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Optimizing Solvent Blends for a Quinary System

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OPTIMIZING SOLVENT BLENDS FOR A QUINARY SYSTEM

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Honors Research Project

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1. Introduction

Choosing the correct solvent is a critical step in every polymerization. If a monomer is not fully soluble in the selected solvent, the reaction will take place in a heterogeneous fashion. Furthermore, if the resulting polymer is not fully soluble, the polymer will precipitate out. Whether a particular solvent will successfully solvate a monomer or polymer is based on the similarities in molecular composition and structure. Even if the molecular structure of solvent and solute are known, this observation is still too qualitative to make consistently correct decisions. The choice of solvents is further complicated when trying to synthesize a copolymer from multiple different monomers. Most solvent choices are based on personal experience or previously established standards, making it difficult to decide on a solvent for a completely new copolymer. These difficulties are compounded if the goal of an experiment is to make several new copolymers which have no previously established acceptable solvent.

The goal of the project funded by the W. M. Keck Foundation is to create a computer aided process which will produce upwards of fifty copolymers at a time, then systematically evaluate these polymers for a given material property. After evaluation a new batch of copolymers is created using the results from the previous experiment as basis for the new copolymers. With an extreme focus on automation and quick turnaround, it is necessary to make the choice of solvents for each copolymer as quickly as possible. This emphasis makes the typical method of prior experience woefully inadequate for the choice of solvents. In

order ensure that picking solvents is not a rate-limiting step for each iteration of copolymer synthesis, it is necessary to create a computer program that can make solvent choices based on reliable and repeatable procedure.

Charles Hansen has created set of parameters which mathematically describe solvents, monomers, and polymers in order to determine the quality of solvents.[1] The Hansen Solubility Parameters (HSP) take into account molecular structure, composition, and size in order to assign numeric values associated with these properties. While HSP do not have a strict theoretical basis, they are closely related to the Hildebrand Solubility Parameter which has an explicit thermodynamic explanation. While the Hildebrand Parameter gives a simple calculation for solubility, it fails to take into account molecular structure, and therefore is insufficient. HSP facilitate creating a numerical algorithm which can consistently determine the quality of solvents.

2. Background

2.1 Hildebrand Solubility Parameter

The Hildebrand Solubility Parameter is a measurable quantity of every molecule, solvents and polymers alike. The parameter δ can be calculated using equation (2.1). In equation (2.1), ΔH is the heat of vaporization, R is the gas constant, T is the absolute temperature, and V_m is the molar volume.[2]

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \quad (2.1)$$

When determining whether a polymer is miscible in a given solvent, equation (2.2) is used to see if the calculated χ is less than χ_c otherwise known as the critical χ value of a polymer solution. For an arbitrarily large polymer χ_c is .5.

$$\chi = \frac{V_m(\delta_1 - \delta_2)^2}{RT} \quad (2.2)$$

$$(\delta_1 - \delta_2)^2 = \frac{\chi RT}{V_m} = R_i \quad (2.3)$$

By rearranging equation (2.2) into (2.3), it can be seen that if R_i is less than χ_c, then the two substances are likely miscible. Using this equation we can create a one-dimensional interaction radius centered on the Hildebrand Parameter for a given polymer. If a solvent lies within the radius of a given polymer, the pair is likely to be miscible. An idealized example of this interaction radius is given in Figure 2.1. As stated before, the Hildebrand Parameter assumes all intermolecular interactions are van der Waals forces.
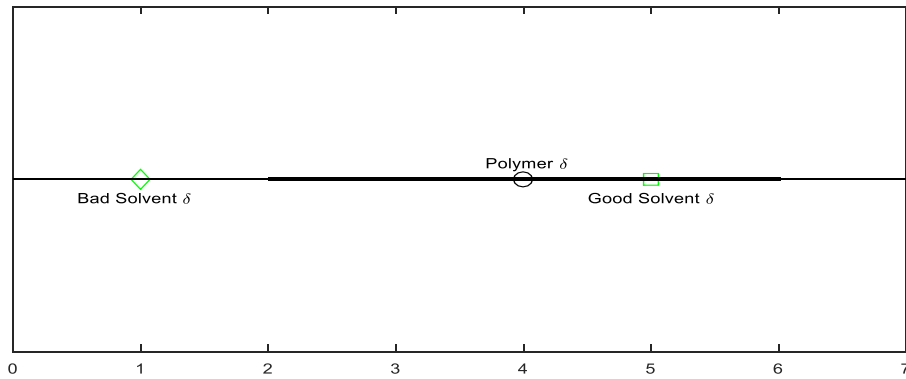
Figure 2.1 The polymer given in figure 2.1 has δ of 4 and an interaction radius of 4. Solvent one lies within the interaction radius, suggesting the two are miscible. Solvent two lies outside of the interaction radius, suggesting they are not miscible

