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Comparison of the solubility of polycyclic aromatic hydrocarbons in non-associated and associated solvents: The hydrophobic effect

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Summary

A remarkable improvement of the predictions of the solubility, Φ_B, of a solute B in a solvent S is achieved by the theory of the mobile order of Huyskens. In this theory, the hydrophobic effect of the associated solvents like alcohols against inert substances is no longer considered as a result from a change in the energy of the molecular interactions, but as a decrease of the entropy due to temporary correlated displacements of two or more hydroxylic groups of solvent molecules. Such correlated displacements create a kind of mobile order. Quantitatively, the hydrophobic effect reduces ln Φ_B by an amount of $r_S \Phi_S V_B / V_S$. A direct consequence of this effect is that an increase in the ratio V_B/V_S of the molar volumes, which in non-H-bonded solvents is favourable for the solubility, becomes unfavourable in alcohols. For polycyclic aromatic hydrocarbons, the prediction of the solubilities in apolar, polar and associated solvents by the mobile order theory necessitates the knowledge of a single parameter only which can be deduced from one experimental solubility.

Introduction

The theory of the mobile order in liquids initiated by Huyskens and Siegel (Huyskens and Siegel, 1988; Huyskens, 1990; Siegel et al., 1990) constitutes the basis of a new thermodynamic treatment of the liquid state. The quantitative development of this theory led to equations describing the effect of solvent-solvent, solute-solvent and solute-solute interactions on the chemical potential of the solute. A universal solubility equation (Ruelle et al., 1991) has therefore been derived for solid (liquid) substances. This equation takes into account the different contributions to the free-energy change when a solid solute B is dissolved in a solvent S. A recent paper (Ruelle et al., 1992) has demonstrated the validity of Huyskens' model in predicting the solubility of naphthalene at 40°C in non-polar, polar and hydrogen-bonded solvents. With respect to the different predictive models against which the results were tested, a remarkable improvement of the prediction was achieved by Huyskens' theory of mobile order, particularly in alcohols.

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In this article, we report the predictions of the solubility of three polycyclic aromatic hydrocarbons, i.e., naphthalene, anthracene and phenanthrene at 25°C. A comparison of the solubility of these solids in non-associated and associated solvents (alcohols), as well as a detailed analysis of the effect of H-bonds in alcohols on the solubility, are presented. However, because of the existence of weak specific interactions between the secondary OH groups of water and the aromatic substances, the solubility in water as associated solvent has not been considered throughout this work.

The Solubility Equation

For inert solutes (inert in the sense that they cannot form themselves H-bonds with the solvents), the solubility, Φ_B, in volume fraction is expressed by the product of three terms (Eqn 1) accounting respectively for the ideal solubility, the effect of differences in molar volumes between the solute and the solvent, and the influence of changes in non-specific cohesion forces upon mixing.

$$\Phi_B = e^A e^B e^D \tag{1}$$

where A is the fluidization constant and e^{-A} denotes the so-called 'ideal solubility'. The fluidization corresponds to the suppression of collective forces or to the suppression of rigidity of the molecules of the solute. At a given temperature, the fluidization term is independent of the solvent and the fluidization constant is calculated from the molar enthalpy of fusion, $\Delta_{melt}H$, and from the equilibrium melting temperature, T_m, of the pure crystalline substance.

$$A = -\Delta_{melt}H(1/T - 1/T_m)/R \tag{2}$$

When the solid undergoes a first-order phase transition between T and T_m, the fluidization constant must include an additional term for the contribution of the transition phase.

$$A = -\Delta_{melt}H(1/T - 1/T_m)/R - \Delta_{trans}H(1/T - 1/T_{trans})/R \tag{2'}$$

B represents a correction factor for the "placing" entropy resulting from the difference in the molar volumes of solvent and solute. According to Huyskens and Haulait-Pirson (1985a), this term depends on the volume fraction Φ_B of the solute and on the ratio V_B/V_S between the molar volumes in solution:

$$B = 0.5\Phi_S(V_B/V_S - 1) + 0.5 \ln(\Phi_B + \Phi_S V_B/V_S) \tag{3}$$

D is related to the changes in the non-specific cohesion forces when fluidized pure solute is mixed with the solvent. To a first approximation, this effect can be represented by a Scatchard-

