Thermochemical Investigation of Molecular Complexation: Estimation of Anthracene-ethyl Acetate and Anthracene-diethyl Adipate Association Parameters from Measured Solubility Data

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THERMOCHEMICAL INVESTIGATION OF MOLECULAR COMPLEXATION: ESTIMATION OF ANTHRACENE-ETHYL ACETATE AND ANTHRACENE-DIETHYL ADIPATE ASSOCIATION PARAMETERS FROM MEASURED SOLUBILITY DATA

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Experimental solubilities are reported for anthracene in binary mixtures containing ethyl acetate or diethyl adipate with *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane and isooctane at 25°C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to evaluate equilibrium constants for presumed anthracene-ethyl acetate and anthracene-diethyl adipate molecular complexes using the Extended Nearly Ideal Binary Solvent model. A single association constant was needed for each assumed complex in order to describe the experimental data to within an average deviation of 2%, though the numerical value did vary with inert hydrocarbon cosolvent. Poor estimates for the binary Gibbs free energies contributed significantly to the equilibrium constant variation.

INTRODUCTION

Solid-liquid equilibrium data of organic systems are becoming increasingly important in the petroleum industry, particularly in light of present trends towards heavier feedstocks and known carcinogenicity/mutagenicity of many larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic hydrocarbons[1-5] (*ie.*, anthracene and pyrene) and heterocyclic polynuclear aromatics[6-9] (*ie.*, carbazole, dibenzothiophene and xanthene) have been published in recent chemical literature. Despite efforts by experimentalists and scientific organizations, both in terms of new experimental measurements and critically-evaluated data compilations, there still exists 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

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methods have proved fairly successful in estimating solid solubility in pure and binary 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–vapour equilibria data, and it is important that the data base contain as many different functional groups as possible. 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 recent 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 relatively simple method for estimating the excess partial molar properties of a solute, $\bar{Z}_A^{ex}$, at infinite dilution in a binary solvent (components B and C)
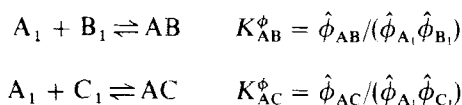
$$\bar{Z}_A^{ex} = f_B^0 (\bar{Z}_A^{ex})_B^* + f_C^0 (\bar{Z}_A^{ex})_C^* - \Gamma_A (X_B^0 \Gamma_B + X_C^0 \Gamma_C)^{-1} \bar{Z}_{BC}^{ex} \tag{1}$$

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

in terms of a weighted mole fraction average of solute properties in the two pure solvents, $(\bar{Z}_A^{ex})_B^*$ and $(\bar{Z}_A^{ex})_C^*$, and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation (1) (with $\bar{Z}^{ex} = \bar{G}^{ex}$) gives accurate predictions for naphthalene, iodine, p-dibromobenzene, benzil, p-benzoquinone, benzoic acid and phenylacetic acid solubilities in systems of nonspecific interactions when molar volumes are used as weighting factors ($\Gamma_i = \bar{V}_i$).[22] 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. The basic NIBS model has also served as the point-of-departure for the development of thermodynamic expressions for describing ternary associated solutions in which the solute complexes with a single solvent[6,7]

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

$$\ln \phi_A^{sat} = \phi_B^0 \ln(\phi_A^{sat})_B + \phi_C^0 \ln(\phi_A^{sat})_C - \ln[1 + \bar{V}_A K_{AC}^\phi \phi_C^0/(\bar{V}_A + \bar{V}_C)]$$

$$- \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^\phi/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A \bar{G}_{BC}^{fh}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \tag{3}$$

or with both solvent components[25]

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

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

$$\ln \phi_A^{sat} = \phi_B^0 \ln(\phi_A^{sat})_B + \phi_C^0 \ln(\phi_A^{sat})_C - \phi_B^0 \ln[1 + \bar{V}_A K_{AB}^\phi/(\bar{V}_A + \bar{V}_B)]$$

$$+ \ln[1 + \bar{V}_A K_{AB}^\phi \phi_B^0/(\bar{V}_A + \bar{V}_B) + \bar{V}_A K_{AC}^\phi \phi_C^0/(\bar{V}_A + \bar{V}_C)]$$

$$- \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^\phi/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A \bar{G}_{BC}^{fh}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \quad (4)$$

Symbols used in the Extended NIBS (Eq. (3)) and Competitive Associated NIBS (Eq. (4)) models are defined in the Appendix. To date, we have calculated association constants for presumed carbazole-dibutyl ether ($K_{AC}^\phi = 25.3 \pm 2.7$),[6,7,23,24] pyrene-dichlorobutane ($K_{AC}^\phi = 14.2 \pm 2.4$),[26] anthracene-chlorobutane ($K_{AC}^\phi = 3.9 \pm 1.3$),[27] anthracene-dichlorobutane ($K_{AC}^\phi = 9.6 \pm 1.8$)[28] and anthracene-butyl acetate ($K_{AC}^\phi = 6.2 \pm 1.4$)[29] from measured solute solubilities.

