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Solubility Parameter for Copolymer used Additives for Lubricating Oil

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Abstract

Obiectives: In this article I have been looking at the determination of the solubility parameter by two methods for an additive hydrogenated poly (isoprene-co-styrene) used in lubricating oils. To determine the solubility parameter, it is necessary to know the intrinsic viscosities of the polymer hydrogenated poly (isoprene-co-styrene) in as many solvents with different solubility parameters. **Methods**: The viscosities of the dilute solutions copolymer hydrogenated poly (isoprene-co-styrene) were determined using Oa and I viscosimeters of the Ubbelodhe Schott capillary-type Viscosimeter set with the 0.04887 and 0.00976 constants at 25°C±0,1°C. From the values obtained for intrinsic viscosities it is concluded that the best solvent for this copolymer is cyclohexane, followed by trichlorethylene, carbon tetrachloride and SAE 10 W oil, and benzene is the weakest. Huggins constants, calculated from the intrinsic viscosity values obtained by extrapolating the reduced viscosities to the zero concentration of the copolymer, have values less than 0.4 for all four solvents. **Findings**: The value of the overall solubility parameter is comparable to the previous copolymer, which reflects its lack of polarity, and those due to polar interactions and hydrogen bonds are also very small: 1.2 (MPa)1/2 for those obtained by the Hansen method and between 1.4 and 2.4 (MPa)1/2 if the improved one is used. Analyzing the values determined by the two methods it is found that for the partial solubility parameters differences between 0.2 and 1.2 (MPa)1/2 are obtained, due to the intrinsic viscosity intake and the method of determination used. The difference between the global solubility parameters determined by the two methods is 0.4 (MPa)1/2. A larger difference also occurs in the sphere of solubility sphere: the obtained with the improved method is almost 30% lower, which means that fewer solvents are found in the sphere of solubility. The improved method applied to the studied copolymer used as an additive for lubricating oils is much more precise than the Hansen method. The solvents used are mostly included within the scope of the action sphere in the improved method. **Application**: Determination of the partial and global solubility parameters hydrogenated poly (isoprene-co-styrene) was done, first, using the Hansen method, then by an improved method. The improved method for determining the solubility parameter is much more precise than the Hansen method.

Keywords: Additives, Copolymer, Lubricating Oil, Solubility Parameter

1. Introduction

The empirical solubility rules established for micromolecular compounds are also valid for polymers: solubility is facilitated by the identical or similar chemical composition of the components: the affinity between the solvent and solvent is maximal when the two components have identical polarity, the solubility decreases with the increase in the molecular weight of the component dissolved.

In[1] called the ratio of the internal energy variation to the passage of one mole of phase-condensed phase sub-

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stance, ΔU^v, and the molar volume, V, the density of the coefficient of energy DEC.:

$$DEC = \Delta U^v / V = \left(\Delta H^v - RT\right)/V \qquad (1)$$

where H^v is the vaporization enthalpy.

The density of cohesive energy is the change in internal energy needed to overcome intermolecular interactions in a cubic centimeter of condensed phase substance. The square root of the density of cohesion energy was named by[2] a solubility parameter, δ:

$$\delta = (DEC)^{1/2} = \left(\Delta U^v / V\right)^{1/2} = \left[\left(\Delta H^v - RT/V\right)\right]^{1/2} \qquad (2)$$

and is measured in $(MPa)^{1/2}$, all sizes being considered at 25^0C (298K).

The relationship (2) allows to determine the solubility parameter of a volatile substance in its entropy of extrapolated vaporization at 25^0C.

Polymers can not be vaporised and other solubility assessment methods should be found for determining the solubility parameters ΔU/V.

For the enthalpy of mixing the following relationship was obtained[2]:

$$H^M = V_m\left(\delta_1 - \delta_2\right)^2 \varphi_1 \varphi_2 \qquad (3)$$

where V_m is the average molar volume of the mixture calculated on the basis of the volume fractions, and δ_1 and δ_2 – solubility parameters of the solvent or solvate respectively.

Mixing enthalpy is 0 when $\delta_1 = \delta_2$ and dissolution is ensured by the entropy factor. Two substances dissolve into one another only when $\delta_1 \approx \delta_2$ and the name of the solubility parameter given by Hildebrand to this magnitude becomes justified.

