The Solubility Parameter Concept Applied to Disperse Dyeing of Polymers

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Synopsis

The solubility parameter concept offers a logical link between the theory of solutions and of nonionic (disperse) dyeing. An attempt has been made to apply the concept to correlate the solubility of several disperse dyes in secondary cellulose acetate, cellulose triacetate, and polypropylene with the calculated solubility parameters of both the polymers and the dyes. When the dyes are applied on hydrophilic polymers from an aqueous dispersion, the correlation between the solubility parameter concept and the dye solubility is not close. One of the reasons for this may be the fact that dyeing of the fibers is, in fact, not a solution in the dry fibers, but consists essentially either in displacement of water molecules from the water swollen fibers and/or, perhaps, in additional swelling by the dye. Consideration of this fact and also correcting for the contribution of hydrogen bonding and dipole interactions to the cohesive energy density brings the disperse dye solubility data into a better agreement with the concept. The concept should be applicable without complications to the dyeing of nonpreswollen fibers, such as polypropylene from aqueous dispersion, or any fiber by the Thermosol process and particularly to dyeing from the vapor phase. The few data available appear to support this view.

INTRODUCTION

Although the phenomenon of the spontaneous transfer of a dye from the dyebath into the fiber is but an example of a highly unsymmetrical distribution of a compound between two phases, its commercial significance and its visually impressive nature has attracted a great deal of attention. In 1890, N. Witt recognized the dyeing process as a solution phenomenon, but in the decades which followed, various kinds of molecular interactions were made responsible for it. It was, however, pointed out[1,2] that it is more logical to expect that all kinds of intermolecular attraction forces, namely, dispersion forces, dipole interaction, and hydrogen bonds, cooperate to bring about the accumulation of the dye in the fiber and that the real task lies in the determination of the contribution of these specific types of forces to the sum total. Progress in this direction depends on the progress of the theory of solutions and the general theory of intermolecular forces.

Ionic dyes complicate the theory of direct dyeing of cellulosics, acid dyeing of wool, and other ion-exchange polymers because of the role of electric

potential.[3]   Nonionic (disperse) dyeing is free from this complication and lends itself better to the analysis of the molecular forces which result in the affinity of the dye for the fiber.   Meyer in 1925 has shown that the equilibrium distribution of nonionic dyes between water and fiber follows the Nernst-Henry law,[4] and this was confirmed by many subsequent observations.[5]   Consequently, at constant temperature the interaction of a given dye with a given polymer can be characterized by a single number.   Usually, the partition coefficient between water and polymer has been used for this purpose, but solubility, i.e., the concentration of the dye in the polymer at saturation, is a more logical choice.   The equilibrium distribution studies with aqueous solution have served well to establish the fact that the activity of the dye on the fiber can be represented by its concentration; but since disperse dyeing is carried out in the presence of undissolved dye, the saturation concentration is fundamentally more significant than the partition coefficient.

The emerging polymer science of the last three decades paid considerable attention to the interaction of solvents with polymers.[6]   There is no a priori reason why the dyes should not be considered as solvents in this relation.   The concept of solubility parameter (sp) has proved useful in the study of the role of various kinds of intermolecular forces acting between polymers and solvents.   Lemons et al.[7] found that compounds which act as good carriers in the dyeing of poly(ethylene terephthalate) have cohesive energy densities close to that of the polymer.   They also noted the contribution of dipole forces in the polymer–solvent interaction.   As far as we are aware of it, the literature does not reveal any explicit application of the sp principle to the dyeing phenomenon per se.   This paper is an attempt to examine the potential usefulness of the sp concept in dyeing, based on data recorded in the literature.

THE CONCEPT

The theoretical basis of the sp concept and its application to polymers have been outlined in several recent articles.[8,9]   Some of the essentials should be repeated here.   The solubility parameter, designated by δ, is defined as the square root of the cohesive energy density, (ced), which can be directly calculated from the molar heat of vaporization ΔH_v:

$$\text{ced} = \delta^2 = -E/V = -N_0 \nu/V = (\Delta H_v - RT)/nV \qquad (1)$$

where E = the potential energy of one mole of material, V = its molar volume, N_0 = Avogadro's number, and ν = potential energy of one molecule.

Assuming that the entropy of mixing is positive, the heat of mixing will determine whether or not two compounds (such as polymer p and a solvent s) will mix, i.e., whether or not the polymer will dissolve in the solvent:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (2)$$

where ΔG_m = free energy of mixing, ΔH_m = heat of mixing, and ΔS_m = entropy of mixing.

