## Solubility of Thioxanthen-9-One in Organic Nonelectrolyte Solvents. Comparison of Observed Versus Predicted Values Based Upon Mobile Order Theory

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# SOLUBILITY OF THIOXANTHEN-9-ONE 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 thioxanthen-9-one dissolved in thirty-five different organic nonelectrolyte solvents containing ester-, ether-, hydroxy-, methyl- and *t*-butyl-functional groups. Results of these measurements are used to test the applications and limitations of expressions derived from Mobile Order theory. For the 26 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* 45%. In comparison, the average absolute deviation increases significantly to 420% when ideal solution behavior is assumed.

*Keywords*: Thioxanthen-9-one solubilities; organic nonelectrolyte solvents; solubility predictions

## 1. 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 poly-nuclear aromatics (*e.g.*, carbazole, dibenzothiophene) 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 of 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 thioxanthen-9-one solubilities in 35 different organic solvents. Functional groups represented include ethers, esters, hydroxy, aromatic and saturated hydrocarbons. Results of these measurements will be used to further test the applications and limitations of predictive expressions derived from Mobile Order theory.

## 2. MATERIALS AND METHODS

Thioxanthen-9-one (Aldrich, 98%) was recrystallized several times from methanol. *n*-Hexane (Aldrich, 99%), *n*-heptane (Aldrich, HPLC), *n*-octane (Aldrich, 99+ %, anhydrous), cyclohexane (Al-

drich, HPLC), methylcyclohexane (Aldrich, 99 + %, anhydrous), cyclooctane (Aldrich, 99 + %), 2,2,4-trimethylpentane (Aldrich, HPLC), *tert*-butylcyclohexane (Aldrich, 99 + %), benzene (Aldrich, 99.9 %), toluene (Aldrich, 99.8 %), o-xylene (Aldrich, 98 + %), m-xylene (Aldrich, 99 + %, anhydrous), p-xylene (Aldrich, 99 + %), dibutyl ether (Aldrich, 99 %), methyl *tert*-butyl ether (Arco, 99.9 + %), methanol (Aldrich, 99.9 + %), ethanol (Aaper alcohol and Chemical Company, absolute), 1-propanol (Aldrich, 99 + %, anhydrous), 2-propanol (Aldrich, 99 + %, anhydrous), 1-butanol (Aldrich HPLC, 99.8 + %), 2-butanol (Aldrich, 99 + %, anhydrous), 1-pentanol (Aldrich, 99 + %), 2-pentanol (Acros, 99 + %), 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), 4-methyl-2-pentanol (Acros, 99 + %), 2-ethyl-1-hexanol (Aldrich, 99 + %), 2-methyl-1-pentanol (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 thioxanthen-9-one 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 378 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 for nine standard solutions ranging in concentration from $5.45 \times 10^{-5}$ Molar to $6.75 \times 10^{-4}$ Molar. The calculated molar absorptivity of $\varepsilon = 6{,}225$ L $mol^{-1}$ $cm^{-1}$ was constant over the concentration range. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of thioxanthen-9-one, 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 thioxanthen-9-one solubilities, $X_A^{sat}$, in 35 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%.

TABLE I  Experimental Thioxanthen-9-one Mole Fraction Solubilities in Select Organic Solvents at 25.0 °C

