

**SOLUBILITY PARAMETER CONCEPTS -  
A NEW LOOK\***

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## INTRODUCTION

The solubility parameter concept, on first discovery appears to offer a rationalized approach for a simplified elastomer selection in various solvents. The original definitive book, "Solubility of Nonelectrolytes" by the title gives the first clue that the problem is more complex than the simple "likes dissolves likes" approach. We live in a world of aqueous and nonaqueous electrolytes. Barton's recent work, "Handbook of Solubility Parameters and Other Cohesion Parameters"<sup>2</sup> is a good starting point for a serious study. Kamlet et al<sup>3</sup> offer some newer thoughts on solubility including more recent references. Jensen<sup>4</sup> in a recent chapter correctly notes that most of the solubility parameter concepts use the historic "similarity matching" of properties rather than the more appropriate "complementary matching" of properties. The former approach still pervades "as a result of an inappropriate extension of the dispersion-only arguments used in the original theory of regular solutions." Consider now, three examples of a mixed-solvent system.

## EXPERIMENTAL

Solvent mixtures are more often the rule rather than the exception; non-latex paints, lacquers, gasohol. Less obvious is high pressure sour gas (a mixture of methane, carbon dioxide and hydrogen sulfide). Consider first, a typical high molecular weight polymer suitable as a paint, lacquer or ink. The following solvents might be utilized to create a solution-based product:

- a. Theta  $\theta$  solvent (one that dissolves the elastomer with the solvated macromolecule size corresponding to its unperturbed [bulk] dimension). This solvent category is necessary to develop high % solids while maintaining low viscosity.
- b. Diluent solvent (one compatible with the theta solvent but incompatible with the polymer).
- c. Viscosity control solvent (a high volatility solvent to reduce overall viscosity for spray painting - typically evaporates before the paint or lacquer coats the object).
- d. Evaporation rate solvent - a low molecular weight, low volatility film-forming (leveling) solvent that allows solvents "a" and "b" to evaporate without forming a hard film first. This is necessary to develop a glossy surface.
- e. Plasticizer solvent - develops flexibility in the polymer.  
A typical range of solvents in a polymer based lacquer system could be:
  - A. tetrahydrofuran (theta solvent)
  - B. ketone (diluent)
  - C. aromatic hydrocarbon (viscosity control)
  - D. glycol ether (evaporation rate control)
  - E. phthalate ester plasticizer (flexibilizer)

Gasoline-alcohol mixtures, -the second example, are "nonideal solutions" as indicated by the increase in both volume and bulk

temperature on mixing. To prevent phase separation during temperature shifts, a third component such as MTBE (methyl tertbutyl ether) or higher molecular weight alcohols must be added to couple the two phases. Simplistically the -OH groups have a strong physical attraction to the alcohol and the -R groups are soluble in the gasoline. Thus a gasoline-alcohol mixture typically contains:

- a. hydrocarbon(s)
- b. alcohol
- c. ether or higher m.w. alcohol

The third case, sour gas is again different, the elevated pressure and temperature increase the density of the CO<sub>2</sub> and H<sub>2</sub>S so they have the mobility of a gas but the solvent power of liquids, each totally dissimilar in their solubility response. The gases are best illustrated by Figure 1 in a molecular thermodynamic sense as:

- a. methane (octopole)
- b. carbon dioxide (quadrupole)
- c. hydrogen sulfide (dipole)

## RESULTS

Hansen and Beerbower<sup>5</sup> give a brief review suitable for a basic explanation of the "similarity matching" concept of solubility parameters. It is less than adequate to develop a reasonable understanding of the solubility problem as defined in the first example noted in the "Experimental" discussion.

The second example, gasoline-methanol is totally incompatible with the Hansen-Beerbower approach. This was noted by Hertz<sup>6</sup> wherein the effect of gasoline, methanol and their mixtures on a 38% ACN nitrile elastomer is tabulated in Figure 2.

