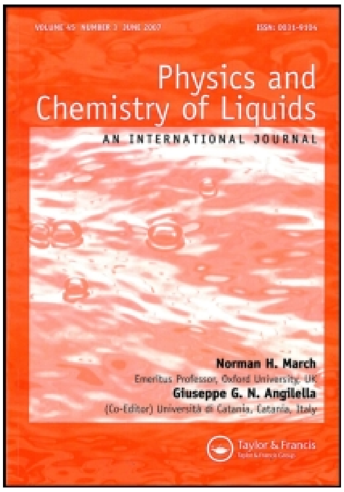

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Solubility of Anthracene in Binary Carbon Tetrachloride Alkane Solvent Mixtures

Sheryl A. Tucker[a]; William E. Acree Jr.[a]
[a] Department of Chemistry, Kent State University, Kent, Ohio, USA

To cite this Article Tucker, Sheryl A. and Acree Jr., William E.(1989) 'Solubility of Anthracene in Binary Carbon Tetrachloride Alkane Solvent Mixtures', Physics and Chemistry of Liquids, 19: 2, 73 — 79

To link to this Article: DOI: 10.1080/00319108908028437

URL: http://dx.doi.org/10.1080/00319108908028437

Phys. Chem. Liq., 1989, Vol. 19, pp. 73–79
Reprints available directly from the publisher
Photocopying permitted by license only

SOLUBILITY OF ANTHRACENE IN BINARY CARBON TETRACHLORIDE + ALKANE SOLVENT MIXTURES

SHERYL A. TUCKER and WILLIAM E. ACREE, Jr.*

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

(Received 19 August 1988)

Experimental solubilities are reported for anthracene in binary solvent mixtures containing carbon tetrachloride with *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane and isooctane at 25°C. Results of these measurements, combined with the excess Gibbs free energies of the binary solvents, are used to test predictive expressions derived from the nearly ideal binary solvent (NIBS) model. Expressions based on a volume fraction average of solute properties in the two pure solvents predict anthracene solubilities to within a maximum deviation of 4.5% and an overall average deviation of 1.8%.

KEY WORDS: Anthracene solubilities, solubilities in binary solvents, solid-liquid equilibria.

I INTRODUCTION

Solid-liquid equilibria is important in many chemical separation processes. For industrial processes concerned with crystallization, solute solubility must be known as a function of both temperature and solvent composition. The chemical literature does contain solubility data for a number of organic compounds. Solubility data for solid solutes dissolved in pure solvents is fairly abundant, data for binary solvents is scarce, and data for higher-order multicomponent solvent mixtures is virtually non-existent. To address this problem, researchers have turned to predictive methods as a means to generate desired quantities. This is especially true in instances where the experimental costs are prohibitive or the measurements are too time-consuming to undertake.

The nearly ideal binary solvent (NIBS) approach developed previously[1–4] provides a relatively simple method for estimating the excess partial molar properties of a solute, $(\Delta \bar{Z}_A^{ex})^*$, at infinite dilution in a binary solvent mixture (components B and C)

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

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

in terms of a weighted mole fraction average of the properties of the solute in the pure solvents, $(\Delta \bar{Z}_A^{ex})_B^*$ and $(\Delta \bar{Z}_A^{ex})_C^*$, and a contribution due to the unmixing of the solvent

---

* To whom correspondence should be addressed.

pair by the presence of the solute. Equation (1) leads to accurate predictions of enthalpies of solution[1], gas-liquid partition coefficients[3], and solubilities[2,4–10] in systems of nonspecific interactions when the weighting factors (Γ_i) are approximated with molar volumes. In addition, Eq. (1) has served as the foundation for approximating the "physical" interactions in systems containing "chemical" interactions such as those between a solute and a complexing solvent.

