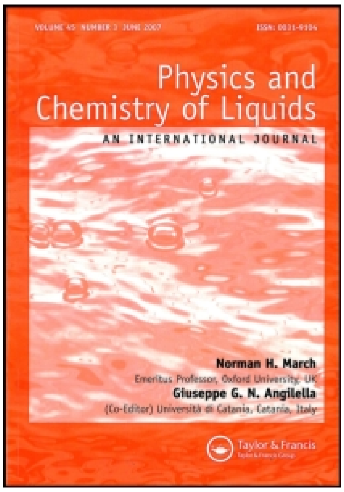

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Thermodynamics of Mobile Order Theory. Part 5. Extension of the Basic Model to Prediction of Anthracene Solubilities in Ternary Alkane Alcohol Solvent Mixtures

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THERMODYNAMICS OF MOBILE ORDER THEORY. PART 5. EXTENSION OF THE BASIC MODEL TO PREDICTION OF ANTHRACENE SOLUBILITIES IN TERNARY ALKANE + ALCOHOL SOLVENT MIXTURES

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Mobile Order theory, which has been used previously to describe the solubility behavior of anthracene and pyrene in binary alkane + alcohol and alcohol + alcohol solvent mixtures, is extended to ternary solvent systems containing alkane and alcohol cosolvents. Expressions are derived for both inert solutes and for systems that have solute – solvent association. Applications and limitations of the newly derived equations were assessed using published anthracene solubility data in 20 different ternary solvent systems. The best expression predicted the observed values to within an overall average absolute deviation of approximately 4.5% using a value of 5,000 $\mathrm{cm^3\,mol^{-1}}$ for all alcohol self-association and cross-association stability constants, and a value of 125 $\mathrm{cm^3\,mol^{-1}}$ for the presumed anthracene-alcohol association constant.

Keywords and Phrases: Anthracene solubilities; Ternary solvent mixtures; Solubility predictions; Hydrogen-bonding; Alcohol solvents

INTRODUCTION

This work continues a systematic search for simple mixing models which will provide reasonable mathematical descriptions of the thermodynamic properties of nonelectrolyte solutions. Of particular interest

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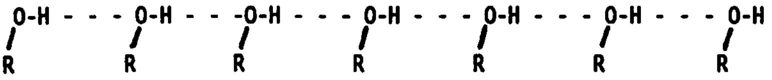
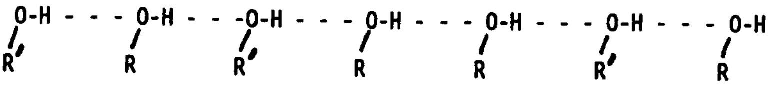
*Corresponding author. Fax: (940) 565-4318, e-mail: acree@unt.edu are those solutions that contain components capable of self-association. To date, we have examined both the applications and limitations of mobile order theory to describe the solubility of anthracene in 34 different binary alkane + alcohol [1 – 5], 57 binary alcohol + alcohol [6 – 10], 50 alcohol + alkoxyalcohol [11 – 13] and 34 alkane + alkoxyalcohol [14], and of pyrene dissolved in 42 different binary alcohol + alcohol [13, 15, 16] and 27 binary alkane + alcohol [5] solvent mixtures. Derived expressions predicted the experimental mole fraction solubilities to within an overall average absolute deviation of less than 4.5%, using a single numerical value of $K_{\text{alcohol}} = 5{,}000\ \text{cm}^3\ \text{mol}^{-1}$ for the association constant of the nine monofunctional alcohol and five alkoxyalcohol cosolvents studied. Nonspecific interactions were expressed in terms of modified solubility parameters. In mixtures containing two alcohol cosolvents, the thermodynamic treatment included the formation of both homogeneous and heterogeneous cross-associated hydrogen-bonded chains. The two polycyclic aromatic hydrocarbons (PAHs) were initially treated as inert solutes incapable of forming molecular complexes with any of the alcohol cosolvents present. Inclusion of a single PAH-alcohol association complex significantly improved the predictive accuracy of the derived expressions.

As part of the afore mentioned studies, we [4] briefly examined the ability of mobile order theory and the Kretschmer-Wiebe stepwise self-association model to mathematically represent vapor – liquid equilibria (VLE) data for binary alkane + alcohol systems. For each model, alcohol-specific association constants and binary interaction parameters were calculated from binary VLE data, and then used in anthracene solubility predictions. Both solution models performed adequately. The Kretschmer-Wiebe model did provide, however, a slightly better mathematical description of the experimental values for the 20 systems for which both VLE and anthracene solubility data could be found. Overall root mean square deviations for the VLE representation were 0.13 and 0.19 kPa for the Kretschmer-Wiebe model and mobile order theory, respectively. Anthracene was considered to be an inert solute in all calculations involving the Kretschmer-Wiebe model. This assumption greatly simplified the computations, particularly in the solvent systems containing two alcohol cosolvents. Here, a reiterative method is required to calculate the concentrations of the alcohol monomers.