The third example, -sour gas/elastomer interactions, is based on original data from Ender<sup>7</sup>. His data, plotted by Hertz<sup>8</sup> in Table I indicates a substantially greater swelling than predicted in propylene-TFE elastomer (AFLAS<sup>®</sup>-ASAHI-3M), as compared to ethylene-propylene elastomer and the perfluoroelastomer (KALREZ<sup>®</sup>-Dupont). Subsequent discussions with Jensen<sup>9</sup> shed new thoughts on this swelling anomaly. This concept was outlined by Hertz<sup>10</sup> using Dr. Jensen's major contribution of Lewis acid-base considerations as a logical mechanism.

#### DISCUSSIONS

Briefly, we will review solubility parameter concepts and comment on them. The basic equation of Hildebrand and Scott designated the energy of vaporization as the *cohesive energy density* (ced) and it's square root as the *solubility parameter*, ( $\delta$ ) thus,

$$\delta = \left( \frac{\Delta H_v - RT}{V} \right)^{1/2} = \left( \frac{\Delta E_v}{V} \right)^{1/2} = (\text{ced})^{1/2} \quad (1)$$

This equation is simply stating that the heat of vaporization  $H_v$  less the volume work ( $-RT$ , where  $R$ =gas constant,  $T$ =absolute temperature) is the estimate of energy to maintain the liquid state

or *cohesive energy*. Dividing this value by molar volume  $V$  corrects for density leading to the term *cohesive energy density*. The values are reported in  $\text{MPa}^{1/2}$  units. This equation is only suitable for vapors obeying the ideal gas law ie: nonpolar fluids (nonelectrolytes).

An area of somewhat generalized agreement was the consideration that polar (aqueous and nonaqueous electrolytes) fluids had three major intermolecular forces to consider:

Dispersion (London) forces "D"-common in all cohesive energy

Hydrogen bonding "H", now referred to as H-bonding

Dipole moment "P", a measure of the *polar* (electrostatic)

aspect of a molecule.

The Hansen modification, utilizing these three intermolecular attractions,

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (2)$$

was intended for polar fluids by assigning a partial solubility parameter equal to the square root of the corresponding partial cohesive energy density. The gasoline-ethanol combination previously noted was an *exothermic* (gave up heat) mixture. Jensen<sup>4</sup> correctly notes that Equation (2) contains only the *squares* of the difference, it can thus only lead to positive or *endothermic* values and is therefore incapable of predicting accurately nonideal fluid/elastomer interactions (square of two *negatives is a positive*). This lack of consistency was previously noted by Hertz<sup>6</sup>

The final insult to the classical solubility parameter concept

is the high pressure sour gas combination noted. Consider the response of the three elastomers (Table 1):

EPDM	(nonfluorinated)
AFLAS <sup>®</sup>	(half-fluorinated EPDM)
KALREZ <sup>®</sup>	(totally fluorinated EPDM)

to very dissimilar gases, CO<sub>2</sub> and H<sub>2</sub>S. One might presume AFLAS<sup>®</sup> to have an intermediate swelling effect somewhere in between EPDM and KALREZ<sup>®</sup> based on the Hansen approach for solubility parameter calculation. Table 1 trend lines indicates approximately double (2X) the anticipated swelling.

The TFE/propylene molar ratio is approximately 48/52. Hydrocarbons respond to electrophilic reactions while fluorocarbons are dominated by a nucleophilic response. This makes it logical to pursue donor/acceptor (Lewis acid-base) possibilities. Adding to this concept, Jensen<sup>4</sup> in his chapter notes that "H-bonding is not really a particular kind of intermolecular 'force' like a dipole or dispersion force, but rather, as emphasized earlier, an example (albeit, a very important one) of a generalized electron-pair, donor-acceptor or Lewis acid-base interaction". He further notes "that most specific electrostatic or polar interactions are already included within conventional measures of electron-pair donor and acceptor strengths, making the separate polar term in the equation potentially redundant." Specifically addressing the sour gas swelling phenomenon, Prof. Jensen<sup>9</sup> states:

"Quantifying these considerations is, however, more difficult.

