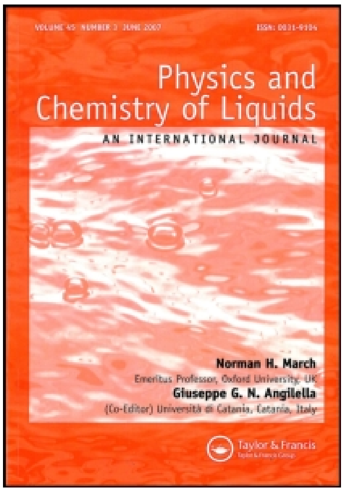

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Thermochemical Investigations of Hydrogen-Bonded Solutions. Part 9. Comparison of Mobile Order Theory and the Kretschmer-Wiebe Association Model for Predicting Pyrene Solubilities in Binary Alcohol Alcohol Solvent Mixtures

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THERMOCHEMICAL INVESTIGATIONS OF HYDROGEN-BONDED SOLUTIONS. PART 9. COMPARISON OF MOBILE ORDER THEORY AND THE KRETSCHMER-WIEBE ASSOCIATION MODEL FOR PREDICTING PYRENE SOLUBILITIES IN BINARY ALCOHOL + ALCOHOL SOLVENT MIXTURES

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A relatively simple expression is developed for predicting the solubility of an inert crystalline solute in binary alcohol + alcohol solvent mixtures based upon the Kretschmer-Wiebe association model. The predictive accuracy of the newly-derived expression is compared to equation(s) derived previously from Mobile Order theory. Computations show that both models accurately describe the solubility behavior of pyrene in the 24 binary solvent systems studied. Average absolute deviations between observed and predicted values were 2.0% and 2.2% for the Kretschmer-Wiebe and Mobile Order predictive equations, respectively.

KEY WORDS: Pyrene solubilities, hydrogen-bonding, self-association, solid-liquid equilibria, binary alcohol solvent mixtures.

1 INTRODUCTION

This work continues a systematic search for mixing models which will provide reasonable mathematical descriptions for the thermochemical properties of a solute at high dilution in mixtures containing an alcoholic cosolvent. To date, we have examined both the application and limitations of Mobile Order theory to describe the solubility of anthracene dissolved in 24 binary alcohol + alkane[1] and 7 binary alcohol + alcohol[2] solvent mixtures. The basic model[3–7] assumes all molecular

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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., Dom $A = V/N_A$. The center of this 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 that 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".

Extension of Mobile Order theory to systems containing an inert solute dissolved in binary solvent mixtures containing two monofunctional self-associating alcoholic solvent components may take one of two different paths, depending upon how one models the hydrogen-bonding. The simplest predictive treatment expresses the volume fraction solubility of the solute ϕ_A^{sat}:[2]

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

in terms of the measured solubility data in both pure solvents, $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$. (The various symbols used in Eqn. (1) are defined in the Appendix.) The two alcohols are permitted to retain their own individual chemical identity and are allowed to form homogeneous self-associated hydrogen bonds with surrounding solvent molecules of the same type. Formation of heterogeneous hydrogen-bonds between two dissimilar alcohols is not allowed.

Monofunctional alcohols do form self-associated species, and there is no a prior experimental evidence or computational reason to preclude formation of heterogeneous B_iC_j complexes, particularly if we are using a single equilibrium constant to describe every monofunctional alcohol's self-association characteristics. For each alcohol, the fraction of time that the alcohol is not involved in hydrogen-bond formation, $\gamma_{\text{Bh:}}$ and $\gamma_{\text{Ch:}}$, is calculated as:

$$\gamma_{\text{Bh:}} = 1/[1 + K_B \phi_B / V_B + K_{BC} \phi_C / V_C] \qquad (2)$$

and

$$\gamma_{\text{Ch:}} = 1/[1 + K_{CB} \phi_B / V_B + K_C \phi_C / V_C] \qquad (3)$$

where K_{BC} and K_{CB} refer to the two additional equilibrium constants needed to describe the formation of the new heterogeneous alcohol-alcohol complexes not found in either neat solvent. It can be readily shown that this set of conditions lead to the following expression for the saturation solubility of a sparingly soluble solute:[2]

$$\begin{aligned}\ln \phi_A^{\text{sat}} = \{&\phi_B^0 \ln (\phi_A^{\text{sat}})_B + \phi_C^0 \ln (\phi_A^{\text{sat}})_C - 0.5\,[\ln (x_B^0 V_B + x_C^0 V_C) - \phi_B^0 \ln V_B \\ &- \phi_C^0 \ln V_C] - (V_A/V_B)\,\phi_B^0[\phi_B^0(K_B/V_B) + \phi_C^0(K_{BC}/V_C)]\}/\{[1 + \phi_B^0(K_B/V_B) \\ &+ \phi_C^0(K_{BC}/V_C)] + (V_A K_B \phi_B^0/V_B^2)(1 + K_B/V_B)^{-1} - (V_A/V_C)\phi_C^0[\phi_B^0(K_{CB}/V_B) \\ &+ \phi_C^0(K_C/V_C)]/[1 + \phi_B^0(K_{CB}/V_B) + \phi_C^0(K_C/V_C)] + (V_A K_C \phi_C^0/V_C^2)(1 + K_C/V_C)^{-1} \\ &+ V_A \phi_B^0 \phi_C^0(\delta'_B - \delta'_C)^2\,(\text{RT})^{-1}\} \qquad (4)\end{aligned}$$

which like Eqn. (1) correctly describes the solubility in both pure self-associating solvents.

An earlier study[2] attempted to assess the applications and limitations of Eqns. (6) and (11) for predicting anthracene solubilities in binary alcohol + alcohol solvent mixtures. Our preliminary computations, using a single value of $K_C = K_B = K_{BC} = K_{CB} \approx 5{,}000$ cm^3 mol^{-1} for all association constants, revealed that both expressions provided a very accurate estimate for how the solubility varies as a function of binary solvent composition. Differences between calculated and observed values were, for the most part, on the order of $\pm$ 2 – 3 relative percent (or less), and were comparable in magnitude both to the experimental uncertainty associated with the measured mole fraction solubility and to the computation uncertainty/error that one might expect in using the modified solubility parameter approximation for the nonspecific physical interactions. Based solely upon "goodness-of-fit", it was impossible for us to determine which of the two derived equations was best with the very limited amount of experimental data available at the time.