Acree and coworkers extended the basic NIBS model to systems containing solute complexation with a single solvent[11–16]

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{\phi}_{AC} = \hat{\phi}_{AC}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\ln \phi_A^{\text{sat}} = \phi_B^0 \ln(\phi_A^{\text{sat}})_B + \phi_C^0 \ln(\phi_A^{\text{sat}})_C + \ln[1 + \bar{V}_A K^{\phi}_{AC}\phi_C^0/(\bar{V}_A + \bar{V}_C)]$$
$$- \phi_C^0 \ln[1 + \bar{V}_A K^{\phi}_{AC}/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A \Delta\bar{G}^{\text{fh}}_{BC}}{RT(X_B^0\bar{V}_B + X_C^0\bar{V}_C)} \tag{2}$$

and to systems where the solute complexes with both solvent components[17]

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{\phi}_{AC} = \hat{\phi}_{AC} = \hat{\phi}_{AC}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$
$$A_1 + B_1 \rightleftharpoons AB \qquad K^{\phi}_{AB} = \hat{\phi}_{AB} = \hat{\phi}_{AB}/(\hat{\phi}_{A_1}\hat{\phi}_{B_1})$$

$$\ln \phi_A^{\text{sat}} = \phi_B^0 \ln(\phi_A^{\text{sat}})_B + \phi_C^0 \ln(\phi_A^{\text{sat}})_C - \phi_B^0 \ln[1 + \bar{V}_A K^{\phi}_{AB}/(\bar{V}_A + \bar{V}_B)]$$
$$+ \ln[1 + \bar{V}_A K^{\phi}_{AC}\phi_C^0/(\bar{V}_A + \bar{V}_C) + \bar{V}_A K^{\phi}_{AB}\phi_B^0/(\bar{V}_A + \bar{V}_B)]$$
$$- \phi_C^0 \ln[1 + \bar{V}_A K^{\phi}_{AC}/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A \Delta\bar{G}^{\text{fh}}_{BC}}{RT(X_B^0\bar{V}_B + X_C^0\bar{V}_C)} \tag{3}$$

(The nomenclature is defined in the List of Symbols at the end of this work.) Equations (2) and (3) enable the determination of solute-solvent equilibrium constants from measured solute solubility as a function of solvent composition. McCargar and Acree[13–16] compared values for the carbazole-dibutyl ether association constant calculated from carbazole solubilities in ten binary dibutyl ether + alkane solvent mixtures. Equation (2) described the carbazole solubilities within an average deviation of 2% using a single association constant, the numerical value ranging from $K^{\phi}_{AC} = 22$ for *n*-heptane to $K^{\phi}_{AC} = 30$ for isooctane cosolvent. The success of the extended NIBS model is even more impressive if one realizes the mole fraction solubilities covered a 25-fold range, and the inert cosolvents included both small (cyclohexane, *n*-hexane) and large (*n*-hexadecane, squalane) hydrocarbons.

While the NIBS and extended NIBS approaches have been very successful in describing solute solubility, additional experimental measurements are still required in order to increase the very limited solubility data bank for solid solutes dissolved in binary solvent mixtures. Development of group contribution methods for predicting solubility from molecular structure (i.e., UNIFAC method[18–20]) require large data bases with all functional groups being adequately represented. For this reason, we report experimental solubilities for anthracene in binary solvent mixtures containing carbon tetrachloride with *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, methylcyclohexane and isooctane. Results of these measurements are compared to predictions based on the NIBS model.

EXPERIMENTAL

Anthracene (Aldrich Gold Label) was used as received. Cyclohexane (Aldrich HPLC), *n*-heptane (Aldrich HPLC), carbon tetrachloride (Aldrich HPLC), *n*-hexane (Aldrich 99%), *n*-octane (Aldrich Gold Label), isooctane (Aldrich HPLC) and methylcyclohexane (Aldrich Gold Label) were stored over molecular sieves to remove trace water. Gas chromatographic analysis showed solvent purities to be 99.8% or better. Binary solvent mixtures were prepared by weight so that compositions could be calculated to 0.0001 mole fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibriate in a constant temperature bath at 25.0 ± 0.1°C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and in some instances by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Aliquots of the saturated 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 356 nm on a Bausch and Lomb Spectronic 2000. Experimental solubilities are listed in Table 1. Numerical values represent the average of 4-6 determinations, with the measurements being reproducible to ±1%. Solubilities in the pure alkane solvents are in excellent agreement with earlier values of Acree and Rytting.[21]

