ_{OH_2} during which the two hydrogen atoms are both not involved in H-bonding (irrespective of the situation of both lone electron pairs on the oxygen atom).

When the solvent does undergo hydrogen bonding, it is considerably more difficult to dissolve an inert foreign substance A . As a matter of fact, the derivative of G^h with respect to the number of moles of the

added inert substance is always positive, and the chemical potential of the dissolved A is therefore increased by an amount

$$\mu_A^h = (\partial G^h / \partial n_A)_{n_B} \quad (9)$$

The hydrogen bonding contribution to the solute's chemical potential, μ_A^h , provides a quantitative description of the so-called *hydrophobic effect* of water, which opposes itself to the dissolution of, for instance, alkanes in this solvent. Similarly, one can define in the same way the *alcoholophobic effect* of the H-bonds in alcohols against the dissolution of substances without hydrogen-bonding activity.

The alcoholophobic effect will be illustrated by considering the dissolution of an inert solute, A , in neat alcohols and select binary solvent mixtures containing one or two alcohol cosolvents. For pure alcohols, or for mixtures of an alcohol with an inert substance, γ_{Bh} is given by Eq. (5). For sake of simplicity, we have assumed that in Dom B the OH finds only one possible insertion site at v^0 . As pointed out by W. Luck [11], there are in liquid alcohols for each molecule two equivalent acceptor sites available, namely, the two one electron pairs on the oxygen atom. This means that the value of K is in fact multiplied by a factor 2, compared to the situation where only one site would be available. The hydrogen-bonding contribution to the Gibbs free energy is given by

$$G^h = -n_B RT \ln [1 + (K_B/V_B)(1 - \phi_A)] \quad (10)$$

and the alcoholophobic effect of the H-bonds on the inert A is quantitatively described by

$$\mu_A^h / (RT) = (V_A/V_B)\phi_B r_B \quad (11)$$

where r_B is

$$r_B = \{(K_B/V_B)\phi_B / [1 + (K_B/V_B)\phi_B]\} \quad (12)$$

a factor characterizing the self-associated solvent. For the lower primary alcohols at room temperature K_B is of the order of $5,000 \text{ cm}^3 \text{ mol}^{-1}$ as indicated by vapor pressure data. As a consequence, with a molar volume V_B of the order of $100 \text{ cm}^3 \text{ mol}^{-1}$, in the pure alcohol r_B

is of the order 0.98 and it is necessary to add a five-fold volume of an inert liquid, bringing ϕ_B as low as 0.2, in order to reduce r_B to the value of 0.90. Thus, for alcohol solvents in the vicinity of 25°C r_B is practically equal to one and the alcoholophobic effect of hydrogen bonding is to a good approximation described by

$$\mu_A^h/(RT) = (V_A/V_B)\phi_B \quad (13)$$

It should be noted that the insertion constant K_B decreases with increasing temperature, and at 45°C the numerical value is about 3,000 cm³ mol⁻¹ for the lower primary alcohols. Even at 45°C, where $r_B = 0.97$, Eq. (13) is still valid. In the temperature range 25–45°C the alcoholophobic effect is practically independent of temperature for the smaller primary alcohols.

The physical significance of the terms ruling the alcoholophobic effect can be discussed in more detail. The quantity μ_A^h results from

$$\mu_A^h/(RT) = n_B(d \ln \gamma_{Bh}/dn_A) = \phi_B(V_A/V_B)(1 - \phi_A)(d \ln \gamma_{Bh}/d\phi_A) \quad (14)$$

the differentiation of $\ln \gamma_{Bh}$ with respect to the number of moles of inert substance A . The latter two quantities in Eq. (14) are mathematically given by

$$(1 - \phi_A)(d \ln \gamma_{Bh}/d\phi_A) = \{(1 - \phi_A)(K_B/V_B)/[1 + (K_B/V_B)(1 - \phi_A)]\} = 1 - \gamma_{Bh} \quad (15)$$

Combination of Eqs. (14) and (15) yields

$$\mu_A^h/(RT) = \phi_B(1 - \gamma_{Bh})(V_A/V_B) \quad (16)$$

From the point-of-view of *mobile order* the four factors of this equation have a clear meaning: the alcoholophobic effect results from the extension of the mobile order existing in volume V_B to a larger volume, consecutive to the introduction of A molecules in the liquid; ϕ_B is the volume fraction of the component exhibiting the mobile order; $(1 - \gamma_{Bh})$ is the fraction of the time during which this happens; and the extension of the domain of the mobile order depends of course on the molar volume of the foreign molecule. It is also noted that the

factor r_B , which characterizes the self-associating alcohol solvent B , is

$$r_B = 1 - \gamma_{Bh} \quad (17)$$

equal to the fraction of time during which the OH proton follows a neighboring oxygen atom in its walk.

