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Prediction of Anthracene Solubilities in Binary Alcohol + Alcohol Solvent Mixtures Using Alcohol-Specific Mobile Order Theory Stability Constants

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Experimental solubilities are reported for anthracene 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 25°C. Results of these measurements, along with previously published solubility data for anthracene 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 57 systems considered, both models provided very accurate predictions of the anthracene solubilities, with an overall average absolute deviation between measured and calculated values being 1.7 and 1.2% for mobile order theory and the Kretschmer–Wiebe association model, respectively.

KEY WORDS: alcohol solvents; anthracene solubilities; hydrogen-bonding; solubility predictions.

1. INTRODUCTION

Solid–liquid equilibrium data on organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in light of present trends toward heavier feedstocks and known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds.

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Solubility data for a number of polycyclic aromatic hydrocarbons (i.e., anthracene and pyrene) and heteroatom polynuclear aromatics (i.e., carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature (for a listing of references see Refs. 1–3). Despite efforts by experimentalists and scientific organizations, in terms of both new experimental measurements and critically evaluated data compilations, there still exist numerous systems for which solubility data are not readily available.

To address this problem, researchers have turned to predictive methods as a means to generate desired quantities. Numerous equations have been suggested for predicting solute solubilities in binary solvent mixtures. For the most part, the predictive methods do provide fairly reasonable estimates for noncomplexing systems. There still remains, however, the need to develop better predictive expressions and mixing models to describe the more nonideal complexing systems believed to contain hydrogen-bonding solvent components. Hydrogen-bonding that occurs in mixtures of alcohols is an example of specific interaction in that highly "preferential" contacts between proton–donor and proton–acceptor sites of neighboring alcohol molecules are established. The resulting H bonds are labile. During their lifetime they confer a higher degree of "order" to the liquid solution. The order introduced in the liquid by the formation of H bonds and the perpetual movement of the H bonds constitute the basic foundations of mobile order theory [4–13].

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 γ_{C_h} and not the concentrations of the various *i*-mers in the ensemble (this does not mean that these *i*-mers do not exist, but that their concentrations do not govern the thermodynamic probability). γ_{C_h} is the fraction of time during which a given molecule of the ensemble is free from H-bonding, that is, does not possess the energy of the H bond. But it is by no means the fraction of 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.

Ruelle and co-workers [6, 7, 14–17] have presented a very impressive set of comparisons between experimental and predicted for anthracene, naphthalene, pyrene (see also Ref. 18), biphenyl, carbazole, benzil (see also Ref. 19), *p*-benzoquinone, thianthrene (see also Ref. 20), tricosane, octacosane, 10-nonadecanone, 11-heneicosanone, and 12-tricosanone over a wide range of both noncomplexing and complexing solvents to document the predictive ability of mobile order theory. More recently, Acree and co-workers successfully extended mobile order theory to binary alkane + alcohol [21], alcohol + alcohol [22–24], and alcohol + 2-alkoxyethanol [25] solvent mixtures. Derived expressions predicted anthracene solubilities in 35 binary alcohol + alcohol and 32 binary alcohol + 2-alkoxyethanol mixtures to within an overall average absolute deviation between predicted and observed mole fraction solubilities of about 1.6 and 3.0%, respectively. A single numerical value of $K_{\text{Alcohol}} = 5000\ \text{cm}^3 \cdot \text{mol}^{-1}$ was assumed for the association constant of all monofunctional alcohol and 2-alkoxyethanol cosolvents studied.

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 alcohol cosolvent studied. As additional solubility data become available, and as mobile order theory is extended to vapor–liquid equilibria [26] and to more complex aqueous–alcohol solvent mixtures [10, 27], it becomes important for us to reexamine 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 hinder sterically 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 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 mobile order theory to predict anthracene solubilities in 57 solvent systems. Predicted values are compared to experimental anthracene solubilities and to calculated values based both upon mobile order theory with the much simpler $K_{\text{Alcohol}} = 5000\ \text{cm}^3 \cdot \text{mol}^{-1}$ approximation and the Kretschmer–Wiebe association model. To increase the number of systems available in our existing solubility database, we also report experimental solubilities for anthracene 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 25°C.

2. METHODS

Anthracene (Acros; 99.9 + %) was recrystallized several times from acetone. 1-Propanol (Aldrich; 99 + %, anhydrous), 2-propanol (Aldrich;

Table I. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + 2-Methyl-1-pentanol (C) Solvent Mixtures at 25.0°C

x_C°	x_A^{sat}
1-Propanol (B) + 2-methyl-1-pentanol (C)	
0.0000	0.000591
0.0737	0.000626
0.1347	0.000654
0.2837	0.000713
0.3727	0.000748
0.4557	0.000771
0.7050	0.000851
0.8395	0.000897
1.0000	0.000966
2-Propanol (B) + 2-methyl-1-pentanol (C)	
0.0000	0.000411
0.0668	0.000453
0.1363	0.000495
0.2887	0.000586
0.3788	0.000634
0.4842	0.000691
0.7035	0.000811
0.8473	0.000876
1.0000	0.000966
1-Butanol (B) + 2-methyl-1-pentanol (C)	
0.0000	0.000801
0.0865	0.000813
0.1692	0.000824
0.3256	0.000848
0.4476	0.000866
0.5278	0.000879
0.7486	0.000916
0.8606	0.000939
1.0000	0.000966
2-Butanol (B) + 2-methyl-1-pentanol (C)	
0.0000	0.000585
0.0844	0.000614
0.1590	0.000643
0.3299	0.000706
0.4255	0.000743

