

## **SOLUBILITIES OF POLYCYCLIC AROMATIC HYDROCARBON SOLIDS IN *n*-OCTADECANE**

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### **ABSTRACT**

Solubilities of five polycyclic aromatic hydrocarbon solids: naphthalene, acenaphthene, anthracene, phenanthrene and pyrene in *n*-octadecane (OD) have been determined over a range of temperatures. Differential scanning calorimetry (DSC) has been used to investigate solid–liquid equilibria. Furthermore, the activity coefficients of the aromatic hydrocarbons in OD have been correlated by Wilson's equation and by the Scatchard–Hildebrand solubility parameter expression. Both approaches offer a useful procedure for estimating, with good accuracy, activity coefficients for aromatic-saturated hydrocarbon systems.

### **INTRODUCTION**

Polycyclic aromatic hydrocarbons (PAH) are of special importance in biological sciences because of their mutagenic and carcinogenic activities. In the field of separation science (gas and liquid chromatography), OD when chemically bonded to a solid support material (usually silica) provides unique selectivity for the separation of polycyclic aromatic hydrocarbons. The mechanism of retention of PAH on a chemically bonded OD phase has not been established and is a topic of much discussion and research [1,2]. In the petrochemical and related industries hydrocarbon mixtures of concern commonly include those containing mono- and polycyclic aromatics with saturated hydrocarbons.

McLaughlin and co-workers investigated the solubility of aromatic hydrocarbons in benzene [3], carbon tetrachloride [4], pyridine [5], thiophene [5] and cyclohexane [6]. Such mixtures are only modestly non-ideal; however, their divergence from ideal behavior must be taken into account. In the present work are reported the solubilities of aromatic hydrocarbon solutes in *n*-octadecane. Furthermore, solute activity coefficients are represented using Scatchard–Hildebrand and Wilson models.

## THEORY

The thermodynamic activity of a solute,  $a_i$ , can be related to its reference supercooled liquid state through the equation [7]

$$\ln a_i = \ln(x_i^l \gamma_i^l) = -(\Delta H_m/RT)[1 - T/T_m] + (\Delta c_p/R) \times [\ln(T/T_m) - (T_m/T) + 1] \quad (1)$$

where  $\Delta H_m$  is solute molar enthalpy of fusion at its melting point  $T_m$ ,  $\Delta c_p$  being the difference in heat capacities between solid and supercooled liquid state of a matter,  $\gamma$  represents the liquid-phase activity coefficient,  $x$  is the solute mole fraction and  $R$  is the gas constant. Terms which integrate  $\Delta c_p$  may be disregarded, if the melting point of the solute is not more than 100 K above the solution temperature. This assumption results in

$$\ln a_i = \ln(x_i^l \gamma_i^l) = -(\Delta H_m/RT_m)[(T_m/T) - 1] \quad (2)$$

or

$$\ln a_i = \ln(x_i^l \gamma_i^l) = -(\Delta S_m/R)[(T_m/T) - 1] \quad (3)$$

where  $\Delta S_m$  is the molar entropy of fusion of the pure solute. Because the activity coefficient of an ideal solution is unity (by definition),  $a_i$  also represents the mole fraction ideal solubility.

In this study two methods, the correlation equations of Scatchard–Hildebrand [7] and Wilson [8], were applied to represent the solute activity coefficients. When the non-ideality arises strictly from differential cohesiveness, the Scatchard–Hildebrand regular solution model

$$RT \ln \gamma_2 = V_2^l [(V_1^l x_1)/(V_1^l x_1 + V_2^l x_2)]^2 (\delta_1 - \delta_2)^2 \quad (4)$$

predicts the solute activity coefficients. The solute activity coefficient in the binary mixture can be calculated at any composition and temperature by implementing only solubility parameters  $\delta_i$  and molar liquid volumes  $V_i^l$  for the pure components. The solubility parameters  $\delta_1$  and  $\delta_2$  are the square root cohesive energy densities  $(-E/V)^{1/2}$  for solvent and solute respectively, where the cohesive energy of the liquid,  $-E$ , is essentially the molal energy of vaporization, and  $V$  is the molal volume of the liquid. At low vapor pressures we may replace  $-E$  by  $\Delta E^v$  so that

$$\delta_i = (\Delta E_i^v/V_i^l)^{1/2} \quad (5)$$

At the temperatures well below the critical temperature  $\Delta E_i^v$  can be computed from the relation

$$\Delta E_i^v = \Delta H_i^v - RT \quad (6)$$

where  $\Delta H_i^v$  is the molar enthalpy of vaporization of the pure liquid at temperature  $T$ . When experimental data are not available for  $\Delta H^v$ , the latter

can be calculated by means of the Clausius – Clapeyron equation, while the Antoine equation is applied for the vapor pressure estimation.

