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

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Experimental solubilities are reported at 26.0°C for pyrene dissolved in twenty different organic nonelectrolyte solvents containing ether-, ester-, chloro-, hydroxy-, and methyl-functional groups. Results of these measurements, combined with our previously published pyrene solubility data in benzene, dibutyl ether, 1,4-dichlorobutane, 1-propanol, 2-propanol and saturated hydrocarbons, are used to test the applications and limitations of expressions derived from Mobile Order theory. For the 30 solvents for which predictions could be made computations show that Mobile Order theory does provide fairly reasonable (though by no means perfect) estimates of the saturation mole fraction solubilities. Average absolute deviation between predicted and observed values is *circa* 79%. In comparison, the average absolute deviation increases significantly to 1380% when ideal solution behavior is assumed.

KEY WORDS: Pyrene, organic solvents, alcohols.

INTRODUCTION

Solid-liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in the 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^{1–5} (i.e., anthracene and pyrene) and hetero-atom polynuclear aromatics^{6–9} (i.e., carbazole, dibenzothiophene and xanthene) have been published in the recent chemical literature. 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 actual 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

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methods have proved fairly successful in estimating solid solubility in pure and binary solvent mixtures from structural information¹⁰⁻¹⁷. Practical application though, is limited to systems for which all group interaction parameters are known. Generally, interaction parameters are evaluated from solid-liquid and liquid-vapor 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 pyrene solubilities in 20 different organic solvents. Functional groups represented include esters, hydroxy, chloro, methyl, and aromatic hydrocarbons. These measurements will supplement our previously reported^{2,3,18-20} pyrene solubility data in benzene, dibutyl ether, 1,4-dichlorobutane, 1-propanol, 2-propanol and saturated alkane hydrocarbon solvents, and will be used to further test the applications and limitations of predictive expressions derived from Mobile Order theory.

Moreover, pyrene is one of the more interesting polycyclic aromatic hydrocarbons (PAHs) in that the molecule is known to exhibit solvatochromic probe behavior as evidenced by selective fluorescence emission intensity enhancement with increasing solvent polarity²¹⁻²³. Measured I/III band emission intensity ratio provides a quantitative measure of the polarity of the microenvironment immediately surrounding the probe. In earlier papers^{24,25} we illustrated how observed I/III intensity ratio variation with binary solvent composition could be used to determine preferential solvation (local composition) around the dissolved PAH probe molecule. Preferential solvation is governed, to a large extent, by the relative magnitude of the various solute-solvent molecular interactions and by solute-solvent shape/size compatibility. Phillips and Brennecke²⁶ recently showed that experimental solubility data in pure solvents can provide valuable insight into preferential solvation, and can be used to complement spectral data obtained from spectroscopic probe methods. Unfortunately, there are very few published solubility studies involving known solvatochromic solute probes in the chemical literature. The present study enlarges the solubility data base for the solvatochromic pyrene probe molecule.

MATERIALS AND METHODS

Pyrene (Aldrich, 99+ %) was recrystallized several times from methanol, giving a melting point temperature of $151.0 \pm 0.5^\circ\text{C}$ (literature values are 151.3^{27} and $149-150^\circ\text{C}^{28}$). Butyl acetate (Aldrich, 99.8+ %), 1-pentanol (Aldrich, 99+ %), 1,2-dichloroethane (Aldrich, 99+ %, anhydrous), 1,4-dioxane (Aldrich, 99.8+ %), toluene (Aldrich, 99.8+ %), ethyl acetate (Aldrich, 99.9%), carbon tetrachloride (Aldrich, 99.9+ %), 1-chlorobutane (Aldrich, 99.9+ %), ethanol (Aaper Alcohol and Chemical Company, absolute), methanol (Aldrich, 99.9+ %), 3-methyl-1-butanol (Aldrich, 99+ %, anhydrous), 2-methyl-1-propanol (Aldrich, 99+ %, anhydrous), *o*-xylene (Al-

drich, 98 + %), *m*-xylene (Aldrich, 99 + %, anhydrous), *p*-xylene (Aldrich, 99 + %), acetone (Aldrich, HPLC grade, 99.9 + %), 1-butanol (Aldrich, 99.8%), 1-octanol (Aldrich, 99 + %, anhydrous), 2-butanol (Aldrich, 99 + %, anhydrous), and cyclopentanol (Aldrich, 99%) were stored over molecular sieves shortly before use. Gas chromatographic analysis showed solvent purities to be 99 mole percent or better. Karl Fisher titration on the alcohol solvents gave water contents (mass/mass %) of <0.02% for methanol, <0.01% for ethanol, <0.01% for 1-butanol, <0.01% for 2-butanol, <0.005% for 1-octanol, <0.04% for cyclopentanol, <0.04% for 1-pentanol, <0.01% for 2-methyl-1-propanol, and <0.01% for 3-methyl-1-butanol.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at $(26.0 \pm 0.1)^\circ\text{C}$ for several days. Attainment of equilibrium was verified 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 pyrene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 372 nm on a Bausch and Lomb Spectronic 2000. Experimental mole fraction pyrene solubilities, X_A^{sat} , in 20 organic solvents studied are listed in Table 1. Numerical values represent the average of between six and eight independent determinations. Reproducibility ranged from $\pm 1.3\%$ for solvents having the lower mole fraction solubilities to $\pm 2.5\%$ for solvents having the larger pyrene solubilities, where an additional dilution was necessary to keep the measured absorbances within the Beer-Lambert law region.

