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Methods of Determination Hansen Solubility Parameters of a Copolymer Paratone 8900

Chemistry

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ABSTRACT

The global and partial solubility parameters and radii of interaction spheres of a copolymer Paratone 8900 were determined from solubility data and intrinsic viscosities using 9 solvents both by the classical Hansen's method and an improved one. The obtained results are in good agreement each other and with intrinsic viscosity data.

INTRODUCTION

Solubility parameters are the most used quantities for the selection of solvents for polymers and to predict their compatibility with some other compounds or materials. That is why the solubility parameters of a polymer must be accurately known. The total solubility parameters, δ, defined by Hildebrand [1] as the square root of the cohesive energy density, CED:

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

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

Hildebrand postulated that interaction, such as salvation should be stronger when the solubility parameters of solvent and solute have equal or very close values.

It was found that it is necessary to describe not only the intensity of interactions, but also their nature.

The first step in differentiation of interactions types was made by Praunsnitz et al. [2, 3], who divided the cohesive energy in two components: one due to the dispersion (d) and the one due to all the other types of forces (a). Thus, the total solubility parameter can be written as [4, 5]:

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

where δ_d and δ_a are corresponding partial solubility parameters.

But it is customary to distinguish three types of intermolecular interactions, which collectively produce the cohesive energy characteristic of the liquid state of phase of non-electrolytes: dispersion, polar (p), and hydrogen bond (h) interactions. Thus, δ_a was divided into its components:

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

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:

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

The determination of the solubility parameters of many substances being a difficult and laborious undertaking, some correlation between solubility parameters and other physical properties were established [6 – 9].

A more accurate method to predict the solubility of a polymer into a solvent was developed using an elaborated equation taking account of entropy effects, polymer-polymer, polymer-solvent and solvent-solvent interactions [10 – 13]. The equation was also used for oligomers [13-16].

The object of this paper is to determine the partial and total solubility parameters of a copolymer produced and recommended and commercialized by Exxon Chemical. Both the Hansen's method [4, 5] and an improved one [14] were used for their determination.

EXPERIMENTAL

The following copolymer was used as: poly (ethylene-co-propylene) (Exxon Chemical) – trade name Paratone 8900.

Solubility parameters were determined from solubility data using Hansen's method [4, 5] as well as an improved, more accurate one [14].

The viscosities of the solvents and solution were determined using two Schott Ubbelohde-type viscometers (0a and Ia), selected according to the values of their constant, so that the margins of the uncertainty, inherent in the Hagenbach-Couette correction, does not exceed the error allowed for the measurements. Intrinsic viscosities were determined from the dependence of reduced viscosity on polymer concentration and their extrapolation to zero polymer concentration.

RESULTS AND DISCUSSIONS

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

The solvents used, their solubility parameters, the intrinsic viscosities obtained and the normed ones are given in Table 1.

The second method considers that good and limiting solvents of a polymer can be represented into the three-dimensional space of coordinate's δ_d, δ_p, δ_h as a system of material points with different weighs. The intrinsic viscosity, [η], being a measure of polymer-solvent interaction (the higher the interactions, the greater the value of intrinsic viscosity), was taken to weight the partial solubility parameters. The coordinates of the mass centre of the system of material points represent the Hansen solubility parameters of the polymer.

In figure 1 the pairs of solubility parameters δ_p -$2\delta_d$, and δ_h-$2\delta_p$ of solvent and non-solvent the polymer Paratone 8900 listed in Table 1 in the axes of rectangular system of, the number 2 in front of solubility parameter indicating dispersion forces due two times greater value taken on the axis. He then traced the circle with the first pair (Figure 1a), so its interior is comprised as many solvents. The coordinates circle center is the partial solubility parameter values corresponding polymer - δ_{pp} şi δ_{pd} - first index indicating the polymer and its radius - radius of interaction. He then made representation to pair δ_h - $2\delta_d$ (Figure 1b) keeping both δ_{pd} and value for the radius of interaction and δ_{ph} value was determined. It was then examined by tracing the correctness of the circle for the pair $\delta_h - \delta_p$ values and range of interaction already determined (Figure 1c).