In the present communication, we extend our earlier studies to ternary solvent mixtures. Expressions are derived for predicting the solubility of crystalline polycyclic aromatic hydrocarbon solutes dissolved in a ternary alcohol (B)+alcohol (C)+alkane (D) solvent mixtures. Such mixtures are characterized not only by the presence of long homogeneous H-bonded chains of the type



caused by self-association of the two alcohol cosolvents, but also by chains



involving hydrogen-bonding between dissimilar alcohol molecules. Application and limitation of the newly-derived equation(s) is illustrated using published anthracene solubility in 12 different ternary propanol+butanol+alkane [17–19] and 8 ternary propanol (or butanol)+alkane+alkane [20, 21] solvent mixtures. The alkane cosolvents studied are heptane, cyclohexane and 2,2,4-trimethylpentane. Predictions for the latter 8 ternary solvent systems were achieved by setting the two cross-association stability constants (K_{BC} and K_{CB}) and self-association constant of solvent component C (K_C) equal to zero.

DEVELOPMENT OF PREDICTIVE EXPRESSION FOR INERT SOLUTES

Essential features of Mobile Order theory, pertaining to a quaternary mixture containing an inert solute (Component A), two alcohol cosolvents (Components B and C) and an alkane cosolvent (Component D), will be briefly reviewed to facilitate development of the final derived equation(s). The Gibbs energy of mixing for the quaternary solution is separated into three contributions:

$$\Delta G^{\text{mix}}_{\text{ABCD}} = (\Delta G_{\text{ABCD}})_{\text{conf}} + (\Delta G_{\text{ABCD}})_{\text{chem}} + (\Delta G_{\text{ABCD}})_{\text{phys}} \quad (1)$$

The first term describes the configurational entropy based upon the Huyskens and Haulait-Pirson [22] definition of solution ideality

$$\begin{aligned}(\Delta G_{\mathrm{ABCD}})_{\mathrm{conf}} = (0.5)\ RT\ [&n_{\mathrm{A}} \ln \phi_{\mathrm{A}} + n_{\mathrm{B}} \ln \phi_{\mathrm{B}} + n_{\mathrm{C}} \ln \phi_{\mathrm{C}} \\ &+ n_{\mathrm{D}} \ln \phi_{\mathrm{D}} + n_{\mathrm{A}} \ln X_{\mathrm{A}} \\ &+ n_{\mathrm{B}} \ln X_{\mathrm{B}} + n_{\mathrm{C}} \ln X_{\mathrm{C}} + n_{\mathrm{D}} \ln X_{\mathrm{D}}]\end{aligned} \tag{2}$$

whereas the last two terms in Eq. (1) result from the formation of hydrogen-bonded complexes and weak nonspecific interactions in the quaternary solution, respectively. (The various symbols used in Eq. (1) and in subsequent equations are defined in the Appendix.)

The chemical contribution depends upon the functional groups present and the characteristics of the self-associating component. Alcohols have one hydrogen "donor" site and the two lone electron pairs on the oxygen atom provide two "acceptor" sites. The maximum possible number of hydrogen bonds is determined by the number of sites that are in minority. Monofunctional alcohols do form self-associated species, and there is no 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:

$$\gamma_{\mathrm{Bh:}} = 1/[1 + K_{\mathrm{B}}\phi_{\mathrm{B}}/V_{\mathrm{B}} + K_{\mathrm{BC}}\phi_{\mathrm{C}}/V_{\mathrm{C}}] \tag{3}$$

and

$$\gamma_{\mathrm{Ch:}} = 1/[1 + K_{\mathrm{CB}}\phi_{\mathrm{B}}/V_{\mathrm{B}} + K_{\mathrm{C}}\phi_{\mathrm{C}}/V_{\mathrm{C}}] \tag{4}$$

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 leads to the following expressions for the Gibbs energy for the hydrogen-bonding contribution

$$\begin{aligned}(\Delta G_{\mathrm{ABCD}})_{\mathrm{chem}} = {}& n_{\mathrm{B}}\, RT \ln[(1 + K_{\mathrm{B}}/V_{\mathrm{B}})/(1 + K_{\mathrm{B}}\phi_{\mathrm{B}}/V_{\mathrm{B}} + K_{\mathrm{BC}}\phi_{\mathrm{C}}/V_{\mathrm{C}})] \\ &+ n_{\mathrm{C}}\, RT \ln[(1 + K_{\mathrm{C}}/V_{\mathrm{C}})/(1 + K_{\mathrm{CB}}\phi_{\mathrm{B}}/V_{\mathrm{B}} + K_{\mathrm{C}}\phi_{\mathrm{C}}/V_{\mathrm{C}}]\end{aligned} \tag{5}$$

