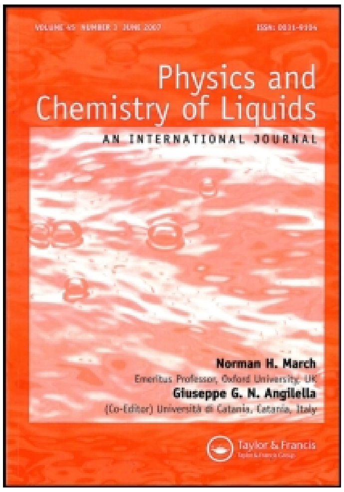

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Solubility of Ferrocene in Organic Nonelectrolyte Solvents. Comparison of Observed *Versus* Predicted Values Based Upon Mobile Order Theory

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SOLUBILITY OF FERROCENE 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 ferrocene dissolved in 46 different organic nonelectrolyte solvents containing ether-, chloro-, hydroxy-, ester, methyl- and *t*-butyl-functional groups. Results of these measurements, combined with previously reported ferrocene solubilities taken from the chemical literature, are used to test the applications and limitations of expressions derived from mobile order theory. For the 42 solvents for which predictions could be made computations show that mobile order theory does provide fairly reasonable estimates of the saturation mole fraction solubilities. Average absolute deviation between predicted and observed values is 107.8%. In comparison, the average absolute deviation is 627% when ideal solution behavior is assumed.

Keywords and Phrases: Ferrocene solubilities; Organic nonelectrolyte solvents; Solubility predictions

INTRODUCTION

Solvation energies for solutes dissolved in organic nonelectrolyte solvents are important in thermodynamic modeling in that they provide valuable information in regards to the interaction of the solute

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*Corresponding author. e-mail: acree@unt.edu with surrounding solvent molecules. Solvation energies can also be used to predict partition coefficients of solutes between water and an immiscible organic solvent and to estimate organic solvent-air partition coefficients, both of which are important properties in understanding the fate and transport of organic chemicals in the environment. There exists in the published chemical literature a fairly large body of experimental solubility and partition coefficient data for organic solvents such as 1-octanol and *n*-hexadecane. Sizeable solubility and partition coefficient databases are also available for several of the saturated alkane solvents, and for benzene, toluene, chloroform and carbon tetrachloride. Very little experimental data has been published for solutes dissolved in many of the other organic solvents commonly encountered in chemical and engineering applications. Scarcity of experimental data seriously hinders development and testing of predictive linear free energy relationships for most of the individual solvents.

Proposed LSERs have taken several different mathematical forms, depending upon whether one wishes to predict gas/organic solvent partition coefficients (as log *L*) [1]

$$\log L = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \Sigma\alpha_2^H + b \cdot \Sigma\beta_2^H + l \cdot \operatorname{Log} L^{16} \qquad (1)$$

$$\log L = c + d \cdot \delta_2 + s \cdot \pi_2^H + a \cdot \Sigma\alpha_2^H + b \cdot \Sigma\beta_2^H + l \cdot \operatorname{Log} L^{16} \qquad (2)$$

$$\log L = c + r \cdot R_2 + q \cdot \mu_2^2 + a \cdot \Sigma\alpha_2^H + b \cdot \Sigma\beta_2^H + l \cdot \operatorname{Log} L^{16} \qquad (3)$$

and water/organic solvent partition coefficients (as log *P*) [1–3]

$$\log P = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \Sigma\alpha_2^H + b \cdot \Sigma\beta_2^H + v \cdot V_x \qquad (4)$$

$$\log P = c + d \cdot \delta_2 + s \cdot \pi_2 + a \cdot \alpha_2 + b \cdot \beta_2 + v \cdot V_x \qquad (5)$$

where R_2 and V_x refer to the excess molar refraction and McGowan volume of the solute, respectively, π_2^H (and π_2) and is the solute dipolarity/polarizability descriptor, and $\Sigma\alpha_2^H$ (and α_2) and $\Sigma\beta_2^H$ (and β_2) are measures of the solute's hydrogen-bond acidity and hydrogen-bond basicity, respectively. δ_2 is a polarizability parameter which was preset by Kamlet *et al.* [4] to 0.0 in the case of nonpolychlorinated aliphatic solutes, to 0.5 for polychlorinated aliphatic solutes, and to

