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# Computer-Aided Theoretical Solvent Selection using the Simplex Method Based on Hansen Solubility Parameters (HSPs)

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## Abstract

Solvent selection is a crucial step in all solvent-involved processes. Using the Hansen solubility parameters (HSPs) could provide a solvent/solvent-mixture, but there are two main challenges: 1) What solvents should be selected? 2) From each solvent, how much should be added to the mixture? There is no straightforward way to answer the two challenging questions. This contribution proposes a computer-aided method for selecting solvents (answer to the question 1) and finding the adequate amount of each solvent (answer to the question 2) to form a mixture of 2, 3 or 4 solvents to dissolve a solute with known HSPs or to replace a solvent. To achieve this, a sophisticated computer software package was developed to find the optimized mixture using the mathematical Simplex algorithm based on HSPs values from a database of 234 solvents. To get a list of solvent-mixtures, polyamide66 was tested using its HSPs. This technique reduces the laboratory effort required in selecting and screening solvent blends while allowing a large number of candidate solvents to be considered for inclusion in a blend. The outcome of this paper significantly diminished the time of solvent development experimentation by decreasing the possible/necessary trials. Thus, the most suitable solvent/solvent-substitution can be found by the least possible effort; hence, it will save time and cost of all solvent-involved processes in the fields of chemistry, polymer and coating industries, chemical engineering, etc.

**Keywords:** Hansen solubility parameters; Solvent mixture; Solvent substitution; Simplex method; Linear programming; Quadratic minimization; Solvent screening

**Abbreviations:** 11dCE:1,1-Dichloroethane; 12dCE: 1,2-diChloroEthane; B2CiPE: Bis(2-chloroisopropyl)ether; bCEE: Bis(chloroethyl) ether; BCM: Bromochloromethane; cHC: Cyclohexyl chloride; dCEthylene: 1,1-Dichloroethylene; DCM: Dichloromethane; dCtFE: 1,2-DichloroTetraFluoroEthane; dEAE: 2-(DiEthylAmino)Ethanol; dEGmBE: Diethylene glycol monoButyl ether; dEGmME: Diethylene glycol monoMethyl ether; EGmMEA: Ethylene glycol monoMethyl ether acetate; MiAK: Methyl isoAmyl ketone; MMA: Methyl methacrylate; odCB: o-diChloroBenzene; oMePh: o-MethoxyPhenol; PG: Propylene glycol; prC: Propyl chloride; THF: Tetrahydrofuran; tMPD: 2,2,4-triMethyl-1,3-pentanediol

## Introduction

Solvents, defined as substances able to dissolve or solvate other substances, are commonly used in many industries and applications [1]. For any solvent-based process, the best-suited solvent or solvent-mixture must be selected [2]. On the other hand, solvent selection and design is a complex problem, which requires decision making in several levels for identifying the best candidates depending on different multi-objective criteria namely environment, health, safety, process feasibility and economics [3]. Currently, solvent selection relies very much on previous experiences, trial and error with different solvent candidates. Use of experimental thermo-physical properties stored in a factual database for the selection has the advantage that the results are very reliable; however, solvent selection is limited to the experimental data pool [2]. Such heuristic approach while valuable on their own, however arguably are not fit to deal with a complex multi-criteria optimization and search problem, which is the case for solvent selection [3].

On the other hand, actual (physical) trials in the laboratory of mixing different solvents and checking the solvation, is a tough and time-consuming job. A number of modern tools are increasingly becoming available to reduce the efforts needed to select the right solvent [4]. The use of prediction models has the advantage that for the selection procedure, any solvent can be considered for which the required group interaction parameters are available and by using predictive methods, an extended variety of solvents can be taken into account for selection [2]. Solubility parameters have found their greatest use in the selection of solvents [5].

Although it is possible to find a solvent mixture based on Hansen solubility parameters (HSPs), the question is: how one can screen the vast number of solvents to find the desired ones? Moreover, which solvents should be selected? Also, how much is the amount of each solvent (volume fraction) in the mixture?

Selection of the appropriate solvents and finding the best volume fractions could be made by computer programming through minimization of $R_A$ formula (discussed in 'background' section); however, finding the minimum of $R_A$ takes much time for each set of solvents by normal linear programming. Because it has to sweep all the decimal values of the volume fraction from 0 to 1 for all the solvents; while by using the Simplex algorithm (discussed in 'background' section), it can be done within a few milliseconds; hence, more combinations of solvents would be taken into account for solvent selection.

