

Improved method to calculate Hansen solubility parameters of a polymer

Ovidiu Segarceanu^{a,*}, Minodora Leca^b

^a*Anticorrosive Protection Varnishes and Paint Research Institute, 49A Theodor Pallady Blvd, Bucharest 74585, Romania*

^b*University of Bucharest, Faculty of Chemistry, Laboratory of Physical Chemistry of Polymers, 13 Carol I Blvd, Bucharest 70346, Romania*

Received 9 February 1996; accepted 15 March 1997

Abstract

An improved method to calculate Hansen solubility parameters δ_d , δ_p and δ_h , as well as the radius of interaction sphere for a given polymer is presented, starting from the idea that the solvents which dissolve a polymer, form in the interior of its solubility range a system of material points, their 'masses' being given by the unity normed intrinsic viscosities of the polymer in the considered solvents. The mass centre coordinates of the material points system represent in fact Hansen solubility parameters of the polymer, and the radius of interaction sphere the distance from this centre to the farthest point of material points system mentioned. © 1997 Elsevier Science S.A.

Keywords: Polymer solubility; Hansen solubility parameters; Radius of interaction sphere; Intrinsic viscosity; Mass center

1. Introduction

Solubility parameters are the most used quantities for the selection of solvents and plasticizers of polymers, to predict their compatibility with some other materials such as polymers and pigments and thus to design coating formulations. That is why the solubility parameters of a polymer must be accurately known.

The total solubility parameter, δ , defined by Hildebrand [1] as the square root of the cohesive energy density, CED:

$$\delta = (\text{CED})^{1/2} = (\Delta E^v / V)^{1/2} \quad (1)$$

where ΔE^v is the energy of vaporization and V , the molar volume, is a measure of all the intermolecular forces, responsible for the material cohesion.

Hildebrand postulated that interactions such as solvation should be strongest when the δ s of solvent and solute are equal.

It was found necessary to describe not only the intensity of interactions but also their quality.

The first step in this direction was made by Praunsnitz et al. [2,3] who divided the cohesive energy in two components: one due to dispersion interaction (d) and the other one

due to all the other types of forces (a). The total solubility parameter can be written as:

$$\delta = (\delta_d^2 + \delta_a^2)^{1/2} \quad (2)$$

where δ_d and δ_a are the corresponding partial solubility parameters.

It is customary to distinguish three types of intermolecular interactions which collectively produce the cohesive energy characteristic of the liquid state of non-electrolytes: dispersion, polar (p), and hydrogen bond (h) interactions, so that δ_a was divided into its components [4,5]:

$$\delta_a = (\delta_p^2 + \delta_h^2)^{1/2} \quad (3)$$

where δ_p and δ_h represent the partial solubility parameters due to polar (dipole–dipole and dipole–induced dipole) and hydrogen bonding forces, respectively, and the total solubility parameter is related to the partial ones by the relation:

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (4)$$

The determination of the solubility parameters of many substances being a difficult and laborious undertaking, correlations between solubility parameters δ_d , δ_p , δ_h and other physical properties of the substance were established [6–9].

A more accurate method to predict the solubility of a polymer into a solvent was developed [10–13] using an

* Corresponding author.

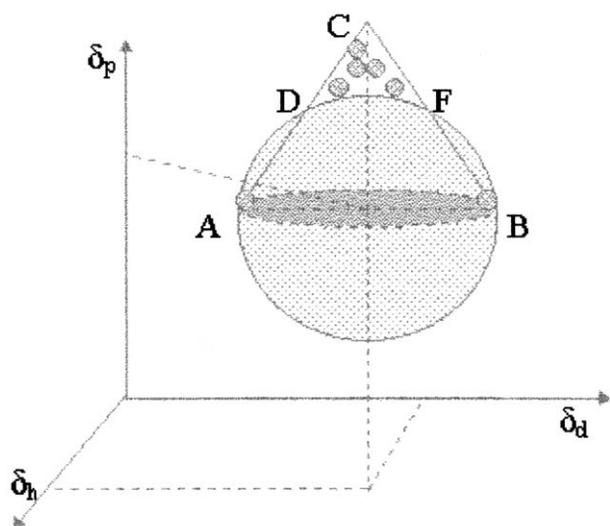


Fig. 1. Scheme of a situation which demonstrates the drawback of the method of [14].

elaborated equation taking account of entropic effects, polymer–polymer, polymer–solvent and solvent–solvent interactions. The equation, a little modified, was also used for oligomers [13].

