SOLUBILITY PARAMETER-A REVIEW

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ABSTRACT

Solubility parameters have found their greatest use in the coatings industry to aid in the selection of solvents. They are used in other industries, however, to predict compatibility of polymers, chemical resistance, and permeation rates, and even to characterize the surfaces of pigments, fibers, and fillers. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own.

The basic principle has been "like dissolves like." More recently, this has been modified to "like seeks like," as many surface characterizations have also been made, and surfaces do not (usually) dissolve. Solubility parameters help put numbers into this simple qualitative idea. This chapter describes the tools commonly used in Hansen solubility parameter (HSP) studies. These include liquids used as energy probes and computer programs to process data. The goal is to arrive at the HSP for interesting materials either by calculation or, if necessary, by experiment and preferably with agreement between the two.

Solubility parameters are sometimes called *cohesion energy parameters* as they are derived from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid's molecules together. All types of bonds holding the liquid together are broken by evaporation, and this has led to the concepts described in more detail later. The term *cohesion energy parameter* is more appropriately used when referring to surface phenomena.

Key Words: - Solubility, Solubility in coating industry.

INTRODUCTION

Solvents are ubiquitous: we depend on them when we apply pastes and coatings, remove stains or old adhesives, and consolidate flaking media. The solubility behavior of an unknown substance often gives us a clue to its identification, and the change in solubility of a known material can provide essential information about its ageing characteristics.

Our choice of solvent in a particular situation involves many factors, including evaporation rate, solution viscosity, or environmental and health concerns, and often the effectiveness of a solvent depends on its ability to adequately dissolve one material while leaving other materials unaffected. The selection of solvents or solvent blends to satisfy such criterion

is a fine art, based on experience, trial and error, and intuition guided by such rules of thumb as "like dissolves like" and various definitions of solvent "strength".

Although it may not be necessary to understand quantum mechanics to remove masking tape, an organized system is often needed that can facilitate the accurate prediction of complex solubility behavior.

The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the **cohesive energy density** of the solvent, which in turn is derived from the **heat of vaporization**.[2]

SOLUBILITY SCALE

The Hildebrand solubility parameter, perhaps the most widely applicable of all the systems, includes such variations as the Hildebrand number, hydrogen bonding value, Hansen parameter, and fractional parameter, to name a few. Sometimes only numerical values for these terms are encountered, while at other times values are presented in the form of two or three dimensional graphs, and a triangular graph called a Teas graph has found increasing use because of its accuracy and clarity.[2]

Hildebrand solubility parameters laying a theoretical foundation, will concentrate on graphic plots of solubility behavior. It should be remembered that these systems relate to non-ionic liquid interactions that are extended to polymer interactions; water based systems and those systems involving acid-base reactions cannot be evaluated by simple solubility parameter systems alone.[12]

THE HILDEBRANDS SOLUBILITY PARAMETER

It is the *total* van der Waals force, however, which is reflected in the simplest solubility value: the **Hildebrand solubility parameter**. The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the **cohesive energy density** of the solvent, which in turn is derived from the **heat of vaporization**. What this means will be clarified when we understand the relationship between vaporization, van der Waals forces, and solubility.[1]

Vaporization

When a liquid is heated to its boiling point, energy (in the form of heat) is added to the liquid, resulting in an increase in the temperature of the liquid. Once the liquid reaches its boiling point, however, the further addition of heat does not cause a further increase in temperature. The energy that is added is entirely used to separate the molecules of the liquid and boil them away into a gas. Only when the liquid has been completely vaporized will the temperature of the system again begin to rise. If we measure the *amount* of energy (in calories) that was added from the onset of boiling to the point when all the liquid has boiled away, we will have a direct indication of the amount of energy required to separate the liquid into a gas, and thus the amount of van der Waals forces that held the molecules of the liquid together.

It is important to note that we are not interested here with the *temperature* at which the liquid begins to boil, but the *amount of heat* that has to be added to separate the molecules. A liquid with a low boiling point may require considerable energy to vaporize, while a liquid with a higher boiling point may vaporize quite readily, or vice versa. What is important is the energy required to vaporize the liquid, called the **heat of vaporization**. (Regardless of the temperature at which boiling begins, the liquid that vaporizes readily has less intermolecular stickiness than the liquid that requires considerable addition of heat to vaporize.[1]

Cohesive Energy Density

From the heat of vaporization, in calories per cubic centimeter of liquid, we can derive the **cohesive energy density** (c) by the following expression

$$c = \frac{\Delta H - RT}{V_m} \quad (1)$$

where:

c=Cohesive energy density

Δh=Heat of vaporization

r=Gas constant

t=Temperature

V_m = Molar volume

In other words, the cohesive energy density of a liquid is a numerical value that indicates the energy of vaporization in calories per cubic centimeter, and is a direct reflection of the degree of van der Waals forces holding the molecules of the liquid together.

