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Thermochemical Investigations of Associated Solutions

Part 11.—Calculation of Pyrene–Dichlorobutane Association Parameters from measured Solubility Data

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Experimental solubilities are reported for pyrene dissolved in binary solvent mixtures containing 1,4-dichlorobutane with n-hexane, n-heptane, n-octane, cyclohexane, methylcyclohexane and iso-octane at 26 °C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to evaluate the equilibrium constant for a presumed pyrene–dichlorobutane molecular complex from the extended nearly ideal binary solvent model. A single equilibrium constant was needed to describe the experimental data to within an average deviation of *ca.* 3%. The numerical value of the calculated association constant varied slightly with inert hydrocarbon cosolvent, the numerical values ranging from a lower limit of $K^{\phi}_{AC} = 11.0$ for iso-octane to $K^{\phi}_{AC} = 18.0$ for the cyclohexane cosolvent.

Molecular complexation occurs in many systems having chemical and engineering significance. Calculation of meaningful association constants is an important first step in understanding molecular interactions and solution nonideality. Previous papers in this series[1–9] were primarily devoted to the development of simple mixing models for describing the thermodynamic excess properties of associated solutions containing AB, AC and/or AC_2 molecular complexes. Expressions were derived for the calculation of solute–solvent association constants from experimental solute solubility based on the infinite dilution form of the extended nearly ideal binary solvent (NIBS) model[1–3]

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

$$\begin{aligned} \ln \phi^{sat}_{A} = {} & \phi^0_B \ln(\phi^{sat}_A)_B + \phi^0_C \ln(\phi^{sat}_A)_C \\ & + \ln[1 + K^{\phi}_{AC}\bar{V}_A\phi^0_C/(\bar{V}_A + \bar{V}_C)] \\ & - \phi^0_C \ln[1 + K^{\phi}_{AC}\bar{V}_A/(\bar{V}_A + \bar{V}_C)] \\ & + \frac{\bar{V}_A \Delta\bar{G}^{fh}_{BC}}{RT(X^0_B\bar{V}_B + X^0_C\bar{V}_C)} \end{aligned} \tag{1}$$

and the competitive associated NIBS model[5,10]

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

$$\mathrm{A_1 + B_1 \rightleftharpoons AB}; \quad K^{\phi}_{AB} = \hat{\phi}_{AB}/(\hat{\phi}_{A_1}\hat{\phi}_{B_1})$$

$$\begin{aligned} \ln \phi^{sat}_{A} = {} & \phi^0_B \ln(\phi^{sat}_A)_B + \phi^0_C \ln(\phi^{sat}_A)_C \\ & - \phi^0_B \ln[1 + K^{\phi}_{AB}\bar{V}_A/(\bar{V}_A + \bar{V}_B)] \\ & + \ln[1 + K^{\phi}_{AB}\bar{V}_A\phi^0_B/(\bar{V}_A + \bar{V}_B) + K^{\phi}_{AC}\bar{V}_A\phi^0_C/(\bar{V}_A + \bar{V}_C)] \\ & - \phi^0_C \ln[1 + K^{\phi}_{AC}\bar{V}_A/(\bar{V}_A + \bar{V}_C)] \\ & + \frac{\bar{V}_A \Delta\bar{G}^{fh}_{BC}}{RT(X^0_B\bar{V}_B + X^0_C\bar{V}_C)}. \end{aligned} \tag{2}$$

In the absence of solute–solvent complexation, eqn (1) (with $K^{\phi}_{AC} = 0$) and eqn (2) (with $K^{\phi}_{AB} = K^{\phi}_{AC} = 0$) reduce to the basic NIBS model which has been shown to provide very reasonable predictions for enthalpies of solution,[11] gas–liquid chromatographic partition coefficients[12,13] and solid–solute solubilities[14–20] in binary solvent mixtures containing only non-specific physical interactions. The symbols used in eqn (1) and (2) are defined in the Appendix.

McCargar and Acree[3,4,6] compared values of the carbazole–dibutyl ether association constant calculated from experimental carbazole solubilities in 10 different binary dibutyl ether–alkane solvent mixtures. A simple stoichiometric complexation model based entirely on specific solute–solvent interactions required at least two equilibrium constants to describe mathematically the observed solubility data. Calculated constants in iso-octane cosolvent were significantly different from values for cyclo-octane. In comparison, the extended NIBS model described the experimental solubilities to within an average deviation of *ca.* ±2% using a single carbazole–dibutyl ether association constant. Variation of the calculated constant with inert hydrocarbon cosolvent was slight, the numerical values ranging from $K^{\phi}_{AC} = 22$ for n-heptane to $K^{\phi}_{AC} = 30$ for both iso-octane and t-butylcyclohexane cosolvents. In two follow-up studies[5,10] the competitive associated NIBS model was derived to explain the observed solubility behaviour of carbazole in binary chloroalkane–dibutyl ether solvent mixtures. Assuming the presence of a very weak chloroalkane–carbazole complex, the authors illustrated the surprisingly large effect that a competing, weak secondary AB complex can have on the calculated K^{ϕ}_{AC} value. Neglect of presumed weak carbazole–chlorohexane, carbazole–chloro-octane, carbazole–chlorotetradecane and carbazole–chlorocyclohexane complexes with $K^{\phi}_{AB} \approx 2$–3 resulted in roughly a two-fold decrease in the calculated carbazole–dibutyl ether equilibrium constant.