Physical nonspecific interactions are expressed in terms of the Scatchard-Hildebrand solubility parameter type model

$$(\Delta G_{ABCD})_{phys} = (n_A V_A + n_B V_B + n_C V_C + n_D V_D)[\phi_A \phi_B (\delta'_A - \delta'_B)^2 + \phi_A \phi_C (\delta'_A - \delta'_C)^2 + \phi_A \phi_D (\delta'_A - \delta'_D)^2 + \phi_B \phi_C (\delta'_B - \delta'_C)^2 + \phi_B \phi_D (\delta'_B - \delta'_D)^2 + \phi_C \phi_D (\delta'_C - \delta'_D)^2] \tag{6}$$

Modified solubility parameters, δ'_i, account only for nonspecific interactions, and in the case of the two alcohol solvents the hydrogen-bonding contributions are removed. Numerical values of δ'_i are available in several published compilations [23–25]. Tabulated values were either estimated using known values for similar solvents, or deduced by regressing experimental solubility data for solid *n*-alkanes in organic solvents in accordance with the configurational entropic model of Huyskens and Haulait-Pirson [22]. Any errors or uncertainties in the measured alkane solubility data would naturally affect the numerical values of δ'_i, as would any shortcomings of the Huyskens and Haulait-Pirson model to back-calculate the observed mole fraction solubilities.

It is noted that other research groups have treated nonspecific interactions differently, and have assumed solution models other than the Scatchard-Hildebrand solubility parameter theory. For example, Ruelle [26] in predicting solubilities in systems involving hydrogen-bond formation between a dissolved solute and surrounding solvent molecules, modified the Scatchard-Hildebrand expression by multiplying it by the fraction of time during which the solute is not bound to the solvent [*i.e.*, during which the distribution between the solvent and unbound solute molecules can still be considered to occur at random]. Ruelle's treatment further assumed that nonspecific interactions involving the bound solute were negligible. The theoretical justification for Ruelle's modification was not given, and it is not clear to us what mathematical form the integral $(\Delta G_{AB})_{phys}$ for the binary solution would have to take in order to give

$$(\Delta G_A)_{phys} = \{1/[1.0 + \max(K_{O_i}, K_{OH_i})(\phi_{solv}/V_{solv})]\} \cdot \phi^2_{solv} V_A (\delta'_A - \delta'_{solv})^2 \tag{7}$$

whenever $(\Delta G_{AB})_{phys}$ is differentiated with respect to the number of moles of solute present. The differentiation is required in deriving the solubility equation. Readers are reminded that any modification in the $(\Delta G_A)_{phys}$ expression must also show up in the corresponding $(\Delta G_B)_{phys}$ expression, the latter expression being obtained by differentiating $(\Delta G_{AB})_{phys}$ with respect to the number of moles of solvent. In Eq. (7) $\max(K_{O_i}, K_{OH_i})$ stands for the association constant governing the strongest intermolecular H-bond displayed by the molecular groups in solution.

We have elected to use the Scatchard-Hildebrand solubility parameter theory, Eq. (6), rather than the Ruelle modification because we have serious concerns about how to mathematically express the $(\Delta G_{ABCD})_{phys}$ contribution for the time that alcohol B is not bound to alcohol C, and for the time that alcohol C is not bound to alcohol B. Moreover, we have serious reservations about whether nonspecific interactions for bound molecules are truly negligible as assumed by Ruelle in proposing Eq. (7). Combining Eqs. (1), (2), (5) and (6), the Gibbs energy of mixing (per stoichiometric mole of mixing) is written as

$$\begin{aligned}
\Delta G^{mix}_{ABCD} = (0.5)\, RT\, [&n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln \phi_C + n_D \ln \phi_D \\
&+ n_A \ln X_A + n_B \ln X_B + n_C \ln X_C + n_D \ln X_D] \\
&+ n_B\, RT \ln [(1 + K_B/V_B)/(1 + K_B \phi_B/V_B + K_{BC}\phi_C/V_C)] \\
&+ n_C\, RT \ln[(1 + K_C/V_C)/(1 + K_{CB}\phi_B/V_B + K_C \phi_C/V_C)] \\
&+ (n_A V_A + n_B V_B + n_C V_C + n_D V_D) \\
&\cdot [\phi_A \phi_B (\delta'_A - \delta'_B)^2 + \phi_A \phi_C (\delta'_A - \delta'_C)^2 \\
&\quad + \phi_A \phi_D (\delta'_A - \delta'_D)^2 + \phi_B \phi_C (\delta'_B - \delta'_C)^2 \\
&\quad + \phi_B \phi_D (\delta'_B - \delta'_D)^2 + \phi_C \phi_D (\delta'_C - \delta'_D)^2]
\end{aligned} \tag{8}$$