RESULTS AND DISCUSSION

The general NIBS equations for predicting solubilities in systems of nonspecific interactions depend on two different models of solution ideality:

$$RT \ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - X_A^{\text{sat}})^2[X_B^0(\Delta\bar{G}_A^{\text{ex}})_B^* + X_C^0(\Delta\bar{G}_A^{\text{ex}})_C^* - \Delta\bar{G}_{BC}^{\text{ex}}] \tag{4}$$

$$\begin{aligned} RT \ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - \phi_A^{\text{sat}})^2[&\phi_B^0(\Delta\bar{G}_A^{\text{ex}})_B^* + \phi_C^0(\Delta\bar{G}_A^{\text{ex}})_C^* \\ &- \bar{V}_A(X_B^0\bar{V}_B + X_C^0\bar{V}_C)^{-1}\Delta\bar{G}_{BC}^{\text{ex}}] \end{aligned} \tag{5}$$

$$\begin{aligned} &RT\left[\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - (1 - \phi_A^{\text{sat}})\left(1 - \frac{\bar{V}_A}{X_B^0\bar{V}_B + X_C^0\bar{V}_C}\right)\right] \\ &\quad = (1 - \phi_A^{\text{sat}})^2[\phi_B^0(\Delta\bar{G}_A^{\text{fh}})_B^* + \phi_C^0(\Delta\bar{G}_A^{\text{fh}})_C^* - \bar{V}_A(X_B^0\bar{V}_B + X_C^0\bar{V}_C)^{-1}\Delta\bar{G}_{BC}^{\text{fh}}] \end{aligned} \tag{6}$$

Equations (4) and (5) are based on Raoult's law and Eq. (6) is based on the Flory-Huggins model. To date, the basic NIBS model has been shown to provide very reasonable predictions of iodine, naphthalene, benzil, *p*-benzoquinone, biphenyl and pyrene solubilities. Predictive applications of Eqs (4-6) requires a prior knowledge of solute solubility in each pure solvent, the excess Gibbs free energy of the binary solvent mixture, and the numerical value of a_A^{solid}, which is calculated from

$$\ln a_A^{\text{solid}} = \frac{-\Delta\bar{H}_A^{\text{fus}}(T_{mp} - T)}{RT_{mp}T}$$

Table 1 Mole fraction solubilities of anthracene in several binary solvent mixtures at 25.0°C.

Solvent (*B*) + *Solvent* (*C*)	X_B^0	X_A^{sat}
n-Hexane + Carbon tetrachloride	0.0000	0.00464
	0.1585	0.00378
	0.3229	0.00299
	0.4318	0.00257
	0.5303	0.00226
	0.7356	0.00176
	0.8631	0.00150
	1.0000	0.00127
n-Heptane + Carbon tetrachloride	0.0000	0.00464
	0.1492	0.00380
	0.3062	0.00311
	0.3935	0.00281
	0.4941	0.00250
	0.7096	0.00201
	0.8448	0.00178
	1.0000	0.00157
n-Octane + Carbon tetrachloride	0.0000	0.00464
	0.1343	0.00392
	0.2818	0.00330
	0.3672	0.00302
	0.4743	0.00268
	0.6934	0.00225
	0.8407	0.00205
	1.0000	0.00184
Cyclohexane + Carbon tetrachloride	0.0000	0.00464
	0.1847	0.00387
	0.3702	0.00318
	0.4715	0.00285
	0.5722	0.00254
	0.8245	0.00191
	1.0000	0.00155
Methylcyclohexane + Carbon tetrachloride	0.0000	0.00464
	0.1921	0.00373
	0.3341	0.00318
	0.4282	0.00289
	0.5316	0.00262
	0.7452	0.00212
	0.8536	0.00190
	1.0000	0.00165
Isooctane + Carbon tetrachloride	0.0000	0.00464
	0.1069	0.00379
	0.2791	0.00285
	0.3652	0.00249
	0.4633	0.00214
	0.6890	0.00157
	0.8367	0.00130
	1.0000	0.00107

Table 2 Comparison between experimental anthracene solubilities and predicted values based on the NIBS model.

