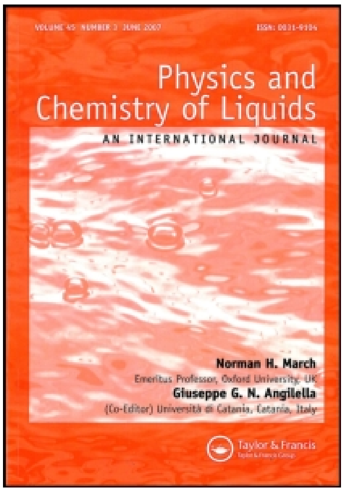

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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Anita I. Zvaigzne[a]; Bradley Smith[a]; Yvonne Cordero[a]; William E. Acree Jr[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA

To cite this Article Zvaigzne, Anita I. , Smith, Bradley , Cordero, Yvonne and Acree Jr, William E.(1992) 'Solubility of Anthracene in Binary Alkane Dimethyl Adipate and Alkane Dibutyl Oxalate Solvent Mixtures', Physics and Chemistry of Liquids, 25: 1, 51 — 58

To link to this Article: DOI: 10.1080/00319109208027287

URL: http://dx.doi.org/10.1080/00319109208027287

Phys. Chem. Liq., 1992, Vol. 25, pp. 51–58
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SOLUBILITY OF ANTHRACENE IN BINARY ALKANE + DIMETHYL ADIPATE AND ALKANE + DIBUTYL OXALATE SOLVENT MIXTURES

ANITA I. ZVAIGZNE, BRADLEY SMITH, YVONNE CORDERO
and WILLIAM E. ACREE, Jr*

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068, USA

(Received 1 May 1992)

Experimental solubilities are reported for anthracene dissolved in three binary mixtures containing dimethyl adipate with cyclohexane, methylcyclohexane and *n*-heptane, and in six solvent mixtures containing dibutyl oxalate with *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane and isooctane at 25°C. Results of these measurements are used to test two mathematical representations based upon the combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister equations and Modified Wilson model. For the systems studied, the combined NIBS/Redlich-Kister equation was found to provide the better mathematical representation with deviations between experimental and back-calculated values being on the order of ±3% or less.

KEY WORDS: Anthracene solubilities, binary solvent mixtures,
mathematical representation of solubility data

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 carcinogencity/mutagenocity 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 methods have proved fairly successful in estimating solid solubility in pure and binary

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* To whom correspondence should be addressed.

solvent mixtures from structural information.[10–17] 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 multifunctional 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. The UNIFAC model[18] now has two sets of group interaction parameters, with the publication of the infinite dilution values by Bastos *et al.*[19]

Predictive expressions for solid–liquid equilibria have also been derived from simple thermodynamic mixing models. The Nearly Ideal Binary Solvent (NIBS) model[20–22] developed previously provides a relative simple method for estimating the excess partial molar properties of a solid, Z_A^{ex}, at infinite dilution in a binary solvent (components B and C)

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

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

in terms of a weighted mole fraction average of solute properties in the two pure solvents, $(Z_A^{ex})_B$ and $(Z_A^{ex})_C$, and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation (1) with $(Z^{ex} = G^{ex})$ gives accurate predictions for naphthalene, iodine, *p*-dibromobenzene, benzil, *p*-benzoquinone, biphenyl, tolylacetic acid, thianthrene, carbazole, benzoic acid and phenylacetic acid solubilities in systems of nonspecific physical interactions when molar volumes are used as weighting factors $(\Gamma_i = V_i)$.[9,22–26] Approximation of weighting factors with molecular surface areas enables Eq. (1) to provide accurate predictions for anthracene[1] and pyrene[3] solubilities in binary solvent mixtures containing benzene. More recently,[27,28] both the NIBS and Modified Wilson[29] models have served as the point-of-departure for the mathematical representation of solute solubility as a function of solvent composition

$$\ln X_A^{sat} = X_B^0 \ln(X_A^{sat})_B + X_C^0 \ln(X_A^{sat})_C + X_B^0 X_C^0 \sum_{i=0}^{n} S_i (X_B^0 - X_C^0)^i \tag{3}$$