As most species are to some extent amphoteric and their EPA (electron-pair acceptor) and EPD (electron-pair donor) properties tend to work in opposite directions as far as the sign and magnitude of the zeta ( $\xi$ ) potential are concerned. Perhaps the simplest approach to this problem would be to use an empirical linear correlation similar to that proposed by Koppel and Palm in 1971 to analyze the solvent dependency of various physico-chemical properties:

$$P = P_0 + \alpha \cdot DN + \beta \cdot AN + \xi \cdot \delta_d \quad (\text{No. 38}) \quad (3)$$

where P is the value of the property in the solvent of interest,  $P_0$  is the value of the property in some reference state (preferably, but not necessarily, the gas phase or some inert solvent).  $\alpha$  describes the sensitivity of the property to solvent basicity,  $\beta$  its sensitivity to solvent acidity,  $\xi$  its sensitivity to nonspecific dispersion forces. The property in question may be a spectral transition, the logarithm of a rate constant or an equilibrium constant, a reaction enthalpy, an NMR shift, or, in our case, the zeta ( $\xi$ ) potential of a colloidal particle. Generally if the EPA-EPD character of the solvent is significant, it tends to swamp the last term."

Jensen(18) further suggests the anomalous swelling of AFLAS<sup>®</sup> is explained in the following manner:



"The equation of interest is NO. 38:

$$\begin{array}{rcc}
 P & = & P_0 \\
 \uparrow & & \uparrow \\
 \text{Property of} & & \text{Property of} \\
 \text{interest} & & \text{reference} \\
 \text{(swell)} & & \text{state} \\
 \\ 
 \alpha \cdot DN & + & \beta \cdot AN & + & \xi \cdot \delta_d \\
 \uparrow & & \uparrow & & \uparrow \\
 \text{Lewis} & & \text{Lewis} & & \text{Nonspecific} \\
 \text{basicity} & & \text{acidity} & & \text{sensitivity} \\
 \text{sensitivity} & & \text{sensitivity} & & \text{(solubility} \\
 & & & & \text{parameter)}
 \end{array}$$

$\alpha$ ,  $\beta$  and  $\xi$  are determined by least squares multiple parameter regression analysis by measuring  $P$  in a variety of systems of known  $DN$ ,  $AN$  and  $\delta_d$ . The values can then be used to calculate  $P$  in other systems.

For your system:

- $P_0$  = volume swell in air = 0
- $P$  = volume swell for gas or liquid
- $DN, AN, \delta_d$  = characterize the gas or liquid
- $\alpha, \beta \& \xi$  = characterize the polymer

For your gases (these are qualitative guesses):

- $\delta$  - ( $H_2S > CO_2$ )
- $DN$  - ( $H_2S > CO_2$ )
- $AN$  - ( $CO_2 > H_2S$ )

For your polymers (these are qualitative guesses):

- EPDM ( $\alpha = \beta = 0$  re only  $\xi$  is operative, polymer is non-specific)
- AFLAS<sup>®</sup> ( $\alpha$  and  $\beta$  large - and swamp  $\xi$ , polymer is amphoteric)
- KALREZ<sup>®</sup> ( $\alpha = 0$ ,  $\beta$  large and swamp  $\xi$ , i.e., polymer is a Lewis base). "

### CONCLUSIONS

Equation (38) offers exciting possibilities for a more rationalized approach using the complementary matching of properties for fluid-elastomer interactions. Unfortunately much work still has to be done at the university level to develop meaningful donor numbers (DN) and acceptor numbers (AN) . Hopefully this paper might spur a renewed effort by encouraging corporate sponsorship to develop these data.

### SUMMARY

Present solubility parameter concepts are only suitable for predicting the simplest elastomer/fluid interactions. The use of donor-acceptor (Lewis acid-base) concepts offer the potential of a more powerful predictive tool. Additional work has to be done at the university level to make this possibility a reality.

### ACKNOWLEDGEMENTS

To the late Alan Beerbower, a long time friend, who introduced me to solubility parameter concepts, once describing it as "a modest part of molecular thermodynamics".

