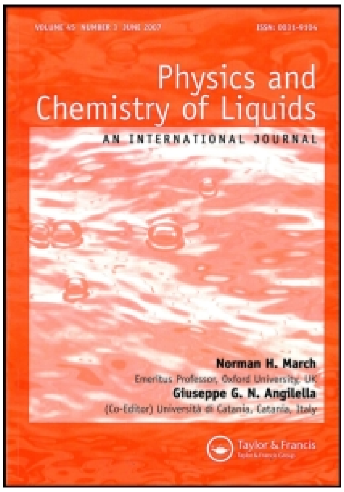

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THERMODYNAMICS OF MOBILE ORDER THEORY. PART 2. EXTENSION OF THE BASIC MODEL TO PREDICTION OF ANTHRACENE SOLUBILITIES IN BINARY ALKANE + ALKOXYALCOHOL SOLVENT MIXTURES

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The unconventional solution model of Mobile Order, which has previously been shown to provide a very reasonable thermodynamic description of anthracene solubilities and chemical potentials in binary alkane + monofunctional alcohol solvent mixtures, is extended to solutions containing an alkoxyalcohol. The ether oxygen atom provides a second site for hydrogen-bond fixation of the hydroxylic proton. The alkoxyalcohol cosolvent is treated as a "pseudo" monofunctional alcohol, having a slightly larger self-association stability constant to reflect the additional H-bond acceptor site. An expression derived from Mobile Order theory is found to predict published anthracene solubility data in 34 binary alkane + alkoxyalcohol solvent systems to within an overall average absolute deviation of *circa* ± 5.0%.

Keywords: Anthracene solubilities; hydrogen bond formation; binary solvents; alkoxyalcohols

INTRODUCTION

This work continues a systematic search for simple mixing models which will provide reasonable mathematical descriptions of the

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thermodynamic 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 32 different binary alkane + monofunctional alcohol [1–3], 57 binary alcohol + alcohol [4–7] and 50 binary alcohol + alkoxyalcohol solvent mixtures [8, 9], and of pyrene dissolved in 27 binary alkane + monofunctional alcohol [3] and 42 binary alcohol + alcohol solvent mixtures [10, 11]. The basic model [12–21] assumes all molecular groups perpetually move in the liquid, and that neighbours of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume V of the liquid divided by the number N_A molecules of the same kind, *i.e.*, Dom $A = V/N_A$. The center of this domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential constants 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 neighbouring 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 $\gamma_{\mathrm{Ch:}}$ and not the concentrations of the various *i*-mers in the ensemble (this does not mean that these *i*-mers do not exist, but rather their concentrations do not govern the thermodynamic probability). $\gamma_{\mathrm{Ch:}}$ is the fraction of 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 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 coworkers have presented a very impressive set of comparisons between experimental and predicted solubilities of crystalline aliphatic and polycyclic aromatic hydrocarbons [16, 17, 22, 23], polychlorinated aromatic hydrocarbons [24], monofunctional proton-acceptor solutes like esters, nitriles, tertiary amides and ketones [25, 26], carbazole [27], methylparaben and testosterone propionate [15, 25] in a wide range of nonpolar, polar and hydrogen-bonded solvents. The authors were even able to predict aqueous solubilities of 86 liquid and crystalline branched- and straight-chain alcohols and of 12 monohydroxysteriods [28].

For an inert crystalline solute dissolved in a binary alkane (B) + alcohol (C) solvent mixture the volume fraction saturation solubility ($\phi_A^{\rm sat}$) is given by [1–3]:

$$\begin{aligned}
\mathrm{RT}\{&\ln(a_A^{\rm solid}/\phi_A^{\rm sat}) - 0.5\,[1 - V_A\,(X_B^{\rm o}V_B + X_C^{\rm o}V_C)]\\
&+ 0.5\,\ln[V_A/(X_B^{\rm o}V_B + X_C^{\rm o}V_C)]\\
&- (V_A/V_C)\,(K_C\phi_C^{\rm o\,2}/V_C)\,/\,(1 + K_C\phi_C^{\rm o}/V_C)\}\\
&= V_A[\phi_B^{\rm o}(\delta'_A - \delta'_B)^2 + \phi_C^{\rm o}(\delta'_A - \delta'_C)^2\\
&- \phi_B^{\rm o}\phi_C^{\rm o}(\delta'_B - \delta'_C)^2]
\end{aligned} \tag{1}$$