2.2 Hansen Solubility Parameters

Charles Hansen, through experimental observation, observed that Hildebrand Solubility Parameter could be improved on by creating sub-parameters relating to the structure of given molecules. The δ_D parameter is the parameter associated with dispersion forces, or the non-polar contributions to solubility. δ_P refers to solubility contributions from polar portions of a molecule brought on by asymmetries in molecular structure. δ_H parameter is associated with hydrogen bonding forces, or intermolecular interactions brought on by the large differences in electronegativity.[1] These three parameters are directly related to the Hildebrand parameter and can easily be substituted in for the equation of miscibility as shown in equations 2.4 and 2.5 respectively.

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \text{ (2.4)}$$

$$\chi = \frac{V_m[(\delta_{D1}-\delta_{D2})^2 + (\delta_{P1}-\delta_{P2})^2 + (\delta_{H1}-\delta_{H2})^2]}{RT} \text{ (2.5)}$$

For calculating the miscibility of polymers in a given solvent, Hansen introduced a deviation in the standard procedure. Observing that dispersion forces carry high weight of importance for the solubility of polymers, he introduced a new set of equations to determine miscibility.

Hansen Space is a three-dimensional plot with perpendicular axes of δ_D, δ_P, and δ_H. Instead of a line segment on a number line, the shape of an interaction radius of a molecule in Hansen Space can be represented by a sphere centered at the HSP of the given Molecule in a three-dimensional space.[1]

$$4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 = R_a^2 \text{ (2.6)}$$

$$RED = {}^{R_a}\!/_{R_o} \text{ (2.7)}$$

Equation (2.6) determines the Relative Affinity (R_a) of a polymer and solvent. Then the Relative Energy Difference (RED) is calculated in equation (2.7) as the quotient of R_a and R_o, where R_o is an experimentally derived parameter of a polymer for arbitrarily high molecular weight. If the RED is less than one, then the polymer and solvent are likely miscible. With this relationship, and combining equations (2.6) and (2.7), equation (2.8) is derived. Equation (2.8) describes all points in Hansen space that describe molecule miscible with a given polymer. As opposed to the non-polymer HSP equation, equation (2.8) describes an ellipsoid in Hansen Space. [1,3]

$$\frac{4(\delta_{D1} - \delta_{D2})^2}{(R_o)^2} + \frac{(\delta_{P1} - \delta_{P2})^2}{(R_o)^2} + \frac{(\delta_{H1} - \delta_{H2})^2}{(R_o)^2} < 1 \text{ (2.8)}$$

It is critical to mention that Hansen describes the HSP of a blend of solvents a simple molar weighted average between the HSP of the two solvent components.[1,3] To calculate the HSP of the copolymers, a similar strategy will be

employed. First, the HSP for the homopolymers of the constituent monomers will be obtained from Hansen's handbook.[1] Then, the weighted average of the homopolymers HSP will be taken as the HSP for the copolymer with the weights being based on the molar percentages of the monomers.

