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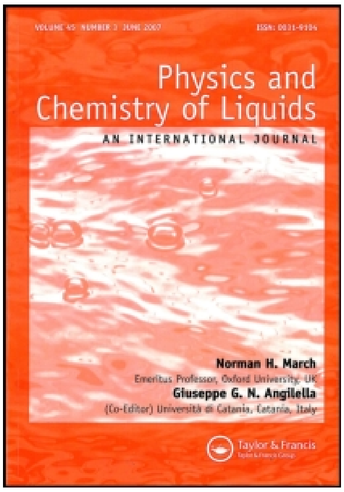

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Solubility of Thianthrene in Organic Nonelectrolyte Solvents: Comparison of Observed Versus Predicted Values Based Upon Mobile Order Theory

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SOLUBILITY OF THIANTHRENE IN ORGANIC NONELECTROLYTE SOLVENTS: COMPARISON OF OBSERVED VERSUS PREDICTED VALUES BASED UPON MOBILE ORDER THEORY

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Experimental solubilities are reported at 25.0 °C for thianthrene dissolved in twenty-one different organic nonelectrolyte solvents containing ether-, hydroxy-, and *t*-butyl-functional groups. Results of these measurements combined, with our previously published thianthrene solubility data in *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane, 2, 2, 4-trimethylpentane and cyclooctane, are used to test the applications and limitations of expressions derived from Mobile Order theory. For the 20 solvents for which predictions could be made computations show that Mobile Order theory does provide fairly reasonable (although by no means perfect) estimates of the saturation mole fraction solubilities. Average absolute deviation between predicted and observed values is *circa* 58%. In comparison, the average absolute deviation increases significantly to 1,940% when ideal solution behavior is assumed.

Keywords: Thianthrene solubilities; organic nonelectrolyte solvents; solubility predictions

INTRODUCTION

Solid-liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly

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in light of present trends towards heavier feedstocks and known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic hydrocarbons (e.g., anthracene and pyrene) and hetero-atom polynuclear aromatics (e.g., carbazole, dibenzothiophene and xanthene) have been published in the recent chemical literature (for listing of references see Acree [1–3]). Despite efforts by experimentalists and scientific organizations, both in terms of 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 group contribution methods and semi-empirical expressions to predict desired quantities. Group contribution methods have proved fairly successful in estimating solid solubility in pure and binary solvent mixtures from structural information [4–11]. Practical application though, is limited to systems for which all group interaction parameters are known. Interaction parameters can be evaluated from liquid–vapor, liquid–liquid and solid-liquid equilibria data. It is important that the data base contain as many different functional groups as possible, preferably with adequate representation from both mono- and multi-functional solute/solvent molecules to permit evaluation to potential synergistic effects. The data base should contain sufficient experimental values near infinite dilution in the event that one wishes to determine separate interaction parameters for finite concentration and infinite dilution activity coefficient predictions. For this reason, we have measured thianthrene solubilities in 21 different organic solvents. Functional groups represented include ethers, hydroxy and saturated hydrocarbons. These measurements will supplement our previously reported [12] thianthrene solubility data in saturated alkane hydrocarbon solvents, and will be used to further test the applications and limitations of predictive expressions derived from Mobile Order theory.

MATERIALS AND METHODS

Thianthrene (Aldrich, 99+%) was recrystallized several times from methanol. 1-Pentanol (Aldrich, 99+%), ethanol (Aaper Alcohol and Chemical Company, absolute), methanol (Aldrich, 99.9+%), 1-propanol

(Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 1-hexanol (Alfa Aesar, 99+%), 1-heptanol (Alfa Aesar, 99+%), 2-methyl-2-butanol (Acros, 99+%), 2-methyl-1-propanol (Aldrich, 99+%, anhydrous), 3-methyl-1-butanol (Aldrich, 99+%, anhydrous), 1-octanol (Aldrich, 99+%, anhydrous), 2-pentanol (Acros 99+%), 4-methyl-2-pentanol (Acros, 99+%), 2-ethyl-1-hexanol (Aldrich, 99+%), 2-methyl-1-pentanol (Aldrich, 99%), dibutyl ether (Aldrich, 99%), methyl *tert*-butyl ether (Arco, 99.9+%), *tert*-butylcyclohexane (Aldrich, 99+%) and cyclopentanol (Aldrich, 99%) were stored over molecular sieves before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent or better.