For a mixture of hydrocarbons, the accuracy of prediction by the Scatchard–Hildebrand equation is improved if an adjustable binary parameter  $l_{12}$  is added to the equation, leading to the expression [9]

$$RT \ln \gamma_2 = V_2^1 \left[ (V_1^1 x_1) / (V_1^1 x_1 + V_2^1 x_2) \right]^2 \{ (\delta_1 - \delta_2)^2 + 2l_{12} \delta_1 \delta_2 \} \quad (7)$$

Calculated activity coefficients are often sensitive to an adjustable constant  $l_{12}$ , although it is generally small compared with unity. As pointed out by Funk and Prausnitz [9], for the aromatic-saturated hydrocarbon mixtures, even a small value of  $l_{12}$  can have a large effect on the predicted activity coefficient. For a special case  $l_{12} = 0$ , eqn. (7) transforms to eqn. (4).

The Wilson equation uses an entropy approach based on the concept of the “local volume fraction”, and has been successfully applied to the representation of both binary and multicomponent mixtures [6,10].

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left[ \Lambda_{21}(x_2 + \Lambda_{21}x_1)^{-1} - \Lambda_{12}(x_1 + \Lambda_{12}x_2)^{-1} \right] \quad (8)$$

where

$$\begin{aligned} \Lambda_{21} &= (V_1^1/V_2^1) \exp[-(\lambda_{21} - \lambda_{22})/RT]; \\ \Lambda_{12} &= (V_2^1/V_1^1) \exp[-(\lambda_{12} - \lambda_{22})/RT] \end{aligned} \quad (9)$$

For practical purposes, only terms  $\lambda_{21} - \lambda_{22}$  and  $\lambda_{12} - \lambda_{22}$  are empirically determined and they represent energy terms related to the difference in cohesive energy between pairs of alike molecules (1–1 or 2–2) and pairs of different molecules (1–2 or 2–1). To a good first approximation, over a modest range of temperature the following relations hold:

$$\Delta\lambda_{21} = \lambda_{21} - \lambda_{22} \neq f(T) \text{ and } \Delta\lambda_{12} = \lambda_{12} - \lambda_{22} \neq f(T); \Lambda_{21} \neq \Lambda_{12}; \Lambda_{11} = \Lambda_{22}$$

Equation (8) can be solved iteratively for both  $\Lambda_{21}$  and  $\Lambda_{12}$ , requiring only two parameters per binary mixture.

## EXPERIMENTAL

All compounds were purchased from Aldrich. Naphthalene, anthracene and phenanthrene were “gold label” quality Aldrich products, while acenaphthene and pyrene were of purity better than 99% and were all used without further purification. Solvent, *n*-octadecane, was vacuum-distilled prior to use. For the determination of the melting points of the pure compounds and binary mixtures a Perkin–Elmer DSC-2 differential scanning calorimeter was used. Temperature programs were calibrated with the melting points of indium (429.8 K) and naphthalene (353.4 K); the latter

was also employed for the determination of the "thermal lag" of the system. Samples of known composition of about 1.5–2.0 mg were weighed into aluminium pans, which were then crimped to preclude sample loss during the heating process. A scan rate of  $5 \text{ K min}^{-1}$  was applied at a sensitivity setting of  $2 \text{ mcal s}^{-1}$ .

## RESULTS AND DISCUSSION

In Table 1 are listed the literature values for the melting points and the molar enthalpies of fusion of the pure compounds together with experimentally measured melting points. We found acceptable agreement between the experimental and reported data.