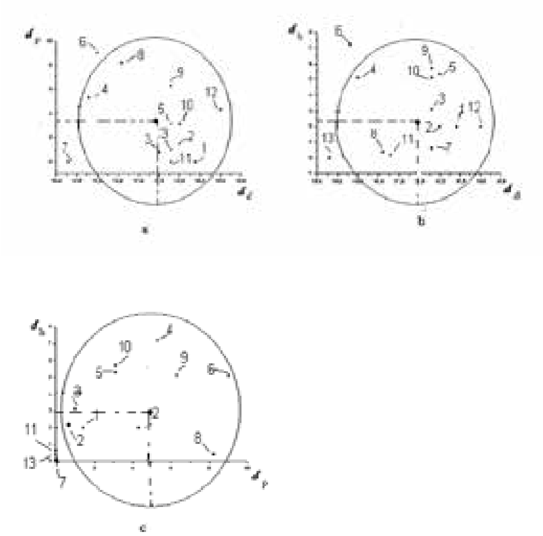

Figure 1: The representation in plan of the pairs of solubility parameter: a – δ_p-$2\delta_d$, b – δ_h-$2\delta_d$ and c – δ_h-δ_p for: 1 – benzene, 2 – toluene, 3 – o-Xylene, 4 – ethyl acetate, 5 – chloroform, 6 – metyl-ethyl-cetone, 7 – n-Heptane, 8 – 1,1-ethane dichloride, 9 – cyclohexanone, 10 – triclorethylene, 11 – carbon tetrachloride, 12 – benzene chloride, 13 – cyclohexane

The equations of the coordinates of the mass centre are [14]:

$$\delta_d = \Sigma\, (\delta_{di}\, x\, [\eta]'_i) / \Sigma\, [\eta]_i \qquad (5)$$

$$\delta_p = \Sigma\, (\delta_{pi}\, x\, [\eta]'_i) / \Sigma\, [\eta]_i \qquad (6)$$

$$\delta_h = \Sigma\, (\delta_{hi}\, x\, [\eta]'_i) / \Sigma\, [\eta]_i \qquad (7)$$

where $[\eta]'_i$ is the intrinsic viscosity of the polymer in solvent i normalized to unity. Normalization to unity was made by dividing the intrinsic viscosities in the solvents given in Table 1 by the maximum value obtained. Once the coordinates of the mass centre of the system of material points was determined, the distances separating the centre from the points was corresponding to good and limiting solvents, R_i, are computed. The highest value of R_i is considered the radius of interaction sphere. The equation used to compute R_i is the well-known Hansen's relation:

$$R_i = [4(\delta_{di} - \delta_d)^2 + (\delta_{pi} - \delta_p)^2 + (\delta_{hi} - \delta_h)^2] \qquad (8)$$

Paratone 8900 has the highest intrinsic viscosity in cyclohexane, followed by trichlorethylene and carbon tetrachloride and the lowest value in benzene.

TABLE – 1
THE SOLVENTS USED, THEIR GLOBAL SOLUBILITY PARAMETERS, INTRINSIC AND NORMED VISCOSITIES AT 25°C

Solvents	δ, (MPa)$^{1/2}$	[η], dl/g	$[\eta]'_i$
n-Heptane	15.3	1.5739	0.6062
Cyclohexane	16.8	2.2385	0.8622
Benzene	18.6	0.6872	0.2646
Toluene	18.2	0.7289	0.2807
o-Xylene	18.0	1.2697	0.4890
Metyl-ethyl-cetone	19.0	-	-
Cyclohexanone	19.6	-	-
Chloroform	19.0	0.4726	0.1820
Ethane dichloride	18.4	-	-
Triclorethylene	19.0	1.6174	0.6229
Carbon tetrachloride	17.8	2.5962*	1.0000
Benzene chloride	19.6	0.6370	0.2453
Ethyl acetate	18.2	-	-

*The maximum value of intrinsic viscosity at which normation was made.

TABLE – 2
THE HANSEN SOLUBILITY PARAMETERS OBTAINED BY THE CLASSICAL AND THE NEW METHOD

Classical		New	
δ, (MPa)$^{1/2}$	17.6	δ,(MPa)$^{1/2}$	17.5
δ_d, (MPa)$^{1/2}$	17.5	δ_d,(MPa)$^{1/2}$	17.4
δ_p, (MPa)$^{1/2}$	0.8	δ_p,(MPa)$^{1/2}$	1.0
δ_h, (MPa)$^{1/2}$	1.0	δ_h,(MPa)$^{1/2}$	1.8
R, (MPa)$^{1/2}$	4.8	R, (MPa)$^{1/2}$	4.5

The Hansen solubility parameters obtained using the two methods are given in Table 2.

CONCLUSIONS

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.

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