2.3 Group Contribution Theory.

In order to take into account the effects that each functional group has on its molecules solubility, HSP employs Group Contribution Theory (GCT). GCT is the idea that every functional group has its own solubility properties and that a molecules solubility properties is a combination of its functional groups. Dispersion forces area simple some of each component divided by the molar volume of the molecule given in equation (2.9). F_{Di} is the contribution of the i_{th} functional group.[4]

$$\delta_D = \frac{\Sigma F_{Di}}{V_m} \quad (2.9)$$

The calculation of the polar parameters and hydrogen bonding parameters differs slightly from the dispersion calculations and are given in equations (2.10) and (2.11) respectively. Additionally, if there are identical functional groups that are distributed symmetrically across the molecule, there are additional coefficients that need to be taken into account. For polar forces, there is a coefficient of .5 is for a single-plane symmetry, .25 for two-plane symmetry, and 0 for more than two planes of symmetry.[4] Hydrogen forces only have an additional coefficient of 0 if there is more than one plane of symmetry.[4]

$$\delta_P = \frac{\sqrt{\Sigma \, F_{Pi}^2}}{V_m} \quad (3.10) \qquad \delta_H = \sqrt{\frac{\Sigma \, F_{Hi}}{V_m}} \quad (3.11)$$

Hansen provides an extensive list of HSP for solvents and polymers, but this list is far from comprehensive.[1] With GCT, it is possible to calculate the HSP of molecule with a known composition and structure. Hansen's handbook contains the solubility contributions of several common functional groups for this purpose. Further work could involve a program that determines the HSP of molecules based on its structure.

3. Application of Hansen Solubility Parameters

3.1 Derivation of the Algorithm

The goal of the procedure is to determine an optimized blend of solvents that could simultaneously dissolve both monomers and the resulting copolymer in order to ensure that polymerization can begin and go to completion. A blend of solvents is necessary because it is highly unlikely that single point in Hansen space, the HSP of a single solvent, will be sufficient to dissolve every possible copolymer system. When using a blend of solvents, every possible HSP of the blend can be represented as points on a line segment between each solvent. The HSP lie on the line segment due to the simple nature of determining HSP for solvent blends, as described by Hansen.[1] An example of how the HSP would be calculated is given in equation (3.1). The coefficient x_1 represents the molar percentage of solvent one in the solvent blend and $(1 - x_1)$ represents the molar percentage of solvent two in the solvent blend.

$$\delta_{D\,total} = x_1\delta_{D1} + (1 - x_1)\delta_{D2} \ (3.1)$$

$$4\frac{(\delta_D - (x_1\delta_{D1} + (1-x_1)\delta_{D2}))^2}{(R_o)^2} + \frac{(\delta_P - (x_1\delta_{P1} + (1-x_1)\delta_{P2}))^2}{(R_o)^2} + \frac{(\delta_H - (x_1\delta_{H1} + (1-x_1)\delta_{H2}))^2}{(R_o)^2} < 1 \ (4.2)$$

Per equations (2.8) and (3.1), equation (3.2) represents all of the possible points in a blend of solvents that are miscible with a given polymer. By expanding the quadranomial of the dispersion forces in equation (3.2) we obtain equation (3.3a) and a simplified version in equation (3.3b).

$$x_1{}^2\left(\delta_{D1}^2 - 2\delta_{D1}\delta_{D2} + \delta_{D2}^2\right) + x_1\left(-2\delta_{Dm}\delta_{D1} + 2\delta_{Dm}\delta_{D2} + 2\delta_{D1}\delta_{D2} - 2\delta_{D2}^2\right) + \left(\delta_{Dm}^2 - 2\delta_{Dm}\delta_{D2} + \delta_{D2}^2\right) \ (3.3a)$$

$$x_1{}^2\Delta_{D2} + x_1\Delta_{D1} + \Delta_{D0} \ (3.3b)$$

By applying the same expansion to the polar and hydrogen bonding forces and summing up all of the analogous (3.3b) equations, equation (3.4) is produced.

$$x_1{}^2(4\Delta_{D2} + \Delta_{P2} + \Delta_{H2}) + x_1(4\Delta_{D1} + \Delta_{P1} + \Delta_{H1}) + (4\Delta_{D0} + \Delta_{P0} + \Delta_{H0} - R_o^2) = 0 \text{ (3.4)}$$

This equation is a quadratic with respects to x_1 and can be solved to find the two points of intersection between the solvent blend and the polymer ellipsoid. All of the points between the two intersections are miscible blends of solvent with the polymer. It is necessary to note that x_1 values that are not between zero and one do not make physical sense. Such an alpha would represent a solvent blend that consists of over one hundred percent of one solvent and a negative percentage of the other.

