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Hansen solubility parameters of polyglycolic acid and interaction parameters between polyglycolic acid and solvents

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ABSTRACT

This article focuses on the solubility parameters and interaction parameters of polyglycolic acid. 43 solvents have been used for polyglycolic acid to study the dissolution property. Then the Hansen three-dimensional solubility parameters and total parameter of polyglycolic acid were obtained by an optimization calculation. The values of δ_d , δ_p , δ_h and δ for polyglycolic acid have been obtained as $17.094 (\text{J}/\text{cm}^3)^{1/2}$, $8.206 (\text{J}/\text{cm}^3)^{1/2}$, $7.912 (\text{J}/\text{cm}^3)^{1/2}$ and $20.546 (\text{J}/\text{cm}^3)^{1/2}$. It was proved that the total parameter of polyglycolic acid is creditable by intrinsic viscosity approach and group contribution method. The values of the interaction parameter and the solubility parameter “distance” between polyglycolic acid and 43 solvents have been calculated. The results of the interaction parameters accords well with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents.

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1. Introduction

Polyglycolic acid (PGA) was first manufactured as a synthetic absorbable suture material, and its success has led to development for other medical applications such as controlled drug release systems, orthopedic fixation and scaffolds [1,2]. In addition, PGA can also be used for beverage packaging material, as a composite container for packing beer, as a single (multi) layer of soft packaging material, and as agricultural biological degradable film, etc. [3]. Either application to medicine or application to industry and agriculture, the solubility or compatibility of PGA with other materials are always involved, that is, the interaction between PGA and other molecules will be touched on. As is known to all, solubility parameter can describe quantitatively the interaction between polymer molecules and other molecules. Therefore, it is necessary to study solubility parameter of PGA. However, to the best of our knowledge, there are very few reports on this investigation for PGA. In literature, only Abhishek et al. researched solubility parameter of PGA [4]. Abhishek et al. estimated the solubility parameters of PGA using intrinsic viscosity method, classical geometric method and group contribution and proposed an optimization method to obtain the Hansen solubility parameters of PGA.

However, the optimization method proposed by Abhishek et al. is very complicated. It contains many vectors functions, matrices functions and scalar functions. The calculation process is too incomprehensible to be convenient for application. Furthermore, Abhishek et al. used only eight solvents (three solvents and five nonsolvents) for PGA. The number of solvents is so small that the results obtained are not representative.

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In this study we measured Hansen solubility parameters of PGA experimentally using 43 solvents. Due to large amount of work, this measurement has not been explored yet. The aim is to acquire more accurate results. Simultaneously, we proposed a simple optimization method to determine the Hansen solubility parameters and compared them with those obtained by other methods.

The concept of a solubility parameter was first presented by Hildebrand. He considered that in a system where the dispersion forces were predominant, the solvent could dissolve the polymer when their parameters were close. However, the molecule polar as well as the hydrogen bonding interaction between the polymer and the solvent must be considered in the solutions of polar polymer–solvent system. In order to predict the miscibility of various polymer–solvent systems, various modifications have been made for the method of solubility parameter. It is the method of Hansen three-dimensional solubility parameters that are recognized widely at present. Hansen divided the total solubility parameter δ into three values – δ_d , δ_p and δ_h , where δ_d , δ_p and δ_h are the contributions of dispersion forces, dipolar forces and hydrogen bonding, respectively. δ can be calculated by $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. Only when the three-dimensional solubility parameters of the polymer and the solvent are all close, can the solvent dissolve the polymer. The objective of this work is to determine the three-dimensional solubility parameters for PGA precisely.

Total solubility parameters of solvents can be obtained from the definition $\delta = (\Delta E/V_m)^{1/2}$ by the energy of vaporization ΔE and the molar volume V_m . Since polymers cannot vaporize normally, total solubility parameters of polymers cannot be acquired by the definition. Their values of three-dimensional and total solubility parameters should be acquired by experiments.

The traditional experimental method to determine the three-dimensional solubility parameters of a polymer is as follows. First, a polymer is dissolved in various solvents under a certain concentration; second, the solvents are divided into good and bad solvents and the solubility parameters of the polymer are calculated using the solubility parameters of the good solvents.

