



Solubility Parameters for Characterizing New Raw Materials

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The chemistry of interactions between molecules produces the physical characteristics of all mixtures. This new understanding of the intermolecular physics, which controls material properties, is among the fastest growing fields of science. "Material science" is producing a revolution in engineering and chemistry, and has influenced medicine and biology. Material science is responsible for the development of new and better consumer products, at lower cost. This article will show you what practical simplifications and clarifications lie behind the revolution in material science, and how to use the "chemistry" of interactions to characterize new raw materials.

What Can a New Material Do?

So, the chemical salesperson has presented you with a new raw material! You already know that new raw materials can be the key to better product performance, the stuff of patents or trade secret technology. Or, however, they can be the time-wasting, fruitless, "blue sky," "try-it-and-see" gambles that get you and your department nowhere—except maybe to the next employer fast! If only you knew ahead of time what that new stuff would do!

Ten years ago such hopes were wishful thinking. Today they have been turned into techniques avidly practiced in the pharmaceutical and coatings industries to improve research and development productivity, in many cases much more than ten-fold!

Imagine emulsion formulas that are stable on the first try. Imagine drug delivery systems that partition into the skin or through the stomach wall faster than your competitor's product. Imagine knowing what preservatives will work before the challenge test is done. Or ... imagine that you will know how the chemical interactions taking place in your mixture will work and what they will do to the mixture.

The Dominance of "Weak" Forces

In general conversation, the term "chemistry" has come to mean "interaction" when applied to markets, social groups and businesses.

Until recently, the interaction "chemistry" of chemistry has remained an elusive and unmeasurable quantity. It is a strange paradox that the physical characteristics which seem most obvious to the nonscientist are controlled by forces so weak that scientists find them most difficult to measure.

The strong intermolecular forces that dominated chemistry during its development and maturity are the forces that cause reactions, the chief subjects of organic chemistry, inorganic chemistry and analytical chemistry. These are forces so strong that they cause electrons to jump off one molecule onto another. Oxidation (burning or rusting) and reduction, decomposition, and combination reactions are the result of these strong forces.

The newly exploited "interactive" forces are relatively weak, but numerous. They have been poorly understood in the past.² Nevertheless, these "weak" forces are responsible for properties ranging from viscosity, adhesion and membrane penetration to the coiling of protein and DNA, and the transcription of genetic code. These interactions produce the real "chemistry" of chemistry.

Weak forces are easier to see than strong forces: Weak forces are always, by their nature, less localized, yet more pervasive than strong forces. Gravity, the "weak force" in physics, is the most pervasive and easy-to-see force we know. Though its effects are easy to measure, gravity itself is the most difficult for physicists to characterize and understand.

Weak forces pull molecules together, but are not strong enough to transform them, only change their orientation. Nevertheless, orientation of molecules is much of what we see; just as the orientation of any building's material is what

we see. A building is a house, a store, or an office, because it is no longer a pile of bricks. In a similar fashion, molecules are the building blocks of life, and of everything around us. Perhaps this analogy helps clarify why their orientation is as important as, and often more obvious than, their substance. As in life, what you do with what you've got can be more significant than how much you have!

Betaine shampoo thickening by dilution: To chemists, an elegant and obvious example of the manipulation of weak field structures is betaine shampoo thickening. A concentrated, mixed solution of surfactants can be from many weak "coupled" structures into fewer, but longer and stronger, oriented bridges of molecules by diluting the solution. Adding water forces the betaine and sulfonate molecules farther apart. Although their attraction becomes weaker, at the same time it is more directed and oriented. Small bridges begin to form.

Viscometer measurements tell us how strong those bridges are. Fast viscometer speeds will break both strong and weak bonds, while slow speeds break only weak bonds. In Figure 1, as we dilute the solution, low-speed viscosity climbs and then drops as high-shear viscosity rises. This shows that weak bonding structures are being converted to strong ones by dilution. The result is shampoo that gets thicker when diluted with water.

The oriented "bridges" that are formed in the diluted shampoo resist weak force effects like pouring. Therefore, they look thick; thus, the dilute product appears to be a gel. From a practical viewpoint, this shampoo is ideal for use in the shower, where water splashing in your hand will not immediately make your shampoo run through your fingers!

This example shows how interactions both produce structure and affect properties in solution. These interactions reflect the cohesive field strengths of each molecular building block; cohesive force, in turn, is responsible for what we term molecular "character."