Since our earlier comparison, two important items have occurred to prompt us to re-evaluate the predictive accuracies of Eqns. (1) and (4). First, experimental pyrene solubility data is available in the chemical literature for 18 binary alcohol + alcohol solvent mixtures, containing both linear and branched alcohols.[8,9] Second, Campbell[10] successfully extended the Kretschmer-Wiebe self-association model to mixtures containing any number of alcohols. Closed form expressions were derived for the Gibbs energy of mixing and the corresponding activity coefficients. This latter achievement now enables us to further compare in *tête-à-tête* fashion the predictive expressions from Mobile Order theory to equations based upon the more conventional thermodynamic treatments. Two earlier papers in this series[11,12] involving anthracene have reported that Mobile Order theory is comparable to, and even sometimes superior than, the corresponding predictive equations of the Mecke-Kempter and Kretschmer-Wiebe models. As part of the current investigation, we have also measured pyrene solubilities in binary 1-butanol + 1-octanol, 2-butanol + 1-octanol, 2-butanol + 1-butanol, 2-butanol + 2-methyl-1-propanol, 3-methyl-1-butanol + 2-methyl-1-propanol and 3-methyl-1-butanol + 1-butanol solvent mixtures at 26 °C. For information purposes, we note that pyrene is approximately ten times more soluble than anthracene. The increased mole fraction solubility enables us to better assess several of the simplifying approximations used in deriving the various predictive expressions.

EXPERIMENTAL METHODS

Pyrene (Aldrich mass fraction 0.99+) was recrystallized several times from anhydrous methanol before use. 1-Propanol (Aldrich mass fraction 0.99+, anhydrous), 2-propanol (Aldrich mass fraction 0.99+, anhydrous), 1-butanol (Aldrich HPLC, mass fraction 0.998+), 2-butanol (Aldrich mass fraction 0.99+, anhydrous), 2-methyl-1-propanol (Aldrich mass fraction 0.99+, anhydrous), 1-octanol (Aldrich mass fraction 0.99+, anhydrous) and 3-methyl-1-butanol (Aldrich mass fraction 0.99+, anhydrous), were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 0.997 mole fraction or better. Karl Fischer titration gave water contents of mass fraction < 0.0001 for all nine alcohols used. Binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at (26.0 ± 0.05) °C for at least three days (often longer). Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Aliquots of saturated pyrene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and then diluted quantitatively with methanol for spectrophotometric analysis at 372 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer-Lambert law absorbance versus concentration working curve derived from measured absorbances of standard solutions of known molar concentrations. Molar absorptivities of the nine standard solutions varied systematically with molar concentration, and ranged from circa $\varepsilon/(\text{Liter mol}^{-1}\ \text{cm}^{-1}) = 235$ to $\varepsilon/(\text{Liter mol}^{-1}\ \text{cm}^{-1}) = 217$ for pyrene concentrations ranging from $C/(\text{Molar}) = 1.25 \times 10^{-3}$ to $C/(\text{Molar}) = 4.15 \times 10^{-3}$. Experimental pyrene solubilities in the six binary alcohol + alcohol mixtures studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ± 1.5 per cent.

MATHEMATICAL REPRESENTATION OF EXPERIMENTAL SOLUBILITY DATA IN BINARY SOLVENT MIXTURES

Expressions for predicting the thermodynamic properties of ternary nonelectrolyte systems have served as the point of departure for mathematical representation of experimental excess molar Gibbs energy, excess molar heat capacity, excess molar

Table 1 Experimental mole fraction solubilities of pyrene (x_A^{sat}) in binary alcohol (*B*) + alcohol (*C*) solvent mixtures at 26.0 °C.

x_C^0	x_A^{sat}
2-Butanol (*B*) + 1-Butanol (*C*)	
0.0000	0.00439
0.1065	0.00465
0.1954	0.00477
0.3926	0.00506
0.5033	0.00527
0.6060	0.00546
0.7875	0.00588
0.8789	0.00611
1.0000	0.00622
2-Butanol (*B*) + 2-Methyl-1-propanol (*C*)	
0.0000	0.00439
0.1070	0.00436
0.1997	0.00425
0.3971	0.00397
0.5005	0.00384
0.6037	0.00371
0.7974	0.00350
0.8933	0.00340
1.0000	0.00326
2-Butanol (*B*) + 1-Octanol (*C*)	
0.0000	0.00439
0.0595	0.00522
0.1303	0.00629
0.2794	0.00853
0.3664	0.00978
0.4708	0.01154
0.6935	0.01506
0.8304	0.01736
1.0000	0.02077
1-Butanol (*B*) + 1-Octanol (*C*)	
0.0000	0.00622
0.0642	0.00720
0.1279	0.00810
0.2677	0.01022
0.3731	0.01168
0.4687	0.01303
0.7018	0.01640
0.8546	0.01870
1.0000	0.02077
3-Methyl-1-butanol (*B*) + 2-Methyl-1-propanol (*C*)	
0.0000	0.00546
0.1214	0.00538
0.2251	0.00514
0.4337	0.00471
0.5369	0.00443
0.6371	0.00415
0.8236	0.00371
0.9131	0.00351
1.0000	0.00326

Table 1 (*Contd.*)

x_C^0	x_A^{sat}
3-Methyl-1butanol (B) + 1-Butanol (C)	
0.0000	0.00546
0.1164	0.00565
0.2450	0.00570
0.4355	0.00581
0.5414	0.00586
0.6364	0.00596
0.8240	0.00606
0.9063	0.00618
1.0000	0.00622

enthalpy and excess molar volume data. Differences between predicted and observed values are expressed as

$$(Z_{ABC}^E)^{\text{obs}} - (Z_{ABC}^E)^{\text{calc}} = x_A x_B x_C Q_{ABC} \tag{5}$$

with Q-functions of varying complexity. For most systems encountered, the experimental data can be adequately represented by a power series expansion

$$Q_{ABC} = A_{ABC} + \sum_{i=1}^{r} B_{AB}^{(i)}(x_A - x_B)^i + \sum_{j=1}^{s} B_{AC}^{(j)}(x_A - x_C)^j + \sum_{k=1}^{t} B_{BC}^{(k)}(x_B - x_C)^k \tag{6}$$

though rarely are experimental data determined with sufficient precision to justify more than a few parameters.

Conceptually, these ideas can be extended to solute solubilities in binary solvent mixtures, however, there has never been up until recently a sufficiently large solid solute solubility data base to warrant computerized storage in equational form. With computerized data storage and retrieval becoming increasingly popular, it seems appropriate to discuss the various mathematical expressions that have been proposed in the chemical literature for describing the variation of solute solubility with binary solvent composition. Mathematical representations provide not only a means to screen experimental data sets for possible outliers in need of redetermination, but also facilitate interpolation at solvent compositions falling between measured data points.