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 limited data base exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, anthracene solubilities were determined in twelve binary ethyl acetate + alkane and diethyl adipate + alkane mixtures, which cover up to a ten-fold range in mole fraction solubilities. Results of these measurements are compared to predictions based on the NIBS and Extended NIBS models.

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), ethyl acetate (Aldrich 99.5 + %, anhydrous) and diethyl adipate (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 $25.0 \pm 0.1°C$ 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. Undissolved material from several containers was removed and analyzed to ensure that the equilibrium solid phase was indeed pure crystalline anthracene. Melting temperatures of the undissolved residues were identical to that of anthracene. Experimental anthracene solubilities in the twelve binary alkane + ethyl acetate and alkane + diethyl adipate mixtures studied are listed in Tables 1 and 2, respectively. Numerical values represent the average of between four and

Table 1 Comparison between predicted and experimental anthracene solubilities in binary alkane + ethyl acetate solvent mixtures at 25.0 °C.

X_C^0	X_A^{sat}	% Deviations of calculated values[a]		
		Eq. (5)	Eq. (6)	Eq. (7)
n-Hexane (B) + Ethyl Acetate (C)				
0.0000	0.00127	—	—	—
0.1336	0.00184	− 13.8	− 16.9	− 16.7
0.2498	0.00241	− 21.6	− 26.4	− 26.2
0.4557	0.00345	− 26.3	− 32.1	− 31.8
0.5662	0.00395	− 24.8	− 30.1	− 29.9
0.6627	0.00428	− 20.7	− 25.3	− 25.0
0.8395	0.00476	− 12.1	− 14.4	− 14.2
0.9192	0.00485	− 6.7	− 7.8	− 7.7
1.0000	0.00484	—	—	—
n-Heptane (B) + Ethyl Acetate (C)				
0.0000	0.00157	—	—	—
0.1476	0.00216	− 1.0	− 5.0	− 4.8
0.2630	0.00269	− 2.2	− 7.6	− 7.4
0.4937	0.00381	− 4.1	− 9.0	− 8.6
0.5949	0.00426	− 4.5	− 8.2	− 7.7
0.6553	0.00445	− 3.6	− 6.4	− 5.8
0.8554	0.00497	− 3.7	− 3.7	− 3.3
0.9222	0.00493	− 1.6	− 1.3	− 1.0
1.0000	0.00484	—	—	—
n-Octane (B) + Ethyl Acetate (C)				
0.0000	0.00184	—	—	—
0.1616	0.00257	− 13.2	− 18.9	− 18.7
0.2990	0.00322	− 19.6	− 28.4	− 28.1
0.5243	0.00423	− 22.6	− 33.2	− 32.6
0.6128	0.00452	− 20.8	− 30.7	− 30.1
0.7155	0.00489	− 19.6	− 28.0	− 27.4
0.8746	0.00508	− 11.7	− 16.0	− 15.6
0.9378	0.00499	− 6.1	− 8.3	− 8.1
1.0000	0.00484	—	—	—
Cyclohexane (B) + Ethyl Acetate (C)				
0.0000	0.00155	—	—	—
0.1178	0.00234	− 12.9	− 8.1	− 8.1
0.2320	0.00310	− 19.4	− 11.6	− 11.6
0.4266	0.00429	− 23.4	− 13.0	− 13.0
0.5274	0.00474	− 21.8	− 11.0	− 11.0
0.6296	0.00513	− 20.0	− 9.6	− 9.6
0.8150	0.00531	− 11.9	− 4.6	− 4.6
0.9051	0.00515	− 6.4	− 2.0	− 2.0
1.0000	0.00484	—	—	—
Methylcyclohexane (B) + Ethyl Acetate (C)				
0.0000	0.00165	—	—	—
0.1410	0.00261	− 28.2	− 30.9	− 30.7
0.2487	0.00329	− 38.4	− 42.3	− 42.2
0.4487	0.00431	− 42.3	− 47.6	− 47.3

