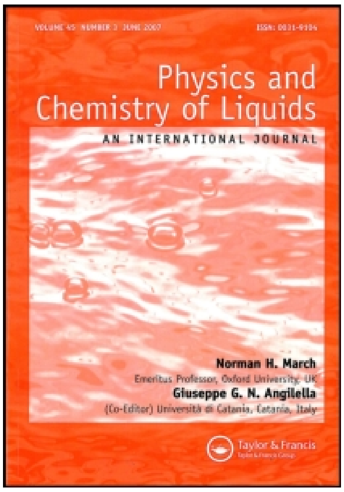

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Thermochemical Investigations of Associated Solutions: Comparison of PAH-chlorobutane Versus PAH-dichlorobutane Equilibrium Constants calculated from Solubility Data

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THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS: COMPARISON OF PAH-CHLOROBUTANE VERSUS PAH-DICHLOROBUTANE EQUILIBRIUM CONSTANTS CALCULATED FROM SOLUBILITY DATA

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Experimental solubilities are reported for anthracene dissolved in binary solvent mixtures containing 1,4-dichlorobutane with *n*-heptane, *n*-octane, cyclohexane and methylcyclohexane at 25°C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to evaluate the equilibrium for a presumed anthracene-dichlorobutane molecular complex using the Extended NIBS model. The calculated equilibrium constant is compared to published values for anthracene-chlorobutane and pyrene-dichlorobutane. Differences in the values for the various polycyclic aromatic hydrocarbons (PAHs) and mono/dichlorobutanes are rationalized at the molecular level in terms of individual microscopic equilibrium constants for distinguishable association species.

KEY WORDS: Equilibrium constants, excess free energy, anthracene solubilities.

INTRODUCTION

Investigations into molecular complexation provide a fertile testing ground for theoretical descriptions of condensed matter, phase transitions, "lock-key" molecular recognition and solvation. Molecular complexation is predicated upon a delicate balance between long-range and short-range intermolecular forces. At one extreme are weakly bonded van der Waals complexes, characterized by loose, nonspecific physical interactions and primarily stabilized by long-range dispersion forces. At the far opposite extreme are the hydrogen-bonded complexes that exhibit relatively strong, specific and highly directional binding of a primarily electrostatic nature. So-called "donor-acceptor" complexes possess intermediate strengths, and are stabilized by both charge transfer interactions, as well as electrostatic and/or dispersion effects. From a thermodynamic standpoint, molecular complexation is generally treated by invoking a dynamic equilibria between the presumed association species

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(A_iC_j) and the uncomplexed monomers $(A_1$ and $C_1)$

$$iA_1 + jC_1 \rightleftharpoons A_iC_j \qquad K^x_{A_iC_j} = \frac{\hat{X}_{A_iC_j}\hat{\gamma}_{A_iC_j}}{(\hat{X}_{A_1}\hat{\gamma}_{A_1})^i(\hat{X}_{C_1}\hat{\gamma}_{C_1})^j}$$

$$K^\phi_{A_iC_j} = \frac{\hat{\phi}_{A_iC_j}\hat{\gamma}_{A_iC_j}}{(\hat{\phi}_{A_1}\hat{\gamma}_{A_1})^i(\hat{\phi}_{C_1}\hat{\gamma}_{C_1})^j}$$

with the equilibrium constant being expressed in either mole fraction $(K^x_{A_iC_j})$ or volume fraction $(K^\phi_{A_iC_j})$ concentration units. Chemical effects are contained in the concentration ratio while the much weaker physical interactions are incorporated into the activity coefficients. Neglect of nonspecific physical interactions can lead to an appreciable error in the calculated equilibrium constant, particularly in the case of weak molecular complexes.[1,2]

Earlier papers in this series have been primarily devoted to the development of simple mixing models for describing thermodynamic excess properties of ternary associated solutions containing AB, AC, and/or AC_2 molecular complexes. Expressions have been derived for the calculation of volume-fraction based[2-5].

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

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

and mole-fraction based[6]

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

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

solute-solvent association constants from experimental solute solubility using the infinite dilution form the Extended Nearly Ideal Binary Solvent (NIBS) model. Activity coefficients are absent from the equilibrium constant expressions as the Extended NIBS model requires that the $\hat{\gamma}_{AC}/\hat{\gamma}_{A_1}\hat{\gamma}_{C_1}$ ratio be independent of mixture composition. This constant ratio does not necessarily equal unity, however, and it is incorporated into the calculated K^ϕ_{AC} and K^x_{AC} values. The superscript (^) denotes "true equilibrium" compositions of the various species in the associated solution, rather than the stoichiometric concentrations. Other symbols used in Eqs. (1) and (2) are defined in the Appendix.