Similar calculations can be used to determine where a solvent blend will miscible with the monomers. By combining equations (2.5) and (3.1), an analogous calculation will be produced and solved in the same fashion. In order to find the section of the solvent blend that is miscible with the monomers and the resulting copolymer, each intersection point will be checked if it within the other two volumes in Hansen Space. For every real solution, two of these intersection points will be found and the midpoint between them will be used as the optimal blend of solvents to solvate the system.

3.2 Cases that Produce Valid Solvent Blends

For the purposes of all examples, the δ_H value of all components will be zero. Setting δ_H to zero will have no effect on the accuracy of the procedure. The

purpose of setting all δ_H values at zero is to make visualization of the procedure

easier to comprehend as it makes the process effectively two-dimensional. The

δ_P-δ_D plane will be displayed in all following figures. Also the temperature is

assumed to be 293 K. Figure 3.1 illustrates how this simplification makes the

procedure easier to interpret as well as gives a visualization of the

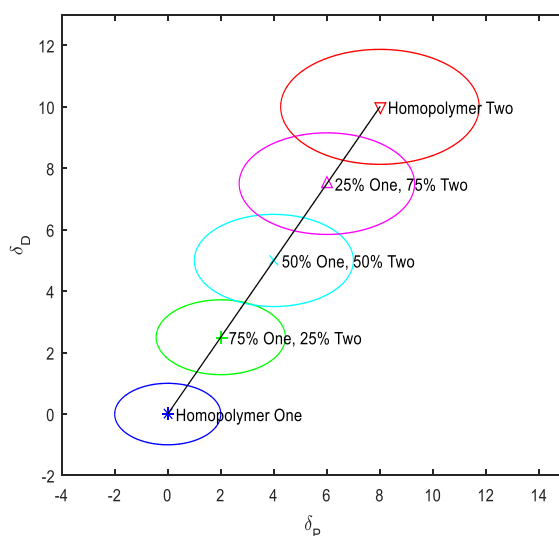aforementioned process of determining the HSP for copolymers.

Figure 3.1 It can be seen that the HSP and the radius of the copolymers are taken as the weighted average of the homopolymers. The key is in the format of (percentage of homopolymer one) / (percentage of homopolymer two).

Figure 3.2 illustrates a ternary system consisting of a monomer and two

solvents. The ternary system is a precursor to the quinary system, and depicts a

how the miscible solvent blends are chosen. This process is repeated for the

second monomer as well as the polymer. The calculations are combined to

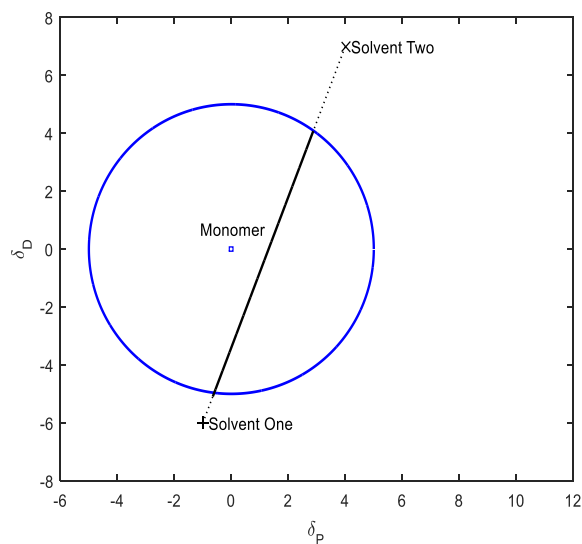determine where the solvent blend intersects the shared volume.

Figure 3.2 Monomer A is centered at (0,0,0) in Hansen Space with a molar volume of 194.8, Solvent A is centered at (,-1,-6, 0) and Solvent B centered at (4,7,0). The area encompassed by the bold segments is the area where monomer is soluble.