and

$$\ln(a_A^{solid}/X_A^{sat}) = 1 - \frac{X_B^0 \{1 - \ln[a_A^{solid}/(X_A^{sat})_B]\}}{X_B^0 + X_C^0 \Lambda_{BC}^{adj}} - \frac{X_C^0 \{1 - \ln[a_A^{solid}/(X_A^{sat})_C]\}}{X_B^0 \Lambda_{CB}^{adj} + X_C^0} \tag{4}$$

with the various S_i and Λ_{ij}^{adj} coefficients computed from measured solubility data *via* least-squares analysis. The various symbols are defined in the Appendix located at the end of the manuscript.

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, anthracene solubilities were determined in three alkane + dimethyl adipate and six alkane + dibutyl oxalate mixtures, which cover up to a ten-fold range in mole fraction solubilities. Results of these measurements are used to further test the descriptive abilities of Eqs. (3) and (4).

MATERIALS AND METHODS

Anthracene (Aldrich 99.9+ %) was used as received. Cyclohexane (Aldrich HPLC), *n*-hexane (Aldrich 99%), *n*-heptane (Aldrich HPLC), *n*-octane (Aldrich 99+ %, anhydrous) methylcyclohexane (Aldrich 99+ %, anhydrous), isooctane (Aldrich HPLC), dimethyl adipate (Aldrich 99%) and dibutyl oxalate (Aldrich 99%) were stored over molecular sieves to remove trace water. Gas chromatographic analysis showed solvent purities to be 99.7% 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 equilibrate in a constant temperature water bath at 25.0 ± 0.1°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 anthracene 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 anthracene solubilities in the nine binary alkane + dimethyl adipate and alkane + oxalate mixtures studied are listed in Tables 1 and 2, respectively. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1.5%.

RESULTS AND DISCUSSION

The ability of Eq. (3) and (4) to mathematically represent the experimental solubility of anthracene in three alkane + dimethyl adipate and six alkane + dibutyl oxalate solvent systems is summarized in Table 3 in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities for the 2-parameter expressions. In the case of Eq. (3) the 3-parameter form was also considered. During the course of evaluating parameters for the Modified Wilson equation, it was noted on a Λ_{BC}^{adj} versus Λ_{CB}^{adj} versus % Deviation three-dimensional map there existed several parameter pairs which described the anthracene solubility to within the same level of error. For example, in the case of anthracene solubilities in isooctane + dibutyl oxalate mixtures,

Table 1 Experimental mole fraction solubilities of anthracene in binary alkane + dimethyl adipate solvent mixtures at 25.0°C.

X_B^0	X_A^{sat}
Cyclohexane (B) + Dimethyl Adipate (C)	
0.0000	0.00871
0.1561	0.00889
0.2940	0.00872
0.4992	0.00765
0.6047	0.00676
0.7014	0.00572
0.8569	0.00368
0.9235	0.00268
1.0000	0.00155
n-Heptane (B) + Dimethyl Adipate (C)	
0.0000	0.00871
0.1193	0.00886
0.2222	0.00878
0.4328	0.00769
0.5267	0.00677
0.6199	0.00590
0.8179	0.00369
0.9072	0.00260
1.0000	0.00157
Methylcyclohexane (B) + Dimethyl Adipate (C)	
0.0000	0.00871
0.1295	0.00898
0.2415	0.00888
0.4605	0.00789
0.5686	0.00697
0.6674	0.00596
0.8357	0.00393
0.9100	0.00295
1.0000	0.00165

the percent deviation was approximately 0.4% for $\Lambda_{BC}^{adj} = 4.302$ and $\Lambda_{CB}^{adj} = 0.514$, 0.8% for $\Lambda_{BC}^{adj} = 3.700$ and $\Lambda_{CB}^{adj} = 0.430$, and 1.1% for $\Lambda_{BC}^{adj} = 4.900$ and $\Lambda_{CB}^{adj} = 0.580$. No special attempt was made to optimize calculated Λ_{ij}^{adj} values as we wished only to learn if Eq. (4) could be used to mathematically represent experimental data in systems covering modest ranges in mole fraction solubilities. Any parameter set having ±2.5% deviation was sufficient for this purpose.