| Organic Solvent | $X_A^{sat}$ |
| --- | --- |
| n-Hexane | 0.000341 |
| n-Heptane | 0.000436 |
| n-Octane | 0.000533 |
| Cyclohexane | 0.000448 |
| Methylcyclohexane | 0.000513 |
| Cyclooctane | 0.001399 |
| 2,2,4-Trimethylpentane | 0.000305 |
| tert-Butylcyclohexane | 0.000674 |
| Benzene | 0.005181 |
| Toluene | 0.005188 |
| o-Xylene | 0.006358 |
| m-Xylene | 0.005543 |
| p-Xylene | 0.005436 |
| Dibutyl ether | 0.001508 |
| Methyl tert-butyl ether | 0.001598 |
| Ethyl acetate | 0.003489 |
| Butyl acetate | 0.004317 |
| Methanol | 0.000260 |
| Ethanol | 0.000738 |
| 1-Propanol | 0.000864 |
| 2-Propanol | 0.000684 |
| 1-Butanol | 0.001140 |
| 2-Butanol | 0.000999 |
| 2-Methyl-1-propanol | 0.000907 |
| 1-Pentanol | 0.001554 |
| 2-Pentanol | 0.001426 |
| 3-Methyl-1-butanol | 0.001193 |
| 2-Methyl-2-butanol | 0.001478 |
| 1-Hexanol | 0.001908 |
| 2-Methyl-1-pentanol | 0.001732 |
| 4-Methyl-2-pentanol | 0.001397 |
| 1-Heptanol | 0.002294 |
| 1-Octanol | 0.002839 |
| 2-Ethyl-1-hexanol | 0.002313 |
| Cyclopentanol | 0.002324 |

## 3. 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 [12 – 19] 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, $\phi_A^{sat}$, as

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

where the $r_{solvent}(V_A/V_{solvent})\phi_{solvent}$ 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

$$
r_{solvent} = (K_{solvent}\ \phi_{solvent}/V_{solvent})/(1 + K_{solvent}\ \phi_{solvent}/V_{solvent}) \quad \text{(Eqn. 2)}
$$

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

If complexation does occur between the crystalline solute and solvent

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

then an additional term involving the solute-solvent equilirbium constant, $K_{A\,solvent}$, must be introduced to describe the solubility enhancement that arises as a result of sepcific interactions. A slightly more complex expression applies in the case of solute complexation with a self-associating solvent. The symbols $\delta_A'$ and $\delta_{solvent}'$ 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

$$
\ln a_A^{solid} = -\Delta H_A^{fus}(T_{mp} - T)/(RTT_{mp}) \qquad \text{(Eqn. 4)}
$$

the solute's molar enthalpy of fusion, $\Delta H_A^{fus}$, at the normal melting point temperature, $T_{mp}$. Contributions from nonspecific interaction are incorporated into Mobile Order theory through the $\phi_{solvent}^2 V_A$ $(\delta_A' - \delta_{solvent}')^2 (RT)^{-1}$ term. Ruelle and coworkers [15–19] have presented a very impressive set of comparisons between experimental and predicted values for anthracene, naphthalene, pyrene (see also Powel et al.[20]), biphenyl, carbazole, benzil (see also Fletcher et al. [21]), p-benzoquinone, tricosane, octacosane, 10-nonadecanone, 11-heneicosanone, and 12-tricosanone solubilities in a wide range of both noncomplexing and complexing solvents to document the predictive ability of Mobile Order theory.

Predictive application of Eqns. (1) and (3) is relatively straightforward. First, an average numerical value of $\delta_{thioxan}' = 20.51\,MPa^{1/2}$ is computed by requiring that each equation (with $r_{solvent} = 0$ and /or

$K_{A\text{solvent}} = 0$) perfectly describes thioxanthen-9-one mole fraction solubility data in $n$-hexane $(\delta'_{\text{thioxan}} = 20.69 MPa^{1/2})$, $n$-heptane $(\delta'_{\text{thioxan}} = 20.46 MPa^{1/2})$, and $n$-octane $(\delta'_{\text{thioxan}} = 20.37 MPa^{1/2})$. The numerical value of $a_A^{\text{solid}} = 0.003813$ is calculated using Eqn. (4) with $\Delta H_A^{\text{fus}} = 35,500 J mol^{-1}$, [22] and $T_{\text{mp}} = 487.88$ K. A numerical value of $V_{\text{thioxan}} = 160$ cm$^3$ mol$^{-1}$ was used for the molar volume of the hypothetical subcooled liquid solute.

