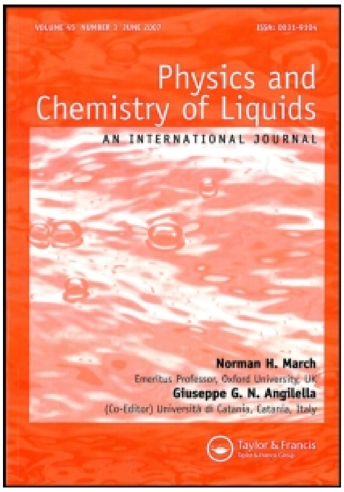

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Solubility of Benzil in Binary Alkane Cyclooctane Solvent Mixtures: Comparison of Predictive Expressions Derived from the Nearly Ideal Binary Solvent (NIBS) Model

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SOLUBILITY OF BENZIL IN BINARY ALKANE + CYCLOOCTANE SOLVENT MIXTURES: COMPARISON OF PREDICTIVE EXPRESSIONS DERIVED FROM THE NEARLY IDEAL BINARY SOLVENT (NIBS) MODEL

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Experimental solubilities are reported for benzil dissolved in seven binary mixtures containing cyclooctane with *n-hexane*, *n*-heptane, *n*-octane, *n*-nonane, methylcyclohexane, 2, 2, 4-trimethylpentane, and *tert*-butylcyclohexane at 25 °C. Results of measurements are compared to the predictions of equations developed previously for solubility in systems of nonspecific interactions. The most successful equation in terms of goodness of fit involved a volume fraction average of the excess Gibbs free energies relative to the Flory-Huggins model, and predicted the experimental solubilities in the seven systems studied to within an overall average absolute deviation of 2.1%and with a maximum deviation of 3.6%.

KEY WORDS: Benzil solubilities, binary solvent mixtures, 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 hydrocarbons (i.e. anthracene and pyrene) and hetero-atom polynuclear aromatics (i.e. carbazole, dibenzothiophene and xanthene) have been published in the recent chemical literature[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 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 methods have proved fairly successful in estimating solid solubility in pure and binary

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solvent mixtures from structural information. 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 both finite concentration and infinite dilution activity coefficient predictions.

Predictive expressions for solid-liquid equilibria have also been derived from simple thermodynamic mixing models. The Nearly Ideal Binary Solvent (NIBS) model[4-6] developed previously provides a relatively simple method for estimating the excess partial molar properties of a solute, ΔZ_A^{ex}, at infinite dilution in a binary solvent (Components B and C)

$$\Delta Z_A^{ex} = f_B^0 (\Delta Z_A^{ex})_B^* + f_C^0 (\Delta Z_A^{ex})_C^* - \Gamma_A (X_B^0 \Gamma_B + X_C^0 \Gamma_C)^{-1} \Delta Z_{BC}^{ex} \qquad (1)$$

$$f_B^0 = 1 - f_C^0 = X_B^0 \Gamma_B / (X_B^0 \Gamma_B + X_C^0 \Gamma_C) \qquad (2)$$

in terms of a weighted mole fraction average of solute properties in the two pure solvents, $(\Delta Z_A^{ex})_B^*$ and $(\Delta Z_A^{ex})_C^*$, and a contribution due to the unmixing of the solvent pair by the presence of the solute. Symbols used in Eqn. (1) are defined in the Appendix. Equation (1) (with $\Delta Z^{ex} = \Delta G^{ex}$) gives accurate predictions for naphthalene, iodine, *p*-benzoquinone, benzil, *p*-dibromobenzene, benzoic acid, carbazole, benzoic acid and phenylacetic acid solubilities in systems of nonspecific interactions when molar volumes are used as weighting factors ($\Gamma_i = V_i$)[1-3,6]. Approximation of weighting factors with molecular surface areas enables Eqn. (1) to provide accurate predictions for anthracene[7] and pyrene[8] solubilities in binary solvent mixtures containing benzene.

Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, benzil solubilities were determined in seven binary alkane + cyclooctane solvent mixtures, which cover upto a 2.5-fold range in mole fraction solubilities. Results of these measurements are compared to predictions based upon the NIBS model.

