

# Using Hansen Solubility Parameters to Model Solvent Blends

Justin Green

## Abstract

Whether or not a chemical or mixture of chemicals will dissolve a polymer is an important area of research in chemistry. This paper is concerned with using the solubility parameters proposed by Charles Hansen to model mixtures of solvents. This model can then be used to find a list of mixtures most likely to dissolve a particular polymer, which would then be subject to experimental verification.

## 1 Introduction

Solvents are used extensively in the chemical industry. But certain solvents may be expensive or harmful to people or the environment. So there is value in finding suitable replacements. Solubility parameters are used to quantify attraction between molecules and (in this case) to predict the miscibility of chemicals. One widely used system of parameters was proposed by Charles Hansen and is known as the Hansen solubility parameters (HSP). It has been observed that, in most cases, mixtures of solvents have HSP values that are approximately proportional to the volume fractions of the component solvents. In other words, in most cases the HSP value of a solvent blend can be assumed to be linearly related to the HSP values of its components. The purpose of this paper is to provide some background information about HSP and show how HSP can be used to model solvent blends, given this linear assumption.

## 2 Solubility Parameters

As stated before, solubility parameters are a way to predict whether or not chemicals will dissolve into each other, and we will use the Hansen solubility parameters. In order to describe HSP we first define the Hildebrand solubility parameter, on which HSP is based.

### 2.1 Hildebrand Solubility Parameter

The Hildebrand solubility parameter,  $\delta$ , of a chemical is defined as

$$\delta = \sqrt{\frac{E}{V}},$$

where  $E$  is the total cohesion energy of the chemical and  $V$  is the molar volume. It should be noted that total cohesion energy is equal to heat of vaporization, which is a value that can be measured relatively easily.

According to the laws of thermodynamics, chemical reactions obey the following equation,

$$\Delta G = \Delta H - \Delta TS, \quad (1)$$

where  $\Delta G$  is free energy,  $\Delta H$  is heat of reaction,  $T$  is absolute temperature, and  $\Delta S$  is entropy of reaction. For negative  $\Delta G$  the reaction will occur spontaneously, for positive  $\Delta G$  the reaction will not occur spontaneously, and the reaction is at equilibrium for  $\Delta G = 0$ .

Suppose we have two chemicals and we mix them together hoping they will dissolve into each other. It has been found that the noncombinational free energy,  $\Delta G_{noncomb}$ , obeys the following equation

$$\Delta G_{noncomb} = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2,$$

where  $\varphi_1$  and  $\varphi_2$  are the volume fractions of the two chemicals,  $V_M$  is the total volume of the mixture, and  $\delta_1$  and  $\delta_2$  are the solubility parameters of the two chemicals.

Noncombinational free energy is defined as the free energy from sources other than the entropy occurring from mixing the solution, or combinational entropy,  $\Delta TS_{comb}$ . We can, therefore, rewrite Equation 1 as

$$\Delta G = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 - \Delta TS_{comb}. \quad (2)$$

We can see from this equation that for a large difference between solubility parameters,  $\Delta G$  is positive and a reaction will not occur spontaneously and for a small difference between solubility parameters,  $\Delta G$  is negative and the reaction will occur spontaneously.

## 2.2 Hansen Solubility Parameters

The problem with the Hildebrand solubility parameter is that it does not take many kinds of intermolecular interactions into account. The idea behind HSP is to divide the total cohesion energy into three separate cohesion energies based on the different kinds of interaction forces most common to organic molecules. These are energy from dispersion interactions, energy from dipole-dipole interactions, and energy from hydrogen bonding.

Energy from dispersion interaction,  $E_D$ , accounts for interaction due to the random nature of the electrons of a molecule. The location of an electron at any given instant can be predicted based on the probability that it will be at that location. So at any instant the electron density of a certain area of the molecule may be particularly high, in which case

a molecule or atom with a positive or partial positive charge can be attracted and given the chance to interact. If the electron density of that area is low, a negative charge can be attracted.

Energy from dipole-dipole interaction,  $E_P$ , accounts for interaction between polar molecules. This differs from dispersion interaction because, in polar molecules, the areas of high and low electron density are said to be permanent. The location of electrons is still random, but the probability they will be in one area is higher than another. Charges can be attracted to those areas accordingly.