Table II summarizes the predicitive ability of Mobile Order theory for the 26 different organic solvents for which both thioxanthen-9-one 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 nonspeccific interactions, and in the case of the alcoholic solvents

TABLE II Comparison Between Experimental Thioxanthen-9-one 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 | 0.000341 | 0.000393 | 15.3 |
| $n$-Heptane | 0.000436 | 0.000420 | −2.7 |
| $n$-Octane | 0.000533 | 0.000483 | −9.4 |
| Cyclohexane | 0.000448 | 0.000494 | 10.3 |
| Methylcyclohexane | 0.000513 | 0.000546 | 6.4 |
| Cyclooctane | 0.001399 | 0.000713 | −49.0 |
| 2,2,4-Trimethylpentane | 0.000305 | 0.000317 | 3.9 |
| $tert$-Butylcyclohexane | 0.000674 | 0.000758 | 12.5 |
| Benzene | 0.005181 | 0.003619 | −30.1 |
| Toluene | 0.005188 | 0.002754 | −46.9 |
| $m$-Xylene | 0.005543 | 0.001922 | −65.3 |
| $p$-Xylene | 0.005436 | 0.002003 | −63.2 |
| Dibutyl ether | 0.001508 | 0.002090 | 38.6 |
| Ethyl acetate | 0.003489 | 0.004064 | 16.5 |
| Butyl acetate | 0.004317 | 0.003675 | −14.9 |
| Methanol | 0.000260 | 0.000148 | −43.1 |
| Ethanol | 0.000738 | 0.000224 | −69.7 |
| 1-Propanol | 0.000864 | 0.000280 | −67.6 |
| 2-Propanol | 0.000684 | 0.000329 | −51.9 |
| 1-Butanol | 0.001140 | 0.000357 | −68.7 |
| 2-Butanol | 0.000999 | 0.000276 | −72.4 |
| 2-Methyl-1-propanol | 0.000907 | 0.000217 | −76.1 |
| 1-Pentanol | 0.001554 | 0.000385 | −75.2 |
| 1-Hexanol | 0.001908 | 0.000364 | −80.9 |
| 1-Heptanol | 0.002294 | 0.000415 | −81.9 |
| 1-Octanol | 0.002839 | 0.000463 | −83.7 |

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

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 |
| Benzene | 89.4 | 18.95 |
| Toluene | 106.84 | 18.10 |
| m-Xylene | 123.2 | 17.20 |
| p-Xylene | 123.9 | 17.30 |
| Dibutyl ether | 170.3 | 17.45 |
| Ethyl acetate | 98.5 | 20.79 |
| Butyl acetate | 132.5 | 19.66 |
| 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 | 158.3 | 16.38 |
| Thioxanthen-9-one[b] | 160.0 | 20.51[c] |

[a] Tabulated values are taken from a compilation given in Ruelle et al.[15,16,19]
[b] The numerical value $a_A^{solid} = 0.003813$ was calculated from the molar enthalpy of fusion, $\Delta H_A^{fus} = 35,500\ J\ mol^{-1}$, [22] at the normal melting point temperature of the solute, $T_{mp} = 487.88\ K$.
[c] Numerical value was calculated using the measured thioxanthen-9-one mole fraction solubilities in n-hexane, n-heptane and n-octane, in accordance with Eqns. (1) and (3); with $r_{solvent} = 0$ and/or $K_{A\ solvent} = 0$.

the hydrogen-bonding contributions have been removed. Numerical values of $\delta'_{solvent}$ were obtained from published compilations [15,16, 19], and were either deduced by regressing actual solubility data of solid n-alkanes in organic solvents in accordance with the configurational entropic model of Huyskens and Haulait-Pirson[23] or estimated using known values for similar organic solvents. Examination of the entries in Table II reveals that Mobile Order theory does provide fairly resonable (though by no means perfect) estimates of the solubility behaviour of thioxanthen-9-one in a wide range of organic

solvents. Average absolute deviation between predicted and observed values is *circa* 45 %. 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 $X_A^{sat} = a_A^{solid} = 0.003813$ for each solvent. The ideal solution approximation corresponds to a considerably larger average absolute deviation of 420 % between predicted and observed values.

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