To date, the Extended NIBS model has described experimental solubilities for carbazole dissolved in ten binary alkane + dibutyl ether mixtures ($K^\phi_{AC} = 25.3 \pm 2.7$),[2,5,6] for pyrene in six binary alkane + 1,4-dichlorobutane mixtures ($K^\phi_{AC} = 14.2 \pm 2.4$),[7] and for anthracene in six binary alkane + 1-chlorobutane mixtures ($K^\phi_{AC} = 3.9 \pm 1.3$)[8] to within an average absolute deviation of about ±2%

using a single equilibrium constant. The equilibrium constant did vary slightly from one inert hydrocarbon cosolvent to another. Success of Eq. (1) in describing these three sets of systems suggests that the Extended NIBS model will provide a suitable basis for investigating weak molecular complexes in organic nonelectrolyte solutions. Further studies are needed though, in order to more firmly establish the possible existence of polycyclic aromatic hydrocarbon (PAH)-chlorobutane complexes and to explain quantitatively differences in the calculated K_{AC}^{ϕ} values at the molecular level. Systems examined thus far contained neither a common PAH solute nor complexing chloroalkane cosolvent. To rectify this problem, we report experimental solubilities for anthracene dissolved in binary solvent mixtures containing 1,4-dichlorobutane with *n*-heptane, *n*-octane, cyclohexane and methylcyclohexane. Results of these measurements are used to calculate association parameters for a presumed anthracene-dichlorobutane molecular complex.

EXPERIMENTAL METHOD

Anthracene (Aldrich Gold Label, 99.9+%) was used as received. Cyclohexane (Aldrich HPLC), methylcyclohexane (Aldrich 99+%, anhydrous), *n*-heptane (Aldrich HPLC), *n*-octane (Aldrich 99%) and 1,4-dichlorobutane (Fluka puriss, 99+%) 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 equilibrate 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 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. Undissolved material from several containers was removed and analyzed to ensure that the equilibrium solid phase was indeed pure crystalline anthracene. Melting point temperatures of the undissolved residues were identical to that of anthracene. Experimental anthracene solubilities are listed in Table 1. Numerical values represent the average of 4–8 determinations, with measurements being reproducible to within ±1.5%.

RESULTS AND DISCUSSIONS

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:[9]

$$\Delta G^{\text{mix}}_{1,2,\ldots,N} = RT\sum_{i=1}^{N} n_i \ln X_i + \left(\sum_{i=1}^{N} n_i\Gamma_i\right)\left(\sum_{i=1}\sum_{j>1}^{N} f_i f_j A_{ij}\right) \tag{3}$$

$$\Delta G^{\text{mix}}_{1,2,\ldots,N} = RT\sum_{i=1}^{N} n_i \ln \phi_i + \left(\sum_{i=1}^{N} n_i\Gamma_i\right)\left(\sum_{i=1}\sum_{j>i}^{N} f_i f_j A_{ij}\right) \tag{4}$$

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

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 generalized mixing models and different weighting factor approximations, Acree and Bertrand[9] derived the following three NIBS expressions for predicting solute solubilities in binary solvent mixtures containing only nonspecific interactions:

$$RT\ln(a^{\text{solid}}_A/X^{\text{sat}}_A) = (1 - X^{\text{sat}}_A)^2[X^0_B(\Delta\bar{G}^{\text{ex}}_A)^*_B + X^0_C(\Delta\bar{G}^{\text{ex}}_{\text{A}})^*_C - \Delta\bar{G}^{\text{ex}}_{BC}] \tag{5}$$

$$\begin{aligned} RT\ln(a^{\text{solid}}_A/X^{\text{sat}}_A) = (1 - \phi^{\text{sat}}_A)^2[&\phi^0_B(\Delta\bar{G}^{\text{ex}}_A)^*_B + \phi^0_C(\Delta\bar{G}^{\text{ex}}_A)^*_C \\ &- \bar{V}_A(X^0_B\bar{V}_B + X^0_C\bar{V}_C)^{-1}\Delta\bar{G}^{\text{ex}}_{BC}] \end{aligned} \tag{6}$$

and

$$\begin{aligned} RT&\left[\ln(a^{\text{solid}}_A/\phi^{\text{sat}}_A) - (1 - \phi^{\text{sat}}_A)\left(1 - \frac{\bar{V}_A}{X^0_B\bar{V}_B + X^0_C\bar{V}_C}\right)\right] \\ &= (1 - \phi^{\text{sat}}_A)^2[\phi^0_B(\Delta\bar{G}^{\text{fh}}_A)^*_B + \phi^0_C(\Delta\bar{G}^{\text{fh}}_{\text{A}})^*_C - \bar{V}_A(X^0_B\bar{V}_B + X^0_C\bar{V}_C)^{-1}\Delta\bar{G}^{\text{fh}}_{BC}] \end{aligned} \tag{7}$$

Equations (5) and (6) are based on Raoult's law for the configurational contribution to the free energy, and Eq. (7) is based on the Flory–Huggins model. In the above expressions a^{solid}_A is the activity of the solid solute relative to the pure subcooled liquid, ϕ_i is the ideal volume fraction and $\bar{V}_i$ is molar volume. Binary solvent properties $\Delta\bar{G}^{\text{ex}}_{BC}$ and $\Delta\bar{G}^{\text{fh}}_{BC}$ 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 $(\Delta\bar{G}^{\text{ex}}_A)^*_i$ and $(\Delta\bar{G}^{\text{fh}}_A)^*_i$. 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 and solute solubility ranges that one can distinguish between the predictive expressions.

Comparisons between experimental and predicted anthracene solubilities are tabulated in the last three columns of Table 1 for the four binary solvent systems studied. Solute properties used in the NIBS predictions include $\bar{V}_A = 150$ cm^3 mol^{-1} and the activity of the solute, $a_A^{\text{solid}} = 0.01049$,[10] which was calculated by integrating the enthalpy of fusion data from the normal melting point temperature to 25°C. Experimental excess Gibbs free energies were not readily available in the chemical literature for the alkane + 1,4-dichlorobutane solvent mixtures, and $\Delta\bar{G}_{BC}^{\text{ex}}$ (and $\Delta\bar{G}_{BC}^{\text{fh}}$) values were thus estimated *via* the Scatchard-Hildebrand solubility parameter model

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

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

where δ_i is the solubility parameter of component *i*. Solvent properties used in the NIBS predictions are given in Table 2.