Thermodynamic principles relate solubility to chemical potential. For a system obeying Eq. (8) the volume fraction solubility, ϕ^{sat}_A, of a sparingly soluble solute ($\phi^{sat}_A \approx 0$) is

$$\begin{aligned}
RT \ln a^{solid}_A = RT\{&\ln \phi^{sat}_A + 0.5[1 - V_A/(X^o_B V_B + X^o_C V_C + X^o_C V_D)] - \\
&0.5 \ln [V_A/(X^o_B V_B + X^o_C V_C + X^o_D V_D)]\} \\
&+ (V_A/V_B)\, RT\, \phi^o_B[\phi^o_B(K_B/V_B) + \phi^o_C(K_{BC}/V_C)]/ \\
&[1 + \phi^o_B(K_B/V_B) + \phi^o_C(K_{BC}/V_C)]
\end{aligned}$$

$$\begin{aligned}&+ (V_A/V_C)\ RT\ \phi_C^o[\phi_B^o(K_{CB}/V_B) + \phi_C^o(K_C/V_C)]/\\&[1 + \phi_B^o(K_{CB}/V_B) + \phi_C^o(K_C/V_C)] + V_A[\phi_B^o(\delta_A' - \delta_B')^2\\&+ \phi_C^o(\delta_A' - \delta_C')^2 + \phi_D^o(\delta_A' - \delta_D')^2 - \phi_B^o\phi_C^o(\delta_B' - \delta_C')^2\\&- \phi_B^o\phi_D^o(\delta_B' - \delta_D')^2 - \phi_C^o\phi_D^o(\delta_C' - \delta_D')^2]\end{aligned} \tag{9}$$

obtained by differentiating Eq. (8) with respect to the number of moles of solute. In Eq. (9), X_i^o and ϕ_i^o denote the mole fraction and volume fraction composition of component i in the initial ternary solvent mixture calculated as if the solute were not present, V_i is the molar volume of component i, 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 subcooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{\text{mp}} - T)/(RT\ T_{\text{mp}}) \tag{10}$$

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

Careful examination of the above expression reveals that it is possible to eliminate the three terms involving the modified solubility parameter of the solute using

$$\begin{aligned}V_A(\delta_A' - \delta_B')^2 = RT\{&\ln [a_A^{\text{solid}}/(\phi_A^{\text{sat}})_B] - 0.5(1 - V_A/V_B)\\&+ 0.5 \ln (V_A/V_B)\}\\&- RT(V_A/V_B)(K_B/V_B)/[1 + (K_B/V_B)]\end{aligned} \tag{11}$$

$$\begin{aligned}V_A(\delta_A' - \delta_C')^2 = RT\{&\ln [a_A^{\text{solid}}/(\phi_A^{\text{sat}})_C] - 0.5(1 - V_A/V_C)\\&+ 0.5 \ln (V_A/V_C)\}\\&- RT(V_A/V_C)(K_C/V_C)/[1 + (K_C/V_C)]\end{aligned} \tag{12}$$

and

$$\begin{aligned}V_A(\delta_A' - \delta_D')^2 = RT\{&\ln [a_A^{\text{solid}}/(\phi_A^{\text{sat}})_D] - 0.5(1 - V_A/V_D)\\&+ 0.5 \ln (V_A/V_D)\}\end{aligned} \tag{13}$$

the measured volume fraction solubilities in the pure solvents, $(\phi_A^{\text{sat}})_B$, $(\phi_A^{\text{sat}})_C$ and $(\phi_A^{\text{sat}})_D$. Substitution of Eqs. (11)–(13) into Eq. (9), followed by suitable algebraic manipulations, yields the following expression