TABLE 1

Physical properties of the polycyclic aromatic hydrocarbons

Property	Naphthalene	Anthracene	Phenanthrene
Melting point, T_m (K)	353.35 [a]	489.65 [a]	369.00 [b]
Enthalpy of fusion, $\Delta_{melt}H$ (kJ/mol)	18.803 [a]	28.800 [b]	18.600 [b]
Molar volume in solution, V_B (cm^3)			
Group contributions [c]	130.2	171.0	171.0
At the melting point [d]	127.1	178.9	169.2
Experimental solubility (X_B) in hexane	0.117 [e]	0.00127 [f]	0.0423 [g]
Modified solubility parameter, δ'_B (MPa$^{1/2}$)	19.400	20.144	19.768
Fluidization constant, A	1.185	4.544	1.507

[a] Gmehling et al. (1978); [b] James (1986); [c] Ruelle et al. (1991); [d] McLaughlin and Zainal (1959); [e] Heric and Posey (1964); [f] Acree (1991a); [g] Acree (1984).

Hildebrand expression (Scatchard, 1931) based on the geometric mean of Berthelot (1898). Using modified solubility parameters, δ', of the solute and of the solvent, the following expression is obtained:

$$D = -\Phi_S^2 V_B(\delta'_B - \delta'_S)^2/(RT) \qquad (4)$$

δ'_B and δ'_S differ from δ_B and δ_S of Hildebrand in that they do not include H-bonding contribution. The value of the modified solubility parameter, δ'_B, of the solute is deduced from an experimental solubility in an apolar solvent.

Results and Discussion

To predict the solubility of naphthalene, anthracene and phenanthrene by applying Eqn 1, one needs to know for each hydrocarbon the following physical properties: its melting point, T_m, its enthalpy of fusion, $\Delta_{melt}H$, its molar volume, V_B, in solution and its modified solubility parameter, δ'_B. The values of these properties for the three polycyclic aromatic hydrocarbons are given in Table 1. Note that the modified solubility parameters of these hydrocarbons have been deduced from their experimental solubility in hexane using the molar volumes calculated from group contributions. Furthermore, as phenanthrene undergoes a lambda point transition from about 331 to 361 K, its fluidization constant, A, at 25°C has been calculated according to the expression developed by Choi and McLaughlin (1983a).

The molar volumes, V_S, and the modified solubility parameters, δ'_S, of the solvents in which the solubilities of the solid hydrocarbons are predicted are listed in Table 2.

From the unique experimental solubility in hexane, and the values given in Tables 1 and 2, Eqn 1 enables predictions of solubility of naphthalene, anthracene and phenanthrene at 25°C in any solvent listed in Table 2. However, predictions have been made in solvents for which experimental solubilities were found in the literature. The results of these predictions as well as the corresponding experimental values are listed in Tables 3–5. The results have been arranged in increasing order of the modified solubility parameter of the solvent. An estimation of the quality

TABLE 2

Molar volume, V_S, and modified non-specific solubility parameter, δ'_S, of various solvents at 25°C