Interestingly, this correlation between vaporization and van der Waals forces also translates into a correlation between vaporization and solubility behavior. This is because the same intermolecular attractive forces have to be overcome to vaporize a liquid as to dissolve it. This can be understood by considering what happens when two liquids are mixed: the molecules of each liquid are physically separated by the molecules of the other liquid, similar to the separations that happen during vaporization. The same intermolecular van der Waals forces must be overcome in both cases.

Since the solubility of two materials is only possible when their intermolecular attractive forces are similar, one might also expect that materials with similar cohesive energy density values would be miscible. This is in fact what happens.[12]

UNITS OF MEASUREMENT

Lists several solvents in order of increasing Hildebrand parameter. Value are shown in both the common form which is derived from cohesive energy *densities* in calories/cc, and a newer form which, conforming to standard international units **(SI units)**, is derived from cohesive *pressures*. The SI unit for expressing pressure is the **pascal**, and SI Hildebrand solubility parameters are expressed in mega-pascals (1 mega-pascal or mpa=I million pascals). Conveniently, SI parameters are about twice the value of standard parameters:

solvent	∂	∂(SI)
n-Pentane	(7.0)	14.4
n-Hexane	7.24	14.9
Freon® TF	7.25	-
n-Heptane	(7.4)	15.3

Diethyl ether	7.62	15.4
1,1,1 Trichloroethane	8.57	15.8
n-Dodecane	-	16.0
White spirit	-	16.1
Turpentine	-	16.6
Cyclo-hexane	8.18	16.8
Amyl acetate	(8.5)	17.1
Carbon tetrachloride	8.65	18.0
Xylene	8.85	18.2
Ethyl acetate	9.10	18.2
Toluene	8.91	18.3
Tetrahydrofuran	9.52	18.5
Benzene	9.15	18.7
Chloroform	9.21	18.7
Trichloroethylene	9.28	18.7
Cellosolve® acetate	9.60	19.1
Methyl ethyl ketone	9.27	19.3
Acetone	9.77	19.7
Diacetone alcohol	10.18	20.0
Ethylene dichloride	9.76	20.2
Methylene chloride	9.93	20.2
Butyl Cellosolve®	10.24	20.2
Pyridine	10.61	21.7
Cellosolve®	11.88	21.9
Morpholine	10.52	22.1
Dimethylformamide	12.14	24.7
n-Propyl alcohol	11.97	24.9
Ethyl alcohol	12.92	26.2
Dimethyl sulphoxide	12.93	26.4
n-Butyl alcohol	11.30	28.7
Methyl alcohol	14.28	29.7

Propylene glycol	14.80	30.7
Ethylene glycol	16.30	34.9
Glycerol	21.10	36.2
Water	23.5	48.0

Table 1. Hildebrand Solubility Parameters

$$\partial/\textbf{cal}^{\frac{1}{2}}\textbf{cm}^{-3/2} = \quad 0.48888 \times \partial /MPa^{1/2} \quad (3)\ [1]$$

$$\partial/\textbf{MPa}^{\frac{1}{2}} = \quad 2.0455 \times \partial /cal^{\frac{1}{2}}cm^{-3/2} \quad (4)\ [1]$$

OTHER SOLUBILITY PARAMETER

Other empirical solubility scales include the *aniline cloud-point* (aniline is very soluble in aromatic hydrocarbons, but only slightly soluble in aliphatic), the *heptane number* (how much heptane can be added to a solvent/resin solution), the *wax number* (how much of a solvent can be added to a benzene/beeswax solution), and many others. The *aromatic character* of a solvent is the percent of the molecule, determined by adding up the atomic weights, that is benzene-structured (benzene is the simplest hexagonal aromatic hydrocarbon). Benzene therefore has 100% aromatic character, toluene 85%, and diethyl benzene 56% aromatic character. By loose

extension, the aromatic character of a mixed solvent, such as V.M. and P. naphtha or mineral spirits, is the percent of aromatic solvent in the otherwise aliphatic mixture.

