Hansen Solubility parameters and Green Solvents for Organic Photovoltaics

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ABSTRACT
The determination and prediction of solubility behavior of organic semiconductors to use them is very important. [1] The concept Hansen solubility parameters is applied for the study. HSPs for PC60BM were determined using HSPiP software. In this experiment, we used 20 and 39 solvents in the first and second phases of the experiment respectively to determine HSPs for PC60BM. The results obtained were 18.23, 3.75, and 4.51 MPa1/2 for dispersive, polar and hydrogen bonding for the first and 17.58, 3.73 and 4.79 MPa1/2 for the second respectively. These results were compared to HSPs of chloroform, Limonene and Benzaldehyde. Limonene is used for cleaning in the electronic and printing industries, and in paint as a solvent. [2] It was selected as a solvent to replace the chlorinated type solvents. (HSPs) of Limonene, with δD, δP and δH of 17.20, 1.8 and 4.3 MPa1/2 respectively, were obtained from the HSPiP list of solvents and the calculated Relative Energy Difference of 0.333 for Limonene to PC60BM suggested that limonene could be a good non-chlorinated for solution processing of fullerene-based polymer solar cells. The Limonene processed active layer in this work displayed a maximum power conversion efficiency of 3.19 % and our results suggest that Limonene would be a promising solvent for environment – friendly fabrication of polymer solar cells if more efforts is done to improve the power conversion efficiency.

Key Words: PC60BM, Dispersive, Polar Bond, Hydrogen Bond, Limonene, Hsip, Photovoltaics.

1. INTRODUCTION
The growing need for energy and inadequate fossil fuel resources on this world need the growth of more sources of renewable energy. [3] To reduce this difficulty, people have been working on solar energy conversion to electricity for years [3] But this cannot be achieved only through Si-based solar cell manufacturing, which is expensive and the main source of solar electricity. [4] This requires alternative sources of solar electricity to be developed and produced [4]. In this case the finding of conducting polymers, the production of OPV devices (organic solar cells) becomes promising.
The main advantages of OPV devices compared to classic solid-state photovoltaic device are; the cost of fabricating OPV device are cheaper, the devices are lightweight, the devices are flexible, and the shape can be customized, and the device can be semitransparent. [5]
The charge transfer from conjugated polymers to fullerene molecules when photon is allowed through the bulk heterojunction of the components is the base for the most organic solar cells of today. [6-10] The Single-Junction organic solar cells with efficiency of (7 – 8) % was reported as the best. [11] The silicon devices gave 15 and 20 % efficiency for amorphous and crystalline respectively. [12,13] But, the organic solar cells still are well known with their low efficiency. [14] This is because the organic components, the blend of donor - acceptor and solvent interaction effect during the solution processing, on film morphology formation is not clearly understood. [15] Many studies show that short circuit density (Jsc) and open circuit voltage (Voc) are mainly affected by the nanostructure of the film morphology.[16-18]

In the same way, the fabrication of polymer solar cells is also affected by the solubility of the components of the blend. [19] Solubility is the key factor in the growth of organic devices. The basis for this work is the concept introduced by Hildebrand and Scott in 1950. [20] Solvents and organic molecules were assigned a value allowing prediction of their solubility. According to this prediction, solvents and organic compounds used in the solar cells of similar cohesive energy density (E/v) would be more miscible. [21] This Hildebrand solubility parameter, δ is defined by eq 1
Limone is a colourless liquid at room temperature. The structural formula for limonene is given below. d-limonene is naturally occurring in fruit. It is also common in cosmetic products, as a solvent for cleaning purposes, and as a flavouring agent. The empirical formula is C_{10}H_{16}, the molecular weight (136.23), boiling point (175.5 – 176 °C), density (g/cm³ at 20 °C) is 0.8411 and vapour pressure (pa at 20 °C) is 190.

