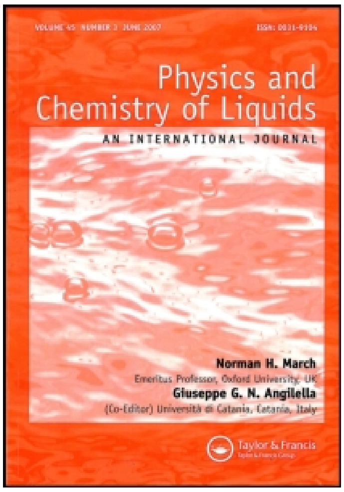

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Thermochemical Investigations of Hydrogen-Bonded Solutions: Part 4. Prediction of Liquid-Vapor Equilibria for Binary 2,2,4-Trimethylpentane 1-Alkanol Mixtures Using Mobile Order Theory

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THERMOCHEMICAL INVESTIGATIONS OF HYDROGEN-BONDED SOLUTIONS: PART 4. PREDICTION OF LIQUID-VAPOR EQUILIBRIA FOR BINARY 2,2,4-TRIMETHYLPENTANE + 1-ALKANOL MIXTURES USING MOBILE ORDER THEORY

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The unconventional solution model of Mobile Order, which previously had been shown to provide a very accurate thermodynamic description of anthracene solubilities and chemical potentials in binary hydrocarbon + alcohol solvent mixtures, is extended to other thermodynamic excess properties. An expression is derived for predicting liquid-vapor equilibria of binary hydrocarbon + alcohol systems. Applications and limitations of the newly-derived predictive expression are assessed using published vapor pressure data for binary mixtures containing 2,2,4-trimethylpentane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol.

KEY WORDS: Vapor pressure, alcohols, Mobile Order theory, liquid-vapor equilibria

INTRODUCTION

For many years one of the more challenging problems facing solution thermodynamicists has been the prediction of phase equilibria in hydrogen-bonding systems containing either a self-associating alcohol or carboxylic acid cosolvent. Self-association decreases the vapor pressure and increases the boiling point temperature of the neat alcohol or carboxylic acid compared to the non-associated hydrocarbon homomorph of comparable molecular size and mass. Moreover, in the case of inert hydrocarbon + alcohol and inert hydrocarbon + carboxylic acid mixtures, hydrogen-bonding may give rise to liquid-liquid immiscibility caused by relatively large positive deviations from Raoult's law. Interpretation of solution nonideality in such nonelectrolyte solutions has historically followed two dissimilar lines, which are predicated upon long-range and short-range molecular forces. At one extreme are weakly bonded van der Waals complexes, characterized by loose, nonspecific physical interactions and primarily stabilized by long-range dispersion forces. At the far opposite extreme are the hydrogen-bonded complexes that exhibit relatively strong, specific and highly directional binding of a primarily electrostatic nature. Even in

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systems known to contain molecular complexation the need to properly account for nonspecific interactions has long been recognized.[1-6]

Much of the earlier research concerning mixtures containing alcohols, as summarized by Pimentel and McClellan,[7] treated hydrogen-bonding as a stepwise polymerization process resulting in a continuum of species. Thus, at low alcohol concentrations dimers would be the predominate polymeric species; with larger polymer chains becoming more significant with increasing alcohol concentration. Van Ness *et al.*[8] compared infrared data to heat of mixing data for ethanol + *n*-heptane and ethanol + methylbenzene and concluded that the results were best explained by a model containing monomers, cyclic dimers and linear polymers having 20 or more units per chain. Tucker and Christian[9] noted that the simplest model ($1\text{–}3-\infty$) that can adequately describe the vapor pressure data for ethanol + *n*-hexadecane systems contained two equilibrium constants, one constant for trimer formation and the second for the sequential addition of the monomer. Other studies have indicated that a simple polymer of definite size may dominate. Fletcher and Heller[10,11] explained the infrared data of 1-octanol in *n*-decane (from dilute solutions to the pure alcohol) in terms of a monomer-tetramer self-association model. Dixon[12] also found that the monomer-tetramer model gave the best correlations for his proton magnetic resonance data on the hydroxyl shift for methanol in cyclohexane. Anderson *et al.*[13,14] explained the vapor pressures of several linear and branched alcohols in 2,2,4-trimethylpentane with a monomer-pentamer model.