EXPERIMENTAL METHODS

Benzil (Aldrich 98%) was recrystallized three times from methanol. Cyclooctane (Aldrich, 99 + %), *n*-hexane (Aldrich, 99%), *n*-heptane (Aldrich, HPLC), *n*-octane (Aldrich, 99 + %, anhydrous), n-nonane (TCI America, 99 + %), methylcyclohexane (Aldrich, 99 + %, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC) and *tert*-butylcyclohexane (Aldrich, 99 + %) were stored over molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent or better. Binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction.

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 last three days (often longer). Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Aliquots of saturated benzil solutions were transferred through a coarse of filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 390 nm on a Bausch and Lomb Spectronic 2000. Experimental benzil solubilities in the seven binary alkane + cyclooctane solvent mixtures studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ± 1.3%. Measured mole fraction solubilities in *n*-hexane, *n*-heptane, *n*-octane, cyclooctane and 2, 2, 4-trimethylpentane are in excellent agreement with published literature values[9–11].

RESULTS AND DISCUSSION

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend upon two different models of ideality

$$RT\ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - X_A^{\text{sat}})^2\,[X_B^0(\Delta G_A^{\text{ex}})_B^* + X_C^0(\Delta G_A^{\text{ex}})_C^* - \Delta G_{BC}^{\text{ex}}] \qquad (3)$$

$$RT\ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - \phi_A^{\text{sat}})^2\,[\phi_B^0(\Delta G_A^{\text{ex}})_B^* + \phi_C^0(\Delta G_A^{\text{ex}})_C^* - V_A(X_B^0 V_B + X_C^0 V_C)^{-1}\Delta G_{BC}^{\text{ex}}] \qquad (4)$$

and

$$RT\{\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - (1 - \phi_A^{\text{sat}})[1 - V_A/(X_B^0 V_B + X_C^0 V_C)]\}$$
$$= (1 - \phi_A^{sat})^2\,[\phi_B^0(\Delta G_A^{\text{fh}})_B^* + \phi_C^0(\Delta G_A^{\text{fh}})_C^* - V_A(X_B^0 V_B + X_C^0 V_C)^{-1}\Delta G_{BC}^{\text{fh}}] \qquad (5)$$

Equations (3) and (4) are based upon Raoult's law and Eqn. (5) is based upon the Flory-Huggins model for the combinatorial entropic contribution. In the above three expressions X_B^0 and X_C^0 refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present, a_A^{solid} is the activity of the solid solute relative to the pure subcooled liquid, ϕ_i denotes volume fraction and V_i is the molar volume of pure component i. Binary solvent properties $\Delta G_{BC}^{\text{ex}}$ and $\Delta G_{BC}^{\text{fh}}$ denote the excess Gibbs energies relative to Raoult's law and the Flory-Huggins model, respectively. Solubility measured in each pure solvent can be used to calculate the excess partial molar Gibbs energy of the solute, $(\Delta G_A^{\text{ex}})_i^*$ and $(\Delta G_A^{\text{fh}})_i^*$. These quantities are then

Table 1 Experimental Mole Fraction Solubilities of Benzil (X_A^{sat}) in Binary Alkane (B) + Cyclooctane (C) Solvent Mixtures at 25.0 °C.