If we denote the sp of polymer and solvent as δ_p and δ_s, respectively, and in accordance with Hildebrand and Scatchard assume that the heat of mixing can be given by

$$\Delta H_m = V_s(\delta_s - \delta_p)^2 v_p \tag{3}$$

where V_s = molar volume of the solvent and v_p = volume fraction of the solute, the dissolution will depend on how small the difference is between the two sp values. The basis of the Hildebrand-Scatchard assumption is that the potential energy of a molecule of s surrounded by molecules of p and vice versa is equal to the geometric mean of the individual potential energies:

$$\nu_{sp} = (\nu_s \nu_p)^{0.5}. \tag{4}$$

Under these assumptions, the solubility is highest when the solubility parameter of solvent and polymer have the same value (zero heat of mixing) and declines with increasing difference (positive heat of mixing).

In applying this concept to the solubility of dyes in polymers, it is to be noted that the solution of the dye in the polymer is, in contrast to the highly exothermic nature of dyeing from aqueous solution, a slightly endothermic process.[5] In general, the interaction of polymers is likewise a slightly endothermic process, and this makes the connection with our problem even closer.

COMPARISON OF SOLUBILITY PARAMETER VALUES AND SOLUBILITIES

For a test of the usefulness of the sp concept we tabulated the solubilities and sp values for (secondary) cellulose acetate, cellulose triacetate, polypropylene and poly(ethylene glycol terephthalate). The solubilities were taken from Majury,[8] Bird and Harris,[9] and Bird and Patel[10] and were determined at 80°C, with the exception of those for poly(ethylene terephthalate) which were taken from Schuler[11] and were determined at 95°C. The dye sp values were calculated for 25°C. The error inherent in these comparisons is similar for the various dyes, and organic compounds as the sp values are expected to decrease with increasing temperature in roughly the same ratio, according to the relation

$$\frac{dln\delta}{dT} = -1.25\alpha$$

where α = coefficient of thermal expansion.

The sp values for two model compounds, azobenzene and p-nitroaniline, were found[12,13] to have been experimentally determined in the literature. The values for the other dyes were calculated by the method of Small[14] using the density values given in Table I. The densities of the dyes G, H,

TABLE I
Comparison of Solubility Parameter (δ) with Solubility

Dye (model compound)	Chemical constitution	Density, g/cm³	δ, cal^{1/2} cm^{-3/2}	Solubility in polymer, g/100 g
	Secondary Cellulose Acetate (δ = 11.0)			
A	4-nitroaniline → N-ethyl N-β-hydroxyethylaniline	1.292	10.51	1.8
B	4-nitro-4'-amino azo-benzene	1.407	11.40	1.6
C	N,N-dimethyl-p-aminoazo-benzene	1.18	9.6	1.9
D	1-methylamino-4-β-hydroxy-ethylanthraquinone	1.25	11.92	2.2
E	2-chloro-4-nitroaniline → N-ethyl-N-β-hydroxy-ethylaniline	1.381	9.77	2.2
F	4-aminoacetanilide → o-cresol	1.334	11.10	2.8
G	azobenzene	1.203[a]	9.85	4.3
H	p-aminoazobenzene	1.17[a]	11.10	14.1
I	p-nitroaniline	1.424[a]	13.40	15.0
	Cellulose Triacetate (δ = 9.1)			
C	as above	1.18	9.6	1.0
G	as above	1.203	9.85	4.9
I	as above	1.424	13.40	15.0
	Polypropylene (δ = 8.0)			
J	p-aminoazobenzene → o-cresol	1.269	10.0	0.14
C	as above	1.18	9.6	0.67
	Poly(ethylene Terephthalate) (δ = 10.70)			
Carrier				
K	ethylene glycol monoethyl ether		11.9	3.7
L	dimethyl formamide		12.14	6.4
M	anisole		9.5	7.4
N	chlorobenzene		9.57	8.4
O	benzyl alcohol		11.97	8.5
P	benzaldehyde		10.40	9.7
Q	acetophenone		9.68	10.0

[a] Density obtained from *Handbook of Physics and Chemistry*.

and I were found in the literature, while the densities of the other dyes were determined experimentally at 25°C using a pycnometer and hexane as the liquid medium.