Careful examination of Table 1 reveals that the NIBS expressions fail to predict the observed anthracene solubilities, particularly in the case of both cyclohexane + dichlorobutane and methylcyclohexane + dichlorobutane mixtures. Deviations between experimental and predicted values are as large as 30+% for many of the individual binary solvent compositions, and exceed those expected for systems containing only nonspecific physical interactions. In past solubility studies, Eqs. (6) and (7) have predicted benzil,[11,12] *p*-benzoquinone,[13] pyrene,[14–16] biphenyl,[17] anthracene,[10,18,19] naphthalene,[9] benzoic acid,[20] thianthrene,[21] iodine,[7,11] and carbazole[22] solubilities in a wide range of binary solvent mixtures to within ±5%. Not too much significance is placed on the predictive ability of Eq. (5) as this particular form of the NIBS model has been shown to be inferior to Eqs. (6) and (7). It is only in systems contaning solute complexation with the smaller complexing solvent, for which the basic NIBS model fails badly, is Eq. (5) superior to the two volume fraction expressions. While one can always argue that the failure of the NIBS model to predict anthracene solubilities in the four binary solvent alkane + dichlorobutane solvent systems results from poor $\Delta\bar{G}_{BC}^{\text{ex}}$ estimates, we believe that complexation between the dissolved anthracene and dichlorobutane cosolvent occurs, in which case the Extended NIBS model [Eqs. (1) and/or (2)] should be used. The Scatchard–Hildebrand equation would have to underestimate the $\Delta\bar{G}_{BC}^{\text{ex}}$ values by over 190 cal mol^{-1} in order to account for the larger 50+% negative deviations.

If one assumes the existence of a weak anthracene-dichlorobutane complex in solution, then the equilibrium constant can be determined using the Extended NIBS model and measured anthracene solubilities as a function of binary solvent composition. Table 3 lists numerical K_{AC}^{ϕ} values, along with the corresponding deviations between observed and predicted anthracene solubilities which are on the order of ±1.5% or less. Inspection of Table 3 reveals that Eq. (1) does describe the experimental data, though the optimized constant does vary slightly with the inert hydrocarbon cosolvent, ranging from a lower limit of $K_{AC}^{\phi} = 8.0$ in *n*-octane to

Table 1 Comparison between predicted and experimental anthracene solubilities in binary alkane + 1,4-dichlorobutane solvent mixtures at 25.0°C.

X_C^0	X_A^{sat}	*% Deviation of Calculated Values*[a]		
		Eqn. 5	*Eqn. 6*	*Eqn. 7*
n-Heptane (B) + 1,4-Dichlorobutane (C)				
0.0000	0.00157	—	—	—
0.1379	0.00276	−19.0	−24.1	−24.0
0.2507	0.00392	−25.7	−33.3	−33.2
0.4470	0.00625	−28.0	−37.1	−37.0
0.5682	0.00768	−24.9	−33.2	−33.1
0.6581	0.00873	−22.1	−29.2	−29.1
0.8425	0.01026	−12.4	−15.8	−15.7
0.9120	0.01049	− 7.1	− 9.0	− 8.9
1.0000	0.01053	—	—	—
n-Octane (B) + 1,4-Dichlorobutane (C)				
0.0000	0.00184	—	—	—
0.1528	0.00312	−14.3	−22.2	−22.1
0.2670	0.00430	−19.7	−31.3	−31.3
0.4983	0.00697	−20.4	−34.3	−34.2
0.5934	0.00807	−18.5	−31.4	−31.2
0.6854	0.00911	−16.5	−27.4	−27.2
0.8550	0.01041	− 9.4	−14.8	−14.6
0.9254	0.01051	− 4.4	− 7.2	− 7.1
1.0000	0.01053	—	—	—
Cyclohexane (B) + 1,4-Dichlorobutane (C)				
0.0000	0.00155	—	—	—
0.1066	0.00278	−34.0	−31.8	−31.8
0.1993	0.00394	−48.3	−44.8	−44.8
0.3903	0.00638	−56.5	−51.5	−51.5
0.4994	0.00754	−51.8	−46.6	−46.6
0.5985	0.00854	−44.7	−39.6	−39.6
0.7962	0.00987	−25.6	−22.3	−22.3
0.8837	0.01023	−15.0	−12.9	−12.9
1.0000	0.01053	—	—	—
Methylcyclohexane (B) + 1,4-Dichlorobutane (C)				
0.0000	0.00165	—	—	—
0.1237	0.00294	−27.6	−28.8	−28.8
0.2298	0.00417	−38.2	−40.0	−40.0
0.4314	0.00646	−39.5	−41.5	−41.5
0.5259	0.00761	−37.8	−39.6	−39.6
0.6270	0.00859	−32.1	−33.5	−33.5
0.8192	0.00996	−17.1	−17.6	−17.6
0.8998	0.01035	+ 0.4	−10.4	−10.4
1.0000	0.01053	—	—	—

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

Table 2 Solvent properties used in the NIBS predictions[a].