Table I. *(Continued)*

x_C^0	x_A^{sat}
0.5327	0.000786
0.7529	0.000872
0.8739	0.000914
1.0000	0.000966
2-Methyl-1-propanol (*B*) + 2-methyl-1-pentanol (*C*)	
0.0000	0.000470
0.0865	0.000516
0.1575	0.000549
0.3292	0.000631
0.4334	0.000678
0.5354	0.000724
0.7468	0.000827
0.8653	0.000893
1.0000	0.000966
1-Octanol (*B*) + 2-methyl-1-pentanol (*C*)	
0.0000	0.002160
0.1359	0.001953
0.2390	0.001844
0.4525	0.001571
0.5583	0.001448
0.6387	0.001354
0.8279	0.001122
0.9165	0.001047
1.0000	0.000966

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 mol% or better. Karl Fischer titration gave water contents (mass/mass, 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 25.0 ± 0.1°C for at least 3 days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature. Aliquots of saturated anthracene 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 356 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 $\varepsilon/(\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}) = 7450$ to $\varepsilon/(\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}) = 7150$ for anthracene concentrations ranging from $C(M) = 6.75 \times 10^{-5}$ to $C(M) = 2.25 \times 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained up to 5 vol% of the neat alcohol cosolvents. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of anthracene, the volume(s) of the volumetric flask(s) used, and any dilutions required to place the measured absorbances on the Beer–Lambert law absorbance-versus-concentration working curve, 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 anthracene solubilities in the six binary solvent mixtures studied are listed in Table I. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1.5%.

3. 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

$$\gamma_i x_i P_i^{\mathrm{sat}} = F_i y_i P \qquad (i = B, C) \tag{1}$$

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 P. The correction factors F_i are defined by

$$F_i = f_i / \{ f_i^{\mathrm{sat}} \exp[(V_i/RT)(P_i - P_i^{\mathrm{sat}})] \} \tag{2}$$

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. The various symbols are defined in greater detail under Nomenclature. The two-term virial equation (expansion in pressure) was used to calculate all fugacity coefficients. The Tsonopoulos correction [28] was used in the second virial coefficient calculations.

Mobile order expressions for the liquid-phase activity coefficients in mixtures of alkane (B) + alcohol (C) are given in Ref. 26:

$$\ln \gamma_B = 0.5[\ln(\phi_B/x_B) + \phi_C(1 - V_B/V_C)] + (V_B/V_C)\, K'_C \phi_C^2/[1 + K'_C \phi_C] + v_B \phi_C^2 \beta_{BC} (RT)^{-1} \tag{3}$$

and

$$\ln \gamma_C = 0.5[\ln(\phi_C/x_C) + \phi_B(1 - V_C/V_B)] + \ln(1 + K'_C) - \ln(1 + K'_C \phi_C) - K'_C \phi_B \phi_C/(1 + K'_C \phi_C) + v_C \phi_B^2 \beta_{BC} (RT)^{-1} \tag{4}$$

where $K'_C = K_C/V_C$. Earlier applications [6–8, 18–25] 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 [see Eq. (6)] with the more general β_{BC} parameter because the binary liquid–vapor equilibrium data that is to be regressed involves several temperatures. Published tabulations [6–8] 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 the binary total pressure using Barker's method [29]. Specifically, for a given set of parameter values, the two equations denoted by Eq. (1) 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 the 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, Eq. (5) was used to correct the numerical values of the association constants to 298.15 K

$$K'_{298}/K'_T = \exp[-(\Delta H^\circ/R)((1/298.15) - (1/T_K))] \tag{5}$$

In the above expression the molar enthalpy of hydrogen-bond formation taken to be $\Delta H^{\circ} = -25.1$ 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 "optimized" 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

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

Alcohol	Alkane	T (K)	$K'_{C,298}$	β_{BC}	ΔP (kPa)	No. Ref.
1-Propanol	*n*-Hexane	318.15	34.7	236.6	0.27	41
	n-Heptane	303.15	29.9	165.5	0.07	30
	2,2,4-Trimethylpentane	328.37	33.3	55.6	0.07	42
2-Propanol	*n*-Heptane	303.15	22.4	169.3	0.13	30
	Cyclohexane	333.15	28.1	387.2	0.29	43
	Methylcyclohexane	323.15	20.7	317.0	0.43	43
1-Butanol	*n*-Heptane	303.15	20.9	187.0	0.06	26
	n-Octane	373.15	37.6	128.4	0.18	44
	Cyclohexane	323.15	37.9	266.8	0.25	45
2-Butanol	*n*-Hexane	333.15	21.7	141.3	0.64	46
	n-Heptane	303.15	12.5	175.5	0.07	26
	Cyclohexane	318.15	16.4	238.0	0.19	47
2-Methyl-1-propanol	*n*-Heptane	303.15	15.8	218.9	0.06	48
1-Pentanol	*n*-Hexane	303.15	16.4	214.0	0.15	49
	n-Heptane	313.15	23.5	162.7	0.09	50
2-Pentanol	*n*-Heptane	313.15	13.1	125.8	0.11	50
3-Methyl-1-butanol	*n*-Heptane	313.15	19.4	192.7	0.10	50
1-Octanol	*n*-Hexane	313.15	16.4	180.8	0.21	51
	n-Heptane	293.15	13.9	86.3	0.05	52
2-Ethyl-1-hexanol	*n*-Hexane	313.15	11.0	−117	[a]	53
Cyclohexanol	*n*-Heptane	303.15	14.4	392.2	0.10	54