whenever the saturation solubility is sufficiently small low so that $1 - \phi_A^{\rm sat} \approx 1.0$. The symbols δ'_A, δ'_B and δ'_C denote the modified solubility parameters of the solute and two solvents, respectively and $a_A^{\rm solid}$ is the activity of the solid solute. The remaining symbols are defined in detail in the Nomenclature. 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 $a_A^{\rm solid}$ can be computed from

$$\ln a_A^{\rm solid} = -\Delta H_A^{\rm fus}\,(T_{\rm mp} - T)/(\mathrm{RT}\;T_{\rm mp}) \tag{2}$$

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

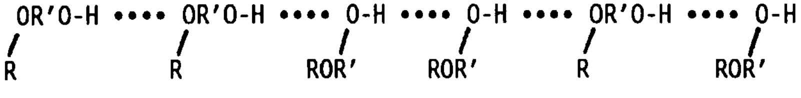
Contributions from nonspecific interactions are incorporated into Mobile Order theory through the $V_A[\phi_B^{\rm o}(\delta'_A - \delta'_B)^2 + \phi_C^{\rm o}(\delta'_A - \delta'_C)^2 - \phi_B^{\rm o}\phi_C^{\rm o}(\delta'_B - \delta'_C)^2]$ term. Through suitable mathematical manipulations, the $V_A\phi_B^{\rm o}(\delta'_A - \delta'_B)^2$ and $V_A\phi_C^{\rm o}(\delta'_A - \delta'_C)^2$ terms were eliminated from the basic model in favor of measured solubility data in both pure solvents, $(\phi_A^{\rm sat})_B$ and $(\phi_A^{\rm sat})_C$. The final derived expression

$$\begin{aligned}
\ln \phi_A^{\rm sat} = &\phi_B^{\rm o}\ln(\phi_A^{\rm sat})_B + \phi_C^{\rm o}\ln(\phi_A^{\rm sat})_C\\
&- 0.5\,[\ln(X_B^{\rm o}V_B + X_C^{\rm o}V_C) - \phi_B^{\rm o}\ln V_B - \phi_C^{\rm o}\ln V_C]\\
&- (V_A/V_C)\phi_C^{\rm o^2}(K_C/V_C)/[1 + \phi_C^{\rm o}(K_C/V_C)]
\end{aligned}$$

$$
\begin{aligned}
&+ (V_A K_C \phi_C^{\circ} / V_C^2)(1 + K_C/V_C)^{-1} \\
&+ V_A \phi_B^{\circ} \phi_C^{\circ} (\delta'_B - \delta'_C)^2 (\mathrm{RT})^{-1} \qquad (3)
\end{aligned}
$$

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. Earlier papers [1–3] have shown that Eq. (3) predicted experimental solubilities of anthracene and pyrene in binary alkane + monofunctional alcohol solvent mixtures to within an overall average absolute deviation of 5.8% and 10.5%, respectively, using alcohol-specific association constants deduced from a regressional analysis of binary alkane + alcohol vapor liquid equilibria (VLE) data. In the absence of binary VLE data a numerical value of $K_C \approx 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ could be assumed for the association constant of the monofunctional alcohol. For the systems studied no loss in predictive accuracy occurred from using the $K_C \approx 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ approximation. Anthracene and pyrene were treated as inert solutes and were not permitted to form association complexes with either the monomeric alcohol or any of the presumed polymeric entities. Inclusion of additional term(s) to account for possible solute–solvent molecular complexation did lead to much smaller deviations of 2.9% (anthracene) and 3.4% (pyrene) between predicted and observed solubilities. Calculated values of the stability constants of the *presumed* anthracene–alcohol and pyrene–alcohol molecular complexes, $K_{AC} \approx 125\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ and $K_{AC} \approx 175\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, suggested very weak specific interactions between alcohols and the two polycyclic aromatic hydrocarbon solutes. In the case of such weak association complexes, very reasonable (through by no means perfect) predictions can still be obtained by treating the solute as an inert, noncomplexing molecule.

