

A New Approach to Estimate Hansen Solubility Parameters using Maple Software

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Abstract

This paper represents the use of Maple software capabilities in the analyses of the polymer- solvent interactions. It illustrates the advantages of using Maple to estimate Hansen solubility parameters and to predict the polymer-solvent miscibility. The study focuses on the polymers and solvents that are employed in the polymer gel electrolytes. The acquired data showed high consistency and flexibility in calculations and estimations processes, especially in regarding with Hansen sphere plotting and relative energy distance calculations.

Keywords: Hansen Solubility Parameters; Polymer-solvent miscibility; Maple software; Hansen Sphere.

INTRODUCTION

Solubility parameters are a measure for the ability of the polymer to dissolve the solvent, or in general, it is the measure of the ability of any two species to be mixed. It is based originally on the cohesive energy of the material such as polymer that is affected by mixing that polymer with solvent. The classic solubility theory has been developed by Hildebrand and Scott who stated that the solubility parameter of a species A (δ_A) is related to its energy of vaporisation (cohesive energy) ΔE_A as follows[1, 2];

$$\delta_A = \sqrt{\frac{\Delta E_A}{V_A}} \quad \dots\dots\dots 1$$

Where V_A is the molar volume of the species A, and $\frac{\Delta E_A}{V_A}$ is known as the cohesive energy density.

$$\Delta E = \Delta H_v - RT$$

Then equation 1 can be written as:

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_A}} \quad \dots\dots\dots 2$$

Where $\Delta H_v, R, T$ are the heat of vaporisation, the gas constant and the absolute temperature respectively.

However, this relation seems not to be effective for polar solvents since it takes only the dispersion force effect, while neglecting the other operative forces such as polarity that

plays a major role in polar solutions.

Moreover, polarity alone also is not enough to control and interpret the dissolving activity. Hydrogen bonds forces have also a great role in bonding the molecules and hence strengthen connections between the polymer chains. Therefore, solubility for swollen materials seems to be more complicated to be predicted using one reaction activity

In 1967, Hansen has developed an approach to find the solubility of solutions by using the well-known ‘‘Hansen Sphere’’ which is constructed by three dimensions including the three major forces that hold the molecules together and hence control the interactions between polymer and the solvent. These parameters represent the three original molecular forces that govern the dissolving activity; the dispersive force (d), the polarity (p) and the hydrogen bond energy (h)[3]. Therefore, the total cohesive energy composed of these components can be written as;

$$E = E_d + E_p + E_h \quad \dots\dots\dots 3$$

Dividing equation 3 by V yields;

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad \dots\dots\dots 4$$

Comparing equation 1 with 4 leads to [4];

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \dots\dots\dots 5$$

Where δ_d, δ_p and δ_h represent the three components of Hansen solubility parameters; the dispersion, the polar and the hydrogen-bonding solubility parameters.

According to these three components, any polymer can be dissolved in a solvent if their solubility parameters are close to each other. This behaviour is also related to the ‘‘like dissolves like’’ role. Hansen has also suggested a relation between the solubility parameters of the mixed species like polymers and solvents, which states that the distance D_{S-P} between the

polymer and the solvent molecules can be given by[5];

$$D_{S-P} = \sqrt{4 * (\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2} \quad 6$$

Where $\delta_{i,p}$ and $\delta_{i,s}$ is the i component of solubility parameter for the polymer and the solvent respectively.

In practice, a sphere can be plotted in three dimensional space includes the three parameters δ_d, δ_p and δ_h as its x, y and z coordinates correspondingly. This sphere is known as Hansen sphere that has a radius R_o called interaction radius which represents a unique characteristic for the required solute and can be obtained experimentally for each polymer or another solute. Hansen sphere is used to measure the miscibility of polymer in the required solvents by plotting it in δ_d, δ_p and δ_h space and then plot HSPs for the other solvents as points with HSPs used as their correspond coordinates. The ratio D_{S-P}/R_o is usually called as the relative energy difference RED. Therefore, the relative energy difference can be considered as one of the best approaches to estimate the miscibility of the solutions, i.e. it can give a good prediction of whether the polymer can dissolve the solvent or not according to the following criteria[3]:

If $D_{S-P}/R_o < 1$ the solvent then is good for that polymer

If $D_{S-P}/R_o = 1$ the mixture is at boundary conditions

And if $D_{S-P}/R_o > 1$ the solvent is poor for that polymer.

