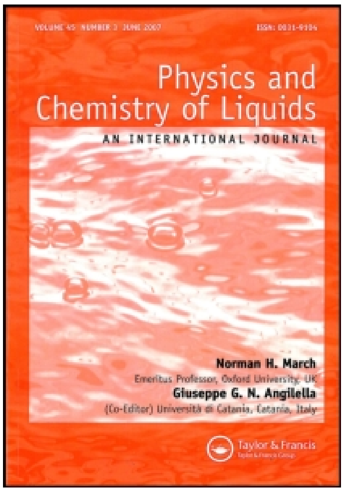

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Thermochemical Investigations of Hydrogen-Bonded Solutions. Part 13. Prediction of Pyrene Solubilities in Binary Alcohol Alcohol Solvent Mixtures Using Alcohol-Specific Mobile Order Theory Stability Constants

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THERMOCHEMICAL INVESTIGATIONS OF HYDROGEN-BONDED SOLUTIONS. PART 13. PREDICTION OF PYRENE SOLUBILITIES IN BINARY ALCOHOL + ALCOHOL SOLVENT MIXTURES USING ALCOHOL-SPECIFIC MOBILE ORDER THEORY STABILITY CONSTANTS

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Experimental solubilities are reported for pyrene dissolved in six binary mixtures containing 2-methyl-1-pentanol with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 1-octanol at 26°C. Results of these measurements, along with previously published solubility data for pyrene in binary alcohol + alcohol solvent mixtures, are used to test the limitations and applications of expressions derived from Mobile Order theory and the Kretschmer-Wiebe association model. Alcohol-specific Mobile Order theory association constants are calculated from vapor-liquid equilibrium data for binary alkane + alcohol solvent mixtures, and used in the solubility predictions. For the 42 different systems considered, both models provided very accurate predictions of the pyrene solubilities, with an overall average absolute deviation between measured and calculated values being 2.0% and 1.6% for Mobile Order theory and the Kretschmer-Wiebe association model, respectively.

Keywords: Pyrene solubilities; alcohol solvents; hydrogen-bonding

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INTRODUCTION

This work continues a systematic search for mixing models which will provide reasonable mathematical descriptions of the thermochemical properties of ternary nonelectrolyte solutions which contain components capable of self-association. To date, we have examined both the application and limitations of Mobile Order theory to describe the solubilities of anthracene dissolved in 24 different binary alcohol + alkane[1], 35 binary alcohol + alcohol[2–4] and 32 binary alcohol + 2-alkoxyethanol solvent mixtures[5], and of pyrene dissolved in 24 binary alcohol + alcohol solvent mixtures[6]. The basic model [7–16] assumes 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 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 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 thermodynamics of Mobile Order expresses the equilibrium condition in terms of time fractions for the time schedule of a given molecule, and not in terms of concentrations of various entities in the ensemble. Thus, in the case of alcohols and alkoxyalcohols one considers the time fraction $\gamma_{\text{ch:}}$ and not the concentrations of the various i-mers in the ensemble (this does not mean that these i-mers do not exist, but their concentrations do not govern the thermodynamic probability). $\gamma_{\text{ch:}}$ is the fraction of the time during which a given molecule of the ensemble is free from H-bonding, this means; 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. A molecule bonded at one side is free from H-bonding only half of the time.

For an inert crystalline solute dissolved in a binary alcohol (B) + alcohol (C) or alcohol (B) + 2-alkoxyethanol (C) solvent mixture the volume fraction saturation solubility ($\phi_{\mathrm{A}}^{\mathrm{sat}}$) is given by:[2, 5]

$$
\begin{aligned}
&\mathrm{RT}\{\ln(a_{\mathrm{A}}^{\mathrm{solid}}/\phi_{\mathrm{A}}^{\mathrm{sat}}) - 0.5[1 - V_A/(x_B^0 V_B + x_C^0 V_C)] \\
&\quad + 0.5\ \ln[V_A/(x_B^0 V_B + x_C^0 V_C)] - (V_A/V_B)\phi_B^0[\phi_B^0(K_B/V_B) + \phi_C^0(K_{BC}/V_C)]/ \\
&\quad [1 + \phi_B^0(K_B/V_B) + \phi_C^0(K_{BC}/V_C)] - (V_A/V_C)\ \phi_C^0[\phi_B^0(K_{CB}/V_B) + \phi_C^0(K_C/V_C)]/ \\
&\quad [1 + \phi_B^0(K_{CB}/V_B) + \phi_C^0(K_C/V_C)]\} \\
&\quad = V_A[\phi_B^0(\delta_A' - \delta_B')^2 + \phi_C^0(\delta_A' - \delta_C')^2 - \phi_B^0\phi_C^0(\delta_B' - \delta_C')^2] \qquad \text{(Eqn. 1)}
\end{aligned}
$$