	Deviations (%) of Calcd Values[a]			
Binary solvent system	*Eq. (4)*	*Eq. (5)*	*Eq. (6)*	$\Delta\bar{G}^{ex}_{BC}$ *(Ref.)*
n-Hexane + Carbon tetrachloride	+ 7.0	0.9	1.2	23
n-Heptane + Carbon tetrachloride	+10.5	+2.4	+2.8	24
n-Octane + Carbon tetrachloride	+11.2	+2.3	+2.9	25
Cyclohexane + Carbon tetrachloride	0.2	−1.5	−1.4	26
Methylcyclohexane + Carbon tetrachloride	+ 4.3	−1.1	0.9	—
Isooctane + Carbon tetrachloride	+12.4	−2.2	−1.8	27

[a] Deviations (%) $= (100/N^{1/2})\left\{\sum^{N} [\ln(X^{\text{calc}}_A/X^{\text{exp}}_A)]^2\right\}^{1/2}$: an algebraic sign indicates that all deviations were of the same sign.

the enthalpy of fusion of the solid $\Delta\bar{H}^{\text{fus}}_A$ at its normal melting point temperature T_{mp}.

Comparisons between experimental and predicted anthracene solubilities are summarized in Table 2. Solute and solvent molar volumes used in these calculations are listed in Table 3. Lack of experimental $\Delta\bar{G}^{ex}_{BC}$ (and $\Delta\bar{G}^{fh}_{BC}$) values for methylcyclohexane + carbon tetrachloride solvent mixtures necessitated that the inputted values be estimated *via* the Scatchard–Hildebrand solubility parameter approach

$$\Delta\bar{G}^{ex}_{BC} = \phi^0_B\phi^0_C(X^0_B\bar{V}_B + X^0_C\bar{V}_C)(\delta_B - \delta_C)^2$$

$$\Delta\bar{G}^{fh}_{BC} = \Delta\bar{G}^{ex}_{BC} + RT[\ln(X^0_B\bar{V}_B + X^0_C\bar{V}_C) - X^0_B \ln \bar{V}_B - X^0_C \ln \bar{V}_C]$$

The solubility parameters of methylcyclohexane and carbon tetrachloride are $\delta = 7.83\ \text{cal}^{1/2}\ \text{cm}^{-3/2}$ and $\delta = 8.55\ \text{cal}^{1/2}\ \text{cm}^{-3/2}$, respectively.[22]

Inspection of Table 2 reveals that the predictive abilities of Eqs (5) and (6) are comparable with overall average deviations of 1.7% and 1.8%, and are superior to Eq. (4) which has an overall average (rms) deviation of 7.6%. The predictive superiority of

Table 3 Molar volumes of anthracene, carbon tetrachloride and alkane solvents used in the NIBS predictions.

Component (i)	$\bar{V}_i$ *(cm³/mole)*
n-Hexane	131.51
n-Heptane	147.48
Methylcyclohexane	128.32
Cyclohexane	108.76
n-Octane	163.46
Isooctane	166.09
Carbon Tetrachloride	97.08
Anthracene[a]	150.00

[a] The numerical value of $a^{\text{solid}}_A = 0.01049$ is taken from Acree and Rytting.[21]

the two volume fraction based equations is particularly noticeable in solvent mixtures containing *n*-octane or isooctane with the much smaller carbon tetrachloride cosolvent. Equation (4) overpredicts the experimental solubility in these two systems by as much as 15%.

Readers are reminded that three measured values are needed for each NIBS prediction. Anthracene solubility in each pure solvent was reproducible to within 1% and $\Delta\bar{G}_{BC}^{ex}$ values are believed to be accurate to at least 6 cal/mol. Ratios of $\Gamma_A/(X_B^0\Gamma_B + X_C^0\Gamma_C)$ greater than unity magnify the effect that errors in the unmixing term has on the solubility predictions. A 6 cal/mole error in $\Gamma_A(X_B^0\Gamma_B + X_C^0\Gamma_C^0)^{-1}\Delta G_{BC}^{ex}$ corresponds to an error of 1% in the predicted value. Based on these observations, "uncertainties" in the NIBS predictions are estimated to be on the order of 2–3% which is comparable to observed deviations between experimental and predicted anthracene solubilities from Eqs (5) and (6).