$$
\begin{aligned}
\ln \phi_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^{o} \ln (\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}} + \phi_{\mathrm{C}}^{o} \ln (\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}} + \phi_{\mathrm{D}}^{o} \ln (\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{D}} \\
& -0.5[\ln(X_{\mathrm{B}}^{o} V_{\mathrm{B}} + X_{\mathrm{C}}^{o} V_{\mathrm{C}} + X_{\mathrm{D}}^{o} V_{\mathrm{D}}) - \phi_{\mathrm{B}}^{o} \ln V_{\mathrm{B}} - \phi_{\mathrm{C}}^{o} \ln V_{\mathrm{C}} \\
& \quad - \phi_{\mathrm{D}}^{o} \ln V_{\mathrm{D}}] - (V_{\mathrm{A}}/V_{\mathrm{B}}) \phi_{\mathrm{B}}^{o} [\phi_{\mathrm{B}}^{o} (K_{\mathrm{B}}/V_{\mathrm{B}}) + \phi_{\mathrm{C}}^{o} (K_{\mathrm{BC}}/V_{\mathrm{C}})]/ \\
& [1 + \phi_{\mathrm{B}}^{o} (K_{\mathrm{B}}/V_{\mathrm{B}}) + \phi_{\mathrm{C}}^{o} (K_{\mathrm{BC}}/V_{\mathrm{C}})] + (V_{\mathrm{A}} K_{\mathrm{B}} \phi_{\mathrm{B}}^{o}/V_{\mathrm{B}}^{2})(1 + K_{\mathrm{B}}/V_{\mathrm{B}})^{-1} \\
& - (V_{\mathrm{A}}/V_{\mathrm{C}}) \phi_{\mathrm{C}}^{o} [\phi_{\mathrm{B}}^{o} (K_{\mathrm{CB}}/V_{\mathrm{B}}) + \phi_{\mathrm{C}}^{o} (K_{\mathrm{C}}/V_{\mathrm{C}})]/[1 + \phi_{\mathrm{B}}^{o} (K_{\mathrm{CB}}/V_{\mathrm{B}}) \\
& + \phi_{\mathrm{C}}^{o} (K_{\mathrm{C}}/V_{\mathrm{C}})] + (V_{\mathrm{A}} K_{\mathrm{C}} \phi_{\mathrm{C}}^{o}/V_{\mathrm{C}}^{2})(1 + K_{\mathrm{C}}/V_{\mathrm{C}})^{-1} \\
& + V_{A} (RT)^{-1} [\phi_{\mathrm{B}}^{o} \phi_{\mathrm{C}}^{o} (\delta_{\mathrm{B}}' - \delta_{\mathrm{C}}')^{2} + \phi_{\mathrm{B}}^{o} \phi_{\mathrm{D}}^{o} (\delta_{\mathrm{B}}' - \delta_{\mathrm{D}}')^{2} + \phi_{\mathrm{C}}^{o} \phi_{\mathrm{D}}^{o} (\delta_{\mathrm{C}}' - \delta_{\mathrm{D}}')^{2}]
\end{aligned}
\tag{14}
$$

for the solubility of an inert solute in a ternary alcohol + alcohol + alkane solvent mixture. Readers will note that $a_{\mathrm{A}}^{\mathrm{solid}}$ was mathematically eliminated from the final derived expression as a consequence of replacing the three terms involving the solute's modified solubility parameter with the measured solute solubilities in pure solvents B, C and D. Elimination of the $a_{\mathrm{A}}^{\mathrm{solid}}$ term from the predictive equation can lead to better solubility estimates, particularly in the case of high melting point solutes. Equation (10) is only an approximate expression. Two additional terms involving differences between the molar heat capacities of the liquid and solid, ΔC_p, were dropped from the more rigorous $a_{\mathrm{A}}^{\mathrm{solid}}$ computation

$$
\begin{aligned}
\ln a_{\mathrm{A}}^{\mathrm{solid}} &= -\Delta H_{\mathrm{A}}^{\mathrm{fus}} (T_{\mathrm{mp}} - T)/(RT\, T_{\mathrm{mp}}) + \Delta C_p (T_{\mathrm{mp}} - T)/RT \\
&\quad - (\Delta C_p/R) \ln (T_{\mathrm{mp}}/T)
\end{aligned}
\tag{15}
$$

because ΔC_p data is generally not available in the chemical literature for high melting point solutes such as anthracene.

SOLUBILITY PREDICTIONS FOR INERT SOLUTES

Despite the complex appearance of Eq. (14) its application to solubilities in ternary alcohol + alcohol + alkane and ternary alcohol + alkane + alkane solvent mixtures is relatively straightforward and is similar to numerical examples presented previously (for example, see McCargar and Acree [27]). The quantities $(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}}$, $(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}}$ and $(\phi_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{D}}$

are calculated from measured mole fraction solubilities of the solid in the pure solvents assuming that the excess molar volume (or alternatively the volume change upon mixing) is zero. These three quantities along with the molar volumes, modified solubility parameters and numerical values of the equilibrium constants for formation of homogeneous (K_B and K_C) and heterogeneous (K_{BC} and K_{CB}) hydrogen-bonded chains are then inserted into Eq. (14) to calculate ϕ_A^{sat} at each ternary solvent composition. Equation (14) assumes that the two alcohol cosolvents undergo both self-association and cross-association. Formation of cross-associated B_iC_j species can be eliminated from the model simply by setting the two cross-association stability constants, K_{BC} and K_{CB}, equal to zero. Our prior studies have shown that in the case of anthracene and pyrene dissolved in binary alkane+alcohol and alcohol+alcohol solvent mixtures that Mobile Order theory provided very reasonable predictions assuming identical numerical values of $K_B = K_C = K_{BC} = K_{CB} = 5{,}000\,\text{cm}^3\,\text{mol}^{-1}$ for the homogeneous and heterogeneous stability constants for all monofunctional alcohols.