3.2.1 Case 1

The simplest case is when the two solvents lie outside of the area where the two monomers and the resulting copolymer are all soluble. If the line segment of the solvent blend intersects the common area, then the optimized blend is chosen as the midpoint between the two points of intersection with the common area. Whether the points of intersection with the common area are on both monomers, or one monomer, has no bearing on the determination of the optimal solvent blend. Figure 3.3 represents the simplest, quinary case.
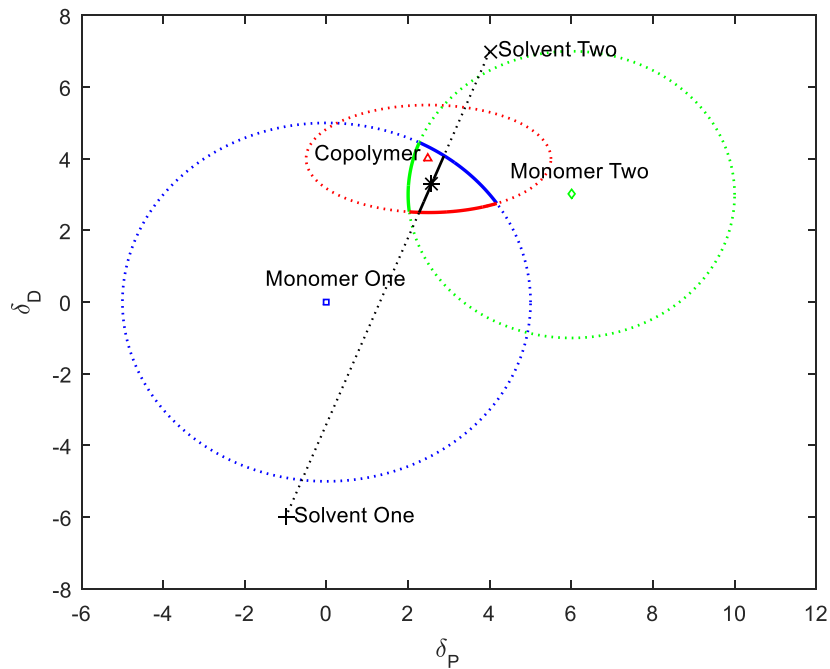
Figure 3.3 The area encompassed by the bold segments is the area where both monomers and the copolymer are soluble. Monomer A is centered at (0,0,0) in Hansen Space with a molar volume of 194.8. Monomer B is centered at (6,4,0) with a molar volume of 304.5, The CoPolymer is centered at (2,4,0) and has an R_o of 4. Solvent A is centered at (,-1,-6, 0) and Solvent B centered at (4,7,0). The optimized blend is determined to be a 28.5:71.5 ratio of Solvent A to Solvent B.

3.2.2 Case 2

Case 2 considers the scenario where only one of the solvents lies outside of the area of common solubility. Case 2 is broken up into two subcases based on how close the solvent within the common area of solubility is to the solute surfaces. With one solvent inside of the common area, one of the calculated points of intersection will represent an impossible blend of solvents that is over one hundred percent of one solvent and a negative percent of the other. Using the midpoint between the two intersection points may or may not yield an impossible blend, creating two distinct sub cases.