In the present investigation Mobile Order theory is extended to an inert crystalline solute dissolved in binary alkane + alkoxyalcohol solvent systems. Such mixtures are characterized by the presence of long H-bonded chains of the type



$$
\underset{\substack{/\\ \mathrm{R}}}{\mathrm{OR'O{-}H}} \cdots\cdots \underset{\substack{/\\ \mathrm{R}}}{\mathrm{OR'O{-}H}} \cdots\cdots \underset{\substack{/\\ \mathrm{ROR'}}}{\mathrm{O{-}H}} \cdots\cdots \underset{\substack{/\\ \mathrm{ROR'}}}{\mathrm{O{-}H}} \cdots\cdots \underset{\substack{/\\ \mathrm{R}}}{\mathrm{OR'O{-}H}} \cdots\cdots \underset{\substack{/\\ \mathrm{ROR'}}}{\mathrm{O{-}H}}
$$

wherein hydrogen-bonding occurs both through the hydroxyl group and ether linkage. From the point-of-view of Mobile Order theory both scenarios lead to extension of the H-bonded chain, and it may be possible to treat alkoxyalcohol as a "pseudo" monofunctional alcohol cosolvent. With this idea in mind we have modified Eq. (3) slightly to allow for the additional site for the fixation of the hydroxylic proton caused by the presence of the ether functional group. Applicability of the proposed modification is evaluated using published [29–33] solubility data for anthracene dissolved in 34 binary alkane + alkoxyalcohol solvent mixtures. The systems should provide a very demanding test of the application and limitations of Mobile Order theory as the alkanes studied include linear (*n*-hexane, *n*-heptane, *n*-octane), branched (2,2,4-trimethylpentane) and cyclic (cyclohexane, methylcyclohexane and *tert*-butylcyclohexane) hydrocarbons.

COMPARISON OF ANTHRACENE SOLUBILITIES IN SIMPLE MONOFUNCTIONAL ALCOHOLS *VERSUS* ALKOXYALCOHOLS

Table I compares published values for the solubility of anthracene in simple monofunctional alcohol solvents to experimental values determined in alkoxyalcohols. Careful examination of the numerical entries reveals that anthracene is considerably more soluble in alkoxyalcohol solvents than in the corresponding monofunctional alcohols of similar size. For example, anthracene is nearly three times more soluble in 2-propoxyethanol than in 1-pentanol, the saturation mole fraction solubilities being $x_A^{\mathrm{sat}} \approx 0.003343$ and $x_A^{\mathrm{sat}} \approx 0.001097$, respectively. Observed solubility enhancement may arise from either differences in the hydrogen-bonding characteristics of alkoxyalcohols *versus* monofunctional alcohols or from differences in nonspecific interactions between the dissolved anthracene solute and the two solvent molecules. From a hydrogen-bonding point-of-view, the alkoxy oxygen atom provides a second site for the fixation of the hydroxylic proton. The fraction of the time that the alkoxyalcohol's hydroxylic proton is free and not involved in hydrogen-bond formation, $\gamma_{\mathrm{Ch:}}$, is

TABLE I Experimental solubilities of anthracene in select alcohol and alkoxyalcohol solvents at 25°C

Solvent	$x_A^{sat,a}$
1-Propanol	0.000591
2-Propanol	0.000411
1-Butanol	0.000801
2-Butanol	0.000585
2-Methyl-1-propanol	0.000470
1-Pentanol	0.001097
2-Pentanol	0.000800
3-Methyl-1-butanol	0.000727
2-Methyl-1-pentanol	0.000966
4-Methyl-2-pentanol	0.000779
1-Octanol	0.002160
2-Ethyl-1-hexanol	0.001397
2-Methoxyethanol	0.002211
2-Ethoxyethanol	0.002921
2-Propoxyethanol	0.003343
2-Isopropoxyethanol	0.003093
2-Butoxyethanol	0.003785
3-Methoxy-1-butanol	0.002702