Of the continuous self-associated solution models currently used to describe thermodynamic properties of alcohol + hydrocarbon mixtures, the more popular models such as the Kretschmer–Wiebe[15-18]

$$C_i + C_1 \rightleftharpoons C_{i+1} \qquad K_c = [\phi_{C_{i+1}}/(\phi_{C_1}\phi_{C_i})][i/(i+1)]$$

$$\phi_C = \sum_{i=1}^{\infty} \phi_{C_i} = (1/K_c) \sum_{i=1}^{\infty} i(K_c\phi_{C_1})^i = \phi_{C_1}(1 - K_c\phi_{C_1})^{-2} \tag{1}$$

Mecke–Kempter[19,20]

$$C_i + C_1 \rightleftharpoons C_{i+1} \qquad K_c = \phi_{C_{i+1}}/(\phi_{C_1}\phi_{C_i})$$

$$\phi_C = \sum_{i=1}^{\infty} \phi_{C_i} = \phi_{C_1} \sum_{i=1}^{\infty} (K_c\phi_{C_1})^{i-1} = \phi_{C_1}(1 - K_c\phi_{C_1})^{-1} \tag{2}$$

and Attenuated Equilibrium Constant (AEC) models[21]

$$C_{i-1} + C_1 \rightleftharpoons C_i \qquad K_C/i = C_{C_i}/(C_{C_{i-1}}C_{C_i}V_c)$$

$$\phi_C = \phi_{C_1}\exp(K_c\phi_{C_1}) \tag{3}$$

assume that the formation of each successive polymeric species is described by an isodesmic association constant in order to reduce the number of "curve-fit" parameters to a single K_c-value. The chemical contribution to the Gibbs free energy of mixing is obtained by assuming that the configurational entropy is described by the Flory-Huggins model, with the $\mathrm{RT} \sum n_i \ln \phi_i$ summation extending over all species believed to be present in the solution. Additional terms are added to account for any nonspecific, physical interactions. Empirically deduced "mixing rules"[22,23] and simplifying assumptions[24–26] allow the models to be applied whenever the solution contains two different alcohols. Through suitable differentiation with respect to temperature, expressions can be derived for excess enthalpies and excess heat capacities. The relative merits of association model are discussed in detail elsewhere.[22,23,27,28]

More recently, we examined both the applications and limitations of Mobile Order theory to describe the solubility behavior of anthracene dissolved in 24 binary alkane + alcohol solvent mixtures. The basic model[29–33] assumes that all molecular groups perpetually move, and that neighbors of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume V of the liquid divided by the number N_A molecules of the same kind, *i.e.*, Dom $A = V/N_A$. The center of this domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential contacts lead to deviations with respect to this "random" visiting. This is especially true in the case of hydrogen-bonding as specific interactions result in a specific orientation of the "donor" molecule with respect to an adjacent "acceptor" molecule.

For an inert crystalline solute dissolved in a binary alkane (B) + alcohol (C) solvent mixture, Mobile Order theory expresses the volume fraction saturation solubility (ϕ_A^{sat}) as:[34]

$$\begin{aligned} RT\{&\ln(a_A^{\mathrm{solid}}/\phi_A^{\mathrm{sat}}) - 0.5[1 - V_A/(x_B^0 V_B + x_C^0 V_C)] + 0.5 \ln [V_A/(x_B^0 V_B + x_C^0 V_C)] \\ &-(V_A/V_C)(K_C \phi_C^{02}/V_C)/(1 + K_C \phi_C^0/V_C)\} = V_A[\phi_B^0(\delta'_A - \delta'_B)^2 \\ &+ \phi_C^0(\delta'_A - \delta'_C)^2 - \phi_B^0 \phi_C^0(\delta'_B - \delta'_C)^2] \end{aligned} \tag{4}$$

whenever the saturation solubility is sufficiently low so that $1 - \phi_A^{\mathrm{sat}} \approx 1.0$. The symbols δ'_A, δ'_B and δ'_C denote the modified solubility parameters of the solute, saturated hydrocarbon solvent and self-associating alcohol, respectively, 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

$$\ln a_A^{\mathrm{solid}} = -\Delta H_A^{\mathrm{fus}}(T_{mp} - T)/(RTT_{mp}) \tag{5}$$