The predictive ability of Eq. (14) is summarized in the middle column of Table I for anthracene dissolved in 12 different ternary propanol+butanol+alkane [17–19] and 8 ternary propanol (or butanol)+alkane+alkane [20, 21] solvent mixtures. Predictions for the latter 8 ternary solvent systems were achieved by setting the two cross-association stability constants (K_{BC} and K_{CB}) and self-association constant of solvent component C (K_C) equal to zero. Each system contains solubility data at nineteen different ternary compositions spanning the entire mole fraction range, as well as measured anthracene solubility in the three pure solvents. The measured mole fraction solubilities were based upon 4–8 replicate measurements and were reproducible to within ± 1.5%. Solvent molar volumes and modified solubility parameters used in the Mobile Order theory computations are listed in Table II. The molar volume of the subcooled anthracene solute is approximated as $V_A = 150\,\text{cm}^3\,\text{mol}^{-1}$. An uncertainty of ± 10% in the numerical value assumed for V_A contributes very little error to the overall solubility predictions.

Examination of the numerical entries in the middle column of Table I reveals that Mobile Order theory predictions the mole fraction solubility of anthracene to within an overall average absolute

TABLE I Summarized comparison between experimental solubilities of anthracene in ternary solvent mixtures and predicted values based upon mobile order theory

Ternary solvent system[a]	*Deviations* (%)[b] *Eq.* (14)	 *Eq.* (16)
Alcohol (B) + Alcohol (C) + Alkane (D) Mixtures		
1-PrOH + 1-BtOH + Cyclohexane	4.4	2.6
1-PrOH + 2-BtOH + Cyclohexane	7.7	3.3
2-PrOH + 1-BtOH + Cyclohexane	7.0	1.6
2-PrOH + 2-BtOH + Cyclohexane	10.1	3.9
1-PrOH + 1-BtOH + Heptane	1.6	6.3
1-PrOH + 2-BtOH + Heptane	3.3	4.5
2-PrOH + 1-BtOH + Heptane	3.7	3.9
2-PrOH + 2-BtOH + Heptane	6.1	1.8
1-PrOH + 1-BtOH + 2,2,4-Trimethylpentane	2.0	9.5
1-PrOH + 2-BtOH + 2,2,4-Trimethylpentane	2.3	7.1
2-PrOH + 1-BtOH + 2,2,4-Trimethylpentane	1.1	7.8
2-PrOH + 2-BtOH + 2,2,4-Trimethylpentane	2.4	5.1
Alcohol (B) + Alkane (C) + Alkane (D) Mixtures		
1-PrOH + 2,2,4-Trimethylpentane + Cyclohexane	6.9	4.1
2-PrOH + 2,2,4-Trimethylpentane + Cyclohexane	7.5	3.4
1-BtOH + 2,2,4-Trimethylpentane + Cyclohexane	4.9	3.2
2-BtOH + 2,2,4-Trimethylpentane + Cyclohexane	11.4	5.2
1-PrOH + Heptane + Cyclohexane	5.2	4.3
2-PrOH + Heptane + Cyclohexane	10.1	2.5
1-BtOH + Heptane + Cyclohexane	5.0	2.9
2-BtOH + Heptane + Cyclohexane	12.5	6.5
Overall Average Absolute Deviation	5.8	4.5

[a] Abbreviation of solvents: 1-propanol (1-PrOH); 2-propanol (2-PrOH); 1-butanol (1-BtOH); and 2-butanol (2-BtOH).

[b] Deviation (%) = $(100/N)\Sigma \mid [(X_A^{\text{sat}})^{\text{calc}} - (X_A^{\text{sat}})^{\text{exp}}]/(X_A^{\text{sat}})^{\text{exp}} \mid$, where N corresponds to the number of data points for each ternary system. In the present study, solubilities were determined at 19 different ternary solvent compositions.

TABLE II Solvent and solute properties used in mobile order predictions

Component (*i*)	$V_i/(cm^3\,mol^{-1})$	$\delta_i'/(MPa^{1/2})$[a]
n-Heptane	147.48	14.66
Cyclohexane	108.76	14.82
2,2,4-Trimethylpentane	166.09	14.30
1-Propanol	75.10	17.29
2-Propanol	76.90	17.60
1-Butanol	92.00	17.16
2-Butanol	92.4	16.60
Anthracene	150.0	

[a] Tabulated values are taken from a compilation given in Ruelle *et al.* [23–25].

deviation of ± 5.8%. Readers are reminded that Eq. (14) does require as input values the experimental mole fraction solubilities in the three pure solvents. The inputed $(\phi_A^{sat})_i$ values do have ± 1.5% uncertainties associated with them. Error propagation analysis, assigning reasonable uncertainties to all the input values, gives a calculational uncertainty of about ±2.5% to each predicted ϕ_A^{sat} value. The propagated uncertainty is slightly less than half of the average absolute deviation between the predicted and observed values.