X_C^0	X_A^{sat}	*% Deviations of Calculated Values*[a]		
		Eqn. (3)	*Eqn. (4)*	*Eqn. (5)*
		n-Hexane (B) + Cyclooctane (C)		
0.0000	0.00575	–	–	–
0.1066	0.00684	−3.9	−2.3	−2.3
0.2026	0.00781	−5.7	−3.0	−3.0
0.3972	0.00975	−6.7	−2.8	−2.8
0.4927	0.01075	−7.1	−3.0	−2.9
0.5940	0.01181	−7.2	−3.1	−3.2
0.8000	0.01380	−6.1	−3.2	−3.5
0.9054	0.01448	−3.5	−2.1	−2.1
1.0000	0.01485	–	–	–
		n-Heptane (B) + Cyclooctane (C)		
0.0000	0.00656	–	–	–
0.1178	0.00758	−2.4	−2.5	−2.5
0.2266	0.00843	−2.4	−2.5	−2.5
0.4214	0.01005	−2.3	−2.4	−2.3
0.5224	0.01102	−3.0	−3.1	−3.0
0.6290	0.01195	−2.7	−2.7	−2.7
0.8110	0.01353	−2.2	−2.1	−2.1
0.9013	0.01436	−2.4	−2.3	−2.3
1.0000	0.01485	–	–	–
		n-Octane (B) + Cyclooctane (C)		
0.0000	0.00724	–	–	–
0.1280	0.00820	−0.8	−1.9	−1.9
0.2381	0.00901	−0.7	−2.4	−2.4
0.4421	0.01063	−0.8	−3.1	−3.1
0.5389	0.01148	−1.4	−3.6	−3.4
0.6497	0.01231	−0.8	−2.6	−2.5
0.8228	0.01380	−1.7	−2.7	−2.6
0.9080	0.01443	−1.6	−2.1	−2.1
1.0000	0.01485	–	–	–
		n-Nonane (B) + Cyclooctane (C)		
0.0000	0.00794	–	–	–
0.1309	0.00869	1.2	−0.6	−0.5
0.2477	0.00943	1.8	−1.4	−1.0
0.4672	0.01098	1.8	−2.1	−1.9
0.5700	0.01185	0.7	−3.0	−2.8
0.6694	0.01262	0.3	−3.0	−2.8
0.8405	0.01368	1.2	−0.7	−0.5
0.9188	0.01423	0.9	−1.0	0.0
1.0000	0.01485	–	–	–
		Methylcyclohexane (B) + Cyclooctane (C)		
0.0000	0.01128	–	–	–
0.0987	0.01163	0.6	1.2	1.2
0.1931	0.01208	0.1	1.1	1.1
0.3870	0.01307	−1.5	−0.1	−0.1
0.4932	0.01359	−2.4	−0.9	−0.9
0.5900	0.01401	−2.9	−1.3	−1.3
0.7907	0.01462	−2.4	−1.5	−1.5
0.8950	0.01483	−1.8	−1.2	−1.2
1.0000	0.01485	–	–	–

Table 1 (*Contd.*)

X_C^0	X_A^{sat}	*% Deviations of Calculated Values*[a]		
		Eqn.(3)	*Eqn.(4)*	*Eqn.(5)*
	2,2,4-Trimethylpentane (B) + Cyclooctane (C)			
0.0000	0.00589	–	–	–
0.1290	0.00703	1.5	0.4	0.5
0.2441	0.00808	3.2	1.7	1.8
0.4460	0.01011	4.4	3.1	3.3
0.5397	0.01119	3.4	2.6	2.7
0.6543	0.01234	3.1	3.1	2.9
0.8314	0.01410	0.3	0.7	0.8
0.9292	0.01464	0.0	0.4	0.4
1.0000	0.01485	–	–	–
	tert-Butylcyclohexane (B) + Cyclooctane (C)			
0.0000	0.01114	–	–	–
0.1296	0.01203	−0.3	−0.9	−0.9
0.2438	0.01256	−0.8	−1.7	−1.6
0.4670	0.01330	0.3	−0.9	−0.7
0.5679	0.01379	−0.7	−1.7	−1.6
0.6680	0.01430	−1.9	−2.8	−2.6
0.8357	0.01472	−1.5	−1.9	−1.8
0.9214	0.01490	−1.3	−1.6	−1.5
1.0000	0.01485	–	–	–

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

combined with the free energy of the binary solvent mixture to predict solubility in mixed solvents. One should note that all equations give identical predictions when $V_A = V_B = V_C$, and it is only in systems having both a large mole fraction solubility range and considerable molecular size disparity that one can distinguish between the descriptive equations.

Initially, testing of the limitations and applications of the basic NIBS model was restricted to binary solvent systems for which ΔG_{BC}^{ex} (or ΔG_{BC}^{fh}) values could be found in the chemical literature, though in more recent studies we have had to estimate the input ΔG_{BC}^{ex} values. This undoubtedly will become more common as more complex systems and multi-functional group solvent components are studied. Excess Gibbs free energies of the binary solvents may be estimated from the Scatchard-Hildebrand solubility parameter approach or the UNIFAC or other group contribution methods. The various group contribution methods have been reviewed in detail in monographs by Acree[6] and Prausnitz *et al.*[12] The Scatchard-Hildebrand approach, perhaps the simplest of the predictive methods, estimates the excess Gibbs free energies from

$$\Delta G_{BC}^{ex} = \phi_B^0 \phi_C^0 (X_B^0 V_B + X_C^0 V_C)(\delta_B - \delta_C)^2 \tag{6}$$

$$\Delta G_{BC}^{fh} = \Delta G_{BC}^{ex} + RT\,[\ln(X_B^0 V_B + X_C^0 V_C) - X_B^0 \ln V_B - X_C^0 \ln V_C] \tag{7}$$

solubility parameters of the pure components, δ_i.