Solvent	V_S (cm^3 mol^{-1})	δ'_S (MPa$^{1/2}$)
n-Hexane	131.6	14.56
n-Heptane	147.5	14.66
n-Octane	163.5	14.85
n-Hexadecane	294.1	15.61
Squalane	525.0	16.25
Cyclohexane	108.8	14.82
Methylcyclohexane	128.3	15.00
Cyclooctane	134.9	15.40
Isooctane	166.1	14.30
Benzene	89.4	18.95
Toluene	106.9	18.10
Ethylbenzene	123.1	18.02
p-Cymene	156.0	20.20
m-Xylene	123.2	17.20
Tetraline	137.1	19.43
Carbon tetrachloride	97.1	17.04
Chloroform	80.7	18.77
1,2-Dichloroethane	78.8	20.99
1,1-Dibromoethane	92.9	18.77
1,2-Dibromoethane	87.0	20.75
n-Chlorobutane	105.0	17.12
1,4-Dichlorobutane	112.1	19.78
Chlorobenzene	102.1	19.48
Bromobenzene	105.3	21.22
Nitrobenzene	102.7	21.77
Pyridine	80.9	20.94
Carbon disulfide	60.0	20.50
Thiophene	79.6	18.70
Acetone	74.0	21.91
Diethyl ether	104.8	18.78
Dibutyl ether	170.3	17.45
Dipentyl ether	204.0	16.16
Dioxane	85.8	20.89
Methyl formate	62.1	22.96
Butyl acetate	132.5	19.66
Methanol	40.7	19.25
Ethanol	58.7	17.81
1-Propanol	75.1	17.29
1-Butanol	92.0	17.16
1-Pentanol	108.6	16.85
1-Octanol	158.3	16.38
Furfuryl alcohol	86.5	18.99

of the prediction is furthermore given by the relative error defined by Eqn 5:

$$\text{deviation } (\%) = 100.0(X^{\text{pred}} - X^{\text{exp}})/X^{\text{exp}} \quad (5)$$

On the basis of the information obtained from Eqn 5, it becomes evident that Eqn 1 is appropriate to predict the solubility of the solid aromatic hydrocarbons in non-associated solvents, but completely fails in predicting the solubilities in alcohols. Therefore, the results will be discussed separately for each of the two sets of solvents.

Solubility in non-associated solvents

For all the non-H-bonded solvents, Eqn 1 predicts the correct order of magnitude of solubility for each of the aromatic hydrocarbons. Except for a few cases, the relative deviations do not exceed ±30% and the largest deviations are observed for ethers, esters and ketones. The origin of these errors is not clear, since, for example, the deviations observed in acetone respectively amount to 21.6, 152.4 and 28.1% for naphthalene, anthracene and phenanthrene. The calculated solubility of naphthalene in acetone at 40°C only deviates by an amount of 11.5% (Ruelle et al., 1992). It can therefore be supposed that part of the deviations are related to the measurements, the values of which originate from different sources. Another part of the deviations should certainly be attributed to the manner in which the changes in the non-specific cohesion forces (term D) are represented in the solubility equation. The term D corresponds to a Scatchard-

TABLE 3

Experimental, X_B^{exp}, and predicted, X_B^{pred} (Eqn 1), solubilities (in molar fraction) of naphthalene at 25°C

Solvent	X_B^{exp}	X_B^{pred}	%	Reference
Non-associated solvent				
Cyclohexane	0.149	0.143	−4.0	Heric and Posey (1964)
Hexadecane	0.204	0.181	−11.4	Heric and Posey (1964)
CCl_4	0.259	0.272	4.8	Heric and Posey (1964)
m-Xylene (25.6°C)[a]	0.293	0.268	−8.5	Rhodes and Eisenhauer (1927)
Ethylbenzene	0.293	0.291	−0.6	Heric and Posey (1964)
Toluene	0.292	0.296	1.2	Heric and Posey (1964)
Thiophene (30.05°C)[a]	0.359	0.311	−13.2	Choi and McLaughlin (1983b)
1,1-Dibromoethane	0.324	0.307	−5.1	Sunier and Rosenblum (1928)
$CHCl_3$	0.332	0.312	−6.2	Williamson (1967)
Benzene	0.295	0.310	4.9	Heric and Posey (1964)
Tetraline (23.0°C)[a]	0.407	0.306	−24.8	Weissenberger (1927)
Chlorobenzene	0.313	0.308	−1.6	Ward (1926)
CS_2	0.292	0.320	9.6	Kröber (1919)
1,2-Dibromoethane	0.302	0.301	−0.4	Sunier and Rosenblum (1928)
Pyridine (24.45°C)[a]	0.303	0.301	−0.5	Choi and McLaughlin (1983b)
1,2-Dichloroethane	0.318	0.301	−5.4	Sunier and Rosenblum (1928)
Nitrobenzene	0.298	0.269	−9.9	Ward (1926)
Acetone	0.233	0.283	21.6	Ward (1926)
Methyl formate	0.137	0.264	92.7	Kröber (1919)
Associated solvent				
n-Octanol	0.132	0.225	70.8	Miller et al. (1985)
n-Pentanol	0.0811	0.259	219.7	Dickhut et al. (1989)
n-Butanol	0.0666	0.278	317.5	Dickhut et al. (1989)
n-Propanol	0.0505	0.293	479.7	Dickhut et al. (1989)
Ethanol	0.0398	0.316	694.0	Dickhut et al. (1989)
Furfuryl alcohol	0.0849	0.311	265.9	Sunier (1931)
Methanol	0.0235	0.342	1355.0	Dickhut et al. (1989)