The success of eqn (1) and (2) in describing carbazole solubilities suggests that the extended NIBS and competitive associated NIBS models will provide a suitable basis for investigating weak molecular complexes in non-electrolyte solutions. Further studies are needed, however, in order to establish more firmly the applications and limitations of both models. For this reason, we report experimental pyrene solubilities in binary solvent mixtures containing 1,4-dichlorobutane with n-hexane, n-heptane, n-octane, cyclohexane, methylcyclohexane and iso-octane. Results of these measurements are used to calculate equilibrium constants for a presumed pyrene–dichlorobutane complex and to ascertain the effect of inert hydrocarbon cosolvents on calculated association parameters.

Experimental

Pyrene (Aldrich 99%) was recrystallized several times from ethanol, giving a melting point of 151.0 ± 0.5 °C (literature

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Table 1. Comparison between predicted and experimental pyrene solubilities in binary alkane–1,4-dichlorobutane solvent mixtures at 26.0 °C

X_C^0	X_A^{sat}	deviation of calculated values[a] (%)		
		eqn (3)	eqn (4)	eqn (5)
	n-hexane (B)–1,4-dichlorobutane (C)			
0.0000	0.0085	—	—	—
0.0928	0.0162	−26.2	−26.4	−26.4
0.1745	0.0243	−34.3	−34.4	−34.4
0.2383	0.0317	−37.5	−37.3	−37.4
0.4437	0.0602	−38.3	−36.8	−36.8
0.5420	0.0733	−34.1	−32.0	−32.0
0.6579	0.0879	−27.9	−25.2	−25.1
0.8223	0.1044	−17.1	−14.7	−14.7
0.9093	0.1084	−9.2	−7.6	−7.5
1.0000	0.1097	—	—	—
	n-heptane (B)–1,4-dichlorobutane (C)			
0.0000	0.0110	—	—	—
0.1019	0.0199	−23.0	−26.0	−25.9
0.1946	0.0306	−33.0	−37.2	−37.2
0.2541	0.0361	−32.4	−37.1	−37.0
0.4668	0.0660	−34.1	−38.9	−38.8
0.5695	0.0811	−31.7	−34.7	−34.5
0.6673	0.0929	−26.9	−30.2	−30.1
0.8323	0.1079	−16.7	−18.1	−18.0
1.0000	0.1097	—	—	—
	n-octane (B)–1,4-dichlorobutane (C)			
0.0000	0.0141	—	—	—
0.1130	0.0233	−15.4	−20.6	−20.6
0.2119	0.0338	−22.8	−30.3	−30.2
0.2735	0.0415	−25.7	−34.1	−33.9
0.4930	0.0683	−23.2	−32.5	−32.4
0.5937	0.0803	−19.7	−28.2	−28.1
0.6867	0.0922	−17.5	−24.4	−24.3
0.8519	0.1074	−10.7	−14.0	−13.9
1.0000	0.1097	—	—	—
	cyclohexane (B)–1,4-dichlorobutane (C)			
0.0000	0.0110	—	—	—
0.0792	0.0200	−31.3	−29.5	−29.5
0.1475	0.0283	−41.6	−38.3	−38.3
0.1952	0.0351	−46.5	−43.2	−43.2
0.3914	0.0613	−49.2	−44.3	−44.3
0.4909	0.0734	−46.0	−40.5	−40.5
0.5860	0.0854	−42.2	−36.5	−36.5
0.7949	0.1015	−24.7	−20.0	−20.0
1.0000	0.1097	—	—	—
	iso-octane (B)–1,4-dichlorobutane (C)			
0.0000	0.0071	—	—	—
0.1163	0.0136	−14.7	−22.1	−22.0
0.2129	0.0214	−19.8	−30.5	−30.4
0.2737	0.0277	−21.9	−33.8	−33.6
0.4940	0.0545	−16.6	−29.7	−29.5
0.6464	0.0763	−11.1	−21.3	−21.1
0.6898	0.0832	−10.5	−19.3	−19.1
0.8535	0.1032	−5.8	−9.2	−9.1
1.0000	0.1097	—	—	—
	methylcyclohexane (B)–1,4-dichlorobutane (C)			
0.0000	0.0130	—	—	—
0.0955	0.0233	−26.7	−27.1	−26.9
0.1782	0.0328	−34.8	−34.9	−34.9
0.2270	0.0389	−37.4	−37.4	−37.4
0.4328	0.0661	−38.7	−38.1	−38.1
0.5356	0.0777	−34.6	−33.5	−33.5
0.6323	0.0882	−29.8	−28.5	−28.5
0.7915	0.1025	−19.9	−18.4	−18.4
1.0000	0.1097	—	—	—