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 $V_A[\phi_B^0(\delta'_A - \delta'_B)^2 + \phi_C^0(\delta'_A - \delta'_C)^2 - \phi_B^0\phi_C^0(\delta'_B - \delta'_C)^2]$ term. Through suitable mathematical manipulations, the $V_A\phi_B^0(\delta'_A - \delta'_B)^2$ and $V_A\phi_C^0(\delta'_A - \delta'_C)^2$ terms were eliminated from the basic model in favor of measured solubility data in both pure solvents, $(\phi_A^{\text{sat}})_B$ and $(\phi_A^{\text{sat}})_C$. The derived expression

$$\begin{aligned}\ln \phi_{\mathrm{A}}^{\text{sat}} = {} & \phi_B^0 \ln (\phi_A^{\text{sat}})_B + \phi_C^0 \ln (\phi_A^{\text{sat}})_C - 0.5[\ln(x_B^0 V_B + x_C^0 V_C) - \phi_B^0 \ln V_B \\ & -\phi_C^0 \ln V_C] + (V_A K_C \phi_C^0/V_C^2)(1 + K_C/V_C)^{-1} \\ & -[V_A K_C \phi_C^{02}/V_C^2](1+\phi_C^0 K_C/V_C)^{-1} + V_A\phi_B^0\phi_C^0(\delta'_B - \delta'_C)^2(RT)^{-1} \qquad (6)\end{aligned}$$

predicted anthracene solubilities in binary solvent mixtures containing either 1-propanol, 2-propanol, 1-butanol or 1-octanol with *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane and 2,2,4-trimethylpentane to within an overall average absolute deviation of *circa* ±4.4% using a single self-association constant of $K_C = 5{,}000$. The various symbols are defined in greater detail in the Appendix.

The success of Eqn. (6) in describing the solubility behavior of anthracene in various alkane + alcohol mixtures suggests that the basic model might be applicable to other thermodynamic properties. To pursue this idea further, we derive an expression for predicting liquid-vapor equilibria of binary inert hydrocarbon + alcohol mixtures based upon Mobile Order theory. The predictive applicability of the newly-derived expression is illustrated using published vapor pressure data for binary mixtures containing 2,2,4-trimethylpentane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol, which were taken from the chemical literature.[13,14,35]

DEVELOPMENT OF PREDICTIVE EXPRESSION BASED UPON MOBILE ORDER THEORY

The Gibbs free energy of mixing for the binary solution containing an inert hydrocarbon (component A) and one alcohol cosolvent (component C) is separated into three contributions:

$$\Delta G_{AC}^{\text{mix}} = (\Delta G_{AC})_{\text{conf}} + (\Delta G_{AC})_{\text{chem}} + (\Delta G_{AC})_{\text{phys}} \qquad (7)$$

The first term describes the configurational entropy based upon the Huyskens and Haulait–Pirson[36] definition of solution ideality

$$(\Delta G_{AC})_{\text{conf}} = (0.5)RT[n_A \ln \phi_A + n_C \ln \phi_C + n_A \ln x_A + n_C \ln x_C] \qquad (8)$$

whereas the latter two terms in Eqn. (7) result from formation of hydrogen-bonded complexes and weak, nonspecific physical interactions in the binary solution, respectively.

The chemical contribution depends upon functional groups present and characteristics of the self-associating component. Alcohols have the one hydrogen "donor" site and the lone pairs on the oxygen atom provide two "acceptor" sites. The maximal possible number of hydrogen-bonds is determined by the number of sites that are in the minority. According to Mobile Order theory[37] the hydrogen-bonding contribution is given by

$$(\Delta G_{AC})_{\text{chem}} = n_C RT \ln[(1 + K_C/V_C)/(1 + K_C\phi_C/V_C)] \tag{9}$$

where K_C refers to the stability (equilibrium) constant of the hydrogen-bond.