[a] Temperature at which the solubility has been measured.

Hildebrand type expression and is based on the assumption that the cohesion energy density between unlike molecules S-B is equal to the geometric mean of the cohesion energy densities of the two equivalent like pairs, S-S and B-B. This rule is applicable to solutes such as polycyclic aromatic hydrocarbons dissolved in hydrocarbons or halogenated hydrocarbons, since solutes and solvents are all predominantly dispersive in nature, but fails when the aromatic hydrocarbons are dissolved in solvents containing small polar molecules like diethyl ether, acetone or methyl formate. For such solvents, it should be borne in mind that Eqn 1 always overpredicts the solubility with respect to the experimental results.

As the logarithm of the solubility, ln Φ_B, results from the sum of three terms, it is interesting to analyze the relative contributions of each of these terms to the solubility. In other words, this entails the evaluation of the relative importance of the melting properties of the solute, of the correction of the placing entropy and of the changes in the non-specific forces with respect to the solubility. For such a purpose, Figs 1–3 demonstrate, for each of the polycyclic hydrocarbons studied, the respective contributions of the

TABLE 4

Experimental, X_B^{exp}, and predicted, X_B^{pred} (Eqn 1), solubilities (in molar fraction) of anthracene at 25°C

Solvent	X_B^{exp}	X_B^{pred}	%	Reference
Non-associated solvent				
Isooctane	0.00107	0.00101	−5.3	Acree (1991a)
n-Heptane	0.00157	0.00135	−13.9	Acree (1991a)
Cyclohexane	0.00155	0.00161	4.1	Acree (1991a)
n-Octane	0.00184	0.00155	−15.8	Acree (1991a)
Methylcyclohexane	0.00165	0.00177	7.2	Acree (1991a)
Cyclooctane	0.00225	0.00231	2.5	Procyk et al. (1987)
n-Hexadecane	0.00380	0.00275	−27.6	McCargar and Acree (1987)
Dipentyl ether	0.00326	0.00361	10.7	Anderson et al. (1980)
Squalane	0.00472	0.00468	−0.8	McCargar and Acree (1987)
CCl_4	0.00630	0.00611	−3.1	Acree (1984)
n-Chlorobutane	0.00586	0.00614	4.8	Acree (1991b)
Dibutyl ether	0.00361	0.00649	79.7	McCargar and Acree (1987)
Toluene	0.00736	0.00856	16.3	Tucker et al. (1988)
Thiophene (24.25°C) [a]	0.0105	0.0112	6.2	Coon et al. (1988)
$CHCl_3$	0.0108	0.0112	3.4	Acree (1984)
Diethyl ether	0.00590	0.0101	70.6	Acree (1984)
Benzene	0.00810	0.0110	35.7	Acree (1984)
Chlorobenzene	0.0102	0.0112	9.4	Mahieu (1936)
Butyl acetate	0.00661	0.0107	61.1	Acree (1991a)
1,4-Dichlorobutane	0.0105	0.0111	5.2	Acree and Zvaigzne (1991)
p-Cymene	0.0117	0.0107	−8.9	Wheeler (1920)
CS_2	0.0109	0.0154	41.0	Acree (1984)
Dioxane	0.00838	0.0119	41.6	Procyk et al. (1987)
Bromobenzene	0.0119	0.0105	−11.5	Mahieu (1936)
Nitrobenzene	0.0103	0.00961	−6.7	Mahieu (1936)
Acetone	0.00431	0.0109	152.4	Mahieu (1936)
Associated solvent				
n-Octanol	0.00187	0.00404	116.2	Miller et al. (1985)
n-Propanol	0.000371	0.00771	1978.0	Mahieu (1936)
Ethanol	0.000800	0.0112	1297.2	Acree (1984)
Methanol	0.000326	0.0221	6684.8	Merck (1989)

[a] Temperature at which the solubility has been measured.