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

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 constant at 298.15 K for each alcohol and that this will lead to some degradation of mobile order theory to represent multisystem and multiproperty data. Computations reported show that the association constants of alcohols are significantly lower than the value of $K_{\text{Alcohol}} = 5000\ \text{cm}^3 \cdot \text{mol}^{-1}$ previously assumed for all alcohols. We strongly suspect that the larger $K_{\text{Alcohol}} = 5000\ \text{cm}^3 \cdot \text{mol}^{-1}$ was based either upon spectroscopic data or upon a thermodynamic treatment which failed to account properly for nonspecific interactions. In the latter case, all solution nonideality would have been attributed to formation of molecular association complexes.

As stated in Section 1 one of the objectives of the present study is to examine critically the ability of mobile order theory to predict anthracene solubilities in binary alcohol + alcohol solvent mixtures. 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 (ϕ_A^{sat}) is given by [22, 25]

$$\begin{aligned} RT\{ &\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - 0.5[1 - V_A/(x_B^{\circ} V_B + x_C^{\circ} V_C)] \\ &+ 0.5\ln[V_A/(x_B^{\circ} V_B + x_C^{\circ} V_C)] - (V_A/V_B)\,\phi_B^{\circ}[\phi_B^{\circ}(K_B/V_B) \\ &+ \phi_C^{\circ}(K_{BC}/V_C)]/[1 + \phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)] \\ &- (V_A/V_C)\,\phi_C^{\circ}[\phi_B^{\circ}(K_{CB}/V_B) \\ &+ \phi_C^{\circ}(K_C/V_C)]/[1 + \phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)]\} \\ = {} & V_A[\phi_B^{\circ}(\delta'_A - \delta'_B)^2 + \phi_C^{\circ}(\delta'_A - \delta'_C)^2 - \phi_B^{\circ}\phi_C^{\circ}(\delta'_B - \delta'_C)^2] \end{aligned} \tag{6}$$

whenever the saturation solubility is sufficiently low that $1 - \phi_A^{\text{sat}} \approx 1.0$. The symbols δ'_A, δ'_B, and δ'_C denote the modified solubility parameters of the solute and self-associating alcohols, respectively, and a_A^{solid} is the activity of the solid solute. The 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

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{\text{mp}} - T)/(RTT_{\text{mp}}) \tag{7}$$

the molar enthalpy of fusion, $\Delta H_A^{\mathrm{fus}}$, at the normal melting-point temperature, T_{mp}.

Contributions from nonspecific interactions are incorporated into mobile order theory through the $V_A[\phi_B^{\circ}(\delta'_A - \delta'_B)^2 + \phi_C^{\circ}(\delta'_A - \delta'_C)^2 - \phi_B^{\circ}\phi_C^{\circ}(\delta'_B - \delta'_C)^2]$ term. Through suitable mathematical manipulations, the $V_A\phi_B^{\circ}(\delta'_A - \delta'_B)^2$ and $V_A\phi_C^{\circ}(\delta'_A - \delta'_C)^2$ 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

$$\begin{aligned}
\ln \phi_A^{\mathrm{sat}} = {} & \phi_B^{\circ} \ln(\phi_A^{\mathrm{sat}})_B + \phi_C^{\circ} \ln(\phi_A^{\mathrm{sat}})_C - 0.5[\ln(x_B^{\circ} V_B + x_C^{\circ} V_C) \\
& - \phi_B^{\circ} \ln V_B - \phi_C^{\circ} \ln V_C] - (V_A/V_B)\, \phi_B^{\circ}[\phi_B^{\circ}(K_B/V_B) \\
& + \phi_C^{\circ}(K_{BC}/V_C)]/[1 + \phi_B^{\circ}(K_B/V_B) + \phi_C^{\circ}(K_{BC}/V_C)] \\
& + (V_A K_B \phi_B^{\circ}/V_B{}^2)(1 + (K_B/V_B))^{-1} \\
& - (V_A/V_C)\phi_C^{\circ}[\phi_B^{\circ}(K_{CB}/V_B) + \phi_C^{\circ}(K_C/V_C)]/[1 + \phi_B^{\circ}(K_{CB}/V_B) \\
& + \phi_C^{\circ}(K_C/V_C)] + (V_A K_C \phi_C^{\circ}/V_C{}^2) \\
& \times (1 + (K_C/V_C))^{-1} + V_A \phi_B^{\circ}\phi_C^{\circ}(\delta'_B - \delta'_C)^2 (RT)^{-1}
\end{aligned} \tag{8}$$

does not require a priori 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. The predictive expression simplifies to the following equation

