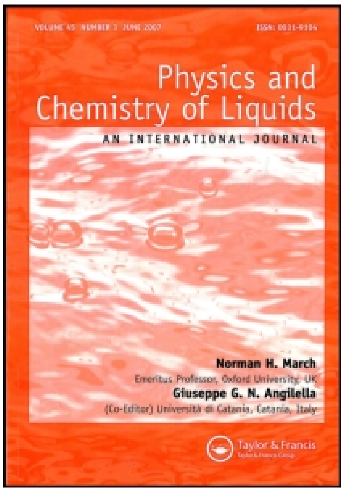

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Thermodynamics of Mobile Order Theory. Part 4. Comparison of Experimental and Predicted Solubilities for *Trans*-Stilbene

Lindsay E. Roy[a]; Carmen E. Hernández[a]; Karina M. De Fina[a]; William E. Acree Jr.[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA

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THERMODYNAMICS OF MOBILE ORDER THEORY. PART 4. COMPARISON OF EXPERIMENTAL AND PREDICTED SOLUBILITIES FOR *TRANS*-STILBENE

LINDSAY E. ROY, CARMEN E. HERNÁNDEZ,
KARINA M. DE FINA and WILLIAM E. ACREE, JR.*

*Department of Chemistry, University of North Texas, Denton,
Texas 76203-5070 (USA)*

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Experimental solubilities are reported for *trans*-stilbene dissolved in sixteen organic solvents at 25.0°C. Solvents studied contained chloro-, cyano-, hydroxy-, fluoro-, and ether-functional groups. Results of these measurements, combined with previously published solubility data, are used to test the applications and limitations of expressions derived from Mobile Order theory. For the 34 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. The average absolute deviation between predicted and observed values is *circa* 20%. The deviation increases significantly to 1,210% when ideal solution behavior is assumed.

Keywords and Phrases: Trans-stilbene solubilities; organic nonelectrolyte solvents; solubility predictions

INTRODUCTION

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

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*Corresponding author. e-mail: Acree@unt.edu hydrocarbons (*e.g.*, anthracene and pyrene) and herero-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]. Abraham and coworkers [12, 13] recently developed a general solvation equation that can be used in the correlation and understanding of physico-chemical and biochemical phenomena. Physical properties that have been correlated include gas/solvent partition coefficients (as $\log L$)

$$\log L = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \sum \alpha_2^H + b \cdot \sum \beta_2^H + d \cdot \log L^{16} \quad (1)$$

and water/solvent partition coefficients (as $\log P$)

$$\log P = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \sum \alpha_2^H + b \cdot \sum \beta_2^H + v \cdot V_x \quad (2)$$

where R_2 and V_x refer to the molar refraction and McGowan volume of the solute, respectively, π_2^H is the solute dipolarity/polarizability descriptor, and $\sum \alpha_2^H$ and $\sum \beta_2^H$ are measures of the solute's hydrogen-bond acidity and hydrogen-bond basicity. For any given solvent, numerical values of the seven curve-fit coefficients (c, r, s, a, b, d and v) are deduced by regressing experimental partition coefficient data in accordance with Eqs. (1) and (2). The input partition coefficients were sometimes calculated as the ratio of the solute molar solubilities in the organic solvent and water, $P = C_A^{\text{org}}/C_A^{\text{aq}}$, and as the ratio of the solute molar solubility in the organic solvent and vapor concentration, $L = C_A^{\text{org}}/C_A^{\text{gas}}$. Published papers [12, 13] have reported curve-fit coefficients for water and a few select organic solvents.

To increase the solubility database available for developing group contribution methods and general solvation correlations, we are in the process of measuring solubility data for polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic nitrogen hetero-atoms (PANHs). In the present communication, we report *trans*-stilbene solubilities in 16 additional organic solvents. Functional groups represented include ethers, hydroxy, chloro, cyano, fluoro, aromatic and saturated hydrocarbons. This brings the number of organic solvents for which we have reported *trans*-stilbene [14] solubility data up to 44. Results of these measurements, combined with our previously published solubility data, are used to further test the applications and limitations of predictive expressions derived from Mobile Order theory. Earlier papers in this series [15, 16] pertained to anthracene and pyrene solubilities in binary alkane + alcohol and alkane + alkoxyalcohol solvent mixtures.