Table 1 Experimental pyrene mole fraction solubilities in select organic nonelectrolyte solvents at 26.0°C

<i>Organic Solvent</i>	X_A^{sat}
Toluene	0.06785
<i>o</i> -Xylene	0.07611
<i>m</i> -Xylene	0.07055
<i>p</i> -Xylene	0.06831
Carbon tetrachloride	0.04229
1,2-Dichloroethane	0.08746
1-Chlorobutane	0.06094
1,4-Dioxane	0.03520
Ethyl acetate	0.04251
Butyl acetate	0.05932
Acetone	0.03612
Methanol	0.00149
Ethanol	0.00317
1-Butanol	0.00622
2-Butanol	0.00433
2-Methyl-1-propanol	0.00319
1-Pentanol	0.00926
3-Methyl-1-butanol	0.00546
1-Octanol	0.02097
Cyclopentanol	0.00994

RESULTS AND DISCUSSION

Solvents studied include both noncomplexing aromatic hydrocarbons 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 model²⁹⁻³⁶ 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., $\text{Dom } A = V/N_A$. 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 solubility, ϕ_A^{sat} , as

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

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

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

with a numerical value of $K_{\text{solvent}} = 5,000 \text{ cm}^3/\text{mole}$ assumed for all monofunctional alcohols.

If complexation does occur between the crystalline solute and solvent

$$\ln \phi_A^{\text{sat}} = \ln a_A^{\text{solid}} - 0.5 \left(1 - \frac{V_A}{V_{\text{solvent}}} \right) \phi_{\text{solvent}}$$

$$\begin{aligned}
& + 0.5 \ln \left[\phi_A^{\text{sat}} + \phi_{\text{solvent}} \left(\frac{V_A}{V_{\text{solvent}}} \right) \right] - \phi_{\text{solvent}}^2 V_A (\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1} \\
& + \ln \left[1 + \frac{K_{A\text{solvent}} \phi_{\text{solvent}}}{V_{\text{solvent}}} \right] \quad (3)
\end{aligned}$$

then an additional term involving the solute-solvent equilibrium constant, $K_{A\text{solvent}}$, 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 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 subcooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}} \frac{T_{\text{mp}} - T}{RT T_{\text{mp}}} \quad (4)$$

the molar enthalpy of fusion, ΔH_A^{fus} , at the normal melting point temperature, T_{mp} . Contributions from nonspecific interactions are incorporated into Mobile Order theory through the $V_A \phi_{\text{solvent}}^2 (\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1}$ term. Ruelle and coworkers³²⁻³⁶ have presented a very impressive set of comparisons between experimental and predicted solubilities for anthracene, naphthalene, pyrene, biphenyl, carbazole, benzil, *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 Eqns. (1) and (3) is relatively straight-forward. First, an average numerical value of $\delta'_{\text{pyrene}} = 20.85 \text{ MPa}^{1/2}$ is computed by requiring that each equation (with $r_{\text{solvent}} = 0$ and/or $K_{A\text{solvent}} = 0$) perfectly describes our previously published^{2,3} pyrene mole fraction solubility data in *n*-hexane ($\delta'_{\text{pyrene}} = 21.03 \text{ MPa}^{1/2}$), *n*-heptane ($\delta'_{\text{pyrene}} = 20.81 \text{ MPa}^{1/2}$), and *n*-octane ($\delta'_{\text{pyrene}} = 20.72 \text{ MPa}^{1/2}$). The numerical value of $a_A^{\text{solid}} = 0.1312$ is based upon the calorimetric measurements by Casellato *et al.*,²⁷ and the molar volume of the hypothetical subcooled liquid pyrene molecule is approximated as the experimentally determined partial molar volume in carbon tetrachloride, $V_{\text{pyrene}} = 166.5 \text{ cm}^3/\text{mole}$ ³⁷. Ruelle *et al.*³⁴ used a slightly larger value of $V_{\text{pyrene}} = 182.0 \text{ cm}^3/\text{mole}$, which was based upon a molar volume of $V_{\text{pyrene}} = 186.8 \text{ cm}^3/\text{mole}$ at pyrene's normal melting point temperature of 151°C, in his earlier calculations involving pyrene solubilities and Mobile Order theory. We feel that our value represents a better estimate of the solute's "true" volume in solution at 26°C as many liquid organic molecules expand by about 1% for every 5–10°C increase in temperature.