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

values are 151.3[21] and 149–150 °C[22]). Cyclohexane (Aldrich HPLC), n-hexane (Aldrich 99%), n-heptane (Aldrich HPLC), iso-octane (Aldrich HPLC), n-octane (Aldrich 99+%), methylcyclohexane (Aldrich 99+%) and 1,4-dichlorobutane (Fluka puriss 99+%) were stored over molecular sieves to remove trace water. Binary solvent mixtures were prepared by weight so that compositions could be calculated to 0.0001 mole fraction.

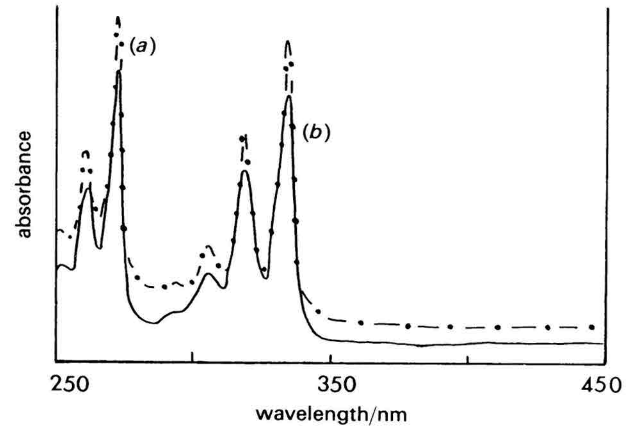

Fig. 1. UV–VIS absorbance spectra of a dilute methanol solution of the equilibrium solid phase (*a*), (— · —) and of recrystallized pyrene (*b*), (——) over the 250–440 nm spectroscopic region. For graphical convenience, spectrum (*a*) has been offset slightly. At higher concentrations, the 372 nm absorption band appears in both spectra.

Excess solute and the solvent were placed in amber glass bottles as a precaution to prevent any possible photochemical reactions between pyrene and dichlorobutane. Carbon tetrachloride, and to a much smaller extent chloroform and dichloromethane, are reported to react with several polycyclic aromatic hydrocarbons *via* a hypothesized concerted transannular addition with free-radical formation.[23–28] The resulting solutions were placed in a constant-temperature water bath and allowed to equilibrate at 26.0 ± 0.1 °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and by approaching equilibrium from supersaturation after first pre-equilibrating the solution at a slightly higher temperature. Aliquots of saturated pyrene 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 372 nm on a Bausch and Lomb Spectronic 2000 UV–VIS spectrophotometer. Experimental solubilities of pyrene in the six binary solvent mixtures studied are listed in table 1. Numerical values represent the

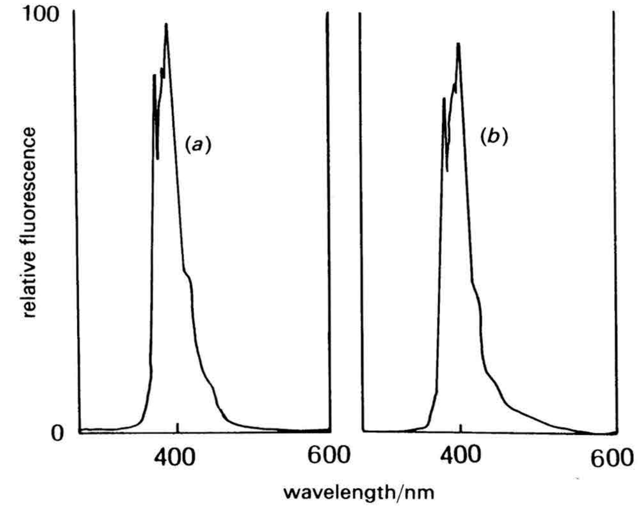

Fig. 2. Fluorescence emission spectra of a dilute methanol solution of the equilibrium solid phase (*a*) and of recrystallized pyrene (*b*). Solutions were excited at 338 nm in a 1 cm² quartz cell.

average of between four and eight independent determinations, with the measured values being reproducible to ±1.5%.

During the course of these studies undissolved material from select containers was removed and analysed to ensure that the equilibrium solid phase was indeed pure crystalline pyrene. Melting point temperatures of $T_{\text{mp}} = 151.0 \pm 0.5\,°\text{C}$ and molar absorptivities of $\varepsilon = 217.7$ dm^3 mol^{-1} cm^{-1} (±1%) in methanol were identical to values for the initial recrystallized pyrene. The solid and saturated liquid phases were further examined by dissolving known quantities in methanol. Absorption and fluorescence emission spectra of the resulting methanol solutions were recorded on an HP 8450A photodiode array spectrophotometer and Shimadzu RF5000 spectrofluorimeter, respectively. For fluorescence measurements the solutions were excited at 338 nm in quartz 1 cm^2 cells with the detector set at the higher sensitivity. Excitation and emission slit widths were 15 and 1.5 nm. As shown in fig. 1 and 2, both sets of spectra indicate that the equilibrium solid phase is pyrene, and no sign of photochemical degradation was observed in either the solid or saturated liquid phases (not shown).