2. Experimental

2.1. Materials

Triethylamine (99.5%), ethyl acetate (99.5%), anhydrous ethyl alcohol (99.7%) and chloroacetic acid (99.0%) were made by the Tianjin Kemiou Chemical Reagent Company (Tianjin, China). The other chemicals were purchased from Sun Chemical & Technology (Shanghai) Company Limited. All the chemicals are of analytical grade and used as received without further purification.

2.2. Synthesis of PGA

The synthesis method has been described in our earlier work [5]. Chloroacetic acid was dissolved in ethyl acetate. Triethylamine was added to the solution. The solution was refluxed with stirring for a period of time. Ethyl acetate was then distilled from the reaction mixture. After all solvent had been removed, the product mixture was obtained. From the product mixture, the byproducts were removed by washing with absolute ethanol. The residue insoluble polymer was PGA. The PGA was dried to constant weight at 60 °C.

2.3. Solubility test

The solubility tests were carried out in 43 organic solvents in order to classify them as good (one-phase systems) or bad (two-phase systems) solvents. The procedure was as follows: 0.1 g of PGA was placed in a glass bottle with 4.9 g of the test solvent [6]. The glass bottle was sealed with a suitable stopper to prevent solvent evaporation. Taking into account the dissolution equilibrium, the sealed solution was allowed to stand for three days at room temperature. The solutions were shaken for a certain time. In the case of solvent in which the solute did not appear to dissolve at room temperature, heat was applied and then cooled to room temperature [6,7]. The heating temperature was below the boiling point of the corresponding solvent. The solubility behavior of PGA was observed by a visual inspection and was judged as soluble or insoluble. Then each solvent was characterized as a bad or good solvent.

2.4. Intrinsic viscosity measurement

The relationship between molecular weight (M) and intrinsic viscosity ($[\eta]$) of PGA can be described by Mark–Houwink equation, $[\eta] = \beta M^\alpha$. $[\eta]$ measurements were performed with an Ubbelohde viscometer at 25 °C. The intrinsic viscosity of each sample was calculated according to the Solomon–Ciuta equation of a single point measurement [8]:

$$[\eta] = \frac{\sqrt{2\left(\frac{t}{t_0} - 1 - \ln \frac{t}{t_0}\right)}}{C} \quad (1)$$

where C is concentration of the solution; t is flow time of solution, t_0 is flow time of pure solvent.

3. Results and discussion

3.1. Results of solubility test

The solubility results of PGA in 43 solvents are listed in Tables 1 and 2. Table 1 lists the nonsolvents and Table 2 lists the solvents.

3.2. Hansen solubility parameters of PGA obtained by optimization method

Hansen proposed the concept of solubility sphere. In general, good solvents are within the sphere while bad solvents are outside the sphere. In a three-dimensional representation, solubility parameters of a solute (δ_d , δ_p , and δ_h) locate in the geometrical center of the sphere. Hansen has developed an empirical equation that predicts the dissolvability of a polymer in a solvent [9].

$$R_i = \sqrt{4(\delta_{ds} - \delta_{dp})^2 + (\delta_{ps} - \delta_{pp})^2 + (\delta_{hs} - \delta_{hp})^2} \quad (2)$$

where R_i is the solubility parameter “distance” (or interaction radius, solubility distance) between the solute and a solvent; subscript index s and p designate the solvent and the polymer, respectively. The solute (polymer) is at the center of the solubility sphere. Once the central coordinates of the solubility sphere, δ_{dp} , δ_{pp} , and δ_{hp} are determined and the solubility distances from its center of the solubility sphere to the points corresponding to solvents, R_i are computed according to Eq. (2). The highest value of R_i in the good solvents is considered the radius of solubility sphere, R . For $R > R_i$, the polymer is soluble in a solvent and for $R < R_i$, the polymer is insoluble in a solvent.

Since plotting in three-dimensional space is not convenient, the solubility parameters of PGA are calculated in present work using an optimization technique of orthogonal design. The procedure of the optimization method is as follows. Based on the known solubility parameters of solvents, δ_{ds} , δ_{ps} , δ_{hs} , the mean values of three-dimensional solubility parameters were calculated for the nonsolvents and the solvents. Two sets of δ_{ds} , δ_{ps} , δ_{hs} were obtained. Then the two sets of data were arrayed using orthogonal design to gain many sets of three-dimensional solubility parameters. Every set of three-dimensional solubility parameters was assigned to the initial value of the polymer's three-dimensional solubility parameters. Table 3 lists the arrangement of three-dimensional solubility parameters for PGA by orthogonal design. Giving a set of three-dimensional solubility parameters of PGA, the values R_i of solvents and nonsolvents can be calculated in terms of Eq. (2). Giving a series of three-dimensional solubility parameters of PGA, a series of values of R_i can be obtained. Based on the values of R_i , a fitting R can be obtained to enable all the points of soluble solvents to be inside the solubility sphere but all the points of insoluble

Table 1
Solubility parameters of nonsolvents, interaction radius as well as interaction parameters between PGA and nonsolvents.