Energy from hydrogen bonding,  $E_H$ , accounts for interaction due to electron exchange. Hydrogen bonding is a specific type of dipole-dipole interaction between a hydrogen atom and an electronegative, or electron seeking, molecule. This category is sometimes divided further based on different types of electron exchange.

The total cohesive energy of a molecule is related to the three separate cohesion energies by

$$E = E_D + E_P + E_H,$$

and the individual Hansen solubility parameters relate to the Hildebrand solubility parameter by

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2.$$

### 2.3 Interaction Sphere

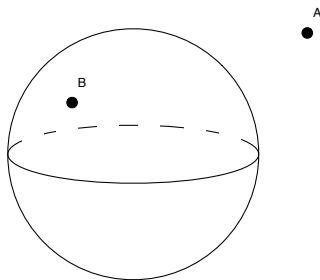
By Equation 2 we have that molecules with similar HSP values will dissolve into each other more readily than molecules with dissimilar HSP values. But the question remains, how close do the HSP values have to be for a spontaneous reaction to occur? This question is answered by experimentation. Solubility tests are done for each polymer to be dissolved and the distance between the HSP values of the polymer and the HSP values of the borderline solvents are taken as the maximum distance allowable for a suitable solvent. This ‘radius of interaction,’  $R_0$ , is given by

$$R_0 = \sqrt{4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2}, \quad (3)$$

where the  $\delta_1$ 's and  $\delta_2$ 's are the HSP values of the polymer to be dissolved and the most outlying suitable solvent. If the distance between the polymer and a solvent is less than  $R_0$ , the solvent is suitable and if the distance is greater than  $R_0$ , the solvent is not suitable.

So, the interaction radius of a polymer creates a sphere enclosing all of the suitable solvents, centered at the HSP values of the polymer. Solvents inside the interaction sphere will dissolve the polymer and solvents outside the sphere will not, as illustrated in Figure 1.

Figure 1: B is a suitable solvent, A is not.



Since we can consider each molecule as a vector in  $\mathbb{R}^3$ , we can simplify this notation to

$$R_0 = |\vec{v} - \vec{s}|,$$

where  $\vec{v}$  represents the polymer and  $\vec{s}$  represents the outlying solvent, considering we multiply each vector by a constant  $\langle 2, 0, 0 \rangle$  to account for the 4 multiplied by the  $\delta_D$  parameter in Equation 3. It should be noted that all vectors represented in this way from this point on are multiplied by this constant vector in the interest of simplifying notation.

## 2.4 Considerations and Limitations

Several considerations must be made when dealing with HSP. The partial HSP values are often difficult to find. Energy from some types of molecular interactions are not taken into account, for example induced dipole and metallic bonds, so other parameters should be added if inorganic molecules are to be considered. HSP values are temperature dependant, so they are usually found for a standard temperature. But as temperature increases the HSP values of solid polymers are often less effected than the values of liquid solvents. Finally, small molecules sometimes perform better as solvents than predicted and large molecules sometimes perform worse than predicted.

## 3 Modeling Solvent Blends

The only way to be sure if a solvent is suitable for dissolving a given polymer is to test it. If we have a list of one hundred solvents and consider all possible combinations of

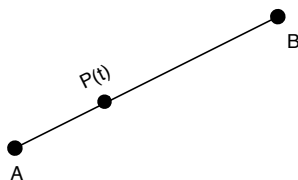
two-solvent blends, we have  $\frac{100!}{2!98!} = 4950$  different combinations to test. If we consider all possible combinations of three-solvent blends, we have  $\frac{100!}{3!97!} = 161,700$  different combinations to test. Considering that we must find the ideal percent composition for each combination, it quickly becomes clear that testing all combinations is not a viable option if we are going to finish in a reasonable amount of time.