The other solvent used was Benzaldehyde. Benzaldehyde is generally regarded as a safe food additive in the United States and is accepted as a flavouring substance in the European Union. The empirical formula is C_{7}H_{10}O, the molecular weight (106.12), boiling point (179.2 °C), density (g/cm³ at 20 °C) is 1.0415 and vapour pressure (pa at 20 °C) is 130.
2. EXPERIMENTAL DETAILS
2.1 Materials and instrumentations
The polymer solar cell devices were fabricated with a configuration of ITO/PEDOT: PSS/TQ1:PC61BM (1:3, w/w) /LiF/Al. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10 Ohm/square was used. It was cleaned under a wet-cleaning process inside ultrasonic bath, which was cleaned in isopropanol in an ultrasonic bath for 60 min and subsequently UV-ozone treated for 20 minutes. The solution of Poly [2,3-bis-(3-octyloxypenyl) quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) was prepared in Limonene and Benzaldehyde with a concentration of 20 mg/ml in a brown vial of 4 ml volume in a glove box. In the same way, the [6,6]-phenyl-C60-butyric acid methyl ester (PC60BM) solution was prepared in a glove box with the concentration of 20 mg/ml in the solvents in a condition to achieve the TQ1:PC60M (1:3) ratio. Then, blend solutions were made by mixing the indicated ratio of the solutions and kept on the plate of temperature 50 – 60 degrees being stirred for 12 hours in the glove box. Blends of TQ1-PC60BM in 1:3 weight/weight ratio were prepared in Limonene and Benzaldehyde. The active layer was deposited by spin coating in a protected N2 atmosphere (<0.1 ppm O2, <0.1 ppm H2O inside a glove box (M. Braun Intergas-systeme GmbH).

After spin coating the active layer, the samples were transferred into the vacuum chamber of the thermal evaporator (Univex 350 G, Oerlikon Lybold Vacuum GmbH) integrated within the glove box. LiF was deposited at the rate of 0.3 Ås⁻¹ to the thickness of 0.3 nm first and then 100 nm Al was deposited with a deposition rate of 1 Å s⁻¹ (Al) at a 10⁻⁶ mbar.

3. RESULTS AND DISCUSSION
Hansen Solubility parameters for [6,6]-phenyl-C60- butyric acid methyl ester (PC60BM) were determined. In the fabrication of conjugated polymer solar cells involving solution processing, the solvent is the key. Hansen solubility parameter determination is the principle that enables to determine dispersive, polar and hydrogen bonding interaction forces for polymers and fullerenes. The solubility tests for PC60BM were performed in the laboratory. The absolute solubility of PC60BM was recorded in ~ 20, 39 solvents with different HSP values. We dissolved 1mg of PC60BM in 1 ml of solvent, for each solvent. 1 for yes, 0 for no were recorded regarding whether each solvent dissolved the PC60BM at the chosen concentration of 1 mg/ml. This information was entered HSPiP and generated HSP and solubility spheres for PC60BM. In this experiment, we used 20 solvents to determine the parameters for PC60BM in the first phase of the experiment. The results obtained were 18.23, 3.75, 4.51 for dispersive, polar and hydrogen bonding respectively. In the same manner 1mg/ml of 39 solvents were taken and 17.58, 3.73 and 4.79 were obtained. These results were compared to results of the Hansen solubility parameters of some solvents like chloroform, Limonene and Benzaldehyde.
3.1 HSP and Solubility spheres for PC61BM _20 solvents_ 1 mg/ml

Table 1 Hansen solubility parameters for PC61BM compared to the parameters of some solvents

| Material     | D     | P     | H     | Remark |
|--------------|-------|-------|-------|--------|
| PC_{61}BM    | 18.23 | 3.75  | 4.51  |        |
| TQ1          | 18.19 | 2.12  | 6.17  |        |
| Chloroform   | 17.8  | 3.1   | 5.7   |        |
| Limonene     | 17.20 | 1.8   | 4.3   |        |
| Benzaldehyde | 19.4  | 7.4   | 5.1   |        |

As it can be seen from the generated Hansen solubility sphere of PC61BM using HSPiP software eight solvents are out of the sphere usually are said non-solvents (red colored squares) and 12 solvents in inside the sphere are called good solvents (blue colored squares).
Table 2 shows the list of 20 solvents with their corresponding Hansen solubility parameters, Score, RED and Mvol.

