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The Solvent Dependence of the Solubility of Organic Solids, and Solubility Parameter Theory: Investigation by Means of an Organic Pigment

A. Grubenmann

Ciba-Geigy AG, Forschungszentrum Marly, CH-1723 Marly, Switzerland

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ABSTRACT

The dependence of the solubility of organic solids on the solvents used is investigated experimentally by means of a test pigment. Due to the much higher molar enthalpy of fusion and melting point, the deviation from ideality or regularity is more pronounced in the case of organic pigments, compared with low-molecular solids, thus causing the amplification of specific effects.

In that context the area of applicability of the Hildebrand/Hansen solubility parameters is tested and discussed. Special findings concern π–π *interactions in solution, which are not described in the solubility parameter model, pigment association in polar-protic solvents, and the need to use virtual states of references for the quantitative description of the solubility of solids. These virtual liquid states are not identical with the hypothetical liquid state of the molten solid at solution temperature.*

NOTATION

a	Activity of solute
C_P	Heat capacity at constant pressure
C_S	Solubility of solid (mg/litre)
ΔE_V	Energy of evaporation
f	Total activity coefficient of solute
f_S^e	Enthalpic part of activity coefficient of solute

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F	Corrected logarithm of solubility of solid
ΔH_F^r	Real enthalpy of fusion
ΔH_F	Virtual enthalpy of fusion
ΔH_F^i	Virtual enthalpy of fusion belonging to the state of reference of solute in the ith solvent class
K, K_1, K_2	Constants
M	Molar weight
n_L, n_S	Number of moles in solution of solvent, and solute
R	Gas constant
T	Temperature of solution
T_F	Melting point
V	Molar volume of liquid
V_L, V_S	Molar volumes of solvent, and solute
x, x_S	Solubility of solid (molar fraction)
δ	Hildebrand solubility parameter
$\delta_D, \delta_P, \delta_H$	Hildebrand/Hansen solubility parameters, concerning dispersion, polarity, hydrogen bonding
$\vec{\delta}$	Vectorial description of $(\delta_D, \delta_P, \delta_H)$
$\vec{\delta}_i^L$	Mean solubility parameter vector of the ith solvent class
$\vec{\delta}^S$	Solubility parameter of solute, in general, or for virtual state of reference
$\vec{\delta}_i^S$	Solubility parameter vector of the solute, describing the state of reference in the ith solvent class
$\vec{\delta}_o^S$	Solubility parameter vector for the primary state of reference of the solute
λ_i	Constants
μ_S	Chemical potential of solid
μ_F'	Standard chemical potential of solute in virtual reference state $(\varphi_S = 1)$
φ_L, φ_S	Volume fractions of solvent, and solute

INTRODUCTION

This investigation is part of a project on crystallization phenomena of organic pigments, where topics like solubility, particle size distributions,[1] interfacial tension and recrystallization are involved. Here we look at means to generalize the influence of solvent characteristics on solubility. The results are valid also for other organic solids. However, due to much stronger intermolecular interactions in the solid state of pigments, the phenomena involved in the process of dissolution are more pronounced with pigments.

Even though the solubility of pigments is very low by usual standards, it plays an important rôle in at least two sectors of pigment technology: at the stage of synthesis and conditioning, solubility considerations govern the appropriate choice of solvents and crystal growth conditions in order to obtain specified particle size distributions, taking into account the rates of formation of the pigment molecules.

On the other hand, the application properties of commercial organic pigments depend strongly on the particle size of the pigment crystals. Not only colouristic properties like colour strength or shade, but also noncolouristic properties like weather fastness, dispersibility and flocculation behaviour are influenced by particle size.

A constant particle size distribution during the storage and manufacture of pigment formulations is of paramount importance. Thus, during the storage of liquid formulations like printing inks, or paints, no particle coarsening through recrystallization is allowed. Within pigmented thermoplastic materials, particle coarsening, or, with inferior pigments, even total dissolution may happen, due to the high manufacturing temperature of up to 300°C. Migration fastness, and resistance to bleeding of pigmented substrate are other effects influenced by particle size.

The cause for these special application properties of pigments is their solubility during the critical phase of application. Generally, of course, it is not necessary to measure the solubilities; results of application tests yield sufficient information on a case-by-case basis, for the selection and development of new pigments. However, knowledge on the general relationships between the solubilities and the substrate properties for particular pigment classes is of a broader usefulness. Therefore, for a representative pigment of the newer generations, the solvent dependence of the solubility was investigated.

Another aim of the investigation was to develop an equation for the quantitative description of the solubility of pigments using solubility parameter theory. This allows one to substitute the discrete properties of individual solvents by means of numerical parameters and to make a quantitative nondiscrete link between the solubilities in different solvents. Experimental testing of the solubility equation exhibits the range of validity and gives indications on exceptions and special effects not accessible by other methods.