These diverse solubility scales are useful because they give concise information about the relative strengths of solvents and allow us to more easily determine what solvents or solvent blends can be used to dissolve a particular material.[13]

Hansen Parameters

The most widely accepted three component system to date is the three parameter system developed by Charles M. Hansen in 1966. **Hansen parameters** divide the total Hildebrand value into three parts: a dispersion force component, a hydrogen bonding component, end a polar component. This approach differs from Crowley's in two major ways: first, by using a dispersion force component instead of the Hildebrand value as the third parameter, and second, by relating the values of all three components to the total Hildebrand value. This means that Hansen parameters are additive: [1]

$$\partial_t^2 = \partial_d^2 + \partial_p^2 + \partial_h^2 \quad (6)$$

where

$\partial_t^2 =$ Total Hildebrand parameter

$\partial_d^2 =$ dispersion component

$\partial_p^2 =$ polar component

$\partial_h^2 =$ hydrogen bonding component

The numerical values for the component parameters are determined in the following way: First, the dispersion force for a particular liquid is calculated using what is called the **homomorph** method. The homomorph of a polar molecule is the nonpolar molecule most closely resembling it in size and structure (n-butane is the homomorph of n-butyl alcohol). The Hildebrand value for the nonpolar homomorph (being due entirely to dispersion forces) is assigned to the polar molecule as its dispersion component value. This dispersion value (squared) is then subtracted from the Hildebrand value (squared) of the liquid, the remainder designated as a value representing the total polar interaction of the molecule ∂_a (not to be confused with the polar component ∂_p). Through trial and error experimentation on numerous solvents and polymers, Hansen separated the polar value into polar and hydrogen bonding component parameters best reflecting empirical evidence.

Solvent	∂/MPa $^{1/2}$			
	∂_t	∂_d	∂_p	∂_h
Alkanes				
n-Butane	14.1	14.1	0.0	0.0
n-Pentane	14.5	14.5	0.0	0.0
n-Hexane	14.9	14.9	0.0	0.0
n-Heptane	15.3	15.3	0.0	0.0
n-Octane	15.5	15.5	0.0	0.0
Isooctane	14.3	14.3	0.0	0.0
n-Dodecane	16.0	16.0	0.0	0.0
Cyclohexane	16.8	16.8	0.0	0.2
Methylcyclohexane	16.0	16.0	0.0	0.0
Aromatic Hydrocarbons				
Benzene	18.6	18.4	0.0	2.0
Toluene	18.2	18.0	1.4	2.0
Napthalene	20.3	19.2	2.0	5.9
Styrene	19.0	18.6	1.0	4.1
o-Xylene	18.0	17.8	1.0	3.1
Ethyl benzene	17.8	17.8	0.6	1.4
p- Diethyl benzene	18.0	18.0	0.0	0.6
Halohydrocarbons				
Chloro methane	17.0	15.3	6.1	3.9
Methylene chloride	20.3	18.2	6.3	6.1
1,1 Dichloroethylene	18.8	17.0	6.8	4.5
Ethylene dichloride	20.9	19.0	7.4	4.1

Chloroform	19.0	17.8	3.1	5.7
1,1 Dichloroethane	18.5	16.6	8.2	0.4
Trichloroethylene	19.0	18.0	3.1	5.3
Carbon tetrachloride	17.8	17.8	0.0	0.6
Chlorobenzene	19.6	19.0	4.3	2.0
o-Dichlorobenzene	20.5	19.2	6.3	3.3
1,1,2 Trichlorotrifluoroethane	14.7	14.7	1.6	0.0
Ethers				
Tetrahydrofuran	19.4	16.8	5.7	8.0
1,4 Dioxane	20.5	19.0	1.8	7.4
Diethyl ether	15.8	14.5	2.9	5.1
Dibenzyl ether	19.3	17.4	3.7	7.4
Ketones				
Acetone	20.0	15.5	10.4	7.0
Methyl ethyl ketone	19.0	16.0	9.0	5.1
Cyclohexanone	19.6	17.8	6.3	5.1
Diethyl ketone	18.1	15.8	7.6	4.7
Acetophenone	21.8	19.6	8.6	3.7
Methyl isobutyl ketone	17.0	15.3	6.1	4.1
Methyl isoamyl ketone	17.4	16.0	5.7	4.1
Isophorone	19.9	16.6	8.2	7.4
Di-(isobutyl) ketone	16.9	16.0	3.7	4.1
Esters				
Ethylene carbonate	29.6	19.4	21.7	5.1
Methyl acetate	18.7	15.5	7.2	7.6
Ethyl formate	18.7	15.5	7.2	7.6
Propylene 1,2 carbonate	27.3	20.0	18.0	4.1
Ethyl acetate	18.1	15.8	5.3	7.2
Diethyl carbonate	17.9	16.6	3.1	6.1
Diethyl sulfate	22.8	15.8	14.7	7.2
n-Butyl acetate	17.4	15.8	3.7	6.3