1.0 for aromatic solutes. Numerical values of the solute descriptors are available in several published tabulations for 500+ common organic molecules and inorganic gas solutes [3–6]. For any given solvent, numerical values of the various regressional coefficients (*c*, *r*, *s*, *a*, *b*, *d*, *l*, *q* and *v*) are deduced by regressing experimental partition coefficient data in accordance with Eqs. (1)–(5). At the present time coefficients are available for only 50 or so different water/organic solvent and gas/solvent systems [2, 3, 7–11]. Equations (1)–(5) allow one to estimate water/organic solvent and gas/solvent partition coefficients for systems for which the solute descriptors and regressional coefficients are known.

If correlation equations are to be developed for still more organic solvents, then additional experimental data must be measured. Activity coefficients, partition coefficients and saturation solubilities for a mininum of 40 or so different solutes are required in order to derive meaningful correlation equations. Moreover, the solutes used should span as wide of a range of solute descriptor values as possible. To increase the solubility database available for developing LSERs, we are in the process of measuring solubility data for polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic nitrogen hetero-atoms (PANHs), and other crystalline sulfur-containing nonelectrolyte solutes. In the present communication, we report ferrocene solubilities at 25°C in 46 different organic solvents containing ether-, chloro-, hydroxy-, ester, methyl- and *t*-butyl-functional groups. Results of these measurements, combined with previously published ferrocene solubility data [12–17], are used to further test the applications and limitations of predictive expressions derived from mobile order theory. Subsequent studies will use the experimental ferrocene solubilities, along with infinite dilution activity coefficient data, in the determination of *c*, *r*, *s*, *a*, *b*, *d*, *q* and *v* values for additional organic solvents.

MATERIALS AND METHODS

Ferrocene (Aldrich, 97%) was used as received. *n*-Hexane (Aldrich, 99%), *n*-heptane (Aldrich, HPLC), *n*-octane (Aldrich, 99+%, anhydrous), *n*-nonane (TCI, 99+%), *n*-decane (TCI, 99+%), *n*-hexadecane (Aldrich, 99%), cyclohexane (Aldrich, HPLC), methylcyclohexane (Aldrich, 99+%, anhydrous), cyclooctane (Lancaster Synthesis, 99+%), 2,2,4-trimethylpentane (Aldrich, HPLC), *tert*-butylcyclohexane (Aldrich, 99+%), benzene (Aldrich, HPLC, 99.9+%), toluene (Aldrich, 99.8%, anhydrous), ethylbenzene (Aldrich, 99.8%, anhydrous), *o*-xylene (Aldrich, HPLC, 99%), *m*-xylene (Aldrich, 99+%, anhydrous), *p*-xylene (Aldrich, 99+%, anhydrous), dibutyl ether (Aldrich, 99%), 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%), 1-decanol (Alfa Aesar, 99+%), cyclopentanol (Aldrich, 99%), methyl *tert*-butyl ether (Arco, 99.9+%), ethyl acetate (Aldrich, HPLC, 99.9%), 2-methyl-2-propanol (Arco Chemical Company, 99+%), 1,2-dichloroethane (Aldrich, HPLC, 99.8%), 1-chlorobutane (Sigma-Aldrich, HPLC, 99.5+%), 1-chlorooctane (Aldrich, 99%), methyl acetate (Aldrich, 99.5%, anhydrous), butyl acetate (Aldrich HPLC, 99.7%) and dimethyl sulfoxide (Aldrich, HPLC, 99.9%) 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 ferrocene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol (or 2-propanol in the case of the larger alkane solvents) for spectrophotometric analysis at 440 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. The concentration of ferrocene in the standard solutions varied from 3.52×10^{-3} molar to 1.18×10^{-2} molar. The calculated molar absorptivity of $\varepsilon \approx 91.5\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ was constant over the concentration range studied.

Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of ferrocene, 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 ferrocene solubilities, X_A^{sat}, in the 46 organic solvents studied are listed in Table I. Numerical values were obtained using ferrocene as received from the supplier and they

TABLE I Comparison between experimental ferrocene mole fraction solubilities and predicted values based upon mobile order theory

Organic solvent	$(X_A^{sat})^{exp,a}$	*Data ref.*	$(X_A^{sat})^{calc}$	*% Dev*[b]
n-Hexane	0.02260	This work	0.02346	3.8
n-Heptane	0.02489	This work	0.02485	−0.2
n-Octane	0.02713	This work	0.02801	3.2
n-Nonane	0.02901	This work	0.03216	10.4
n-Decane	0.03097	This work	0.03372	8.9
n-Hexadecane	0.03963	This work	0.04672	17.9
Cyclohexane	0.03300	This work	0.02877	−12.8
Methylcyclohexane	0.03372	This work	0.03121	−7.4
Cyclooctane	0.04680	This work	0.03927	−16.1
2,2,4-Trimethylpentane	0.02179	This work	0.01950	−10.5
tert-Butylcyclohexane	0.03612	This work	0.04111	13.8
Benzene	0.08756	This work	0.1339	52.9
Toluene	0.08321	This work	0.1138	36.8
Ethylbenzene	0.07703	This work	0.1098	42.5
o-Xylene	0.08014	This work		
m-Xylene	0.07436	This work	0.08817	18.6
p-Xylene	0.07785	This work	0.09090	16.8
Dibutyl ether	0.05107	This work	0.09365	83.4
Methyl *tert*-butyl ether	0.04120	This work		
1,4-Dioxane	0.0683	[12]	0.1447	111.9
Methanol	0.003298	This work	0.008894	169.8
Ethanol	0.005976	This work	0.01322	121.2
1-Propanol	0.008917	This work	0.01629	82.7
2-Propanol	0.007078	This work	0.01866	163.6
1-Butanol	0.01181	This work	0.02027	71.6
2-Butanol	0.01027	This work	0.01634	59.1
2-Methyl-1-propanol	0.009621	This work	0.01333	38.6

TABLE I (Continued)

Organic solvent	$(X_A^{sat})^{exp,a}$	*Data ref.*	$(X_A^{sat})^{calc}$	% *Dev*[b]
2-Methyl-2-propanol	0.009215	This work	0.01135	23.2
1-Pentanol	0.01352	This work	0.02184	61.5
2-Pentanol	0.01263	This work		
3-Methyl-1-butanol	0.01225	This work		
2-Methyl-2-butanol	0.01554	This work		
1-Hexanol	0.01735	This work	0.02101	21.1
2-Methyl-1-pentanol	0.01426	This work		
4-Methyl-2-pentanol	0.01343	This work		
1-Heptanol	0.02050	This work	0.02366	15.4
1-Octanol	0.02215	This work	0.02606	17.7
2-Ethyl-1-hexanol	0.01667	This work		
1-Decanol	0.02767	This work	0.03029	9.5
Cyclopentanol	0.01774	This work		
Butyl acetate	0.05580	This work	0.1367	145.0
Ethyl acetate	0.04300	This work	0.1421	230.5
Methyl acetate	0.03258	This work	0.1400	329.7
1,2-Dichloroethane	0.07735	This work	0.1466	89.5
1-Chlorobutane	0.05962	This work	0.08863	48.7
1-Chlorooctane	0.06062	This work	0.1083	78.7
Tetrachloromethane	0.0692	[12]	0.0882	27.5
2-Propanone	0.024	[16]	0.140	483.3
Acetonitrile	0.007557[c]	[14]	0.1257	1563.4
Dimethyl sulfoxide	0.01410	This work		
Carbon disulfide	0.0669	[12]	0.1585	136.9
Pyridine	0.07048[c]	[14]	0.1461	107.3

[a] Numerical values represent the average of between four and eight independent determinations, with the measurements being reproducible to ± 1.5%.

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

[c] Calculated from the published molar solubility [14] using the molar volumes given in Table III.

represent the average of between four and eight independent determinations. The measurements were reproducible to ± 1.5%. For each solvent studied, all experimental measurements fell within ± 1.5% of the average value listed in Table I. We did recrystallize several grams of the solid from *n*-hexane for solubility determinations in a few select solvents (*n*-hexane, cyclohexane, benzene, methanol, dimethyl sulfoxide and butyl acetate). To within the stated experimental uncertainty of ± 1.5%, there was no difference in the experimental solubilities using the recrystallized and unrecrystallized samples.