Acree and coworkers[13–15] suggested possible mathematical representations for isothermal solubility data in binary solvent mixtures based upon either a Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister model

$$\ln x_A^{\text{sat}} = x_B^0 \ln (x_A^{\text{sat}})_B + x_C^0 \ln (x_A^{\text{sat}})_C + x_B^0 x_C^0 \sum_{i=0}^{N} S_i (x_B^0 - x_C^0)^i \tag{7}$$

or Modified Wilson equation[16]

$$\ln[a_A^{\text{solid}}/x_A^{\text{sat}}] = 1 - x_B^0\{1 - \ln[a_A^{\text{solid}}/(x_A^{\text{sat}})_B]\}/(x_B^0 + x_C^0\Lambda_{BC}^{\text{adj}})$$
$$- x_C^0\{1 - \ln[a_A^{\text{solid}}/(x_A^{\text{sat}})_C]\}/(x_B^0\Lambda_{CB}^{\text{adj}} + x_C^0) \qquad (8)$$

where the various S_i and $\Lambda_{ij}^{\text{adj}}$ "curve-fit" parameters can be evaluated via least squares analysis. Both expressions can be derived from published solution models that assume either two-body and/or three-body interactions between molecules in the fluid solution. In Eqns. (7) and (8), x_B^0 and x_C^0 refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present, a_A^{solid} is the activity of the solid solute, and $(x_A^{\text{sat}})_i$ is the saturated mole fraction solubility of the solute in pure solvent i. The numerical value of $a_A^{\text{solid}} = 0.1312$[17] used in the Modified Wilson computations was calculated from the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature of the solute, T_{mp}/K.

The ability of Eqns. (7) and (8) to represent mathematically the experimental solubility of pyrene in the six binary alcohol + alcohol solvent systems is summarized in Table 2 in the form of "curve-fit" parameters and percent deviations in

Table 2 Mathematical representation of pyrene solubilities in several binary alcohol (B) + alcohol (C) solvent mixtures.

Binary Solvent System Component (B) Component (C)	*Eqn. (7)*		*Eqn. (8)*	
	S_i^a	*% Dev.*[b]	$\Lambda_{ij}^{adj,c}$	*% Dev.*[b]
1-Butanol + 1-Octanol	0.676	0.2	1.823	0.7
	0.314		0.555	
	0.221			
2-Butanol + 1-Octanol	0.891	0.4	1.843	1.4
	0.519		0.545	
	0.143			
2-Butanol + 1-Butanol	0.007	0.3	0.565	0.8
	-0.011		2.002	
	0.326			
2-Butanol + 2-Methyl-1-propanol	0.052	0.1	2.128	0.4
	0.092		0.528	
	0.206			
3-Methyl-1-butanol + 2-Methyl-1-propanol	0.259	0.5	1.293	0.5
	0.072		0.904	
	0.206			
3-Methyl-1-butanol + 1-Butanol	0.003	0.3	1.263	0.6
	0.085		0.788	
	0.171			

[a] Combined NIBS/Redlich-Kister curve-fit parameters are ordered as S_0, S_1 and S_2.
[b] Deviation (%) = (100/N) Σ | $[(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}]/(x_A^{\text{sat}})^{\text{exp}}$ |.
[c] Adjustable parameters for the Modified Wilson equation are ordered as $\Lambda_{BC}^{\text{adj}}$ and $\Lambda_{CB}^{\text{adj}}$.

back-calculated solubilities. The parameters S_i were computed from a polynomial least squares analysis of

$$[\ln x_A^{\text{sat}} - x_B^0 \ln(x_A^{\text{sat}})_B - x_C^0 \ln(x_A^{\text{sat}})_C]/(x_B^0 x_C^0) = S_0 + S_1(x_B^0 - x_C^0) + S_2(x_B^0 - x_C^0)^2 \quad (9)$$

using the commercial software Table Curve (Jandel Scientific, Corte Madera, California).

In the case of the Modified Wilson equation the two curve-fit parameters were determined by an "inhouse" computer program. Briefly, the program calculated the mole fraction solubility of pyrene at each of the seven different binary solvent compositions studied using pre-selected values for $\Lambda_{BC}^{\text{adj}}$ and $\Lambda_{CB}^{\text{adj}}$. Values for both $\Lambda_{BC}^{\text{adj}}$ and $\Lambda_{CB}^{\text{adj}}$ were initially set at 0.100. Each subsequent calculation increased one of the parameters by a 0.003 increment. The program selected every possible set of parameters between the ordered pairs of ($\Lambda_{BC}^{\text{adj}} = 0.100$, $\Lambda_{CB}^{\text{adj}} = 0.100$) and ($\Lambda_{BC}^{\text{adj}} = 10.000, \Lambda_{CB}^{\text{adj}} = 10.000$) that differed by the preset distance. The ordered pair that gave the lowest average absolube deviation was taken as the "optimized" values listed in Table 2. The alternative criterion of "goodness-of-fit" of lowest root mean square deviation gave essentially identical numerical values for both Modified Wilson parameters. Careful examination of Table 2 reveals that the Combined NIBS/-Redlich-Kister equation provided the better mathematical representation for how the solubility varied with solvent composition. For the six pyrene systems studied the overall average absolute standard deviation between experimental and calculated values was 0.3%, which is less than the experimental uncertainty. Slightly larger deviations were noted in the case of the Modified Wilson equation.

DEVELOPMENT OF PREDICTIVE EXPRESSION BASED UPON KRETSCHMER-WIEBE ASSOCIATION MODEL

Essential features of the Kretschmer-Wiebe association model, pertaining to a ternary mixture containing an inert solute (component *A*) and two alcohol cosolvents (components *B* and *C*), will be briefly reviewed to facilitate development of the final derived predictive expression. The basic model[10] assumes that two alcohols form both continuous homogeneous hydrogen-bonded

$$B_i + B_1 \rightleftharpoons B_{i+1} \qquad K_B = \hat{C}_{B_{i+1}}/(\hat{C}_{B_1}\hat{C}_{B_i})$$

$$C_i + C_1 \rightleftharpoons C_{i+1} \qquad K_C = \hat{C}_{C_{i+1}}/(\hat{C}_{C_1}\hat{C}_{C_i})$$

and heterogeneous hydrogen-bonded polymers

$$C_1 + \text{Polymer-}B \rightleftharpoons \text{Polymer-}B\text{-}C \qquad K_{BC} = \hat{C}_{\text{Polymer}-B-C}/(\hat{C}_{C_1}\,\hat{C}_{\text{Polymer}-B})$$

$$B_1 + \text{Polymer-}C \rightleftharpoons \text{Polymer-}C\text{-}B \qquad K_{CB} = \hat{C}_{\text{Polymer}-C-B}/(\hat{C}_{B_1}\,\hat{C}_{\text{Polymer}-C})$$

by successive chemical reactions. Formation of homogeneous hydrogen-bonded polymers B_{i+1} and C_{i+1} are described by isodesmic equilibrium constants K_B and K_C, respectively, which are expressed in terms of molar concentrations of the true species in solution. The overbar (Λ) denotes the true species that exist in the associated solution.