The numerical value of $a_A^{solid} = 0.01049^1$ used in the Modified Wilson computations was calculated from

$$\ln a_A^{solid} = -\Delta H_A^{fus}(T_{mp} - T)/(RTT_{mp}) \qquad (5)$$

The molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature of the solute, T_{mp}. Attempts to eliminate a_A^{solid} from the mathematical representation in

Table 2 Experimental mole fraction solubilities of anthracene in binary alkane + dibutyl oxalate solvent mixtures at 25.0°C.

X_B^0	X_A^{sat}	X_B^0	X_A^{sat}
n-Hexane (B) + Dibutyl Oxalate (C)		Cyclohexane (B) + Dibutyl Oxalate (C)	
0.0000	0.01043	0.0000	0.01043
0.1575	0.00965	0.1683	0.00957
0.2995	0.00850	0.3317	0.00860
0.5129	0.00648	0.5625	0.00673
0.6130	0.00551	0.6557	0.00579
0.6999	0.00456	0.7420	0.00484
0.8623	0.00277	0.8818	0.00314
0.9293	0.00201	0.9402	0.00235
1.0000	0.00127	1.0000	0.00155
n-Heptane (B) + Dibutyl Oxalate (C)		Methylcyclohexane (B) + Dibutyl Oxalate (C)	
0.0000	0.01043	0.0000	0.01043
0.1459	0.00959	0.1702	0.00960
0.2630	0.00881	0.2855	0.00880
0.4833	0.00694	0.5185	0.00702
0.5799	0.00597	0.6203	0.00606
0.6797	0.00498	0.7115	0.00514
0.8500	0.00313	0.8603	0.00346
0.9195	0.00240	0.9196	0.00271
1.0000	0.00157	1.0000	0.00165
n-Octane (B) + Dibutyl Oxalate (C)		Isooctane (B) + Dibutyl Oxalate (C)	
0.0000	0.01043	0.0000	0.01043
0.1164	0.00991	0.1279	0.00941
0.2387	0.00915	0.2522	0.00832
0.4527	0.00734	0.4556	0.00627
0.5566	0.00646	0.5538	0.00531
0.6628	0.00542	0.6501	0.00436
0.8339	0.00364	0.8312	0.00258
0.9144	0.00275	0.9151	0.00180
1.0000	0.00184	1.0000	0.00107

favor of a simplified version ($a_A^{solid} = 1$)

$$\ln(1/X_A^{sat}) = 1 - \frac{X_B^0\{1 - \ln[1/(X_A^{sat})_B]\}}{X_B^0 + X_C^0\Lambda_{BC}^{adj}} - \frac{X_C^0\{1 - \ln[1/(X_A^{sat})_C]\}}{X_B^0\Lambda_{CB}^{adj} + X_C^0} \tag{6}$$

proved unsuccessful.

Careful examination of Table 3 reveals that Eq. (4) provides fairly reasonable (though by no means perfect) mathematical representations of all nine systems studied, which cover up to a *circa* ten-fold mole fraction solubility range in the case of isooctane + dibutyl oxalate. Back-calculated and experimental values generally differ by less than ±3%, except for dimethyl adipate mixtures containing cyclohexane, methylcyclohexane and *n*-heptane. These three systems exhibit maximum anthracene solubilities near pure dimethyl adipate. The maxima in the X_A^{sat} versus X_B^0 curves

Table 3 Mathematical representation of anthracene solubilities in several binary alkane (B) + dimethyl adipate (C) and alkane (B) + Dibutyl oxalate (C) solvent mixtures.