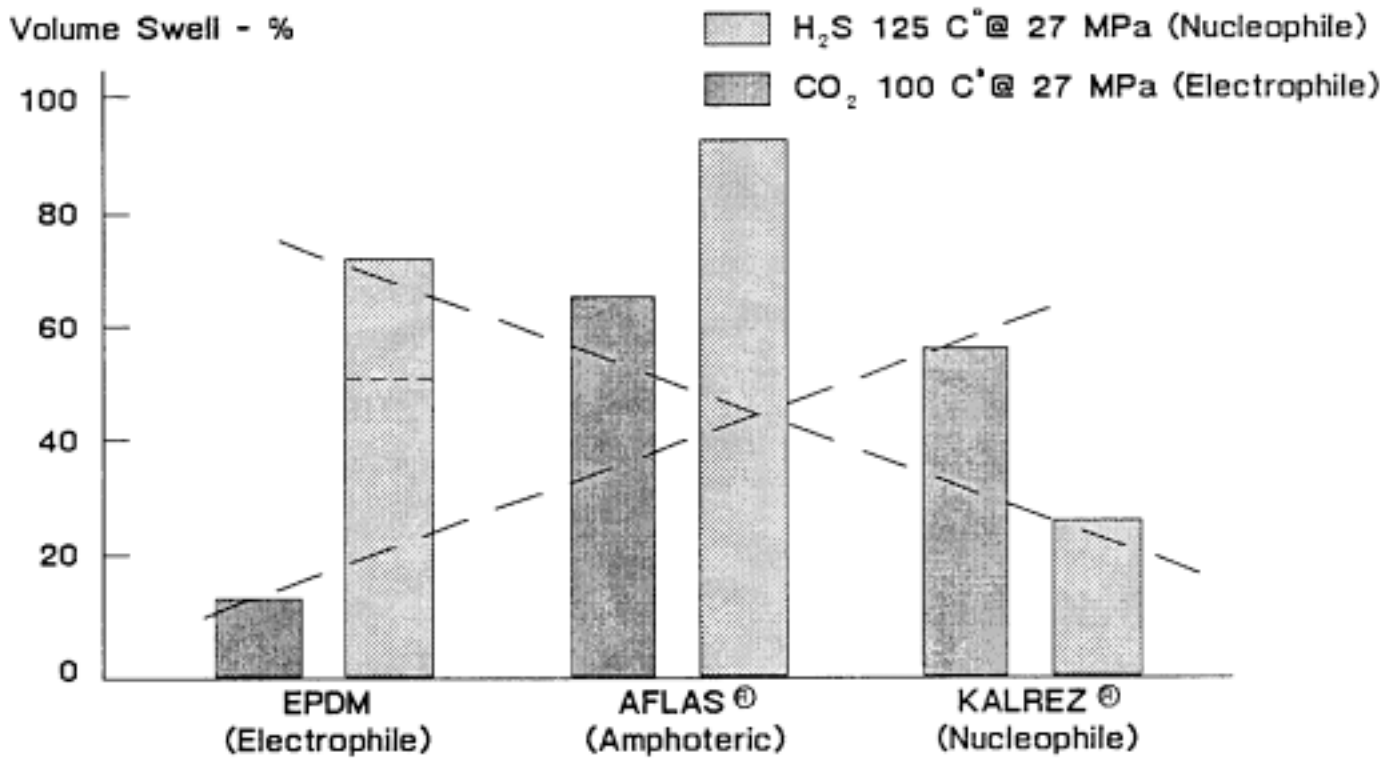
To Professor William B. Jensen, for his keen insight and help in applying Lewis acid-base theory to the solubility parameter puzzle.

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TABLE I

## GAS-ELASTOMER SWELLING\*



\* D. Ender, Shell Dev. Co. - Paper no. 44 ACS - Rubber Div. 10/83

## ELECTRIC CHARGE DISTRIBUTION

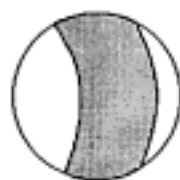
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**Methane  
(Neutral)**



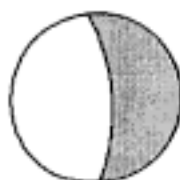
**(Octopole)**

**Carbon Dioxide  
(Electrophile or  
Lewis Acid)**



**(Quadrupole)**

**Hydrogen Sulfide  
(Nucleophile or  
Lewis Base)**



**(Dipole)**

FIGURE 2

ELASTOMER SWELL vs GASOLINE-ALCOHOL RATIO  
(Room Temperature - Long Term)