Under these conditions, many of researchers have investigated the compatibility of different of solvents to different polymers experimentally [6-11] . Others have used HSPs and RED to study thermodynamics of polymer solutions [10, 12-14]. On the other hand, other researchers have developed computational approaches based on the collected data out of the older experimental works to estimate the compatibility of polymers solutions and blends [15, 16]. Gharagheizi and Angaji have presented a computer method based on Nelder–Mead optimization algorithm to calculate HSPs for a group of polymers and solvents[17]. The results from this study have shown a good agreement with the previous experimental data. Vebber et al. have also had their contributions on calculating HSPs of polymers using computer procedure based on the genetic algorithm. Their calculations yielded a correlated data for Hansen and latter practical works.

In this study, Maple 18 software has been employed to calculate the compatibility of number of polymers with a number of solvents.

Table 1 shows HSPs and R_o for the polymers under the current study, while Table 2 shows HSPs values for the solvents. The reason behind choosing these polymers and solvents specifically is the common relation between them which is that all of these polymers and solvents are used in

polymer gel electrolytes preparation [18, 19]. These types of PGEs are commonly used in lithium-ion batteries manufacturing which is the main field in the author research work.

Table 1: Hansen solubility parameters and R_o for the polymers under study[8, 20]

Polymer	δ_d MPa ^{1/2}	δ_p MPa ^{1/2}	δ_h MPa ^{1/2}	R_o
PVDF	17.2	12.1	10.2	9.6
PMMA	17.7	6.7	6.2	8.96
PAN	21.7	14.1	9.1	10.9
PVC	19.2	7.9	3.4	3.5

Table 2: Hansen solubility parameters for the solvents that have been chosen for this study [4, 8, 9, 20]

Solvent	δ_d MPa ^{1/2}	δ_p MPa ^{1/2}	δ_h MPa ^{1/2}
PC	20	18	4.1
EC	18	21.7	5.1
DEC	16.6	3.1	6.1
DMF	17.4	13.7	11.3
GBL	18	16.6	7.4

MAPLE SOFTWARE PROCEDURE

The use of Maple system here to evaluate the interactions between solvents and solutes mathematically is due to its distinctive advantages. These advantages include the outstanding three dimensions graphics, the flexibility in programming and data processing, and apparently the simplicity and speed in dealing with long and complex procedures. The system is used seemingly for the first time and the procedure has been written by the author not based on previous studies; therefore, the result data have to be validated with a previous practical work. This has been already done by collecting some data from Hansen and the latter relative works[4], which will be stated accordingly in the results and discussion. Figure 1 shows flow chart of Maple procedure that has been used to estimate the miscibility of polymers in the studied solvents. The procedure starts with defining HSPs for the polymer and the solvent and the radius of Hansen sphere R_o (which has already been found either experimentally or by a reference). The processes then start by calculating the distance between the polymer and the solvent D_{S-P} , using equation 6. The program then starts comparing the result with R_o ; if the distance is less than the radius of polymer sphere then the solvent is good, otherwise, there are two possibilities: one is that the distance is greater than the radius which means

that the solvent is poor to dissolve that polymer and the user needs to choose another solvent (new trial by defining HSPs for another solvent). The last probability is this routine when the distance is equal to the radius, i.e. the boundary condition of the relative energy difference at which the polymer is said to be swollen rather than dissolved in the solvent. The system then uses all the nominated parameters to plot Hansen sphere for the polymer and to plot solvent parameters as straight lines which are represented by the polymer sphere centre as their start points and their HSPs as the their end points.