According to Eq. (14) the alcoholophobic effects in the pure lower primary alcohols at room temperature are purely entropic in nature, and are not related to an absorption of heat. It is thus completely wrong to ascribe the alcoholophobicity to the necessity of breaking hydrogen bonds in order to bring about the dissolution of the foreign substance in the alcohols. This error is very often encountered in the chemical literature. The reason for the lack of thermicity in the dissolution process is quite simple, namely, the mobile hydrogen bonded chains move along the invading molecules. No (or practically no) hydrogen bonds have to be broken.

To mathematically understand the entropic effect which lies at the origin of the alcoholophobicity, we need to carefully examine Eq. (6). For the primary alcohols under consideration $(1 - \gamma_{Bh})$ is practically equal to unity, and Eq. (6) reduces to

$$G = n_B RT \ln[\langle \text{Dom } B \rangle v^0] - n_B RT \ln K + G^{0, \text{free}} \quad (18)$$

The first term in this equation is positive and purely entropic. The free energy of the alcohols is higher and the entropy lower because hydrogen bonding forces the hydroxylic hydrogen to occupy the small part v^0 of the domain. Thus, hydrogen-bonding imposes in $\langle \text{Dom } B \rangle$ the obligations of the mobile order and Eq. (18) shows that the effect on G (or on S) is more important whenever $\langle \text{Dom } B \rangle$ is larger, as would be the case whenever a foreign substance is dissolved. The alcoholophobicity thus arises because: (1) the addition of small amounts of an inert substance does not destroy the hydrogen bonds; (2) mobile order is preserved; and (3) mobile order is now extended over a larger volume. Thus when pentane is added to an alcohol, the OH hydrogen atom goes on to follow a neighboring oxygen in its walk through the liquid, but it follows it in a larger volume. The alcoholophobic effect consists essentially in an extension of the mobile order over a larger volume. It is ruled therefore by the increase of

volume brought about by the addition of one mole of the inert substance to the hydrogen-bonded liquid.

These arguments can be extended to binary solvent mixtures as follows. In the case of an inert substance (A) dissolved in a binary alcohol (B) + alkane (C) solvent mixture the fraction of time γ_{Bh} during which a given molecule of alcohol B is free from hydrogen bonding is

$$1/\gamma_{\text{Bh}} = 1 + K_B C_B = 1 + (K_B/V_B)\phi_B^0(1 - \phi_A) \quad (19)$$

where ϕ_B^0 denotes the initial volume fraction composition of the alcohol cosolvent calculated as if the solute were not present. For simplicity, it will be assumed that the numerical value of K_B is independent of alkane cosolvent. Small changes in K_B 's numerical value will have an insignificant effect on the alcoholophobicity. The alcohol's mobile domain, Dom B , is larger due to the presence of the alkane cosolvent. Under such circumstances, the hydrogen bonding contribution to the solute's chemical potential is

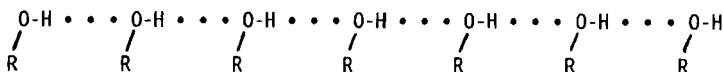
$$\mu_A^h/(\text{RT}) = (V_A/V_B)\phi_B^0(1 - \phi_A)r_B = (V_A/V_B)\phi_B^0(1 - \phi_A)(1 - \gamma_{\text{Bh}}) \quad (20)$$

where

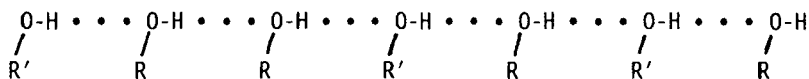
$$r_B = (1 - \gamma_{\text{Bh}}) = \{(K_B/V_B)\phi_B^0(1 - \phi_A)/[1 + (K_B/V_B)\phi_B^0(1 - \phi_A)]\} \quad (21)$$

Careful examination of Eqs. (20) and (21) reveals that the alcoholophobic effect decreases with decreasing alcohol proportion in the binary solvent mixture. Decreased alcoholophobicity results because both the fraction of time $(1 - \gamma_{\text{Bh}})$ and r_B become markedly less than unity, especially at low values of ϕ_B^0 .