whenever the saturation solubility is sufficiently low that $1 - \phi_A^{\mathrm{sat}} \approx 1.0$. The symbols δ_A', δ_B' and δ_C' denote the modified solubility parameters of the solute and self-associating alcohols, respectively. The remaining symbols are defined in detail in the Appendix. Contributions from nonspecific interactions are incorporated into Mobile Order theory through the $V_A[\phi_B^0(\delta_A' - \delta_B')^2 + \phi_C^0(\delta_A' - \delta_C')^2 - \phi_B^0\phi_C^0(\delta_B' - \delta_C')^2]$ term. Through suitable mathematical manipulations, the $V_A\ \phi_B^0(\delta_A' - \delta_B')^2$ and $V_A\ \phi_C^0(\delta_A' - \delta_C')^2$ terms were eliminated from the basic model in favor of measured solubility data in both pure solvents, $(\phi_A^{\mathrm{sat}})_B$ and $(\phi_A^{\mathrm{sat}})_C$. The final derived expression

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

does not require a *prior* knowledge of the solute's enthalpy of fusion and melting point temperature, which would be needed to calculate the numerical value of a_A^{solid} at the temperature corresponding to the solubility measurements. In the above treatment the two alcohols retain their own individual chemical identity, and are allowed to form homogeneous self-associated and heterogeneous cross-associated hydrogen-bonded chains with neighboring alcohol molecules. Constants K_{BC} and K_{CB} are set equal to zero whenever cross-association is neglected.

Four previous papers[2–4, 6] have shown that Eqn. (2) provides very reasonable predications of the saturated mole fraction solubilities of both anthracene and pyrene dissolved in binary alcohol + alcohol solvent mixtures using a single equilibrium constant of $K_B = K_C = 5{,}000\,\mathrm{cm^3\,mol^{-1}}$ for self-association and of $K_{BC} = K_{CB} = 5{,}000\,\mathrm{cm^3\,mol^{-1}}$ for heterogeneous H-bond chain formation. The overall average absolute deviations between predicted and observed solubilities were 1.6 % and 2.2 %, respectively, for anthracene and pyrene. More recently, McHale *et al.* [5] showed that Mobile Order theory provided reasonably accurate predications for anthracene solubility in 32 different binary alcohol + 2-alkoxyethanol solvent mixtures. Here, the 2-alkoxyethanol cosolvent was treated as a pseudo-monofunctional alcohol, with hydrogen-bond formation occurring largely through the hydroxylic OH group, rather than the oxygen ether linkage. All homogeneous self-association and heterogeneous cross-association stability constants were again set equal to $K_i = 5{,}000\,\mathrm{cm^3\,mol^{-1}}$. Acree[17] and Pandey *et al.*[18] successfully extended Mobile Order theory to excess enthalpies of ternary hydrocarbon + hydrocarbon + alcohol and hydrocarbon + alcohol + alcohol systems. Several published papers[2–4, 6, 19–24] have further documented that the predictive accuracy of Mobile Order theory equations are often comparable to (and sometimes even superior than) the corresponding expressions derived from the more conventional thermodynamic treatments such as the Nearly Ideal Binary Solvent (NIBS), Extended NIBS, Wilson, Mecke-Kempter and Kretschmer-Wiebe models.

Experimental solubility data for mixtures containing highly branched alcohols were very limited at the time of our earlier solubility investigations. We did not believe that any slight improvement in predictive accuracy that might be gained from using "alcohol-specific" association constants necessarily warranted the very time-consuming computations required to obtain an optimized K_{Alcohol}-value for each different alcohol cosolvent studied. As additional solubility data becomes available, and as Mobile Order theory is extended to vapor-liquid equilibria[24] and to more complex aqueous-alcohol solvent mixtures[13,25], it becomes important for us to re-examine the assumption that a single association constant is valid for all primary, secondary, branched and cyclic alcohols. A methyl-substituent in close proximity of the hydroxyl group is expected to sterically hinder both self - and cross-association, thereby increasing the fraction of time during which a given alcohol molecule is free from hydrogen-bonding.

In the present study, we report computation of "alcohol-specific" association constants for 11 different alcohols by curve-fitting published liquid-vapor equilibria data for binary alkane + alcohol mixtures in accordance with Mobile Order theory. Calculated alcohol-specific association constants are then used in conjunction with Eqn. (2) to predict pyrene solubilities in 42 solvent systems. Predicted values are compared to experimental pyrene solubilities, and to calculated values based both upon Mobile Order theory with the much simpler $K_{\mathrm{Alcohol}} = 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ approximation and the Kretschmer-Wiebe association model. To increase the number of systems available in our existing solubility data base, we also report experimental solubilities for pyrene dissolved in six binary alcohol + 2-methyl-1-pentanol solvent mixtures containing 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 1-octanol at 26°C.