The object of this paper is to describe a more rapid and accurate method to determine the partial or Hansen solubility parameters as well as the radius of interaction sphere for a given polymer using the tabulated Hansen solubility parameters of solvents. Intrinsic viscosities of polymer in different solvents were used as ‘weights’ of dissolving capacities of polymer. Equations corresponding to a system of material points placed into a tridimensional space were used, and a computer program was elaborated.

2. Mathematical considerations on the most used existing methods

Determination of Hansen solubility parameters of a polymer by classical method [4,5] consists in testing polymer solubility in different solvents with known partial solubility parameters. Solvents which interact with the given polymer (dissolve or swell it) are represented as points in planes having as coordinates (δ_p, δ_h) , $(2\delta_d, \delta_p)$, $(2\delta_d, \delta_h)$ and are comprised into circles of radius, R , which represents the radius of interaction sphere. The coordinates of the centre of the sphere represent Hansen solubility parameters of polymers. Any of the three planes can be considered first for drawing of circle, which results in different values for R and Hansen solubility parameters.

An effort to eliminate this shortcoming was made by Shareef at al. [14] who used a computer program to calculate the partial interaction parameters of pigments in the three-dimensional space. The method was developed to determine partial solubility or interaction parameters of pigments but can be also used for polymers. The method con-

sists in determining all the possible distances between the points placed into the above mentioned three-dimensional space. The points represent good solvents as well as solvents which swell the polymer, named in the following ‘limiting solvents’. The maximum separation distance is selected as the diameter of the interaction sphere and the coordinates of its middle represent the three Hansen parameters. The main drawback of the method is that there can exist several equal maximum separation distances; thus the position of the diameter of the sphere is not well-defined, and some good and limiting solvents are outside the sphere. Such an example is given below.

Let us suppose that good and limiting solvents for a given polymer, represented by small circles, are placed into an equilateral cone ABC as Fig. 1 shows. The maximum distance computed according to this method is $AB = BC = CD$. Considering AB as the diameter of the interaction sphere, the solvents placed between the top of the cone and the surface of the sphere are not included despite the fact that they dissolve the polymer.

Thus, we can affirm that even this method does not always determine accurately the coordinates of the centre of the interaction sphere and its radius. In the above-mentioned case the problem is which of the three maximum separation distances is the most probable diameter of the interaction sphere. Some other situations can be conceived.

3. The new problem statement and method of solution

The authors of this paper consider that good and limiting solvents of a polymer can be represented into the three-dimensional space of coordinate δ_d , δ_p , δ_h as a system of material points with different weights. The weights of solvents are determined by the intrinsic viscosities, normed to unity, of the polymer in the corresponding solvents, as it is well known that the intrinsic viscosity of a polymer in a given solvent is a measure of polymer–solvent interactions:

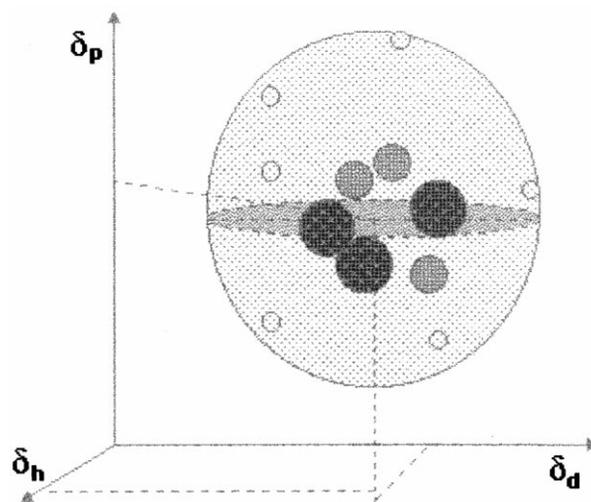


Fig. 2. Scheme of interaction sphere of the studied resin.