Solvent mixtures containing two alcohol cosolvents are characterized by



and



both formation of self-associated and cross-associated hydrogen-bonds. The OH proton of alcohol molecule B finds not only an insertion site with the neighboring B but also $n_{B'}/n_B$ sites of the B' alcohol molecules occupying its domain. The equation of the mobile order becomes

$$\begin{aligned} (1 - \gamma_{Bh})/\gamma_{Bh} &= K_B^{\text{mix}} v^0 [1 + (n_{B'}/n_B)] / \langle \text{Dom } B \rangle \\ &= K_B^{\text{mix}} [(\phi_B/V_B) + (\phi_{B'}/V_{B'})] \end{aligned} \tag{22}$$

where K_B^{mix} is the insertion constant of alcohol B in the mixed chain, which may differ from K_B . A similar expression

$$(1 - \gamma_{B'h})/\gamma_{B'h} = K_{B'}^{\text{mix}} [(\phi_B/V_B) + (\phi_{B'}/V_{B'})] \tag{23}$$

with $K_{B'}^{\text{mix}}$ being the insertion constant for alcohol B' in the mixed chains. The effect of the H-bonds on the Gibbs free energy of the system and the alcoholophobic effect for an inert substance A dissolved in a binary alcohol (B) + alcohol (B') solvent mixture are given by

$$G^h = n_B RT \ln \gamma_{Bh} + n_{B'} RT \ln \gamma_{B'h} \tag{24}$$

$$\mu_A^h / (RT) = V_A (1 - \phi_A) [(\phi_B^0 r_B / V_B) + (\phi_{B'}^0 r_{B'} / V_{B'})] \tag{25}$$

Eqs. (24) and (25) respectively. The two structuration factors, r_B and $r_{B'}$, can be expressed

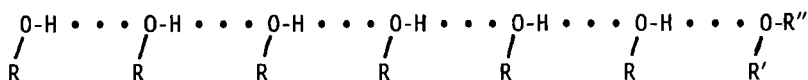
$$\begin{aligned} r_B = (1 - \gamma_{Bh}) &= K_B^{\text{mix}} (1 - \phi_A) [(\phi_B^0 / V_B) \\ &+ (\phi_{B'}^0 / V_{B'})] / \{1 + K_B^{\text{mix}} (1 - \phi_A) [(\phi_B^0 / V_B) + (\phi_{B'}^0 / V_{B'})]\} \end{aligned} \tag{26}$$

and

$$\begin{aligned} r_{B'} = (1 - \gamma_{B'h}) &= K_{B'}^{\text{mix}} (1 - \phi_A) [(\phi_B^0 / V_B) \\ &+ (\phi_{B'}^0 / V_{B'})] / \{1 + K_{B'}^{\text{mix}} (1 - \phi_A) [(\phi_B^0 / V_B) + (\phi_{B'}^0 / V_{B'})]\} \end{aligned} \tag{27}$$

in terms of the two insertion stability constants. This particular application differs slightly from our earlier solubility treatment [2] in binary alcohol+alcohol solvent mixtures in that we now assume *mixture H-bond stability constants* for insertion of the two alcohol molecules into the hydrogen-bonded chain. Earlier application distinguished between the point of insertion, and whether the hydrogen bonds formed involved similar or dissimilar alcohol molecules. The two treatments are identical if a single insertion constant is used for the two alcohols.

Finally, in binary alcohol (*B*) + ether (*C*) solvent mixtures, molecule *C* cannot be inserted into the hydrogen-bonded chain because it lacks a proton donor site. Solvent *C* can be added, however, to the end of the chain of *B* molecules



This particular case involves a combination of insertion and addition H-bonds. In the mixture, the domain of the *proton donor* (which is the alcohol molecule) is

$$\langle \text{Dom } h \rangle = V/N_B = V/(Ln_B) \quad (28)$$

partitioned into two parts, ϕ_B^0 and ϕ_C^0 . When the proton donor site is in the part ϕ_B^0 it finds in this region the proton acceptor site *B*., and may follow this site in its walk through the liquid. When the proton donor site is in the part ϕ_C^0 of its domain it may follow a *C* : site in its motions. Hydrogen bonds can at a given time only be found in the part ϕ_B of the volume because only this part contains donor sites. But the number of acceptor sites present in a part ϕ_B of the volume is only equal to the number donor sites in the same volume when V_B and V_C are equal. When V_C is larger than V_B this number is smaller. Now, each alcohol molecule in its domain may be in charge of $[\phi_B^0 + \phi_C^0(V_B/V_C)]$ hydrogen bonds. Whenever $V_C > V_B$ the number of H-bonds in which the $n_{B's}$ may be involved is thus equal to $n_B L [\phi_B^0 + \phi_C^0(V_B/V_C)]$.