Results and Discussion

The NIBS equations which have been most successful for describing the excess chemical potential of solutes in multicomponent solvent mixtures are derived from the following two simple mixing models:[15]

$$\Delta G^{\text{mix}}_{1,2,\ldots,N} = RT \sum_{i=1}^{N} n_i \ln X_i + \left(\sum_{i=1}^{N} n_i \Gamma_i\right)\left(\sum_{i=1}^{N} \sum_{j>i}^{N} f_i f_j A_{ij}\right)$$

$$\Delta G^{\text{mix}}_{1,2,\ldots,N} = RT \sum_{i=1}^{N} n_i \ln \phi_i + \left(\sum_{i=1}^{N} n_i \Gamma_i\right)\left(\sum_{i=1}^{N} \sum_{j>i}^{N} f_i f_j A_{ij}\right)$$

$$f_i = n_i \Gamma_i \Big/ \left(\sum_{j=1}^{N} n_j \Gamma_j\right)$$

where X_i and f_i refer to the mole fraction and weighted mole fraction of component i, respectively, n_i is the number of moles of component i and A_{ij} is a binary interaction parameter which is independent of composition. The weighting factors (Γ_i) represent a rough measure of the skew of the binary excess property from a symmetric curve with an extremum at the equimolar composition. For simplicity, weighting factors are assumed to be independent of both temperature and pressure. Therefore, molar volumes and other experimentally determined weighting factors must be regarded as approximations of these 'true' weighting factors. Replacement of weighting factors with molar volumes requires that the values be referred to a specified condition, such as 25 °C and 1 atm, or to an extrapolated state such as 'close-packed' volume.

Based on the two mixing models and different weighting-factor approximations, Acree and Bertrand[15] derived the following three NIBS expressions for predicting solute solubilities in binary solvent mixtures containing only nonspecific interactions:

$$RT \ln(a_{\text{A}}^{\text{solid}}/X_{\text{A}}^{\text{sat}}) = (1 - X_{\text{A}}^{\text{sat}})^2[X_{\text{B}}^0(\Delta\bar{G}_{\text{A}}^{\text{ex}})_{\text{B}}^* + X_{\text{C}}^0(\Delta\bar{G}_{\text{A}}^{\text{ex}})_{\text{C}}^* - \Delta\bar{G}_{\text{BC}}^{\text{ex}}] \tag{3}$$

$$RT \ln(a_{\text{A}}^{\text{solid}}/X_{\text{A}}^{\text{sat}}) = (1 - \phi_{\text{A}}^{\text{sat}})^2[\phi_{\text{B}}^0(\Delta\bar{G}_{\text{A}}^{\text{ex}})_{\text{B}}^* + \phi_{\text{C}}^0(\Delta\bar{G}_{\text{A}}^{\text{ex}})_{\text{C}}^* - \bar{V}_{\text{A}}(X_{\text{B}}^0 \bar{V}_{\text{B}} + X_{\text{C}}^0 \bar{V}_{\text{C}})^{-1}\Delta\bar{G}_{\text{BC}}^{\text{ex}}] \tag{4}$$

and

$$RT\left[\ln(a_{\text{A}}^{\text{solid}}/\phi_{\text{A}}^{\text{sat}}) - (1 - \phi_{\text{A}}^{\text{sat}})\left(1 - \frac{\bar{V}_{\text{A}}}{X_{\text{B}}^0 \bar{V}_{\text{B}} + X_{\text{C}}^0 \bar{V}_{\text{C}}}\right)\right] = (1 - \phi_{\text{A}}^{\text{sat}})^2[\phi_{\text{B}}^0(\Delta\bar{G}_{\text{A}}^{\text{fh}})_{\text{B}}^* + \phi_{\text{C}}^0(\Delta\bar{G}_{\text{A}}^{\text{fh}})_{\text{C}}^* - \bar{V}_{\text{A}}(X_{\text{B}}^0 \bar{V}_{\text{B}} + X_{\text{C}}^0 \bar{V}_{\text{C}})^{-1}\Delta\bar{G}_{\text{BC}}^{\text{fh}}]. \tag{5}$$

Eqn (3) and (4) are based on Raoult's law for the configurational contribution to the free energy, and eqn (5) is based on the Flory–Huggins model. In the above expressions $a_{\text{A}}^{\text{solid}}$ is the activity of the solid solute relative to the pure subcooled liquid, X_i is mole fraction and ϕ_i is the ideal volume fraction. Binary solvent properties $\Delta\bar{G}_{\text{BC}}^{\text{ex}}$ and $\Delta\bar{G}_{\text{BC}}^{\text{fh}}$ refer to 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 $(\Delta\bar{G}_{\text{A}}^{\text{ex}})_i^*$ and $(\Delta\bar{G}_{\text{A}}^{\text{fh}})_i^*$. The 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 $\bar{V}_{\text{A}} = \bar{V}_{\text{B}} = \bar{V}_{\text{C}}$, and it is only in systems having considerable molecular size disparity that one can distinguish between the predictive expressions.