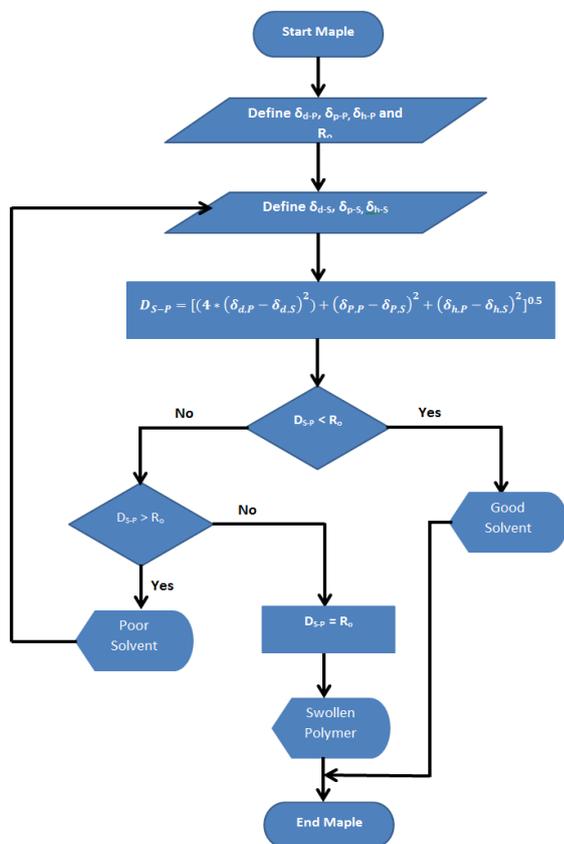


Figure 1: Flow chart of Maple procedure

RESULTS AND DISCUSSION

Figures from Figure2 down to Figure5 illustrate solubility spheres for PVDF, PMMA, PAN and PVC created by Maple procedure.

The program shows that the polymers miscibility varies in accordance with the different solubility components of the solvents. The figures show that DMF has a good compatibility for all the polymers except for PVC, which exhibits high resistance to all the tested solvents. This incompatibility is confirmed experimentally by Grause and others [21, 22].

In Figure 2, PVDF is apparently compatible with DMF and GBL. According to the technical guides and previous studies [23-26], PVDF tends to be dissolved in aprotic polar solvents very well and these two solvents have been referred as good

solvents for it; meanwhile PVDF is normally resistant to ethers and esters [27-29]. This is why PVDF shows incompatibility with the other solvents. However, PC and EC are considered as latent solvents which mean that they can substantially swell PVDF at specific circumstances. This may explain why these two solvents have very short distance to PVDF sphere although they are outside it.

PMMA shows lower miscibility for DMF than DEC; meanwhile it exhibits immiscible behaviour for the other solvents. The literature states that polar dimethylformamide (DMF) dissolves PMMA in a less amount than DEC, which is evidently illustrated in Figure 3 [30-32].

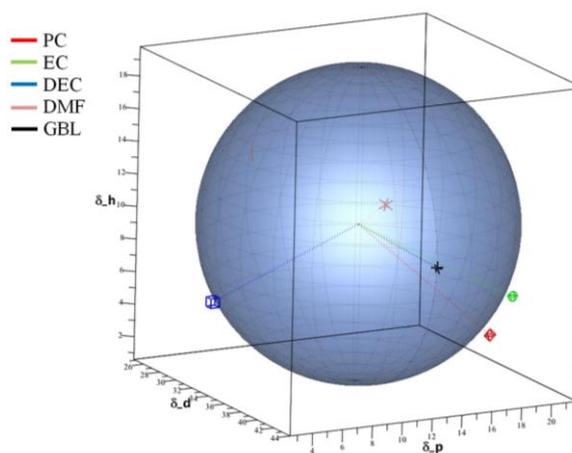


Figure 2: Solubility Sphere for PVDF.

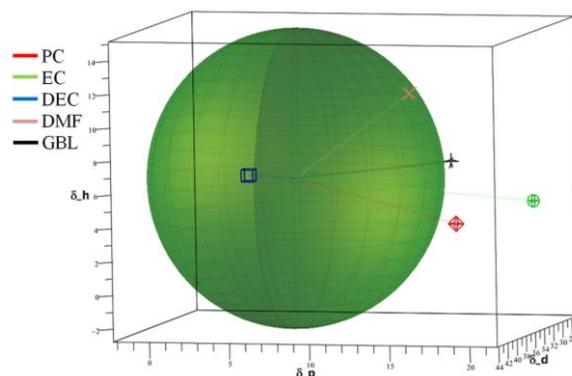


Figure 3: Solubility Sphere for PMMA.

PC and GBL show slightly higher dissolving power to PAN. DMF shows less power to dissolve PAN. EC and DEC show similar behaviour with PAN to that of PVDF. Similar behaviour has been reported in [33, 34].

In Figure 6, all the study species have been grouped and compared corresponding to the relative energy difference RED. In this figure EC has the greater RED value of the other

solvents with all the polymers except for PAN, where which DEC is differed more relatively. However, its value is still by far greater than the unity. DMF has the lowest value of RED with PVDF, which again confirms the behaviour illustrated in Figure 2. The compatibility between DEC and PMMA is confirmed in this figure, likewise the large immiscibility between PMMA and PC along with EC.