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 three days (often longer). Attainment of equilibrium was verified both by repetitive measurements after several additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Aliquots of saturated thianthrene 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 255 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. Calculated molar absorptivities of the nine standard solutions varied systematically with molar concentration, and ranged from about $\varepsilon \approx 35{,}230\ \mathrm{L\ mol^{-1}\ cm^{-1}}$ to $\varepsilon \approx 33{,}450\ \mathrm{L\ mol^{-1}\ cm^{-1}}$ for thianthrene concentrations ranging from 1.48×10^{-5} Molar to 5.57×10^{-5} Molar. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of thianthrene, volume(s) of volumetric flask(s) used and any dilutions required to place the measured absorbances on the Beer-Lambert law absorbance versus concentration working curve, and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from (mass/mass) solubility fractions using the molar masses of the solute and solvent. Experimental thianthrene solubilities, X_A^{sat}, in 21 organic solvents studied are listed in Table I. Numerical values represent the average of between four and eight independent determinations, with the measurements being reproducible to ±2%.

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TABLE I Experimental Thianthrene Mole Fraction Solubilities in Select Organic Solvents at 25.0°C

Organic Solvent	X_A^{sat}
Methanol	0.000472
Ethanol	0.001038
1-Propanol	0.00162
2-Propanol	0.001007
1-Butanol	0.00227
2-Butanol	0.00166
2-Methyl-1-propanol	0.00149
1-Pentanol	0.00308
2-Pentanol	0.00208
3-Methyl-1-butanol	0.00243
2-Methyl-2-butanol	0.00235
1-Hexanol	0.00390
2-Methyl-1-pentanol	0.00287
4-Methyl-2-pentanol	0.00230
1-Heptanol	0.00501
1-Octanol	0.00553
2-Ethyl-1-hexanol	0.00415
Cyclopentanol	0.00408
Dibutyl ether	0.00970
Methyl *tert*-butyl ether	0.00939
tert-Butylcyclohexane	0.00658

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RESULTS AND DISCUSSION

Solvents studied include both noncomplexing alkanes and self-associating alcohols. Of the many solution models proposed in recent years, Mobile Order theory is perhaps the only one that is capable of describing solute behavior in such a wide range of solvent mixtures. The basic model [13–20] assumes that all molecular groups perpetually move, and that neighbors of a given kind of 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 of molecules of the same kind, i.e. Dom $A = V/N_A$. The center of this domain perpetually moves. The 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.

In the case of an inert crystalline solute dissolved in a self-associating solvent, Mobile Order theory expresses the volume fraction saturation solubility, ϕ_A^{sat}, as

$$\begin{aligned}\ln \phi_A^{\mathrm{sat}} = \ln a_A^{\mathrm{solid}} - 0.5(1 - V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}} + 0.5 \ln [\phi_A^{\mathrm{sat}} \\ + \phi_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})] - \phi_{\mathrm{solvent}}^2\, V_A(\delta_A' - \delta_{\mathrm{solvent}}')^2 (RT)^{-1} \\ - r_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}} \qquad (1)\end{aligned}$$

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 most 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 alcoholic solvents can be calculated based upon

$$r_{\mathrm{solvent}} = (K_{\mathrm{solvent}}\,\phi_{\mathrm{solvent}}/V_{\mathrm{solvent}})/(1 + K_{\mathrm{solvent}}\,\phi_{\mathrm{solvent}}/V_{\mathrm{solvent}}) \qquad (2)$$

with a numerical value of $K_{\mathrm{solvent}} = 5{,}000\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ assumed for all monofunctional alcohols.