The observed melting points and activity coefficients ( $\gamma_2 = a_2/x_2$ ) of PAH in OD at designated solute mole fraction  $x_2$  are listed in Table 2. Solute activities  $a_2$ , were computed from eqn. (2) and the values of  $\Delta H_m$

TABLE 1

Solubility parameters  $\delta_i$ , molar liquid volumes  $V_i$  of solutes and solvent at the melting point  $T_m$  of the solutes with molar enthalpy of melting  $\Delta H_m$

Solute	$T_m$ (K)	$\Delta H_m$ (kJ mol <sup>-1</sup> )	$10^{-4} \delta_2$ ((J m <sup>-3</sup> ) <sup>1/2</sup> )	$10^6 V_2$ (m <sup>3</sup> mol <sup>-1</sup> )	n-Octadecane	
					$10^{-4} \delta_1^f$ ((J m <sup>-3</sup> ) <sup>1/2</sup> )	$10^6 V_1^g$ (m <sup>3</sup> mol <sup>-1</sup> )
Naphthalene	352.5 353.3 <sup>d</sup>	18.77 <sup>a</sup>	1.9396 <sup>c</sup>	130.86 <sup>c</sup>	1.5486	343.1
Acenaphthene	367.3 367.2 <sup>a</sup>	21.86 <sup>c</sup>	1.8930 <sup>d</sup>	149.8 <sup>c</sup>	1.5382	347.3
Phenanthrene	372.9 372.3 <sup>a</sup>	18.60 <sup>a</sup>	1.9772 <sup>c</sup>	168.05 <sup>c</sup>	1.5337	349.1
Anthracene	490.1 489.2 <sup>a</sup>	28.80 <sup>a</sup>	1.7688 <sup>f</sup>	178.9 <sup>a</sup>	1.2666	382.7
Pyrene	423.6 423.3 <sup>a</sup>	15.31 <sup>b</sup>	1.8111 <sup>e</sup>	186.8 <sup>d</sup>	1.3868	363.4

<sup>a</sup> Ref. 3.

<sup>b</sup> Ref. 13.

<sup>c</sup> Ref. 5.

<sup>d</sup> Ref. 14.

<sup>e</sup> Enthalpy of vaporization was taken from ref. 14.

<sup>f</sup> Enthalpy of vaporization was evaluated by using the Clausius–Clapeyron equation with Antoine equation constants given in ref. 15.

<sup>g</sup> Extrapolated using data from ref. 16.

TABLE 2

Solubility, experimental activity coefficients at saturation of five aromatic hydrocarbon solids in *n*-octadecane and calculated activity coefficients using eqns. (7) and (8)

Solute	$x$	$T$ (K)	$\gamma_{\text{expt}}$	$\gamma_{\text{pred}}^{\text{a}}$	$\Delta$ (%)	$\gamma_{\text{pred}}^{\text{b}}$	$\Delta$ (%)
Naphthalene	0.9184	348.7	1.003	1.007	0.4	1.003	0.0
	0.8850	347.0	1.009	1.013	0.4	1.007	0.2
	0.8650	346.0	1.013	1.017	0.4	1.010	0.3
	0.7996	342.5	1.028	1.033	0.5	1.021	0.7
	0.5956	330.0	1.082	1.091	0.9		
	0.5224	325.1	1.114				
Acenaphthene	0.9208	363.5	1.008	1.007	0.1	1.014	0.6
	0.8185	359.0	1.042	1.031	1.1	1.043	0.1
	0.7590	356.2	1.058	1.048	0.9		
	0.6925	352.4	1.071				
Phenanthrene	0.8956	367.5	1.040	1.032	0.8	1.032	0.8
	0.8849	367.0	1.045	1.038	0.7	1.038	0.7
	0.8224	364.2	1.078	1.084	0.5	1.082	0.4
	0.8186	364.1	1.080	1.087	0.6	1.085	0.5
	0.8081	363.5	1.086	1.096	0.9	1.094	0.7
	0.6667	359.9	1.246	1.246	0.0		
	0.6315	358.8	1.294	1.286			
Anthracene	0.9011	483.0	1.000	1.020	2.0	1.011	1.1
	0.8513	480.8	1.024	1.042	1.7	1.026	0.2
	0.8142	478.5	1.034	1.062	2.7	1.041	0.7
	0.8000	477.5	1.035	1.070	3.0	1.047	1.2
	0.7615	477.0	1.082	1.094	1.1	1.068	1.3
	0.6774	472.6	1.136	1.154	1.6	1.127	0.8
	0.5909	468.0	1.212	1.225	1.0		
	0.5577	466.5	1.253				
Pyrene	0.9502	419.0	1.003	1.000	0.3	1.009	0.6
	0.8986	417.2	1.041	1.033	0.7	1.033	0.7
	0.8235	412.5	1.080	1.093	1.2	1.088	0.7
	0.7612	411.2	1.152	1.159	0.6	1.151	0.1
	0.7329	410.5	1.188	1.194	0.5	1.185	0.2
	0.7028	409.7	1.228	1.234	0.5	1.225	0.2
	0.6905	409.1	1.242	1.251	0.7		
	0.6061	407.0	1.381				