EXPERIMENTAL METHODS

Pyrene (Aldrich, 99%) was recrystallized several times from anhydrous methanol, giving a purified sample that melted at $T_{mp}/K = 426.2 \pm 0.5$. 1-Propanol (Aldrich, 99+ %, anhydrous), 2-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, HPLC, 99.8 %), 2-butanol (Aldrich 99+ %, anhydrous), 2-methyl-1-propanol (Aldrich, 99+ %, anhydrous), 1-octanol (Aldrich, 99+ %, anhydrous) and 2-methyl-1-pentanol (Aldrich, 99%) were stored over anhydrous sodium sulfate and molecular sieves before use. Gas chromatographic analysis showed solvent purities to be 99.5 mole percent or better. Karl Fischer titration gave water contents (mass/mass %) of <0.01% for the seven alcohols. 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 ± 0.1)°C for at least three days (often longer). Attainment of equilibrium was verified both 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 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. Molar absorptivities of the nine standard solutions varied systematically with molar concentration, and ranged from about $\varepsilon/(\mathrm{L} \bullet \mathrm{mol}^{-1} \bullet \mathrm{cm}^{-1}) = 234$ to $\varepsilon/(\mathrm{L} \bullet \mathrm{mol}^{-1} \bullet \mathrm{cm}^{-1}) = 220$ for pyrene concentrations ranging from $C/(\mathrm{Molar}) = 8.31 \times 10^{-4}$ to $C/(\mathrm{Molar}) = 4.15 \times 10^{-3}$. Identical molar absorptivities were obtained for select pyrene standard solutions that contained up to 5 volume percent of the neat alcohol cosolvents. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of pyrene, volume(s) of volumetric flask(s) used and any dilutions required to place the measured absorbances on the Beer-Lambert law absorbance versus concentration working curve, and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from (mass/mass) solubility fractions using the molar masses of the solute and solvent. Experimental pyrene solubilities in the six binary solvent mixtures studied are listed in Table I.

RESULTS AND DISCUSSION

Optimized values of the Mobile Order theory association constants were obtained by fitting the Mobile Order model to isothermal vapor-liquid equilibrium data for binary mixtures of alkane (B) + alcohol (C). The criteria for the equilibrium are:

$$\gamma_i x_i P_i^{\mathrm{sat}} = F_i y_i P \quad (i = B, C) \qquad \text{(Eqn. 3)}$$

TABLE I Experimental Mole Fraction Solubilities of Pyrene (X_A^{sat}) in Binary Alcohol (B) + 2-Methyl-1-pentanol (C) Solvent Mixtures at 26.0°C

X_C^0	X_A^{sat}
1-Propanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.00426
0.0722	0.00462
0.1297	0.00487
0.2858	0.00543
0.3802	0.00582
0.4824	0.00612
0.7020	0.00684
0.8413	0.00737
1.0000	0.00789
2-Propanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.00290
0.0688	0.00327
0.1382	0.00364
0.2911	0.00438
0.3598	0.00477
0.4844	0.00536
0.7069	0.00648
0.8384	0.00702
1.0000	0.00789
1-Butanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.00622
0.0775	0.00645
0.1592	0.00656
0.3283	0.00679
0.4240	0.00697
0.5041	0.00709
0.7403	0.00745
0.8629	0.00773
1.0000	0.00789
2-Butanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.00439
0.0815	0.00481
0.1605	0.00508
0.3241	0.00560
0.4217	0.00594
0.5009	0.00616
0.7466	0.00709
0.8416	0.00735
1.0000	0.00789

TABLE I (Continued)

X_C^0	X_A^{sat}
2-Methyl-1-propanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.00326
0.0902	0.00366
0.1581	0.00400
0.3354	0.00480
0.4290	0.00518
0.5515	0.00572
0.7443	0.00661
0.8454	0.00714
1.0000	0.00789
1-Octanol (B) + 2-Methyl-1-pentanol (C)	
0.0000	0.02077
0.1356	0.01881
0.2438	0.01733
0.5035	0.01378
0.5605	0.01286
0.6287	0.01216
0.8331	0.00979
0.9165	0.00865
1.0000	0.00789

where γ_i, x_i, y_i and P_i^{sat} are the liquid phase activity coefficient, liquid phase mole fraction, vapor phase mole fraction, and pure component vapor pressure, respectively, of species i. The equilibrium (total) pressure is denoted as P. The correction factors F_i are defined by

$$F_i = f_i / \{ f_i^{sat} \exp[(V_i/RT)(P_i - P_i^{sat})]\} \qquad \text{(Eqn. 4)}$$

where f_i^{sat} and f_i denote the fugacity coefficients for the pure saturated species i at the temperature of the mixture and for species i in the vapor mixture, respectively, and V_i is the molar saturated liquid volume of pure species i. All fugacity coefficients were evaluated using the two-term virial equation (expansion in pressure). Second virial coefficients were calculated using the Tsonopoulos correction [26].