TEST PIGMENT

Contrary to the high-grade pigments of earlier generations, the extremely low solubility of more recent products is not mainly due to a very high molecular weight of larger than 1000 and, in some cases, rigid molecular geometry.

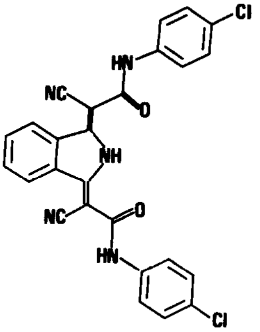

Fig. 1. Test substance: 1,3-bis(cyano-*p*-chlorophenylcarbamoyl-methylen)isoindolin.

With newer pigments the 'insolubility' depends to a large degree on the strength of the intermolecular hydrogen bonding in the solid.

For the present investigation, a member of the isoindoline pigment class[2] was selected (Fig. 1), which shows sufficiently high solubilities in solvents, according to the needs of the analytical method used. However, typical high-grade pigments show appreciably lower solubilities than the selected specimen.

As is known from X-ray structure analysis,[2] hydrogen bonding occurs between amide-protons and cyano groups of neighbouring molecules in the solid state. This leads to ribbon-like linking (Fig. 2) and consequently to solubility depression. On the other hand, the imide group contributes nothing to the insolubility through intermolecular hydrogen bonding, because of existing intramolecular bonds towards the two carbonyl groups.

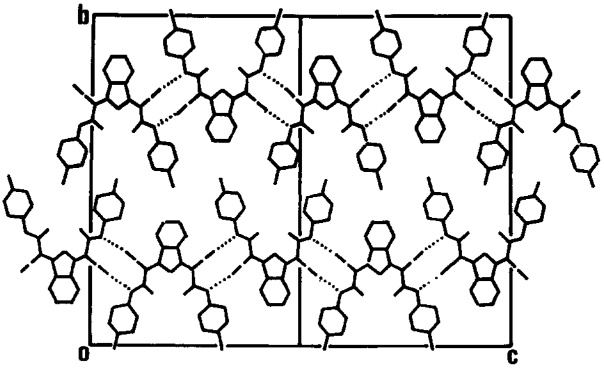

Fig. 2. Formation of linear chains via hydrogen bonding in the solid state of the test pigment.

THERMODYNAMICS OF THE SOLUBILITY OF SOLIDS

In thermodynamics, the solubility in solvents may be described by the following equation[3] (for a list of symbols, see Notation):

$$a = f \cdot x = \exp\left[-\frac{\Delta H_{\mathrm{F}}^{\mathrm{r}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{F}}}\right)\right] \tag{1}$$

In accordance with the extremely small solubilities of good organic pigments, the molar enthalpies of fusion and the melting points are fairly large, in fact much larger than those of common organic solids of lower molecular weight (Table 1). This is also an indication of considerably different behaviour, be it in the solid state or in solution.

Equation (1) describes the process of mixing the hypothetically liquefied solid with solvent at the temperature T of solution. Thus, the state of reference for mixing consists of the substance, fused at the melting point T_F and cooled down to the temperature of mixing. T, as a hypothetical liquid. The solubility in any solvent could be calculated, if the relationships between the activity coefficient f and the properties of the solvents and the liquefied solid were known.

In that context, thermodynamic models like UNIFAC,[4–6] or its extended form SUPERFAC[7], are of interest. They allow the calculation of intermolecular interactions by means of group increments, for example, to determine the activity coefficient f in (1). Other group-increment models for the calculation of activity coefficients for liquid mixtures, such as NRTL, ASOG or MOSCED are formally equivalent.[8,9] Such models are applied with good success in chemical engineering for problems concerning liquid/vapour and liquid/liquid equilibria, e.g. distillation and extraction.[10–12] Also, problems concerning polymer solutions may be solved by means of UNIFAC.[13,14] Recently solubility problems concerning the area of pharmaceutical chemistry were treated with this model.[15–18]

In many fields of technical chemistry, such as the pigment sector, qualitative surveys on the solvent dependence of solubility are needed rather than exact solubility data. For that purpose Hildebrand/Hansen solubility parameters[19] are rather better suited than the more sophisticated models.

TABLE 1
Thermodynamic Data of the Test Pigment

M (*g/mol*)	ρ (*g/cm*^{3})	T_F (°*C*)	ΔH_F (*kJ/mol*)	C_P (*J/g K; t in °C*)
500·36	1·498	406	123 ± 10	$0{\cdot}7141 + 4{\cdot}9112 \times 10^{-3}t - 2{\cdot}768 \times 10^{-6}t^2$

For chemists, that system is of special interest, because they are used to classifying solvents by means of similar criteria (polarity, proticity).