No.	Solvent	Solubility parameters (J/cm^3) ^{1/2}			Interaction radius (J/cm^3) ^{1/2}	Interaction parameters $\alpha = 1.56$
		δ_d	δ_p	δ_h		
1	Dimethylbenzene	17.80	1.00	3.10	8.78	1.47
2	Toluene	18.00	1.40	2.00	9.20	1.42
3	Chlorobenzene	19.00	4.30	2.00	8.05	1.04
4	Carbon tetrachloride	17.80	0.00	0.60	11.08	1.88
5	Methyl isobutyl ketone	15.30	6.10	4.10	5.64	0.63
6	Isopropanol	15.80	6.10	17.40	10.06	1.20
7	Bromobenzene	19.20	5.50	4.10	6.29	0.66
8	Carbon bisulfide	20.20	0.00	0.60	12.63	1.52
9	n-Butyl alcohol	16.00	5.70	15.80	8.56	1.06
10	Isobutyl alcohol	15.10	5.70	15.90	9.27	1.26
11	n-Amyl alcohol	15.90	5.90	13.90	6.85	0.80
12	Secondary butyl alcohol	15.80	5.70	14.50	7.51	0.82
13	n-Propyl alcohol	16.00	6.80	17.40	9.84	1.14
14	Absolute ethyl alcohol	15.80	8.80	19.40	11.80	1.28
15	Acetonitrile	15.30	18.00	6.10	10.59	0.93
16	Trichloroethylene	18.00	3.10	5.30	6.01	0.51
17	Styrene	18.60	1.00	4.10	8.69	1.37
18	1-Chlorbutane	16.20	5.50	2.00	6.74	0.75
19	Ethyl sulfide	16.89	3.10	2.10	7.75	1.02
20	Ethylbenzene	17.80	0.60	1.40	10.11	1.98
21	Isobutyl acetate	15.10	3.70	6.30	6.23	0.82
22	Isopropyl acetate	14.90	4.50	8.20	5.75	0.61
23	2-Hexanone	15.30	6.10	4.10	5.64	0.62
24	1-Chloropropane	16.00	7.80	2.00	6.32	0.56
25	Cis-decahydronaphthalene	17.60	0.00	0.00	11.44	3.19
26	1,2,3,4-Tetrahydronaphthalene	19.60	2.00	2.90	9.42	1.90

Table 2

Solubility parameters of solvents, interaction radius as well as interaction parameters between PGA and solvents.

No.	Solvent	Solubility parameters (J/cm ³) ^{1/2}			Interaction radius (J/cm ³) ^{1/2}	Interaction parameters $\alpha = 1.56$
		δ_d	δ_p	δ_h		
1	1,1,2,2-Tetrachloroethane	18.80	5.10	5.30	5.30	0.47
2	Pyridine	19.00	8.80	5.90	4.35	0.24
3	Methyl-2-pyrrolidinone	18.00	12.30	7.20	4.53	0.31
4	Dimethylacetamide	16.80	11.50	9.40	3.66	0.20
5	Trifluoroacetic acid	15.60	9.70	11.40	4.83	0.28
6	1,1,3,3-Tetramethylurea	16.80	8.20	11.10	3.24	0.20
7	Triethyl phosphate	16.70	11.40	9.20	3.53	0.34
8	Benzaldehyde	19.40	7.40	5.30	5.36	0.46
9	Ethyl lactate	16.00	7.60	12.50	5.12	0.47
10	Ethyl formate	15.50	8.40	8.40	3.23	0.13
11	Cyclohexanone	17.80	8.40	5.10	3.15	0.15
12	Methyl isobutenyl ketone	16.40	7.20	5.00	3.38	0.21
13	2,2'-Dichloroethyl ether	18.80	9.00	5.70	4.14	0.32
14	Diethylene glycol monoethyl ether acetate	16.20	5.10	9.20	3.81	0.40
15	Butyl lactate	15.80	6.50	10.20	3.85	0.35
16	Isophoron	17.00	8.00	5.00	2.93	0.20
17	Propylamine	16.00	4.90	8.60	4.02	0.21

Table 3

Orthogonal table of three-dimensional solubility parameters for PGA.