The standard Gibbs free energy for heterogeneous H-bond formation is independent of the composition of the polymeric chain, and hence, depends only on the fact that a chain terminating with alcohol B and a single alcohol C monomer are in equilibrium, in accordance to the chemical reaction given above for formation of heterogeneous Polymer-B-C. It is further assumed that the standard free energy change is the same for a single alcohol B monomer in equilibrium with a polymer chain ending in alcohol C (ie., $K_{BC} = K_{CB}$). If a Polymer-B chain reacts with an alcohol B monomer, then the chemical reaction is mathematically described by the isodesmic equilibrium constant K_B. True species range in size from the monomers of each stoichiometric component to a linear chain of essentially infinite length composed of any combination of alcohols B and C.

From a thermodynamic standpoint, the ternary associated solution can be modeled either in terms of the concentrations for the three stoichiometric components calculated as if self-association did not occur, or in terms of the concentrations of species believed to exist in solution. The volume fraction ϕ_i and molar concentration C_i of stoichiometric species i are defined as

$$\phi_i = x_i v_i/\sum x_j v_j = n_i v_i/\sum n_j v_j \tag{10}$$

$$C_i = \phi_i/v_i = n_i/\sum n_j v_j \tag{11}$$

respectively, where x_i is the stoichiometric mole fraction and n_i is the stoichiometric number of molecules of components i. The above summation extends over the three components in the solution. The parameter v_i in Eqns. (10) and (11) is a measure of molecular size for the stoichiometric species and is arbitrarily normalized to the molar volume of methanol at 303.15 K ($V_{\text{methanol}} = 41.0\ \text{cm}^3\ \text{mol}^{-1}$) according to $v_i = (V_i/V_{\text{methanol}})_{303.15\text{K}}$. Similarly, the volume fraction and molar concentrations of a true species s are

$$\hat{\phi}_s = \hat{x}_s v_s/\sum \hat{x}_t v_t = \hat{n} v_s/\sum \hat{n}_t v_t \tag{12}$$

$$\hat{C}_s = \hat{\phi}_s/v_s = \hat{n}_s/\sum \hat{n}_t v_t \tag{13}$$

expressed in terms of true mole fractions and mole numbers. Numerical values of the size parameters of the true species are assumed to be additive and size parameters of the alcohol monomers are the same as for the corresponding stoichiometric species. For example, the size parameter for true species $BCBBC$ in the ternary mixture would be $v_{BCBBC} = 3v_{B1} + 2v_{C1} = 3v_B + 2v_C$.

It now becomes necessary to distinguish between the different true polymeric entities. The counting scheme employed will be that of Campbell.[10] True species are identified by the chain length (total number of various alcohol monomers in the chain) and by the monomer that is at the terminal position on the chain. The molar concentration of the H-bonded complex of length n that ends in alcohol monomer B will be denoted by $\hat{C}_{B,n}$, and similarly by $\hat{C}_{C,n}$ if the chain ends with alcohol cosolvent C. As examples of the notation, C_B and C_C are the overall stoichiometric concentrations of alcohols B and C, respectively, $\hat{C}_{B,1}$ is the molar concentration of alcohol B monomer, and $\hat{C}_{B,4}$ would be the molar concentration of H-bonded polymers having chains that are 4 molecules in length and whose terminal group is alcohol B.

Concentrations of the true alcohol species are expressed in terms of the monomer group that ends the chain and in terms of the total chain length. The total concentration of complexes is given by

$$\Psi_{\text{Total}} = \hat{C}_A + \hat{C}_{B,1} + \hat{C}_{B,2} + \hat{C}_{B,3} + \ldots\ldots + \hat{C}_{C,1} + \hat{C}_{C,2} + \hat{C}_{C,3} + \ldots\ldots \tag{14}$$

For a binary mixture containing two alcohols, Eqn. (14) can be reduced to the following closed mathematical form (see Campbell[10])

$$\Psi_{\text{Total}} = C_A + \Psi_B + \Psi_C \tag{15}$$

where Ψ_B and Ψ_C are obtained from simultaneous (iterative) solution of

$$\Psi_B = C_B/(1 + K_B\Psi_B + K_{BC}\Psi_C) \tag{16}$$

$$\Psi_C = C_C/(1 + K_{BC}\Psi_B + K_C\Psi_C) \tag{17}$$

Computation requires a prior knowledge of both homogeneous self-association constants (K_B and K_C), as well as the single cross-association constant (K_{BC}). This latter quantity has been approximated[10,18] as a simple geometric average of K_B and K_C (i.e., $K_{BC} = (K_B\,K_C)^{0.5}$) in binary alcohol-alcohol liquid-vapor equilibrium studies.

Having reviewed the essential features and notation of the Kretschmer-Wiebe model, attention is now focussed on the development of a predictive expression for solute solubility in binary solvent mixtures containing two alcohol cosolvents. The Gibbs free energy of mixing (relative to the pure liquids) is described by the sum of two separate contributions, one contribution representing chemical interactions and the other representing physical interactions. The chemical contribution is based upon the Kretschmer-Wiebe model discussed above, and is

$$\begin{aligned}(\Delta G_{ABC})_{\text{chem}} = \mathrm{RT}[&n_A \ln\hat{\phi}_A + n_B \ln(\hat{C}_{B,1}/\hat{C}^*_{B,1}) + n_C \ln(\hat{C}_{C,1}/\hat{C}^*_{C,1}) \\ &+ n_A(1-\phi_A) + n_B v_B C_A + n_C v_C C_A - (n_A v_A + n_B v_B + n_C v_C)(\Psi_B + \Psi_C) \\ &+ n_B\Psi^*_B + n_C\Psi^*_C]\end{aligned} \tag{18}$$

written in terms of stoichiometric concentrations wherever possible. Quantities $\hat{C}_{B(\text{or}\,C),1}$ and $\hat{C}^*_{B(\text{or}\,C),1}$ refer to the molar concentrations of the monomers in the mixture and in the neat alcohols, respectively. Numerical values of $\Psi^*_{B(\text{or}\,C)}$ and $\hat{C}^*_{B(\text{or}\,C),1}$ for the two pure alcohols are obtained through application of Eqns. (16)

and (17) and $\hat{C}_{B(\mathrm{or}\,C),1} = \Psi^2_{B(\mathrm{or}\,C)}/C_{B(\mathrm{or}\,C)}$. In the neat alcohols $C_{B(\mathrm{or}\,C)}$ is simply the reciprocal of $V_{B(\mathrm{or}\,C)}$, and $\Psi_{B(\mathrm{or}\,C)}$ are the only non-zero values of Ψ_i. These simplifications result in a set of equations

$$1/V_{B(\mathrm{or}\,C)} = \hat{C}^*_{B(\mathrm{or}\,C),1}/(1 - K_{B(\mathrm{or}\,C)}\hat{C}^*_{B(\mathrm{or}\,C),1})^2 \tag{19}$$

$$\Psi^*_{B(\mathrm{or}\,C)} = \hat{C}^*_{B(\mathrm{or}\,C),1}/(1 - K_{B(\mathrm{or}\,C)}\hat{C}^*_{B(\mathrm{or}\,C),1}) \tag{20}$$

that can be solved for $\hat{C}^*_{B(\mathrm{or}\,C),1}$ and $\Psi^*_{B(\mathrm{or}\,C)}$.