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3.2.2.1 Case 2.1

When the procedure encounters a scenario that falls under case 2, it initially does not apply any additional steps in determining the optimal solvent blends, even though there is the potential to produce an impossible blend. That is because there are cases such as subcase 2.1 where the normal procedure produces an acceptable result. This result will be farther from the common surface than a midpoint between the inclusive solvent and the intersection with the surface. Figure 3.4 illustrates such a subcase. In order to emphasize the important differences between sub case 2.1 and other subcases of case 2, the window of this figure is much smaller and encompasses only the common area.
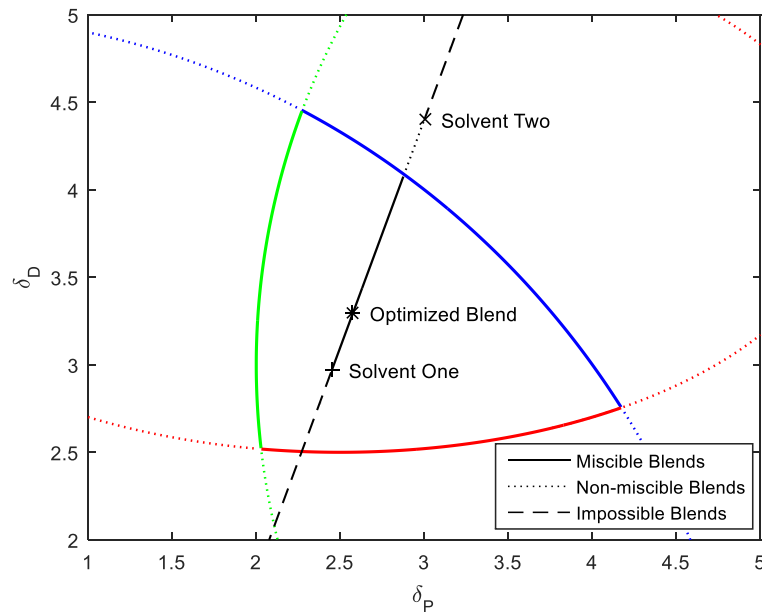

Figure 3.4 One solvent is inside the common area, but the initial optimized blend is a represents a possible blend. The same monomers and copolymer are used as in Figure 3.3. Solvent A is located at (2.75,2.97,0) Slolvent B is located at (3.2,4.5,0) the calculated ratio of Solvent A to Solvent B is 91.9:8.1. It is important to note that this result produces the same point in Hansen Space as the conditions form Figure 3.3.

3.2.2.2 Subcase 2.2

      Subcase 2.2 differs from subcase 2.1 in that the midpoint between points of intersection is not a possible blend of solvents. The procedure has subroutine built in for just such a case. The procedure is able to detect that a non-valid blend has been calculated, and recalculate the optimal solvent as the pure solvent that lies inside the shared volume. This subcase is illustrated in Figure 3.5
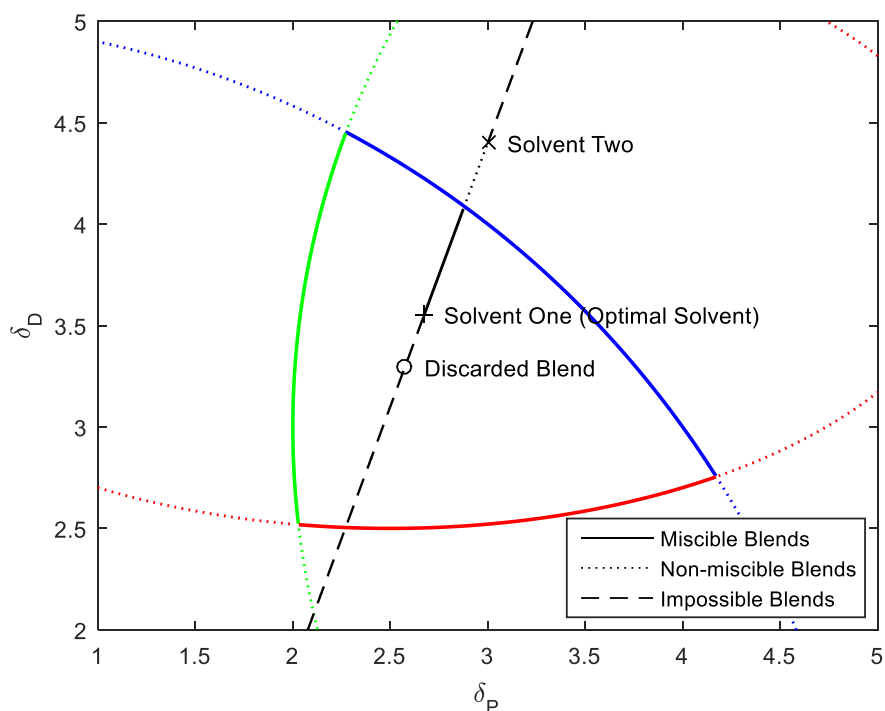

Figure 3.5 In this case, the initial optimized blend represented an impossible blend, thus the new optimization was calculated. Solvent A is centered at (2.675,3.555,0), the HSP of all other components are all equivalent to the HSP of Figure 3.4. It is important to note that the discarded solvent blend is in the same point of Hansen Space as the optimized blend of the previous two Figures.