Binary solvent system	*Eq. (3)*		*Eq. (3)*		*Eq. (4)*	
	S_i^a	% *Dev.*[b]	S_i^a	% *Dev.*[b]	$\Lambda_{ij}^{adj,c}$	% *Dev.*[b]
Cyclohexane + Dimethyl adipate	3.306 2.273	6.3	2.950 1.813 1.447	1.6	7.336 0.138	6.7
n-Heptane + Dimethyl adipate	2.818 1.212	3.4	2.580 1.032 0.859	1.2	5.536 0.180	6.8
Methylcyclohexane + Dimethyl adipate	3.124 1.809	14.0	2.760 1.447 1.337	1.6	6.593 0.152	6.6
n-Hexane + Dibutyl oxalate	2.716 1.765	5.0	2.350 1.449 1.375	0.7	3.825 0.290	0.8
n-Heptane + Dibutyl oxalate	2.252 1.305	3.0	2.100 1.156 0.626	1.0	3.323 0.304	0.6
n-Octane + Dibutyl oxalate	2.065 1.076	3.0	1.860 0.988 0.712	0.4	3.263 0.308	0.7
Cyclohexane + Dibutyl oxalate	2.714 2.256	6.0	2.400 1.726 1.368	2.0	5.353 0.279	0.3
Methylcyclohexane + Dibutyl oxalate	2.512 1.929	5.6	2.100 1.567 1.550	1.2	6.037 0.345	0.5
Isooctane + Dibutyl oxalate	2.512 1.519	4.1	2.250 1.348 0.968	0.9	4.302 0.514	0.4

[a] Combined NIBS/Redlich-Kister curve-fit parameters are ordered as S_0, S_1 and S_2.

[b] Deviation (%) = $(100/N)\sum|\ln(X^{calc}/X^{exp})|$.

[c] Adjustable parameters for the Modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

undoubtedly arises because of strong nonidealities in the binary solvent systems. Published liquid–liquid equilibria data[30,31] shows that at 25°C (or slightly below) *n*-heptane + dimethyl adipate mixtures will separate into two immiscible liquid phases as the upper critical solution composition and temperature are $X_{Hp}^0 = 0.65$ and $T_{crit} = 298.5$ K, respectively. Phase separation was noted during the initial preparation of various *n*-heptane + dimethyl adipate solutions; however, only one liquid phase observed in mixtures saturated with anthracene. Solubilities were not measured in *n*-hexane + dimethyl adipate, *n*-octane + dimethyl adipate and isooctane + adipate mixtures because two liquid phases were present. Surprisingly, Eq. (4) is able to describe accurately the sharp, pronounced solubility enhancement that occurs when dibutyl oxalate is added to a pure alkane cosolvent, but grossly over-estimates the observed solubilities in alkane + dimethyl adipate mixtures at low dimethyl adipate mole fractions. Furthermore, the "optimum" set of Λ^{adj} values fail to predict the observed solubility maxima. In comparison, the three-parameter mathematical representation based upon the combined NIBS/Redlich-Kister models, Eq. (3), describes the solubility data to within an average absolute deviation of $\pm 1.2\%$, which is comparable to the experimental uncertainty. There may be one or two individual data points within each system; however, for which the deviations exceed $\pm 3\%$.

Readers are reminded that the nine anthracene systems considered in the present study were judiciously selected so as to encompass typically encountered solubility ranges. Many of the systems currently being studied cover less than a ten-fold mole fraction range, and can be described by either the combined NIBS/Redlich-Kister [Eq. (3)] or Modified Wilson [Eq. (4)] mathematical representations. From a computational standpoint, Eq. (3) will likely be preferred because most research groups involved in reporting thermodynamic properties have computer programs for evaluating the Redlich-Kister coefficients. In the case of the two-parameter Redlich-Kister fit, the computations require only a simple linear least squares analysis of $[\ln X_A^{sat} - X_B^0 \ln(X_A^{sat})_B - X_C^0 \ln(X_A^{sat})_C]/X_B^0 X_C^0$ versus $X_B^0 - X_C^0$. With this idea in mind, we recommend that the future presentation of experimental isothermal solubility data for solid solutes dissolved in binary solvent mixtures include not only a tabulation of the actual observed values but if possible, that the solubility data be mathematically represented by Eq. (3). Realizing that a single equation will not be applicable to all systems encountered, we further suggest Eq. (4) as an alternative mathematical representation for systems having extremely large solubility ranges and/or highly asymmetrical $\ln X_A^{sat}$ versus X_B^0 curves, such as the carbazole + alkane + tetrahydropyran systems reported previously.[28]

Acknowledgements

This research was supported in part by a grant from the National Science Foundation (Grant No. CTS-8922485). Yvonne Cordero and Bradley Smith also thank the US Department of Education for support provided to them under the Upward Bound Math and Science Program.