Mobile Order expressions for the liquid phase activity coefficients in mixtures of alkane (B) + alcohol (C) are given by[24]:

$$\ln \gamma_B = 0.5[\ln(\phi_B/x_B) + \phi_C(1 - V_B/V_C)] + (V_B/V_C)\, K_C' \phi_C^2/[1 + K_C' \phi_C] + V_B \phi_C^2 \beta_{BC} (RT)^{-1} \qquad \text{(Eqn. 5)}$$

and

$$\ln \gamma_C = 0.5[\ln(\phi_C/x_C) + \phi_B(1 - V_C/V_B)] + \ln(1 + K_C') - \ln(1 + K_C' \phi_C)$$

$$- K_C' \phi_B \phi_C/(1 + K_C' \phi_C) + V_C \phi_B^2 \beta_{BC} (RT)^{-1} \qquad \text{(Eqn. 6)}$$

where $K_C' = K_C/V_C$. Earlier applications[2–6, 9–11] involving Mobile Order theory described nonspecific physical interactions in terms of a modified solubility parameter model. In computing alcohol-specific association constants we have elected to replace the $(\delta_B' - \delta_C')^2$ parameter with the more general β_{BC}-parameter because the binary liquid-vapor equilibrium data that is to be regressed involves several different temperatures. Published tabulations[9–11] of δ_i' pertain to 298.15 K, and to our knowledge there has been no systematic study examining how modified solubility parameters vary with temperature.

Values for the two parameters K_C' and β_{BC} were obtained from binary total pressure using Barker's method [27]. Specifically, for a given set of parameter values, Eqn. (3) for components B and C are solved by trial and error for the total pressure P and vapor phase mole fraction y_B corresponding to each liquid mole fraction x_B of an isothermal set of total pressure data. The sum of the squares of the differences between the calculated and measured pressures is evaluated and a new set of parameter values is assumed according to the Nelder-Mead flexible polyhedron search method. The process is repeated until the sum of the squares is minimized. The optimized values of K_C' and β_{BC} are those numerical values which produce this minimum. Several binary vapor - liquid equilibrium data sets involved temperatures other than 298.15 K. For these systems, the numerical values of the association constants were corrected to 298.15 K using

$$K_{298}'/K_T' = \exp[-(\Delta H^\circ/R)(1/298.15 - 1/T_K)] \qquad \text{(Eqn. 7)}$$

with the molar enthalpy of hydrogen-bond formation taken to be $\Delta H^\circ = -25.1\ \text{kJ mol}^{-1}$.

Numerical values of the calculated association constants (corrected to 298.15 K) are tabulated in Table II, along with the calculated β_{BC}-values and overall root mean square deviations in the back-calculated total pressures. Careful examination of Table II reveals that the "opti-

TABLE II Mobile Order Theory Association Constants ($K'_{C,298}$) and Physical Interaction Constants (β_{BC}, J mol^{-1}) Calculated from Binary Alkane (B) + Alcohol (C) Vapor-Liquid Equilibrium Data

Alcohol	*Alkane*	*T/K*	$K'_{C,298}$	β_{BC}	$\Delta P/kPa$	*Data Ref.*
1-Propanol	*n*-Hexane	318.15	34.7	236.6	0.27	[36]
	n-Heptane	303.15	29.9	165.5	0.07	[28]
	2,2,4-Trimethylpentane	328.37	33.3	55.6	0.07	[37]
2-Propanol	*n*-Heptane	303.15	22.4	169.3	0.13	[28]
	Cyclohexane	333.15	28.1	387.2	0.29	[38]
	Methylcyclohexane	323.15	20.7	317.0	0.43	[38]
1-Butanol	*n*-Heptane	303.15	20.9	187.0	0.06	[24]
	n-Octane	373.15	37.6	128.4	0.18	[39]
	Cyclohexane	323.15	37.9	266.8	0.25	[40]
2-Butanol	*n*-Hexane	333.15	21.7	141.3	0.64	[41]
	n-Heptane	303.15	12.5	175.5	0.07	[24]
	Cyclohexane	318.15	16.4	238.0	0.19	[42]
2-Methyl-1-propanol	*n*-Heptane	303.15	15.8	218.9	0.06	[43]
1-Pentanol	*n*-Hexane	303.15	16.4	214.0	0.15	[44]
	n-Heptane	313.15	23.5	162.7	0.09	[45]
2-Pentanol	*n*-Heptane	313.15	13.1	125.8	0.11	[45]
3-Methyl-1-butanol	*n*-Heptane	313.15	19.4	192.7	0.10	[45]
1-Octanol	*n*-Hexane	313.15	16.4	180.8	0.21	[46]
	n-Heptane	293.15	13.9	86.3	0.05	[47]
2-Ethyl-1-hexanol	*n*-Hexane	313.15	11.0	− 177	**[a]	[48]
Cyclohexanol	*n*-Heptane	303.15	14.4	392.2	0.10	[49]

[a] K'_C and β_{BC} were estimated from limited *x*-*y* data.