<sup>a</sup> Using eqn. (7).

<sup>b</sup> Using eqn. (8).

and  $T_m$  of the pure compounds provided in Table 1. Solubility equations were determined by the method of least squares subject to the condition that

$$\ln x = A/T + B \quad (10)$$

satisfies the point  $(0, 1/T_m)$ . In Table 3 are listed parameters  $A$  and  $B$  of

TABLE 3

Best-fit constants (applicable over specified temperature span  $\Delta T$ ) of eqn. (10) for indicated solutes ( $R = 8.314 \text{ J mol}^{-1}$ )

Solute	$\Delta T$ (K)	$B$	$-RA$ ( $\text{kJ mol}^{-1}$ )
Naphthalene	352.5–325.1	7.564	22.15
Acenaphthene	367.3–352.4	8.831	26.93
Phenanthrene	372.9–358.8	14.274	43.90
Anthracene	490.1–466.5	13.760	55.65
Pyrene	423.6–407.0	14.427	50.39

the solubility equation (10), and the temperature range over which linearity was observed for each binary mixture. It was found that the solubility curves did not have the slopes conforming with ideal values ( $\Delta H_m/R$ ). In all instances the solubility curves had slopes corresponding to negative deviation from Raoult's law,  $\gamma_2 > 1$  (solubility was less than that obeying ideal behavior). For pyrene, the low entropy change upon melting, compared with the rest of the investigated solutes, points toward an inherent ordering in the liquid state, implying that factors inhibiting rotation in the solid also restrain rotation in the liquid state. Owing to preserved molecular ordering, it was not surprising that pyrene demonstrated the uppermost deviation from ideality. Naphthalene exhibited the smallest departure from ideality.

The melting process can be separated into three subprocesses: translational, rotational, and internal melting [11]. Translational melting comprises change from the ordered line-up of the molecular centers of gravity in the solid to the dilated and more randomized arrangement in the liquid. A value of  $14.6 \text{ J mol}^{-1} \text{ K}^{-1}$  can be regarded as a reasonable estimate for the translational entropy of melting for all molecules [12]. For spherical molecules, only translational melting is feasible. Rotational melting embraces transformation from the ordered disposition of the major axes of crystalline molecules to the randomly oriented arrangement in the liquid. For rigid non-spherical molecules both translational and rotational melting are conceivable;  $\Delta S_m = 54.4 \text{ J mol}^{-1} \text{ K}^{-1}$  is a sound approximation [12] for both subprocesses. Internal melting represents interchange from the equable conformation of flexible molecules of the crystal to the random conformation of such molecules in the liquid. All three steps are relevant to the melting of the flexible molecules that can go through conformational changes.

To scrutinize the general pattern of the solubility of the aromatic hydrocarbons in OD the solubility data were plotted in the form  $\ln$  mol-fraction against inverse reduced temperature  $T_m/T$ . In Fig. 1 are depicted experimental data for investigated systems. The solubility data for PAH solutes under investigation were fitted to a straight line (dashed line in Fig. 1) with slope, intercept and correlation coefficient of  $-9.4778$ ,  $9.4842$  and  $0.9367$ ,