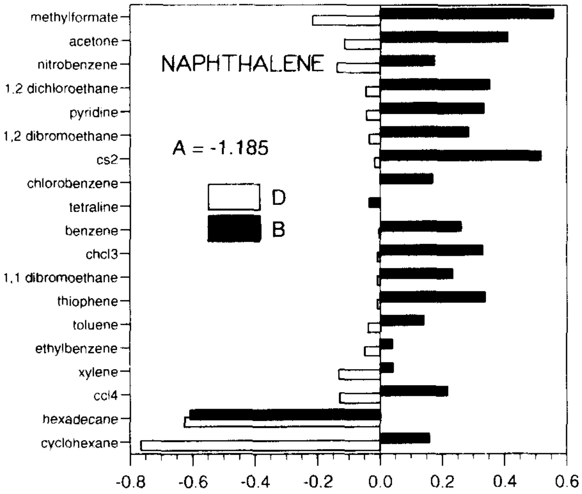

Fig. 1. Contributions of the fluidization (A), of the mixing entropy correction (B) and of the change in cohesion forces (D) to the solubility of naphthalene in non-associated solvents at 25°C.

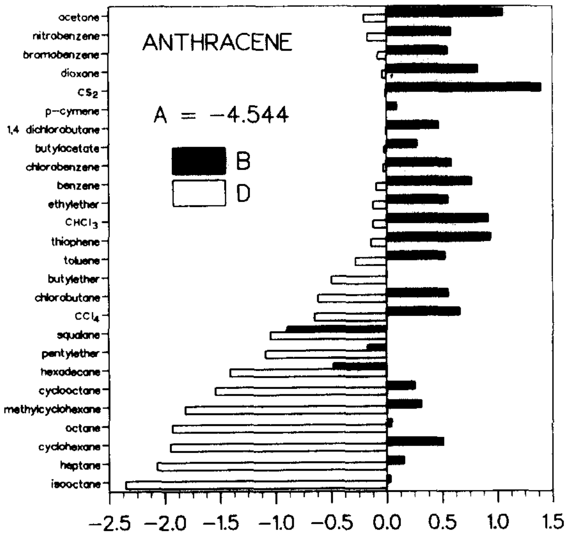

Fig. 2. Contributions of the fluidization (A), of the mixing entropy correction (B) and of the change in cohesion forces (D) to the solubility of anthracene in non-associated solvents at 25°C.

terms A, B and D vs the solvents arranged in increasing order of their modified solubility parameter, δ'_S. First of all, the diagrams show that the solubility of the solid aromatic hydrocarbons is mainly governed by their melting properties: the melting process represents the most important hindrance to the solubility (the absolute value of A is greater than the two other terms but has a negative sign). For anthracene in particular, the energy which must be supplied in order to lead to the disruption of the crystal is so high that its solubility remains low. Irrespective of the solvent, the solubility of anthracene is about 25-times

TABLE 5

Experimental, X_B^{exp}, and predicted, X_B^{pred} (Eqn 1), solubilities (in molar fraction) of phenanthrene at 25°C