The sp values for the polymers and the compounds K through Q were taken from the literature[12,13,15,16] and refer to room temperature. The sp of polypropylene was obtained from Shawali.[17]

The results, as tabulated in Table I, do not reveal any obvious correlations between the sequence of solubility parameters and solubilities. As an

empirical rule, a good solvent for a polymer should have an sp within a range of ±1 or 2 units of that of the polymer, but the best solvent should have an sp of the same magnitude as the polymer.   The table shows the highest solubility in secondary cellulose acetate attained by p-nitroaniline, with an sp of 2.4 units higher than the polymer.   Almost the same solubility is exhibited by p-aminoazobenzene, which matches closely the sp of the polymer.   Dye F, which has the same sp as p-aminoazobenzene and matches the sp of acetate, is only one-fifth as soluble as the latter.   Dye I (p-nitroaniline) again has the highest solubility in cellulose triacetate, with an sp value 4.30 units higher than the polymer.   Dye C, with an sp value only 0.5 units higher than that of cellulose triacetate, has very low solubility in it.

The solubility of dyes in polypropylene shows much more concordance with the sp concept.   The dye with the highest solubility in polypropylene,[10] dye C (N,N-dimethyl-p-aminoazobenzene; C.I. Solvent Yellow 2) has an sp value of only 1.4 units higher than that of the polymer.   It is also nonpolar.   Dye J, which has hydrogen bonding groups and has an sp 1.8 units higher than that of the polymer, is not as soluble as dye C.   With simple organic compounds, which act as carriers in polyester dyeing (compounds K through Q), the trend is much the same.   The sp values of the compounds lie within ±1.4 units of the sp of poly(ethylene terephthalate).   Cellosolve (K), with an sp of 1.2 units higher than that of the polymer, has almost 30% the solubility of acetophenone which has an sp of 1.0 units lower than that of the polymer.   Benzaldehyde, with an sp only 0.3 units lower than that of the polymer, has an appreciable (9.7%) solubility in it.

In order to bring these results into proper perspective, several factors should be considered:

1.   The phenomenon of dye solubility in fibers is, strictly speaking, not a solution phenomenon, but rather one of swelling.[18]   Although no covalent crosslinks are present in the fiber-forming polymers studied, they are partially ordered ("crystalline") and the ordered regions act as crosslinks. (The nature of crystalline order in polymers is still a controversial subject, but has no direct bearing upon our problem.)   Due to the restriction imposed by the supramolecular structures, unless a solvent is capable of entering the ordered region, it only swells the polymer but does not dissolve it.   The extent of swelling is related to sp; maximum swelling is attained if sp of the swelling agent is the same as that of the polymer. Therefore, the solubilities given can be considered as characterizing the swelling action of the dye.

2.   Assuming that only the disordered portion of the polymer is accessible to the dye, the true "solubility" of the dye is attained by multiplying values observed with a factor equal to the ordered/disordered ratio or accessibility.

3.   The solubility values tabulated were determined not with the dry polymers, but with those containing water taken up in equilibrium with liquid water.   For instance, cellulose acetate has taken up some 12%

water.   The disordered regions contain a correspondingly higher concen-
tration of water and the dye is dissolved in the cellulose acetate–water
mixture rather than in cellulose acetate.   If the dye is uniformly distrib-
uted in this region, the sp of the matrix is that of the polymer–water mix-
ture which is much higher than that listed for the polymer.   Polypropylene
is possibly free from water.

4.   Since water already has swollen the fiber, the entering dye molecules
are not necessarily expected to increase the swelling, but to replace some of
the water of swelling.

5.   Since the fibers are swollen with water when they are equilibrated
with the dye, the dye molecules in entering the fiber have either to displace
water molecules or cause additional swelling.   Experimental data are lack-
ing for determining which of these alternatives predominate, but the possi-
bility cannot be disregarded that the observed solubilities are the results, to
some extent, of competition against the attraction forces between polymer
and water.   This might be significant at high dye concentration in the
fiber, although the linearity of dye partition, in contrast to the sigmoidal
shape of the moisture regain curve, does not reveal it.   The presence of
cavities in the fibers could make possible a third alternative, but these
cavities are not offering sufficient space to accommodate large amounts of
dyes.

It could be asked, how can the large swelling of acetate, triacetate, and
polyester by water which has a high sp value ($\sim$23) be reconciled with the
sp concept?   The answer is that water is absorbed by hydrogen bonding
(to the hydroxyl and ester groups of the polymers) and for this case the
concept does not apply.   The same is true also of the absorption of simple
organic compounds, e.g., alcohols, esters, etc., by hydrophilic polymers.
This, however, does not necessarily vitiate the validity of the concept for
the interaction of the water-swollen polymer with the dye.