RESULTS AND DISCUSSION

Solubility data are available in the chemical literature for 10 of the 46 organic solvents for which we measured ferrocene solubilities. As shown in Table II, there is considerable scatter in the published literature values. Values reported by one research group may differ by as much as ± 25% from values reported by different groups. Part of the experimental uncertainty is undoubtedly caused by differences in chemical purities and by differences in experimental methodologies. For example, three of the earlier studies [14, 15, 17] were concerned with ferrocene solubilities in binary aqueous-organic solvent mixtures. It is not clear from reading the three experimental descriptions whether the organic solvents were dried prior to use. Trace water in the organic solvent would have minimal effect on the measured values in the binary solvent mixtures. There is no reason for us to believe that one set of data is any better than another, however, we do note that in the case of ferrocene solubilities in the three alkane solvents (*n*-hexane, *n*-heptane and cyclohexane) that values reported by Matveev and Statsenko [17] are consistently less than values reported by other researchers. Similarly, Matveev and Statsenko's values in the two aromatic solvents (benzene and toluene) are considerably greater than values reported by other researchers. For the most part, our experimental data falls in the range bracketed by the literature values.

TABLE II Comparison of observed and literature values for the mole fraction solubilities, X_A^{sat}, of ferrocene

Solvent	*This work*	*Literature*	*Ref.*
n-Hexane	0.02260	0.02197[a]	[16]
		0.01968[a]	[17]
n-Heptane	0.02489	0.0262	[12]
		0.024	[13]
		0.02502[a]	[16]
		0.02238[a]	[17]
n-Octane	0.02713	0.0232[a]	[17]
Cyclohexane	0.03300	0.0388	[12]
		0.0342	[13]
		0.03680[a]	[16]
		0.02625[a]	[17]
Benzene	0.08756	0.071	[13]
		0.08391[a]	[16]
		0.1311[a]	[17]
Toluene	0.08321	0.08269[a]	[16]
		0.1269[a]	[17]
Methanol	0.003298	0.003657[a]	[14]
Ethanol	0.005976	0.004731[a]	[16]
1-Butanol	0.01181	0.00853[a]	[16]
Dimethyl sulfoxide	0.01410	0.01474[a]	[15]

[a] The published molar solubilities were converted to mole fractions using the molar volumes given in Table III.

Solvents listed in Table I 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 [18–25] 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.*, $\mathrm{Dom}\,A = V/N_A$. 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

$$\begin{aligned}\ln \phi_A^{\mathrm{sat}} = {} & \ln a_A^{\mathrm{solid}} - 0.5(1 - V_A/V_{\mathrm{solvent}})\phi_{\mathrm{solvent}} \\ & + 0.5 \ln [\phi_A^{\mathrm{sat}} + \phi_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})] \\ & - \phi_{\mathrm{solvent}}^2 V_A(\delta_A' - \delta_{\mathrm{solvent}}')^2 (RT)^{-1} \\ & - r_{\mathrm{solvent}}(V_A/V_{\mathrm{solvent}})\phi_{\mathrm{solvent}} \end{aligned} \tag{6}$$

where the r_{solvent} $(V_A/V_{\mathrm{solvent}})$ 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 alcoholic solvents can be calculated based upon

$$r_{\mathrm{solvent}} = (K_{\mathrm{solvent}}\ \phi_{\mathrm{solvent}}/V_{\mathrm{solvent}})/(1 + K_{\mathrm{solvent}}\ \phi_{\mathrm{solvent}}/V_{\mathrm{solvent}}) \tag{7}$$

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

$$\begin{aligned}\ln \phi_A^{\text{sat}} = \ln a_A^{\text{solid}} &- 0.5(1 - V_A/V_{\text{solvent}})\phi_{\text{solvent}} \\ &+ 0.5\ln[\phi_A^{\text{sat}} + \phi_{\text{solvent}}(V_A/V_{\text{solvent}})] \\ &- \phi_{\text{solvent}}^2 V_A(\delta_A' - \delta_{\text{solvent}}')^2 (RT)^{-1} \\ &+ \ln[1 + \phi_{\text{solvent}}(K_{A\text{solvent}}/V_{\text{solvent}})] \qquad (8)\end{aligned}$$