Isobutyl acetate	16.8	15.1	3.7	6.3
2-Ethoxyethyl acetate	20.0	16.0	4.7	10.6
Isoamyl acetate	17.1	15.3	3.1	7.0
Isobutyl isobutyrate	16.5	15.1	2.9	5.9
Nitrogen Compounds				
Nitromethane	25.1	15.8	18.8	5.1
Nitroethane	22.7	16.0	15.5	4.5
2-Nitropropane	20.6	16.2	12.1	4.1
Nitrobenzene	22.2	20.0	8.6	4.1
Ethanolamine	31.5	17.2	15.6	21.3
Ethylene diem me	25.3	16.6	8.8	17.0
Pyridine	21.8	19.0	8.8	5.9
Morpholine	21.5	18.8	4.9	9.2
Analine	22.6	19.4	5.1	10
N-Methyl-2-pyrrolidone	22.9	18.0	12.3	7.2
Cyclohexylamine	18.9	17.4	3.1	6.6
Quinoline	22.0	19.4	7.0	7.6
Formamide	36.6	17.2	26.2	19.0
N,N-Dimethylformamide	24.8	17.4	13.7	11.3
Sulfur Compounds				
Carbon disulfide	20.5	20.5	0.0	0.6
Dimethylsulphoxide	26.7	18.4	16.4	10.2
Ethanethiol	18.6	15.8	6.6	7.2
Alcohols				
Methanol	29.6	15.1	12.3	22.3
Ethanol	26.5	15.8	8.8	19.4
Allyl alcohol	25.7	16.2	10.8	16.8
1-Propanol	24.5	16.0	6.8	17.4
2-Propanol	23.5	15.8	6.1	16.4
1-B utanol	23.1	16.0	5.7	15.8
2-Butanol	22.2	15.8	5.7	14.5

Isobutanol	22.7	15.1	5.7	16.0
Benzyl alcohol	23.8	18.4	6.3	13.7
Cyclohexanol	22.4	17.4	4.1	13.5
Diacetone alcohol	20.8	15.8	8.2	10.8
Ethylene glycol monoethyl ether	23.5	16.2	9.2	14.3
Diethylene glycol monomethyl ether	22.0	16.2	7.8	12.7
Diethylene glycol monoethyl ether	22.3	16.2	9.2	12.3
Ethylene glycol monobutyl ether	20.8	16.0	5.1	12.3
Diethylene glycol monobutyl ether	20.4	16.0	7.0	10.6
1 -Decanol	20.4	17.6	2.7	10.0
Acids				
Formic acid	24.9	14.3	11.9	16.6
Acetic acid	21.4	14.5	8.0	13.5
Benzoic acid	21.8	18.2	7.0	9.8
Oleic acid	15.6	14.3	3.1	14.3
Stearic acid	17.6	16.4	3.3	5.5
Phenols				
Phenol	24.1	18.0	5.9	14.9
Resorcinol	29.0	18.0	8.4	21.1
m-Cresol	22.7	18.0	5.1	12.9
Methyl salicylate	21.7	16.0	8.0	12.3
Polyhydric Alcohols				
Ethylene glycol	32.9	17.0	11.0	26.0
Glycerol	36.1	17.4	12.1	29.3
Propylene glycol	30.2	16.8	9.4	23.3
Diethylene glycol	29.9	16.2	14.7	20.5
Triethylene glycol	27.5	16.0	12.5	18.6
Dipropylene glycol	31.7	16.0	20.3	18.4
Water	47.8	15.6	16.0	42.3

Table 2 . Hasen parameter for the solvent at 25^0c [1]

Solvent Mixtures

It is an interesting aspect of the Hildebrand solvent spectrum that the Hildebrand value of a solvent mixture can be determined by averaging the Hildebrand values of the individual solvents by volume. For example, a mixture of two parts toluene and one part acetone will have a Hildebrand value of 18.7 (18.3 x 2/3 + 19.7 x 1/3), about the same as chloroform. Theoretically, such a 2:1 toluene/acetone mixture should have solubility behavior similar to chloroform. If, for example, a resin was soluble in one, it would probably be soluble in the other. What is attractive about this system is that it attempts to predict the properties of a mixture *a priori* using only the properties of its components (given the solubility parameters of the polymer and the liquids); no information on the mixture is required.
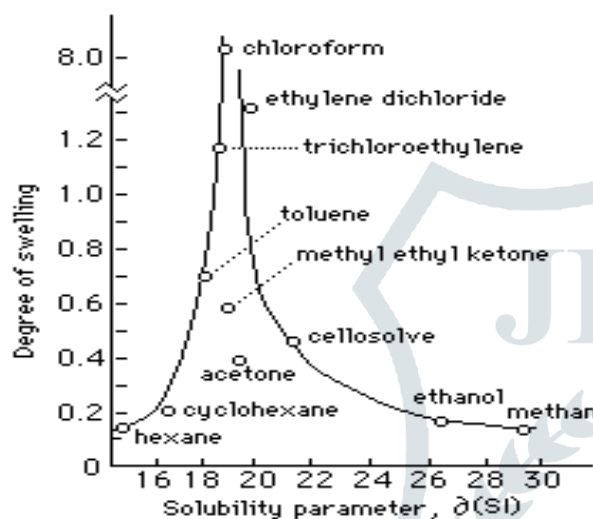
Fig.1 Swelling of Linseed Oil Film in Solvents Arranged According to Solubility Parameter[13]