| No  | Solvent            | δD   | δP   | δH   | Score | RED  | Mvol |
|-----|--------------------|------|------|------|-------|------|------|
| 156 | Chloroform         | 17.80| 3.10 | 5.701| 1     | 0.315| 80.5 |
| 148 | Chlorobenzene      | 19.00| 4.30 | 2.00 | 1     | 0.587| 102.1|
| 181 | Cyclohexane        | 16.80| 0.00 | 0.2  | 0     | 1.254| 108.9|
| 7   | Acetone            | 15.50| 10.40| 7.00 | 0     | 1.756| 73.8 |
| 234 | O-Dichlorobenzene  | 19.20| 6.30 | 3.30 | 1     | 0.671| 113  |
| 617 | Tetrahydrofuran (THF) | 16.80 | 5.70 | 8.00 | 1     | 0.894| 81.9 |
| 451 | Mesitylene         | 18.00| 0.60 | 0.60 | 1     | 0.990| 139.5|
| 397 | Formamide          | 17.20| 26.20| 19.00| 0     | 5.254| 39.9 |
| 870 | 1-Chloronaphthalene| 20.50| 4.90 | 2.50 | 1     | 0.999| 138.9|
| 697 | P-xylene           | 17.80| 1.00 | 3.10 | 1     | 0.630| 121.1|
| 637 | Toluene            | 18.00| 1.40 | 2.00 | 1     | 0.681| 106.6|
| 696 | Water              | 15.50| 16.00| 42.3 | 0     | 7.862| 18   |
| 297 | Dimethyl Formamide (DMF) | 17.40 | 13.70| 11.30| 0     | 2.383| 77.4 |
| 367 | Ethylene Dichloride| 18.00| 7.40 | 4.10 | 0     | 0.725| 79.4 |
| 524 | Methylene Dichloride| 17.00| 7.30 | 7.10 | 1     | 0.987| 64.4 |
| 325 | Ethanol            | 15.80| 8.80 | 19.40| 0     | 3.226| 58.6 |
| 570 | 2-Propanol         | 15.80| 6.10 | 16.40| 0     | 2.560| 76.9 |
| 368 | Ethylene Glycol    | 17.00| 11.00| 26.00| 0     | 4.472| 55.9 |
| 698 | O-Xylene           | 17.80| 1.00 | 3.10 | 1     | 0.630| 121.1|
| 1078| Indene             | 18.70| 2.60 | 9.00 | 1     | 0.927| 116.9|

In= 12 Out= 8 Total= 20
D= 18.23 P=3.75 H=4.51
Tot = 19.15
R= 5.1
Fit= 1.000
Core= ± [0.20, 0.50, 0.45]
Wrong In= 0
Wrong Out= 0
3.2 HSP and solubility spheres for PC61BM _39 solvents_ 1 mg/ml

As it can be seen from the generated Hansen solubility sphere of PC61BM using HSPiP software 13 solvents are out of the sphere usually are said non-solvents (red colored squares) and 26 solvents in inside the sphere are called good solvents (blue colored squares).