To date, testing of the limitations and applications of the NIBS model has been primarily restricted to binary solvent systems for which $\Delta\bar{G}_{\text{BC}}^{\text{ex}}$ values could be found in the chemical literature, though in a few instances we have had to estimate the input $\Delta\bar{G}_{\text{BC}}^{\text{ex}}$ values. This undoubtedly will become more common as we apply the extended NIBS and competitive associated NIBS models to the more complex systems. Excess Gibbs free energies of such systems 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[14] and Prausnitz *et al.*[29] The Scatchard–Hildebrand approach, perhaps the simplest of the predictive methods, estimates the excess Gibbs free energies from the solubility parameters of the pure components, δ_i.

$$\Delta\bar{G}_{\text{BC}}^{\text{ex}} = \phi_{\text{B}}^0 \phi_{\text{C}}^0(X_{\text{B}}^0 \bar{V}_{\text{B}} + X_{\text{C}}^0 \bar{V}_{\text{C}})(\delta_{\text{B}} - \delta_{\text{C}})^2 \tag{6}$$

$$\Delta\bar{G}_{\text{BC}}^{\text{fh}} = \Delta\bar{G}_{\text{BC}}^{\text{ex}} + RT[\ln(X_{\text{B}}^0 \bar{V}_{\text{B}} + X_{\text{C}}^0 \bar{V}_{\text{C}}) - X_{\text{B}}^0 \ln \bar{V}_{\text{B}} - X_{\text{C}}^0 \ln \bar{V}_{\text{C}}]. \tag{7}$$

Comparisons between experimental and predicted pyrene solubilities are tabulated in the last three columns of table 1 for the six binary solvent systems studied. Properties used in the calculations include $\bar{V}_{\text{A}} = 166.5$ cm^3 mol^{-1}, based on the partial molar volume of pyrene in carbon tetrachloride,[30] and the activity of the solute, $a_{\text{A}}^{\text{solid}} = 0.1312$, calculated from the enthalpy of fusion data, $\Delta\bar{H}_{\text{A}}^{\text{fus}} = 4.09$ kcal mol^{-1},†[21] at the normal melting point temperature of $T_{\text{mp}} = 424.4$ K. $\ln a_{\text{A}}^{\text{solid}} = -\Delta\bar{H}_{\text{A}}^{\text{fus}}(T_{\text{mp}} - T)/RTT_{\text{mp}}$. Solvent properties used in the NIBS predictions are listed in table 2.

Careful examination of table 1 reveals that all three NIBS expressions fail to predict the observed pyrene solubilities. Deviations between experimental and predicted values are on the order of 30–50% 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 eqn (4) and (5) have predicted benzil,[16,31] *p*-benzoquinone,[32] pyrene,[18,33,34] biphenyl,[35] anthracene,[17,19,20] thianthrene,[36] benzoic acid[37] and iodine[13,31] solubilities in a wide range of binary solvent mixtures to within *ca.* ±5%. While one can always argue that the failure of the basic NIBS model to predict pyrene

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† 1 cal = 4.184 J.

Table 2. Solvent properties used in NIBS predictions

component (i)	$\bar{V}_i$/cm^3 mol^{-1}	δ_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
cyclohexane	108.76	8.19
methylcyclohexane	128.32	7.83
iso-octane	166.09	6.86
1,4-dichlorobutane	112.12	9.67[b]

[a] Except for 1,4-dichlorobutane, values are taken from tabulations in ref. (3) and (4). [b] Solubility parameter is calculated from the enthalpy of vaporization in ref. (38).

solubilities in the six binary alkane–dichlorobutane solvent mixtures results from poor $\Delta\bar{G}^{ex}_{BC}$ estimates, we believe that complexation between the dissolved pyrene and dichlorobutane cosolvent occurs, in which case the extended NIBS model [eqn (1)] should be used. The Scatchard–Hildebrand equation would have to underestimate the $\Delta\bar{G}^{ex}_{BC}$ values by over 170 cal mol^{-1} in order to account for the larger 40+% negative deviations in table 1. For a few select solvent systems and compositions we did look at using the UNIFAC and Modified UNIFAC group contribution methods to estimate $\Delta\bar{G}^{ex}_{BC}$ values. While the solubility predictions did improve by 2–3% in some instances, we did not feel that this small improvement warranted the extra computational time, nor would it change the fact that the simple NIBS expressions failed to predict the observed pyrene solubilities.