Relationship (3) allows to determine the solubility parameters of the polymers if solubility parameters of the solvents are known and the mixing temperatures are determined experimentall[3]

Intermolecular interaction forces are of four types: dispersion forces or London; dipol-dipol forces or Keesom; Dipole-dipole-induced or Debye forces; hydrogen bonds.

For different substances, the contribution of the four types of forces to cohesion energy is different and their weight should be determined.

In[4] divided energy of vaporization into a non-polar, dispersion component, ΔU^v_d, and a polar one, ΔU^v_a and the solubility parameter is:

$$\delta = \left[\left(\Delta U^v_d + \Delta U^v_a / V\right)\right]^{1/2} = \left(\delta_d^2 + \delta_a^2\right) \qquad (4)$$

where δ_d is the non-polar solubility parameter, and δ_a the polarity solubility parameter.

Subsequent[5] have divided the polar side into the contribution due to dipol-dipol interactions, δ_p, and contribution due to hydrogen bonds, δ_h, and therefore the total solubility parameter is given by the relationship:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (5)$$

For substances to dissolve in one another, all three solubility parameters must have equal or close values.

The non-polar solubility parameter of a polar substance is determined on the basis of the homomorph. It is the closest saturated hydrocarbon as the size and shape of the polar substance considered.

In[6] have proposed to obtain the solubility parameter due to hydrogen bonds by calculation using the relationship:

$$\delta_h = \left(5000 N / V\right)^{1/2} \qquad (6)$$

where N represents the number of OH groups in the molecule and V - the molar volume.

In[7] was the pairs of solubility parameters δ_p - δ_h, δ_p - δ_d and δ_h - δ_d in a system of cartesian axes taking the unit on the axis δ_d twice as high as on the axles δ_p and δ_h. The solubility parameter of a substance is a point, and the solubility parameters of its solvents are found on a radius circle called the radius of interaction. Solvents are found in a spherical volume with R_A radius called volume of interaction or solubility. The magnitude of the interaction radius is given by:

$$R_A^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \tag{7}$$

index 1 denoting solvent from the sphere, and 2 substance.

If the enthalpy of vaporization of a compound is not known but its boiling temperature is known, T_f, the solubility parameter can be obtained using the Hildebrand rule:

$$\Delta H^v = 23{,}7T_f + 0{,}02T_f^2 + 2950 \tag{8}$$

Knowing the vaporization enthalpy, the solubility parameter can be determined by the relationship (37) to which positive corrections should be added: 1.4 for alcohols, 0.6 for esters and 0.5 for ketones.

The solubility parameter can also be calculated from the defined group calculations, calculated and tabulated by[8], if the structural formula of the substance is known. Each functional group has an approximately constant value of the product of the cohesive energy and its molar volume at 298 K. Radical of this product, F_i, has been called constant molar attraction. Molar attraction constants are additive and related to the solubility parameter through the relationship[9]:

$$\delta = \left(\rho \sum_i F_i\right) \Big/ M \tag{9}$$

where ρ is the density and M molecular mass, the summation being done for all the groups present in the molecule.

The classic experimental methods for determining the solubility parameters of the polymers are: intrinsic solubility, impregnation and viscosity.

The solubility method consists of choosing a series of liquids or mixtures thereof with increasing solubility parameters in which the polymer is dissolved. As the polymer dissolves in liquids whose solubility parameters are within a range of higher or lower values, its parameter is considered to be the middle of the solubility range[9].

The softening method is used for cross-linked polymers, replacing that of the solubility. The crosslinked polymer is immersed in liquids with increasing solubility parameters and equilibrium imbibition is determined. The solubility parameter of the polymer is determined from the peak of the equilibrium curve according to the solubility parameter.

The intrinsic viscosity method consists in determining the intrinsic viscosities of the polymer in a series of solvents with different solubility parameters. The solubility parameter of the polymer is considered equal to that of the solvent for which intrinsic viscosity has the maximum value (macromolecular scales have maximum dimensions, intrinsic viscosity being a measure of their size in solutions in various solvents)[10].

To determine the solubility parameters of polymers, other properties were also used: refractive index, dipole moment, surface tension, turbidimetric titration.

In this article I have been looking at the determination of the solubility parameter by two methods for an additive hydrogenated poly (isoprene-co-styrene) used in lubricating oils.