**Tabel 3 shows the list of 39 solvents with their corresponding Hansen solubility parameters, Score, RED and Mvol**

| No | Solvent                  | δD    | δP    | δH    | Score | RED  | Mvol |
|----|--------------------------|-------|-------|-------|-------|------|------|
| 156| Chloroform               | 17.80 | 3.10  | 5.701 | 1     | 0.315| 80.5 |
| 148| Chlorobenzene            | 19.00 | 4.30  | 2.00  | 1     | 0.587| 102.1|
| 181| Cyclohexane              | 16.80 | 0.00  | 0.2   | 0     | 1.254| 108.9|
| 7  | Acetone                  | 15.50 | 10.40 | 7.00  | 0     | 1.756| 73.8 |
| 234| O-Dichlorobenzene        | 19.20 | 6.30  | 3.30  | 1     | 0.671| 113  |
| 617| Tetrahydrofuran (THF)    | 16.80 | 5.70  | 8.00  | 1     | 0.894| 81.9 |
| 451| Mesitylene               | 18.00 | 0.60  | 0.60  | 1     | 0.990| 139.5|
| 397| Formamide                | 17.20 | 4.90  | 2.50  | 1     | 0.999| 138.9|
| 870| 1-Chloronaphthalene      | 20.50 | 4.90  | 2.50  | 1     | 0.999| 138.9|
| 697| P-xylene                 | 17.80 | 1.00  | 3.10  | 1     | 0.630| 121.1|
| 637| Toluene                  | 18.00 | 1.40  | 2.00  | 0     | 0.681| 106.6|
| 696| Water                    | 15.50 | 16.00 | 42.3  | 0     | 7.862| 18   |
| 297| Dimethyl Formamide (DMF) | 17.40 | 13.70 | 11.30 | 0     | 2.383| 77.4 |
| 367| Ethylene Dichloride      | 18.00 | 7.40  | 4.10  | 0     | 0.725| 79.4 |
| 524| Methylene Dichloride     | 17.00 | 7.30  | 7.10  | 1     | 0.987| 64.4 |
| 325| Ethanol                  | 15.80 | 8.80  | 19.40 | 1     | 3.226| 58.6 |
| 570| 2-Propanol              | 15.80 | 6.10  | 16.40 | 0     | 2.560| 76.9 |
| 368| Ethylene Glycol          | 17.00 | 11.00 | 26.00 | 0     | 4.472| 55.9 |
| 698| O-Xylene                 | 17.80 | 1.00  | 3.10  | 1     | 0.630| 121.1|
| 1078| Indene                  | 18.70 | 2.60  | 9.00  | 1     | 0.927| 116.9|
| 333| Ethyl Benzene            | 17.80 | 0.60  | 1.40  | 1     | 0.724| 122.8|
| 303| Dimethyl Sulfoxide (DMSO)| 18.40 | 16.40 | 10.20 | 0     | 2.168| 71.3 |
| 1253| d-limonene              | 17.20 | 1.80  | 4.30  | 1     | 0.333| 162.9|
| 440| Isopropyl Acetate        | 14.90 | 4.50  | 8.20  | 1     | 0.999| 117.6|
| 430| Isobutyl Acetate         | 15.10 | 3.70  | 6.30  | 1     | 0.872| 133.8|
Photovoltaic performances of Limonene or Benzaldehyde – processed TQ1:PC61BM active layers were investigated in polymer solar cells with a device configuration of ITO/PEDOT: PSS/TQ1:PC61BM (1:3) LiF/Al. The measurements of the polymer solar cell were carried out under illumination of AM1.5G simulated solar light at 100 mW/cm². The J-V characteristics are shown in fig 5 and their photovoltaic parameters are summarized in Table 4. The Limonene – processed polymer solar cell shown a maximum open circuit voltage (Voc) of 0.7780, a short circuit current (Jsc) maximum of 9.4400, a fill factor (FF) of 51.7000 %, giving a power conversion efficiency of 3.19 %.

The Benzaldehyde – processed polymer solar cell as fig 6 and table 5 show also exhibited an open circuit voltage (Voc) of maximum 0.7580, a short circuit current (Jsc) of 5.4700, a fill factor (FF) of 42.6000 %. The Benzaldehyde processed polymer solar displayed a much lower PCE of 1.6300 %. The results show that the Limonene processed polymer solar cell is relatively better effective than the Benzaldehyde-processed solar cells even if both showed lower power conversion efficiency.
Figure 5 J-V characteristics for Limonene processed TQ1-PC61BM active layers in polymer solar cells

Table 4 Photovoltaic performances of the Limonene-processed BHJ films

| No | Device                        | Voc [V] | Jsc [mA/cm²] | FF (%) | PCE (%) |
|----|-------------------------------|---------|--------------|--------|---------|
| 1  | TQ1-PC61BM, Limo(1 to 3)      | 0.7780  | 6.3000       | 46.2000| 2.2600  |
| 2  | TQ1-PC61BM, Limo(1 to 3)      | 0.7680  | 7.1300       | 51.7000| 2.8300  |
| 3  | TQ1-PC61BM, Limo(1 to 3)      | 0.7620  | 9.4400       | 44.2000| 3.1900  |
| 4  | TQ1-PC61BM, Limo(1 to 3)      | 0.7590  | 9.4000       | 44.0000| 3.1400  |

Figure 6 J-V characteristics for Benzaldehyde processed TQ1-PC61BM active layers in polymer solar cells
Table 5 Photovoltaic performances of the Benzaldehyde processed BHJ films

| No | Device | Voc [V] | Jsc [mA/cm²] | FF (%) | PCE (%) |
|----|--------|---------|--------------|--------|---------|
| 1  | TQ1-PC61BM, Bez(1to3) | 0.7350 | 5.4700 | 40.6000 | 1.6300 |
| 2  | TQ1-PC61BM, Bez(1to3) | 0.7580 | 3.4100 | 42.6000 | 1.1000 |

4. CONCLUSIONS

The solubility of different organic semiconductors in various solvents were determined by Hansen solubility parameters. In this case, the substituted fullerene (PCBM) and TQ1 were chosen. The Hansen Solubility parameters for both [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) and TQ1 were determined using HSPiP software. We observed a good quality of fitting parameters for PC₆₁BM and TQ1. Therefore, Hansen solubility parameters can be taken for describing and predicting the solubility behavior of organic semiconductors.