Solvent	X_B^{exp}	X_B^{pred}	%	Reference
Non-associated solvent				
Cyclohexane (27.4°C)	0.0402	0.0570	41.9	McLaughlin and Zainal (1960)
CCl_4	0.185	0.179	−3.1	Acree (1984)
Toluene	0.221	0.209	−5.5	Speyers (1902)
Thiophene (26.3°C) [a]	0.238	0.234	−1.6	Choi and McLaughlin (1983b)
$CHCl_3$	0.268	0.234	−12.6	Henstock (1922)
Diethyl ether	0.151	0.223	47.5	Acree (1984)
Benzene	0.2078	0.231	11.7	Acree (1984)
CS_2	0.255	0.252	−1.0	Acree (1984)
Pyridine (26.7°C) [a]	0.246	0.232	−5.7	Choi and McLaughlin (1983b)
Acetone	0.171	0.219	28.1	Henstock (1922)
Methyl formate	0.0808	0.204	153.0	Kröber (1919)
Associated solvent				
n-Octanol	0.0597	0.122	104.3	Miller et al. (1985)
Ethanol	0.0140	0.240	1616.3	Henstock (1922)
Methanol	0.00749	0.274	3562.4	Henstock (1922)

[a] Temperature at which the solubility has been measured.

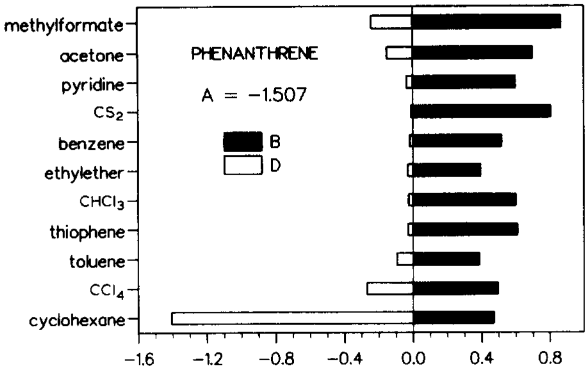

Fig. 3. Contributions of the fluidization (A), of the mixing entropy correction (B) and of the change in cohesion forces (D) to the solubility of phenanthrene in non-associated solvents at 25°C.

lower than that of its isomer phenanthrene. Besides the contribution of the term A in Eqn 1, the relative effects of the correction of the placing entropy (B) and of the changes in the nonspecific cohesion forces (D) depend on the solvent in which the solute is dissolved. The contribution of the term D can be neglected for solvents the modified solubility parameter of which is close to that of the aromatic hydrocarbon. In contrast, this contribution, which is always negative, results in a decrease of the solubility as much as the modified solubility parameter of the solvent differs from that of the solute. This endothermic effect explains the relatively low solubility of the aromatic hydrocarbons in aliphatic alkanes or cycloalkanes. Finally, the contribution of B is important only when the volumes of the solvent and of the solute are markedly different from each other. When the volume of the solvent is smaller than that of the solute, the sign of B is positive and the corresponding effect leads to an increase in the solubility. In the opposite case, as for hexadecane, tetraline or squalane, the contribution of B is negative and the solubility decreases.

Solubility in alcohols

As can be seen from Tables 3–5, the experimental solubilities of the solid aromatic hydrocarbons are lower in alcohols than in the non-associated solvents, and Eqn 1 completely fails in predicting the solubilities in such solvents. Not only are the calculated values always largely overestimated, but their evolution within the series of alcohols proceeds in the opposite direction to the measured values. The lower solubilities must be assigned to the presence in alcohols of H-bonded chains of the type OH--OH--OH--OH--OH. To account for the influence of such self-associations on the solubility, Huyskens and Haulait-Pirson (1985b) proposed a new model for H-bonded liquids. This model differs from the classical ones in considering a single equilibrium between two possible situations for the hydroxylic proton: the free and the bonded state. Owing to the labile character of these H-bond associations, the alcohol molecules regularly pass through the free state which remains the reference state. The formation of a hydrogen bond by the OH group of an alcohol will bring the hydroxylic proton into the vicinity of the oxygen atom of a neighbouring molecule during a much longer fraction of time than that governed by random contacts. These preferential contacts introduce a kind of order into the liquid, referred to as the 'mobile' order because of their perpetually changing character. The fact that the OH proton of a liquid alcohol has to follow the oxygen atom of a neighbouring molecule during more than 99% of the time restricts the freedom of this proton to visit the other parts of its domain. The mobile order corresponds to a decrease in the molar entropy. The dissolution of a foreign inert substance like a polycyclic hydrocarbon in the alcohol further increases the reduction in the freedom of the proton. This constitutes the main part of what is called the 'hydrophobic effect' which is at the origin of the lowered solubility of an inert substance in associated solvents.