Component (i)	$\bar{V}_i/cm^3\ mol^{-1}$	$\delta_i/(cal\ cm^{-3})^{1/2}$
n-Heptane	147.48	7.50
n-Octane	163.46	7.54
Cyclohexane	108.76	8.19
Methylcyclohexane	128.32	7.83
1,4-Dichlorobutane	112.12	9.67

[a] Values are taken from a tabulation in ref. (7).

$K^{\phi}_{AC} = 12.0$ in cyclohexane cosolvent. 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 free energies in the computations. It must be remembered that four measured quantities are needed to evaluate the equilibrium constant. Anthracene solubilities in each pure solvent and binary solvent mixture were reproducible to within $\pm 1.5\%$, and it is hoped that the $\Delta\bar{G}^{fh}_{BC}$ estimates are accurate to within ± 20 cal mol^{-1}. Furthermore, Eq. (1) is derived from the basic NIBS model and any errors in predicting the nonspecific physical contributions, which are perhaps as large as 4–5%, would naturally carry over into the equilibrium constant determination. A calculated anthracene-dichlorobutane association constant of $K^{\phi}_{AC} = 8.0$ in

Table 3 Summary of association parameters for presumed PAH-chloroalkane and PAH-dichloroalkane molecular complexes as calculated from measured solubilities.

Hydrocarbon cosolvent	K^{ϕ}_{AC}[a]	*Dev. (%)*[b]
Complex = Anthracene-Dichlorobutane		
n-Heptane	8.5	0.9
n-Octane	8.0	1.1
Cyclohexane	12.0	1.2
Methylcyclohexane	10.0	1.0
Complex = Anthracene-Chlorobutane[c]		
n-Heptane	3.5	0.6
n-Octane	3.0	0.6
Cyclohexane	6.0	1.3
Methylcyclohexane	5.0	0.3
Complex = Pyrene-Dichlorobutane[d]		
n-Heptane	15.0	1.2
n-Octane	12.5	1.8
Cyclohexane	18.0	1.9
Methylcyclohexane	15.0	1.1

[a] Numerical values subject to re-evaluation when $\Delta\bar{G}^{ex}_{BC}$ data becomes available.

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

[c] Numerical values taken from ref. (8).

[d] Numerical values taken from ref. (7).

n-octane may be identical, at least to within the limitations of the Extended NIBS model, to a value of $K^{\phi}_{AC} = 12.0$ in cyclohexane. An average volume fraction based association constant of $K^{\phi}_{AC} = 9.6$ indicates that roughly 15% of the total anthracene solubility in pure dichlorobutane corresponds to the uncomplexed solute. [Note: $\phi^{\text{sat}}_{A}/\hat{\phi}_{A_1} \approx 1 + \bar{V}_A K^{\phi}_{AC} \phi^{0}_{C}/(\bar{V}_A + \bar{V}_C)$]. In the absence of specific solute-solvent association, the expected mole fraction solubility in dichlorobutane is *circa* $X^{\text{sat}}_{A} \approx 0.00162$ and falls between values in *n*-heptane ($X^{\text{sat}}_{A} = 0.00157$) and *n*-octane ($X^{\text{sat}}_{A} = 0.00184$). Based on these observations, it is believed that the Extended NIBS model provides a more realistic description of the thermochemical properties of anthracene dissolved in binary alkane + 1,4-dichlorobutane mixtures than did the simpler NIBS model discussed previously.

Equilibrium constants for various PAH-chloroalkane complexes can be compared directly by remembering that the solubility method measures only the total solute solubility and cannot distinguish between the different molecular forms. For example, assuming that the single chlorine atom on 1-chlorobutane may complex with each aromatic ring on anthracene, then three molecular complexes are possible (see Figure 1)

$$\text{Anthracene} + \text{1-Chlorobutane} \rightleftharpoons \text{A1Cl} \qquad k^{\phi}_{\text{A1Cl}} = \hat{\phi}_{\text{A1Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\text{Anthracene} + \text{1-Chlorobutane} \rightleftharpoons \text{A2Cl} \qquad k^{\phi}_{\text{A2Cl}} = \hat{\phi}_{\text{A2Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\text{Anthracene} + \text{1-Chlorobutane} \rightleftharpoons \text{A1}'\text{Cl} \qquad k^{\phi}_{\text{A1}'\text{Cl}} = \hat{\phi}_{\text{A1}'\text{Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

Complexes A1Cl and A1′Cl are not really distinguishable and thus have identical microscopic equilibrium constants, *ie*., $k^{\phi}_{\text{A1Cl}} = k^{\phi}_{\text{A1}'\text{Cl}}$. The measured anthracene solubility represents the uncomplexed solute plus the sum of all complexed forms. Through mathematical manipulations it can be shown that the macroscopic K^{ϕ}_{AC} value for the anthracene-chlorobutane complex is

$$K^{\phi}_{AC} = \frac{\hat{\phi}_{AC}}{\hat{\phi}_{A_1}\hat{\phi}_{C_1}} = \frac{\hat{\phi}_{\text{A1Cl}} + \hat{\phi}_{\text{A2Cl}} + \hat{\phi}_{\text{A1}'\text{Cl}}}{\hat{\phi}_{A_1}\hat{\phi}_{C_1}} \tag{10}$$

$$K^{\phi}_{AC} = k^{\phi}_{\text{A1Cl}} + k^{\phi}_{\text{A2Cl}} + k^{\phi}_{\text{A1}'\text{Cl}} \tag{11}$$