[a] Experimental solubility data is taken from references [1–11] and [29–33].

$$\begin{aligned}\gamma_{\mathrm{Ch:}} &= 1/[1 + K_{\mathrm{OH}}\ \phi_C/V_C + K_{\mathrm{OC}}\ \phi_C/V_C] \\ &= 1/[1 + (K_{\mathrm{OH}} + K_{\mathrm{OC}})\ \phi_C/V_C] \qquad (4)\end{aligned}$$

where K_{OH} and K_{OC} refer to the microscopic stability constants for H-bond formation through the OH and alkoxy ether groups, respectively.

As noted in the *Introduction* previous studies assumed identical numerical values of $K_{\mathrm{Alcohol}} \approx 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for the stability constant(s) of all monofunctional alcohols before alcohol-specific association constants became available from regressional analysis of binary VLE data. For the systems that we have studied there is very little difference in the predicted anthracene and pyrene solubilities based upon alcohol-specific association constants and the much simpler $K_{\mathrm{Alcohol}} \approx 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ approximation. There is no reason for us to believe that the value(s) for hydrogen-bond formation through the OH should be any different for alcohols and alkoxyalcohols. The numerical value of K_{OH} in Eq. (4) is set at $K_{\mathrm{OH}} = 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. Stability constants for H-bond formation involving alcohols and ethers, however, are much weaker. Here, the calculated values typically range between $K_{OC} = 100\,\mathrm{cm^3\,mol^{-1}}$ and $K_{OH} = 300\,\mathrm{cm^3\,mol^{-1}}$. Given the relative magnitudes of the two stability constants, combined with the fact that the alkoxy hydroxylic OH and ether O atom molar concentrations are equal, it is expected that hydrogen-bond formation should occur largely through the OH group. Close proximity of the OH and O functional groups may further encourage proton fixation at the OH "acceptor" site. Assuming for the moment numerical values of $K_{OH} = 5{,}000\,\mathrm{cm^3\,mol^{-1}}$, $K_{OC} = 100\,\mathrm{cm^3\,mol^{-1}}$ and $V_C = 100\,\mathrm{cm^3\,mol^{-1}}$, we calculate that a typical alkoxyalcohol would be engaged in hydrogen-bonding approximately 98% of the time. Similarly, the corresponding alcohol solvent molecule of comparable molecular size ($K_{\mathrm{Alcohol}} = 5{,}000\,\mathrm{cm^3\,mol^{-1}}$ and $V_{\mathrm{Alcohol}} = 100\,\mathrm{cm^3\,mol^{-1}}$) would also be involved in hydrogen-bond formation *circa* 98% of the time. The calculations, albeit only approximate, suggest that the observed solubility enhancement does not result from differences in hydrogen-bonding.

Rather, we believe that a more plausible explanation involves differences in the nonspecific interactions between the dissolved anthracene solute and the two different solvent molecules. In the case of an inert solute dissolved in a self-associating solvent Mobile Order theory expresses the volume fraction solubility as

$$\begin{aligned} \ln\phi_A^{\mathrm{sat}} = {} & \ln a_A^{\mathrm{solid}} - 0.5\,(1 - V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}} \\ & + 0.5\ln\left[\phi_A^{\mathrm{sat}} + \phi_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})\right] \\ & - \phi_{\mathrm{solvent}}^2 V_A(\delta'_A - \delta'_{\mathrm{solvent}})^2(\mathrm{RT})^{-1} \\ & - r_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}} \end{aligned} \qquad (5)$$

where the $r_{\mathrm{solvent}}\,(V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}}$ term represents the contributions resulting from hydrogen-bond formation between the solvent molecules. For many of the published applications, r_{solvent} was assumed to be unity for strongly associated solvents with single hydrogen-bonded chains such as monofunctional alcohols, to be two for water or diols, and to equal zero for non-associated solvents such as saturated hydrocarbons. A more exact value for simple monofunctional alcoholic solvents can be calculated based upon

$$r_{\mathrm{solvent}} = (K_{\mathrm{solvent}}\,\phi_{\mathrm{solvent}}/V_{\mathrm{solvent}})/(1 + K_{\mathrm{solvent}}\,\phi_{\mathrm{solvent}}/V_{\mathrm{solvent}}) \qquad (6)$$