In contrast to what is generally assumed, the hydrophobic effect is not caused by the necessity of breaking H-bonds of the solvent in order to introduce the molecule of the solute, but has a purely entropic nature that cannot be explained on the basis of the classical thermodynamic treatments of the liquid which consider this phase as a kind of deformed crystal (pseudo-lattice). In fact, the hydrophobic effect finds a natural explanation and also a quantitative prediction in the frame of the mobile order in liquids.

This theory starts from the statement that, in a liquid, all molecular groups perpetually move, and that the neighbours of a given external atom of a molecule constantly change identity. If we consider for instance an H atom of a CH_3 group of hexane in the liquid phase, this atom will be successively in contact with other CH_3 groups and with CH_2 groups. It can be said that the H atom being considered perpetually visits the various parts of its domain, characterized by different neighbours. The theory of the mobile order considers that this freedom of 'visiting' constitutes an essential part of the entropy of liquids compared to that of crystals.

This freedom of visiting is suppressed during a large part of the time for the H atom involved in a hydrogen bond. In pure methanol, the OH proton follows the oxygen atom of a neighbouring molecule for 99% of the time of its peregrination through the liquid, or renounces its right of visiting its domain for 99% of the time. If methanol is diluted by the same volume of hexane, the hydroxylic proton will follow a neighbouring oxygen atom for 98% of the time. The effect of this temporary renouncement of the OH group to visit its domain on the entropy of the liquid can be evaluated. During the fraction $(1-\gamma)$ of the time that it is involved in H-bonding, the proton under consideration occupies a small part V_0 at the border of its domain instead of visiting the whole. The domain DomA is the volume of the liquid V divided by the number, N_{alc}, of alcohol molecules. Both V_0 and DomA are perpetually moving and not localisable with respect to external axes but the ratio V_0/DomA has a well defined value.

The reduction of the entropy caused by the mobile order is given, when γ is very small, by the expression:

$$\Delta S_{\text{mobile order}} = R\ \ln(V_0/\text{DomA})$$
$$= R\ \ln(V_0 N_{alc}) - R\ \ln V$$

When a hydrocarbon is added to the alcohol, $V_0 N_{alc}$ remains unchanged but the volume V of the liquid increases and ΔS becomes more negative. *Such a decrease in entropy constitutes the essence of the hydrophobic effect.*

The quantitative treatment of this effect (Huyskens and Haulait-Pirson, 1988a,b) shows

TABLE 6

Experimental X_B^{exp} and predicted (Eqn 7) X_B^{pred} solubilities (in molar fraction) of naphthalene, anthracene and phenanthrene at 25°C, in alcohols along with the contributions, B, D and F to the solubility

Solvent	X_B^{exp}	X_B^{pred}	%	B	D	F
Naphthalene ($A = -1.185$)						
Methanol	0.0235	0.0252	7.4	1.570	−0.001	−2.954
Ethanol	0.0398	0.0438	10.2	0.925	−0.109	−2.013
n-Propanol	0.0505	0.0567	12.4	0.587	−0.192	−1.570
n-Butanol	00666	0.0707	6.2	0.347	−0.215	−1.278
n-Pentanol	0.0811	0.0783	−3.4	0.173	−0.281	−1.088
n-Octanol	0.132	0.0965	−26.8	−0.171	−0.405	−0.756
Furfuryl alcohol	0.0849	0.0841	−1.0	0.406	−0.007	−1.322
Anthracene ($A = -4.544$)						
Methanol	0.000326	0.000366	12.3	2.315	−0.055	−4.195
Ethanol	0.000800	0.000608	−24.0	1.489	−0.374	−2.908
n-Propanol	0.000371	0.000785	111.5	1.048	−0.560	−2.273
n-Octanol	0.00187	0.00137	−26.9	0.079	−0.974	−1.079
Phenanthrene ($A = -1.507$)						
Methanol	0.00749	0.00878	17.2	2.247	−0.017	−4.051
Ethanol	0.0140	0.0160	14.3	1.433	−0.241	−2.781
n-Octanol	0.0597	0.0380	−36.3	0.076	−0.728	−1.036