(Continued)

Table 1 (*Continued*)

X_C^0	X_A^{sat}	% Deviations of calculated values[a]		
		Eq. (5)	Eq. (6)	Eq. (7)
0.5783	0.00485	−40.1	−45.2	−44.8
0.6645	0.00507	−35.6	−40.2	−39.9
0.8433	0.00516	−20.0	−22.7	−22.5
0.9173	0.00505	−11.3	−12.7	−12.6
1.0000	0.00484	—	—	—
	Isooctane (B) + Ethyl Acetate (C)			
0.0000	0.00107	—	—	—
0.1306	0.00147	−3.6	−11.4	−11.3
0.3215	0.00221	−6.4	−21.1	−20.8
0.5273	0.00313	−5.4	−21.6	−21.1
0.6250	0.00362	−5.5	−20.1	−19.5
0.7106	0.00402	−4.8	−17.1	−16.4
0.8682	0.00465	−3.5	−9.4	−8.9
0.9290	0.00477	−1.8	−5.0	−4.7
1.0000	0.00484	—	—	—

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

eight independent determinations, with the measured values being reproducible to within $\pm 1.5\%$.

RESULTS AND DISCUSSION

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend on two different models of ideality[21,22]

$$RT \ln(a_A^{solid}/X_A^{sat}) = (1 - X_A^{sat})^2 [X_B^0 (\bar{G}_A^{ex})_B^* + X_C^0 (\bar{G}_A^{ex})_C^* - \bar{G}_{BC}^{ex}] \tag{5}$$

$$RT \ln(a_A^{solid}/X_A^{sat}) = (1 - \phi_A^{sat})^2 [\phi_B^0 (\bar{G}_A^{ex})_B^* - \phi_C^0 (\bar{G}_A^{ex})_C^* - \bar{V}_A (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)^{-1} \bar{G}_{BC}^{ex}] \tag{6}$$

and

$$RT \left[\ln(a_A^{solid}/\phi_A^{sat}) - (1 - \phi_A^{sat}) \left(1 - \frac{\bar{V}_A}{X_B^0 \bar{V}_B + X_C^0 \bar{V}_C} \right) \right]$$
$$= (1 - \phi_A^{sat})^2 [\phi_B^0 (\bar{G}_A^{fh})_B^* + \phi_C^0 (\bar{G}_A^{fh})_C^* - \bar{V}_A (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)^{-1} \bar{G}_{BC}^{fh}] \tag{7}$$

Equations (5) and (6) are based on Raoult's law and Eq. (7) is based on the Flory-Huggins model for the combinatorial entropic contribution. In the above three expressions a_A^{solid} refers to the activity of the solid solute relative to the pure subcooled liquid, X_i is mole fraction, ϕ_i denotes volume fraction and $\bar{V}_i$ is the molar volume of

Table 2 Comparison between predicted and experimental anthracene solubilities in binary alkane + diethyl adipate solvent mixtures at 25.0°C.

X_C^0	X_A^{sat}	% Deviations of calculated values[a]		
		Eq. (5)	Eq. (6)	Eq. (7)
n-Hexane (B) + Diethyl Adipate (C)				
0.0000	0.00127	—	—	—
0.0624	0.00199	−26.7	−19.9	−19.9
0.1414	0.00296	−44.8	−31.5	−31.6
0.3032	0.00482	−53.4	−33.3	−33.4
0.3960	0.00591	−52.9	−31.8	−32.0
0.4999	0.00699	−47.8	−27.6	−27.8
0.7181	0.00887	−30.5	−16.5	−16.7
0.8282	0.00952	−18.8	−9.7	−9.9
1.0000	0.01033	—	—	—
n-Heptane (B) + Diethyl Adipate (C)				
0.0000	0.00157	—	—	—
0.0887	0.00254	−26.2	−20.8	−20.9
0.1544	0.00328	−36.4	−28.1	−28.2
0.3278	0.00522	−45.3	−32.8	−33.0
0.4176	0.00619	−44.4	−31.5	−31.6
0.5344	0.00735	−39.7	−27.4	−27.6
0.7352	0.00896	−25.3	−16.8	−17.0
0.8621	0.00962	−12.7	−7.9	−8.0
1.0000	0.01033	—	—	—
n-Octane (B) + Diethyl Adipate (C)				
0.0000	0.00184	—	—	—
0.0868	0.00280	−22.2	−19.5	−19.5
0.1721	0.00377	−33.5	−28.9	−29.0
0.3402	0.00567	−40.8	−34.3	−34.4
0.4447	0.00679	−39.8	−33.1	−33.2
0.5480	0.00776	−35.5	−29.3	−29.4
0.6732	0.00877	−28.0	−22.8	−22.9
0.8715	0.00989	−11.9	−9.6	−9.6
1.0000	0.01033	—	—	—
Cyclohexane (B) + Diethyl Adipate (C)				
0.0000	0.00155	—	—	—
0.0611	0.00245	−33.2	−24.1	−23.9
0.1187	0.00327	−50.5	−34.6	−34.4
0.2661	0.00511	−70.0	−39.7	−39.5
0.3541	0.00616	−67.6	−38.9	−38.8
0.4508	0.00716	−64.2	−35.2	−35.2
0.6832	0.00886	−42.0	−20.4	−20.5
0.8279	0.00952	−22.8	−9.7	−9.7
1.0000	0.01033	—	—	—
Methylcyclohexane (B) + Diethyl Adipate (C)				
0.0000	0.00165	—	—	—
0.0682	0.00258	−29.8	−23.1	−23.1
0.1344	0.00344	−44.6	−32.9	−32.9
0.2960	0.00540	−57.3	−38.5	−38.6
0.3889	0.00645	−57.3	−37.2	−37.4