Physical effects are expressed in terms of the Scatchard–Hildebrand solubility parameter model[28,38,39]

$$(\Delta G^{\text{ex}}_{AC})_{\text{phys}} = (n_A V_A + n_C V_C)\phi_A\phi_C(\delta'_A - \delta'_C)^2 \tag{10}$$

where δ'_i refers to the modified solubility parameter of pure component i, which ideally should have all specific effects removed. Ruelle *et al.*[32] deduced numerical values of δ'_i by regressing solubility data of solid n-alkanes in organic solvents in accordance to the Huyskens and Haulait–Pirson[36] model. Any errors or uncertainties in the measured data would naturally affect the calculated numerical values of δ'_i, as would any shortcomings of the Huyskens and Haulait–Pirson model to back-calculate the observed n-alkane mole fraction solubilities.

Combining Eqns. (8)–(10) the Gibbs free energy of mixing (per stoichiometric mole of solution) is written as

$$\begin{aligned}\Delta G^{\text{mix}}_{AC} &= (0.5)RT[x_A \ln \phi_A + x_C \ln \phi_C + x_A \ln x_A + x_C \ln x_C] \\ &\quad + x_C\, RT \ln[(1 + K_C/V_C)/(1 + K_C\phi_C/V_C] + (x_A V_A + x_C V_C)\phi_A\phi_C(\delta'_A - \delta'_C)^2\end{aligned} \tag{11}$$

Standard thermodynamic principles relate liquid-vapor equilibria to chemical potential, which in the case of the alcohol is

$$\begin{aligned}(\mu_C - \mu_C^{\bullet})/RT = \ln(f_C/f_C^{\bullet}) \approx \ln(P_C/P_C^{\bullet}) &= 0.5[\ln(x_C\phi_C) + \phi_A(1 - V_C/V_A)] \\ &\quad + \ln[(1 + K_C/V_C)/(1 + K_C\phi_C/V_C)] \\ &\quad - \phi_A\phi_C(K_C/V_C)/(1 + K_C\phi_C/V_C) + V_C\phi_A^2(\delta'_A - \delta'_C)^2(RT)^{-1}\end{aligned} \tag{12}$$

found by differentiating $\Delta G^{\text{mix}}_{AC}$ with respect to the number of moles of component C, holding the temperature, pressure and n_A constant. Thermodynamic rigor requires that the fugacity, f_C, be used in Eqn. (12). At total pressures of 2 atm or less vapor phase ideality can be assumed with little (if any) loss of accuracy. Under these conditions, fugacities are replaced by partial pressures, P_C.

RESULTS AND DISCUSSION

Tables 1–6 provide a summarized comparison between published vapor pressure data[35] and predictions based upon Mobile Order theory for binary mixtures containing 2,2,4-trimethylpentane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol,

Table 1 Comparison between experimental partial pressures of 1-propanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-propanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.0048	0.594	0.766	0.945
0.0104	1.317	1.589	1.940
0.01923	2.42	2.75	3.31
0.03237	3.87	4.22	4.99
0.05867	6.16	6.48	7.43
0.09714	7.74	8.71	9.67
0.1968	9.93	11.62	12.35
0.2945	10.99	12.87	13.39
0.5967	12.91	14.16	14.37
1.1134	14.42	14.60	14.68
1.9959	15.29	14.76	14.78
3.992	16.30	15.04	15.05
8.009	18.19	16.53	16.53
10.91	19.52	18.50	18.50
13.31 (neat)	20.85	20.85	20.85

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 75.13\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 17.29\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we have listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order predictions.

Table 2 Comparison between experimental partial pressures of 1-butanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-butanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.004316	0.142	0.192	0.237
0.01165	0.395	0.490	0.596
0.01501	0.498	0.615	0.745
0.01809	0.589	0.725	0.874
0.02180	0.736	0.851	1.019
0.04259	1.295	1.444	1.682
0.06358	1.669	1.896	2.162
0.0853	1.938	2.257	2.526
0.1485	2.425	2.929	3.163
0.4030	3.14	3.78	3.88
0.9962	3.77	4.07	4.10
1.979	4.35	4.17	4.18
4.079	4.82	4.38	4.38
6.875	5.34	4.88	4.88
9.644	5.91	5.69	5.69
10.87 (neat)	6.18	6.18	6.18

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 92.00\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 17.16\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order predictions.