Some authors proposed methods to find a proper solvent mixture for very specific applications like electro-spinning [6]; however, a more general method applicable to a broader range of processes seems to be necessary to propose. Some publications use HSPs to predict solvent systems that are likely to dissolve, like Aghanouri and Sun [7], but they are empirically based and not computer-assisted, meaning that they

cannot consider a large range of solvents. Nelson developed a computer-based formulating technique that allows selection of minimum cost solvent blends, but it was not capable of suggesting a solvent-substitution or solvent mixture for a solute with known HSPs [8]. Moreover, they used Hildebrand solubility parameters which have been updated and replaced by a more reliable and more accurate value, HSPs. To our knowledge, there is no report about a general computer-assisted method of finding a solvent-mixture for a solute with known HSPs. This contribution proposes a computer-assisted selection of solvents out of a vast number of solvents' HSPs values stored in a database.

The purpose of this paper is to illustrate how to develop a systematic framework using HSPs to aid in finding a solvent-mixture/-substitution for many applications including organic synthesis, complex reaction systems, and solvent-based separations that decreases the laboratory labour and saves the experimentation time. The approach taken is the traditional one used in HSPs theory: matching the solvent's HSPs to the polymer's. HSPs values of the solvents will be those matched to the polymer.

Our contributions are:

- We found a way to decrease the experimental effort in solvent screening.
- We decreased the computational process time in minimization of RA formula, by uing the Simplex method.

To set the scene for this paper, we bring a brief description of the Hansen approach for solving the problem of finding a solvent-mixture. Then the linear programming and the Simplex algorithm are briefly introduced. The following overview is to facilitate reading for those who are not familiar with these concepts; therefore, experts can skip it.

## Background

Solubility parameters help put numbers into this simple qualitative idea [5]. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own [5]. Several graphing and modelling techniques have been developed to aid in the prediction of polymer solubility [9]. The basic principle has been "like dissolves like" [5]. By 1950, Hildebrand had defined the solubility parameter as the sum of all the intermolecular attractive forces, which he found to be empirically related to the extent of mutual solubility of many chemical species [10,11]. Solubility behavior cannot be accurately predicted by only the Hildebrand solubility parameter [9]. In 1967, Charles Hansen improved the concept and introduced his three-dimensional solubility parameters. The Hansen approach provides an empirical, yet effective method for determining the dissolution possibility of solutes [9]. The solubility parameter has been used for many years to select solvents for coatings materials [5].

The Hansen model is usually considered as a sphere. The center of the sphere has the $\delta d$, $\delta p$, and $\delta h$ values of the polymer in question (solute) [9]. $\delta$ is square root of cohesion energy density, $\delta d$, $\delta p$, and $\delta h$ represent the dispersive forces, polar interactions, and hydrogen bonding, respectively. The radius of the sphere, $R_O$, is termed the interaction radius [9]. The values of $R_O$ have been reported for some polymers in the literature. $R_A$ is the distance in HSPs space between the solute/polymer and the solvent [12]. The boundary of the spherical characterization is based on the requirement that 'good' solvents have a distance from the center of the sphere, $R_A$ (also termed the solubility parameter distance) less than $R_O$ [9]. $R_A$ is given by the following relation:

$$R_A \ \text{Solution} = \sqrt{\left[4 \times \left(\delta d_s - \delta d_f\right)^2\right] + \left(\delta p_s - \delta p_f\right)^2 + \left(\delta h_s - \delta h_f\right)^2} \quad (3)$$

where $\delta d_f$, $\delta p_f$, and $\delta h_f$ are the Hansen solubility components for the polymer/solute (our favourite values), and $\delta d_s$, $\delta p_s$, and $\delta h_s$ are the Hansen solubility components for the solvent [9]. Eq. 1 was developed from plots of experimental data where the constant '4' was found convenient and correctly represented the solubility data as a sphere encompassing the good solvent [9].