It has been observed that, in most cases, the HSP values of a mixture of solvents are proportional to the volume fractions of its component solvents. This means that the HSP values of a mixture are approximately linearly related to the HSP values of its component solvents. We can, therefore, model a mixture of two solvents with a parametric equation for a line,

$$P(t) = (\vec{b} - \vec{a})t + \vec{a},$$

where  $0 \leq t \leq 1$  and  $\vec{a}$  and  $\vec{b}$  represent the two component solvents  $A$  and  $B$ , respectively. The volume fraction of component  $B$  is represented by the parameter  $t$  and the volume fraction of  $A$  is  $1 - t$ . Pictorially, this is a line segment between the components  $A$  and  $B$  with the mixture,  $P(t)$ , lying somewhere on the line, as in Figure 2.

Figure 2: A two-solvent blend.

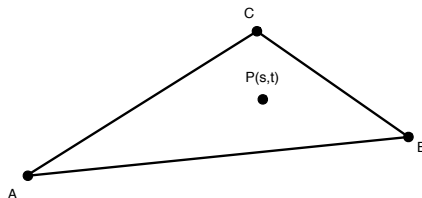


Similarly we can model a mixture of three solvents with a parametric equation for a plane,

$$P(s, t) = (\vec{b} - \vec{a})t + (\vec{c} - \vec{a})s + \vec{a},$$

where  $0 \leq s + t \leq 1$  and  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$  represent the three components  $A$ ,  $B$  and  $C$ . In this case the volume fractions of components  $B$  and  $C$  are represented by the parameters  $t$  and  $s$ , respectively, while  $A$  is  $1 - t - s$ . Pictorially, this is a triangle defined by  $A$ ,  $B$ , and  $C$  with the mixture,  $P(s, t)$ , lying somewhere inside the triangle, as in Figure 3. We can model any  $n$ -solvent blend for  $n \in \mathbb{N}$  similarly, but it is probably unnecessary to go beyond three or four solvents.

Figure 3: A three-solvent blend.



To determine whether or not a solvent is suitable, we need to know its distance in Hansen space from the polymer we want to dissolve. In the case of a two-solvent mixture, we define distance function,

$$D(t) = |\vec{v} - P(t)|,$$

where  $\vec{v}$  represents the polymer we want to dissolve. In the case of a three-solvent blend, the distance function is

$$D(s, t) = |\vec{v} - P(s, t)|.$$

Consider the functions  $P$  and  $D$  for a three-solvent blend. The other cases work similarly. The function  $P$  is a linear function from  $[0, 1] \times [0, 1]$  to  $\mathbb{R}^3$ , so it is a continuous function. The function  $D$ , defined as the distance between a constant and  $P$ , is a linear function from  $[0, 1] \times [0, 1]$  to  $\mathbb{R}$ , so  $D$  is a continuous function on a closed domain. Therefore, by the Extreme Value Theorem,  $D$  obtains a minimum on its domain. This means that a minimum distance between the solvent blend and the polymer exists and we can calculate it. We can also find the values of  $s$  and  $t$  (and hence the volume fractions of the component solvents) where this minimum occurs.

Once we determine the minimum distance,  $D_0$ , for a particular solvent blend, we can determine if that distance is small enough so that the blend is suitable for dissolving our polymer. Recall from Section 2.3 that each polymer has an interaction radius,  $R_0$ , associated with it. If we have  $D_0 > R_0$  then the solvent blend is not suitable. If we have  $D_0 < R_0$  then the solvent blend is suitable and we can add it to the list of solvents to be tested. This process of finding and minimizing the distance function and comparing it to the interaction radius is repeated for each combination of solvents.

## 4 Conclusions

HSP is a system which can be used to determine whether or not a solvent will dissolve a polymer. If we assume that the HSP values of a mixture of solvents is linearly related to

the HSP values of its component solvents we can model the mixture of solvents as a linear parametric equation. We can then minimize the distance in Hansen space between the mixture and a polymer to determine whether the minimum distance results in a mixture which is a suitable solvent of the polymer. This will also give us the volume fractions of the component solvents.

HSP has been used for years to successfully predict the behaviour of single solvents. Assuming that the linear assumption is valid for enough solvent blends, we can extend the use of HSP to mixtures of solvents as well. This method could be used to increase the range of polymers that can be dissolved by cheaper solvents and help reduce the usage of dangerous chemicals. Further research could be done in this area to determine how valid this linear assumption is.

## References

- [1] C. A. Hansen, Hansen Solubility Parameters: A User's Handbook, CRC Press (2000), 1-39.