$$K^{\phi}_{AC} = 2k^{\phi}_{\text{A1Cl}} + k^{\phi}_{\text{A2Cl}} \tag{12}$$

the degeneracy sum of the individual microscopic constants. One can devise a similar complexation scheme between anthracene and 1,4-dichlorobutane (see Figure 2), in which case

$$K^{\phi}_{AC} = 4k^{\phi}_{\text{A1Cl}} + 2k^{\phi}_{\text{A2Cl}} \tag{13}$$

Again only two distinguishable complexes are formed as both chlorine atoms behave independently. From a statistical standpoint, the anthracene-dichlorobutane constant should be exactly twice the value for anthracene-chlorobutane, in complete agreement with experimental ratios which fall in the 2–2.7 range. Uncertainties on calculated K^{ϕ}_{AC} values are believed to be *circa* ±2 and would account for the slight discrepancy. A much larger K^{ϕ}_{AC} ratio would have required postulating that both chlorine atoms simultaneously interact with anthracene to form a doubly-degenerate A1ClA1′Cl′

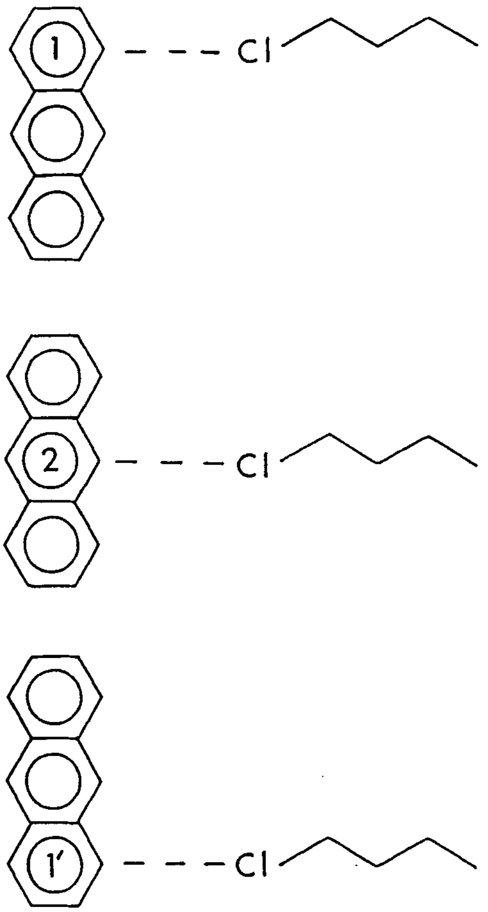

Figure 1 Hypothetical structures of anthracene-chlorobutane molecular complexes. The chlorine atom is permitted to interact with each aromatic ring. Three molecular complexes are formed, but only two are distinguishable because complexes A1Cl and A1'Cl are identical.

(equal to A1'ClA1Cl') complex. Unfortunately, the solubility data is inconclusive in regards to the "double chlorine complex".

The magnitude of the PAH-chloroalkane equilibrium constant is further affected by the size and electron distribution around the PAH aromatic ring, as reflected in K^{ϕ}_{AC} values for anthracene-dichlorobutane ($K^{\phi}_{AC} = 9.6 \pm 1.8$) versus pyrene-dichlorobutane ($K^{\phi}_{AC} = 14.2 \pm 2.4^{7}$). In our naive pictorial representation, pyrene has four polarizable aromatic rings available for complexation. Two distinguishable P1Cl and P2Cl complexes would be formed

$$K^{\phi}_{AC} = 4k^{\phi}_{\mathrm{P1Cl}} + 4k^{\phi}_{\mathrm{P2Cl}} \tag{14}$$

each having degeneracies of 4. Rationalization of equilibrium constant differences between various PAH solutes is possible only if one assumes that all microscopic constants are independent of aromatic ring position, *ie*., $k^{\phi}_{\mathrm{P1Cl}} = k^{\phi}_{\mathrm{P2Cl}} = k^{\phi}_{\mathrm{A1Cl}} = k^{\phi}_{\mathrm{A2Cl}}$,