Table 2 summarizes the predictive ability of Mobile Order theory for the 30 different organic solvents for which both pyrene solubility data and modified solubility parameters could be found. Solvent molar volumes and modified solubility

Table 2 Comparison between experimental pyrene mole fraction solubilities and predicted values based upon mobile order theory

<i>Organic Solvent</i>	$(X_A^{\text{sat}})^{\text{exp}}$	$(X_A^{\text{sat}})^{\text{calc}}$	%Dev ^a
<i>n</i> -Hexane	0.00852	0.00998	17.1
<i>n</i> -Heptane	0.01101	0.01068	- 3.0
<i>n</i> -Octane	0.01379	0.01243	- 9.9
Cyclohexane	0.01089	0.01323	21.5
Methylcyclohexane	0.0130	0.0146	12.3
2,2,4-Trimethylpentane	0.00721	0.00769	6.7
Cyclooctane	0.01956	0.01987	1.6
<i>t</i> -Butylcyclohexane	0.0159	0.0207	30.2
Benzene	0.06316	0.12217	93.4
Toluene	0.06785	0.09409	38.7
<i>m</i> -Xylene	0.07055	0.06323	- 10.4
<i>p</i> -Xylene	0.06831	0.06612	- 3.2
Carbon tetrachloride	0.04229	0.06472	53.0
1,2-Dichloroethane	0.08746	0.14649	67.5
1-Chlorobutane	0.06094	0.06470	6.2
1,4-Dichlorobutane	0.1097	0.1286	17.2
1,4-Dioxane	0.03520	0.14314	306.6
Dibutyl ether	0.0298	0.0665	123.2
Ethyl acetate	0.04251	0.13864	226.1
Butyl acetate	0.05932	0.12378	108.7
Acetone	0.03612	0.14379	298.1
Methanol	0.00149	0.00455	205.4
Ethanol	0.00317	0.00655	106.6
1-Propanol	0.00426	0.00802	88.3
2-Propanol	0.00290	0.00964	232.4
1-Butanol	0.00622	0.01021	64.1
2-Butanol	0.00433	0.00756	74.6
2-Methyl-1-propanol	0.00319	0.00573	79.6
1-Pentanol	0.00926	0.01081	16.8
1-Octanol	0.02097	0.01259	- 40.0

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

parameters are listed in Table 3. 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^{32,33,36}, 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-Pirson³⁸ or estimated using known values for similar organic solvents. Examination of the entries in Table 2 reveals that Mobile Order theory does provide fairly reasonable (though by no means perfect) estimates of the solubility behavior of pyrene in a wide range of organic solvents. Average absolute deviation between predicted and observed values is *circa* 79%. It should be noted that Ruelle and coworkers³⁴ previously presented a similar comparison involving Mobile Order theory; however, the author's solvent set included primarily saturated alkane hydrocarbons. Our comparison is more

Table 3 Solvent and solute properties used in mobile order predictions.

Component (i)	$V_i/(\text{cm}^3 \text{ mole}^{-1})$	$\delta'_i/(\text{MPa}^{1/2})^a$
<i>n</i> -Hexane	131.51	14.56
<i>n</i> -Heptane	147.48	14.66
<i>n</i> -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
<i>t</i> -Butylcyclohexane	173.9	15.50
Benzene	89.4	18.95
Toluene	106.9	18.10
<i>m</i> -Xylene	123.2	17.20
<i>p</i> -Xylene	123.9	17.30
Carbon tetrachloride	97.1	17.04
1, 2-Dichloroethane	78.8	20.99
1-Chlorobutane	105.0	17.12
1, 4-Dichlorobutane	112.1	19.78
Dibutyl ether	170.3	17.45
1, 4-Dioxane	85.8	20.89
Ethyl acetate	98.5	20.79
Butyl acetate	132.5	19.66
Acetone	74.0	21.91
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-Octanol	158.30	16.38
Pyrene ^b	166.50 ³⁷	20.85 ^c

^a Tabulated values are taken from a compilation given in Ruelle *et al.*^{32,33,36}

^b The numerical value of $a_A^{\text{solid}} = 0.1312$ was calculated from the molar enthalpy of fusion, $\Delta H_A^{\text{fus}} = 4.09 \text{ kcal/mole}$,²⁷ at the normal melting point temperature of the solute, $T_{\text{mp}} = 424.4 \text{ K}$

^c Numerical value was calculated using the measured pyrene mole fractions solubility in *n*-hexane, *n*-heptane and *n*-octane, in accordance with Eqns. (1) and (3); with $r_{\text{solvent}} = 0$ and/or $K_{\text{Asolvent}} = 0$

complete in that seventeen additional solvents are considered. 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 70-fold range in mole fraction. Had an ideal solution been assumed, then the predicted mole fraction solubility would be $X_A^{\text{sat}} = a_A^{\text{solid}} = 0.1312$ for each solvent. The ideal solution approximation corresponds to a considerably larger average absolute deviation of 1380% between predicted and observed values.

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