$$\begin{aligned}
\ln \phi_A^{\mathrm{sat}} = {} & \phi_B^{\circ} \ln(\phi_A^{\mathrm{sat}})_B + \phi_C^{\circ} \ln(\phi_A^{\mathrm{sat}})_C \\
& - 0.5[\ln(x_B^{\circ} V_B + x_C^{\circ} V_C) - \phi_B^{\circ} \ln V_B - \phi_C^{\circ} \ln V_C] \\
& - (V_A/V_B)\, \phi_B^{\circ}\phi_B^{\circ}(K_B/V_B)/[1 + \phi_B^{\circ}(K_B/V_B)] \\
& + (V_A K_B \phi_B^{\circ}/V_B{}^2)(1 + ((K_B/V_B))^{-1} \\
& - (V_A/V_C)\, \phi_C^{\circ}\phi_C^{\circ}(K_C/V_C)/[1 + \phi_C^{\circ}(K_C/V_C)] \\
& + (V_A K_C \phi_C^{\circ}/V_C{}^2)(1 + (K_C/V_C))^{-1} + V_A \phi_B^{\circ}\phi_C^{\circ}(\delta'_B - \delta'_C)^2 (RT)^{-1}
\end{aligned} \tag{9}$$

whenever the two cross-association constants, K_{BC} and K_{CB}, are set equal to zero.

The predictive ability of mobile order theory is summarized in Table III for the self-association only ($K_{BC} = K_{CB} = 0$) and heterogeneous cross-association forms of mobile order theory. Vapor–liquid equilibrium data could not be found in the chemical literature for binary alkane + 2-methyl-1-pentanol and alkane + 4-methyl-2-pentanol, hence, all mobile order theory entries for the six 2-methyl-1-pentanol and six 4-methyl-2-pentanol systems were made assuming that $K_{\text{Alcohol}} = 5000$ cm^{3}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 in Table III. In the case of cross-association the stability constants were approximated as the geometric average of the equilibrium constants for the pure alcohols, 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. [30] 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.

Fifty-seven systems [22, 24, 31–34] are considered in the present study. Each system reports solubility data at seven binary solvent compositions spanning the entire mole fraction range, plus anthracene solubilities in both pure alcohol solvents. Systems selected include both linear and branched alcohols ranging in size from $V_i = 75.10$ cm$^3\cdot$mol^{-1} to $V_i = 158.30$ cm$^3\cdot$mol^{-1}. 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 compilations [6–8] 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 [35] or estimated using known values for similar organic solvents. The alcohol-specific association constants, which are listed in the second column in Table IV, represent the arithmetic average of values deduced by curve-fitting vapor–liquid equilibrium data of binary alkane + alcohol mixtures as discussed above. The molar volume of anthracene was approximated as $V_{\text{Anth}} = 150$ cm$^3\cdot$mol^{-1}, which is considerably less than the numerical value of $V_{\text{Anth}} = 171.0$ cm$^3\cdot$mol^{-1} assumed by Ruelle et al. [7] in their set of published calculations for anthracene dissolved in neat organic solvents. We feel that the smaller value represents a better estimate of anthracene's molecular size when dissolved in fluid solution. Shahidi et al. [36] cited an experimental value of $V_{\text{Anth}} = 156.8$ cm$^3\cdot$mol^{-1} for the partial molar volume of anthracene dissolved in carbon tetrachloride.

Table III. Summarized Comparison Between Experimental Anthracene Solubilities and Predicted Values Based Upon Mobile Order Theory Eqs. (8) and (9) and Upon Kretschmer Wiebe Eqs. (10) and (15)