that, at the equilibrium between the solid phase B and the solution, the logarithm of the solubility, ln Φ_B, is diminished by an amount expressed by the F term (Eqn 6):

$$F = r_S \Phi_S V_B / V_S \qquad (6)$$

where r_S represents the 'structuration factor' of the solvent that takes the value -1 for strongly associated solvents with single H-bond chains like alcohols and 0 for non-associated solvents.

Hence, the predictive solubility equation for hydrocarbons in alcohols becomes:

$$\Phi_B = e^A e^B e^D e^F \qquad (7)$$

The last term represents the hydrophobic effect of the association of the solvent on the solubility of a solid inert substance.

The solubilities of naphthalene, anthracene and phenanthrene in alcohols as predicted according to Eqn 7 are compared to the experimental values in Table 6. Now, the predictions always give the correct values of solubilities, the relative errors being of the same order of magnitude as those observed for the non-associated solvents.

If one excludes the importance of the melting properties of the solid solute previously mentioned, the comparison among each of the values of the three contributions B, D and F (Table 6) to the solubility demonstrates the predominant influence of the hydrophobic effect. Without this term, it is quite impossible to correctly predict the solubility in alcohols. Furthermore, a direct consequence of this effect is that, for a given solute, any increase in the molar volume, V_S, of the solvent which normally disfavours the solubility of the aromatic hydrocarbons in non-associated solvents, promotes it in alcohols as shown for naphthalene in Fig. 4.

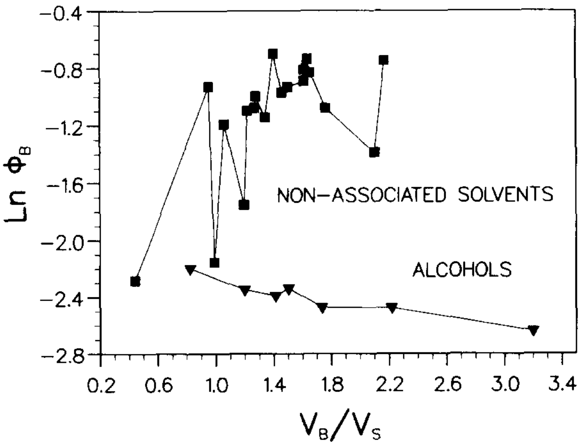

Fig. 4. Experimental solubility (ln Φ_B) of naphthalene at 25°C in alcohols and non-associated solvents vs the ratio, V_B/V_S, of the molar volumes of the naphthalene, B, and of the solvent S.

Moreover, a final consequence of the hydrophobic effect is that associated solvents will never form regular solutions, hence explaining the inability of the classical models of solubility to predict the solubility in associated solvents without the inclusion of adjustable parameters.

Conclusion

Based on a limited number of characteristics of the solutes and of the solvents, the solubility equation (Eqn 7) derived from the mobile order thermodynamics allows one to quantitatively predict the solubilities of solid polycyclic aromatic hydrocarbons in non-associated and associated solvents. The equation takes into account the various contributions to the free energy change when a solid solute B is dissolved in a solvent S: the fluidization of B, the entropy of mixing, the change in the non-specific cohesion forces, and for self-associated solvents the hydrophobic effect. In contrast to what is generally assumed, the hydrophobic effect results neither from the breaking of H-bonded chains in order to create a cavity necessary for placing the hydrocarbon molecule, nor from the breaking of some special cohesion forces that should bind the hydrocarbons together, the so-called hydrophobic interactions. The hydrophobic effect which is at the origin of the lowered solubility of the hydrocarbons in alcohols with respect to the non-associated solvents has a purely entropic nature: it originates from the extension of the domain, DomA, of one alcohol molecule as a consequence of the addition of the inert substance which increases the negative value of the entropy of mobile order.

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