If complexation does occur between the crystalline solute and solvent

$$\begin{aligned}\ln \phi_A^{\mathrm{sat}} = \ln a_A^{\mathrm{solid}} - 0.5(1 - V_A/V_{\mathrm{solvent}})\,\phi_{\mathrm{solvent}} + 0.5 \ln [\phi_A^{\mathrm{sat}} \\ + \phi_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})] - \phi_{\mathrm{solvent}}^2\, V_A(\delta_A' - \delta_{\mathrm{solvent}}')^2 (RT)^{-1} \\ + \ln [1 + \phi_{\mathrm{solvent}}(K_{A\,\mathrm{solvent}}/V_{\mathrm{solvent}})] \qquad (3)\end{aligned}$$

then an additional tern involving the solute-solvent equilibrium constant, $K_{A\,\mathrm{solvent}}$, must be introduced to describe the solubility enhancement that arises as a result of specific interactions. A slightly more complex expression applies in the case of solute complexation with a

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self-associating solvent. The symbols δ'_A and δ'_{solvent} denote the modified solubility parameters of the solute and solvent, respectively, V_i is the molar volume, and a_A^{solid} is the activity of the solid solute. This latter quantity is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical supercooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{\text{mp}} - \text{T})/(R\,T\,T_{\text{mp}}) \tag{4}$$

the solute's molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature, T_{mp}. Contributions from nonspecific interaction are incorporated into Mobile Order theory through the $\phi_{\text{solvent}}^2 V_A(\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1}$ term. Ruelle and coworkers [16–20] have presented a very impressive set of comparisons between experimental and predicted for anthracene, naphthalene, pyrene (see also Powell *et al.*, [21]), biphenyl, carbazole, benzil (see also Fletcher *et al.*, [22]), *p*-benzoquinone, tricosane, octacosane, 10-nonadecanone, 11-heneicosanone, and 12-tricosanone in a wide range of both noncomplexing and complexing solvents to document the predictive ability of Mobile Order theory.

Predictive application of Equations (1) and (3) is relatively straightforward. First, an average numerical value of $\delta'_{\text{thianthrene}} = 21.02\,\text{MPa}^{1/2}$ is computed by requiring that each equation (with $r_{\text{solvent}} = 0$ and/or $K_{A\,\text{solvent}} = 0$) perfectly describes our previously published [12] thianthrene mole fraction solubility data in *n*-hexane ($\delta'_{\text{thianthrene}} = 21.00$ $\text{MPA}^{1/2}$), *n*-heptane ($\delta'_{\text{thianthrene}} = 21.00\,\text{MPa}^{1/2}$), and *n*-octane ($\delta'_{\text{thianthrene}} = 21.05\,\text{MPa}^{1/2}$). The numerical value of $a_A^{\text{solid}} = 0.04411$ is calculated using Equation (4) with $\Delta H_A^{\text{fus}} = 25{,}400$ J mol^{-1}, [23] and $T_{\text{mp}} = 428.4\,\text{K}$. A numerical value of $V_{\text{thianthrene}} = 156\,\text{cm}^3\,\text{mol}^{-1}$ was used for the molar volume of hypothetical subcooled liquid solute [12].