Solubility parameters of mixtures are linear [13]. That is, each of the three HSPs of a solvent mixture is a linear function of composition. In this case, the composition value to be used in calculating solubility parameters for solvent mixtures is the volume fraction ($\varphi$) for each component [13]. For a binary (two-solvent) mixture, the equation for all three solubility parameters is eqn. (2) [13].

$$\delta_{\text{blend}} ° \left[\varphi_{\text{comp1}} \times \sigma_{\text{comp1}}\right] + \left[\varphi_{\text{comp2}} \times \sigma_{\text{comp2}}\right] \quad (2)$$

This equation is correct for more than two components where the HSPs values are known [13]. Traditionally, without specific data, it is usually assumed that there is no volume change upon mixing of solvents. That is:

$$\left(\text{vol. Fraction}\right)_1 = \frac{\left(\dfrac{\text{Wt. Fraction}}{\text{Density}}\right)_1}{\left(\dfrac{\text{Wt. Fraction}}{\text{Density}}\right)_1 + \left(\dfrac{\text{Wt. Fraction}}{\text{Density}}\right)_2} \quad (3)$$

In eqn. (2), $\varphi$ is the volume fraction of component 1, and $\delta$ is any solubility parameter. It is understood that $\varphi \text{comp1} + \varphi \text{comp 2} = 1$. The volume fraction is easy to compute because solvents are stored in pails or drums and used by volume, although they are sold by weight.

Linear programming (LP) is a technique for the optimization of a linear objective function, subject to linear equality and linear inequality constraints. Although the R formula is not linear (it is quadratic), its constraint are linear. It's feasible region is a convex poly-tope, which is a set defined as the intersection of finitely many half spaces, each of which is defined by a linear inequality [14]. Its objective function is a real-valued affine (linear) function defined on this polyhedron. A linear programming algorithm finds a point in the polyhedron where this function has the smallest (or largest) value if such a point exists. There are a few LP methods such as ellipsoid and interior-point, but for more than 35 years now, George B. Dantzig's Simplex-Method has been the most efficient mathematical tool for solving linear programming problems [15]. It is probably that mathematical algorithm for which the most computation time on computers is spent. This fact explains the great interest of experts and of the public to understand the method and its efficiency [15].

A convenient single parameter to describe solvent quality is the relative energy difference, RED, number: RED=$R_A$/$R_O$ [9]. According to the basic principle in dissolution, "like dissolves like" [5], the more similarity, the less $R_A$ and hence, the higher the probability of dissolution. In other words, the distance in HSPs space between the solute/polymer, the Hansen space, should be as small as possible ($R_A$≈0) [12]. By taking square root from both sides of eqn. (4), we have:

$$R_A^2 \ \text{Solution} = \left[4 \times \left(\delta d_s - \delta d_f\right)^2\right] + \left(\delta p_s - \delta p_f\right)^2 + \left(\delta h_s - \delta h_f\right)^2 \quad (4)$$

Therefore, we need to minimize $R_A^2$, as much as possible. In this paper, we minimize the $R_A^2$, with the Simplex method by development the t of a computer program.

## Methodology

The Microsoft Visual Studio software package was used to develop the program. The Microsoft.SolverFoundation.Services.dll library that contains the Simplex algorithm was imported at the beginning of the program's codes. The codes were written in the Visual Basic programming language that operates within the Microsoft. Net framework. All the HSPs values of 234 solvents together with their names and CAS number, health NFPA index were imported into a database. The database was connected to the program in a way that each time the program initiates, it loads the solvents' $\delta d$, $\delta p$ and $\delta h$ values to predefined arrays–D(), P(), and H(), respectively. Out of 234 solvents, 81085 different combinations were examined for polyamide66 (PA66) as the case study. It was counted by a counter variable in the program's code (this will be mentioned later, in "the code" section). The HSPs values of the solvents obtained from ASTM STP1133, Hansen [5], Mark [16], and Barton [17]. The values for NFPA health index were obtained from Sigma-Aldrich material safety data sheets, sciencelab. com, cameochemicals.noaa.gov, synquestlabs.com, and mathesongas.com.

## The solution: the program's codes

To count the different combinations in an integer variable, called "Processes":

```
Processes=0
For i=0 To NumberOfSolventsInDB - 4
For j=i+1 To NumberOfSolventsInDB - 3
Processes=Processes+1
Next
Next
For i=0 To NumberOfSolventsInDB - 3
For j=i+1 To NumberOfSolventsInDB - 2
Processes=Processes+1
Next
Next
For i=0 To NumberOfSolventsInDB - 2
For j=i+1 To NumberOfSolventsInDB - 1
Processes=Processes+1
Next
Next.
```