SOLUBILITY PARAMETERS

The solubility parameter as originally derived by Hildebrand[20] is defined in terms of the cohesion energy density:

$$\delta = \left(\frac{\Delta E_V}{V}\right)^{1/2} \tag{2}$$

This single parameter model was extended by Hansen[21-23] to a three-component system with contributions from dispersion forces δ_D, polar interactions δ_P, and hydrogen bonding δ_H. The relation to the former single parameter is given by

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{3}$$

For a variety of solvents, compilations of such parameters are given in Refs 19 and 24. Also, for polymers solubility parameters are available.[25] However, for typical solids no such compilation exists. One reason lies in the fact, that with solids, the meaning of solubility parameters depends on the properties involved in the application, e.g. surface properties, or the properties of the molten or dissolved solid.

Taking into account solubility parameters, and the Flory–Huggins size correction for dissimilar molar volumes of solute and solvents[25] (eqn (1)) can be expanded to:

$$\ln x_S = -\frac{\Delta H_F^r}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_F}\right) - \ln\left(\frac{\varphi_S}{x_S}\right) - \varphi_L\left(1 - \frac{V_S}{V_L}\right) - \ln f_S^e \tag{4}$$

with

$$\ln f_S^e = \frac{V_S \varphi_L^2}{RT} \cdot [(\delta_D^S - \delta_D^L)^2 + (\delta_P^S - \delta_P^L)^2 + (\delta_H^S - \delta_H^L)^2] = \frac{V_S \varphi_L^2}{RT} \cdot (\vec{\delta}^S - \vec{\delta}^L)^2 \tag{5}$$

where $\vec{\delta}$ is the vector notation of the Hildebrand/Hansen solubility parameter,

$$\vec{\delta} = (\delta_D, \delta_p, \delta_H) \tag{6}$$

φ is volume fraction, V is molar volume and indices S, L are solute and solvent.

According to eqn (5) the activity coefficient f_S^e cannot be smaller than 1. The model, therefore, is only valid for mixtures with positive enthalpy of mixing,[26] i.e. for substances where the effective solubility is smaller than the

TABLE 2
Quasiideal and Experimental Solubility (mg/litre at 20°C)

Solvent	C_S *(quasiideal)*	C_S *(experimental)*
N-methyl pyrrolidone	$3{\cdot}6 \times 10^{-3}$	780
N,N-dimethyl acetamide	$3{\cdot}0 \times 10^{-3}$	240

quasi-ideal solubility (with $f_S^e = 1$ in eqn (4)). This requirement is not fulfilled with the test pigment, as is obvious from the values given in Table 2; the experimental solubility is much higher than predicted by eqn (4), even taking into account the temperature dependence of the heat of fusion and the entropy term. Thus, for the test pigment, and presumably for others as well, solubilities cannot be described by eqn (4). Similar discrepancies between experimental and calculated solubilities were also found with *p*-hydroxybenzoic acid, methyl *p*-hydroxybenzoate, and benzoic acid.[16] The reason lies in the fact, that the hypothetical, liquid state of reference at the mixing temperature T is a highly excited state compared with the energy level of the solute in solution. Thus, during the mixing process energy of solvation is evolved.

In order to avoid this conceptual discrepancy, one may define another, virtual, liquid state of reference, characterized by means of the standard chemical potential μ_F^1 (at volume fraction $\varphi_S = 1$). The energy level of this virtual reference state is shifted in such a way that the Hildebrand/Hansen eqn (4) is valid. This state of reference corresponds, therefore, not with the supercooled fused substance but rather with a virtual state which lies energetically between the solid and liquid state. As a consequence, this defines a virtual heat of fusion ΔH_F. From the equation for the chemical equilibrium:

$$\mu_S = \mu_F^1 + RT \ln a \tag{7}$$

it follows through differentiation:

$$\frac{1}{R} \cdot \frac{\partial\left(\dfrac{\mu_S - \mu_F^1}{T}\right)}{\partial T} = \frac{\partial \ln a}{\partial T} \equiv \frac{\Delta H_F}{RT^2} \tag{8}$$

Integration of (8) and combination with (7) yields an expression which relates the virtual heat of fusion to the standard chemical potential.

$$\mu_F^1 = \lambda_1 \# \Delta H_F\left(1 - \frac{T}{T_F}\right) + \text{const.} \tag{9}$$

On the other hand, the standard chemical potential can roughly be set proportional to the energy of evaporation. The justification lies in the fact that both of them show a uniform development as a function of the difference between the virtual state of reference and the liquid state

$$\mu_F^1 = -\lambda_2 \# \Delta E_V \tag{10}$$

From the definition of the solubility parameters (eqn (2)), and in combination with eqns (9) and (10), an expression is obtained which relates virtual heat of fusion ΔH_F to the solubility parameter vector $\vec{\delta}^S$ of the state of reference.

$$V \cdot (\vec{\delta}^S)^2 = \lambda_3 \cdot \Delta H_F \left(1 - \frac{T}{T_F}\right) + \text{const.} \tag{11}$$

According to (11) the added constant turns out to define a primary state of reference $(\Delta H_F^0, \vec{\delta}_0^S)$, therefore:

$$\Delta H_F = \Delta H_F^0 + \lambda \cdot ((\vec{\delta}^S)^2 - (\vec{\delta}_0^S)^2) \tag{12}$$