6.   Another apparent discrepancy is that, as is well known, low molec-
ular solvents of suitable sp value dissolve cellulose acetate, i.e., enter the
highly ordered region, whereas dyes of the same sp cause only limited swell-
ing.   In general, solubility of polymers increases with molecular size of the
solvent, but the rate of the diffusion of the solvents in the polymer decreases.
We can tentatively conclude that dye molecules are much too large to enter
the highly ordered regions at any appreciable rate under the experimental
conditions prevailing in the technique of disperse dyeing, and the experi-
ments.   The situation is different at the high temperature of Thermosol
dyeing and especially of vapor phase dyeing.   Data obtained by Jones and
Seddon[19] and Majury[20] who studied the vapor phase dyeing of cellulose
acetate are shown in Table II.   The equilibrium dye concentration in the
fiber was obtained at each temperature with saturated vapor.

The contrast between vapor phase dyeing (high temperature) and dyeing
from the aqueous phase (low temperature and H_2O as solvent) is immedi-
ately obvious on comparing Tables I and II.   The dye H with an sp value
only 0.1 units higher than that of the polymer has a very high solubility in

TABLE II
Vapor Phase Dyeing of Secondary Cellulose Acetate (δ = 11.0)

Dye (model compound)	Chemical constitution	δ, cal$^{1/2}$ cm$^{-3/2}$	Temp. of dyeing, °C	Solubility in polymer, g/100 g
B	4-nitro-4'-amino-azobenzene	11.40	195.4	7.7
			164.7	9.9
G	azobenzene	9.85	105.0	16.4
H	p-aminoazobenzene	11.10	129.7 liquid	16.6
			100.2	31.0
			114.9	46.7
I	p-nitroaniline	13.40	120	50.0

TABLE III
The Contribution of Hydrogen Bonding and Polar Forces to Solubility Parameter (δ)

Dye	Chemical constitution	Density, g/cm	δ_A, cal$^{1/2}$ cm$^{-3/2}$	Solubility in polymer, g/100 g
	Secondary Cellulose Acetate (δ_A = 5.3)			
A	4-nitroaniline → N-ethyl-N-β-hydroxyethylaniline	1.292	4.3	1.8
B	4-nitro-4'-aminoazobenzene	1.407	6.8	1.6
C	N,N-dimethyl-p-amino-azobenzene	1.18	3.8	1.9
D	1-methylamino-4-β-hydroxyethylanthraquinone	1.25	4.9	2.2
E	2-chloro-4-nitroaniline-→ N-ethyl-N-β-hydroxyethyl-aniline	1.381	5.9	2.2
F	4-aminoacetanilide → o-cresol	1.334	4.5	2.8
G	azobenzene	1.203	4.0	4.3
H	p-aminoazobenzene	1.17	4.4	14.1
I	p-nitroaniline	1.424	5.4	15.0
	Cellulose Triacetate (δ_A = 4.4)			
C	as above	1.18	3.8	1.0
G	as above	1.203	4.0	4.9
I	as above	1.424	5.4	15.0
	Polyethylene Terephthalate (δ_A = 4.8)			
			δ_A	
	ethylene glycol mono-ethyl ether		8.55	3.7
	dimethyl formamide		8.5	6.4
	anisole		3.9	7.4
	chlorobenzene		2.4	8.4
	benzyl alcohol		7.9	8.5
	benzaldehyde		4.9	9.7
	acetophenone		4.7	10.0

it. Dye B, which had a solubility of only 1.6% at 80°C, now has a solubility six times greater at, 164.7°C. p-Nitroaniline again shows a high solubility despite the mismatch between its sp and that of the polymer. This could be due to either its small size enabling it to diffuse deeper into the accessible regions and/or the role of dipole interactions, which are seen in Table III. Both for high and low temperature dyeing, the influence of the dye molecular size on the solubility is evident. The dyes of small size have comparatively high solubility in the polymers.

7. The ced and sp concepts were originally developed for interaction by dispersion (London) forces alone. Later, the contribution of permanent dipoles, dipole-induced dipoles, and hydrogen bonding were included to give the sp a three-dimensional parameter,[13] as follows:

$$\delta^2 = \delta^2_d + \delta^2_h + \delta^2_p$$

δ = solubility parameter, δ_d = solubility parameter representing the contribution of London dispersion forces to the cohesive energy density, δ_h = solubility parameter representing the contribution of hydrogen bonding forces to the cohesive energy density, and δ_p = solubility parameter representing the contribution of dipole-dipole and dipole-induced dipole forces to the cohesive energy density. The sum of the last two contributions will be defined by

$$\delta^2_A = \delta^2_h + \delta^2_p$$

and represent the contribution of both polarity and the presence of hydrogen bonding on the cohesive energy density.