MATERIALS AND METHODS

Trans-stilbene (Aldrich, 96%) was recrystallized several times from methanol. *n*-Nonane (TCI, 99 + %), *n*-decane (TCI, 99 + %), *n*-hexadecane (Aldrich, 99 + %), ethylene glycol (Aldrich, 99 + %), acetonitrile (Aldrich, HPLC, 99.9 + %), benzene (Aldrich, HPLC, 99.9 + %), toluene (Aldrich, 99.8%), 2,2,2-trifluoroethanol (Aldrich, 99 + %), tetrachloromethane (Aldrich, HPLC, 99.9 + %), chlorobenzene (Aldrich, HPLC, 99.9%), *o*-xylene (Aldrich, HPLC, 99 + %), *m*-xylene (Aldrich, 99 + %, anhydrous), *p*-xylene (Aldrich, 99 + %, anhydrous), ethylbenzene (Aldrich, 99.8%, anhydrous), 1,4-dioxane (Aldrich, HPLC, 99.9%) and tetrahydrofuran (Aldrich, 99.9%, anhydrous) were stored over activated molecular sieves and distilled shortly 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 either 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 *trans*-stilbene 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 294 nm on a Bausch and Lomb Spectronic 2000. In the case of *n*-hexadecane and *n*-decane solvent systems, dilutions were made with ethanol because of miscibility problems encountered when trying to dilute the saturated solutions with methanol. Concentrations of the dilute solutions were determined from a Beer-Lambert law absorbance *versus* concentration working curve derived from measured absorbances of standard solutions of known molar concentration ranging from 1.38×10^{-5} Molar to 4.62×10^{-5} Molar. The calculated molar absorptivity of $\varepsilon \approx 28{,}850$ Liter $\text{mol}^{-1}\,\text{cm}^{-1}$ was constant over the concentration range. Identical molar absorptivities were obtained for select *trans*-stilbene standard solutions that contained up to 5 volume percent of the neat organic cosolvents.

Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by molar mass of the solute, 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 solutes and solvents. Numerical values represent the average of between four and eight independent determinations, with the measurements being reproducible to ± 2.0%.

RESULTS AND DISCUSSION

Experimental *trans*-stilbene solubilities, X_A^{sat}, in the 16 different organic solvents studied are listed in Table I. 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 [17–24] assumes that all molecules in the solution move. Such motion brings about a change in the instantaneous partners for molecular interaction. When two molecules approach each other, their mutually attractive forces lead to molecular interaction. After a sufficient time each functional group in the molecule under consideration will have visited all places in its domain, and will have experienced all possible

TABLE I Experimental *trans*-stilbene mole fraction solubilities in select organic solvents at 25.0°C

Organic solvent	X_A^{sat}
n-Nonane	0.01383
n-Decane	0.01511
n-Hexadecane	0.02178
Benzene	0.06232
Toluene	0.06066
o-Xylene	0.06126
m-Xylene	0.05690
p-Xylene	0.06342
Ethylbenzene	0.05331
Chlorobenzene	0.07363
Tetrachloromethane	0.03970
Ethylene glycol	0.000296
2,2,2-Trifluoroethanol	0.000666
Acetonitrile	0.00995
1,4-Dioxane	0.06615
Tetrahydrofuran	0.1035

contacts with the functional groups of the other neighboring molecules. 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

$$\begin{aligned}\ln \phi_A^{\text{sat}} = {} & \ln a_A^{\text{solid}} - 0.5(1 - V_A/V_{\text{solvent}})\phi_{\text{solvent}} \\ & + 0.5 \ln [\phi_A^{\text{sat}} + \phi_{\text{solvent}}(V_A/V_{\text{solvent}})] \\ & - \phi_{\text{solvent}}^2 V_A(\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1} \\ & - r_{\text{solvent}}(V_A/V_{\text{solvent}})\phi_{\text{solvent}}\end{aligned} \tag{3}$$

where ϕ_{solvent} is the volume fraction of the solvent [*i.e.*, $\phi_{\text{solvent}} = 1 - \phi_A^{\text{sat}}$], and the r_{solvent} (V_A/V_{solvent}) ϕ_{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 monofunctional alcoholic solvents can be calculated based upon

$$r_{\text{solvent}} = (K_{\text{solvent}}\phi_{\text{solvent}}/V_{\text{solvent}})/(1 + K_{\text{solvent}}\phi_{\text{solvent}}/V_{\text{solvent}}) \tag{4}$$

with a numerical value of $K_{\text{solvent}} = 5{,}000\,\text{cm}^3\,\text{mol}^{-1}$ assumed for all monofunctional alcohols. This numerical value was determined by regressing spectroscopic and vapor pressure data. Solute properties used in Eq. (3) and in subsequent equations refer to the properties that the solute would have if it were a liquid at 298.15 K. The thermodynamic standard state is thus the hypothetical subcooled liquid. This standard state is commonly used in thermodynamic descriptions of solid–liquid equilibria [25–27].