No.	Solubility parameters (J/cm ³) ^{1/2}		
	δ_{dp}	δ_{pp}	δ_{hp}
1	I	I	I
2	II	I	II
3	I	II	II
4	II	II	I

I represents the average value of one-dimensional solubility parameters of all good solvents. II represents the average value of one-dimensional solubility parameters of all bad solvents.

In the first column, I represents the average value of δ_d of all good solvents and II represents the average value of δ_d of all bad solvents. In the second and third columns, I and II represent the average value of δ_p and δ_h , respectively.

solvents to be outside the solubility sphere. The solubility parameters corresponding to the fitting R are just the solubility parameters of PGA by the optimization method. The results are obtained by a computer procedure.

The optimization method is superior to the traditional experimental method because it considers the nonsolvent data also as a part of the procedure. This translates to obtaining a better fit of the data.

According to the solubility results and the three-dimensional solubility parameters of solvents and nonsolvents listed in Tables 1 and 2, the three-dimensional solubility parameters of PGA acquired by the optimization method are: $\delta_d = 17.094$ (J/cm³)^{1/2}, $\delta_p = 8.206$ (J/cm³)^{1/2}, $\delta_h = 7.912$ (J/cm³)^{1/2}, $\delta = 20.546$ (J/cm³)^{1/2}. The results are satisfactory. The biggest value of R_i of the soluble solvents, $R_{\max} = 5.36$ (J/cm³)^{1/2}, is clearly less than the least value of the insoluble solvents, $R_{\min} = 5.64$ (J/cm³)^{1/2}. All the points of soluble solvents are inside the solubility sphere and all the points of insoluble solvents are outside the solubility sphere. A clear boundary to judge good or bad solvents for PGA exists according to the values of R_i . The values of R_i of PGA in various solvents are listed in Tables 1 and 2.

3.3. Verification of the total solubility parameters for PGA

3.3.1. Intrinsic viscosity method

Study of the solvent-solute interaction is perhaps more appropriate through $[\eta]$, which is an inherent property of a material [4,10]. The intrinsic viscosity $[\eta]$ is the viscosity at infinite dilution, where a solute molecule is surrounded only by solvent molecules and intermolecular forces between the solute molecules are essentially zero. In other words, $[\eta]$ implies maximum dissolution of the solute molecules. Therefore, the maximum $[\eta]$ value would be obtained in the case of a good solvent where solvent-solute interaction is maximal. The relationship between $[\eta]$ and δ are shown by the Mangaraj equation [4,10],

$$[\eta] = [\eta]_{\max} \exp[-A(\delta_{ts} - \delta_t)^{-2}] \quad (3)$$

where δ_{ts} and δ_t are the total solubility parameters of the solvent and polymer, respectively. The maximum value, $[\eta]_{\max}$ is attributed to the solvent with the highest solvency power, and is expected when $\delta_{ts} = \delta_t$.

A representative plot of $[\eta]$ versus δ_{ts} for a polymer can be drawn. The δ_{ts} value at the maximum $[\eta]$ corresponds to the solubility parameter for the polymer. Sharper inflection in the curve could be obtained by using solvents with δ_{ts} values in the vicinity of the inflection point.

According to the solubility experiment, trifluoroacetic acid, propylamine, mixture of chloroform and trifluoroacetic acid (3:7, w/w) can dissolve PGA at room temperature. The intrinsic viscosity data obtained for PGA in these solvents are listed in Table 4.

The solubility parameter of a mixed solvent is calculated by the following equation [8]:

$$\delta_{sm} = \delta_1\varphi_1 + \delta_2\varphi_2 \quad (4)$$

where δ_1 , φ_1 , δ_2 and φ_2 are the volume fraction and solubility parameter of solvent 1 and solvent 2, respectively.

From the plot of $[\eta]$ versus δ_{ts} for PGA, mixture of chloroform and trifluoroacetic acid is at the the inflection point, the solubility parameter at the inflection point is $21.226 \text{ (J/cm}^3)^{1/2}$, namely, the total solubility parameter of PGA.