Nonspecific interactions are incorporated into the basic model through the $\phi^2_{\text{solvent}} V_A(\delta'_A - \delta'_{\text{solvent}})^2 (\text{RT})^{-1}$ term. The modified solubility parameters δ'_i account for only nonspecific interactions, and in the case of both alcohol and alkoxyalcohols, the hydrogen-bonding contributions would have been removed.

To illustrate this point, we calculate the solubility parameter of anthracene by requiring that Eq. (5) must accurately describe the published mole fraction solubility of anthracene in *n*-hexane ($X_A^{\text{sat}} = 0.001274$), *n*-heptane ($X_A^{\text{sat}} = 0.001571$), *n*-octane ($X_A^{\text{sat}} = 0.001838$), cyclohexane ($X_A^{\text{sat}} = 0.001553$), methylcyclohexane ($X_A^{\text{sat}} = 0.001649$), *tert*-butylcyclohexane ($X_A^{\text{sat}} = 0.001978$) and 2,2,4-trimethylpentane ($X_A^{\text{sat}} = 0.001074$). For solvents incapable of self-association K_{solvent} equals zero. Performing the aforementioned computations, the numerical value of δ'_A is found to range from $\delta'_A = 20.25\,\text{MPa}^{1/2}$ (in *n*-octane) to $\delta'_A = 21.10\,\text{MPa}^{1/2}$ (in cyclohexane). The average of $\delta'_A = 20.64\,(\pm 0.31)\,\text{MPa}^{1/2}$, when substituted back into Eq. (5) back-calculates the observed mole fraction solubilities to within ± 15–25%, which will be taken as a rough indication of the ability of the Scatchard-Hildebrand solubility parameter equation to describe the nonspecific physical contributions in systems free of specific interactions and molecular complexation. Solvent and solute properties used in the Mobile Order computations are listed in Table II.

Inspection of Eq. (5) (with $K_{\text{solvent}} = 0$) reveals that nonspecific effects influence solubility behavior as follows: the saturation solubility increases as δ'_{solvent} approaches δ'_A with a maximum value being reached whenever $\delta'_A = \delta'_{\text{solvent}}$. Assuming for the moment that alcohols and alkoxyalcohols have similar hydrogen-bonding characteristics, then anthracene should exhibit greater solubility in solvents having δ'_{solvent} values closer to $\delta'_A = 20.64\,\text{MPa}^{1/2}$. Tabulated modified solubility parameters [5, 10, 15–17, 22] for alcohol solvents range from *circa* $\delta'_{\text{solvent}} = 16.00\,\text{MPa}^{1/2}$ for 3-methyl-1-butanol to $\delta'_{\text{solvent}} = 17.29\,\text{MPa}^{1/2}$ for 1-propanol. Although numerical δ'_{solvent} values for 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol, 2-butoxyethanol and 3-methoxy-1-butanol were not given in the published tabulations, it can be argued that modified solubility parameters of alkoxyalcohols should exceed the tabulated values of the corresponding alcohols of comparable molecular size. An

TABLE II Solute and solvent properties used in the mobile order theory computations

Solvent	V_i *(cm³ mol⁻¹)*	$\delta_i'(MPa^{1/2})$ [a]
n-Hexane	131.51	14.56
n-Heptane	147.48	14.66
n-Octane	163.46	14.85
Cyclohexane	108.76	14.82
Methylcyclohexane	128.32	15.00
tert-Butylcyclohexane	173.9	15.50
2,2,4-Trimethylpentane	166.09	14.30
2-Ethoxyethanol	97.50	20.30
2-Propoxyethanol	114.92	19.80
2-Isopropoxyethanol	116.2	19.30
2-Butoxyethanol	131.92	19.20
3-Methoxy-1-butanol	115.09	19.80
Anthracene	150.0	$a_A^{\text{solid}} = 0.01049$ [b]