mized" association constant for any given alcohol does vary slightly from one binary alkane + alcohol system to another. For example, in the three binary systems containing 2-propanol the calculated association constant ranged from a lower value of $K_C' = 20.7$ for methylcyclohexane to an upper limit of $K_C' = 28.1$ for the cyclohexane cosolvent. Some variation in calculated values for the association constant of a given alcohol is to be expected. First, the hydrogen-bonding treatment assumed in the original development of Mobile Order theory is probably much simpler than the actual situation. Second, values of the association constants will depend both upon the uncertainties in the experimental vapor-liquid equilibrium data and upon the particular solution model used to describe nonspecific physical interactions. The point to be made here is simply that the practical application of Mobile Order theory will eventually require a fixed value of the association at 298.15 K for each alcohol, and that this will lead to some degradation of Mobile Order theory to represent multi-system and multi-property data. Computations reported show that the association constants of alcohols are significantly smaller than the value of $K_{\text{Alcohol}} = 5{,}000\,\text{cm}^{-3}\,\text{mol}^{-1}$ previously assumed for all alcohols. We strongly suspect that the larger $K_{\text{Alcohol}} = 5{,}000\,\text{cm}^{-3}\,\text{mol}^{-1}$ was based either upon spectroscopic data or upon a thermodynamic treatment which failed to properly account for nonspecific interactions. In the latter case, all solution nonideality would have been attributed to formation of molecular association complexes.

As stated in the Introduction one of the objectives of the present study is to critically examine the ability of Mobile Order theory to predict pyrene solubilities in binary alcohol + alcohol solvent mixtures. Table III summarizes results of these computations for the self-association only ($K_{BC} = K_{CB} = 0$) and heterogeneous cross-association forms of Eqn. (2). Vapor-liquid equilibrium data could not be found in the chemical literature for binary alkane + 2-methyl-1-pentanol, hence, all Mobile Order theory entries for the six 2-methyl-1-pentanol systems were made assuming $K_{\text{Alcohol}} = 5{,}000\,\text{cm}^{-3}\,\text{mol}^{-1}$. Columns 2 and 4 list results for the self-association only treatment.

Predictions including cross-association are listed in the third and fifth columns of Table III under the headings of (2a) and (2a*). In the case of cross-association the stability constants were approximated as the geometric average of the equilibrium constants for the pure alco-

TABLE III Summarized Comparison Between Experimental Pyrene Solubilities and Predicted Values Based Upon Mobile Order Theory Eqn. (2) and Upon Kretschmer-Wiebe Eqns. (8) and (14)

Solvent (B) + Solvent (C)	% *Deviations*[a,b]		% *Deviations*[a,b]		% *Deviations*[a]	
	(2)	(2a)	(2*)	(2a*)	(8)	(14)
1-Octanol + 1-Butanol	1.1	−1.9	+3.0	−2.0	−1.2	−1.4
1-Octanol + 2-Butanol	1.9	3.3	+3.5	3.2	1.4	1.3
2-Butanol + 1-Butanol	+2.1	1.0	+5.6	−1.2	0.9	0.9
2-Butanol + 2-Methyl-1-propanol	+1.7	−1.4	+7.0	−1.4	−1.4	−1.4
1-Butanol + 3-Methyl-1-butanol	+3.5	0.9	+6.0	0.9	0.8	0.8
3-Methyl-1-butanol + 2-Methyl-1-propanol	1.1	−3.8	+3.5	−3.7	−3.1	−3.2
1-Butanol + 1-Propanol	+2.3	−1.7	+4.6	−0.8	0.7	0.7
2-Butanol + 1-Propanol	+4.1	+1.1	+8.1	+0.8	0.2	0.2
2-Propanol + 1-Propanol	+2.4	−0.7	+6.0	0.7	0.5	0.5
1-Octanol + 1-Propanol	1.3	−3.9	+1.6	−3.9	−2.8	−3.3
1-Butanol + 2-Propanol	+1.9	−1.1	+5.0	−1.2	0.9	0.8
2-Butanol + 2-Propanol	+1.0	−2.1	+5.6	−2.1	−2.5	−2.5
3-Methyl-1-butanol + 2-Propanol	+6.4	+3.3	+10.1	+3.4	+2.7	+2.6
2-Methyl-1-propanol + 2-Propanol	+2.8	0.5	+7.8	0.5	−1.5	−1.4
1-Propanol + 2-Methyl-1-Propanol	+3.9	1.1	+7.9	0.9	0.9	0.9
3-Methyl-1-butanol + 1-Propanol	+4.4	+1.4	+7.4	1.3	0.4	0.4
1-Octanol + 2-Propanol	3.3	−6.0	2.1	−5.8	−2.5	−3.0
1-Propanol + 2-Ethyl-1-hexanol	+6.2	+3.3	+9.4	+2.9	+3.5	+3.3
2-Propanol + 2-Ethyl-1-hexanol	+6.2	3.3	+10.2	3.3	+6.0	+5.7
1-Butanol + 2-Ethyl-1-hexanol	+6.6	+3.7	+9.4	3.3	+3.8	+3.7
2-Butanol + 2-Ethyl-1-hexanol	+3.3	0.5	+7.7	0.6	+2.9	+2.7
2-Methyl-1-propanol + 2-Ethyl-1-hexanol	+3.7	1.6	+8.3	1.7	2.1	2.0
3-Methyl-1-butanol + 2-Ethyl-1-hexanol	+6.7	3.8	+10.2	3.7	4.1	4.0