3.2.3 Case 3

Case 3 represents the scenario when both solvents are included inside the

common area. As in case 2, case 3 is broken up into two subcases, depending on if the

initial optimized blend lies within the range of possible solvent blends.

3.2.3.1 Subcase 3.1

In this subcase the initial optimized blend lies within the possible blend of

solvents. The initial optimized blend will be better suited to dissolve the system

throughout polymerization as it lies as far away from the common area surface as

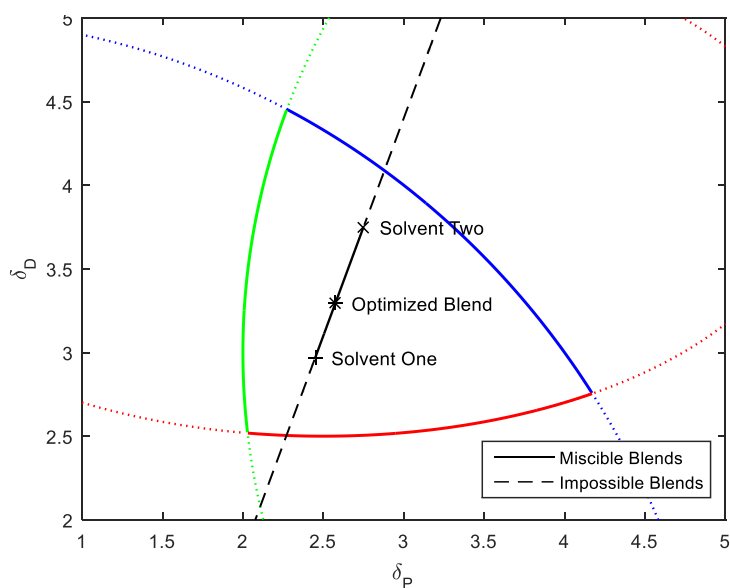possible along the solvent blend line segment. This case is illustrated in Figure 3.6.

Figure 3.6 Case 3.1 is an analogue of case 2.1, in that the initial optimized blend represents a possible solvent blend. The HSP of the monomers and copolymer are the same in this figure as in Figure 3.3. Solvent A is centered at (2.45,2.97,0) and Solvent B is centered at (3.75,2.95,0). The calculated blend is 58.2:41.8 ratio of Solvent A to Solvent B.

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3.2.3.2 Subcase 3.2

This subcase is similar to subcase 2.2 in that the initial calculation for the optimized blend is outside of the possible blend of solvents. Because there are two solvents in the shared volume, the subroutine from case 2.2 is insufficient. The distance between the discarded blend and each pure solvent will be calculated and the pure solvent with the shortest distance will be chosen as the optimal solvent. This case is illustrated in Figure 3.7
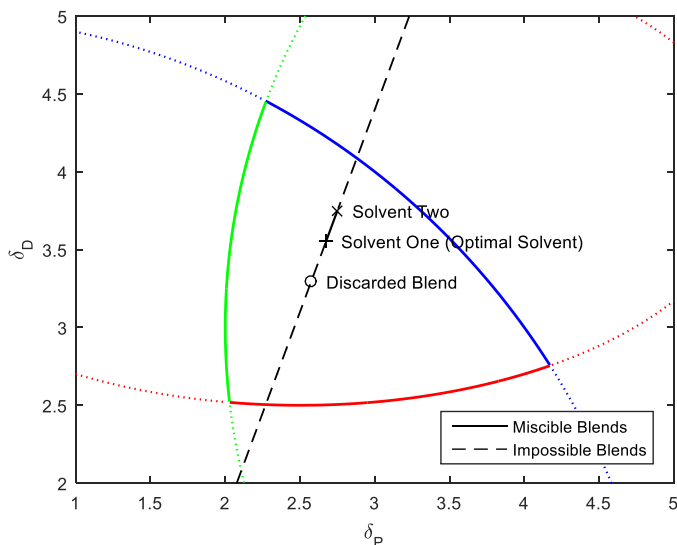