Table 2 (*Continued*)

X_C^0	X_A^{sat}	% Deviations of calculated values[a]		
		Eq. (5)	Eq. (6)	Eq. (7)
0.4862	0.00731	−51.9	−32.1	−32.2
0.6317	0.00856	−41.9	−25.0	−25.2
0.8405	0.00967	−18.9	−10.3	−10.4
1.0000	0.01033	—	—	—
Isooctane (B) + Diethyl Adipate (C)				
0.0000	0.00107	—	—	—
0.0894	0.00182	−21.6	−19.0	−19.0
0.1723	0.00264	−31.9	−27.7	−27.7
0.3411	0.00443	−35.2	−29.7	−29.8
0.4555	0.00565	−31.2	−25.9	−26.0
0.5626	0.00678	−26.1	−21.4	−21.5
0.7615	0.00865	−14.3	−11.6	−11.6
0.8684	0.00949	−7.7	−6.3	−6.4
1.0000	0.01033	—	—	—

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

pure component *i*. Binary solvent properties $\bar{G}_{BC}^{ex}$ and $\bar{G}_{BC}^{fh}$ denote the excess Gibbs free energies relative to Raoult's law and the Flory–Huggins model, respectively. Solubility data measured in each pure solvent can be used to calculate the excess partial molar Gibbs free energy of the solute $(\bar{G}_A^{ex})_i^*$ and $(\bar{G}_A^{fh})_i^*$. These quantities are then 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 $\bar{V}_A = \bar{V}_B = \bar{V}_C$, and it is only in systems having 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 $\bar{G}_{BC}^{ex}$ (or $\bar{G}_{BC}^{fh}$) values could be found in the chemical literature, though in more recent studies we have had to estimate the input $\bar{G}_{BC}^{ex}$ values. This undoubtedly will become more common as the Extended NIBS and Competitive Associated NIBS models are applied to more complex systems having presumed solute-solvent complexation. 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 recent monographs by Acree[22] and Prausnitz *et al.*[30] The Scatchard-Hildebrand approach, perhaps the simplest of the predictive methods, estimates the excess Gibbs free energies from

$$\bar{G}_{BC}^{ex} = \phi_B^0 \phi_C^0 (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)(\delta_B - \delta_C)^2 \tag{8}$$

$$\bar{G}_{BC}^{fh} = \bar{G}_{BC}^{ex} + RT[\ln(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C) - X_B^0 \ln \bar{V}_B - X_C^0 \ln \bar{V}_C] \tag{9}$$

solubility parameters of the pure components, δ_i.

Comparisons between experimental and predicted anthracene solubilities are summarized in the last three columns of Tables 1 and 2. Solute properties used in the NIBS predictions include $\bar{V}_A = 150 \text{ cm}^3 \text{ mol}^{-1}$ and the activity of the solute, $a_A^{solid} = 0.01049$,[1] which was calculated by integrating the enthalpy of fusion data from the normal melting point temperature to 25°C. For two of the binary solvent systems studied, n-heptane + ethyl acetate[31] and cyclohexane + ethyl acetate,[32] experimental excess Gibbs free energies are available in the chemical literature. Values for the remaining ten systems were estimated via Eq. (8). Solvent molar volumes and solubility parameters are listed in Table 3.