This equation shows that ΔH_F and $\vec{\delta}^S$ are functionally interdependent. Accordingly, the difficulties in defining the appropriate states of reference $(\Delta_F, \vec{\delta}^S)$ are focused on the solubility parameter vectors. However, no algorithm for the calculation of $\vec{\delta}^S$ is known. It is however of principal interest to know what extent deviation from the regular solution concept[26] occurs. From experimental results it was found that a functional relationship between $\vec{\delta}^S$, $\vec{\delta}_0^S$ and $\vec{\delta}^L$ approximately holds:

$$(\vec{\delta}^S - \vec{\delta}_0^S) = f(\vec{\delta}^L - \vec{\delta}_0^S) \tag{13}$$

where

$$\vec{\delta}^S = \vec{\delta}_0^S, \quad \text{if} \quad \vec{\delta}^L = \vec{\delta}_0^S \tag{14}$$

The solubility eqn (4) can now be re-formulated, taking into account eqns (12)–(14) for the description of the respective virtual state of reference $(\Delta H_F, \vec{\delta}^S)$.

$$\ln C_S = -\frac{\Delta H_F}{R}\left(\frac{1}{T} - \frac{1}{T_F}\right) - \ln\left(\frac{V_S}{M}\right) + \left(\frac{V_S}{V_L} - 1\right) - \frac{V_S}{RT}\left(\vec{\delta}^S - \vec{\delta}^L\right)^2 \tag{15}$$

In eqn (15) an additional approximation for the volume fraction is involved. In view of the low solubility of pigments,

$$n_S \cdot V_S \ll n_L \cdot V_L \tag{16}$$

the following approximations result (n_S, n_L are number of moles of solute and solvent, C_S is solubility of solid (in g/litre)):

$$\frac{\varphi_S}{x_S} = \frac{V_S}{V_L} \tag{17}$$

$$C_S = \varphi_S \cdot \frac{M}{V_S} \tag{18}$$

$$\varphi_L \approx 1 \tag{19}$$

Inspection of eqns (12)–(15) shows that the pigment solubility can entirely be expressed as a function of the solubility parameters of solvent $\bar{\delta}^L$ and the volume fraction V_S/V_L, if eqn (13) is expanded into a power series.

$$\ln C_S = \frac{V_S}{V_L} + k_o + \sum_j \sum_n (k_{jn} \cdot (\delta^L_{jn})^n, \quad j = \mathrm{D, P, H} \tag{20}$$

In the simplest case, an equation with the highest power $n = 2$, with 7 adjustable constants, results. This equation corresponds to the equation of Richardson *et al.*,[27] which showed a high level of correlation, when applied to pharmaceuticals. Due to the fact that pigments show much higher melting points, and also much higher heats of fusion than common pharmaceuticals, probably the simplest equation should not give a correlation as good as with pharmaceuticals. In fact, the test pigment shows a five times higher heat of fusion and a melting point 159° higher than the compound applied by Richardson *et al.*

In accord with the equations shown the principal aim of the experimental investigation using a test pigment can thus be reformulated:

—to test the power series, eqn (20) on its reliability for pigments;
—to determine virtual enthalpies of fusion and to compare with the real enthalpy of fusion;
—to investigate special features not covered by the solubility equation.

EXPERIMENTAL CONDITIONS AND SOLUBILITIES

In order to determine the solubilities, solvents were equilibrated with excess pigment, decanted, and concentrations measured by spectrophotometry. To test the model described in the preceding section, solubilities had to be measured in pure solvents and in mixtures of solvents. Due to the weakly acid character of the imide group it was necessary to add small amounts of acetic acid to some of the solvent in order to prevent dissociation, which may increase the solubility. However, in acidified mixtures containing water, considerable decomposition of the pigment takes place. Here it was thus necessary to make the measurements at pH 7.

A pigment sample was used, which was recrystallized from dimethylformamide at 90°C under argon, resulting in pigment crystals larger than 5 μm. To prepare the saturated solutions, a maximum excess of 10 times the amount of dissolved pigment was used, depending on the solubilities. The pigment slurries were stirred (magnetic bars) during 24 h at 60°C. To prevent reaction with oxygen in some of the solvents (probably due to the formation of hydroperoxides) the equilibration was performed under argon. After removing the stirring bars, and after a sedimentation time of 24 h, aliquots of the solutions were carefully taken with pipettes, then diluted with tetrahydrofuran. After addition of 1% formic acid the concentrations were determined spectrophotometrically on a Perkin-Elmer-Lambda 9 spectrophotometer by comparing with standard solutions. With some of the measurements, corrections to the observed extinction values had to be made due to interfering decomposition products. The accuracies of the measurements differ, and depend on the solvents used. The maximum error is estimated to ±20% of the measured concentration. Commercial solvents of quality purissimum, or purum (Fluka, Merk) were used, without further purification. The method used to measure the solubility in water is based on ultrafiltration through 0·2 μm Teflon Millipore filters and up-concentration by means of extraction (20 ml hexane/2 litres water, taking into account the partition coefficient).