Figure 3.7 Represented is the only where both solvents are used as the endpoints of the optimized solvent search space. Also worth noting is that the procedures successfully discards the initial optimized blend. Solvent A is centered at (2.65,3.49,0) and Solvent B is centered at (2.8,3.88,0). The HSP of the monomers and copolymer are the same as Figure 3.3.

3.3 Solvent Bank

It is likely that two solvents and their resulting blends will not be sufficient to solvate every possible copolymer system. In order to increase the likelihood that an

optimal solvent blend will be obtained, multiple pairs of solvents will be tested with the

procedure for each copolymer system. The selection of solvents will be referred to as the

solvent bank. The first step in this system will be deciding which solvent pairs are

miscible with each other. Each miscible pair will then be used in the normal procedure

and all optimal blends will be output. This procedure is illustrated in Figure 3.8
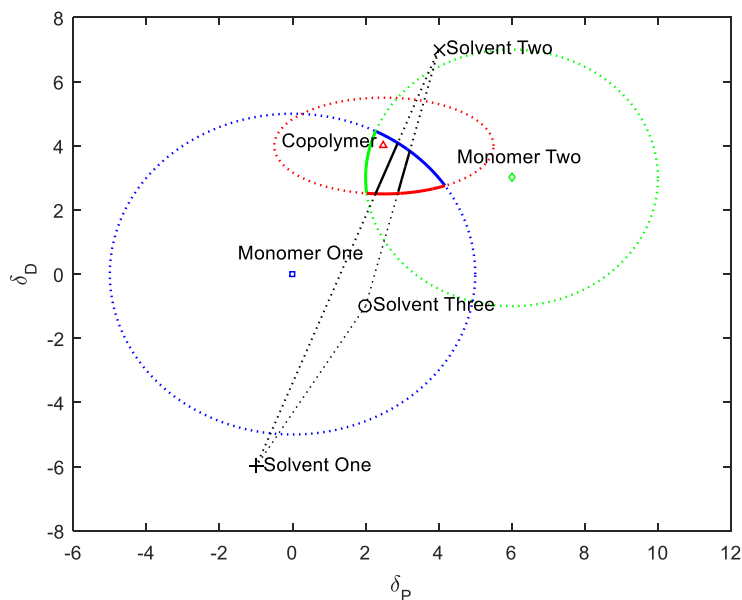

Figure 3.8 It is shown how multiple solutions can be obtained by testing multiple
pairs of solvents. Areas not accessible by a single solvent blend are accessible
by using multiple solvent pairs.

4. Conclusion

The goal of creating an Algorithm using the Hansen Solubility parameters has been derived and verified. With this procedure in place it will be possible to quickly and accurately determine optimal solvent blends. By providing a mathematical description based on molecular structure, HSP has facilitated the development of a consistent and successful procedure. Despite the lack of a theoretical basis for HSP, it is shown that they are effective and accurate in determining the miscibility of solvents and polymers.

Automating this process will eliminate one of the many rate limiting steps of the high throughput Keck Foundation project. The end product of the Keck project will be able to create and analyze new copolymers at unprecedented speeds. To contribute to this project requires a novel approach to determining solvent blends, as given in this thesis. Without this procedure, it would not be possible to run through an iteration of copolymers quickly and efficiently.

It has been shown that HSP have a wide range of applications across the field of polymers. From coatings to gloves, HSP plays a relevant role in determining key characteristics of these systems[12,27]. The HSP provides a much needed quantification of molecular structure as it relates to solubility.

There is a known improvement to the procedure that can be implemented but is left out to lower the time it takes for the procedure to produce results. These improvements involve calculating distances from the surface of the polymer ellipsoids in Hansen Space which is computationally expansive. Future

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work can be done to improve this procedure when speed of results is not a

primary focus

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