Two Component Parameters

A scheme to overcome the inconsistencies caused by hydrogen bonding was proposed by Harry Burrell in 1955. This simple solution divides the solvent spectrum into three separate lists: one for solvents with poor hydrogen bonding capability, one for solvents with moderate hydrogen bonding capability, and a third for solvents with strong hydrogen bonding capability, on the assumption that solubility is greatest between materials with similar polarities. This system of classification is quite successful in predicting solvent behavior, and is still widely used in practical applications. The classification according to Burrell may be briefly summarized as follows:

Weak hydrogen bonding liquids: hydrocarbons, chlorinated hydrocarbons, and nitrohydrocarbons.

Moderate hydrogen bonding liquids: ketones, esters, ethers, and glycol monoethers

Strong hydrogen bonding liquids: alcohols, amines, acids, amides, and aldehydes

Later systems assign specific values to hydrogen bonding capacity, and plot those values against Hildebrand values on a two dimensional graph. Although hydrogen bonding values are generally determined using IR spectroscopy (by measuring the frequency shift a particular solvent causes in deuterated methanol), another interesting method uses the speed of sound through paper that has been wet with the solvent being tested. Since paper fibers are held together largely by hydrogen bonds, the presence of a liquid capable of hydrogen bonding will disrupt the fiber-fiber bonds in preference to fiber-liquid bonds. This disruption of paper fiber bonding will decrease the velocity of sound travelling through the sheet. Water, capable of a high degree of hydrogen bonding,

is used as a reference standard, and the hydrogen bonding value of a liquid is the ratio of its sonic disruption relative to water. In this test, alkanes have no effect on fiber hydrogen bonding, giving the same sonic velocities as air dried paper.

Hydrogen bonding is a type of electron donor-acceptor interaction and can be described in terms of Lewis acid-base reactions. For this reason other systems have attempted the classification of solvents according to their electron donating or accepting capability. Such extensions of the Hildebrand parameter to include acidity-basicity scales, and ultimately ionic systems, are relatively recent and outside the scope of this pape.[4]

Three Component Parameters

Solubility behavior can be adequately described using Hildebrand values, although in some cases differences in polar composition give unexpected results, for example). Predictions become more consistent if the Hildebrand value is combined with a polar value (i.e. hydrogen bonding number), giving two parameters for each liquid. Even greater accuracy is possible if all three polar forces (hydrogen bonding, polar forces, and dispersion forces) are considered at the same time. This approach assigns three values to each liquid and predicts miscibility if all three values are similar.

As long as data is presented in the form of a single list, or even a two dimensional graph, it can be easily understood and applied. With the addition of a third term, however, problems arise in representing and using the information; the manipulation of three separate values presents certain inconveniences in practical application. It is for this reason that the development and the use of three component parameter systems has centered on solubility maps and models. [5]

3-D Models

While polymer solubilities may be easily presented as a connected group of solvents on a list, or as a specific area on a graph, the description of solubilities in three dimensions is understandably more difficult. Most researchers have therefore relied on three-dimensional constructions within which all three component parameters could be represented at once.

In 1966, Crowley, Teague, and Lowe of Eastman Chemical developed the first three component system using the Hildebrand parameter, a hydrogen bonding number, and the dipole moment as the three components. A scale representing each of these three values is assigned to a separate edge of a large empty cube. In this way, any point within the cube represents the intersection of three specific values. A small ball, supported on a rod, is placed at the intersection of values for each individual solvent.
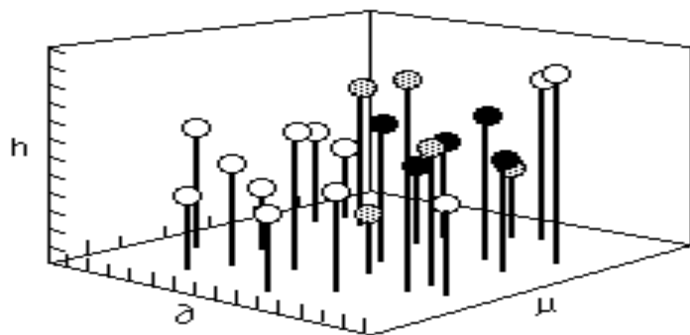

Fig 2. A three dimensional box used to plot solubility information (after Crowley, Teague and Lowe) a=Hildebrand value, p=dipole moment, h=hydrogen bonding value.[6]

Once all the solvent positions have been located within the cube in this way, solubility tests are performed on individual polymers. The position of solvents that dissolve a polymer are indicated by a black ball, nonsolvents by a white one, and partial solubilities are indicated by a grey ball. In this way a solid volume (or three dimensional area) of solubility is formed, with liquids within the volume being active solvents (black balls), and liquids outside the volume being non-solvents (white balls). Around the surface of the volume, at the interface between the area of solubility and the surrounding non-solvent area, the balls are grey.