Solvent (B) + solvent (C)	% deviations[a,b]		% deviations[a,c]		% deviations[a]	
	(9)	(8)	(9)	(8)	(10)	(15)
1-Butanol + 1-propanol	+1.7	−1.0	+3.9	−0.9	−0.4	−0.4
2-Butanol + 1-propanol	+3.1	0.5	+6.8	0.4	−0.5	−0.5
2-Propanol + 1-propanol	+2.0	1.5	+5.1	1.3	0.5	0.5
1-Octanol + 1-propanol	0.6	−2.9	+2.1	−2.8	−2.3	−2.3
1-Butanol + 2-propanol	+1.1	−1.9	+3.8	−1.8	0.6	0.6
2-Butanol + 2-propanol	+3.1	0.3	+7.6	0.4	0.1	0.1
1-Octanol + 2-Butanol	−1.5	−4.1	+2.0	−3.9	−1.2	−1.3
3-Methyl-1-butanol + 2-propanol	+4.5	+1.8	+8.0	+1.5	1.2	1.1
2-Methyl-1-propanol + 2-propanol	+3.8	+1.0	+8.3	+1.0	0.4	0.4
1-Propanol + 2-methyl-1-propanol	+2.0	−0.7	+5.7	−0.9	−2.1	−2.1
1-Octanol + 2-methyl-1-propanol	−2.1	−4.7	+1.4	−4.6	−2.5	−2.5
3-Methyl-1-butanol + 1-Butanol	+2.8	0.3	+5.1	0.3	−1.2	−1.2
3-Methyl-1-butanol + 2-Butanol	+2.3	1.1	+6.1	0.9	0.9	0.9
2-Butanol + 2-methyl-1-propanol	+3.0	0.4	+7.8	0.4	0.4	0.3
3-Methyl-1-butanol + 1-Octanol	1.7	−1.7	+3.4	−1.7	0.9	0.9
3-Methyl-1-butanol + 2-methyl-1-propanol	+1.8	−0.9	+5.7	−0.9	−0.5	−0.5
3-Methyl-1-butanol + 1-propanol	+2.8	0.3	+5.5	0.2	−1.1	−1.1
1-Octanol + 2-propanol	−3.8	−6.4	1.0	−6.3	−3.8	−3.8
1-Octanol + 1-butanol	+0.8	−1.9	+2.6	−2.0	−1.5	−1.5
2-Butanol + 1-butanol	+4.5	+1.8	+7.6	+1.5	+2.0	+2.0
2-Methyl-1-propanol + 1-butanol	+1.6	−1.1	+4.9	−1.3	−2.0	−2.0
1-Propanol + 2-ethyl-1-hexanol	+6.0	+3.4	+8.9	+3.1	+3.3	+3.3
2-Propanol + 2-ethyl-1-hexanol	+3.4	1.1	+7.1	1.1	+2.7	+2.7
1-Butanol + 2-ethyl-1-hexanol	+4.2	1.5	+6.6	1.2	1.5	1.5
2-Butanol + 2-ethyl-1-hexanol	+2.1	1.0	+6.0	1.0	+1.4	+1.4
2-Methyl-1-propanol + 2-ethyl-1-hexanol	0.8	−2.7	+4.1	−2.6	−1.9	−1.9
3-Methyl-1-butanol + 2-ethyl-1-hexanol	+3.0	−0.4	+5.2	−0.5	0.4	0.4
1-Octanol + 2-ethyl-1-hexanol	+1.6	−1.0	+4.3	−1.1	−1.0	−1.0
1-Propanol + 1-pentanol	+3.0	0.5	+5.8	0.5	+0.9	+0.9

2-Propanol + 1-pentanol	0.9	−2.4	+4.4	−2.4	0.2	0.2
1-Butanol + 1-pentanol	+2.8	0.4	+5.1	0.4	0.5	0.5
2-Butanol + 1-pentanol	+2.9	0.5	+6.7	0.5	+1.4	+1.4
2-Methyl-1-propanol + 1-pentanol	+0.6	−2.1	+4.6	−2.1	−1.9	−1.9
3-Methyl-1-butanol + 1-pentanol	2.7	0.7	+5.7	0.7	0.8	0.8
1-Octanol + 1-pentanol	+2.2	0.5	+4.8	0.5	0.8	0.5
1-Propanol + 2-pentanol	+4.8	+2.0	+8.4	+1.7	+1.2	+1.2
2-Propanol + 2-pentanol	+3.4	1.0	+7.8	0.9	0.9	0.9
1-Butanol + 2-pentanol	+3.3	+0.6	+6.5	0.3	0.5	0.5
2-Butanol + 2-pentanol	+3.7	+1.0	+8.4	+1.0	+1.5	+1.5
2-Methyl-1-propanol + 2-pentanol	+3.4	0.8	+8.3	0.8	0.8	0.8
1-Pentanol + 2-pentanol	+2.9	0.5	+7.0	0.5	0.6	0.6
3-Methyl-1-butanol + 2-pentanol	+2.4	−0.4	+6.2	−0.5	−0.3	−0.3
1-Octanol + 2-pentanol	1.0	−3.4	+2.5	−3.4	−1.6	−1.6
1-Propanol + 4-methyl-2-pentanol	+7.2	+4.5			1.1	1.1
2-Propanol + 4-methyl-2-pentanol	+8.3	+5.6			+2.4	+2.4
1-Butanol + 4-methyl-2-pentanol	+5.8	+3.1			0.4	0.4
2-Butanol + 4-methyl-2-pentanol	+3.5	+0.8			0.3	0.3
2-Methyl-1-propanol + 4-methyl-2-pentanol	+4.2	+1.5			+0.6	+0.5
1-Pentanol + 4-methyl-2-pentanol	+4.4	+1.7			0.6	0.5
3-Methyl-1-butanol + 4-methyl-2-pentanol	+2.3	−0.4			−0.9	−0.9
1-Octanol + 4-methyl-2-pentanol	−2.0	−4.6			−2.5	−2.8
2-Methyl-1-pentanol + 1-propanol	+5.2	+2.5			0.8	0.8
2-Methyl-1-pentanol + 2-propanol	+4.5	+1.8			0.6	0.6
2-Methyl-1-pentanol + 1-butanol	+5.7	+3.0			+1.1	+1.1
2-Methyl-1-pentanol + 2-butanol	+3.8	+1.2			+1.8	+1.8
2-Methyl-1-pentanol + 2-methyl-1-propanol	+2.3	0.8			0.7	0.7
2-Methyl-1-pentanol + 1-Octanol	+3.5	+0.9			+1.5	+1.2
Overall average absolute % deviation	3.1	1.7	5.6	1.5	1.2	1.2

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

[b] A numerical value of $K_{Alcohol} = 5000$ cm$^3 \cdot$ mol^{-1} was assumed for the self-association constant of alcohol cosolvents. In the case of Eq. (8) the cross-association constants were set equal to $K_{BC} = K_{CB} = (K_B K_C)^{0.5}$.