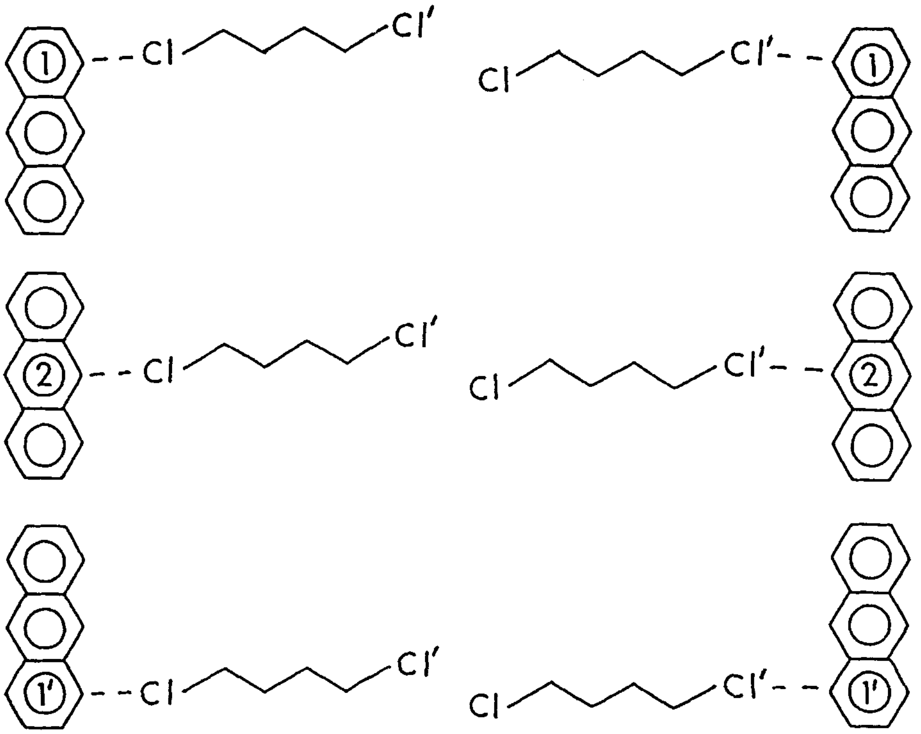

Figure 2 Hypothetical structures of anthracene-dichlorobutane molecular complexes. Interactions between the two chlorine atoms and each aromatic ring results in the formation of distinguishable A1Cl (degeneracy of 4) and A2Cl (degeneracy of 2) molecular complexes.

etc. This particular approximation, while not justified by direct experimental evidence, allows Eqs. (13) and (14) to be simplified to the point where the pyrene-dichlorobutane association constant is expected to be roughly 33% larger than the value for anthracene-dichlorobutane. Examination of Table 3 reveals that the K^{ϕ}_{AC} values follow this trend, at least to within the combined propagated experimental uncertainties inherent in the Extended NIBS computations.

The possibility exists that both 1:1 and 2:1 anthracene-dichlorobutane and pyrene-dichlorobutane complexes might be formed, in which case the pentanary form (A_1, B, C_1, AC, and A_2C) of the Extended NIBS model would be required to explain the observed solubility data. Macroscopic equilibrium constants, K^{ϕ}_{AC} and $K^{\phi}_{A_2C}$, are defined in terms of two step-wise equilibria

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

$$A_1 + AC \rightleftharpoons A_2C \qquad K^{\phi}_{A_2C} = \hat{\phi}_{A_2C}/(\hat{\phi}_{A_1}\hat{\phi}_{AC})$$

with the saturated volume fraction solubility of the *uncomplexed* solute, $\hat{\phi}^{\text{sat}}_{A_1}$, given by

$$\ln \hat{\phi}^{\text{sat}}_{A_1} = \phi^0_B \ln(\phi^{\text{sat}}_A)_B + \phi^0_C \ln(\phi^{\text{sat}}_{A_1})_C + \frac{\bar{V}_A \Delta\bar{G}^{\text{fh}}_{BC}}{RT(X^0_B\bar{V}_B + X^0_C\bar{V}_C)} \tag{15}$$

where

$$\phi_A^{\text{sat}} = \hat{\phi}_{A_1}^{\text{sat}}[1 + \bar{V}_A K_{AC}^{\phi} \phi_C^0/(\bar{V}_A + \bar{V}_C) + 2\bar{V}_A K_{AC}^{\phi} K_{A_2C}^{\phi} \phi_C^0 \hat{\phi}_{A_1}^{\text{sat}}/(2\bar{V}_A + \bar{V}_C)] \tag{16}$$

$$(\phi_A^{\text{sat}})_C = (\hat{\phi}_{A_1}^{\text{sat}})_C[1 + \bar{V}_A K_{AC}^{\phi}/(\bar{V}_A + \bar{V}_C) + 2\bar{V}_A K_{AC}^{\phi} K_{A_2C}^{\phi} (\hat{\phi}_{A_1}^{\text{sat}})_C/(2\bar{V}_A + \bar{V}_C)] \tag{17}$$

Equation (15) differs slightly from previously published expressions[23,24] in that the equilibrium constants are expressed in terms of volume fractions rather than mole fractions. Like Eq. (1), the two-complex Extended NIBS model is derived for solutes having very limited solubility, and contains only a single association parameter whenever the two end chlorine atoms act independently.

The twenty-four assumed microscopic equilibrium constants depend upon whether anthracene complexes with the Cl′ chlorine atom after first complexing with the Cl chlorine atom

First:

$$\text{Anthracene} + \text{Dichlorobutane} \rightleftharpoons \text{A1Cl} \qquad k_{\text{A1Cl}}^{\phi} = \hat{\phi}_{\text{A1Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\text{Anthracene} + \text{Dichlorobutane} \rightleftharpoons \text{A2Cl} \qquad k_{\text{A2Cl}}^{\phi} = \hat{\phi}_{\text{A2Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

$$\text{Anthracene} + \text{Dichlorobutane} \rightleftharpoons \text{A1'Cl} \qquad k_{\text{A1'Cl}}^{\phi} = \hat{\phi}_{\text{A1'Cl}}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1})$$