Once the volume of solubility for a polymer is established, it becomes necessary to translate that information into a form that is practical. This means transforming the 3-D model (difficult to carry around) into a 2-D graph (easier to publish). This is usually done in one of two similar ways. In both cases, the data is plotted on a rectangular graph that represents only two of the three component parameter scales (one side of the cube).
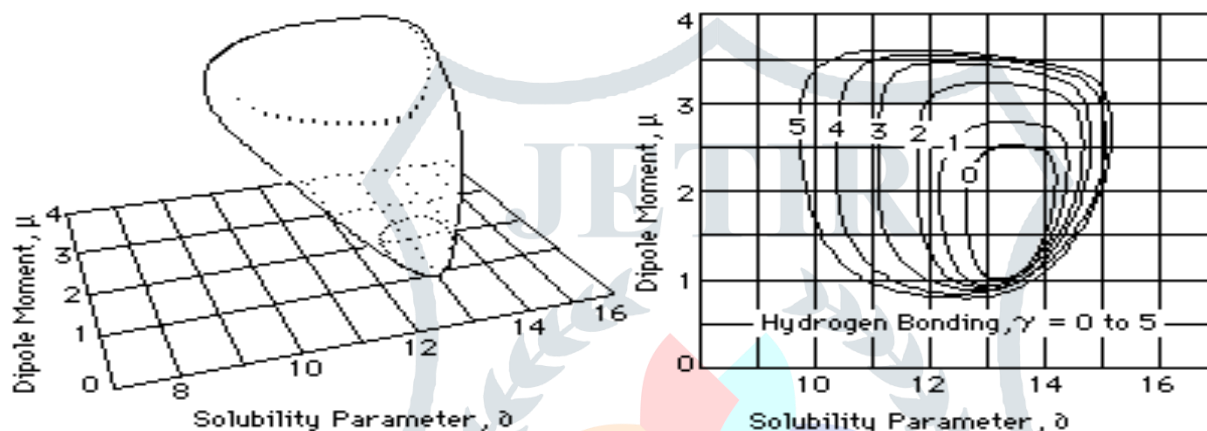
Fig 3. Approximate Representations of Solid Model and Solubility Map for Cellulose Acetate (ref.13) (´from Crowley, at al, *Journal of Paint Technology* **Vol 39, 504, Jan 1967) graph that represents either a single slice through the volume at a specified value on the third component parameter scale, or a topographic map that indicats several values of the third parameter at the same time. Because the volume of solubility for a polymer usually has an unusual shape, several graphs are often needed for an individual polymer if its total solubility behavior is to be shown.**

Maps such as these can' be used in conjunction with a table of three component parameters for individual solvents, and in this way provide useable information about solvent-polymer interactions and allow the formulation of polymer or solvent blends to suit specific applications. Data presented in this way is not only concise, but saves considerable time by allowing the prediction of solubility behavior without recourse to extensive empirical testing. !t is for these reasons that solubility maps are often included in technical reports and manufacturer's product data sheets. How graphs are actually used to accomplish these purposes will be described later in terms of the triangular Teas graph, in which these procedures are similar but greatly simplified.

POLYMER SOLUBILITY WINDOWS

Given the solvent positions, it is possible to indicate polymer solubilities using methods similar to those used by Crowley and Hansen: a polymer is tested in various solvents, and the results indicated on the graph (a 3-D model is no longer necessary). At first, individual liquids from diverse locations on the graph are mixed with the polymer under investigation, and the degree of swelling or dissolution noted. Liquids that are active solvents, for example, might have their positions on the graph marked with a red dot. Marginal solvents might be marked with a yellow

dot, and nonsolvents marked with black. Once this is done, a solid area on the Teas graph will contain all the red dots, surrounded with yellow dots.