1-Octanol + 2-Ethyl-1-hexanol	+4.8	+1.9	+7.7	+1.9	+2.0	+2.0
1-Propanol + 1-Pentanol	+3.1	0.7	+6.2	0.7	+1.0	+0.9
2-Propanol + 1-Pentanol	+1.3	−1.8	+5.2	−1.7	0.5	0.4
1-Butanol + 1-Pentanol	+1.1	−1.9	+3.8	−2.1	−1.5	−1.6
2-Butanol + 1-Pentanol	+2.5	0.5	+6.8	0.5	1.0	1.0
2-Methyl-1-propanol + 1-Pentanol	0.6	−2.9	+4.6	−2.9	−2.5	−2.5
3-Methyl-1-butanol + 1-Pentanol	+2.5	0.5	+5.8	0.5	−1.2	−1.2
2-Pentanol + 1-Pentanol	+1.6	−1.4	+6.0	−1.5	−1.1	−1.1
1-Propanol + Cyclohexanol	+1.3	−1.8	+5.1	−2.1	0.5	0.6
2-Propanol + Cyclohexanol	0.7	−2.8	+4.9	−2.9	1.4	1.3
1-Butanol + Cyclohexanol	+1.6	−1.4	+5.0	−1.8	−0.8	−0.8
2-Butanol + Cyclohexanol	+0.8	−2.2	+5.8	−2.2	−1.6	−1.7
2-Methyl-1-propanol + Cyclohexanol	+5.2	2.3	+10.4	2.3	0.8	0.8
2-Methyl-1-pentanol + 1-Propanol	+4.7	1.7			0.8	0.8
2-Methyl-1-pentanol + 2-Propanol	+4.7	+1.7			0.7	0.7
2-Methyl-1-pentanol + 1-Butanol	+4.9	1.9			0.6	0.5
2-Methyl-1-pentanol + 2-Butanol	+2.0	1.1			1.0	0.9
2-Methyl-1-pentanol + 2-Methyl-1-propanol	1.3	−1.7			−1.2	−1.2
2-Methyl-1-pentanol + 1-Octanol	+2.0	1.2	--	–	0.7	0.7
Overall Average Absolute % Deviation	3.0	2.0	6.2	2.0	1.6	1.6

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

[b] Mobile Order theory Eqns. (2) and (2*) have the two cross-association constants K_{BC} and K_{CB} set equal to zero. Eqns. (2*) and (2a*) use the calculated alcohol-specific association constants. In the case of cross-association $K_{BC} = K_{CB} = (K_B K_C)^{0.5}$.

hols, i.e. $K_{BC} = K_{CB} = (K_B\ K_C)^{0.5}$. The geometric mean approximation is often invoked in applying association models to mixtures containing two alcohols. For example, Pradhan *et al.*[28] regressed isothermal vapor-liquid equilibrium data for five binary alcohol + alcohol mixtures in accordance with the Kretschmer-Wiebe model. The computed K_{ij} cross-association constants differed only slightly from the geometric mean approximation.

Forty-two different systems[6, 29–31] are considered in the present study. Each system reports solubility data at seven binary solvent compositions spanning the entire mole fraction range, plus pyrene solubilities in both pure alcohol solvents. Systems selected include both linear and branched alcohols ranging in size from $V_i = 75.10$ cm^{-3}mol^{-1} to $V_i = 158.30$ cm^{-3}mol^{-1}. Solute and solvent molar volumes and modified solubility parameters used in the Mobile Order predictions are listed in Table IV. The modified solubility parameters account for only nonspecific interactions, and in the case of the alcohol solvents the hydrogen-bonding contributions have been removed. Numerical values of δ_i' were obtained from published compilation[9–11], and were either deduced by regressing actual solubility data of solid *n*-alkanes in organic solvents in accordance with the configurational entropic model of Huyskens and Haulait-Pirson[32] or estimated using known values for similar organic solvents. The alcohol-specific association constants, which are listed in the second column of Table IV, represent the arithmetic average of values deduced by curve-fitting vapor-liquid equilibrium data of binary alkane + alcohol mixtures as discussed above.

Careful examination of Table III reveals that Mobile Order theory does provide very reasonable (though by no means perfect) predictions for the solubility behavior of pyrene in binary mixtures containing two alcohol solvents, particularly when cross-association is included in the theoretical treatment. Both cross association treatments gave overall average absolute deviations of about 2% between predicted and observed pyrene mole fraction solubilities. For many of the systems studied, the deviation between predicted and observed values was only slightly larger than the experimental uncertainty associated with the measured solubility data. In the case of cross-association treatment, no improvement in predictive accuracy was found for the alcohol-specific association constant computations. The much simpler

TABLE IV Solvent and Solute Properties Used in Mobile Order Predictions

Component (i)	K_i^{opt}/(cm^3/mol)	V_i/(cm^3/mol)	$\delta_i'/(MPa^{1/2})^a$
1-Propanol	2450	75.10	17.29
2-Propanol	1825	76.90	17.60
1-Butanol	2960	92.00	17.16
2-Butanol	1560	92.4	16.60
2-Methyl-1-propanol	1470	92.8	16.14
1-Pentanol	2015	108.60	16.85
2-Pentanol	1435	109.50	16.45
3-Methyl-1-butanol	2130	109.8	16.00
2-Methyl-1-pentanol		124.52	15.85
4-Methyl-2-pentanol		127.25	15.85
1-Octanol	2400	158.30	16.38
2-Ethyl-1-hexanol	1730	157.09	16.60
Cyclohexanol	1530	106.00	17.88
Pyrene[b]		166.5	

[a] Tabulated values are taken from a either compilation given in Ruelle *et al.* [9–11], or are estimated using known values for similar alcohols.