If one assumes the existence of a weak pyrene–dichlorobutane complex in solution, then the equilibrium constant can be determined using the extended NIBS model[1] and measured pyrene solubilities as a function of binary solvent composition.

$$RT\left[\ln(a^{solid}_{A}/\hat{\phi}^{sat}_{A_1}) - 1 + \bar{V}_A\left(\frac{\hat{\phi}^{sat}_{A_1}}{\bar{V}_A} + \frac{\phi_B}{\bar{V}_B} + \frac{\phi_C}{\bar{V}_C}\right)\right]$$
$$= (1 - \phi^{sat}_{A})^2[\phi^0_B(\Delta\bar{G}^{fh}_{A})^*_B + \phi^0_C(\Delta\bar{G}^{fh}_{A})^*_C - \bar{V}_A(X^0_B\bar{V}_B + X^0_C\bar{V}_C)^{-1}\Delta\bar{G}^{fh}_{BC}] \qquad (8)$$

where

$$\phi^{sat}_{A} = \hat{\phi}^{sat}_{A_1}[1 + \bar{V}_A K^{\phi}_{AC}\hat{\phi}_{C_1}/(\bar{V}_A + \bar{V}_C)]$$
$$\phi_C = \hat{\phi}_{C_1}[1 + \bar{V}_C K^{\phi}_{AC}\hat{\phi}^{sat}_{A_1}/(\bar{V}_A + \bar{V}_C)].$$

Eqn (8), rather than eqn (1), is the more rigorous of the extended NIBS expressions. Many of the approximations that were used in the original simplification of eqn (8) to obtain eqn (1) are not valid at the higher dichlorobutane concentrations where pyrene is more soluble. Furthermore, depending upon the numerical value of K^{ϕ}_{AC} an appreciable amount of dichlorobutane may be complexed, in which case the uncomplexed and stoichiometric dichlorobutane volume fractions are no longer equal, *i.e.* $\hat{\phi}_{C_1} \neq \phi_C$.

Despite the complex appearance of eqn (8), its application to solubilities in mixed solvents is relatively straightforward and similar in concept to the numerical example presented in an earlier paper[3] for calculating K^{ϕ}_{AC} values using eqn (1). First, the quantities $(\Delta\bar{G}^{fh}_{A})^*_B$ and $(\Delta\bar{G}^{fh}_{A})^*_C$ are calculated from the measured volume fraction solubility of the solid in the pure solvents using an *assumed* value for the equilibrium constant. This latter calculation requires values of $\hat{\phi}^{sat}_{A_1}$ and $\hat{\phi}_{C_1}$ which simultaneously satisfy eqn (8)–(10). In practice, a re-iterative procedure can be set up whereby the initial guess of $\hat{\phi}_{C_1} = \phi_C$ is continually improved by the preceding $\hat{\phi}^{sat}_{A_1}$ calculated value. The convergence rarely takes more than six or seven iterations. Calculated $(\Delta\bar{G}^{fh}_{A})^*_B$ and $(\Delta\bar{G}^{fh}_{A})^*_C$ values, along with the excess Gibbs free energy of the binary solvent mixture (obtained from the chemical literature or estimated as in the present study), are then inserted into eqn (8) to compute the predicted volume fraction solubility, ϕ^{sat}_{A}, again *via* the afore-mentioned re-iterative approach. The equilibrium constant is varied until one obtains the 'optimum' K^{ϕ}_{AC} value which best describes the entire set of solubility data for any given binary solvent system.