## The core part of the program

```
Dim solver=SolverContext.GetContext()
Dim model=solver.CreateModel()
Dim x1=New Decision(Domain.RealNonnegative, "QuantA" & i & j)
Dim x2=New Decision(Domain.RealNonnegative, "QuantB" & i & j)
Dim x3=New Decision(Domain.RealNonnegative, "QuantC" & i & j)
Dim x4=New Decision(Domain.RealNonnegative, "QuantD" & i & j)
model.AddDecisions(x1, x2, x3, x4)
model.AddGoal("Goal" & i & j, GoalKind.Minimize, 4 * (D(i) *
```

x1+D(j)*x2+D(j+1)*x3+D(j+2)*x4 - FD)*(D(i)*x1+D(j)*x2+D(j+1)*x3+D(j+2)*x4 - FD)+(P(i)*x1+P(j)*x2+P(j+1)*x3+P(j+2)*x4 - FP)*(P(i)*x1+P(j)*x2+P(j+1)*x3+P(j+2)*x4 - FP)+(H(i)*x1+H(j)*x2+H(j+1)*x3+H(j+2)*x4 - FH)*(H(i)*x1+H(j)*x2+H(j+1)*x3+H(j+2)*x4 - FH))

```
model.AddConstraint("sigmaN" & i & j, x1+x2+x3+x4=1)
model.AddConstraint("rangeX1" & i & j, x1 <= Maximum PercentageOfComponent)
model.AddConstraint("rangeX2" & i & j, x2 <= Maximum PercentageOfComponent)
model.AddConstraint("rangeX3" & i & j, x3 <= Maximum PercentageOfComponent)
model.AddConstraint("rangeX4" & i & j, x4 <= Maximum PercentageOfComponent)
solver.Solve()
n1=x1.GetDouble()
n2=x2.GetDouble()
n3=x3.GetDouble()
n4=x4.GetDouble()
```

R=4 * (D(i) * n1+D(j) * n2+D(j+1) * n3+D(j+2) * n4 - FD) * (D(i) * n1+D(j) * n2+D(j+1) * n3+D(j+2) * n4 - FD)+(P(i) * n1+P(j) * n2+P(j+1) * n3+P(j+2) * n4 - FP) * (P(i) * n1+P(j) * n2+P(j+1) * n3+P(j+2) * n4 - FP)+(H(i) * n1+H(j) * n2+H(j+1) * n3+H(j+2) * n4 - FH) * (H(i) * n1+H(j) * n2+H(j+1) * n3+H(j+2) * n4 - FH)

And once the R is calculated, the program checks if the calculated R (based on the found n1, n2, n3 and n4 to the minimized valued with respect to Hansen space) is less than the maximmum accepted R (Rlimite) or not:

```
If R<= Rlimite Then
"copy the results to listview"
End if
```

This code is for a four-solvent mixture system. For two- and three-solvent mixture system the code is the same, with the difference that only the parameters are 3 and 2, respectively. As the calculation of taking squre root is far slower than normal calculations, to increase the speed of the program, we calculated the squre root of R ($R_A$) and compared with the squre root of Rlimite which gives the same result but is faster. Rlimite is the highest accepted $R_A$ which the user of the program inputs to the program.

## The sweeping loops

The aforementioned calculation is only for one single combination while we need to check all the possible combination. To do this, we have to take the values of the all the solvents in the database:

```
For i=0 To NumberOfSolventsInDB - 4
For j=i+1 To NumberOfSolventsInDB - 3
"the core part of the program"
Next
Next
For i=0 To NumberOfSolventsInDB - 3
```

*For j=i+1 To NumberOfSolventsInDB - 2*

*"the core part of the program"*

*Next*

*Next*

*For i=0 To NumberOfSolventsInDB - 2*

*For j=Me.i+1 To NumberOfSolventsInDB - 1*

*"the core part of the program"*

*Next*

*Next*

in which, the first, second and third 'for loop' sweeps $\delta d$, $\delta p$ and $\delta h$ values for the four-solvent mixture, three-solvent mixture and two-solvent mixture, respectively. In a non-technical word, the 'for loop' means the variable i is increasing by 1 each time the process inside the loop is done (in this case: "the core part of the program") and this will be continued until the i valued is less than "NumberOfSolventsInDB - 4" which is 4 subtracted from the number of the solvents in the stored database that contains the HSPs of the 234 solvents. This is true for the other 'for loops' as well as NumberOfSolventsInDB - 3 and NumberOfSolventsInDB - 2.

All the $\delta d$, $\delta p$ and $\delta h$ values are stored in D(), P() and H() arrays, respectively; and by changing the i and j variables' vales in the three 'for loops', the $\delta d$, $\delta p$ and $\delta h$ values of the corresponding solvent are taken and considered for the core part of the program.