Sticky Molecules

The cohesive energy of ingredients is measured by the solubility parameter (δ). It is the source of such properties as viscosity, adhesion, miscibility and even the boiling point. Cohesive energy is simply an attractive force that is generated inside molecular particles of all ingredients. Some, like water, have more; some have less, like oil. We call highly cohesive ingredients "polar;" those less cohesive are oily or "nonpolar." The stickiness of molecules comes directly from the electronegativity of the atoms that make up the molecules.³ This relationship is shown in Figure 2, which compares the electronegativity numbers (EN) of Linus Pauling⁴ and the solubility parameters (δ) of Joel Hildebrand.⁵

When one invisible molecule sticks to the next, and the next, like a string of magnets, suddenly the tiny weak forces produce effects on a scale we can see. So, when we understand where these cohesive forces come from, we can then control the visible effects they produce.

For example, Teflon[®] is very nonpolar and has very weak

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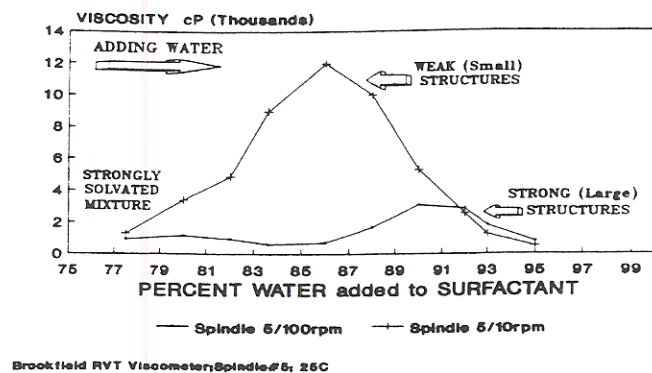


Figure 1. Rheology of betaine shampoo base

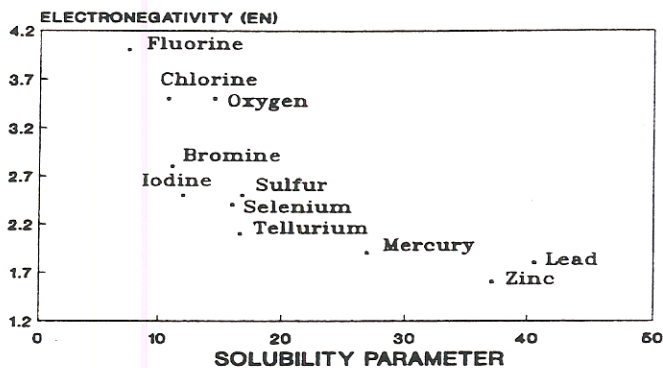


Figure 2. Electronegativity, the source of "stickiness," plotted versus solubility parameter

cohesion. Therefore, it can only form weakly attached molecular aggregates. Taken together, many individual noncohesive Teflon molecules form a continuous nonsticky barrier. This is why it is so widely used for nonstick surfaces. Low cohesion on the molecular level produces a nonsticky surface in the macro world. The molecular cohesion is most accurately measured as the solubility parameter.

How to Characterize Ingredients

Over 1000 cosmetic, pharmaceutical and fragrance materials have solubility parameters (δ) published in the *Cosmetic Bench Reference*.⁶ Other materials are listed in the *Handbook of Solubility Parameters and Other Cohesion Parameters*.⁷ But for new raw materials, you will have to determine the cohesive energy or solubility parameter from one or several methods available: Hildebrand's equation, Fedor method, the Drop Weight Method and Hansen's Three-Parameter Method.

By using these four different methods, I will demonstrate how this can be done using three new materials of current interest in the cosmetics field. These materials are pyruvic acid (an α -hydroxy acid), triclosan and cetyl ethoxylate. Look at their values for cohesive energy—are they "sticky" or not? Materials mix best with similarly cohesive materials. Then, compare the implied attributes with what the manufacturer says the ingredients will do!

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Hildebrand's Equation

Hildebrand⁸ showed us that the solubility parameter could be determined from boiling point, molecular weight and specific gravity (density). This equation was based on the fact that cohesive energy is overcome when liquids boil. The energy that holds the molecules together is overcome by the applied heat. Knowing that heat, we can arithmetically calculate the opposing cohesive energy.