The effect of these hydrogen bonds on the free energy of the system:

$$\begin{aligned} G^h &= (N_{\text{possible H-bonds}}/L) \ln (\text{chance to escape}) \\ &= n_B [\phi_B^0 + \phi_C^0(V_B/V_C)] \ln \gamma_{BH} \end{aligned} \quad (29)$$

depends upon their number and upon the possibility in the time γ_{Bh} to escape from their action. The chance in the time for the proton donor site of B to escape for H-bonding depends upon the concentration of the insertion and of the addition sites, and on the corresponding insertion and/or addition constants:

$$(1 - \gamma_{\text{Bh}})/\gamma_{\text{Bh}} = \{K_B(\phi_B^0/V_B) + (\phi_C^0/V_C)\}(1 - \phi_A) \quad (30)$$

The alcoholophobic effect on an inert substance A dissolved in a binary mixture containing an alcohol and ether is given by

$$\mu_A^h/(\text{RT}) = V_A(1 - \phi_A)\phi_B^0\{(\phi_B^0/V_B) + (\phi_C^0/V_C)\}r_S \quad (31)$$

with

$$r_S = \{\langle K_S \rangle [(\phi_B^0/V_B) + (\phi_C^0/V_C)](1 - \phi_A)\} / \{1 + \langle K_S \rangle [(\phi_B^0/V_B) + (\phi_C^0/V_C)](1 - \phi_A)\} \quad (32)$$

The fixation (insertion or addition) constant $\langle K_S \rangle$ depends on the composition of the solvent mixture. At high alcohol content $\langle K_S \rangle$ will be of the order of magnitude of the insertion constant K_B . For high values of K_S , the structuration factor, r_S , is approximately equal to unity and Eq. (31) reduces to

$$\begin{aligned} \mu_A^h/(\text{RT}) &= V_A(1 - \phi_A)\phi_B^0\{(\phi_B^0/V_B) + (\phi_C^0/V_C)\} \\ &= (1 - \phi_A)\phi_B^0(V_A/V_{\text{Solvent}}) \end{aligned} \quad (33)$$

where V_{Solvent} is the molar volume of the mixed solvent.

It should be noted that the above equation differs from that calculated without correction in Eq. (29). Without this correction one would have obtained

$$\mu_A^h/(\text{RT}) = (1 - \phi_A)\phi_B^0(V_A/V_B) \quad (34)$$

for the hydrogen-bonding contribution to the solute's chemical potential.

DEVELOPMENT OF A PREDICTIVE EXPRESSION FOR SOLUBILITY IN BINARY ALCOHOL (B) + ETHER (C) SOLVENT MIXTURES

For an inert crystalline solute dissolved in a self-associating alcohol solvent, Mobile Order theory describes the volume fraction saturation solubility $(\phi_A^{\text{sat}})_B$ as the sum of four separate contributions

$$\begin{aligned} \ln(\phi_A^{\text{sat}})_B = & \ln a_A^{\text{solid}} - 0.5[1 - (V_A/V_B)](1 - \phi_A^{\text{sat}}) \\ & + 0.5 \ln[\phi_A^{\text{sat}} + \phi_B(V_A/V_B)] - \phi_B^2 V_A (\delta'_A - \delta'_B)^2 (RT)^{-1} \\ & - r_B (V_A/V_B) (1 - \phi_A^{\text{sat}}) \end{aligned} \quad (35)$$