[b] The numerical value of $a_A^{solid} = 0.1312$ [50] was calculated from the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature of the solute, $T_{mp} = 424.4$ K.

$K_{\text{Alcohol}} = 5{,}000\,\text{cm}^{-3}\,\text{mol}^{-1}$ approximation gave nearly identical predicted values. Such was not the case, however, with the self-association only treatment. Here, significant degradation in predictive ability was noted each time the alcohol-specific association constants were used. Moreover, predicted values were almost always larger than the observed values, as is indicated by the numerous algebraic positive signs in column 4.

Also included in Table III (last two columns) are predictions based upon the Kretschmer-Wiebe association model. The model assumes that the alcohol molecules form complexes of linear *n*-mers, the distribution of which is governed by chemical equilibria. The collection of all different complexes plus the inert components comprises the set of "true" species which mix according to the Flory-Huggins equation. The degree of association of the alcohol is given by the value of a single association constant K_{Alcohol} which is assumed to be independent of complex size.

For an inert crystalline solute dissolved in a binary alcohol (B) + alcohol (C) solvent mixture, the Kretschmer-Wiebe model expresses the volume fraction saturation solubility as:[3, 6]

$$RT\ln\phi_A^{\text{sat}} = RT\,[\ln a_A^{\text{solid}} - (1-\phi_A^{\text{sat}}) + v_A(\Psi_B + \Psi_C)]$$

$$- v_A[\phi_B^2\beta_{AB} + \phi_C^2\beta_{AC} + \phi_B\phi_C(\beta_{AB} + \beta_{AC} - \beta_{BC})] \quad \text{(Eqn. 8)}$$

and

$$\Psi_B = C_B/(1 + K_B\Psi_B + K_{BC}\Psi_C) \qquad \text{(Eqn. 9)}$$

$$\Psi_C = C_C/(1 + K_{BC}\Psi_B + K_C\Psi_C) \qquad \text{(Eqn. 10)}$$

where β_{ij} represents a binary interactional parameter describing nonspecific interactions between components i and j, ϕ_i is volume fraction, C_i is molar concentration and a_A^{solid} is the activity of the solid solute. This latter quantity is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical supercooled liquid at the same temperature and pressure. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{mp} - T)/(R\;T\;T_{mp}) \qquad \text{(Eqn. 11)}$$

the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature, T_{mp}. The parameter v_A in Eqn. (8) is a measure of the molecular size for the solute 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 $v_A = (V_A/V_{\text{methanol}})_{303.15\,\text{K}}$.

The two solute-solvent interaction parameters are calculated from the appropriate binary reduction of Eqn. (8).

$$RT\ln(\phi_A^{\text{sat}})_B = RT\,[\ln a_A^{\text{solid}} - 1 + (\phi_A^{\text{sat}})_B + v_A\Psi_B^*] - v_A\phi_B^2\beta_{AB} \quad \text{(Eqn. 12)}$$

and

$$RT\ln(\phi_A^{\text{sat}})_C = RT[\ln a_A^{\text{solid}} - 1 + (\phi_A^{\text{sat}})_C + v_A\,\Psi_C^*] - v_A\,\phi_C^2\beta_{AC} \quad \text{(Eqn. 13)}$$

and measured volume fraction solubilities in both pure alcohol cosolvents $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$. Alternatively, if the saturation solubility is sufficiently small ($\phi_A^{\text{sat}} = 0$; $1 - \phi_A^{\text{sat}} = 1$) Eqns. (8), (12) and (13) can be combined to yield

$$RT\ln\phi_A^{\text{sat}} = RT\{\phi_B^0[\ln(\phi_A^{\text{sat}})_B - v_A\psi_B^*] + \phi_C^0[\ln(\phi_A^{\text{sat}})_C - v_A\Psi_C^*]$$

$$+ v_A(\Psi_B + \Psi_C)\} + v_A\,\phi_B^0\phi_C^0\beta_{BC} \qquad \text{(Eqn. 14)}$$

Numerical values of Ψ_B and Ψ_C are obtained from simultaneous (iterative) solutions of Eqns. (9) and (10). In the neat alcohols $C_{B(or\,C)}$ is simply the reciprocal of $v_{B(or\,C)}$. Computational procedure is described in greater elsewhere [3, 6].