Careful examination of Tables 1 and 2 reveals that all three NIBS expressions grossly underpredict the observed anthracene solubilities. Deviations between experimental and predicted values are of the order of 20–30% (often larger) for many of the individual binary solvent compositions, and are considerably larger than what would be expected for systems containing only nonspecific physical interactions. In past studies Eqs. (6) and (7) predicted benzil,[33,34] p-benzoquinone,[35] pyrene,[2,3,36] biphenyl,[37] anthracene,[1,38,39] thianthrene,[40] carbazole,[9] benzoic acid[41] and iodine[21,34] solubilities in a wide range of binary organic solvent mixtures to within circa ±5%. While one can always argue that poor $\bar{G}_{BC}^{ex}$ estimates contribute significantly to the failure of the basic NIBS model, one cannot overlook the fact that the model still fails to describe the solubility behavior in both n-heptane + ethyl acetate and cyclohexane + ethyl acetate mixtures for which measured $\bar{G}_{BC}^{ex}$ data exists. Out of curiosity, solubility predictions were also performed in these latter two solvent systems using estimated $\bar{G}_{BC}^{ex}$ values. Replacement of actual binary $\bar{G}_{BC}^{ex}$ data with estimated values led to reduced mole fraction solubilities, ie., $X_{Anthr}^{sat} = 0.00253$ versus $X_{Anthr}^{sat} = 0.00377$ (Eq. (6)), for cyclohexane + ethyl acetate at $X_C^0 = 0.4266$, with deviations now being comparable to those noted in the other four binary alkane + ethyl acetate solvent systems. The Scatchard-Hildebrand solubility parameter approach under-estimates solution nonideality in alkane + ethyl acetate mixtures, perhaps because of the moderately polar ester functional group.

Table 3   Solvent properties used in the NIBS predictions.

Component i	$\bar{V}_i / \text{cm}^3 \text{ mol}^{-1}$	$\delta_i / (\text{cal cm}^{-3})^{1/2}$ [a]
n-Hexane	131.51	7.27
n-Heptane	147.48	7.50
n-Octane	163.46	7.54
Cyclohexane	108.76	8.19
Methylcyclohexane	128.32	7.83
Isooctane	166.09	6.86
Ethyl Acetate	98.54	8.91[b]
Diethyl Adipate	202.25	8.88[c]

[a] Except or ethyl acetate and diethyl adipate, values are taken from tabulations contained in Ref. 26–29.

[b] Numerical value taken from compilation by Hoy.[46]

[c] Arithmetic average of estimated values contained in a paper by Ahmad and Yaseen.[47]

If one assumes the existence of weak anthracene-ethyl acetate and anthracene-diethyl adipate complexes in solution, then the equilibrium constants can be calculated using the Extended NIBS model and measured anthracene solubilities as a function of binary solvent composition. Aromatic solutes are capable of undergoing several types of molecular interactions, depending upon the chemical nature of the surrounding solvent molecules. In hydrogen-bond donating solvents, the electron-rich aromatic compounds serve as hydrogen-bond acceptor sites. Aromatic compounds also have the ability to form electron donor-acceptor complexes, in which case an aromatic solute may act as either acceptor or donor.[42,43] Specific interactions between aromatic hydrocarbons and esters have been suggested in the past. Stephenson and Fuchs[44] reported that the enthalpy of transfer for benzene from the vapor phase to ethyl acetate was considerably more exothermic than the corresponding transfer enthalpy for cyclohexane, which served as an inert model compound of comparable molecular size.

Table 4 lists numerical K_{AC}^ϕ parameters, along with the corresponding deviations between observed and predicted anthracene solubilities which are on the order of $\pm 1.8\%$ or less, except for the cyclohexane + ethyl acetate system. Two values are calculated for both cyclohexane + ethyl acetate and n-heptane + ethyl acetate mixtures in order to show that poor $\bar{G}_{BC}^{ex}$ estimates (or in the extreme case, the neglect of binary solvent nonideality) can lead to appreciable errors/uncertainties in K_{AC}^ϕ computations. Careful examination reveals that Eq. (3) does describe the solubility data, though the

Table 4 Volume fraction based association constants for presumed anthracene-ethyl acetate and anthracene-diethyl adipate molecular complexes.