which, respectively, result from the breaking of collective solute-solute interactions in the crystalline lattice leading to solute fluidization, the entropy of mixing as given by the Huyskens and Haulait-Pirson model, [12] the changes in the nonspecific cohesion forces upon mixing, and the effect of solvent self-association. In Eq. (35) r_B is the mobile order structuration factor, and δ'_A and δ'_B denote the modified solubility parameters of the solute and self-associating solvent. For most published applications, r_B was assumed to be unity for strongly associated solvents with single hydrogen-bond chains like monofunctional alcohols, two for water and diols, and zero for non-associated solvents such as saturated hydrocarbons. Modified solubility parameters account for only nonspecific physical interactions, and in the case alcoholic (and other self-associating) solvents the hydrogen bonding contributions have been removed. Numerical values of δ'_{solvent} can be obtained from published compilations [7–9, 13–15] and were deduced either from experimental solubilities of solid alkanes or estimated using known values for similar organic solvents. The quantity a_A^{solid} refers to the fugacity of the pure hypothetical subcooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{\text{mp}} - T)/(RT T_{\text{mp}}) \quad (36)$$

the solute's molar enthalpy of fusion, ΔH_A^{fus} , and the normal melting point temperature, T_{mp} .

An earlier study in this series [1] has examined the extension of Mobile Order theory to the case of an inert solute dissolved in a binary

alcohol (B) + alcohol (C) solvent mixtures. The molar volume of the binary solvent was given by $V_{\text{solvent}} = x_B^0 V_B + x_C^0 V_C$, and δ'_{solvent} was approximated as a volume fraction of the modified solubility parameters of the two pure solvents, i.e., $\delta'_{\text{solvent}} = \phi_B^0 \delta'_B + \phi_C^0 \delta'_C$. Gordon and Scott [16] invoked a similar approximation, $\delta_{\text{solvent}} = \phi_B^0 \delta_B + \phi_C^0 \delta_C$, in using the Scatchard-Hildebrand solubility parameter theory to explain the solubility maximum observed in the phenanthrene-cyclohexane-methylene iodide system. Performing the aforementioned substitutions (with μ_A^h described by Eq. (20)), a relatively simple expression

$$\begin{aligned} \ln [a_A^{\text{solid}}/(\phi_A^{\text{sat}})] - 0.5[1 - V_A/(x_B^0 V_B + x_C^0 V_C)](1 - \phi_A^{\text{sat}}) \\ + 0.5 \ln [\phi_A^{\text{sat}} + \phi_B^0 V_A/(x_B^0 V_B + x_C^0 V_C)] \\ - (V_A/V_B)(K_B \phi_B^{02}/V_B)/[1 + K_B \phi_B^0/V_B] \\ = V_A[\phi_B^0(\delta'_A - \delta'_B)^2 + \phi_C^0(\delta'_A - \delta'_C)^2 \\ - \phi_B^0 \phi_C^0(\delta'_B - \delta'_C)^2](RT)^{-1} \end{aligned} \quad (37)$$

was obtained for the saturation solubility of a sparingly soluble solute (i.e., $\phi_A^{\text{sat}} \approx 0$). Through suitable mathematical manipulations, Acree *et al.* [1] eliminated the $V_A \phi_B^0(\delta'_A - \delta'_B)^2$ and $V_A \phi_C^0(\delta'_A - \delta'_C)^2$ terms from the basic model in favor of the measured solubility data in both pure solvents, $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$. The final derived expression

$$\begin{aligned} \ln \phi_A^{\text{sat}} = \phi_B^0 \ln (\phi_A^{\text{sat}})_B + \phi_C^0 \ln (\phi_A^{\text{sat}})_C - 0.5[\ln (x_B^0 V_B + x_C^0 V_C) \\ - \phi_B^0 \ln V_B - \phi_C^0 \ln V_C] + (V_A K_B \phi_B^0/V_B^2)/[1 + K_B/V_B] \\ - (V_A K_B \phi_B^{02}/V_B^2)/[1 + K_B \phi_B^0/V_B] + V_A \phi_B^0 \phi_C^0(\delta'_B - \delta'_C)^2(RT)^{-1} \end{aligned} \quad (38)$$

predicted anthracene solubilities in binary solvent mixtures containing either 1-propanol, 2-propanol, 1-butanol or 1-octanol with n -hexane, n -heptane, n -octane, cyclohexane, methylcyclohexane and 2, 2, 4-trimethylpentane to within an overall average absolute deviation of *circa* $\pm 4.4\%$ using a single self-association constant of $K_B = 5,000 \text{ cm}^3 \text{ mol}^{-1}$ for the four primary alcohols studied [1]. For informational purposes, we note that Eq. (38) was comparable to (and sometimes superior to) expressions based upon the more classical thermodynamic

models like the Mecke-Kempter and Kretschmer-Wiebe treatments [17, 18].