The melting point and enthalpy of fusion were measured with a Perkin-Elmer DSC-2 apparatus under nitrogen. Due to thermal decomposition of the pigment, the melting point and the heat of fusion could be established approximately only at heating rates of 40 K/min and 160 K/min. Also due to decomposition it was not possible to measure the specific heat of the liquefied pigment.

Solubility parameters and molar volumes of the solvents were taken from Ref. 19. For mixtures of solvents the respective values were calculated by means of the following approximations:

$$\delta_j^{\mathrm{L\,mixture}} = \varphi_{\mathrm{L1}} \cdot \delta_j^{\mathrm{L1}} + (1 - \varphi_{\mathrm{L1}}) \cdot \delta_j^{\mathrm{L2}}; \quad j = D, P, H \tag{21}$$

$$V_{\mathrm{L}}^{\mathrm{mixture}} = \frac{1}{\dfrac{\varphi_{\mathrm{L1}}}{V_{\mathrm{L1}}} + \dfrac{(1 - \varphi_{\mathrm{L1}})}{V_{\mathrm{L2}}}} \tag{22}$$

Although the solubilities were determined at 60°C, the errors resulting from the use of solubility parameters valid at 25°C are negligible. Besides, temperature corrected values, if necessary, could be calculated according to Ref. 19.

RESULTS

The solvents used, the appropriate solubility parameters and molar volumes, and the measured solubilities are presented in Table 3. They are grouped into classes which proved to be useful for the analysis of the data.

As can be seen, the experimental solubilities span a range of eight decades, indicating strongly different interactions between pigment and solvent molecules. A nonlinear regression analysis according to eqn (20) showed, as expected, that the correlation for the test pigment is indeed not so good as for pharmaceuticals. Only with a highest power of 5 in the power series does a leveling of the standard error occur. However, also in this case, the residuals for some of the solvents are still very large, as can be seen in Table 3. Obviously, the model developed is not adequate enough for compounds of very high heats of fusion and high melting points. Even if taking account of virtual liquid reference states the solute does not show the same interaction behaviour as the solvents in the thought process of mixing. This fact will cause severe problems not only in models using solubility parameters, but also in more sophisticated models for the solubility of solids.

However, part of the residuals for some of the solvents may still have other causes. In order to find the special features which could cause a deviation from normal behaviour, a graphical evaluation was performed. For every solvent class of Table 3 a particular virtual state of reference was defined, which is characterized by individual ΔH_F^i, δ_D^i, δ_P^i, δ_H^i. As an example, the logarithms of the corrected solubilities of the pigment in one group of solvents are presented in Fig. 3 as a linear function of $(\vec{\delta}_i^{\,S} - \vec{\delta}^{\,L})^2$, according to:

$$F \equiv \left(\ln C_S - \frac{V_S}{V_L}\right) = K - \frac{V_S}{RT}\cdot(\vec{\delta}_i^S - \vec{\delta}^L)^2 \tag{23}$$

where

$$K = -\frac{\Delta H_F^i}{R}\cdot\left(\frac{1}{T} - \frac{1}{T_F}\right) - \ln\left(\frac{V_S}{M}\right) - 1 \tag{24}$$

In the calculation of F values a constant V_S value of 350 cm^3 was used. For δ_D^S only a mean value of 11 cal$^{1/2}$ cm$^{-3/2}$ was estimated, due to lack of large differences of the δ_{Dj}^S within the individual solvent classes. Then, for each class δ_{Pi}^S and δ_{Hi}^S were optimized. The determined virtual reference states of the pigment with regard to individual solvent classes are grouped in Table 4. As expected, for strongly protic solvents, showing only weak interactions with the pigment, the difference between the virtual and real enthalpy of fusion is small, indicating a reference state which is similar to the standard state of the liquified, undercooled solid. On the other hand, for good solvents the shift of the virtual state of reference is large.

TABLE 3
Solubilities of the Test Pigment, and Solubility Parameters and Molar Volumes of the Solvents