The edges of this area, or **polymer solubility window**, can be more closely determined in the following way. Two liquids near the edge of the solubility window are chosen, one within the window (red dot), and one outside the window (black dot). Dissolution (or swelling) of the polymer is then tested in various mixtures of these two liquids, using cloud-point determinations if accuracy is essential, and the mixture just producing solubility is noted on the graph, thus determining the edge of the solubility window. (The mixture would be located on a line between the two liquids, at a point corresponding in distance to the ratio of the liquids in the mixture.) If this procedure is repeated in several locations around the edge of the solubility window, the boundaries can be accurately determined. Interestingly, some composite materials (such as rubber/resin pressure sensitive adhesives, or wax resin mixtures) can exhibit two or more separate solubility windows, more or less overlapping, that reflect the degree of compatibility and the concentration of the original components.
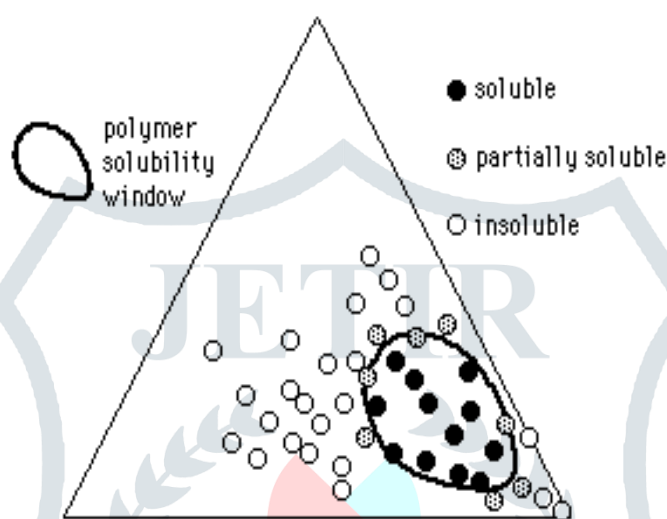

Figure 4. The solubility window of a hypothetical polymer (circles indicate solvents).[13]

This method of solubility window determination can be performed on samples under a microscope, and the results plotted on a Teas graph. In cases where the solubilities of artifactual materials are to be assessed prior to treatment, it is often unnecessary to delineate the entire solubility window of the materials in question. It can suffice to record the reaction of the materials to the progressive mixtures of a few selected solvents under working conditions in order to determine appropriate working solutions.

Temperature, concentration, viscosity

The solubility window of a polymer has a specific size, shape, and placement on the Teas graph depending on the polarity and molecular weight of the polymer, and the temperature and concentration at which the measurements are made. Most published solubility data are derived from 10% concentrations at room temperature.[5]

Heat has the effect of increasing the size of the solubility window, due to an increase in the disorder (**entropy**) of the system. The more disordered a system is (increased entropy), the less it matters how dissimilar the solubility parameters of the components are. Since entropy also relates to the number of elements in a system (more elements=more disorder), polymer grades of lower molecular weight (many small molecules) will have larger solubility windows than polymer grades of higher molecular weight (fewer large molecules).[5]

Concentration also has an effect on solubility. As stated, most polymer solubility windows are determined at 10% concentration of polymer in solvent. Because an increase in polymer concentration causes an increase in the entropy of the system (more elements=more disorder), solubility information can be considered accurate for solutions of higher concentration as well. Solvent evaporation as a polymer film dries serves to increase the polymer concentration in the solvent, thus insuring that the two materials stay mixed. It is possible, however, for polymer solutions of less than 10% to phase separate (become immiscible), due to a decrease in entropy. This is

particularly likely with polymer-solvent combinations at the edge of the polymer solubility window. In other words, with lower polymer concentration there is an increase in the order of the system (less entropy); therefore, the size of the solubility window becomes smaller (there is less difference tolerated between solvent and polymer solubility values).[5]

Solution viscosity also varies depending on where in the polymer solubility window the solvent is located. One might expect viscosity to be at a minimum when a solvent near the center of a polymer solubility window is used. However, this is not the case. Solvents at the center of a polymer solubility window dissolve the polymer so effectively that the individual polymer molecules are free to uncoil and stretch out. In this condition molecular surface area is increased, with a corresponding increase in intermolecular attractions. The molecules thus tend to attract and tangle on each other, resulting in solutions of slightly higher than normal viscosity.[5]

When dissolved in solvents slightly off-center in the solubility window, polymer molecules stay coiled and grouped together into microscopic clumps which tend to slide over one another, resulting in solutions of lower viscosity. As solvents nearer and nearer the edge of the solubility window are used to dissolve the polymer, however, these clumps become progressively larger and more connected and viscosity again increases until ultimately polymer-liquid phase separation occurs as the region of the solubility window boundary is crossed.[5]

Dried film properties

The position of a solvent in the solubility window of a polymer has a marked effect on the properties of not only the polymer-solvent solution, but on the dried film characteristics of the polymer as well. Because of the uncoiling of the polymer molecule, films (whether adhesives or coatings) cast from solvent solutions near the center of the solubility window exhibit greater adhesion to compatible substrates. This is due to the increase in polymer surface area that comes in contact with the substrate. (Hildebrand parameters can be related to surface tension, and adhesion is greatest when the polarities of adhesive and adhered are similar.)