Using the fundamental principles discussed in the preceding section, we now extend Mobile Order theory to systems containing an inert solute dissolved in a mixed solvent having both a self-associating alcohol (*B*) and a proton acceptor ether (*C*) cosolvent. Here the alcoholophobic effect is given by Eq. (31). The derived expression

$$\begin{aligned} \ln \phi_A^{\text{sat}} = & \phi_B^0 \ln (\phi_A^{\text{sat}})_B + \phi_C^0 \ln (\phi_A^{\text{sat}})_C - 0.5 [\ln (x_B^0 V_B + x_C^0 V_C) \\ & - \phi_B^0 \ln V_B - \phi_C^0 \ln V_C] + (V_A/V_B) \phi_B^0 \gamma_B - (V_A/V_{\text{solvent}}) \phi_B^0 r_S \\ & + V_A \phi_B^0 \phi_C^0 (\delta'_B - \delta'_C)^2 (RT)^{-1} \end{aligned} \quad (39)$$

with

$$r_B = (K_B/V_B)/[1 + (K_B/V_B)] \quad (40)$$

and

$$r_S = \langle K_S \rangle [(\phi_B^0/V_B) + (\phi_C^0/V_C)] / \{1 + \langle K_S \rangle [(\phi_B^0/V_B) + (\phi_C^0/V_C)]\} \quad (41)$$

mathematically describes solute solubility in both pure solvents, and does not require a prior knowledge of the solute's enthalpy of fusion and melting point temperature. Elimination of the a_A^{solid} term from the predictive equation can lead to better solubility estimates, particularly in the case of high melting point solutes. Eq. (36) used to calculate a_A^{solid} is only an approximate expression. Two additional terms involving differences between the molar heat capacities of the subcooled liquid and solid were dropped from the more rigorous a_A^{solid} computation [19].

Readers should note that without the correction introduced in Eq. (29), one would obtain an almost identical predictive expression:

$$\begin{aligned} \ln \phi_A^{\text{sat}} = & \phi_B^0 \ln (\phi_A^{\text{sat}})_B + \phi_C^0 \ln (\phi_A^{\text{sat}})_C - 0.5 [\ln (x_B^0 V_B + x_C^0 V_C) \\ & - \phi_B^0 \ln V_B - \phi_C^0 \ln V_C] + (V_A/V_B) \phi_B^0 r_B - (V_A/V_B) \phi_B^0 r_S \\ & + V_A \phi_B^0 \phi_C^0 (\delta'_B - \delta'_C)^2 (RT)^{-1} \end{aligned} \quad (42)$$

except that V_B (rather than V_{solvent}) now appears in the term describing the alcoholophobic effect in the binary solvent mixture. The above derivation assumes that the ether can form an addition hydrogen-bond with alcohols. Solute-solvent complexation is not included in the model. While this may be an oversimplification in our application of Eq. (39) to anthracene solubilities in binary alcohol + dibutyl ether solvent mixtures, we feel at this time there is insufficient experimental data to warrant inclusion of an anthracene-alcohol hydrogen-bonded complex/interaction. Any slight reduction in the percent deviation would not outweigh the increased calculational complexity created by the additional solute-solvent association complexes.

RESULTS AND DISCUSSION

The descriptive ability of Eqs. (39) and (42) will be critically assessed using published solubility data for anthracene dissolved in seven binary alcohol + dibutyl ether solvent mixtures [10]. Each system contains solubility data at seven different binary solvent compositions spanning the entire mole fraction range, as well as measured anthracene solubility in dibutyl ether and pure alcohol cosolvents. The experimental mole fraction solubilities listed in the second column of Table I represent the arithmetic average of between four and eight independent determinations, with the measured values being reproducible to within ± 1.3 . Table I also contains the calculated values from Eqs. (39) and (42) assuming r_B and r_S to be approximately equal to unity. Moreover, the next to last column of Table I also gives "adjusted" values of r_S which were back-calculated from the experimental anthracene solubility data using Eq. (39) and assuming $r_B = 1$. Solute and solvent properties used in the Mobile Order theory predictions are listed in Table II.