Solvent	V_L	δ_D^L	δ_P^L	δ_H^L	*Solubility*	$ln(C_{exp}/C_{calc})$
	(cm^3/mol)	*($cal^{1/2}\ cm^{-3/2}$; 25°C)*			*(mg/litre; 60°C)*	
Aprotic-polar solvents, and carboxylic acids						
N-methyl pyrrolidone	96·5	8·8	6	3·5	9 100	1·57
N,N-dimethyl acetamide	92·5	8·2	5·6	5	3 060	1·14
N,N-dimethyl formamide	77·0	8·5	6·7	5·5	1 600	−0·58
Dimethyl sulphoxide	71·3	9	8	5	1 480	−0·09
Propionitrile	70·9	7·5	7	2·7	53·6	−0·81
Butyronitrile	87·0	7·5	6·1	2·5	16·1	−0·84
Acetonitrile	52·6	7·5	8·8	3	10·7	−0·82
Nitroethane	71·5	7·8	7·6	2·2	22·0	−2·31
Nitromethane	54·3	7·7	9·2	2·5	16·0	0·38
Acetic acid	57·1	7·1	3·9	6·6	4·9	1·06
Formic acid	37·8	7·0	5·8	8·1	2·0	−0·90
Ketones and esters						
Cyclohexanone	104	8·7	3·1	2·5	180	0·38
Isophorone	150·5	8·1	4·0	3·6	89	0·62
Methyl ethyl ketone	90·1	7·8	4·4	2·5	42	−0·32
Diethyl ketone	106·4	7·7	3·7	2·3	23·3	0·45
Ethyl acetate	98·5	7·7	2·6	3·5	17·4	0·10
n-Butyl acetate	132·5	7·7	1·8	3·1	11·5	0·77
Methyl isobutyl ketone	125·8	7·5	3·0	2·0	11·3	1·51
Diacetone alcohol	124·2	7·7	4·0	5·3	7·8	−0·40

Aromates						
Nitrobenzene	102·7	9·8	4·2	2	137	0·64
Bromobenzene	105·3	10	2·7	2	31·4	−0·33
o-Dichlorobenzene	112·8	9·4	3·1	1·6	20	−0·15
Chlorobenzene	102·1	9·3	2·1	1	19·2	−0·24
Benzene	89·4	9	0	1	8·37	−0·26
Toluene	106·8	8·8	0·7	1	6·35	−0·92
Ethylbenzene	123·1	8·7	0·3	0·7	3·6	−0·68
Alcohols[a]						
2-Methoxyethanol	79·1	7·9	4·5	8	13·9	−0·51
2-Methoxyethanol/ 1-butanol 1:1[b]	84·8	7·85	3·65	7·85	6·5	−0·43
2-Methoxyethanol/ 1,3-butanediol 2:1	82·4	7·97	4·63	8·83	5·3	−0·56
Triethylene glycol/ 1-pentanol 1:3	110·2	7·8	3·18	7·38	4·0	−0·13
Triethylene glycol/ 1-butanol 1:3	96·2	7·8	3·63	8·05	2·77	−0·36
1-Pentanol	109	7·8	2·2	6·8	1·98	−0·86
1-Butanol	91·5	7·8	2·8	7·7	1·39	−1·08
2-Methyl-2-butanol	108·8	7·4	2·2	5·9	0·67	−0·34
Alcohols[a] (pigment dissolved as associates)						
Triethylene glycol	114	7·8	6·1	9·1	17·2	1·24
Triethylene glycol/ 2-methoxyethanol 2:1	99·3	7·83	5·57	8·73	21·1	0·81
Triethylene glycol/ diethylene glycol 1:2	100·8	7·87	6·83	9·7	9·6	0·77
Diethylene glycol	95·3	7·9	7·2	10	6·1	0·59

(*continued*)

TABLE 3—*cont.*

Solvent	V_L (*cm*^{3}*/mol*)	δ_D^L	δ_P^L	δ_H^L	*Solubility* (*mg/litre; 60°C*)	$ln(C_{exp}/C_{calc})$
		(*cal*$^{1/2}$ *cm*$^{-3/2}$*; 25°C*)				
Strongly protic solvents I[c]						
Diethylene glycol/ water 3:1	46·0	7·83	7·35	12·68	9·6	1·33
Diethylene glycol/ water 1:1	30·3	7·75	7·50	15·35	4·7	0·93
Ethanol/water 3:1	37·4	7·68	5·18	12·30	4·1	−0·07
Ethanol/water 3:2	30·8	7·66	5·70	13·98	2·1	−0·52
Ethanol/water 1:1	27·5	7·65	6·05	15·10	0·60	−1·51
Ethanol/water 2:3	24·9	7·64	6·40	16·22	0·49	−1·54
Strongly protic solvents II[c]						
Diethylene glycol/ water 1:3	22·6	7·68	7·65	18·03	1·54	1·2
Diethylene glycol/ water 1:4	21·5	7·66	7·68	18·56	0·72	1·18
Ethanol/water 1:3	21·8	7·63	6·93	17·90	0·41	−0·75
Ethanol/water 1:4	20·9	7·62	7·10	18·46	0·41	−0·04
Water	18·0	7·6	7·8	20·7	5×10^{-5}	−0·41

C_{exp}/C_{calc}: experimental solubility/calculated solubility, according to eqn (20); nonlinear regression analysis with highest power of 5; standard error 1·29.

[a] Solvents contain 2% acetic acid.

[b] Volume ratios.

[c] Solubility measured at pH 7.