Many other properties of dried films, such as plastic crazing or gas permeability are related to the relative position that the original solvent occupied in the solubility window of the polymer. The degree of both crazing and permeability is predictably less when solvents more central to the solubility window have been used.[7]

Evaporation rates and solubility

Solvent evaporation rates can also have a marked affect on dried film properties. The solubility parameters of solvent blends can change during film drying because of the difference in evaporation rates of the component liquids. If a volatile true solvent is mixed with a slow evaporating non-solvent, the compatibility between solvents and polymer can shift as the true solvent evaporates. The predominance of theu non-solvent during the last stages of drying can result in a discontinuous, porous film with higher opacity and decreased resistance to water and oxygen deterioration. (There may be instances where these properties are desirable.)

This can be avoided, however, by either blending a small amount of a high boiling true solvent into the solvent mixture (this solvent remains to the last and insures miscibility), or by making sure that, if an azeotropic mixture is formed on evaporation, the parameters of the azeotrope lie within the polymer solubility window.[3]

An azeotrope is a mixture of two or more liquids that has a constant boiling point at a specific concentration. When two liquids are mixed that are capable of forming an azeotrope, the more volatile liquid will evaporate more quickly until the concentration reaches azeotropic proportions. At that point, the concentration will remain constant as evaporation continues. If the position of the azeotropic mixture lies within the solubility window, compatibility with the polymer will continue throughout the drying process. This can be determined by consulting a table of azeotropes and checking the location of the mixture on the Teas graph in relation to the polymer solubility window. (Methods of plotting solvent mixtures are described in the next section.)(ref.3)

Blending solvents

Teas graph is particularly useful as an aid to creating solvent mixtures for specific applications. Solvents can easily be blended to exhibit selective solubility behavior (dissolving one material but not another), or to control such properties as evaporation rate, solution viscosity, degree of toxicity or environmental effects. The use of the Teas graph can reduce trial and error experimentation to a minimum, by allowing the solubility behavior of a solvent mixture to be predicted in advance.

Because solubility properties are the net result of intermolecular attractions, a mixture with the same solubility parameters as a single liquid will, in many cases, exhibit the same solubility behavior. Determining the solubility behavior of a solvent mixture, therefore, is simply a matter of locating the solubility parameters of the mixture on the Teas graph. There are two ways by which this may be accomplished: mathematically, by calculating the fractional parameters of the mixture from the fractional parameters of the individual solvents, and geometrically, by simply drawing a line between the solvents and measuring the ratio of the mixture on the graph. The mathematical method is the most accurate, and is appropriate for mixtures of three or more solvents. The geometrical method is the most convenient and is suitable for mixtures of two solvents, or for very rough guesses when three solvents are involved.[5]

HANSEN SOLUBILITY PARAMETERS FOR WATER

Water is such an important material that a special section is dedicated to its HSP at this point. The behavior of water often depends on its local environment, which makes general predictions very difficult. Water is still so unpredictable that its use as a test solvent in solubility parameter studies is not recommended. This is true of water as a pure liquid or in mixtures. Table includes data from various HSP analyses of the behavior of water. The first set of data is derived from the energy
of vaporization of water at 25°C. The second set of data is based on a correlation of the solubility of various solvents in water, where "good" solvents are soluble to more than 1% in water. "Bad" solvents dissolve to a lesser extent. The third set of data is for a correlation of total miscibility of the given solvents with water.

HSP Correlations Related to Water
Correlation δD δP δH Ro FIT G/T(ref.1)

Water — Single molecule 15.5 16.0 42.3 — — —
Water — >1% soluble ina 15.1 20.4 16.5 18.1 0.856 88/167
Water — Total miscibility 1a 18.1 17.1 16.9 13.0 0.880 47/166
Water — Total miscibility "1b" 18.1 12.9 15.5 13.9 1.000 47/47

The HSP for water as a single molecule, based on the latent heat at 25°C is sometimes used in connection with mixtures with water to estimate average HSP. More recently, it has been found in a study involving water, ethanol, and 1,2-propanediol that the HSP for water indicated by the total water solubility correlation could be used to explain the behavior of the mixtures involved.
The averaged values are very questionable as water can associate, and water has a very small molar volume as a single molecule. It almost appears to have a dual character. The data for the 1% correlation,52 as well as for the total water miscibility, suggest that about six water molecules associate into units.
Traditionally, solvents are considered as points. This is practical and almost necessary from an experimental point of view as most solvents are so miscible as to not allow any experimental characterization in terms of a solubility sphere. An exception to this is the data for water reported in Table. The HSP reported here are the center points of HSP spheres where the good solvents are either those that are completely miscible or those that are miscible to only 1% or more, as
discussed previously. It should also be mentioned that amines were a major source of outliers in these correlations. No solids were included. Their use to predict solubility relations for amines and for solids must therefore be done with caution.

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