2. Material and methods

The viscosities of the dilute solutions copolymer hydrogenated poly(isoprene-co-styrene) were determined using Oa and I viscosimeters of the Ubbelodhe Schott capillary-type Viscosimeter set with the 0.04887 and 0.00976 constants at 25°C±0,1°C[9]. Viscosimeters were selected in such a way that the allowed measurement error limits and Hagenbach-Couette correction[11] for kinetic energy could not be exceeded in order to increase the accuracy of the determinations.

Dissolution was carried out at room temperature, allowing the copolymer hydrogenated poly(isoprene-co-styrene) to soak for a long period of time and then gently shaking manually to avoid its degradation by agitation.

3. Results and discussion

Considering that it is a non-polar copolymer, 14 solvents, together with the global and partial solubility parameters, were used to determine the overall and partial solubility parameters of the hydrogenated isoprene-co-styrene copolymer in Table 1[12].

Solvents used, global solubility parameters, δ, and partial, δ_d, δ_p and δ_h,[3] in order of increase of the global solubility parameter values, as well as the results of the dissolution tests, are presented in Table 1[12].

With respect to solubility in various solvents, it should be noted that the copolymer hydrogenated poly (isoprene-co-styrene) is slightly soaked in methyl ethyl ketone and cyclohexanone and very little in ethyl acetate and 1, 2-dichloroethane.

From the values obtained for intrinsic viscosities it is concluded that the best solvent for this copolymer is cyclohexane, followed by trichlorethylene, carbon tetrachloride and SAE 10 W oil, and benzene is the weakest. Huggins constants, calculated from the intrinsic viscosity values obtained by extrapolating the reduced viscosities to the zero concentration of the copolymer, have values less than 0.4 for all four solvents. This means that the oil is a good solvent for copolymer hydrogenated poly (isoprene-co-styrene).

The values obtained for intrinsic viscosities and those normalized to the unit are shown in Table 2.

Table 1. Solvents used, partial solubility parameters and the solubility of the copolymer[12]

Solvents	**Δ (MPa)$^{1/2}$**	**δ_d (MPa)$^{1/2}$**	**δ_p (MPa)$^{1/2}$**	**δ_h (MPa)$^{1/2}$**
n-Heptane	15.3	15.3	0	0
Cyclohexane	16.8	16.8	0	0.2
Benzene	18.6	18.4	0	2
Toluene	18.2	18	1.4	2
o-xylene	18	17.8	1	3.1
Methyl-ethyl cetone	19	16	9	5.1
Cyclohexanone (20°C)	19.6	17.8	6.3	5.1
Ehyl acetate (20°C)	18.2	15.8	5.3	7.2
Ethane dichloride	18.4	16.6	8.2	0.4
Chloroform	19	17.8	3.1	5.7
Carbon tetrachloride	17.8	17.8	0	0.6
Trichlorethylene (20°C)	19	18	3.1	5.3
Benzene chloride	19.6	19	4.3	2

Table 2. The solvents used, the intrinsic viscosities of the copolymer therein and the viscosities normed at the unit[3,9,12]

Solvent	**$[\eta]$, dL/g**	**$[\eta]'$**
n-Heptane	0.7903	0.3190
Cyclohexane	2.4767*	1.0000
Benzene	0.4923	0.1988
Toluene	0.6836	0.2760
o-xylene	0.8309	0.3355
Methyl-ethyl cetone	-	-
Cyclohexanone	-	-
Ehyl acetate	-	-
Ethane dichloride	-	-
Chloroform	1.4131	0.5705
Carbon tetrachloride	2.0413	0.8240
Trichlorethylene	2.2608	0.9128
Benzene chloride	0.7777	0.3140
oil SAE 10W	1.8733	0.7563

* the maximum intrinsic viscosity value

Table 3. Hansen parameters and the sphere of solubility sphere calculated by the Hansen method and the improved method[12]

Method	**δ_{dp} (MPa)$^{1/2}$**	**δ_{pp} (MPa)$^{1/2}$**	**δ_{hp} (MPa)$^{1/2}$**	δ (MPa)$^{1/2}$	**R(MPa)$^{1/2}$**
Classical	17.3	1.2	1.2	17.4	4.8
Improved	17.6	1.4	2.4	17.8	3.7

The representations of the solubility parameter pairs are given in Figure 1.