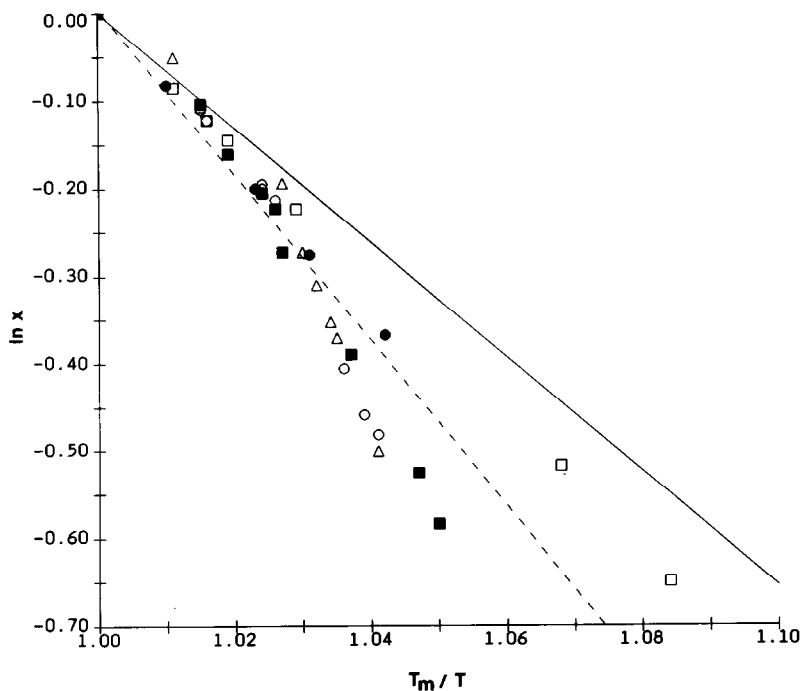


Fig. 1. Solubilities of naphthalene ( $\square$ ), acenaphthene ( $\bullet$ ), phenanthrene ( $\circ$ ), anthracene ( $\blacksquare$ ) and pyrene ( $\Delta$ ). Ideal solubility (—), data fitted to eqn. (10) (- - - -).

respectively. A full line represents ideal slope ( $\Delta S_m/R = 54.4/R$ ) presuming that only translational and rotational melting are conceivable. In Fig. 2 are presented solubility curves for PAH solutes, in different solvents, derived from the published data [5]. Even though the same PAH solutes were not examined with listed solvents, important conclusions could still be made from plots such as Fig. 2. A dashed line represents the ideal solubility curve with slope  $54.4/R$ . It was intriguing to observe that the solubility of PAH in OD is closer to ideality than in cyclohexane. In Fig. 3 are represented solubilities of naphthalene, as a model solute, in different solvents. A dashed line depicts ideal solubility. It was pointed out [17] that the solubility of aromatics is influenced by electron donor-acceptor interactions, in which the aromatic ring acts as electron donor. Utilizing solvents that have stronger electron-accepting capability, the solubility of naphthalene approaches the ideal value, and as in the case of chloroform positive deviation from Raoult's law, i.e. higher than ideal solubilities, was confirmed. A binary mixture, naphthalene-thiophene, most closely approximates ideal behavior. When spherical or straight chain hydrocarbons were used positive aberration was observed. In addition, it could be reasoned that *n*-octadecane was a better solvent for naphthalene than cyclohexane or *n*-hexane. This was related to the chain flexibility of the solvent molecule. A dissolved solute is