## Results and Discussion

The subset of solvent-mixtures results was obtained from running the software with the HSPs of the selected polymer (PA66) out of 234 organic solvents. Using five main descriptors, namely, the dispersive ($\delta d$), polar ($\delta p$), and hydrogen ($\delta h$) Hansen solubility parameters, CAS registry number, and the health indexes according to the NFPR classifications. The Rlimite was assigned equally to "0.2".

### Miscibility challenge

Solvents used in this study are of different sorts–polar, non-polar, protic, aprotic, etc. The closeness of HSPs values of solvent-mixture and the solute only guarantees the likeness of the interactions between the solvent-mixture and the solute; however, there is no guarantee for miscibility of all the components of a solvent-mixture.

As the "polar" interactions of molecules are enumerated in $\delta p$ values (in Hansen theory, see the 'background' section), we assumed that the closeness in $\delta p$ values of the components could increase the possibility of miscibility, i.e., the difference in $\delta p$ values (called $\Delta P$, hereinafter) will decrease the chance of immiscibility of each solvent in the other one.

### Results for PA66

The Hansen solubility parameters of PA66 have been reported as 18.5, 5.1 and 12.2 for $\delta D$, $\delta P$ and $\delta H$, respectively [18]. The results were sorted first by $\Delta P$, and then R and then by health index, descendingly. The used solvents are listed in Table 1.

As shown in Table 1, 30 records of 50 records of the results have R=0, meaning that they have the same HSPs with PA66's HSPs. In other words, theoretically, they are exactly the same with PA66 regarding dispersion forces ($\delta d$), polar interactions ($\delta p$) and hydrogen bonding ($\delta h$). However, some results with a large $\Delta P$ are not good candidates

for being a solvent for PA66. For instance, the record #50 has the $\Delta P=8.4$ (ethylene glycol $\delta P$: 9.4 — o-Xylene $\delta P$: 1), that they are not miscible in each other. Even without knowing the $\delta P$ values of ethylene glycol (a polar solvent) and o-Xylene (a non-polar organic solvent), it is obvious that preparation of one-phase liquid from those two solvents is not possible. However, for example, the record #2 and #3 have the $\Delta P=1.8$, which shows a higher possibility of giving a one-phase liquid. Proposed solvents using the developed software for PA66: only the first 50 are shown here. The full 196 records of results shown in Table 1.

Therefore, according to our above-mentioned proposal about miscibility, the record #=1 is the best candidate regarding miscibility. On the other hand, the record #2 and #3 have the higher possibility of dissolving PA66 (the closer R than record #1). Thus, the best candidates in terms of having the lowest chance of immiscibility (lowest $\Delta P$) and at the same time having the highest possibility of dissolving PA66 (the closest possible R) is the record #2 and #3.

Some of the results may seem weird, as one might notice that how a solvent that is considered a non-solvent for a polymer could be part of the solvent-mixture for that polymer? For example in the result number #50 for polyamide 66, biphenyl is a part of the four-solvent mixture system, while it is non-solvent for polyamide 66. As Hansen discussed [5], a solvent can dissolve a given polymer in a mixture of two solvents, neither of which can dissolve the polymer by itself. Although Hansen discussed it for a binary system, but, as Durkee [13] discussed later, the relationship between HSPs are correct for more than two components where the HSPs values for a given polymer/solute are known.

As Hansen approach is a theoretical approach, all the suggested solvents are "theoretically proposed" solvents. As Hansen argued [9], solubility can be affected by any specific interactions, especially H-bonds, polymer morphology (crystallinity) and cross-linking, temperature, and changes in temperature [9]. Also, of importance is the size and shape of the solvent molecules. Therefore, according to Gmehling, by using predictive methods (such as using HSPs), a vast number of solvents can be considered for selection, but, of course, the quality of the predicted separation factors, etc. is less accurate than the use of highly reliable experimental data [2]. More specifically about PA66, as Anda argues, due to the presence of polar amide groups along polyamide chains, strong interactions between the polyamide and polar solvents like water can be formed [19]. Although there have been some co-solvent studies for polyamide [20], but they were obtained by practical trial and error, and one cannot generalize that method to other polymers/solutes. While, using the method proposed in this paper, as mentioned before, has the advantage of being applicable to all polymers/solutes and at the same time, is less time-consuming than the practical method. Therefore, a greater number of applicants can be taken into account to be the candidates (Table 1).