Example 1: Pyruvic acid (an "α-hydroxyacid")

CH₃COCO₂H
Molecular weight = 88.06
Boiling point = 165°C
Specific gravity = 1.267 g/cc

$$S.P.(\delta) = \left(\frac{(23.7BP + 0.02BP^2 - 2950) - (1.98T)^{1/2} \cdot 3910.5 \text{ cal/cc}}{MW / \text{Sp. Grav.} \cdot 581.9 \text{ mol/cc}} \right)$$

where T = Temperature of specific gravity measurement

$$S.P.(\delta) = 12.40 \text{ plus H bond adjustment: Alcohol } +1.4$$

Ester +0.6

Ald/ketone(BP > 100°C) +0.5

$$\text{If Keto: } S.P. = 12.40 + 0.50 = 12.90 \text{ (cal/cc)}^{1/2}$$

$$\text{If Enol: } S.P. = 12.40 + 1.40 = 13.80 \text{ (cal/cc)}^{1/2}$$

Pyruvic acid is known to exist in a keto and an enol form. Each form has different polarity; therefore, each offers a different drive to penetrate skin. It is valuable to know which tautomeric form is most effective, since other formula ingredients can cause a shift from the keto to the enol form.

Fedors' Method

Hildebrand's equation is especially good for liquids that boil. Many published results use this method. For all mate-

rials, including those that do not boil, or materials which only have parts of their molecule exposed. Fedors' method will calculate the amount of sticky molecular surface from atomic geometry.

Fedors⁹ compiled a table of molecular parts (chemical groups) and their contribution to cohesive energy and molecular volume. In Examples 2 and 3, you can add them up, and find the maximum stickiness the keto and enol forms can exert. Fedors' method is especially useful when two parts of a single molecule have different polarity, as in surfactants and proteins. Thus, you can calculate the stickiness of various parts of molecules separately.

Example 2: Pyruvic acid (keto form)

Group	No.	Energy		Volume	
		Each	Total	Each	Total
CH ₃	1	1125	1125	33.5	33.5
COOH	1	6600	6600	28.5	28.5
>C=O	1	4150	4150	10.8	10.8
		11,875 cal/mol		72.8 cc/mol	
		11,875/72.8 = 163.1 cal/cc		S.P.(δ) = 163.1 ^{1/2} = 12.77 (cal/cc) ^{1/2}	

Example 3: Pyruvic acid (enol form)

Group	No.	Energy		Volume	
		Each	Total	Each	Total
CH ₂ =	1	1125	1125	33.5	33.5
COOH	1	6600	6600	28.5	28.5
>C=	1	1030	1030	-5.5	-5.5
-OH(Adj)	1	4150	4150	10.8	10.8
		13,880 cal/mol		64.5 cc/mol	
		13,880/64.5 = 215.1 cal/cc		S.P.(δ) = 215.1 ^{1/2} = 14.66 (cal/cc) ^{1/2}	

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α -Hydroxy acids have recently found popularity as "fruit acids" with "skin renewal" properties. Irritancy and control of penetration when using these materials is extremely important. The percutaneous absorption and the release from the vehicle are both related to solubility of the acid in skin and in the formula base. Van Scott has recommended 5 to 10% of glycolic and pyruvic acids for best effect.¹⁰

Now compare the Fedors' results for the two molecular forms to the Hildebrand result from boiling point. Using either Hildebrand's or Fedors' method, you can tell what structure you have. It is clear that pyruvic acid is predominantly in the keto form when concentrated; and its solubility parameter $12.77 \text{ (cal/cc)}^{1/2}$ is close enough to that for skin, $14.2 \text{ (cal/cc)}^{1/2}$, to favor limited penetration.

Drop Weight Method

For mixtures which do not have a definite molecular structure or sharp boiling point, the drop weight comparison is a good quick method for estimating the solubility parameter.¹¹ Drop weights are related directly to the cohesive energy of a liquid mixture through the surface tension it produces. A comparison of drop weights of two bracketing "known" materials will give a good estimate of the cohesive energy of the unknown.

We have found that you must use the same dropper type, consistently, to get good results.