The Hansen solubility parameters of δD, δP, δH, of Limonene were obtained from HSPiP software package and the calculation of Ra and RED of Limonene to PC₆₁BM and TQ1 suggested that Limonene could be a good green solvent for solution processing of fullerene-based polymer solar cells. Our results suggest that Limonene would have potential to be used as green solvent for polymer solar cells fabrication if the power conversion efficiency is more increased by using suitable solvent additives.

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REFERENCES

[1] F. Machui, S. Abbott, D. Waller, M. Koppe, C. J. Brabec, 2011, 2159-2165.
[2] Florida, Industrial Cleaning, Pollution Prevention Fact Sheet, 1-3.
[3] https://www.oecd.org/greengrowth/greening-energy/49157219.pdf.
[4] https://www.irena.org/documentdownloads/publications/re_technologies_cost_analysis-solar_pv.pdf.
[5] Y. Galagan, R. Andriessen, 61-83.
[6] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science (80-. ). 1995, 270, 1789-1791.
[7] S. Günes, H. Neugebauer, N. S. Sariciftci, Chem. Rev. 2007, 107, 1324-1338.
[8] K. M. Coakley, M. D. McGehee, Chem. Mater. 2004, 16, 4533-4542.
[9] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, Adv. Mater. 2006, 18, 789-794.
[10] R. Jean, Acc. Chem. Res. 2009, 42, 1719-1730.
[11] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, 2015, 1-6.
[12] D. E. Carlson, C. R. Wronski, 2012, 671, 1-4.
[13] O. Schultz, S. W. Glunz, G. P. Willeke, 2004, 553-558.
[14] O. S. Cells, 2015, 4, DOI 10.4172/2169-0022.1000203, 1-2.
[15] O. Wodo, B. Ganapathysubramanian, 2012, 1-31.
[16] W. Geens, T. Martens, J. Poortmans, T. Aernouts, J. Manca, L. Lutsen, 2004, 452, 498-502.
[17] F. I. Interchain, Z. Shang-you, R. Xue-song, Q. Shi-xiong, 2004, 498-502.
[18] T. Yamanari, T. Taima, J. Sakai, K. Saito, 2009, 93, 759-761.
[19] F. MacHui, S. Abbott, D. Waller, M. Koppe, C. J. Brabec, Macromol. Chem. Phys. 2011, 212, 2159-2165.
[20] L. R. Brantley, 1952, 51.
[21] D. T. Duong, B. Walker, J. Lin, C. Kim, J. Love, B. Purushothaman, J. E. Anthony, T. Q. Nguyen, J. Polym. Sci. Part B Polym. Phys. 2012, 50, 1405-1413.
[22] S. Abbott, C. M. Hansen, H. Yamamoto, Hansen Solubility Parameters in Practice Complete with eBook, Software and Data 5th Edition, 2015, 5-40.
[23] S. Parameters, A. Introduction, 2000, 2-10.
[24] S. Morphology, 2012, 2-8.
[25] Z. He, C. Zhong, X. Huang, W. Wong, H. Wu, 2011, 4636-4643.
[26] V. A. Online, D. Kim, H. P. Kim, F. K. Shneider, J. Jang, 2015, 303-316.
[27] Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, 2014, 4-9.
[28] A. Manuscript, 2016, DOI 10.1039/C6CC08939A, 2-6.
[29] L. Xiao, C. Liu, K. Gao, Y. Yan, J. Peng, Y. Cao, X. Peng, RSC Adv. 2015, 5, 92312-92317.
[30] K. Tada, Sol. Energy Mater. Sol. Cells 2013, 108, 82-86.
[31] H. W. Choi, T. Zhou, M. Singh, G. E. Jabbour, 2015, DOI 10.1039/C4NR03915G, 2-10.
[32] T. M. Eggenhuisen, Y. Galagan, E. W. C. Coenen, W. P. Voorthuijzen, M. W. L. Slaats, S. A. Kommeren, S. Shanmuganam, M. J. J. Coenen, R. Andriessen, W. A. Groen, Sol. Energy Mater. Sol. Cells 2015, 134, 364-372.