Careful examination of Table I reveals that Eq. (39) with $r_B = 1$ and $r_S = 1$ provides remarkably accurate predictions for the two smaller alcohols, 1-propanol and 2-propanol. Deviations between predicted and observed values are less than 5% in these two systems. Deviations do increase, however, with increasing alcohol size. This is undoubtedly due to the low concentration of the OH sites and the reduction of the

TABLE I Comparison between experimental anthracene solubilities in binary alcohol (B) + dibutyl ether (C) solvent mixtures and predicted values based upon Mobile Order theory

x_C^0	$x_A^{sat, exp}$	$\phi_A^{sat, exp}$	Calculated Values		
			$\phi_A^{sat, a}$ Eqn. (39)	r_S^{adpt}	$\phi_A^{sat, a}$ Eqn. (42)
<i>1-Propanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000591	0.001180			
0.0532	0.000787	0.001473	0.001497		0.001338
0.0984	0.000961	0.001707	0.001755		0.001470
0.2230	0.001463	0.002278	0.002365		0.001811
0.3074	0.001784	0.002564	0.002674		0.002023
0.3948	0.002175	0.002895	0.002910		0.002225
0.6368	0.003018	0.003335	0.003220	0.84	0.002691
0.8042	0.003409	0.003372	0.003248	0.60	0.002945
1.0000	0.003615	0.003184			
<i>2-Propanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000411	0.000802			
0.0517	0.000570	0.001046	0.001044		0.000942
0.1011	0.000750	0.001303	0.001280		0.001079
0.2268	0.001226	0.001875	0.001846		0.001430
0.3126	0.001606	0.002275	0.002176		0.001665
0.4112	0.001989	0.002587	0.002487	0.92	0.001927
0.6286	0.002827	0.003127	0.002933	0.73	0.002455
0.7938	0.003267	0.003244	0.003104	0.56	0.002806
1.0000	0.003615	0.003184			
<i>1-Butanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000801	0.001306			
0.0564	0.001004	0.001562	0.001538		0.001438
0.1215	0.001246	0.001841	0.001794		0.001589
0.2719	0.001822	0.002412	0.002306		0.001924
0.3541	0.002085	0.002612	0.002529		0.002097
0.4627	0.002513	0.002940	0.002764	0.87	0.002314
0.6851	0.003259	0.003356	0.003059	0.55	0.002715
0.8369	0.003526	0.003357	0.003152	0.30	0.002954
1.0000	0.003615	0.003184			
<i>2-Butanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000585	0.000950			
0.0642	0.000807	0.001243	0.001186		0.001102
0.1203	0.001019	0.001502	0.001394		0.001237
0.2536	0.001544	0.002065	0.001862		0.001562
0.3457	0.001901	0.002390	0.002149		0.001785
0.3916	0.002085	0.002545	0.002278	0.80	0.001895
0.6777	0.003067	0.003169	0.002873	0.55	0.002546
0.7413	0.003211	0.003208	0.002960	0.50	0.002679
1.0000	0.003615	0.003184			

TABLE I (Continued)

x_C^0	$x_A^{sat, exp}$	$\phi_A^{sat, exp}$	Calculated Values		
			$\phi_A^{sat, a}$ Eqn. (39)	r_S^{adpr}	$\phi_A^{sat, a}$ Eqn. (42)
<i>2-Methyl-1-propanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000470	0.000760			
0.0627	0.000668	0.001026	0.000972		0.000905
0.1127	0.000837	0.001237	0.001147		0.001025
0.2427	0.001323	0.001778	0.001603		0.001351
0.3429	0.001693	0.002127	0.001932		0.001609
0.4450	0.002093	0.002466	0.002233	0.80	0.001871
0.6767	0.002936	0.003032	0.002764	0.58	0.002451
0.8164	0.003345	0.003215	0.002986	0.30	0.002780
1.0000	0.003615	0.003184			
<i>3-Methyl-1-butanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.000727	0.000993			
0.0753	0.000964	0.001264	0.001208		0.001151
0.1270	0.001142	0.001458	0.001358		0.001263
0.2884	0.001737	0.002048	0.001820		0.001623
0.3892	0.002076	0.002335	0.002090		0.001852
0.4656	0.002350	0.002555	0.002280	0.75	0.002026
0.6713	0.003026	0.003018	0.002717	0.57	0.002488
0.7950	0.003343	0.003176	0.002925	0.40	0.002758
1.0000	0.003615	0.003184			
<i>1-Octanol (B) + Dibutyl Ether (C)</i>					
0.0000	0.002160	0.002047			
0.0964	0.002415	0.002272	0.002170		0.002157
0.1982	0.002665	0.002488	0.002298		0.002273
0.3832	0.003114	0.002867	0.002525		0.002486
0.4861	0.003299	0.003015	0.002647	0.72	0.002604
0.5892	0.003459	0.003138	0.002765	0.65	0.002723
0.7847	0.003792	0.003393	0.002976	0.30	0.002944
0.8897	0.003722	0.003304	0.003081	0.25	0.003062
1.0000	0.003615	0.003184			