Table 3 Comparison between experimental partial pressures of 1-pentanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-pentanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.01019	0.124	0.149	0.182
0.01582	0.188	0.222	0.269
0.02657	0.300	0.346	0.411
0.04246	0.443	0.497	0.579
0.05987	0.569	0.630	0.720
0.08189	0.662	0.761	0.854
0.09997	0.726	0.847	0.938
0.14939	0.827	1.014	1.094
0.2006	0.925	1.123	1.190
0.2927	1.031	1.237	1.285
0.3868	1.073	1.302	1.337
0.6116	1.213	1.376	1.395
0.9821	1.333	1.426	1.434
1.9945	1.552	1.492	1.494
3.033	1.637	1.557	1.558
3.976	1.756	1.628	1.628
6.014	1.907	1.833	1.833
8.035	2.21	2.13	2.13
9.20 (neat)	2.35	2.35	2.35

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 108.70\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 16.85\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order predictions.

Table 4 Comparison between experimental partial pressures of 1-hexanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-hexanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.00337	0.0143	0.0160	0.0197
0.00669	0.0260	0.0309	0.0379
0.01106	0.0421	0.0494	0.0601
0.01531	0.0573	0.0662	0.0801
0.02119	0.0792	0.0879	0.1052
0.03149	0.1108	0.1215	0.1434
0.04230	0.1371	0.1521	0.1770
0.05967	0.176	0.193	0.220
0.1015	0.220	0.262	0.290
0.1989	0.280	0.345	0.365
0.2930	0.314	0.382	0.397
0.5936	0.370	0.427	0.433
0.9125	0.422	0.446	0.449
2.0775	0.514	0.487	0.488
3.990	0.599	0.561	0.561
6.011	0.694	0.670	0.670
7.985 (neat)	0.820	0.820	0.820

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 125.23\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 16.40\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order prediction.

Table 5 Comparison between experimental partial pressures of 1-heptanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-heptanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.00562	0.00563	0.00718	0.00882
0.01092	0.01116	0.01339	0.01629
0.01567	0.0160	0.0185	0.0224
0.02073	0.0207	0.0236	0.0283
0.03083	0.0284	0.0328	0.0387
0.05023	0.0412	0.0471	0.0543
0.08319	0.0545	0.0647	0.0723
0.15117	0.0679	0.0859	0.0925
0.2472	0.0806	0.1007	0.1053
0.2959	0.0829	0.1051	0.1090
0.4399	0.0970	0.1130	0.1154
0.7892	0.1027	0.1213	0.1223
2.005	0.137	0.136	0.136
3.963	0.164	0.162	0.162
6.012	0.211	0.204	0.204
7.045 (neat)	0.232	0.232	0.232

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 141.94\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 16.39\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order predictions.

Table 6 Comparison between experimental partial pressures of 1-octanol and predicted values based upon Mobile Order theory for 2,2,4-trimethylpentane (A) + 1-octanol (C) mixtures at 25°C.

$m_C/(mol\ L^{-1})$	$P_C^{exp}/(Torr)$	$P_C^{pred,a}/(Torr)$	$P_C^{pred,b}/(Torr)$
0.00963	0.00296	0.00376	0.00458
0.01541	0.00453	0.00576	0.00695
0.01936	0.00574	0.00703	0.00843
0.02475	0.00737	0.00865	0.01029
0.03899	0.01026	0.01238	0.01444
0.08034	0.0159	0.0200	0.0224
0.15808	0.0200	0.0276	0.0296
0.4081	0.0258	0.0353	0.0361
0.8213	0.0306	0.0386	0.0389
1.5271	0.0367	0.0417	0.0418
2.004	0.0379	0.0437	0.0437
3.150	0.0463	0.0493	0.0493
6.313 (neat)	0.0750	0.0750	0.0750

[a] Predicted values of P_C based upon Eqn. (12) with an assumed equilibrium constant of $K_C = 4{,}000$. Numerical values of the molar volumes of $V_A = 166.09\ cm^3\ mol^{-1}$ and $V_C = 158.40\ cm^3\ mol^{-1}$ and modified solubility parameters of $\delta'_A = 14.30\ MPa^{1/2}$ and $\delta'_C = 16.38\ MPa^{1/2}$ were used in the computations. Modified solubility parameters were taken from the chemical literature,[32,33] as was the vapor pressure data.[35] To conserve journal space, we listed only every other experimental value for the vapor pressure data.

[b] An assumed equilibrium constant of $K_C = 5{,}000$ was used in the Mobile Order predictions.