TABLE 4
States of Reference for the Different Classes of Solvents

Solvent class	ΔH_F^i (*kJ/mol*)	δ_{Di}^S	δ_{Pi}^S (*cal*$^{1/2}$/*cm*$^{3/2}$)	δ_{Hi}^S	V_S [a](*slope*) (*cm*^{3})
Aprotic-polar; carboxylic acids	31	11	6·35	4·15	350
Ketones, esters	38	11	4·4	3·8	340
Aromates	—	11	4·9	2·1	50
Alcohols	42	11	4·5	7	335
Strongly protic I	72	11	7·3	12	350
Strongly protic II	82	11	8	14	325
To compare:					
Primary state of reference	—	11	5·8	5	—
Experimental enthalpy of fusion	123	—	—	—	—
Molar volume of solid	—	—	—	—	334

[a] From slope of curves of $\ln C_S - V_S/V_L$ versus $(\vec{\delta}_i^S - \vec{\delta}^L)^2$; see Fig. 3.

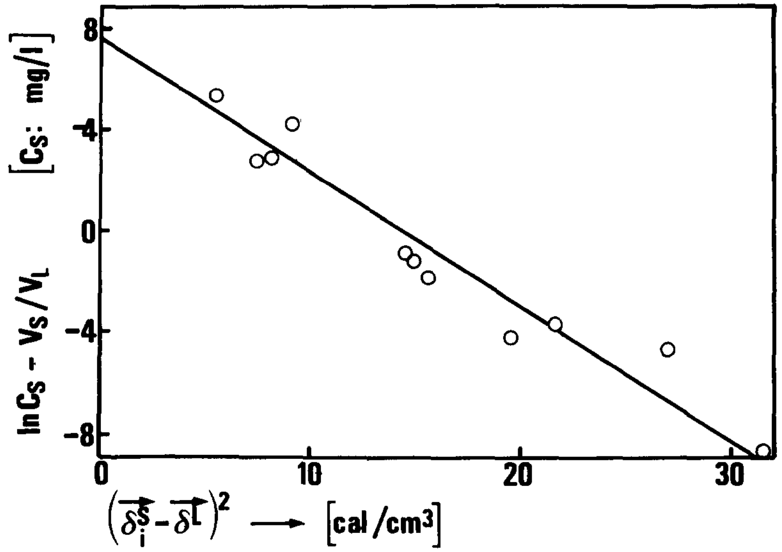

Fig. 3. Fit of solubility data according to eqn (23) for aprotic-polar solvents, and carboxylic acids.

Concerning the quantitative interpretations of the results of Table 3 some pecularities have to be mentioned. Many pigments, like our test pigment, show strong π–π interactions with aromatic solvents. These interactions are not described by the Hildebrand/Hansen solubility parameters. This fact can be seen from the curve of Fig. 4, which obviously does not reflect a simple linear relationship. Moreover, the molar volume, calculated from the slope of this curve amounts only to 50 cm^3 instead of 350 cm^3. This is an indication of quite similar strong interactions between solute and solvents, irrespective of the solubility parameters of the different aromates. This result suggests the curve of Fig. 4 to be an incomplete description of the solute/solvent interactions. For such substances the cohesive energy density ought to be partitioned not only to δ_D^2, δ_P^2, δ_H^2, but in a more general way, taking also into account π–π interactions.

Some of the solubilities in alcoholic solvents could not be fitted satisfactorily according to eqn (23), using a molar volume of 350 cm^3. Inspection of the absorbance as a function of solute concentration (Figs 5 and 6) showed large deviations from the Lambert–Beer law for alcohols such as triethylene glycol (Fig. 5), indicating molecular association with higher pigment concentration.

A largest number-mean degree of association amounting to about three was tentatively estimated by means of eqn (23) and variation of V_S, using the data for solvents with similar relative deviation of absorbance at the saturation concentration. Such associations are quite common with

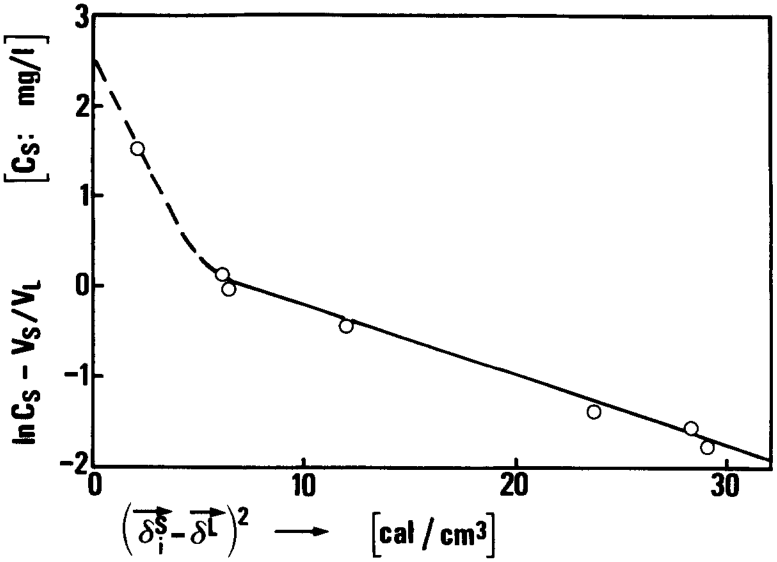

Fig. 4. Fit of solubility data according to eqn (23) for aromatic solvents.