Second:

$$\text{Anthracene} + \text{A1Cl} \rightleftharpoons \text{A1ClCl'A1} \qquad k_{\text{A1ClCl'A1}}^{\phi} = \frac{\hat{\phi}_{\text{A1ClCl'A1}}}{\hat{\phi}_{A_1}\hat{\phi}_{\text{A1Cl}}}$$

$$\text{Anthracene} + \text{A1Cl} \rightleftharpoons \text{A1ClCl'A2} \qquad k_{\text{A1ClCl'A2}}^{\phi} = \frac{\hat{\phi}_{\text{A1ClCl'A2}}}{\hat{\phi}_{A_1}\hat{\phi}_{\text{A1Cl}}}$$

$$\text{Anthracene} + \text{A1Cl} \rightleftharpoons \text{A1ClCl'A1'} \qquad k_{\text{A1ClCl'A1'}}^{\phi} = \frac{\hat{\phi}_{\text{A1ClCl'A1'}}}{\hat{\phi}_{A_1}\hat{\phi}_{\text{A1Cl}}}.$$

+6 ADDITIONAL EQUILIBRIA

and vice versa. Again, both chlorine atoms are permitted to interact with each aromatic ring. Using this particular complexation scheme, macroscopic and microscopic constants are inter-related as follows

$$K_{AC}^{\phi} = 4k_{\text{A1Cl}}^{\phi} + 2k_{\text{A2Cl}}^{\phi} \tag{18}$$

$$\begin{aligned} K_{A_2C}^{\phi} = {} & \frac{\hat{\phi}_{\text{A1ClCl'A1}} + \hat{\phi}_{\text{A1ClCl'A2}} + \hat{\phi}_{\text{A1ClCl'A1'}}}{(\hat{\phi}_{\text{A1Cl}} + \hat{\phi}_{\text{A2Cl}} + \hat{\phi}_{\text{A1'Cl}} + \hat{\phi}_{A1Cl'} + \hat{\phi}_{\text{A2Cl'}} + \hat{\phi}_{\text{A1'Cl}})\hat{\phi}_{A_1}} \\ & + \frac{\hat{\phi}_{\text{A2ClCl'A1}} + \hat{\phi}_{\text{A2ClCl'A2}} + \hat{\phi}_{\text{A2ClCl'A1'}}}{(\hat{\phi}_{\text{A1Cl}} + \hat{\phi}_{\text{A2Cl}} + \hat{\phi}_{\text{A1'Cl}} + \hat{\phi}_{\text{A1Cl'}} + \hat{\phi}_{\text{A2Cl'}} + \hat{\phi}_{\text{A1Cl}})\hat{\phi}_{A_1}} \\ & + \frac{\hat{\phi}_{\text{A1'ClCl'A1}} + \hat{\phi}_{\text{A1'ClCl'A2}} + \hat{\phi}_{\text{A1'ClCl'A1'}}}{(\hat{\phi}_{\text{A1Cl}} + \hat{\phi}_{\text{A2Cl}} + \hat{\phi}_{\text{A1'Cl}} + \hat{\phi}_{\text{A1Cl'}} + \hat{\phi}_{\text{A2Cl'}} + \hat{\phi}_{\text{A1Cl}})\hat{\phi}_{A_1}} \end{aligned} \tag{19}$$

$$\begin{aligned} K_{AC}^{\phi} K_{A_2C}^{\phi} = {} & k_{\text{A1Cl}}^{\phi}(k_{\text{A1ClCl'A1}}^{\phi} + k_{\text{A1ClCl'A2}}^{\phi} + k_{\text{A1ClCl'A1'}}^{\phi}) + k_{\text{A2Cl}}^{\phi}(k_{\text{A2ClCl'A1}}^{\phi} + k_{\text{A2ClCl'A2}}^{\phi} \\ & + k_{\text{A2ClCl'A1'}}^{\phi}) + k_{\text{A1'Cl}}^{\phi}(k_{\text{A1'ClCl'A1}}^{\phi} + k_{\text{A1'ClCl'A2}}^{\phi} + k_{\text{A1'ClCl'A1'}}^{\phi}) \end{aligned} \tag{20}$$

which is simplifiable to a single macroscopic constant

$$K^{\phi}_{AC}K^{\phi}_{A_2C} = 9(k^{\phi}_{\mathrm{A1Cl}})^2 = 0.25(K^{\phi}_{AC})^2 \tag{21}$$

under the very specialized set of conditions that the chlorine atoms act independently, *ie.*, equal k^{ϕ}_i values.

Despite the complex appearance of Eqs. (15)–(17), their application to solubilities in mixed solvents is relatively straightforward. The solubility of the uncomplexed solute in the pure complexing solvent, $(\hat{\phi}^{\mathrm{sat}}_{A_1})_C$, is first computed using an assumed K^{ϕ}_{AC} (and corresponding $K^{\phi}_{A_2C}$) value. This quantity, along with the measured solubility in the inert hydrocarbon cosolvent and excess Gibbs free energies of the binary solvent, is then substituted into Eqs. (15) and (16) to calculate $\hat{\phi}^{\mathrm{sat}}_{A_1}$ and ϕ^{sat}_{A} at each solvent composition. The entire computational procedure is repeated until the numerical value of K^{ϕ}_{AC} that "best" describes the experimental solubility in a particular binary solvent system is obtained. Computations show that the two-complex model with $K^{\phi}_{A_2C} = 0.25$ (K^{ϕ}_{AC}) also describes the observed data to *circa* ±1.5% and the K^{ϕ}_{AC} values, which range from $K^{\phi}_{AC} = 7.7$ (% dev. = 1.3%) for *n*-octane to $K^{\phi}_{AC} = 11.5$ (% dev. = 0.8%) for cyclohexane, differ by a few-tenths unit from those given in Table 3. Unfortunately, no firm conclusion can be reached regarding the possible formation of an A_2C anthracene-dichlorobutane molecular complex. The "extra" $2K^{\phi}_{AC}K^{\phi}_{A_2C}\phi^0_C\hat{\phi}^{\mathrm{sat}}_{A_1}\bar{V}_A/(2\bar{V}_A + \bar{V}_C)$ term makes only a minor contribution in the computations because of the low anthracene solubilities and small $\hat{\phi}^{\mathrm{sat}}_{A_1}$ values. Readers should note that pyrene solubilities in binary alkane + dichlorobutane mixtures could be treated in a similar fashion, and that the Extended NIBS model could be expanded so as to include a 1:2 PAH-dichlorobutane complex. In this latter case, the uncomplexed and overall PAH solubilities would be related by a second degree polynomial in ϕ^0_C, which is not consistent with the present experimental data. Additional measurements are planned on much larger PAH molecules in hopes of developing a better estimational method for PAH-polychloroalkane association parameters.