Table 3 contains the values of the partial and global solubility parameters and the interaction angle for the

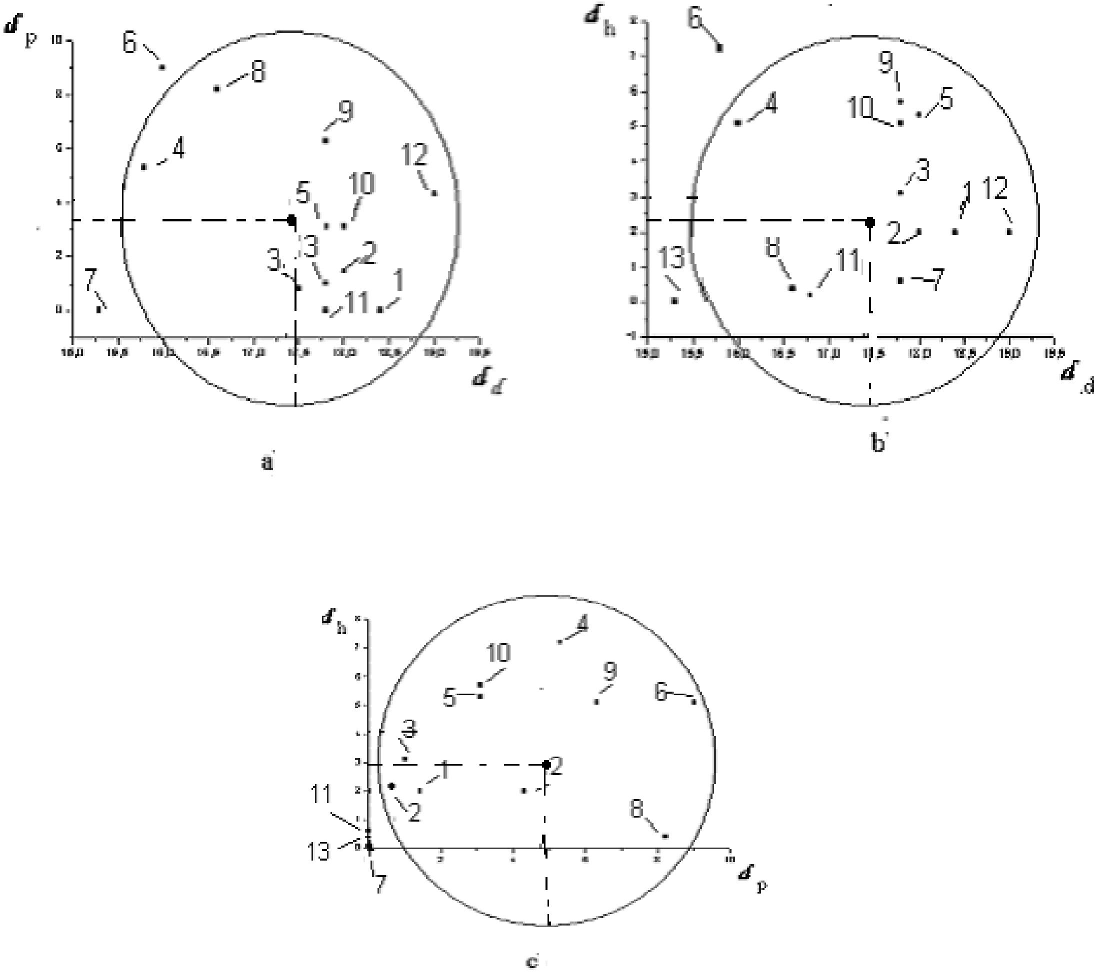

Figure 1. Plane representation of pairs of solubility parameters: a – δp-2δd, b – δh-2δd şi c – δh-δp for the solvents in Table 1.

copolymer hydrogenated poly (isoprene-co-styrene) obtained by both the Hansen method and the improved method.

Analyzing the values determined by the two methods it is found that for the partial solubility parameters differences between 0.2 and 1.2 $(MPa)^{1/2}$ are obtained, due to the intrinsic viscosity intake and the method of determination used. The difference between the global solubility parameters determined by the two methods is 0.4 $(MPa)^{1/2}$. A larger difference also occurs in the sphere of solubility sphere: the obtained with the improved method is almost 30% lower, which means that fewer solvents are found in the sphere of solubility.

4. Conclusion

The value of the overall solubility parameter is comparable to the previous copolymer, which reflects its lack of polarity, and those due to polar interactions and hydrogen bonds are also very small: 1.2 $(MPa)^{1/2}$ for those obtained by the Hansen method and between 1.4 and 2.4 $(MPa)^{1/2}$ if the improved one is used.

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