Example 4. Drop weight solubility parameter calculation

	Drop Weight	Solubility Parameter(δ)
Water	58 mg	$23.40 \text{ (cal/cc)}^{1/2}$ (known)
Unknown	32 mg	-Interpolated-
Mineral oil	21 mg	$7.09 \text{ (cal/cc)}^{1/2}$ (known)

Water - mineral oil = 37 milligram difference
= $16.3 \text{ (cal/cc)}^{1/2}$ difference

This gives $0.44 \text{ (cal/cc)}^{1/2}$ per mg

For unknown: 11 mg/drop heavier than mineral oil:
 $7.09 \text{ (cal/cc)}^{1/2} + (11 \text{ mg/drop} \cdot 0.44 \text{ (cal/cc)}^{1/2}/\text{mg})$

Solubility Parameter(δ) = $7.09 + 4.84 = 11.93 \text{ (cal/cc)}^{1/2}$

Hansen's Three-Parameter Approach

To account for unexplained (at the time) deviations from theory, such as chameleonic solubility, Hansen developed the three-dimensional solubility parameter approach.¹² He placed hydrogen bond cohesion on one axis, polarizable charge cohesion on another axis, and nonpolar "London" contributions on the third axis. These are the three sources of the cohesive energy [i.e., the solubility parameter(δ)]. There is a large body of three-dimensional solubility parameter data available which has great practical use and precision.¹³

The problem of nonsymmetrical molecules: Very few molecules are symmetrical; this means that most are more sticky on one end than the other. Scientists call this "anisotropy" (different properties in different directions).¹⁴ This contributes to orientation and structure formation, as in crystals, quasi-crystals, liquid crystal phases,¹⁵ aggregation,¹⁶ helical coiling, and ternary polymer and protein forms.

Most every molecule is anisotropic in one way or another. Some more than others—surfactants, for example. Their anisotropy is so pronounced that there is a special name for it ... amphiphilic. Because the two molecule ends will not dissolve in the same solvents, surfactants are attracted to

SOLUBILITY

Balances The Interfacial
Membrane Structure

Solubility Parameters (SP) of
System Parts Must Match.

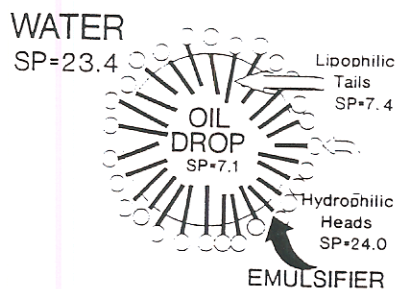


Figure 3. Interfacial membrane structures from anisotropy: solubility parameters of the system parts must match

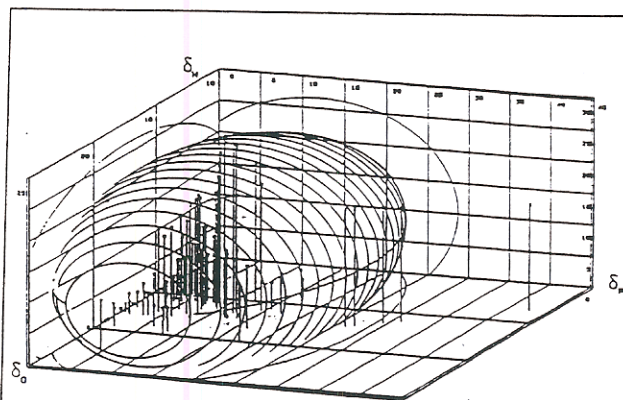


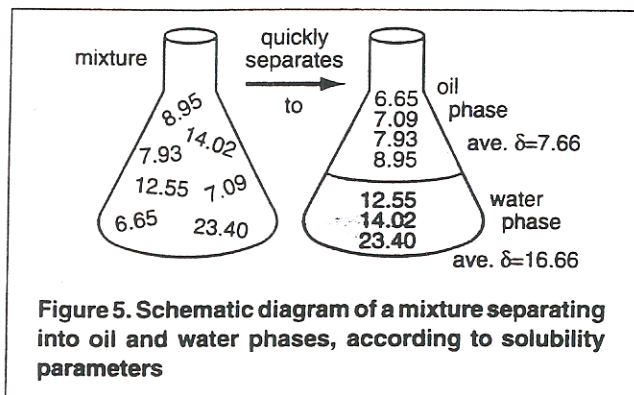
Figure 4. Hansen 3D solubility map, from *Rheological Properties of Cosmetics & Toiletries*, Dennis Laba, ed (1993), courtesy of Marcel Dekker, Inc, New York.

interfaces where they can stick each tail into its preferred solvent type. In cases like this, each end of the molecule should be characterized separately.