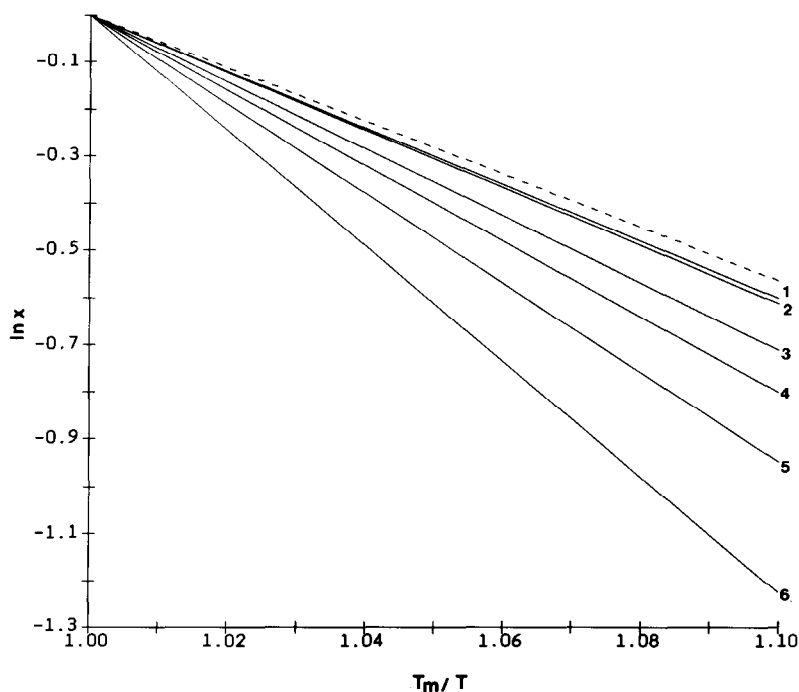


Fig. 2. Generalization of solid solubility of PAH in different solvents: thiophene (1), pyrene (2), benzene (3), carbon tetrachloride (4), *n*-octadecane (5) and cyclohexane (6), ideal solubility (-----).

small enough to rest within the skeleton of the solvent molecule (OD) without substantially affecting the intermolecular bonding. The same solute may have to break many bonds to create a hole for itself when dissolved in cyclohexane or *n*-hexane.

*Correlation of results based on Scatchard–Hildebrand regular solution theory and Wilson equations*

The Scatchard–Hildebrand regular solution model with binary parameter  $l_{12}$  (eqn. (7)) was applied to forecast  $\gamma_2$ . Only one experimental data point was required for the evaluation of the binary parameter  $l_{12}$ . It was reckoned for every binary mixture (values listed in Table 4) at the lowest temperature at which the solubility was measured. Itemized in Table 1 are the solubility parameters and liquid molar volumes of the solutes (index 2) and solvent (index 1) evaluated at the melting point of the solutes. The divergence of the values predicted for the activity coefficients, from the experimental results was estimated utilizing the relationship [5]

$$\Delta = 100 \left\{ \left[ (\gamma_2)_{\text{expt}} - (\gamma_2)_{\text{pred}} \right] / (\gamma_2)_{\text{expt}} \right\} \quad (11)$$



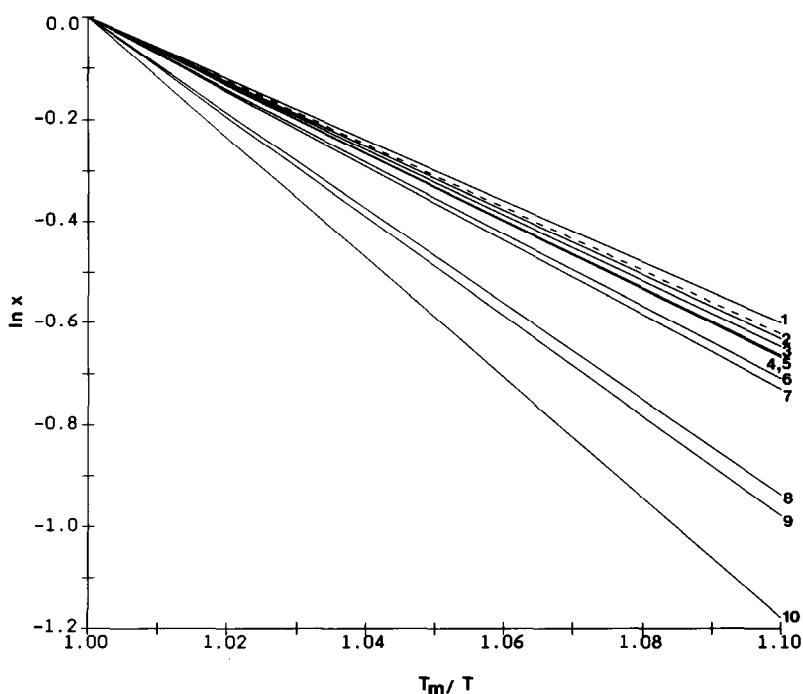


Fig. 3. Solubilities of naphthalene in various solvents: chloroform (1), thiophene (2), pyrene (3), benzene (4), carbon disulfide (5), carbon tetrachloride (6), toluene (7), *n*-octadecane (8), cyclohexane (9) and *n*-hexane (10), ideal solubility (-----). All curves, except curve 8, were constructed using literature data: for curves 1, 5 and 10 the data are from ref. 18, for curves 2 and 3 from ref. 5, for curves 4 and 9 from ref. 6 and for curve 6 from ref. 4.

and is given in Table 2. An average deviation was 0.9%, while individual deviation never exceeded 3.0% of the experimental values.