[c] Mobile order theory predictions used the alcohol-specific association constants given in Table IV. In the case of Eq. (8) the cross-association constants were set equal to $K_{BC} = K_{CB} = (K_B K_C)^{0.5}$.

Table IV. Solvent and Solute Properties Used in Mobile Order Predictions

Component (i)	K_i^{opt} (cm$^3\cdot$mol^{-1})	V_i (cm$^3\cdot$mol^{-1})	δ_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
Anthracene[b]		150.0	

[a] Tabulated values are either taken from compilation given by Ruelle et al. [6–8] or estimated using known values for similar alcohols.

[b] The numerical value of $a_A^{\mathrm{solid}} = 0.01049$ [40] was calculated from the molar enthalpy of fusion, $\Delta H_A^{\mathrm{fus}}$, at the normal melting-point temperature of the solute, $T_{\mathrm{mp}} = 490$ K.

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 anthracene 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 1.7% between predicted and observed anthracene 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 $K_{\mathrm{Alcohol}} = 5000$ cm$^3\cdot$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 indicated by the numerous algebraic positive signs in column 4 in Table III.

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 the 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 [23, 24]:

$$RT\ln\phi_A^{\mathrm{sat}} = RT[\ln a_A^{\mathrm{solid}} - (1-\phi_A^{\mathrm{sat}}) + v_A(\Psi_B+\Psi_C)] - v_A[\phi_B^2\beta_{AB} + \phi_C^2\beta_{AC} + \phi_B\phi_C(\beta_{AB}+\beta_{AC}-\beta_{BC})] \quad (10)$$

and

$$\Psi_B = C_B/(1+K_B\Psi_B + K_{BC}\Psi_C) \quad (11)$$

$$\Psi_C = C_C/(1+K_{BC}\Psi_B + K_C\Psi_C) \quad (12)$$

where β_{ij} represents a binary interactional parameter describing nonspecific interactions between component i and component j, ϕ_i is the volume fraction, and C_i is the molar concentration. The parameter v_A in Eq. (10) is a measure of the molecular size for the solute and is arbitrarily normalized to the molar volume of methanol at 303.15 K ($V_{\mathrm{methanol}} = 41.0\ \mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) according to $v_A = (V_A/V_{\mathrm{methanol}})_{303.15\ \mathrm{K}}$.

The two solute–solvent interaction parameters are calculated from the appropriate binary reduction of Eq. (10):

$$\beta_{AB} = RT\{\ln[a_A^{\mathrm{solid}}/(\phi_A^{\mathrm{sat}})_B] - 1 + (\phi_A^{\mathrm{sat}})_B + v_A\Psi_B^*\}/(v_A\phi_B^2) \quad (13)$$

and

$$\beta_{AC} = RT\{\ln[a_A^{\mathrm{solid}}/(\phi_A^{\mathrm{sat}})_C] - 1 + (\phi_A^{\mathrm{sat}})_C + v_A\Psi_C^*\}/(v_A\phi_C^2) \quad (14)$$

and measured volume fraction solubilities in both pure alcohol cosolvents, $(\phi_A^{\mathrm{sat}})_B$ and $(\phi_A^{\mathrm{sat}})_C$. Alternatively, if the saturation solubility is sufficiently small ($\phi_A^{\mathrm{sat}} \approx 0$; $1-\phi_A^{\mathrm{sat}} \approx 1$), Eqs. (10), (13), and (14) can be combined to yield

$$RT\ln\phi_A^{\mathrm{sat}} = RT\{\phi_B^{\circ}[\ln(\phi_A^{\mathrm{sat}})_B - v_A\Psi_B^*] + \phi_C^{\circ}[\ln(\phi_A^{\mathrm{sat}})_C - v_A\Psi_C^*] + v_A(\Psi_B+\Psi_C)\} + v_A\phi_B^{\circ}\phi_C^{\circ}\beta_{BC} \quad (15)$$

Numerical values of Ψ_B and Ψ_C are obtained from simultaneous (iterative) solution of Eqs. (11) and (12). In the neat alcohols $C_{B(\text{or } C)}$ is simply the reciprocal of $v_{B(\text{or } C)}$. The computational procedure is described in greater elsewhere [23, 24].

Predictive ability of Eqs. (10) and (15) is summarized in the last two columns in Table III. The 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:

$$\beta_{BC} = 91.43[(\text{Cne}_2/\text{Cne}_1) - 1] \qquad (16)$$

where β_{BC} is in $\text{J} \cdot \text{mol}^{-1}$ and Cne is the effective carbon number of the alcohol [37]. 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 [38] 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 [39]. Numerical values for the association constants are listed in Table V along with a relation that allows their estimation at other temperatures. The numerical value of $a_A^{\text{solid}} = 0.01049$ [40] used in the Kretschmer–Wiebe solubility predictions was calculated via Eq. (7).