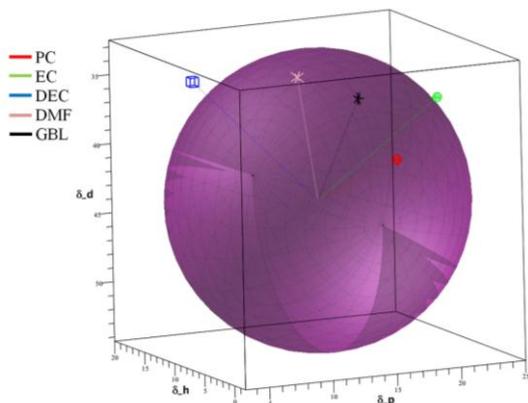


Figure 4: Solubility Sphere for PAN.

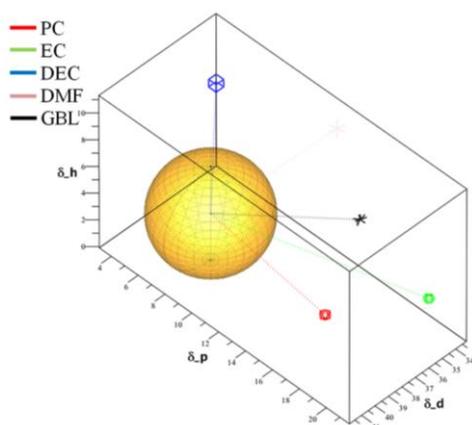


Figure 5: Solubility Sphere for PVC

Table 3: RED values for each polymer with the corresponding solvent

Solvent	RED			
	PVDF	PMMA	PAN	PVC
PC	1.06	1.38	0.66	2.93
EC	1.14	1.68	1.04	4.03
DEC	1.04	0.47	1.4	2.16
DMF	0.21	0.97	0.81	2.98
GBL	0.58	1.11	0.73	2.82

Table 4: Solvent Miscibility as Calculated By Maple.

Polymer	Solvent Quality	
	Good	Non solvent or swelling agent
PVDF	DMF	PC
	GBL	EC
		DEC
PMMA	DEC	PC
	DMF	EC
		GBL
PAN	PC	EC
	DMF	DEC
	GBL	
PVC		PC
		EC
		DEC
		DMF
		GBL

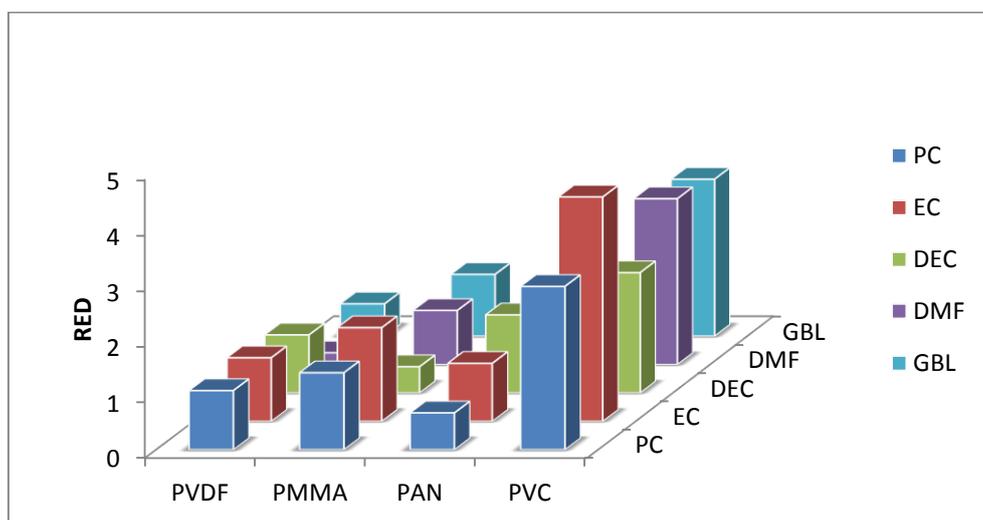


Figure 6: Comparison of calculated RED values for the study solvents in the selected polymers

CONCLUSION

Maple software shows reliable calculation and data extraction in regarding with polymer-solvent interaction through Hansen solubility theory. The computed data indicate a good agreement with the validated data from earlier experimental works. Maple plots techniques shows precise and outstanding presentation for polymer sphere. Overall, Maple succeeds to present a new promises technique for this type of calculations.

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