Table 1

The solvents used, their solubility parameters, intrinsic and normed viscosities at 25°C

Crt. no.	Solvents	δ_d ((MPa) ^{1/2})	δ_p ((MPa) ^{1/2})	δ_h ((MPa) ^{1/2})	$[\eta]_{25^\circ\text{C}}$ (dl/g)	$[\eta]'_{25^\circ\text{C}}$ (dl/g)
1	N-Methylpyrrolidone	18.0	12.3	7.2	0.1014	0.9703
2	Dimethylformamide	16.8	13.3	14.3	0.0990	0.9473
3	Dimethylsulfoxide	18.4	16.4	10.2	0.0190	0.1818
4	γ -Butyrolactone	19.1	16.6	6.6	0.0700	0.6898
5	Morpholine	18.9	4.9	9.2	0.1045 ^a	1.0000
6	Cyclohexanone	17.8	8.4	5.1	0.0750	0.7177
7	Acetone	15.6	11.7	4.1	–	–
8	Methyldiethylene glycol	16.2	7.8	12.7	–	–
9	Cellosolve	16.0	9.2	16.4	–	–
10	Diacetonolcohol	15.6	8.2	10.9	–	–
11	Cellosolve acetate	15.8	4.7	10.4	–	–

^aThe maximum value of intrinsic viscosity at which normation was made.

the higher the interactions, the greater the values of intrinsic viscosity. The coordinates of the mass centre of the system of material points represent the Hansen solubility parameters of the polymer. It is obvious that the mass centre is closer to solvents with higher ‘weights’, the ones which dissolve it better, and away from those with smaller ‘weights’ which are not good solvents for the polymer.

The equations of the coordinates of the mass centre, adapted to the present situation, are:

$$\delta_{dp} = \frac{\sum (\delta_{di} \times [\eta]_i)}{\sum [\eta]_i} \quad (5)$$

$$\delta_{pp} = \frac{\sum \delta_{pi} \times [\eta]_i}{\sum [\eta]_i} \quad (6)$$

$$\delta_{hp} = \frac{\sum (\delta_{hi} \times [\eta]_i)}{\sum [\eta]_i} \quad (7)$$

where subscript index p designates the polymer and $[\eta]_i$ is the intrinsic viscosity of polymer in solvent i, normed to unity. Normation to unity was made by dividing by the maximum obtained intrinsic viscosity. Once the coordinates of the interaction sphere — δ_{dp} , δ_{pp} and δ_{hp} — are determined, the separating distances from its centre to the points corresponding to good and limiting solvents, R_i , are computed. The highest value of R_i is considered the radius of interaction sphere, R . The equation used to compute R_i is the well-known Hansen’s relation:

$$R_i = [4(\delta_{di} - \delta_{dp})^2 + (\delta_{pi} - \delta_{pp})^2 + (\delta_{hi} - \delta_{hp})^2] \quad (8)$$

Using this method to compute the Hansen solubility parameters of a polymer, all the good and ‘limiting’ solvents are

comprised into the interior of the sphere or are at least on its surface, and a scheme of the interaction sphere of a polymer is given (Fig. 2). Larger and more black circles represent good solvents, which have greater ‘weights’ and are placed closer to the mass centre of the sphere which, in fact, is also its geometric centre.

4. Proving of the method

The Hansen solubility parameters of a polyesterimide resin used as electroinsulator were determined by the classical method and compared to those obtained by the new method. The solvents used, their solubility parameters, the intrinsic viscosities obtained and the normed ones are given in Table 1. Solvents 1–6 solve the resin, while 7–11 swell it, and zero values were taken for normed intrinsic viscosities, $[\eta]'$, in solvents 7–11.

The Hansen solubility parameters obtained using the two methods are given in Table 2. Comparing the values obtained by the two methods, positive and negative differences are obtained, ranging between 0.2 and 1.2 (MPa)^{1/2}, due to the contribution of intrinsic viscosities and to the method in itself.

In the case the intrinsic viscosities where data are not available, Hansen solubility parameters can be determined using Eqs. (5)–(7), and the value 1 for $[\eta]_i$, considering that all the solvents have the same capacity to dissolve the polymer. In these conditions the above-mentioned equations compute some average values for parameters.

Table 2

The Hansen solubility parameters obtained by the classical and the new method

Method	Hansen solubility parameters ((MPa) ^{1/2})			R ((MPa) ^{1/2})
	δ_{dp}	δ_{pp}	δ_{hp}	
Classical	17.4	12.3	8.6	4.1
New	18.0	11.1	8.8	8.6

5. Conclusions

1. The method presented in the paper determines more accurately the Hansen solubility parameters and the radius of interaction sphere of a polymer, due to the combination of intrinsic viscosity data (used to determine the Hildebrand solubility parameters) with Hansen

solubility parameters and an improved mathematical method.

2. The method is simple, uses literature data on solvents and polymers, and can be easily implemented on a computer.
3. The equations used to determine Hansen parameters are simple and do not imply special processing.

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