Physical effects are expressed in terms of the Nearly Ideal Binary Solvent (NIBS) model developed by Bertrand and coworkers[19–21]

$$(\Delta G_{ABC})_{\mathrm{phys}} = (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)^{-1} \times (n_A\Gamma_A n_B\Gamma_B\beta_{AB} + n_A\Gamma_A n_C\Gamma_C\beta_{AC}$$

$$+ n_B\Gamma_B n_C\Gamma_C\beta_{BC}) \tag{21}$$

where Γ_i is the weighting factor for component i and β_{ij} is a binary interaction parameter that is independent of composition. The NIBS model has been shown[22] to provide reasonably accurate predictions for naphthalene, iodine, *p*-dibromobenzene, benzil, *p*-benzoquinone, anthracene, pyrene and carbazole solubilities in systems containing only nonspecific interactions. Precise applicability of Eqn. (21) to Gibbs free energy and its temperature and pressure derivatives requires that weighting factors be independent of both variables. Therefore, molar volumes and experimentally determined weighting factors must be regarded as approximations of these true weighting factors, and for applications to conditions of varying temperature and/or pressure, they should be referred to a specific condition, such as 303.15 and 1 atm, or to an extrapolated state, such as a "close-packed" volume. For our applications, weighting factors will be approximated by the stoichiometric size parameter v_i.

Combination of Eqns. (18) and (21) yields the following expression for the total Gibbs free energy of mixing of the ternary system (per stoichiometric mole of solution)

$$\Delta G_{ABC} = \mathrm{RT}[n_A \ln\hat{\phi}_A + n_B \ln(\hat{C}^*_{B,1}/\hat{C}_{B,1}) + n_C \ln(\hat{C}_{C,1}/\hat{C}^*_{C,1})$$

$$+ n_A(1 - \phi_A) + n_B v_B C_A + n_C v_C C_A - (n_A v_A + n_B v_B + n_C v_C)(\Psi_B + \Psi_C)$$

$$+ n_B\Psi^*_B + n_C\Psi^*_C] + (n_A v_A + n_B v_B + n_C v_C)^{-1} \times (n_A v_A n_B v_B \beta_{AB}$$

$$+ n_A v_A n_C v_C \beta_{AC} + n_B v_B n_C v_C \beta_{BC}) \tag{22}$$

when weighting factors are replaced with the molecular size parameters v_i. Thermodynamic principles relate solubility to chemical potential. For a system obeying

Eqn. (22) the volume fraction solubility of a crystalline solute A in alcohols B and C is

$$\mathrm{RT}\ln\phi_A^{\mathrm{sat}} = \mathrm{RT}[\ln a_A^{\mathrm{solid}} - (1-\phi_A^{\mathrm{sat}}) + v_A(\Psi_B + \Psi_C)] - v_A[\phi_B^2\beta_{AB} + \phi_C^2\beta_{AC} + \phi_B\phi_C(\beta_{AB} + \beta_{AC} - \beta_{BC})] \quad (23)$$

obtained by differentiating ΔG_{ABC} with respect to n_A. Careful examination of the above expression reveals that the two solute-solvent interaction parameters, β_{AB} and β_{AC}, can be calculated from the appropriate binary reduction

$$\mathrm{RT}\ln(\phi_A^{\mathrm{sat}})_B = \mathrm{RT}[\ln a_A^{\mathrm{solid}} - 1 + (\phi_A^{\mathrm{sat}})_B + v_A\Psi_B^*] - v_A\phi_B^2\beta_{AB} \quad (24)$$

and

$$\mathrm{RT}\ln(\phi_A^{\mathrm{sat}})_C = \mathrm{RT}[\ln a_A^{\mathrm{solid}} - 1 + (\phi_A^{\mathrm{sat}})_C + v_A\Psi_C^*] - v_A\phi_C^2\beta_{AC} \quad (25)$$

and measured volume fraction solubilities in both pure alcohol cosolvents, $(\phi_A^{\mathrm{sat}})_B$ and $(\phi_A^{\mathrm{sat}})_C$.

RESULTS AND DISCUSSION

Despite the complex appearance of Eqn. (23), its application to solubilities in binary alcohol + alcohol solvent mixtures is relatively straight forward. The quantities $(\phi_A^{\mathrm{sat}})_B$ and $(\phi_A^{\mathrm{sat}})_C$ are calculated from the measured mole fraction solubility of the solid in the two pure solvents assuming that the excess molar volume (or alternatively, the volume change upon mixing) is zero. These values, along with the various molecular size parameters v_i and $a_A^{\mathrm{solid}} = 0.1312$,[22] are inserted into Eqns. (24) and (25) and the two β_{Ai} solute-solvent parameters are computed. The molar volume of the subcooled pyrene solute is approximated as $V_A = 166.5\mathrm{cm}^3\mathrm{mol}^{-1}$. An uncertainty of ± 10% in the numerical value assumed for V_A contributes very little error to the overall solubility predictions. The binary alcohol-alcohol interaction parameter is estimated using an unpublished correlation developed by one of the authors (S. W. Campbell) from binary liquid-vapor equilibria data for mixtures of straight chain alcohols

$$\beta_{BC}(\mathrm{in\,J\,mol^{-1}}) = 91.43[(\mathrm{Cne}_2/\mathrm{Cne}_1) - 1] \quad (26)$$

where Cne is the effective carbon number of the alcohol (see Table 3). Cne_2 is the larger of the two effective carbon numbers and Cne_1 is the smaller one. The β_{BC}-parameter is assumed to be independent of temperature. The cross association equilibrium constant, K_{BC}, is approximated as the geometric average of K_B and K_C, i.e., $K_{BC} = (K_B K_C)^{0.5}$. Values of self-association constants at 30 °C for a number of alcohols have been obtained by Schmidt and Campbell[23] from alcohol-alkane binary vapor-liquid equilibrium data. These are listed in Table 3 along with a relation that allows their estimation at other temperatures. Next, Eqns. (16) and (17) are solved simultaneously (iterative) for Ψ_B and Ψ_C. All calculated quantities and pure component properties are then substituted directly into Eqn. (23), and the satuation volume fraction solubility calculated at each desired binary solvent composition.

The descriptive ability of Eqn. (23) will be critically assessed using published solubility data for pyrene dissolved in three binary alcohol + alcohol solvent mixtures (see references 8 and 9 for published solubility data taken from chemical literature). Each system contains solubility data at seven different binary compositions spanning the entire mole fraction range, as well as the measured pyrene solubility in both pure alcohol cosolvents. The experimental mole fractions listed in Table 4 for three of the 24 systems considered represent the average of between four and eight independent determinations, with the measured values being reproducible to within ± 1.5% (or better). Columns 3 and 4 of the table list calculated values based upon Eqns. (23) and (29), respectively. The latter equation will be discussed shortly. A complete summarized comparison for the entire set of 24 systems is presented in Table 5. The various solute-solvent (β_{AB} and β_{AC}) and solvent-solvent (β_{BC}) binary interaction parameters generated during the course of the solubility predictions

Table 3 Self-association constants K_i and molar volumes V_i at T_{ref} = 303.15 K, and effective carbon numbers Cne_i for select $C_1 - C_{12}$ linear and branched alcohols.