The Mobile Order theory predictions (though by no means perfect) are in accord with our earlier experiences using this particular solution model. As stated in the Introduction past studies have shown that Mobile Order theory described the solubility of anthracene in 34 different binary alkane + alcohol [1–5], 57 binary alcohol + alcohol [6–10], 50 alcohol + alkoxyalcohol [11–13] and 34 alkane + alkoxyalcohol [14], and of pyrene dissolved in 42 different binary alcohol + alcohol [13, 15, 16] and 27 binary alkane + alcohol [5] solvent mixtures to within an overall average absolute deviation of less than 4.5%, using a single numerical value of $K_{alcohol} = 5{,}000\,cm^3\,mol^{-1}$ for the association constant of the nine monofunctional alcohol and five alkoxyalcohol cosolvents studied. Of all the binary systems studied, deviations between predicted and observed anthracene solubilities were largest in solvent mixtures containing both an alkane and alcohol cosolvent. The binary alkane + alcohol solvent mixtures covered the larger range of anthracene mole fraction solubilities. The predictive accuracy of most solution models does decrease with increasing solution nonideality and with greater dissimilarities between the solute solubility in the pure solvents. A fair comparison would be to compare the ternary solvent predictions to those involving anthracene dissolved in binary alkane + alcohol solvent mixtures, which cover comparable ranges in mole fraction solubilities. Mobile Order theory predicted the solubility behavior of anthracene in binary alkane + alcohol solvent mixtures to within an average absolute deviation of ± 5.7%. [2, 3] Statistically, there is no difference in the predictive ability of Mobile Order theory when used to predict anthracene solubilities in binary and ternary solvent mixtures containing both an alkane and alcohol cosolvent. Based upon the comparisons presented above, we conclude that there is no loss in predictive ability in extending Mobile Order theory to higher-order multicomponent solvent mixtures.

EXTENSION OF THE MODEL TO INCLUDE SOLUTE-ALCOHOL COMPLEXATION

The thermodynamic treatment thus far has assumed that anthracene is an inert solute. It may be possible to improve the predictive ability of Mobile Order theory by including solute–solvent association terms into the basic model. Complexation involving a polycyclic aromatic hydrocarbon's (PAH's) polarizable π-electron cloud and the alcohol's OH functional group is not unreasonable. In fact published vapor–liquid and liquid–liquid equilibria [28–34], calorimetric [35,36] and spectroscopic [37,38] data are often interpreted with theoretical models that assume formation of a PAH-alcohol complex. Moreover, Ruelle *et al.* [39] assumed a weak PAH-water complex in rationalizing the aqueous solubility behavior of crystalline polycyclic aromatic hydrocarbons. The calculated stability constant, albeit very small ($K_{\text{complex}} \approx 80\,\text{cm}^3\,\text{mol}^{-1}$) did have an appreciable effect in terms of explaining the enhanced PAH solubilities. Without the complexation term, Mobile Order theory predictions for the PAH solutes were systematically low. Ruelle and Kesselring [40] also used Mobile Order theory to predict aqueous solubilities of proton-acceptor oxygen-containing solutes. Again, the authors assumed a numerical value of $K_{\text{complex}} \approx 80\,\text{cm}^3\,\text{mol}^{-1}$ for the stability constant for water's OH functional group interacting with a fused aromatic ring.

Extension of Eq. (14) to systems containing both AB and AC molecular complexation is relatively straightforward. Three terms are added to the final derived equation

$$\begin{aligned}\ln \phi_A^{\text{sat}} = {} & \phi_B^o \ln (\phi_A^{\text{sat}})_B + \phi_C^o \ln (\phi_A^{\text{sat}})_C + \phi_D^o \ln (\phi_A^{\text{sat}})_D \\ & - 0.5[\ln(X_B^o V_B + X_C^o V_C + X_D^o V_D) - \phi_B^o \ln V_B \\ & \qquad - \phi_C^o \ln V_C - \phi_D^o \ln V_D] \\ & + \ln [1 + \phi_B^o K_{AB}/V_B + \phi_C^o K_{AC}/V_C] \\ & - \phi_B^o \ln [1 + K_{AB}/V_B] - \phi_C^o \ln [1 + K_{AC}/V_C] \\ & - (V_A/V_B)\phi_B^o[\phi_B^o(K_B/V_B) \\ & + \phi_C^o(K_{BC}/V_C)]/[1 + \phi_B^o(K_B/V_B) + \phi_C^o(K_{BC}/V_C)] \\ & + (V_A K_B \phi_B^o/V_B^2)(1 + K_B/V_B)^{-1}\end{aligned}$$