Obviously, $21.226 \text{ (J/cm}^3)^{1/2}$ is close to $20.546 \text{ (J/cm}^3)^{1/2}$ calculated by the optimization method. It illustrates that the three-dimensional solubility parameters acquired by optimization calculation are precise.

3.3.2. The group contribution method

Abhishek et al. [4] calculated the solubility parameter of PGA using Fedors and Van Krevelen group contribution method. The results are $23.82 \text{ (J/cm}^3)^{1/2}$ and $19.24 \text{ (J/cm}^3)^{1/2}$, respectively. The average value is $21.53 \text{ (J/cm}^3)^{1/2}$ which approaches the total solubility parameter ($20.546 \text{ (J/cm}^3)^{1/2}$) acquired by optimization method in this work.

3.4. The Flory–Huggins interaction parameters between PGA and its solvents

Interaction parameter plays an important role in the theory of polymer solutions. It provides a measure of the thermodynamic affinity of a solvent to the polymer, or a measure of the quality of the solvent. The smaller interaction parameter is, the more stable the solution is relative to the pure components and the more likely that the system is miscible. On the basis of interaction parameter values, solvents may be classified as good interaction parameter $<1/2$ or poor interaction parameter $>1/2$ solvents [8,11].

The interaction parameter can be calculated on the basis of Flory–Huggins and Hildebrand–Scatchard theories in terms of solubility parameters [12]. Thomas Lindvig suggested that the Flory–Huggins interaction parameters were related to the three-dimensional solubility parameters of polymers and solvents [13]. The relation is as follows:

$$\chi_{12} = \alpha \frac{v_s}{RT} \left((\delta_{ds} - \delta_{dp})^2 + 0.25(\delta_{ps} - \delta_{pp})^2 + 0.25(\delta_{hs} - \delta_{hp})^2 \right) \quad (5)$$

where χ_{12} is the interaction parameter; v_s is the molar volume of a solvent; δ_{ds} , δ_{ps} and δ_{hs} are the solubility parameters of solvents and δ_{dp} , δ_{pp} , and δ_{hp} are the solubility parameters of PGA; R is the universal gas constant, and T is the kelvin absolute temperature. Hansen suggested to use this expression with $\alpha = 1$ [11,13–15]. However, Thomas Lindvig et al. found that the average absolute deviation is minimum with $\alpha = 0.6$ when they studied the activity coefficients of poly(butyl methacrylate) and poly(vinyl acetate) [13]. We discover that $\alpha = 1.54$ – 1.62 is suitable for PGA–solvent system.

When $\alpha = 1.56$, the calculated results of the interaction parameters between PGA and its solvents are also listed in Tables 1 and 2.

The results in Tables 1 and 2 shows that when $\chi_{12} > 0.5$, PGA cannot dissolve and while $\chi_{12} < 0.5$, PGA can dissolve. That is, $\chi_{12} = 0.5$ is the critical point to distinguish good solvents from bad solvents. The results are distinctly in accord with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents [8,11].

4. Conclusions

The following conclusions can be drawn from the work:

- (1) The three-dimensional solubility parameters and the total solubility parameter of PGA acquired by optimization calculation are: $\delta_d = 17.094 \text{ (J/cm}^3)^{1/2}$, $\delta_p = 8.206 \text{ (J/cm}^3)^{1/2}$, $\delta_h = 7.912 \text{ (J/cm}^3)^{1/2}$, $\delta = 20.546 \text{ (J/cm}^3)^{1/2}$. They are verified by intrinsic viscosity method and group contribution method. The optimization method is superior to the traditional

Table 4
The intrinsic viscosities of PGA in different solvents.

No.	Solvents	$\delta \text{ (J/cm}^3)^{1/2}$	Intrinsic viscosity (L/g)
1	Trifluoroacetic acid	21.816	0.00673
2	Mixture of chloroform and trifluoroacetic acid (3:7)	21.226	0.02017
3	Propylamine	19.585	0.01894

experimental method because it considers the nonsolvent data also as a part of the procedure. In the optimization technique, bad solvents were used to improve the accuracy of the three-dimensional solubility parameters. Hence the optimized solubility parameters are reliable.

- (2) The values of χ_{12} and R_i have been reported for PGA for the first time to the best of our knowledge. The results of χ_{12} are consistent with the boundary of complete miscibility suggested by Flory–Huggins for polymers and solvents.

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