[a] Tabulated δ_i' values for the alkanes were taken from a compilation given in Ruelle *et al.* [15–17]. Modified solubility parameters for the five alkoxyalcohols were estimated by the authors, and were calculated by adding an incremental ether-group contribution value to the known modified solubility parameters of alcohols of comparable molecular size. The numerical value of the ether-group contribution value to δ_i' was computed from differences between the known modified solubility parameters of dialkyl ethers and the corresponding alkane homomorph hydrocarbon, taking into account the length of the alkyl chain.

[b] Numerical value was calculated using Eq. (2) and the solute's molar enthalpy of fusion, $\Delta H_A^{\text{fus}} = 28,860\,\text{J mol}^{-1}$ [34], at the normal melting point temperature.

alkoxyalcohol possesses an ether oxygen atom in addition to the alcohol OH functional group. In molecules where an ether oxygen atom is present, one generally finds a significant increase in the numerical value of the modified solubility parameter relative to that of the *n*-alkane homolog, *i.e.*, $\delta'_{\text{solvent}} = 17.96\,\text{MPa}^{1/2}$ for dipropyl ether *vs.* $\delta'_{\text{solvent}} = 14.56\,\text{MPa}^{1/2}$ for *n*-hexane, $\delta'_{\text{solvent}} = 17.45\,\text{MPa}^{1/2}$ for dibutyl ether *vs.* $\delta'_{\text{solvent}} = 14.85\,\text{MPa}^{1/2}$ for *n*-octane and $\delta'_{\text{solvent}} = 16.16\,\text{MPa}^{1/2}$ for dipentyl ether *vs.* $\delta'_{\text{solvent}} = 15.14\,\text{MPa}^{1/2}$ for *n*-decane [15–17, 22]. The effect does level off with increasing alkyl chain length. Based upon the above observations we estimate that the modified solubility parameters of the five alkoxyalcohol solvents studied should lie somewhere in the range of $\delta'_{\text{solvent}} = 19.0\,\text{MPa}^{1/2}$ to $\delta'_{\text{solvent}} = 21.0\,\text{MPa}^{1/2}$, which is very close to the calculated modified solubility of anthracene of $\delta'_A = 20.64(\pm 0.31)\,\text{MPa}^{1/2}$. (Values of $\delta'_{\text{solvent}} = 20.3\,\text{MPa}^{1/2}$ for 2-ethoxyethanol, $\delta'_{\text{solvent}} = 19.8\,\text{MPa}^{1/2}$ for 2-propoxyethanol, $\delta'_{\text{solvent}} = 19.3\,\text{MPa}^{1/2}$ for 2-isopropoxyethanol, $\delta'_{\text{solvent}} = 19.2\,\text{MPa}^{1/2}$ for 2-butoxyethanol and $\delta'_{\text{solvent}} = 19.8\,\text{MPa}^{1/2}$ for 3-methoxy-1-butanol will be used in the Mobile Order predictions to be presented in the next section). This suggests that the significant solubility enhancement noted in the alkoxyalcohol solvents (mole fraction solubility in 2-butoxyethanol is $x_A^{\text{sat}} = 0.003785$ [29]) results largely from differences in nonspecific interactions, as opposed to differences in the hydrogen-bonding characteristics of the two solvent types.

EVALUATION OF PREDICTIVE EXPRESSION FOR ALKANE + ALKOXYALCOHOL SOLVENT MIXTURES

Discussion in the preceding section focussed exclusively on the solubility of anthracene in either a neat alcohol and/or neat alkoxyalcohol solvent, where hydrogen-bond formation involved self-association of the single solvent component. These ideas can be extended to binary alkane (B) + alkoxyalcohol (C) solvent mixtures as the presence of the saturated hydrocarbon merely dilutes the molar concentration of the OH and ether functional groups. The alkoxyalcohol can be treated as a "pseudo" monofunctional alcohol having perhaps a slightly larger H-bond stability constant to reflect the presence a second site for fixation of the hydroxylic OH proton. The maximum number of hydrogen bonds that can be formed remains the same, and is determined by the number of OH protons present.