aqueous solutions of dyes. Stacking of the delocalized π-systems seems to be the mechanism of formation of the associates.[28] In view of the π–π interactions between test pigment and aromatic solvents in solution, the formation of associates in alcoholic solution may be due to π–π interactions among solute molecules, analogous to the water-soluble dyes. A proper balance of the intersolute π–π interactions and the solute/solvent interactions is of importance. Thus, according to the absorbance curves of Figs 5 and 6 the highest degree of association of the test pigment is observed in solvents like triethylene glycol, whereas in good solvents like dimethyl

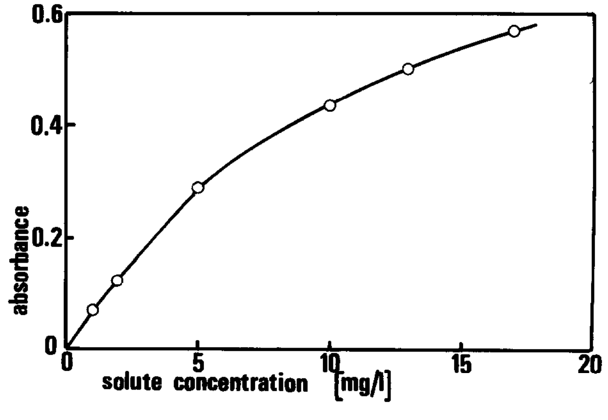

Fig. 5. Absorbance of test pigment in triethylene glycol + 1% formic acid.

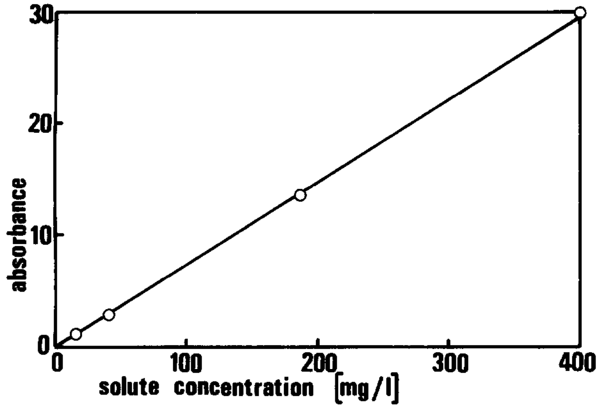

Fig. 6. Absorbance of test pigment in dimethyl sulphoxide + 1% formic acid (60°C; $\lambda_{max} = 434$ nm; cell length = 10 mm).

sulphoxide the solute/solvent interactions predominate, and no measurable association occurs. On the other hand, in solvents like methanol, or water, the solubility is too low to allow appreciable association, according to suitable equilibria equations.

CONCLUSIONS

Thermodynamic models for the solubility of solids describe the process of dissolution as the mixing of solvent with the hypothetically liquefied solid at the temperature of solution. Hildebrand/Hansen solubility parameters are suitable to estimate the enthapic contribution to the mixing process for the two liquids, if the enthalpy of mixing is positive. However, substances with a high molar enthalpy of fusion, and high melting point, like a pigment, usually show negative enthalpies of mixing. This is due to the energetically highly excited states of the hypothetically liquefied solids relative to the dissolved solids. Probably to a lesser extent this may be true for most of the organic solids, as can be estimated from the deviation from ideality.[16] This problem can be avoided by defining virtual liquid states of reference with much smaller enthalpies of fusion. The states of reference are fixed in such a way that the enthalpy of mixing is positive. Then the interactions in the virtual liquids resemble those of crystal lattices disordered to some extent.

However, the model loses its universality: there no longer exists a single state of reference. For every class of solvents—in a strict sense even for every solvent—a proper virtual state of reference must be defined, which is characterized by its own ΔH^i_F, δ^S_{Di}, δ^S_{Pi}, δ^S_{Hi}. However, by means of the solubility parameters of the solvents an empirical relationship between the individual states of reference and a primary state of reference may be derived.

Solids which consist of molecules featuring large delocalized π-systems, like organic pigments, may be dissolved in aromatic solvents generating additional π–π interactions. These interactions are not accounted for in the Hildebrand/Hansen solubility parameter model.

In some of the solvents the investigated test pigment forms associates, probably through stacking of the π-system. The existence of associates is bound to a proper balance of the intersolute π–π interactions and solute/solvent interactions.

To summarize, it can be stated that the quantitative assessment of the solvent-dependence of the solubility of solids cannot be realized as universally with the help of solubility parameters as is possible, for example, for the mixing of solvents. The condition of strongly dissimilar interactions in a liquefied solid at the mixing temperature, and its solution causes problems, and may also cause problems in more sophisticated models.

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