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References

1. T. E. Burchfield and G. L. Bertrand, *J. Solution Chem.*, **4**, 205 (1975).
2. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **81**, 1170 (1977).
3. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **83**, 2355 (1979).
4. W. E. Acree, Jr. and G. L. Bertrand, *J. Solution Chem.*, **12**, 101 (1983).
5. W. E. Acree, Jr., *Thermodynamic Properties of Nonelectrolyte Solutions* (Academic Press, Inc., Orlando, FL, 1984).
6. W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, **71**, 201 (1982).
7. W. E. Acree, Jr. and J. H. Rytting, *Int. J. Pharm.*, **10**, 231 (1982).
8. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *J. Chem. Eng. Data*, **32**, 60 (1987).
9. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *Phys. Chem. Liq.*, **16**, 179 (1987).
10. M. V. Marthandan and W. E. Acree, Jr., *J. Chem. Eng. Data*, **32**, 301 (1987).
11. W. E. Acree, Jr., D. R. McHan and J. H. Rytting, *J. Pharm. Sci.*, **72**, 929 (1983).
12. W. E. Acree, Jr., *Int. J. Pharm.*, **15**, 159 (1983).
13. J. W. McCargar and W. E. Acree, Jr., *Phys. Chem Liq.*, **17**, 123 (1987).
14. J. W. McCargar and W. E. Acree, Jr., *J. Pharm Sci.*, **76**, 572 (1987).
15. J. W. McCargar and W. E. Acree, Jr., *J. Solution Chem.*, in press.
16. W. E. Acree, Jr. and J. W. McCargar, *J. Mol. Liq.*, **37**, 251 (1988).
17. W. E. Acree, Jr. and J. W. McCargar, *J. Pharm. Sci.*, **76**, 575 (1987).
18. Aa Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, **21**, 1086 (1975).
19. W. E. Acree, Jr. and J. H. Rytting, *Int. J. Pharm.*, **13**, 197 (1983).
20. W. E. Acree, Jr., *Int. J. Pharm.*, **18**, 47 (1984).
21. W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, **72**, 292 (1983).
22. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
23. D. V. S. Jain, V. K. Gupta and B. S. Lark, *Indian J. Chem.*, **8**, 815 (1970).
24. T. G. Bissell and A. G. Williamson, *J. Chem. Thermodyn.*, **7**, 131 (1975).
25. D. V. S. Jain, V. K. Gupta and B. S. Lark, *Indian J. Chem.*, **9**, 465 (1971).
26. J. R. Goates, R. J. Sullivan and J. B. Ott, *J. Phys. Chem.*, **63**, 589 (1959).
27. R. Battino, *J. Phys. Chem.*, **72**, 4503 (1968).

APPENDIX: LIST 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
$(\Delta \bar{G}_A^{\text{ex}})^*$	partial molar Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution
$(\Delta \bar{G}_A^{\text{fh}})^*$	partial molar Gibbs free energy of the solute (Flory-Huggins model), extrapolated back to infinite dilution
$\Delta \bar{G}_{BC}^{\text{ex}}$	excess Gibbs free energy of the binary solvent mixture based on Raoult's law
$\Delta \bar{G}_{BC}^{\text{fh}}$	excess Gibbs free energy of the binary solvent mixture based on the Flory-Huggins model
$\Delta \bar{H}_A^{\text{fus}}$	molar enthalpy of fusion of solute
$\bar{V}_i$	molar volume of component i
X_B^0, X_C^0	mole fraction composition of the solvent mixture, calculated as if the solute were not present
X_A^{sat}	saturated mole fraction solubility of the solute
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
ϕ_A^{sat}	ideal volume fraction solubility of solute
RMS Dev	$(100/N^{1/2})\left\{\sum^{N} [\ln(X_A^{\text{calc}}/X_A^{\text{exp}})]^2\right\}^{1/2}$