It was suggested and confirmed that for optimum solubility (maximum swelling) not only the sp values of polymer and solvent, but also their polarities should match.[12] We have made calculations of δ_A values for the polymers and dyes as follows, using the method of Hansen[15]: The sp contribution from London dispersion forces can be determined experimentally by considering a hydrocarbon homomorph. To a first approximation, from the data of Hansen, the following empirical relations were established:

for acetates and triacetates, $\delta_A/\delta = 0.48 \ (\simeq)$
for amines, $\delta_A/ = 0.41$
for nitrocompounds, $\delta_A/\delta = 0.60$.

The calculated δ_A values for the polymers and dyes are shown in Table III.

We find that consideration of the contribution of dipole and hydrogen bonding forces improves considerably the correlation between sp and solubility. For instance, dyes F, H, and I, which have δ_A values close to cellulose acetate, have high solubility in it. The same holds for dyes G and I in cellulose triacetate. Furthermore, dyes A, B, C, which have δ_A values greatly differing with that of cellulose acetate, have low solubility. The same holds for dye C in cellulose triacetate. Equally remarkable is the absorption of simple organic solvents by poly(ethylene terephthalate). High solubility in the polymer is shown by benzaldehyde and acetophenone

whose δ_A values approximately match that of the polymer, whereas low solubility in the polyester is exhibited by Cellosolve with a high disparity between its δ_A value and that of the polymer. The improved correlation buttresses the important role of dipole-dipole, dipole-induced dipole, and hydrogen bonding forces in solubility phenomena, involving fibers pre-swollen by water.

Probably more important than some of the complications enumerated above is the fact that the dyes are applied below their melting point, i.e., in crystalline state. The mutual attraction potential of the dye molecules is therefore increased by the heat of fusion. It is true that this is to some extent compensated by the entropy of crystallization. The compensation is less complete with decreasing temperature. For correct application of the sp concept, the dyes should be applied in the liquid state. The solubilities of dyes A and B in cellulose acetate at their melting points have been obtained by Milicevic[21] by extrapolation. Dye A has a solubility of 2.82% at its melting point 165°C, while dye B has a solubility of 4.7% at 215°C. These few data reflect the fact that the closer the sp of the dye is to the polymer sp, the higher the solubility—a fact that is somewhat obscured at the low-temperature aqueous disperse dyeing shown in Table I, but they do not correlate with the role of the polar and hydrogen bonds (δ_A).

CONCLUSIONS

From the data available in the literature and presented in this paper, the following inferences can be drawn:

1. Dyes that are commercially used for dyeing cellulose acetate and cellulose triacetate have a solubility parameter (sp) within ± 1.4 units of that of the polymer. The same relationship holds for organic compounds that are commercially used as carriers in the dyeing of poly(ethylene terephthalate). This trend may also explain why there are very few dyes with high solubility in polypropylene.

2. The application of the sp concept to dyeing of hydrophilic polymers from aqueous dispersions is complicated by the presence of the water of swelling in these polymers. A better correlation is obtained by considering the contributions of hydrogen bonding and dipole interactions to the total sp.

3. The question of whether differences of accessibility by large dye molecules have an effect on solubility should be investigated.

4. For a more valid, more promising test of the sp concept of dyeing, we had better turn to the systems which deal with dry polymers unswollen by water or carriers. Eminently suitable is polypropylene. The difficulty of obtaining a commercially acceptable disperse dyeing of unmodified poly-propylene is that the sp of polypropylene is so close to the sp of the dry cleaning solvents that those dyes which are readily exhausted by the fiber are read-ily extracted by the solvents. The fact that these dyes could serve for the quantitative study of the application of the sp concept is already shown by

the solubilities of *p*-amino azobenzene → *o*-cresol and N,N-dimethylamino-azobenzene in polypropylene.

5.   The few available data show that the sp concept shows better correlation if the dyes are applied on cellulose acetate either in the vapor phase (crystalline), as in the Thermosol process, or in the molten state. More such data are necessary for complete characterization.   Even more suitable for such a study is the behavior of hydrophobic fibers in the Thermosol process.   The increased tempo of commercial and scientific research in this field justifies the hope that the required data will soon be available and thus the missing link between the theory of solution and theory of dyeing will be more firmly established for this sector of the dyeing technology.

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