Alcohol	K_i^a	Cne_i	V_i (303.15 *K*)
Methanol	365.6	1.00	41.0[c]
Ethanol	382.7	2.00	59.0
1-Propanol	282.9	3.00	75.5
2-Propanol	77.7	2.30	77.4
1-Butanol	230.8	4.00	92.4
2-Butanol	71.0	3.10	92.9
2-Methyl-1-propanol	154.1	3.53	93.4
2-Methyl-2-propanol	18.2	2.26	99.6
1-Pentanol	204.9	5.00	109.1
2-Pentanol	86.7	4.06[b]	110.0
3-Pentanol	58.2	3.88[b]	108.6
2-Methyl-1-butanol	154.2	4.54[b]	108.7
3-Methyl-1-butanol	196.8	4.67[b]	109.7
2-Methyl-2-butanol	24.6	3.23[b]	110.2
1-Hexanol	234.8	6.00	125.7
2,3,3-Trimethyl-2-butanol	2.6	2.07[b]	139.6
1-Octanol	153.8	8.00	160.1
2-Ethyl-1-hexanol	50.1	7.41[b]	157.8
1-Decanol	171.3	10.00	192.3
1-Dodecanol	216.2	12.00	225.3

[a] Self-association constants K_i at 298.15 K are calculated from the following correlation: $\ln[K_i(T)/K_i(303.15\ \mathrm{K})] = -10.783\ (T/303.15)$.
[b] Effective carbon numbers were calculated using correlation of Ambrose and Sprake.[24]
[c] Molar volumes were calculated using density data from the TRC Thermodynamic Tables of Non-Hydrocarbons.[25]

Table 4 Comparison between experimental pyrene solubilities in binary alcohol (*B*) + alcohol (*C*) solvent mixtures and predicted values based upon the Kretschmer-Wiebe Model.

x_C^0	x_A^{sat}	*Predicted Values*	
		Eqn. (23)	*Eqn. (29)*
	1-Butanol (*B*) + 1-Propanol (*C*)		
0.0000	0.00622	-----	-----
0.1265	0.00606	0.00599	0.00599
0.2295	0.00587	0.00580	0.00580
0.4508	0.00543	0.00538	0.00538
0.5503	0.00515	0.00519	0.00518
0.6450	0.00496	0.00500	0.00500
0.8337	0.00460	0.00461	0.00461
0.9162	0.00443	0.00444	0.00444
1.0000	0.00426	-----	-----
	2-Methyl-1-propanol (*B*) + 2-Ethyl-1-hexanol (*C*)		
0.0000	0.00326	-----	-----
0.0639	0.00376	0.00376	0.00376
0.1292	0.00433	0.00429	0.00428
0.2622	0.00537	0.00542	0.00542
0.3592	0.00615	0.00629	0.00628
0.4824	0.00722	0.00743	0.00742
0.7042	0.00920	0.00956	0.00955
0.8052	0.01022	0.01055	0.01055
1.0000	0.01250	-----	-----
	1-Butanol (*B*) + 2-Propanol (*C*)		
0.0000	0.00622	-----	-----
0.1320	0.00581	0.00577	0.00576
0.2301	0.00545	0.00543	0.00543
0.4486	0.00467	0.00468	0.00468
0.5611	0.00424	0.00430	0.00430
0.6423	0.00398	0.00403	0.00403
0.8276	0.00339	0.00343	0.00343
0.9133	0.00315	0.00316	0.00316
1.0000	0.00290	-----	-----

are tabulated in Table 6. Careful examination of Tables 4 and 5 reveals that the Kretschmer-Wiebe model provides very accurate predictions for the solubility of pyrene dissolved in binary alcohol + alcohol solvent mixtures. Average absolute deviations between observed and predicted values were 2.0% for both Eqns. (23) and (29). For many of the systems studied the predictive error was less than the experimental uncertainty associated with the measured pyrene mole fraction solubilities.

The computational procedure can be simplified in the case of a sparingly soluble solute ($\phi_A^{sat} \approx 0$; $1 - \phi_A^{sat} \approx 1$) by completely eliminating the calculation of the two solute-solvent interaction parameters. Rather than calculating actual numerical values, Eqns. (24) and (25) are solved explicitly for β_{AB} and β_{AC}, and the resulting expressions

$$\beta_{AB} = \mathrm{RT}\ \{\ln [a_A^{solid}/(\phi_A^{sat})_B] - 1 + (\phi_A^{sat})_B + v_A \Psi_B^*\}/(v_A \phi_B^2) \qquad (27)$$

Table 5 Summarized comparison between experimental pyrene solubilities and predicted values based upon Kretschmer-Wiebe Eqns. (23) and (29) and upon mobile order theory Eqns. (1) and (4).

Solvent (B) + Solvent (C)	*% Deviations*[a]		*% Deviations*[a]	
	Eqn. (23)	*Eqn.* (29)	*Eqn.* (1)	*Eqn.* (4)
1-Octanol + 1-Butanol	− 1.2	− 1.4	1.1	− 1.9
1-Octanol + 2-Butanol	1.4	1.3	1.9	3.3
2-Butanol + 1-Butanol	0.9	0.9	+ 2.1	1.0
2-Butanol + 2-Methyl-1-propanol	− 1.4	− 1.4	+ 1.7	− 1.4
1-Butanol + 3-Methyl-1-butanol	0.8	0.8	+ 3.5	0.9
3-Methyl-1-butanol + 2-Methyl-1-propanol	− 3.1	− 3.2	1.1	− 3.8
1-Butanol + 1-Propanol	0.7	0.7	+ 2.3	− 1.7
2-Butanol + 1-Propanol	0.2	0.2	+ 4.1	+ 1.1
2-Propanol + 1-Propanol	0.5	0.5	+ 2.4	− 0.7
1-Octanol + 1-Propanol	− 2.8	− 3.3	1.3	− 3.9
1-Butanol + 2-Propanol	0.9	0.8	+ 1.9	− 1.1
2-Butanol + 2-Propanol	− 2.5	− 2.5	+ 1.0	− 2.1
3-Methyl-1-butanol[b] + 2-Propanol	+ 2.7	+ 2.6	+ 6.4	+ 3.3
2-Methyl-1-propanol[b] + 2-Propanol	− 1.5	− 1.4	+ 2.8	0.5
1-Propanol + 2-Methyl-1-propanol	0.9	0.9	+ 3.9	1.1
3-Methyl-1-butanol + 1-Propanol	0.4	0.4	+ 4.4	+ 1.4
1-Octanol + 2-Propanol	− 2.5	− 3.0	3.3	− 6.0
1-Propanol + 2-Ethyl-1-hexanol	+ 3.5	+ 3.3	+ 6.2	+ 3.3
2-Propanol + 2-Ethyl-1-hexanol	+ 6.0	+ 5.7	+ 6.2	3.3
1-Butanol + 2-Ethyl-1-hexanol	+ 3.8	+ 3.7	+ 6.6	+ 3.7
2-Butanol + 2-Ethyl-1-hexanol[b]	+ 2.9	+ 2.7	+ 3.3	0.5
2-Methyl-1-propanol + 2-Ethyl-1-hexanol	2.1	2.0	+ 3.7	1.6
3-Methyl-1-butanol + 2-Ethyl-1-hexanol	4.1	4.0	+ 6.7	3.8
1-Octanol + 2-Ethyl-1-hexanol	+ 2.0	+ 2.0	+ 4.8	+ 1.9