Table 3 lists numerical values of the pyrene–dichlorobutane association constant calculated *via* the extended NIBS model for each of the six binary solvents. Also tabulated are the corresponding deviations between observed and calculated pyrene solubilities, which are of the order of ±2% except for the iso-octane–dichlorobutane system. Inspection of table 3 reveals that the optimized constants do vary slightly with the inert hydrocarbon cosolvent, the numerical values ranging from $K^{\phi}_{AC} = 11$ in iso-octane to $K^{\phi}_{AC} = 18$ in cyclohexane. Part of the observed variation in K^{ϕ}_{AC} undoubtedly arises from the manner in which experimental uncertainties are propagated in the extended NIBS model and from having to use estimated $\Delta\bar{G}^{fh}_{BC}$ values rather than actual experimental data in the calculations. It must be remembered that four measured quantities are needed to determine the equilibrium constant. Pyrene solubilities in each pure solvent and binary solvent mixture were reproducible to within ±1.5%, and it is hoped that the $\Delta\bar{G}^{fh}_{BC}$ estimates are accurate to within ±20 cal mol^{-1}. This may not be the case for binary iso-octane–dichlorobutane mixtures since the large difference in solubility parameters, $\delta_{iso\text{-}octane} = 6.86$ cal$^{1/2}$ cm$^{-3/2}$ and $\delta_{dichlorobutane} = 9.67$ cal$^{1/2}$ cm$^{-3/2}$, leads to what we consider to be extremely large $\Delta\bar{G}^{fh}_{BC}$ values of 275 cal mol^{-1} near the equimolar composition. Furthermore, eqn (8) is derived from the basic NIBS model[1,14,15] and any errors in predicting the nonspecific interaction contributions, which are perhaps as large as 4–5%, would carry over into the equilibrium constant computation as would the possible formation of a weak 2 : 1 pyrene–dichlorobutane A_2C molecular complex at the higher dichlorobutane concentrations. In performing the K^{ϕ}_{AC} calculations, we noted that the volume fraction of the uncomplexed pyrene varied with binary solvent composition, reaching a maximum value near the equivolume concentration of $\phi^0_B \approx \phi^0_C$ where the contribution from the unmixing of the binary solvent pair (*i.e.* the $\Delta\bar{G}^{fh}_{BC}$ term) is maximized. A calculated pyrene–dichlorobutane association constant of $K^{\phi}_{AC} = 12.5$ in the n-octane cosolvent may be identical, at least to within the limitations of the extended NIBS model, to a value of $K^{\phi}_{AC} = 18$ in the cyclohexane cosolvent. Based on these observations we believe that the extended NIBS model does provide a more realistic description of the thermochemical properties of pyrene dissolved in binary alkane–dichlorobutane mixtures than did the simpler NIBS model discussed previously. Additional experimental studies are currently underway to measure both anthracene and pyrene solubilities in a wider range of binary dichloroalkane–alkane and chloroalkane–alkane mixtures to test further the limitations and applications of the extended NIBS model. The present

Table 3. Volume fraction based association constant for presumed pyrene–dichlorobutane molecular complex

inert hydrocarbon cosolvent	K^{ϕ}_{AC}	dev.[a] (%)
n-hexane	13.5	1.6
n-heptane	15.0	1.2
n-octane	12.5	1.8
cyclohexane	18.0	1.9
methylcyclohexane	15.0	1.1
iso-octane	11.0	3.9

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

study provided the first real test of the extended NIBS model away from the conditions of infinite dilution.

Readers are reminded that it is fundamentally impossible to prove that a particular solution is correct simply by comparing predicted and experimental values. One can demonstrate, however, that a model is consistent with a wide range of experimental observations, which implies that the model and equations derived therefrom may be correct. Similarly, it can be shown that a given model is inconsistent with experimental data so that the model must be either incorrect or incomplete. In the present study, we started with the prior knowledge that the extended NIBS model had provided a very reasonable description of the thermochemical properties of carbazole dissolved in binary alkane–dibutyl ether mixtures[3–5] and of iodine dissolved in several binary alkane–benzene mixtures.[2] Comparisons presented in this paper for pyrene dissolved in six alkane–dichlorobutane solvent systems have shown the applicability of the extended NIBS model to additional non-electrolyte solutions. It is hoped that the knowledge gained will further our understanding of molecular interactions in solution and will encourage the development of better thermodynamic mixing models.

Appendix: Glossary of Symbols

$a_{\mathrm{A}}^{\mathrm{solid}}$	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$(\Delta\bar{G}_{\mathrm{A}}^{\mathrm{ex}})_i^*$	partial molar Gibbs free energy of the solute (Raoult's law) in pure solvent *i*, extrapolated back to infinite dilution
$(\Delta\bar{G}_{\mathrm{A}}^{\mathrm{fh}})_i^*$	partial molar Gibbs free energy of the solute (Flory–Huggins model) in pure solvent *i*, extrapolated back to infinite dilution
$\Delta\bar{G}_{\mathrm{BC}}^{\mathrm{ex}}$	excess molar Gibbs free energy of the binary solvent mixture based on Raoult's law
$\Delta\bar{G}_{\mathrm{BC}}^{\mathrm{fh}}$	excess molar Gibbs free energy of the binary solvent mixture based on the Flory–Huggins model
$\Delta\bar{H}_{\mathrm{A}}^{\mathrm{fus}}$	molar enthalpy of fusion of the solute
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 solvent mixture, calculated as if the solute were not present
$X_{\mathrm{A}}^{\mathrm{sat}}$	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
$\phi_{\mathrm{A}}^{\mathrm{sat}}$	ideal volume fraction solubility of solute
$\hat{\phi}_i$	true mole fraction of component *i* in the associated solution
δ_i	solubility parameter of component *i*
Γ_i	weighting factor of component *i*