Inspection of the last two columns in Table III reveals that the Kretschmer–Wiebe association model also provides very accurate predictions for the solubility of anthracene dissolved in binary alcohol + alcohol solvent mixtures. Overall average absolute deviations between observed and predicted values were 1.2% for both Eq. (10) and Eq. (15). The aromatic hydrocarbon solute, anthracene, 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 anthracene–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 when one realizes that it is possible to predict anthracene solubilities at all 399 binary solvent compositions (seven compositions for each of the 57 binary

Table V. Self-Association Constants K_i and Molar Volumes V_i at $T_{\mathrm{ref}} = 303.15$ 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) ($\mathrm{cm^3 \cdot mol^{-1}}$)
1-Propanol	282.9	3.00	75.5[b]
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
1-Pentanol	204.9	5.00	109.1
2-Pentanol	86.7	4.06[c]	110.0
3-Methyl-1-butanol	196.8	4.67[c]	109.7
2-Methyl-1-pentanol	41.5[d]	5.51	125.1
4-Methyl-2-pentanol	20.8[d]	4.17	127.8
1-Octanol	153.8	8.00	160.1
2-Ethyl-1-hexanol	50.1	7.41[c]	157.8
Cyclohexanol	104.4	6.17[c]	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] Molar volumes were calculated using density data from the TRC Thermodynamic Tables of Non-Hydrocarbons [55].

[c] Effective carbon numbers were calculated using the correlation of Ambrose and Sprake [37].

[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 [39]. 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.

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 Eqs. (11) and (12)] that must be solved by trial and error.

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NOMENCLATURE

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°	Standard enthalpy of hydrogen-bond formation
K_B	Kretschmer–Wiebe equilibrium constant describing the stepwise 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 stepwise 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 stepwise 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* to the molar volume of methanol at 303.15 K

x_i	Liquid-phase mole fraction of component *i*
$x_i^{\mathrm{o}}, x_j^{\mathrm{o}}$	Mole fraction compositions of the *ij* binary mixture, calculated as if the third component were not present
$x_{\mathrm{A}}^{\mathrm{sat}}$	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*
$\gamma_{\mathrm{C}_{\mathrm{h1}}}$	Fraction of time that alcoholic solvent *C* is not involved in hydrogen-bond formation
δ_i'	Modified solubility parameter of component *i*
$\phi_{\mathrm{B}}^{\mathrm{o}}, \phi_{\mathrm{C}}^{\mathrm{o}}$	Ideal volume fraction compositions of the binary solvent mixture, calculated as if the third component were not present
$\phi_{\mathrm{A}}^{\mathrm{sat}}$	Ideal volume fraction solubility of the solute
ϕ_i	Ideal volume fraction of component *i*
$\Psi_{\mathrm{B}}^{*}, \Psi_{\mathrm{C}}^{*}$	Total molar concentration of all species in the neat alcohol cosolvents
$\Psi_{\mathrm{B}}, \Psi_{\mathrm{C}}$	Quantities defined by Eqs. (11) and (12), respectively

REFERENCES

1. W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*, Vol. 54 in IUPAC Solubility Data Series (Oxford University Press, Oxford, 1994).
2. W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 1 (Solutes A-E)*, Vol. 58 in IUPAC Solubility Data Series (Oxford University Press, Oxford, 1995).
3. W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 2 (Solutes F Z)*, Vol. 59 in IUPAC Solubility Data Series (Oxford University Press, Oxford, 1995).
4. P. L. Huyskens and G. G. Siegel, *Bull. Soc. Chem. Belg.* **97**:821 (1988).
5. G. G. Siegel, P. L. Huyskens, and G. Vanderheyden, *Ber. Bunsen-Ges. Phys. Chem.* **94**:549 (1990).
6. P. Ruelle, C. Rey-Mermet, M. Buchmann, H. Nam-Tran, U. W. Kesselring, and P. L. Huyskens, *Pharm. Res.* **8**:840 (1991).
7. P. Ruelle, M. Buchmann, H. Nam-Tran, and U. W. Kesselring, *Int. J. Pharm.* **87**:47 (1992).
8. P. Ruelle, M. Buchmann, H. Nam-Tran, and U. W. Kesselring, *Pharm. Res.* **9**:788 (1992).
9. P. L. Huyskens, *J. Mol. Struct.* **270**:197 (1992).
10. K. Nelis, L. Van den Berge-Parmentier, and F. Huyskens, *J. Mol. Liq.* **67**:157 (1995).
11. P. L. Huyskens, D. P. Huyskens, and G. G. Siegel, *J. Mol. Liq.* **64**:283 (1995).
12. P. L. Huyskens and K. Seghers, *J. Mol. Struct.* **322**:75 (1994).
13. P. L. Huyskens, *J. Mol. Struct.* **297**:141 (1993).
14. P. Ruelle, M. Buchmann, and U. W. Kesselring, *J. Pharm. Sci.* **83**:396 (1994).