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

$$\begin{aligned}\ln a_A^{\text{solid}} = &-\Delta H_A^{\text{fus}}(T_{mp} - T)/(RT\,T_{mp}) + (\Delta C_{p,A}/RT)(T_{mp} - T) \\ &- (\Delta C_{p,A}/T)\ln(T_{mp}/T) \qquad (9)\end{aligned}$$

the solute's molar enthalpy of fusion, ΔH_A^{fus}, and heat capacity difference, $\Delta C_{p,A}$, 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 [21–25] have presented an 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. (6) and (8) is relatively straightforward. First, an average numerical value of $\delta_{\text{ferro}}' = 20.43\ \text{MPa}^{1/2}$ is computed by requiring that each equation (with $r_{\text{solvent}} = 0$ and/or $K_{A\text{solvent}} = 0$) perfectly describes ferrocene mole fraction solubility data in *n*-hexane ($\delta_{\text{ferro}}' = 20.48\ \text{MPa}^{1/2}$), *n*-heptane ($\delta_{\text{ferro}}' = 20.33\ \text{MPa}^{1/2}$), and *n*-octane ($\delta_{\text{ferro}}' = 20.48\ \text{MPa}^{1/2}$). The numerical values of

$a_A^{\mathrm{solid}} = 0.140$ and $V_{\mathrm{ferro}} = 135.0\,\mathrm{cm^3\,mol^{-1}}$ were both taken from the chemical literature [12].

Table I summarizes the predictive ability of mobile order theory for the 42 different organic solvents for which both ferrocene 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 $\delta'_{\mathrm{solvent}}$ were obtained from published compilations [21, 22, 24, 25], and were either deduced by regressing actual solubility data of solid *n*-alkanes in

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
Cyclooctane	134.9	15.40
2,2,4-Trimethylpentane	166.09	14.30
tert-Butylcyclohexane	173.9	15.50
Benzene	89.4	18.95
Toluene	106.84	18.10
Ethylbenzene	123.1	18.02
m-Xylene	123.2	17.20
p-Xylene	123.9	17.30
Dibutyl ether	170.3	17.45
1,4-Dioxane	85.8	20.89
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
2-Methyl-2-propanol	94.3	15.78
1-Pentanol	108.6	16.85
1-Hexanol	125.2	16.40
1-Heptanol	141.9	16.39
1-Octanol	158.3	16.38
1-Decanol	191.6	16.35
Methyl acetate	79.8	21.71
Ethyl acetate	98.5	20.79
Butyl acetate	132.5	19.66

TABLE III (Continued)

Component (*i*)	$V_i/(cm^3\,mol^{-1})$	$\delta_i'/(MPa^{1/2})^a$
1,2-Dichloroethane	78.8	20.99
1-Chlorobutane	105.0	17.12
1-Chlorooctane	171.1	18.00
Tetrachloromethane	97.08	17.04
2-Propanone	74.0	21.91
Acetonitrile	52.9	23.62
Pyridine	80.9	20.94
Carbon disulfide	60.0	20.50
Ferrocene[b]	135.0[c]	20.43[d]

[a] Tabulated values are taken from a compilation given in Ruelle *et al.* [21,22,24,25].

[b] The numerical value of $a_A^{solid} = 0.140$ was taken from the chemical literature [12].

[c] Numerical value of $V_{ferro} = 135.0\,cm^3\,mol^{-1}$ was taken from the chemical literature [12].

[d] Numerical value was calculated using the measured ferrocene mole fraction solubilities in *n*-hexane, *n*-heptane and *n*-octane, in accordance with Eqs. (6) and (8); with $r_{solvent} = 0$ and/or $K_{A solvent} = 0$.

organic solvents in accordance with the configurational entropic model of Huyskens and Haulait-Pirson [26] or estimated using known values for similar organic solvents. Examination of the entries in Table I reveals that mobile order theory does provide fairly reasonable (though by no means perfect) estimates of the solubility behavior of ferrocene in a wide range of organic solvents. Average absolute deviation between predicted and observed values is 107.8%. Expressed on a natural logarithmic mole fraction scale, mobile order theory predicts the ferrocene solubilities to within ±0.51 ln units. The arithmetic average of the ln X_A^{sat} difference is 0.49, which indicates a systematic overprediction in the predicted value. 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 26-fold range in mole fraction. Had an ideal solution been assumed, then the predicted mole fraction solubility would be $X_A^{sat} = a_A^{solid} = 0.140$ for each solvent. The ideal solution approximation corresponds to a considerably larger average absolute deviation of 627% between predicted and observed values.

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