Further improvement in the correlation of the activity coefficients for the examined systems was achieved using Wilson's equation. The lowest solubility data point was implemented in these determinations as it was reasoned that the matching value of activity coefficient would presumably be more rigorous, due to its magnitude, for the computations of the characteristic

TABLE 4

Binary parameters used in eqn. (7) and characteristic energy differences used in eqn. (8)

Solute	$l_{12}$	$\Delta\lambda_{21}$ (J mol <sup>-1</sup> )	$\Delta\lambda_{12}$ (J mol <sup>-1</sup> )
Naphthalene	-0.0180	2447.6	3859.7
Acenaphthene	-0.0127	-5012.8	7252.7
Phenanthrene	-0.0076	-700.4	6916.0
Anthracene	-0.0287	1248.7	5381.7
Pyrene	0.0015	1701.4	7747.7

energy differences listed in Table 4. The procedure was iterated for all solute-solvent binary mixtures. When Wilson's equation was used computed activity coefficients had an average deviation of 0.6% while discrete deviation never exceeded 1.3%.

## CONCLUSION

The solubilities of polycyclic aromatic hydrocarbons in *n*-octadecane have been determined and the corresponding activity coefficients have been computed. It has been demonstrated that, by using Wilson's equation or the Scatchard-Hildebrand regular solution model, the solute activity coefficients can be predicted with good accuracy.

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## REFERENCES

- 1 H. Colin and G. Guiochon, *J. Chromatogr.*, 141 (1977) 289.
- 2 S.A. Wise, W.J. Bonnett, F.R. Guenther and W.E. May, *J. Chromatogr. Sci.*, 19 (1981) 457.
- 3 E. McLaughlin and H.A. Zainal, *J. Chem. Soc.*, (1959) 863.
- 4 E. McLaughlin and H.A. Zainal, *J. Chem. Soc.*, (1960) 2485.
- 5 P.B. Choi and E. McLaughlin, *Ind. Eng. Chem. Fundam.*, 22 (1983) 46.
- 6 P.B. Choi, C.P. Williams, K.G. Kenneth, G. Buehring and E. McLaughlin, *J. Chem. Eng. Data*, 30 (1985) 403.
- 7 J.M. Prausnitz, R.N. Lichtenthaler and E. Gomes de Azevedo, *Molecular Thermodynamic of Fluid Phase Equilibria*, 2nd Edn., Prentice-Hall, Englewood Cliffs, NJ, 1986.
- 8 G.M. Wilson, *J. Am. Chem. Soc.*, 86 (1964) 127.
- 9 E.W. Funk and J.M. Prausnitz, *Ind. Eng. Chem.*, 62 (1970) 8.
- 10 J.E. Coon, M. Troth and E. McLaughlin, *J. Chem. Eng. Data*, 32 (1987) 233.
- 11 E. Martin, S.H. Yalkowsky and J.E. Wells, *J. Pharm. Sci.*, 68 (1979) 565.
- 12 S.H. Yalkowsky and S.C. Valvani, *J. Pharm. Sci.*, 69 (1980) 912.
- 13 D.R. Wauchop and F.W. Getzen, *J. Chem. Eng. Data*, 17 (1972) 38.
- 14 E. McLaughlin and R.A. Ubbelohde, *Trans. Faraday Soc.*, 53 (1957) 628.
- 15 R.C. Reid, J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, 4th Edn., McGraw-Hill, New York, 1987, pp. 729, 732.
- 16 C.-F. Chien and R.J. Laub, *Bull. Soc. Chem. Beograd*, 48 (1983) 319.
- 17 N.M. Djordjevic, *Thermochim. Acta*, 143 (1989) 171.
- 18 J.H. Hildebrand and C.A. Jenks, *J. Am. Chem. Soc.*, 42 (1920) 2180.