## Conclusion

A sophisticated software package for the selection of the most suitable solvent-mixture for a solute/polymer with known HSPs or solvent-substitution for any solvent-involved process, e.g., liquid-liquid extraction was developed. The technique introduced in this paper decreases the time of solvent selection process tremendously by screening the vast number of different combination of an enormous number of solvents and narrow it down to a smaller set of solvents. This technique reduces the laboratory effort required in screening solvent blends while allowing a large number of candidate solvents to be considered for inclusion in a blend. Using Hansen solubility parameters (HSPs) to find solvent mixture for a polymer/solute with known HSPs is a very good tool but still is not the perfect method;

| # | R | n1 | n2 | n3 | n4 | Health | d, p, h | ΔP | max & min δP |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.093 | 2-Phenoxyethano : 35.21% | Cyclohexanol: 19.05% | Aniline: 45.74% | - | 2.619 | 18.46, 5.12, 12.18 | 1.6 | 2-Phenoxyethanol {P: 5.7} - Cyclohexanol {P: 4.1} |
| 2 | 0 | 2-Phenoxyethanol: 13.98% | Cyclohexanol: 21.95% | Aniline: 47.12% | Phenol: 16.95% | 2.561 | 18.5, 5.1, 12.2 | 1.8 | Phenol{P: 5.9}-Cyclohexanol {P: 4.1} |
| 3 | 0 | m-Cresol: 15.87% | Cyclohexanol: 18.08% | Aniline: 43.46% | Phenol: 22.6% | 2.638 | 18.5, 5.1, 12.2 | 1.8 | Phenol{P: 5.9}- Cyclohexanol {P: 4.1} |
| 4 | 0.144 | m-Cresol: 59.5% | Aniline: 31.41% | Phenol: 9.09% | - | 3 | 18.44, 5.17, 12.17 | 1.8 | Benzoic acid {P: 6.9} - m-Cresol {P: 5.1} |
| 5 | 0 | Benzyl alcohol: 13.31% | Cyclohexanol: 27.9% | Aniline: 43.87% | Phenol: 14.92% | 2.176 | 18.5, 5.1, 12.2 | 2.2 | Benzyl alcohol {P: 6.3} - Cyclohexanol {P: 4.1} |
| 6 | 0.069 | Benzyl alcohol: 28.39% | Cyclohexanol: 32.45% | Aniline: 39.17% | - | 1.783 | 18.47, 5.12, 12.19 | 2.2 | Benzyl alcohol {P: 6.3} - Cyclohexanol {P: 4.1} |
| 7 | 0 | Cyclohexanol: 24.92% | Aniline: 46.14% | Phenol: 27.17% | Benzoic acid: 1.77% | 2.484 | 18.5, 5.1, 12.2 | 2.8 | Benzoic acid {P: 6.9} - Cyclohexanol {P: 4.1} |
| 8 | 0.114 | 3-Chloro-1-propanol: 70.62% | Amyl acetate: 2.88% | Bromoform: 26.5% | - | 1.53 | 18.48, 5.21, 12.17 | 3.5 | dCEthylene (1,1-Dichloroethylene) {P: 6.8} - Amyl acetate {P: 3.3} |
| 9 | 0.156 | 2-Phenoxyethanol: 73.93% | Amyl acetate: 4.63% | Bromoform: 21.44% | - | 2.907 | 18.48, 5.25, 12.16 | 3.5 | dCEthylene (1,1-Dichloroethylene) {P: 6.8} - Amyl acetate {P: 3.3} |
| 10 | 0.168 | Phenol: 68.86% | Amyl acetate: 10.38% | Bromoform: 20.76% | - | 2.792 | 18.48, 5.26, 12.16 | 3.5 | dCEthylene (1,1-Dichloroethylene) {P: 6.8} - Amyl acetate {P: 3.3} |
| 11 | 0.195 | Benzyl alcohol: 60.7% | 1-Octanol: 13.67% | Ethylene diBromide: 25.63% | - | 1.513 | 18.41, 5.17, 12.15 | 3.6 | Benzyl alcohol {P: 6.3} - 1-Decanol {P: 2.7} |
| 12 | 0.107 | 3-Chloro-1-propanol: 70.31% | Bromoform: 26.78% | IsoAmyl acetate: 2.91% | - | 1.536 | 18.48, 5.2, 12.17 | 4.3 | 12dCE {P: 7.4} - IsoAmyl acetate {P: 3.1} |
| 13 | 0.135 | Phenol: 67.89% | Bromoform: 22% | IsoAmyl acetate: 10.11% | - | 2.798 | 18.48, 5.22, 12.17 | 4.3 | 12dCE {P: 7.4} - IsoAmyl acetate {P: 3.1} |