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APPENDIX: GLOSSARY OF SYMBOLS

a^{solid}_A	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$(\Delta\bar{G}^{\mathrm{ex}}_A)^*_i$	partial molar Gibbs free energy of the solute (Raoult's law in pure solvent *i*, extrapolated back to infinite dilution
$(\Delta\bar{G}^{\mathrm{fh}}_A)^*_i$	partial molar Gibbs free energy of the solute (Flory-Huggins model) in pure solvent *i*, extrapolated back to infinite dilution
$\Delta\bar{G}^{\mathrm{ex}}_{BC}$	excess molar Gibbs free energy of the binary solvent mixture based on Raoult's law

$\Delta \bar{G}^{fh}_{BC}$	excess molar Gibbs free energy of the binary solvent mixture based on the Flory-Huggins model
$\Delta \bar{H}^{fh}_{A}$	molar enthalpy of fusion of the solute
K^{ϕ}_{AC}	volume fraction-based macroscopic equilibrium constant for the formation of the AC molecular complex
K^{x}_{AC}	mole fraction-based macroscopic equilibrium constant for the formation of the AC molecular complex
k^{ϕ}_{A1C1}	volume fraction-based microscopic equilibrium constant for the formation of the "distinquishable" A1C1 molecular complex
$\bar{V}_i$	molar volume of component i
X^0_B, X^0_C	mole fraction composition of the solvent mixture, calculated as if the solute were not present
X^{sat}_A	saturated mole fraction solubility of the solute
$\hat{X}_i$	true equilibrium mole fraction of component i in the associated solution
ϕ^0_B, ϕ^0_C	ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
ϕ^{sat}_A	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

References

1. G. L. Bertrand, *J. Phys. Chem.*, **79**, 48 (1975).
2. J. W. McCargar and W. E. Acree, Jr., *Phys. Chem. Liq.*, **17**, 123 (1987).
3. W. E. Acree, Jr., D. R. McHan and J. H. Rytting, *J. Pharm. Sci.*, **72**, 929 (1983).
4. W. E. Acree, Jr., *Int. J. Pharm.*, **15**, 159 (1983).
5. J. W. McCargar and W. E. Acree, Jr., *J. Pharm. Sci.*, **76**, 572 (1987).
6. J. W. McCargar and W. E. Acree, Jr., *J. Solution Chem.*, **17**, 1081 (1988).
7. W. E. Acree, Jr., S. A. Tucker and A. I. Zvaigzne, *J. Chem. Soc., Faraday Trans.*, **86**, 2197 (1990).
8. W. E. Acree, Jr., *J. Solution Chem.*, in press.
9. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **81**, 1170 (1977).
10. W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, **72**, 292 (1983).
11. W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, **71**, 201 (1982).
12. W. E. Acree, Jr. and G. L. Bertrand, *J. Solution Chem.*, **12**, 101 (1983).
13. W. E. Acree, Jr. and J. H. Rytting, *Int. J. Pharm.*, **10**, 231 (1982).
14. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *Phys. Chem. Liq.*, **16**, 179 (1987).
15. J. R. Wallach, S. A. Tucker, B. M. Oswalt, D. J. Murral and W. E. Acree, Jr., *J. Chem. Eng. Data*, **34**, 70 (1989).
16. C. L. Judy, N. M. Pontikos and W. E. Acree, Jr., *J. Chem. Eng. Data*, **32**, 60 (1987).
17. W. E. Acree, Jr., *Int. J. Pharm.*, **18**, 47 (1984).
18. S. A. Tucker, D. J. Murral, B. M. Oswalt, J. L. Halmi and W. E. Acree, Jr., *Phys. Chem. Liq.*, **18**, 279 (1988).
19. M. V. Marthandan and W. E. Acree, Jr., *J. Chem. Eng. Data*, **32**, 301 (1987).
20. W. E. Acree, Jr. and G. L. Bertrand, *J. Pharm. Sci.*, **70**, 1033 (1981).
21. W. E. Acree, Jr., S. A. Tucker and A. I. Zvaigzne, *Phys. Chem. Liq.*, **21**, 45 (1990).
22. W. E. Acree, Jr., *Phys. Chem. Liq.*, **22**, 157 (1990).
23. W. E. Acree, Jr. and S. A. Tucker, *Phys. Chem. Liq.*, **19**, 23 (1989).
24. W. E. Acree, Jr., S. A. Tucker and L. E. Cretella, *Thermochim. Acta*, **145**, 245 (1989).