References

1 W. E. Acree Jr, D. R. McHan and J. H. Rytting, *J. Pharm. Sci.*, 1983, **72**, 929.
2 W. E. Acree Jr, *Int. J. Pharm.*, 1983, **15**, 159.
3 J. W. McCargar and W. E. Acree Jr, *Phys. Chem. Liq.*, 1987, **17**, 123.
4 J. W. McCargar and W. E. Acree Jr, *J. Pharm. Sci.*, 1987, **76**, 572.
5 W. E. Acree Jr and J. W. McCargar, *J. Pharm. Sci.*, 1987, **76**, 575.
6 J. W. McCargar and W. E. Acree Jr, *J. Solution Chem.*, 1988, **17**, 1081.
7 W. E. Acree Jr and J. W. McCargar, *J. Mol. Liq.*, 1988, **37**, 251.
8 W. E. Acree Jr and S. A. Tucker, *Phys. Chem. Liq.*, 1989, **19**, 23.
9 W. E. Acree Jr, S. A. Tucker and L. E. Cretella, *Thermochim. Acta*, 1989, **145**, 245.
10 J. W. McCargar and W. E. Acree Jr, *J. Solution Chem.*, 1989, **18**, 151.
11 T. E. Burchfield and G. L. Bertrand, *J. Solution Chem.*, 1975, **4**, 205.
12 W. E. Acree Jr and G. L. Bertrand, *J. Phys. Chem.*, 1979, **83**, 2355.
13 W. E. Acree Jr and J. H. Rytting, *Anal. Chem.*, 1980, **52**, 1765.
14 W. E. Acree Jr, *Thermodynamic Properties of Nonelectrolyte Solutions* (Academic Press, Orlando, FL, 1984).
15 W. E. Acree Jr and G. L. Bertrand, *J. Phys. Chem.*, 1977, **81**, 1170.
16 W. E. Acree Jr and J. H. Rytting, *J. Pharm. Sci.*, 1982, **71**, 201.
17 W. E. Acree Jr and J. H. Rytting, *J. Pharm. Sci.*, 1983, **72**, 292.
18 C. L. Judy, N. M. Pontikos and W. E. Acree Jr, *Phys. Chem. Liq.*, 1987, **16**, 179.
19 S. A. Tucker, D. J. Murral, B. M. Oswalt, J. L. Halmi and W. E. Acree Jr, *Phys. Chem. Liq.*, 1988, **18**, 279.
20 M. V. Marthandan and W. E. Acree Jr, *J. Chem. Eng. Data*, 1987, **32**, 301.
21 F. Casellato, C. Vecchi, A. Girelli and B. Casu, *Thermochim. Acta*, 1973, **6**, 361.
22 J. Buckingham, *Dictionary of Organic Compounds* (Chapman and Hall, New York, 5th edn, 1982), p. 4840.
23 S. A. Tucker, L. E. Cretella, R. Waris, K. W. Street Jr, W. E. Acree Jr and J. C. Fetzer, *Appl. Spectrosc.*, 1990, **44**, 269.
24 N. Selvarajan, M. M. Panicker, S. Vaidyanathan and V. Ramakrishnan, *Indian J. Chem., Sect. A*, 1979, **18**, 23.
25 M. V. Encinas, M. A. Rubio and E. A. Lissi, *Photochem. Photobiol.*, 1983, **37**, 125.
26 M. V. Encinas, M. A. Rubio and E. A. Lissi, *J. Photochem.*, 1982, **18**, 137.
27 W. M. Wiczk and T. Latowski, *Z. Naturforsch., Teil A*, 1987, **42**, 1290.
28 E. J. Bowen and K. K. Rohatgi, *Discuss. Faraday Soc.*, 1953, **14**, 146.
29 J. M. Prausnitz, R. N. Lichtenthaler and E. Gomez de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria* (Prentice-Hall, Englewood Cliffs, NJ, 2nd edn 1986).
30 F. Shahidi, P. G. Farrell, J. T. Edward and P. Cannone, *J. Org. Chem.*, 1979, **44**, 950.
31 W. E. Acree Jr and G. L. Bertrand, *J. Solution Chem.*, 1983, **12**, 101.
32 W. E. Acree Jr and J. H. Rytting, *Int. J. Pharm.*, 1982, **10**, 231.
33 J. R. Wallach, S. A. Tucker, B. M. Oswalt, D. J. Murral and W. E. Acree Jr, *J. Chem. Eng. Data*, 1989, **34**, 70.
34 C. L. Judy, N. M. Pontikos and W. E. Acree Jr, *J. Chem. Eng. Data*, 1987, **32**, 60.
35 W. E. Acree Jr, *Int. J. Pharm.*, 1984, **18**, 47.
36 W. E. Acree Jr, S. A. Tucker and A. I. Zvaigzne, *Phys. Chem. Liq.*, 1990, **21**, 45.
37 W. E. Acree Jr and G. L. Bertrand, *J. Pharm. Sci.*, 1981, **70**, 1033.
38 V. Majer and V. Svoboda, *Enthalpies of Vaporization of Organic Compounds*, IUPAC Chemical Data Series No. 32 (Blackwell Scientific Publications, Oxford, 1985).

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