If complexation does occur between the crystalline solute and solvent

$$\begin{aligned} \ln \phi_A^{\text{sat}} = \ln a_A^{\text{solid}} &- 0.5(1 - V_A/V_{\text{solvent}})\phi_{\text{solvent}} \\ &+ 0.5 \ln [\phi_A^{\text{sat}} + \phi_{\text{solvent}}(V_A/V_{\text{solvent}})] \\ &- \phi_{\text{solvent}}^2 V_A(\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1} \\ &+ \ln [1 + \phi_{\text{solvent}}(K_{A\,\text{Solvent}}/V_{\text{solvent}})] \end{aligned} \tag{5}$$

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 supercooled liquid. The numerical value of a_A^{solid} can be computed from

$$\ln a_A^{\text{solid}} = -\Delta H_A^{\text{fus}}(T_{\text{mp}} - T)/(R\,T\,T_{\text{mp}}) \tag{6}$$

the solute's molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature, T_{mp}. Equation (6) assumes that the enthalpy of fusion is independent of temperature, and that there are no solid phase transitions between the melting point and system temperature, T. Lack of heat capacity data for *trans*-stilbene as a function of temperature necessitated this assumption. Additional term(s) must be included if the solid undergoes a phase transition [28, 29]. Contributions from nonspecific interaction are incorporated into Mobile Order theory through the $\phi^2_{\text{solvent}} V_A (\delta'_A - \delta'_{\text{solvent}})^2 (RT)^{-1}$ term. Ruelle and coworkers [20–24] have presented a very impressive set of comparisons between experimental and predicted values for anthracene, naphthalene, pyrene, biphenyl, carbazole, benzil, *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 Eqs. (3) and (5) is relatively straight-forward. First, an average numerical value of $\delta'_{\text{stilbene}} = 19.69\,\text{MPa}^{1/2}$ is computed by requiring that each equation (with $r_{\text{solvent}} = 0$ and/or $K_{A\,\text{Solvent}} = 0$) perfectly describes published [14] *trans*-stilbene mole fraction solubility data in *n*-hexane ($\delta'_{\text{stilbene}} = 19.78\,\text{MPa}^{1/2}$), *n*-heptane ($\delta'_{\text{stilbene}} = 19.68\,\text{MPa}^{1/2}$), and *n*-octane ($\delta'_{\text{stilbene}} = 19.60\,\text{MPa}^{1/2}$). The numerical value of $a_A^{\text{solid}} = 0.06227$ is calculated using Eq. (4) with $\Delta H_A^{\text{fus}} = 27{,}400\,\text{J mol}^{-1}$ [30] and $T_{\text{mp}} = 398.15\,\text{K}$. A numerical value of $V_{\text{stilbene}} = 177.0\,\text{cm}^3\,\text{mol}^{-1}$ was used for the molar volume of the hypothetical subcooled liquid solute. Calculation of the solute's modified solubility parameter in this fashion eliminates any computational errors/uncertainties that might occur as a result of solubility enhancement from either specific solute–solvent interactions or formation of solute–solvent association complexes. Saturated hydrocarbons are incapable of molecular complexation.

Table II summarizes the predictive ability of Mobile Order theory for the 34 different organic solvents for which both experimental solubility data and modified solubility parameters could be found. Predicted values were computed using an iterative method in which all ϕ_{solvent} values in Eq. (3) were initially set equal to zero. The computed volume fraction solubility was used to calculate a better estimate for ϕ_{solvent}, which was then substituted into Eq. (3) for the second iteration. The calculations converged after three or four iterations. Solvent molar volumes and modified solubility parameters are listed in Table III. Solvent molar volumes were calculated as the molar mass of

TABLE II Comparison between experimental *trans*-stilbene mole fraction solubilities and predicted values based upon Mobile Order theory