Table III provides a summarized comparison between measured anthracene solubilities in 34 different binary alkane + alkoxyalcohol solvent systems and predicted values based upon Eq. (3). Each system reports solubility data at seven binary compositions spanning the solvent's entire mole fraction range, plus the measured solute solubilities in both the neat alkane and alkoxyalcohol cosolvent. Each mole fraction solubility represents the average of between four and eight independent experimental determinations, with the measured values being reproducible to ± 1.8% (or better). For convenience, we have assumed a numerical value of $K_C = K_{\text{OH}} + K_{\text{OC}} \approx 5{,}000\,\text{cm}^3\,\text{mol}^{-1}$ for all five alkoxyalcohols studied. Computations using slightly smaller or larger values of K_C indicate that the predicted mole fraction solubility is not too sensitive to the actual numerical value assumed. Stability constants from $K_C = 4{,}000\,\text{cm}^3\,\text{mol}^{-1}$ to $K_C = 6{,}000\,\text{cm}^3\,\text{mol}^{-1}$ gave essentially identical predicted values. This

TABLE III Comparison between experimental solubilities and mobile order theory predictions for anthracene dissolved in binary alkane (B) + alkoxyalcohol (C) solvent mixtures

Binary Solvent System	*% Dev.*[a]
n-Hexane + 2-Ethoxyethanol	6.10
n-Heptane + 2-Ethoxyethanol	6.84
n-Octane + 2-Ethoxyethanol	5.93
Cyclohexane + 2-Ethoxyethanol	4.26
Methylcyclohexane + 2-Ethoxyethanol	4.86
2,2,4-Trimethylpentane + 2-Ethoxyethanol	8.75
n-Hexane + 2-Propoxyethanol	5.62
n-Heptane + 2-Propoxyethanol	+ 8.17
n-Octane + 2-Propoxyethanol	5.62
Cyclohexane + 2-Propoxyethanol	5.94
Methylcyclohexane + 2-Propoxyethanol	4.76
tert-Butylcyclohexane + 2-Propoxyethanol	3.50
2,2,4-Trimethylpentane + 2-Propoxyethanol	8.21
n-Hexane + 2-Isopropoxyethanol	3.23
n-Heptane + 2-Isopropoxyethanol	4.47
n-Octane + 2-Isopropoxyethanol	4.40
Cyclohexane + 2-Isopropoxyethanol	3.46
Methylcyclohexane + 2-Isopropoxyethanol	3.77
tert-Butylcyclohexane + 2-Isopropoxyethanol	5.26
2,2,4-Trimethylpentane + 2-Isopropoxyethanol	6.39
n-Hexane + 2-Butoxyethanol	4.35
n-Heptane + 2-Butoxyethanol	5.23
n-Octane + 2-Butoxyethanol	4.51
Cyclohexane + 2-Butoxyethanol	4.98
Methylcyclohexane + 2-Butoxyethanol	4.98
tert-Butylcyclohexane + 2-Butoxyethanol	4.18
2,2,4-Trimethylpentane + 2-Butoxyethanol	6.71
n-Hexane + 3-Methoxy-1-butanol	3.70
n-Heptane + 3-Methoxy-1-butanol	5.50
n-Octane + 3-Methoxy-1-butanol	4.59
Cyclohexane + 3-Methoxy-1-butanol	3.20
Methylcyclohexane + 3-Methoxy-1-butanol	– 3.17
tert-Butylcyclohexane + 3-Methoxy-1-butanol	3.97
2,2,4-Trimethylpentane + 3-Methoxy-1-butanol	7.72
Overall Average Absolute Deviation	5.04

[a] % Deviation = $(100/N)\Sigma \ln[(X_A^{\mathrm{sat}})^{\mathrm{calc}}/(X_A^{\mathrm{sat}})^{\mathrm{exp}}]$, where N is the number of binary solvent compositions in the system under consideration.

is not surprising given the mathematical form of the two chemical contributions in Eq. (3). Any time that K_C/V_C is much larger than unity, the denominators of the fourth and fifth terms simplify to $\phi_C^0\ (K_C/V_C)$ and K_C/V_C, respectively. This leads to a cancellation of K_C between the numerator and denominator of the two hydrogen-bonding terms.