Chameleonic solubility: Materials with ends of opposing polarity can also exhibit a behavior called "chameleonic solubility." That is, they may dissolve in either polar or nonpolar solvent, but not in between!¹⁷ Acrylates/ C_{10} - C_{30} alkyl acrylate crosspolymer^b does this very nicely; this is why you can disperse it in either a water or oil phase. But, of course, if you found the solubility parameter(s) for this crosspolymer, you would have known what would happen. The carboxylic groups on this molecule have a solubility parameter of about $15.2 \text{ (cal/cc)}^{1/2}$, and the grafted hydrocarbon links have a solubility parameter of about $8.1 \text{ (cal/cc)}^{1/2}$. In a water phase, the crosspolymer sticks out its carboxyls; in an oil phase, it sticks out its hydrocarbon chains to match similar cohesive forces.

Hansen's method was very successful in finding ideal solvents and plasticizers for polymers, carriers for dyes, and

^bCarbomer 1342, BFGoodrich



even an ideal vehicle for triclosan.¹⁸

Characterizing triclosan: Willemin at Rhône-Poulenc Researchers used Hansen's technique to characterize triclosan, and fully explain its unusual ability to dissolve and partition in formulation. The best match for triclosan is defined by a spherical area in the three-dimensional graph matrix shown in Figure 4.

Hansen's three-dimensional solubility approach was based on empirical solubility measurements, but is supported by a mechanistic model. As successful as Hansen's maps have become, this author believes that even they will eventually be replaced by yet more successful computer analyses of interactions of chemical groups on anisotropic molecules. An approach that will permit us to make successful estimates of formulation properties without all the trial-and-error experimental work, will be the sign that the science of materials has matured. Today, however, is its youth.

What Can You Do, Knowing Character?

No matter how you decided to determine the cohesive energies of your ingredients, you are probably wondering what you can do with those numbers, once you've found them.

Solubility parameters tell you which ingredients interact and which do not. Whether values are high or low, the ingredients with close solubility parameters interact strongly—"like dissolves like."¹⁹ For example, consider a mixture of ingredients as shown in Figure 5.

In this example, cetyl ethoxylate, with nonpolar δ of 7.02 and polar end δ of 10.45, could be used as an emulsifier. Oil- or water-phase ingredients could be adjusted to make them better match the emulsifier tails. Then, you could use less emulsifier, or achieve a more stable emulsion at the chosen emulsifier level. This technique was discovered just a few years ago by Hans Schott at Temple University.²⁰

Mechanistics—The Future

Mechanisms in all areas of science are the keys to great leaps in creativity. Albert Einstein spent five years at Princeton working on a mechanistic explanation for gravity and time. Although he was unsuccessful, he knew that if he could uncover the mechanism behind these fundamental processes, it would allow their manipulation.

Remember, this is the same Einstein who, when he was a chemist (a very short time), in 1906 developed the very successful Stokes-Einstein equation, accurately explaining relative viscosities of dilute particles in suspension. He based his equation on his mechanical model of the interaction of the particles with the fluid. So, was Albert Einstein a

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better chemist than physicist? Or, is there really a difference any more?

Characterizing raw materials offers all chemists the same advantage which Einstein hoped to find by characterizing the nature of time and gravity. Solubility parameter characterization offers the key to a mechanistic model of what happens when we mix stuff. This mechanism is basically identifying materials with similar cohesive power, since those share the dominant interactions.

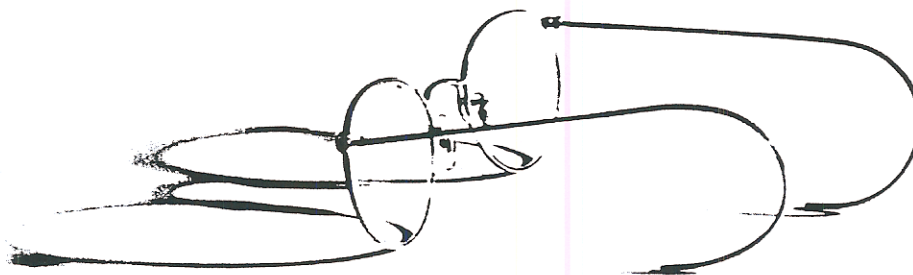
Knowing what is happening is the first step in solving any problem. Knowing why something happens is the second step. But, knowing how something happens is the explanation with a future.

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