[a] Deviation = $(100/N)\ \%\,\Sigma|\ln[(x_A^{\text{sat}})^{\text{calc}}/(x_A^{\text{sat}})^{\text{exp}}]|$. The algebraic sign indicates that all deviations were of the same sign.

[b] Molar volumes and modified solubility parameters used in Mobile Order predictions: $V_i = 92.8\ \text{cm}^3\ \text{mol}^{-1}$ and $\delta_i' = 16.14\ \text{MPa}^{1/2}$ for 2-methyl-1-propanol; $V_i = 109.8\ \text{cm}^3\ \text{mol}^{-1}$ and $\delta_i' = 16.00\ \text{MPa}^{1/2}$ for 3-methyl-1-butanol; and $V_i = 157.09\ \text{cm}^3\ \text{mol}^{-1}$ and $\delta_i' = 16.60\ \text{MPa}^{1/2}$ for 2-ethyl-1-hexanol. Numerical values for the remaining alcohol solvents are given elsewhere.[1,2,5,6]

and

$$\beta_{AC} = \text{RT}\ \{\ln[a_A^{\text{solid}}/(\phi_A^{\text{sat}})_C] - 1 + (\phi_A^{\text{sat}})_C + v_A \Psi_C^*\}/(v_A \phi_C^2) \tag{27}$$

are substituted directly into Eqn. (23). After suitable algebraic manipulation, the final derived expression

$$\begin{aligned}\text{RT}\ \ln \phi_A^{\text{sat}} = \text{RT}\ &\{\phi_B^0[\ln(\phi_A^{\text{sat}})_B - v_A \psi_B^*] + \phi_C^0[\ln(\phi_A^{\text{sat}})_C - v_A \Psi_C^*] \\ &+ v_A(\Psi_B + \Psi_C)\} + v_A \phi_B^0\, \phi_C^0 \beta_{BC}\end{aligned} \tag{29}$$

Table 6 Solute-Solvent and Solvent-Solvent Binary Interaction Parameters Used in the Kretschmer-Wiebe Predictions.

Component i + Component j	β_{ij} *(J mol^{-1})*
Solute-Solvent	
Pyrene + 1-Propanol	1127.7
Pyrene + 2-Propanol	1451.1
Pyrene + 1-Butanol	1021.5
Pyrene + 2-Butanol	1302.2
Pyrene + 1-Octanol	617.8
Pyrene + 2-Methyl-1-propanol	1432.6
Pyrene + 3-Methyl-1-butanol	1199.2
Pyrene + 2-Ethyl-1-hexanol	971.1
Solvent-Solvent	
1-Butanol + 1-Propanol	30.5
2-Butanol + 1-Propanol	3.0
2-Propanol + 1-Propanol	27.9
1-Octanol + 1-Propanol	152.5
1-Butanol + 2-Propanol	67.6
2-Butanol + 2-Propanol	31.8
1-Octanol + 2-Butanol	144.6
3-Methyl-1-butanol + 2-Propanol	94.2
2-Methyl-1-propanol + 2-Propanol	48.9
1-Propanol + 2-Methyl-1-propanol	16.2
1-Octanol + 2-Methyl-1-propanol	115.8
3-Methyl-1-butanol + 1-Butanol	15.3
2-Butanol + 2-Methyl-1-propanol	12.7
3-Methyl-1-butanol + 2-Methyl-1-propanol	29.5
3-Methyl-1-butanol + 1-Propanol	50.9
1-Octanol + 2-Propanol	226.6
1-Octanol + 1-Butanol	91.4
2-Butanol + 1-Butanol	26.5
1-Propanol + 2-Ethyl-1-hexanol	134.4
2-Propanol + 2-Ethyl-1-hexanol	203.1
1-Butanol + 2-Ethyl-1-hexanol	77.9
2-Butanol + 2-Ethyl-1-hexanol	127.1
2-Methyl-1-propanol + 2-Ethyl-1-hexanol	100.5
3-Methyl-1-butanol + 2-Ethyl-1-hexanol	53.6
1-Octanol + 2-Ethyl-1-hexanol	7.3

is obtained. The above expression, like Eqn. (23), is "anchored by" the solubilities in the two pure alcohol cosolvents, requires both $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$ as needed input parameters, and hence, can only predict the solute solubility as a function of binary solvent composition.

The third and fourth columns in Tables 4 and 5, respectively, provide a summarized comparison between measured pyrene solubilities and calculated values based upon this simplified predictive expression. Careful examination of Tables 4 and 5 reveals that there is essentially no difference regarding the predictive accuracy of Eqns. (23) and (29) for the systems considered here. Pyrene has a sufficiently low mole fraction (and volume fraction) solubility in alcohol cosolvents, and the infinite dilution approximation of $\phi_A^{\text{sat}} \approx 0$ is completely valid. This will not necessarily be the case, however, in planned subsequent studies which will involve the more soluble phenanthrene polycyclic aromatic hydrocarbon solute.

As stated in the *Introduction*, one of the objectives of the present study is to compare in tête-à-tête fashion the applications and limitations of predictive expressions based upon Mobile Order theory against those derived from the more conventional thermodynamic association models, such as the Kretschmer-Wiebe model. Earlier papers in this series[11,12] reported that Mobile Order theory was comparable to, and sometimes superior than, both the Kretschmer-Wiebe and Mecke-Kempter models in regards to predicting the solubility of anthracene in binary alcohol + saturated hydrocarbon solvent systems. The two afore mentioned comparisons involved only a single self-associating alcohol cosolvent, and did not consider formation of heterogeneous hydrogen bonded polymers that results whenever two dissimilar alcohol cosolvents are present.