Predictive ability of Eqns. (8) and (14) is summarized in the last two columns of Table III. Binary alcohol–alcohol interaction parameter is estimated using an unpublished correlation developed by one of the authors (S. W. Campbell) from binary data for mixtures of straight chain alcohols

$$\beta_{BC}(\text{in J mol}^{-1}) = 91.43\,[(\text{Cne}_2/\text{Cne}_1) - 1] \qquad \text{(Eqn. 15)}$$

where Cne is the effective carbon number of the alcohol [33]. Cne_2 is the larger of the two effective carbon numbers and Cne_1 is the smaller one. Effective carbon numbers used in the Kretschmer-Wiebe solubility predictions are listed in Table V. 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 [34] from alcohol-alkane binary vapor-liquid equilibrium data. Vapor-liquid equilibrium data could not be found in the case of binary alkane + 2-methyl-1-pentanol mixtures, and the Kretschmer-Wiebe association constant for this alcohol was estimated using the method of Bender and Nath. [35] Numerical values for the association constants are listed in Table V along with a relation that allows their estimation at other temperatures.

Inspection of the last two columns of Table III reveals that the Kretschmer-Wiebe association model also provides very accurate predictions for the solubility of pyrene dissolved in binary alcohol + alcohol solvent mixtures. Overall average absolute deviations between observed and predicted values were 1.6 % for both Eqns. (8) and (14).

TABLE V 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, Branched and Cyclic 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-Methyl-1-pentanol	41.5[d]	5.51	125.1
4-Methyl-2-pentanol	20.8[d]	4.17	127.8
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
Cyclohexanol	104.4	6.17[b]	106.4

[a] Self-association constants K_i at 298.15 K are calculated from the following correlation: $\ln [K_i(T)/K_i(303.15\ \mathrm{K})] = -10.783 \ln (T/303.15)$.

[b] Effective carbon numbers were calculated using correlation of Ambrose and Sprake. [33].

[c] Molar volumes were calculated using density data from the TRC Thermodynamic Tables of Non-Hydrocarbons. [51].

[d] Experimental vapor-liquid equilibrium for binary alkane + 2-methyl-1-pentanol and alkane + 4-methyl-2-pentanol mixtures could not be found in the published chemical literature. Kretschmer-Wiebe association constants were estimated from experimental molar enthalpies of vaporization and normal boiling point temperatures of the neat alcohols and hydrocarbon homomorphs according to the method proposed by Nath and Bender [35]. Antoine constants used in the equilibrium constant computations were: $A = 6.80909$, $B = 1662.71$ and $C = -75.01$ for 2-methyl-1-pentanol; and $A = 7.07349$, $B = 1751.56$ and $C = -57.93$ for 4-methyl-2-pentanol.

The aromatic hydrocarbon solute, pyrene, is assumed to be inert and is not permitted to form association complexes with either the monomeric alcohol or any of the presumed polymeric entities. Introduction of additional "curve-fit" association parameters for formation of pyrene-alcohol molecular complexes would lead to reduced deviations between observed and calculated values. At this time, we do not feel that the slight reduction in percentage deviation necessarily warrants the increased calculational complexity whenever one realized that it is possible to predict pyrene solubilities at all 294 binary solvent compositions (seven compositions for each of the 42 binary solvents) to within an overall average absolute deviation of less than 2%. In a direct comparison of Mobile Order theory versus the Kretschmer-Wiebe model, the latter model does have an ever so slightly lower overall average absolute deviation. For informational purposes, the "apparent" superiority of the Kretschmer-Wiebe model is significantly less than the experimental uncertainty associated with the measured solubility data. Without a more clear-cut distinction between models, we are hesitant to claim that either one is superior to the other for binary alcohol + alcohol solvent mixtures. Mobile Order theory does provide the simpler computational method for mixtures containing two alcohols. The extension of the Kretschmer-Wiebe model to systems containing multiple associating alcohols resulted in a set of coupled, nonlinear equations [See Eqns. (9) and (10)] that must be solved by trial and error.

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APPENDIX: GLOSSARY OF SYMBOLS

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure supercooled 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.
ΔH^0	standard enthalpy of hydrogen-bond formation.
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 alcohols *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*.
P	equilibrium (total) pressure.
R	gas constant.
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	liquid phase mole fraction of component *i*.
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.
y_i	vapor phase mole fraction of component *i*.

Greek letters

β_{ij}	binary interaction parameter for components *i* and *j*, used in the mathematical description for nonspecific interactions.
γ_i	liquid phase activity coefficient of component *i*.
$\gamma_{\mathrm{ch:}}$	fraction of time that alcoholic solvent *C* is not involved in hydrogen-bond formation.
δ_i'	modified solubility parameter of component *i*.
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the binary solvent mixture, calculated as if the third component were not present.
ϕ_A^{sat}	ideal volume fraction solubility of the solute.
ϕ_i	ideal volume fraction of component *i*.
Ψ_B^*, Ψ_C^*	total molar concentration of all species in the neat alcohol cosolvents.
Ψ_B, Ψ_C	quantities defined by Eqns. (9) and (10), respectively.