15. P. Ruelle, E. Sarraf, and U. W. Kesselring, *Int. J. Pharm.* **104**:125 (1994).
16. P. Ruelle, E. Sarraf, L. Van den Berge, K. Seghers, M. Buchmann, and U. W. Kesselring, *Pharm. Acta Helv.* **68**:49 (1993).
17. P. Ruelle and U. W. Kesselring, *J. Mol. Liq.* **67**:81 (1995).
18. J. R. Powell, D. Voisinet, A. Salazar, and W. E. Acree, Jr., *Phys. Chem. Liq.* **28**:269 (1994).
19. K. A. Fletcher, S. Pandey, M. E. R. McHale, and W. E. Acree, Jr., *Phys. Chem. Liq.* **33**:181 (1996).
20. K. A. Fletcher, M. E. R. McHale, J. R. Powell, K. S. Coym, and W. E. Acree, Jr., *Phys. Chem. Liq.* **34**:41 (1997).
21. W. E. Acree, Jr., A. I. Zvaigzne, and S. A. Tucker, *Fluid Phase Equil.* **92**:223 (1994).
22. W. E. Acree, Jr., and A. I. Zvaigzne, *Fluid Phase Equil.* **99**:167 (1994).
23. A. I. Zvaigzne, J. R. Powell, W. E. Acree, Jr., and S. W. Campbell, *Fluid Phase Equil.* **121**:1 (1996).
24. J. R. Powell, M. E. R. McHale, A.-S. M. Kauppila, W. E. Acree, Jr., and S. W. Campbell, *J. Solut. Chem.* **25**:1001 (1996).
25. M. E. R. McHale, J. R. Powell, A.-S. M. Kauppila, W. E. Acree, Jr., and P. L. Huyskens, *J. Solut. Chem.* **25**:1089 (1996).
26. J. R. Powell, M. E. R. McHale, A.-S. M. Kauppila, W. E. Acree, Jr., P. H. Flanders, V. G. Varanasi, and S. W. Campbell, *Fluid Phase Equil.* **134**:185 (1997).
27. M. E. R. McHale, S. Pandey, and W. E. Acree, Jr., *Phys. Chem. Liq.* **33**:93 (1996).
28. C. Tsonopoulos, *AIChE J.* **20**:263 (1974).
29. J. A. Barker, *Aust. J. Chem.* **6**:207 (1953).
30. A. G. Pradham, V. R. Bhethanabotla, and S. W. Campbell, *Fluid Phase Equil.* **84**:183 (1993).
31. J. R. Powell, M. E. R. McHale, A.-S. M. Kauppila, P. Otero, M. Jayasekera, and W. E. Acree, Jr., *J. Chem. Eng. Data* **40**:1270 (1995).
32. A. I. Zvaigzne and W. E. Acree, Jr., *J. Chem. Eng. Data* **40**:917 (1995).
33. 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).
34. J. R. Powell, M. E. R. McHale, A.-S. M. Kauppila, and W. E. Acree, Jr., *J. Chem. Eng. Data* **41**:728 (1996).
35. P. L. Huyskens and M. C. Haulait-Pirson, *J. Mol. Liq.* **31**:135 (1985).
36. G. Shahidi, P. G. Farrell, J. T. Edward, and P. Canonne, *J. Org. Chem.* **44**:950 (1979).
37. D. Ambrose and C. H. S. Sprake, *J. Chem. Thermodyn.* **2**:631 (1970).
38. C. A. Schmidt and S. W. Campbell, *Int. J. Thermophys.* **16**:1299 (1995).
39. A. Nath and E. Bender, *Fluid Phase Equil.* **7**:275 (1981).
40. W. E. Acree, Jr., and J. H. Rytting, *J. Pharm. Sci.* **72**:292 (1983).
41. I. Brown, W. Fock, and F. Smith, *J. Chem. Thermodyn.* **1**:273 (1969).
42. C. Berro, E. Neau, and M. Rogalski, *Fluid Phase Equil.* **7**:41 (1981).
43. I. Nagata, T. Ohta, and Y. Uchiyama, *J. Chem. Eng. Data* **18**: 54 (1973).
44. P. Gierycz, J. Gregorowicz, and S. Malanowski, *J. Chem. Thermodyn.* **20**:385 (1988).
45. P. Vonka, V. Svoboda, K. Strubl, and R. Holub, *Collect. Czech. Chem. Commun.* **36**:18 (1971).
46. D. O. Hanson and M. Van Winkle, *J. Chem. Eng. Data* **12**:319 (1967).
47. H. T. French, *J. Solut. Chem.* **12**:869 (1983).
48. V. R. Bhethanabotla and S. W. Campbell, *Fluid Phase Equil.* **62**: 239 (1991).
49. H. C. Van Ness and M. M. Abbott, *Int. DATA Ser. Sel. Data Mix. Ser. A* (1977), p. 11.
50. J. Rhodes, M.S. thesis (University of South Florida, Tampa, 1996).
51. A. Heintz, E. Dolche, and R. N. Lichtenthaler, *Fluid Phase Equil.* **27**:61 (1986).
52. G. Geiseler, K. Quitzsch, H. G. Vogel, D. Pilz, and H. Sachse, *Z. Phys. Chem.* (*Frankfurt*) **56**:288 (1967).

53. A. M. Kiryukhin, T. M. Lesteva, N. P. Markvzin, and L. S. Budantseva, *Prom-St. Sint. Kauch.* **7**:4 (1982).
54. J. T. Sipowska and S. A. Wieczorek, *J. Chem. Thermodyn.* **16**:693 (1984).
55. K. N. Marsh (ed.), *TRC Thermodynamic Tables: Non-Hydrocarbons* (Thermodynamics Research Center, Texas A&M University, College Station, 1994).