Comparison between experimental and predicted benzil solubilities are summarized in the last three columns of Table 1. Solute properties used in the NIBS predictions include $V_A = 183\ \text{cm}^3\ \text{mol}^{-1}$[19,13] and the activity of the solute, $a_A^{\text{solid}} = 0.224$[9], which was calculated by integrating the molar enthalpy of fusion data from the normal melting point temperature to 25 °C. Experimental excess Gibbs free energies of mixing could not be found in the chemical literature for the seven binary alkane + cyclooctane solvent mixtures, hence we have used estimated $\Delta G_{BC}^{\text{ex}}$ values in all NIBS predictions. The $\Delta G_{BC}^{\text{ex}}$ values are estimated *via* Eqn. (6) using solvent properties listed in Table 2. Use of estimated $\Delta G_{BC}^{\text{ex}}$ values will unfortunately introduce additional errors/uncertainties in the NIBS predictions; however, we do not believe that this error will be very large. A 5–10 cal mol^{-1} underestimation in $\Delta G_{BC}^{\text{ex}}$ translates to roughly a -2% error in the predicted mole fraction benzil solubility, which is only slightly larger than the experimental uncertainty.

Careful examination of Table 1 reveals that Eqns. (4) and (5) provide reasonably accurate predictions for how the solubility of benzil varies with binary solvent composition, and both equations are slightly superior to the mole fraction based expression, Eqn. (3). Values predicted from Eqns. (4) and (5) differ from the observed values by an overall average absolute deviation of 2.1%. For the most part, both equations underpredict the observed mole fraction solubility by a few relative percent. As noted above, we believe that the underpredictions result in part from uncertainties/errors associated with $\Delta G_{BC}^{\text{ex}}$ (and $\Delta G_{BC}^{\text{fh}}$) estimations.

Table 2 Solvent Properties used in the NIBS Predictions.

Component i	$V_i/(cm^3\ mol^{-1})$	$\delta_i/(cal\ cm^{-3})^{1/2,a}$
n-Hexane	131.51	7.27
n-Heptane	147.48	7.50
n-Octane	163.46	7.54
n-Nonane	179.44	7.64
Cyclohexane	108.76	8.19
Methylcyclohexane	128.32	7.83[b]
Cyclooctane	134.88	8.51[c]
2,2,4-Trimethylpentane	166.09	6.86
tert-Butylcyclohexane	173.93	7.82[d]

[a] Unless otherwise noted, solubility parameters taken from Ref. 18.
[b] Calculated from data in Ref. 19.
[c] Calculated from the calorimetric data in Cox and Pilcher[20].
[d] Calculated from data in Majer and Svoboda[21].

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APPENDIX: GLOSSARY OF SYMBOLS

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$(\Delta \bar{G}_A^{\text{ex}})_i^*$	partial molar Gibbs free energy of the solute (Raoult's law) in pure solvent i, extrapolated back to infinite dilution
$(\Delta \bar{G}_A^{\text{fh}})_i^*$	partial molar Gibbs free energy of the solute (Flory-Huggins model) in pure solvent i, extrapolated back to infinite dilution
$\Delta G_{BC}^{\text{ex}}$	excess molar Gibbs free energy of the binary solvent mixture based upon Raoult's law
$\Delta G_{BC}^{\text{fh}}$	excess molar Gibbs free energy of the binary solvent mixture based upon the Flory-Huggins model
$\bar{V}_i$	molar volume of component i
X_B^0, X_C^0	mole fraction composition of the binary solvent mixture, calculated as if the solute were not present
X_A^{sat}	mole fraction saturation solubility of the solute
ϕ_B^0, ϕ_C^0	ideal volume fraction composition of the binary solvent mixture, calculated as if the solute were not present
ϕ_A^{sat}	ideal volume fraction saturation solubility of the solute
δ_i	solubility parameter of component i
Γ_i	weighting factor of component i