Inert hydrocarbon cosolvent	K_{AC}^ϕ [a]	Dev. (%)[b]
Complex = Anthracene-Ethyl Acetate		
n-Hexane	6.8	0.9
n-Heptane	6.5	1.6
	2.0[c]	1.2
n-Octane	6.8	0.6
Cyclohexane	13.0	5.2
	3.0[c]	1.4
Methylcyclohexane	11.0	1.4
Isooctane	4.5	1.5
Complex = Anthracene-Diethyl Adipate		
n-Hexane	10.5	0.6
n-Heptane	10.5	0.9
n-Octane	10.5	0.9
Cyclohexane	13.0	1.6
Methylcyclohexane	12.5	1.1
Isooctane	9.0	1.8

[a] Numerical values are subject to re-evaluation whenever experimental $\bar{G}_{BC}^{ex}$ data becomes available.
[b] Deviation (%) = $(100/N) \sum |\ln(X_A^{calc}/X_A^{exp})|$.
[c] Calculated using measured excess Gibbs free energies for the binary solvent.

computed association constants do vary with the inert hydrocarbon cosolvent. For example, values for the anthracene-ethyl acetate constant range from a lower limit of $K_{AC}^{\phi} = 4.5$ for isooctane to an upper value of $K_{AC}^{\phi} = 13.0$ for cyclohexane whenever estimated $\bar{G}_{BC}^{ex}$ values are used in the Extended NIBS equation. The solubility parameters of cyclohexane and ethyl acetate differ only slightly, $\delta_{cyclo} = 8.19$ cal$^{1/2}$ cm$^{-3/2}$ versus $\delta_{ethyl} = 8.91$ cal$^{1/2}$ cm$^{-3/2}$, and thus the $\bar{G}_{BC}^{fh}$ term makes only a minor contribution to the overall K_{AC}^{ϕ} computation. For all practical purposes, the cyclohexane + ethyl acetate mixture was assumed to be ideal (with $\bar{G}_{BC}^{ex} < 14$ cal mol^{-1}). Unfortunately, experimental vapor pressure data[32] shows cyclohexane + ethyl acetate mixtures to exhibit greater nonideality than what is predicted by Eq. (8). A much smaller range, $K_{AC}^{\phi} = 2.0$ to $K_{AC}^{\phi} = 3.0$, is noted if one considers only the cyclohexane + ethyl acetate and n-heptane + ethyl acetate systems for which actual $\bar{G}_{BC}^{ex}$ data exists. Poor $\bar{G}_{BC}^{ex}$ estimates lead to an error of over 300% in the K_{AC}^{ϕ} determinations, and further document earlier contentions[6,45] that neglect of nonspecific interactions can lead to appreciable errors in calculated equilibrium constants, particularly in the case of the weaker molecular complexes.

No significance is placed on the various K_{AC}^{ϕ} values or ranges at the present time as numerical values will be subject to re-evaluation whenever experimental $\bar{G}_{BC}^{ex}$ data becomes available. It is impossible to ascertain whether the two ester groups behave independently in their presumed complexation with anthracene as would be the case if the association constant for anthracene-diethyl adipate were exactly twice the K_{AC}^{ϕ} value for anthracene-ethyl acetate. Anthracene could complex with either ester group thereby doubling the degeneracy of each distinguishable microscopic complex.[28] Measured solubilities in both alkane + ethyl acetate and alkane + diethyl adipate mixtures make a valuable addition to our existing data base. These systems, along with previously studied anthracene in binary alkane + 1-chlorobutane[27] and alkane + 1,4-dichlorobutane mixtures,[28] represent the only solubility data sets having complexing solvents with common mono- and di-functional groups.

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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
$(\bar{G}_A^{ex})_i^*$	partial molar Gibbs free energy of the solute (Raoult's law) in pure solvent i, extrapolated back to infinite dilution
$(\bar{G}_A^{fh})_i^*$	partial molar Gibbs free energy of the solute (Flory-Huggins model) in pure solvent i, extrapolated back to infinite dilution
$\bar{G}_{BC}^{ex}$	excess molar Gibbs free energy of the binary solvent mixture based on Raoult's law
$\bar{G}_{BC}^{fh}$	excess molar Gibbs free energy of the binary solvent mixture based on the Flory–Huggins model

K_{AC}^{ϕ} volume fraction-based equilibrium constant for the formation of the AC molecular complex

$\bar{V}_i$ 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

ϕ_B^0, ϕ_C^0 ideal volume fraction composition of the solvent mixture, calculated as if the solute were not present

ϕ_A^{sat} ideal volume fraction solubility of solute

$\hat{\phi}_i$ true equilibrium volume fraction of component i in the associated solution

δ_i solubility parameter of component i

Γ_i weighting factor of component i