1-heptanol and 1-octanol. Published vapor pressure data is in the form of the partial pressure and molarity of the 1-alkanol. Mixtures were originally prepared by mass and molarities calculated using the densities of the neat liquids. Solution concentrations range from near infinite dilution up to the neat 1-alkanol, which is listed as the last entry in each table. Partial pressures were determined *via* a gas chromatographic headspace method, and according to the author[35] the estimated precision was 1.6% or better, except in the case of 1-octanol where the reproducibility was on the order of 2.7%. 1-Alkanol volume fractions used in the Mobile Order predictions were obtained by multiplying by the experimental molarity by V_C, this latter quantity calculated as the reciprocal of the neat alcohol molarity. Modified solubility parameters of $\delta'_A = 14.30\ \mathrm{MPa}^{1/2}$, $\delta'_C = 17.29\ \mathrm{MPa}^{1/2}$ (1-propanol), $\delta'_C = 17.16\ \mathrm{MPa}^{1/2}$ (1-butanol), $\delta'_C = 16.85\ \mathrm{MPa}^{1/2}$ (1-pentanol), $\delta'_C = 16.40\ \mathrm{MPa}^{1/2}$ (1-hexanol), $\delta'_C = 16.39\ \mathrm{MPa}^{1/2}$ (1-heptanol) and $\delta'_C = 16.38\ \mathrm{MPa}^{1/2}$ (l-octanol) were taken from published compilations in the chemical literature.[32,33]

The last two columns of Tables 1–6 show that the Mobile Order predictions are fairly sensitive to the numerical value assumed for the K_C self-association equilibrium constant, particularly at low alcohol concentrations. Our initial computations assumed that $K_C = 5{,}000$, which was the numerical value suggested in many of the earlier solubility studies involving alcohol solvents. After completing predictions on the 2,2,4-trimethylpentane + 1-propanol and 2,2,4-trimethylpentane + 1-butanol systems, however, we noted that at low alcohol concentrations every predicted value exceeded the experimental partial pressure, sometimes by as much as 2.5 torr. Through a series of trial-and-error computations, the value of K_C was varied in an attempt to find the best single equilibrium constant that would describe the entire combined data set. Based upon these computations, we concluded that the so-called "best" value was $K_C \approx 4{,}000$. Smaller K_C values under-estimated the partial pressure, whereas larger numerical values (such as $K_C = 5{,}000$) over-estimated the partial pressure at low alcohol concentrations. Results of our computations show that Mobile Order does provide fairly reasonable (though by no means perfect) predictions of the experimental vapor pressures for binary 2,2,4-trimethylpentane + 1-propanol, 2,2,4-trimethylpentane + 1-butanol, 2,2,4-trimethylpentane + 1-pentanol, 2,2,4-trimethylpentane + 1-hexanol, 2,2,4-trimethylpentane + 1-heptanol and 2,2,4-trimethylpentane + 1-octanol mixtures.

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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 subcooled liquid.
C_i	molar concentration of component i.
f_C	fugacity of the self-associating alcohol in the binary mixture, the superscript "$\bullet$" denotes the pure alcohol.
$\Delta G_{BC}^{\text{ex}}$	excess Gibbs free energy of the binary solvent mixture based upon Raoult's law.
$\Delta G_{BC}^{\text{fh}}$	excess Gibbs free energy of the binary solvent mixture based upon the Flory–Huggins model.
ΔH_A^{fus}	molar enthalpy of fusion of the solute at its normal melting point temperature.

K_C	equilibrium constant describing the step-wise self-association of monofunctional alcohols, where the concentration units are either volume fraction or molarity depending upon the particular association model considered.
m_C	molarity of component C in the binary mixture.
n_i	number of moles of component *i*.
P_C	partial pressure of component C above the binary mixture.
T_{mp}	normal melting point temperature of the solute.
V_i	molar volume of component *i*.
x_i^0, x_j^0	mole fraction compositions of the *ij* binary mixture, calculated as if the third component were not present.
x_A^{sat}	mole fraction solubility of the solute.
δ_i	Scatchard-Hildebrand solubility parameter of component *i*.
δ_i'	modified solubility parameter of component *i*.
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the binary solvent mixture, calculated as if the third component were not present.
ϕ_A^{sat}	ideal volume fraction solubility of the solute.
μ_C	chemical potential of component C.