| 14 | 0.144 | 2-Phenoxyethanol: 73.43% | Bromoform: 21.93% | IsoAmyl acetate: 4.64% | - | 2.907 | 18.47, 5.23, 12.16 | 4.3 | 12dCE {P: 7.4} - IsoAmyl acetate {P: 3.1} |
| 15 | 0.143 | Benzyl alcohol: 75.27% | 1,4-Dioxane: 24.73% | - | - | 1.247 | 18.55, 5.19, 12.14 | 4.5 | Benzyl alcohol {P: 6.3} - 1,4-Dioxane {P: 1.8} |
| 16 | 0.138 | Benzyl alcohol: 75.16% | 1,4-Dioxane: 24.7% | PG monoMethyl ether: 0.14% | - | 1.247 | 18.54, 5.19, 12.14 | 4.7 | butyl lactate {P: 6.5} - 1,4-Dioxane {P: 1.8} |
| 17 | 0.007 | Phenol: 74.99% | Styrene: 4.62% | 1-bromonaphthalene: 20.39% | - | 2.75 | 18.5, 5.1, 12.2 | 4.9 | Phenol {P: 5.9} - Styrene {P: 1} |
| 18 | 0.117 | Phenol: 43.75% | Ethylene diBromide: 43.32% | Furfuryl alcohol: 12.93% | - | 3 | 18.44, 5.08, 12.2 | 4.9 | Furfuryl alcohol {P: 7.6} - 1-Decanol {P: 2.7} |
| 19 | 0 | Ethylene diBromide: 59.85% | isoButyl isoButyrate: 4.61% | Methyl isoAmyl ketone: 4.23% | Resorcinol: 31.32% | 2.464 | 18.5, 5.1, 12.2 | 5.5 | Resorcinol {P: 8.4} - isoButyl isoButyrate {P: 2.9} |
| 20 | 0.095 | Benzyl alcohol: 72.09% | 2-Butanol: 2.99% | 1,4-Dioxane: 24.92% | - | 1.249 | 18.47, 5.16, 12.15 | 6.2 | Methyl salicylate {P: 8} - 1,4-Dioxane {P: 1.8} |
| 21 | 0.176 | Napthalene: 48.95% | Methyl isoAmyl ketone: 8.47% | Resorcinol: 42.58% | - | 1.915 | 18.42, 5.04, 12.22 | 6.4 | Resorcinol {P: 8.4} - Napthalene {P: 2} |
| 22 | 0.008 | Bromoform: 51.68% | Lactic acid: 31.86% | Dichlorodifluoromethane: 16.45% | - | 2.835 | 18.5, 5.09, 12.2 | 6.5 | Lactic acid {P: 8.3} - dCtFE {P: 1.8} |
| 23 | 0.182 | Phenol: 74.92% | 1-bromonaphthalene: 25.08% | - | - | 2.749 | 18.58, 5.2, 12.19 | 6.5 | DEP (diEthyl phthalate) {P: 9.6} - 1-bromonaphthalene {P: 3.1} |
| 24 | 0.192 | Ethylene diBromide: 72.77% | 1,3-Butanediol: 27.23% | - | - | 2.455 | 18.49, 5.27, 12.11 | 6.5 | 1,3-Butanediol {P: 10} - Ethylene diBromide {P: 3.5} |
| 25 | 0.192 | Ethylene diBromide: 72.76% | 1,3-Butanediol: 27.23% | tEGmOE: 0.01% | - | 2.455 | 18.49, 5.27, 12.11 | 6.9 | 1,3-Butanediol {P: 10} - tEGmOE {P: 3.1} |
| 26 | 0 | Resorcinol: 46.22% | DEK (diEthyl ketone): 5.85% | 1-MethylNaphthalene: 34.51% | di(isoButyl) ketone: 13.42% | 1.807 | 18.5, 5.1, 12.2 | 7.6 | Resorcinol {P: 8.4} - 1-MethylNaphthalene {P: 0.8} |
| 27 | 0 | isoButyl isoButyrate: 10.95% | dibutyl sebacate: 1.42% | PG: 45.74% | Biphenyl: 41.89% | 0.433 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 28 | 0 | Butyric acid: 9.11% | dibutyl sebacate: 3.89% | PG: 43.83% | Biphenyl: 43.17% | 0.471 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 29 | 0 | Methylal: 5.07% | dibutyl sebacate: 6.32% | PG: 45.69% | Biphenyl: 42.92% | 0.543 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 30 | 0 | tEGmOE: 6.29% | dibutyl sebacate: 3.9% | PG: 45.61% | Biphenyl: 44.2% | 0.544 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 31 | 0 | Oleyl alcohol: 6.3% | dibutyl sebacate: 4.71% | PG: 45.65% | Biphenyl: 43.35% | 0.544 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 32 | 0 | MethylAmyl acetate: 10.67% | dibutyl sebacate: 2.07% | PG: 45.28% | Biphenyl: 41.98% | 0.547 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 33 | 0 | 1-Tridecanol: 6.72% | dibutyl