$$
\begin{aligned}
&-(V_A/V_C)\phi_C^o[\phi_B^o(K_{CB}/V_B)+\phi_C^o(K_C/V_C)]/[1+\phi_B^o(K_{CB}/V_B)\\
&+\phi_C^o(K_C/V_C)]+(V_AK_C\phi_C^o/V_C^2)(1+K_C/V_C)^{-1}\\
&+V_A(RT)^{-1}[\phi_B^o\phi_C^o(\delta'_B-\delta'_C)^2+\phi_B^o\phi_D^o(\delta'_B-\delta'_D)^2\\
&+\phi_C^o\phi_D^o(\delta'_C-\delta'_D)^2]
\end{aligned}
\qquad (16)
$$

to describe complexation in the ternary solvent mixture, the $\ln[1 + \phi_B^o K_{AB}/V_B + \phi_C^o K_{AC}/V_C]$ term, and in the two pure alcohol cosolvents, the $\phi_B^o \ln [1 + K_{AB}/V_B] - \phi_C^o \ln [1 + K_{AC}/V_C]$ terms. The latter two terms are introduced whenever the $\phi_B^o V_A(\delta'_A - \delta'_B)^2$ and $\phi_C^o V_A(\delta'_A - \delta'_C)^2$ nonspecific interactions are eliminated from the basic model in favor of the measured PAH solute solubilities in the pure alcohol cosolvents. As before, the final derived expression applies to solutes of limited solubilities, (*i.e.*, $\phi_A^{sat} \approx 0$). Equation (16) can be used to predict anthracene solubilities in ternary alcohol+alkane+alkane solvent mixtures by setting all stability constants involving component C (K_C, K_{BC}, K_{CB} and K_{AC}) equal to zero.

Predictive application of Eq. (16) requires *a priori* knowledge of the numerical value for a given PAH-alcohol stability constant. In principle, one could have a different numerical value for each alcohol cosolvent. Such approaches would restrict predictions to alcohols already studied, and would represent more of a "curve-fitting" exercise rather than an outright solubility prediction. To maintain as much generality as possible, we elected to define a single stability constant for all four anthracene-alcohol complexes. The stability constant is thus independent of the alcohol cosolvent. This assumption seems reasonable in that only monofunctional alcohols were studied in the present investigation, and the molecular size of the single OH functional group (H-bond donor site) is approximately the same for linear and branched alcohols. Based upon eight sample computations, we decided upon a numerical value of $K_{AB} = K_{AC} = 125\,\text{cm}^3\,\text{mol}^{-1}$ for the *presumed* anthracene-alcohol complexes. This value accurately reproduced the observed anthracene data in our set of preliminary computations. No attempt was made to optimize the value of K_{AB} (and K_{AC}) as we wanted the computations to represent outright solubility predictions to the extent possible. The last column of Table I compares the predictions of Eq. (16) to the experimental anthracene solubility data. Examination of the numerical entries reveals that deviations between the observed and predicted values does decrease whenever the model includes the formation of an anthracene-alcohol complex. The overall average deviation went from approximately ±5.8% to ±4.5% for the ternary solvent mixtures studied.

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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.
ΔH_A^{fus}	molar enthalpy of fusion of the solid solute at its normal melting point temperature.
K_B, K_C	Mobile Order stability (equilibrium) constant describing the homogeneous self-association of monofunctional alcohols B and C, where the concentration units are molarity.
K_{AB}, K_{AC}	Mobile Order stability (equilibrium) constant describing the association between the solute (anthracene) and the alcohol cosolvent (Components B and C).
K_{BC}, K_{CB}	Mobile Order cross-association stability (equilibrium) constant describing the heterogeneous association of monofunctional alcohols B and C, where the concentration units are molarity.
T_{mp}	normal melting point temperature of the solute.
V_i	molar volume of component *i*.
X_B^o, X_C^o, X_D^o	mole fraction compositions of ternary solvent mixture, calculated as if the solute were not present.
X_A^{sat}	mole fraction solubility of the solute.

Greek Letters

γ_{Ih}:	fraction of time that alcoholic solvent I is not involved in hydrogen-bond formation.
δ_i'	modified solubility parameter of component *i*.
ϕ_{B}^{o}, ϕ_{C}^{o}, ϕ_{D}^{o}	volume fraction compositions of ternary solvent mixture, calculated as if the solute were not present and assuming that the excess volume of mixing is zero.
$\phi_{\mathrm{A}}^{\mathrm{sat}}$	volume fraction solubility of the solute, calculated assuming that the excess volume of mixing is zero.
ϕ_{solv}	volume fraction of solvent, calculated assuming that the excess volume is zero.