Careful examination of the numerical entries in Table III reveals that Mobile Order predicts the observed solubility behavior to within an overall average absolute deviation of ± 5%. Individual deviations in a given system; however, may be as large as ± 15%. An algebraic sign in front of the numerical value indicates that Eq. (3) either overpredicted (+ sign) or underpredicted (−sign) the solubility at all seven binary solvent compositions. For 32 of the 34 systems investigated deviations were both positive and negative, hence, the absence of an algebraic sign. We note that part of the large deviations between the predicted and observed values is undoubtedly a result of failure of the Scatchard-Hildebrand solubility parameter equation to accurately describe the nonspecific interactions in these highly nonideal solvent mixtures. Deviations may also be caused by errors/uncertainties associated with the estimational scheme used in computing the modified solubility parameters of the alkoxyalcohols. An uncertainty of $\pm 0.2\,\mathrm{MPa}^{1/2}$ in the numerical value of δ'_i can lead to a $\pm 1-2\%$ difference in the calculated mole fraction solubility of anthracene. This is particularly true in mixtures of solvent components having vastly dissimilar δ'_i values as was the case here.

In evaluating the applicability of Mobile Order theory one must remember that no solution model is perfect. Often one wishes a reasonable estimate for the saturation solubility in the absence of an experimental value. Earlier studies [1 – 3] have documented that Eq. (3) predicted anthracene solubilities in 32 binary alkane + monofunctional alcohol solvent mixtures to within an overall average absolute deviation of ± 5.8%, which is comparable in magnitude to the deviations noted in the current study. There appears to be no loss in predictive accuracy in extending Mobile Order theory to systems containing an alkoxyalcohol. It may be possible in the future to reduce the deviations by including additional term(s) to account for specific solute – solvent interactions, as was the case in a recently published study [3] involving pyrene and anthracene dissolved in alkane + monofunctional alcohol mixtures. At the present time we feel uncomfortable trying to calculate stability constant(s) for the anthracene – alkoxyalcohol complexes that are likely present solution. We know that there is some error in the $V_A\ \phi_B^{\circ}\ \phi_C^{\circ}(\delta'_B - \delta'_C)^2(\mathrm{RT})^{-1}$ term caused by our inability to describe nonspecific interactions in the binary solvent mixtures. When vapor – liquid equilibria data becomes available for alkane + alkoxyalcohol mixtures we plan to re-estimate the solubility parameters of the alkoxyalcohols. This should reduce the error in the $V_A\ \phi_B^o\ \phi_C^o(\delta'_B - \delta'_C)^2(\mathrm{RT})^{-1}$ term and permit a more meaningful computation of the solute–solvent stability constant(s).

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NOMENCLATURE

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_C	Mobile Order theory stability constant used to describe the formation of hydrogen-bonded chain of the monofunctional alcohol *C*.
K_{AC}	Mobile Order theory stability constant used to describe the formation of the *AC* molecular complex.
n_i	number of moles of component *i*.
T_{mp}	normal melting point temperature of the solute.
V_i	molar volume of component *i*.
x_i^o, x_j^o	mole fraction composition of the *ij* binary mixture, calculated as if the third component were not present.
x_A^{sat}	mole fraction solubility of the solute.

Greek Letters

γ_{Ch}:	fraction of time during which molecule *C* of the ensemble is free from H-bonding.
δ'_i	modified solubility parameter of component *i*.

ϕ_B^o, ϕ_C^o 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.

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