^aPredicted values are based upon the assumption that $r_B = 1.0$ and $r_S = 1.0$.

value of r_S . In 1-octanol, the predictions are low by as much as 13%. In comparison, Eq. (42) systematically underestimates the observed anthracene solubilities by 15–30% in the case of the smaller alcohols. One must thus conclude that the correction factor introduced into Eq. (39), which takes into account the reduction of the concentration of acceptor sites as a consequence of the higher value of V_C compared with V_B , is completely justified.

Our computations further indicate that Eq. (39) (with r_S) underestimates the observed mole fraction solubility in the presence of

TABLE II Solute and solvent properties used in Mobile Order solubility predictions

Component	$V_{ij}/(\text{cm}^3 \text{mol}^{-1})$	$\delta'_i/(\text{MPa}^{1/2})^a$
1-Propanol	75.1	17.29
2-Propanol	76.9	17.60
1-Butanol	92.0	17.16
2-Butanol	92.4	16.60
2-Methyl-1-propanol	92.8	16.14
3-Methyl-1-butanol	109.8	16.0
1-Octanol	158.3	16.38
Dibutyl ether	170.3	17.45
Anthracene	150.0	21.648

^aModified solubility parameters of dibutyl ether and the alcohol cosolvents were taken from published tabulations [7–9].

excess dibutyl ether. In the vicinity of $x_C^0 = 0.80$, this underestimation is of the order of 4% for the propanols, 8% for the butanols, 9% for 3-methyl-1-butanol and 11% for octanol. This is likely due to the reduction of r_S in this composition range. It must be borne in mind that the “adjusted” r_S values given in the next to last column of Table I represent very rough estimations, because the numerical value of r_S is very sensitive to experimental errors in ϕ_A^{sat} . Nevertheless, several observations can be made. Careful examinations of Table I reveals that the numerical values of the adjusted r_S decrease with increasing dibutyl ether concentration. The extrapolated values for pure dibutyl ether (i.e., at $\phi_C^0 = 1.0$) lie between $r_S = 0.15$ for the larger alcohols and $r_S = 0.5$ for the smaller alcohols. The corresponding $\langle K_S \rangle$ value, describing the H -bonds of the alcohol at large dilution in the ether lies between 40 and 175 $\text{cm}^3 \text{mol}^{-1}$. This is considerably less than the K_B insertion constants which are of the order 1,000 $\text{cm}^3 \text{mol}^{-1}$ to 5,000 $\text{cm}^3 \text{mol}^{-1}$. The variation of $\langle K_S \rangle$ as a function of dibutyl ether volume fraction is not linear, but rather the drop is accelerated in the last part of the binary solvent composition range. The accelerated drop likely results from the disappearance of the cooperativity effect in H -bonded chains, the ether-alcohol bond being stronger when the alcohol is already bonded to another alcohol molecule.

A more refined quantitative data treatment is not possible at the present time, in part because of the very limited amount of experimental data, uncertainties ($\pm 1.3\%$) associated with the measured mole fraction solubilities, and deficiencies inherent in the Scatchard-

Hildebrand solubility parameter model to accurately describe non-specific interactions in the seven binary alcohol + dibutyl ether solvent mixtures. Our past experiences with Mobile Offer theory have shown that errors in the $V_A\phi_B^0\phi_C^0(\delta'_B - \delta'_C)^2](RT)^{-1}$ term can lead to deviations between predicted and observed values of anywhere between 3–10 %. Readers may recall that numerical values of the modified solubilities were calculated from measured solubility data for solid alkanes, and not from the observed thermodynamic properties for the actual binary alcohol + dibutyl ether systems being described. Moreover, Eq. (39) with the simple assumption that $r_S=1$ still gives satisfactory (though by no means perfect) predictions for the anthracene solubilities.

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