Organic solvent	$(X_A^{sat})^{exp}$	*[Data Ref.]*	$(X_A^{sat})^{calc}$	*%Dev* [a]
n-Hexane	0.00960	[14]	0.01025	6.8
n-Heptane	0.01085	[14]	0.01080	−0.4
n-Octane	0.01241	[14]	0.01224	−1.4
n-Nonane	0.01383	This Work	0.01416	2.4
n-Decane	0.01511	This Work	0.01482	−1.9
n-Hexadecane	0.02178	This Work	0.02062	−5.3
Cyclohexane	0.01374	[14]	0.01316	−4.3
Methylcyclohexane	0.01413	[14]	0.01414	0.1
Cyclooctane	0.02080	[14]	0.01814	−12.8
2,2,4-Trimethylpentane	0.00803	[14]	0.00812	1.1
tert-Butylcyclohexane	0.01570	[14]	0.01864	18.7
Benzene	0.06232	This Work	0.06809	9.3
Toluene	0.06066	This Work	0.05724	−5.6
m-Xylene	0.05690	This Work	0.04361	−23.4
p-Xylene	0.06342	This Work	0.04496	−29.1
Ethylbenzene	0.05331	This Work	0.05429	1.8
Chlorobenzene	0.07363	This Work	0.06699	−9.0
Dibutyl ether	0.02783	[14]	0.04498	61.6
1,4-Dioxane	0.06615	This Work	0.06597	−0.3
Tetrahydrofuran	0.1035	This Work	0.07213	−30.3
Tetrachloromethane	0.03970	This Work	0.04486	13.0
Methanol	0.00196	[14]	0.00209	6.5
Ethanol	0.00321	[14]	0.00387	20.5
1-Propanol	0.00403	[14]	0.00519	28.8
2-Propanol	0.00279	[14]	0.00597	114.0
1-Butanol	0.00533	[14]	0.00682	27.9
2-Butanol	0.00382	[14]	0.00547	43.1
2-Methyl-1-propanol	0.00330	[14]	0.00441	33.7
1-Pentanol	0.00691	[14]	0.00761	10.1
1-Hexanol	0.00841	[14]	0.00746	−11.4
1-Heptanol	0.01092	[14]	0.00858	−21.4
1-Octanol	0.01251	[14]	0.00955[b]	−23.6[b]
Ethylene glycol	0.000296	This Work	0.000186	−37.2
Acetonitrile	0.00995	This Work	0.00431	−56.7

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

[b] An incorrect value was used for the molar volume of 1-octanol in calculating the predicted solubility reported in Table II of Ref. [14]. The values given here correct the miscalculated values from our earlier paper.

the solvent divided by the liquid density at 298.15 K. 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 $\delta'_{solvent}$ were obtained from published compilations [20, 21, 23, 24], 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

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
n-Nonane	179.87	15.07
n-Decane	195.88	15.14
n-Hexadecane	294.12	15.61
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
1,4-Dioxane	85.8	20.89
Tetrahydrofuran	81.4	19.30
Benzene	89.4	18.95
Toluene	106.84	18.10
m-Xylene	123.2	17.20
p-Xylene	123.9	17.30
Ethylbenzene	123.1	18.02
Chlorobenzene	102.1	19.48
Tetrachloromethane	97.08	17.04
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
Ethylene glycol	56.0	19.90
Acetonitrile	52.9	23.62
trans-Stilbene[b]	177.0	19.69[c]

[a] Tabulated values are taken from a compilation given in Ruelle *et al.* [20, 21, 23, 24].

[b] The numerical value of $a_A^{solid} = 0.06227$ was calculated from the molar enthalpy of fusion, $\Delta H_A^{fus} = 27,400\,J\,mol^{-1}$ [30], at the normal melting point temperature of the solute, $T_{mp} = 398.15\,K$.

[c] Numerical value was calculated using the measured *trans*-stilbene mole fraction solubilities [14] in *n*-hexane, *n*-heptane and *n*-octane, in accordance with Eqs. (3) and (5); with $r_{solvent} = 0$ and/or $K_{A\,Solvent} = 0$.

and Haulait-Pirson [31] or estimated using known values for similar organic solvents. The predicted values do depend upon the numerical values assumed for the various input parameters. Computations using slightly different numerical values for the solubility parameters ($\pm 0.10\,MPa^{1/2}$) and molar volumes ($\pm 1\,cm^3\,mol^{-1}$) indicate that the predicted value can vary 5–10% as a result of small changes in these two input parameters. This would be true of any predictive model that uses solubility parameters, functional group contribution energies, or other similar input parameters.

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 *trans*-stilbene in a wide range of organic solvents. Average absolute deviation between predicted and observed values are *circa* 20%. Readers are reminded that in evaluating the applicability of Mobile Order theory one must realize that many of these particular systems are highly nonideal, and that the experimental solubility data covers over a 340-fold range in mole fraction. Had an ideal solution been assumed, then the predicted mole fraction solubility would be $X_A^{\text{sat}} = a_A^{\text{solid}} = 0.06227$ for each organic solvent studied. The ideal solution approximation corresponds to a considerably larger average absolute deviation of 1,210% between predicted and observed values.

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