Table 5 also compares measured pyrene solubilities to calculated values based upon Eqns. (1) and (4). Solvent properties used in the Mobile Order predictions are given elsewhere[5,6]. Equation (1) assumes only formation of homogeneous B_i and C_i alcohol hydrogen-bonded polymers, whereas the latter expression includes provisions for mixed B_iC_j heterogeneous polymers as well. Careful examination of Table 5 reveals that inclusion of mixed polymers improves the Mobile Order predictions slightly; an average absolute deviation of 3.4% for Eqn. (1) versus a slightly lower deviation fo 2.2% for Eqn. (4). In a tête-à-tête comparison of Mobile Order theory versus the Kretschmer-Wiebe model, we find that both approaches provide reasonably accurate predictions for the measured pyrene solubilities in the 28 systems considered. The Kretschmer-Wiebe model does have an ever-so-slightly lower average absolute deviation between observed and predicted values of 2.0% for Eqn. (29). For informational purposes, the "apparent" superiority of the Kretschmer-Wiebe model is much less than the experimental uncertainty associated with the measured solubility data. Each individual data point represent the average of four to eight independent deteterminations, the reproducibility of which was *circa* ± 1.5%. Without a more clear-cut distinction between models, we are hesitant to claim that either one is superior to the other. Moreover, it is impossible for us to determine a *prior* which of the two models will give the "better" set of predicted values for any given binary solvent system.

APPENDIX: GLOSSARY OF SYMBOLS

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugactity of the pure subcooled liquid.
C_i	molar concentration of component *i*.
ΔH_A^{fus}	molar enthalpy of fusion of the solid solute at its normal melting point temperature.
K_B	Kretschmer-Wiebe equilibrium constant describing the step-wise homogeneous self-association of monofunctional alcohol *B*, where the concentration units are molarity. Also used as the Mobile Order theory self-association constant.

K_C	Kretschmer-Wiebe equilibrium constant describing the step-wise homogeneous self-association of monofunctional alcohol C, where the concentration units are molarity. Also used as the Mobile Order theory self-association constant.
K_{BC}, K_{CB}	Kretschmer-Wiebe equilibrium constant describing the step-wise heterogeneous association of monofunctional alcohol B and C, where the concentration units are molarity. Also used as the Mobile Order theory self-association constant.
n_i	number of moles of component i.
T_{mp}	normal melting point temperature of the solute.
V_i	molar volume of component i.
v_i	normalized molecular size parameter used in the Kretschmer-Wiebe model, defined as the ratio of the molar volume of component i divided by the molar volume of methanol at 303.15 K.
x_i^0, x_j^0	mole fraction compositions of the ij binary mixture, calculated as if the third component were not present.
x_A^{sat}	mole fraction solubility of the solute.

Greek Letters

β_{ij}	binary interaction parameter for components i and j, used in the mathematical description for nonspecific interactions.
Γ_i	generalized weighting factor for component i, used in the Nearly Ideal Binary Solvent (NIBS) model for nonspecific interactions.
γ_{Bh}	fraction of time that alcoholic solvent B is not involved in hydrogen-bond formation.
δ_i	Scatchard-Hildebrand solubility parameter of component i.
δ'_i	modified solubility parameter of component i.
$\Lambda_{ij}^{\mathrm{adj}}$	adjustable "curve-fit" parameter in the modified Wilson mathematical representation.
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the binary solvent mixture, calculated as if the solute were not present.
ϕ_A^{sat}	ideal volume fraction solubility of the solute.
ϕ_{solvent}	ideal volume fraction of solvent.
ϕ_i	ideal volume fraction of component i in the "true" associated solution.
Ψ_{Total}	total molar concentration of all *true* species in associated solution.
Ψ_B^*, Ψ_C^*	total molar concentration of all species in the neat alcohol cosolvents.
Ψ_B, Ψ_C	quantities defined by Eqs. (16) and (17), respectively.

References

1. W. E. Acree, Jr., A. I. Zvaigzne and S. A. Tucker, *Fluid Phase Equilibr.*, **92**, 233 (1994).
2. W. E. Acree, Jr. and A. I. Zvaigzne, *Fluid Phase Equilibr.*, **99**, 167 (1994).
3. P. L. Huyskens and G. G. Siegel, *Bull. Soc. Chim. Belg.*, **97**, 821 (1988).
4. G. G. Siegel, P. L. Huyskens and G. Vanderheyden, *Ber. Bunsen-Ges. Phys. Chem.*, **94**, 549 (1990).
5. P. Ruelle, C. Rey-Mermet, M. Buchmann, H. Nam-Tran, U. W. Kesselring and P. L. Huyskens, *Pharm. Res.*, **8**, 840 (1991).

6. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Int. J. Pharm.*, **87**, 47 (1992).
7. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Pharm. Res.*, **9**, 788 (1992).
8. A. I. Zvaigzne, B. J. Miller and W. E. Acree, Jr., *J. Chem. Eng. Data*, **40**, 1267 (1995).
9. A. I. Zvaigzne, M. E. R. McHale, J. R. Powell, A.-S. M. Kauppila and W. E. Acree, Jr., *J. Chem. Eng. Data*, **40**, 1273 (1995).
10. S. W. Campbell, *Fluid Phase Equilibr.*, **102**, 61 (1994).
11. W. E. Acree, Jr., A. I. Zvaigzne and S. A. Tucker, *Fluid Phase Equilibr.*, 92, 1. (1994), [Corrigendum, **101**, 267 (1994)]
12. W. E. Acree, Jr. and S. A. Tucker, *Fluid Phase Equilibr.*, **102**, 17 (1994).
13. W. E. Acree, Jr., *Thermochim. Acta*, **198**, 71 (1992).
14. W. E. Acree, Jr. and A. I. Zvaigzne, *Thermochim. Acta*, **178**, 151 (1991).
15. W. E. Acree, Jr., J. W. McCargar, A. I. Zvaigzne and I.-L. Teng, *Phys. Chem. Liq.*, **23**, 27 (1991).
16. J. F Comer and M. M Kopecni, *Anal. Chem.*, **62**, 991 (1990).
17. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *Phys. Chem. Liq.*, **16**, 179 (1987).
18. A. G. Pradhan, V. R. Bhethanabotla and S. W. Campbell, *Fluid Phase Equilibr.*, **84**, 183 (1993).
19. T. E.Burchfield and G. L. Bertrand, *J. Solution Chem.*, **4**, 205 (1975).
20. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **81**, 1170 (1977).
21. W. E. Acree, Jr. and G. L. Bertrand, *J. Solution Chem.*, **12**, 101 (1983).
22. W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*; Vol. **54** in *IUPAC Solubility Data Series*, Oxford University Press, Oxford, U. K. (1994).
23. C. P. Schmidt and S. W. Campbell, *Int. J. Thermophys.*, **16**, 1299 (1995).
24. D. Ambrose and C. H. S. Sprake, *J. Chem. Thermodyn.*, **2**, 631 (1970).
25. K. N. Marsh, (Editor). *TRC Thermodynamic Tables: Non-Hydrocarbons*, Thermodynamics Research Center, Texas A & M University, College Station, Texas.