References

1. W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, **72**, 292 (1983).
2. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *J. Chem. Eng. Data*, **32**, 60 (1987).
3. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *Phys. Chem. Liq.*, **16**, 179 (1987).
4. P. B. Choi, C. P. Williams, K. G. Buehring and E. McLaughlin, *J. Chem. Eng. Data*, **30**, 403 (1985).
5. J. E. Coon, M. Troth and E. McLaughlin, *J. Chem. Eng. Data*, **32**, 233 (1987).
6. J. W. McCargar and W. E. Acree, Jr., *Phys. Chem. Liq.*, **17**, 123 (1987).
7. J. W. McCargar and W. E. Acree, Jr., *J. Pharm. Sci.*, **76**, 572 (1987).
8. J. E. Coon, W. B. Sediawan, J. E. Auwaerter and E. McLaughlin, *J. Solution Chem.*, **17**, 519 (1988).
9. W. E. Acree, Jr., *Phys. Chem. Liq.*, **22**, 157 (1990).
10. W. E. Acree, Jr. and J. H. Rytting, *Int. J. Pharm.*, **13**, 197 (1983).
11. W. E. Acree, Jr., *Int. J. Pharm.*, **18**, 47 (1984).
12. U. Domanska and T. Hofman, *J. Solution Chem.*, **14**, 531 (1985).
13. U. Domanska, *Fluid Phase Equilibr.*, **35**, 217 (1985).
14. R. S. Basu, H. Pham and D. P. Wilson, *Int. J. Thermophysics*, **7**, 319 (1986).
15. A. B. Ochsner and T. D. Sokoloski, *J. Pharm. Sci.*, **74**, 634 (1985).
16. R. Carta and S. Dernini, *J. Chem. Eng. Data*, **28**, 328 (1983).
17. A. Martin, P. L. Wu, A. Adjei, A. Beerbower and J. M. Prausnitz, *J. Pharm. Sci.*, **70**, 1260 (1981).

18. A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, **21**, 1086 (1975).
19. J. C. Bastos, M. E. Soares and A. G. Medina, *Ind. Eng. Chem. Res.*, **27**, 1269 (1988).
20. T. E. Burchfield and G. L. Bertrand, *J. Solution Chem.*, **4**, 205 (1975).
21. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **81**, 1180 (1977).
22. W. E. Acree, Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, (Academic Press, Inc., Orlando, FL, 1984).
23. W. E. Acree, Jr., *J. Chem. Eng. Data*, **30**, 70 (1985).
24. C. L. Judy and W. E. Acree, Jr., *Int. J. Pharm.*, **27**, 39 (1985).
25. W. E. Acree, Jr., N. M. Pontikos and C. L. Judy, *Int. J. Pharm.*, **31**, 225 (1986).
26. W. E. Acree, Jr., S. A. Tucker, A. I. Zvaigzne and I.-Lih Teng, *Phys. Chem. Liq.*, **21**, 45 (1990).
27. W. E. Acree, Jr. and A. I. Zvaigzne, *Thermochim. Acta*, **178**, 151 (1991).
28. W. E. Acree, Jr., J. W. McCargar and A. I. Zvaigzne, *Phys. Chem. Liq.*, **23**, 27 (1991).
29. J. F. Comer and M. M. Kopecni, *Anal. Chem.*, **62**, 991 (1990).
30. G. Manzini and V. Crescenzi, *Int. DATA Ser., Sel. Data Mix., Ser. A*, **53**, (1977).
31. G. Manzini and V. Crescenzi, *J. Phys. Chem.*, **81**, 431 (1977).

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
ΔH_A^{fus}	molar enthalpy of fusion of the solute
S_i	adjustable "curve-fit" parameter in the combined NIBS/Redlich-Kister mathematical representation
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}	saturated mole fraction solubility of the solute
$(X_A^{sat})_i$	saturated mole fraction solubility of the solute in pure solvent component *i*
Λ_{ij}^{adj}	adjustable "curve-fit" parameter in the Modified Wilson mathematical representation