sebacate: 4.56% | PG: 45.23% | Biphenyl: 43.49% | 0.548 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 34 | 0 | IsoAmyl acetate: 10.53% | dibutyl sebacate: 2.39% | PG: 45.18% | Biphenyl: 41.9% | 0.548 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 35 | 0 | DiisoButyl carbinol: 6% | dibutyl sebacate: 5.98% | PG: 44.82% | Biphenyl: 43.2% | 0.552 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 36 | 0 | sec-Butyl acetate: 12.66% | dibutyl sebacate: 0.57% | PG: 44.5% | Biphenyl: 42.27% | 0.555 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 37 | 0 | 1-Decanol: 8.34% | dibutyl sebacate: 7.44% | PG: 44.02% | Biphenyl: 40.2% | 0.56 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 38 | 0 | 1-Octanol: 7.59% | dibutyl sebacate: 7.46% | PG: 43.62% | Biphenyl: 41.33% | 0.564 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 39 | 0 | 1-Pentanol: 8.11% | dibutyl sebacate: 6.52% | PG: 42.71% | Biphenyl: 42.65% | 0.573 | 18.5, 5.1, 12.2 | 8.4 | dCEthylene {P: 9.4} - Biphenyl {P: 1} |
| 40 | 0 | Cyclohexanol: 9.3% | dibutyl sebacate: 7.89% | PG: 42.09% | Biphenyl: 40.72% | 0.579 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 41 | 0 | isobutanol: 9.06% | dibutyl sebacate: 5.68% | PG: 41.37% | Biphenyl: 43.89% | 0.586 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 42 | 0 | 2-Ethoxyethyl acetate: 17.42% | dibutyl sebacate: 0.89% | PG: 40.77% | Biphenyl: 40.92% | 0.592 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 43 | 0 | 1-Butanol: 11.26% | dibutyl sebacate: 6.03% | PG: 40% | Biphenyl: 42.71% | 0.6 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 44 | 0 | 2-Octanol: 20.27% | dibutyl sebacate: 0.24% | PG: 39.3% | Biphenyl: 40.19% | 0.607 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 45 | 0 | 2-Butanol: 14.06% | dibutyl sebacate: 4.11% | PG: 39.23% | Biphenyl: 42.6% | 0.608 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 46 | 0 | 2-Propanol: 12.27% | dibutyl sebacate: 5.56% | PG: 39.04% | Biphenyl: 43.13% | 0.61 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 47 | 0 | 4-Methyl-2-pentanol: 5.85% | dibutyl sebacate: 6.76% | PG: 44.39% | Biphenyl: 43% | 0.615 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 48 | 0 | 2-Ethyl-1-hexanol: 6.56% | dibutyl sebacate: 6.74% | PG: 44.2% | Biphenyl: 42.49% | 0.624 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Biphenyl {P: 1} |
| 49 | 0 | Xylene (Xylol): 10.47% | dibutyl sebacate: 4.6% | PG: 46.89% | Biphenyl: 38.04% | 0.636 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - Xylene (Xylol) {P: 1} |
| 50 | 0 | o-Xylene: 10.94% | dibutyl sebacate: 4.68% | PG: 46.86% | Biphenyl: 37.53% | 0.641 | 18.5, 5.1, 12.2 | 8.4 | PG {P: 9.4} - o-Xylene {P: 1} |

**Table 1:** Proposed solvents using the developed software for PA66.

therefore, more research is needed in this field to increase the quality of the proposed set of solvent-mixtures. As Jiaa studied [21], there is a relationship between HSPs and acidity of the polymers/solutes. Therefore, in the future studies in this regard, pKa/pKb values could be taken into account in order to get the better results.

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