Table II summarizes the predictive ability of Mobile Order theory for the 20 different organic solvents for which both thianthrene solubility data and modified solubility parameters could be found. Solvent molar volumes and modified solubility parameters are listed in Table III. The modified solubility parameters account for only nonspecific interactions, and in the case of the alcoholic solvents the hydrogen-bonding contributions have been removed. Numerical values of δ'_{solvent} were obtained from published compilations [16, 17, 20], and were

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TABLE II Comparison Between Experimental Thianthrene Mole Fraction Solubilities and Predicted Values Based Upon Mobile Order Theory

Organic Solvent	$(X_A^{\text{sat}})^{\text{exp}}$	$(X_A^{\text{sat}})^{\text{calc}}$	*%Dev*[a]
n-Hexane	0.00320[12]	0.00331	1.1
n-Heptane	0.00346[12]	0.00353	2.0
n-Octane	0.00392[12]	0.00409	4.3
Cyclohexane	0.00587[12]	0.00418	−28.8
Methylcyclohexane	0.00631[12]	0.00467	−26.0
Cyclooctane	0.01232[12]	0.00625	−49.3
2,2,4-Trimethylpentane	0.00273[12]	0.00261	−4.4
tert-Butylcyclohexane	0.00658	0.00665	1.1
Dibutyl ether	0.00970	0.02040	110.3
Methanol	0.000472	0.00169	258.1
Ethanol	0.001038	0.00232	123.5
1-Propanol	0.00162	0.00279	72.2
2-Propanol	0.001007	0.00334	231.7
1-Butanol	0.00227	0.00352	55.1
2-Butanol	0.00166	0.00264	59.0
2-Methyl-1-propanol	0.00149	0.00201	34.9
1-Pentanol	0.00308	0.00371	20.5
1-Hexanol	0.00390	0.00341	−12.6
1-Heptanol	0.00501	0.00388	−22.6
1-Octanol	0.00553	0.00432	−21.9

[a] Deviations (%) = $100[(X_A^{\text{sat}})^{\text{calc}} - (X_A^{\text{sat}})^{\text{exp}}]/(X_A^{\text{sat}})^{\text{exp}}$.

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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 [24] or estimated using known values for similar organic solvents. Examination of the entries in Table II reveals that Mobile Order theory does provide fairly reasonable (though by no means perfect) estimates of the solubility behavior of thianthrene in a wide range of organic solvents. Average absolute deviation between predicted and observed values is *circa* 58%. Readers are reminded that in evaluating the applicability of Mobile Order theory one must realize that many of these particular systems are highly non-ideal, and that the experimental solubility data covers over a 20-fold range in mole fraction. Had an ideal solution been assumed, then the predicted mole fraction solubility would be $X_A^{\text{sat}} = a_A^{\text{solid}} = 0.04411$ for each solvent. The ideal solution approximation corresponds to a considerably larger average absolute deviation of 1,940% between predicted and observed values.

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TABLE III Solvent and Solute Properties Used in Mobile Order Predictions

Component (i)	$V_i/(cm^3\ mol^{-1})$	$\delta'_i/(MPa^{1/2})^a$
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
2,2,4-Trimethylpentane	166.09	14.30
Cyclooctane	134.9	15.40
tert-Butylcyclohexane	173.9	15.50
Dibutyl ether	170.3	17.45
Methanol	40.7	19.25
Ethanol	58.7	17.81
1-Propanol	75.10	17.29
2-Propanol	76.90	17.60
1-Butanol	92.00	17.16
2-Butanol	92.4	16.60
2-Methyl-1-propanol	92.8	16.14
1-Pentanol	108.6	16.85
1-Hexanol	125.2	16.40
1-Heptanol	141.9	16.39
1-Octanol	108.6	16.38
Thianthrene[b]	156.0	21.02[c]

[a] Tabulated values are taken from a compilation given in Ruelle *et al.* [16,17,20].

[b] The numerical value of $a_A^{solid} = 0.04411$ was calculated from the molar enthalpy of fusion, $\Delta H_A^{fus} = 25{,}440$ J mol^{-1}, [23] at the normal melting point temperature of the solute, $T_{mp} = 428.4$ K.

[c] Numerical value was calculated using the measured thianthrene mole fraction solubilities in *n*-hexane, *n*-heptane and *n*-octane, in accordance with Equations (1) and (3); with $r_{solvent} = 0$ and/or $K_{A\ solvent} = 0$.

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