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STUDY SOLUBILITY OF TWO COPOLYMERS USED AS VISCOSITY IMPROVERS FOR MULTI-GRADE OIL

Ioana Stanciu

University of Bucharest, Department of Physical Chemistry, Romania
email: ioasta@yahoo.com

ABSTRACT

This paper presents a calculation method of intrinsic viscosity of copolymers in different solvents and oil SAE 10W, Huggins and Schulz-Blascheke coefficients, of two copolymers used as viscosity improvers for multi-grade oil. Intrinsic viscosities were determined from the dependence of reduced viscosity on polymer concentration and their extrapolation to zero polymer concentration. Huggins and Schulz-Blascheke coefficients of two copolymers were determining their intrinsic viscosity.

KEYWORDS: intrinsic viscosities, Huggins, coefficients, Schulz-Blascheke.

1. INTRODUCTION

The concentration dependence of the viscosity of dilute polymer solutions can be expressed in a power series in concentration:

$$\eta = \eta_0(1 + H_1c_2 + H_2c_2^2 + H_3c_2^3 + ...) \quad (1)$$

wherein η and η_0 denote the viscosity of solution and solvent, respectively. This equation may be rewritten in the more familiar form:

$$(\eta - \eta_0)/\eta_0c_2 = \eta_{SP}/c_2 = [\eta] + k_1[\eta]^2c_2 + k_2[\eta]^3c_2 + \ldots\ldots\ldots\ldots \quad (2)$$

were [η] is the intrinsic viscosity, $k_i = (k_1, k_2\ldots,$ etc.) a dimensionless parameter, and k_1 corresponds to the Huggins coefficient k_H. For low concentration c_2 we obtained Huggins' (1) well knew relationship [1]:

$$\eta_{SP}/c_2 = [\eta](1 + k_H[\eta]c_2) \quad (3)$$

By an earlier, empirical approach of Schultz and Blascheke [2, 3] equation (4) had been found:

$$\eta_{SP}/c_2 = [\eta](1 + k_{SB}\eta_{SP}) \quad (4)$$

Numerous studies revealed that Huggins' coefficient k_H is always higher that Schulz-Blaschke's coefficient k_{SB}, whereas it is the opposite with the viscosity values. Comparing equations (3) and (4) leads to the quantitative relationship:

$$k_H = k_{SB}([\eta]_{SB}\eta_{SP})/ [\eta]^2c_2 \quad (5)$$

This shows that the coefficient differences largely depend on the investigated specific viscosity region as well as on the concentration.

k_H şi k_{SB} not only depend on the intermolecular hydrodynamic interaction but also on many other factors, which certainly include the intermolecular thermodynamic interaction [4, 5].

According to a hydrodynamic theory of Riseman and Ullman [6], the value of k_H would be 3/5 for a coil and 11/15 for rods. $k_H \geq 1$ results for spherical particles, and therefore k_H is often found to be between 0.8 and 1.3 in the case of aggregated chain molecules.

The limiting value $k_{H\theta}$ for an untrained coil under θ conditions is according to Sakai [7,8] k_H is 0.52 relatively close to corresponding measurements [9]. In suitable solvents, $k_H < 0.52$ should be obtained with uncharged systems, provided coils of sufficiently high molecular weight are available.

The object of this paper is to determine the intrinsic viscosities of copolymers in different solvents and oil SAE 10W, Huggins and Schulz-Blascheke coefficients of two copolymers produced and recommended by DSM Elastomers Europe B.V. and Infieum UK LIMITED respectively as viscosity improvers for multi-grade mineral oils, to estimate their efficiency as lubricating additive components for the mineral oil SAE 10W. The obtained values were correlated with the intrinsic viscosities.

2. EXPERIMENTAL ANALYSIS AND RESULTS

The following copolymers were used as viscosity improvers: poly (ethylene-co-propylene) (DSM Elastomers Europe B.V.), trade name KELTAN 4200, and hydrogenated poly (isoprene-co-styrene) (Infieum UK LIMITED), trade name INFINEUM SV 260. As mineral oil SAE 10W (INCERP, Romania) was used.

The two copolymers is insoluble in water, soluble in hydrocarbons such as (alkanes: hexane, heptanes, octane, decane, dodecane, iso-octane, isododecane, cycloalkanes: cyclo-octane, decaline, cyclododecane, aromatic substances: butyl benzene, octylbenyene, and oil: paraffinic naphthenic, aromatic [10,11] .

The viscosities of the solvents and solutions 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 [12].

The results of the dissolving tests showed that the hydrocarbures and the derivates halogenations – except the ethane dichloride – dissolve the copolymer, when the two cetons and the ethyl acetate don't dissolve it. They interact, with the ethyl acetate and the cyclohexanone and with 1,2 - ethane dichloride and methyl-ethyl-cetone do not interact.

Form determining value intrinsic viscosities in a given solvent, it has been made data viscosimetric measures in every solvent to many concentrations of copolymer (3 or 4 measures in every concentration and used the media), then calculated the reduced viscosities, η_{sp}/c_2, that were represented in function of concentration c_2 of copolymer and the extrapolation of the detained lines to zero polymer concentration.

The dependence reduced viscosity of the copolymers concentration for the used solvents is represented in Figs. 1-3, grouped in the same graphic in function of the reduced value viscosity and for the obtained lines not to interact.

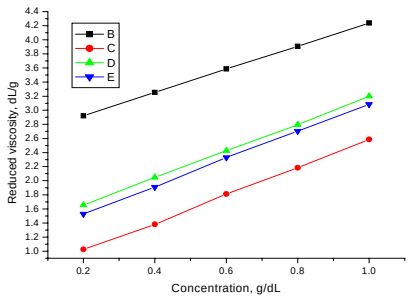

Fig. 1. The dependence reduced viscosity of concentration for solutions at 25^0C: B – Carbontetrachloride, C – Benzene chloride, D – n-Heptane and E – o-Xylene

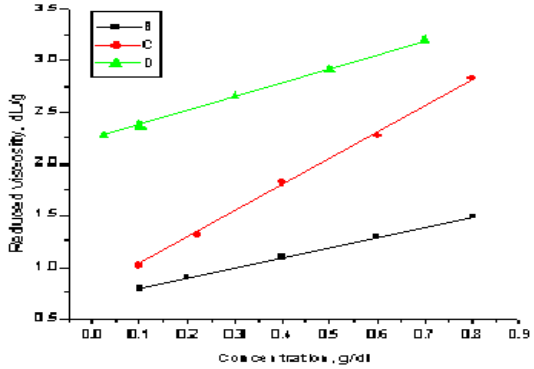

Fig. 2. The dependence reduced viscosity of concentration for solutions at 25^0C: B – Benzene, C - Toluene, D – Cyclohexane

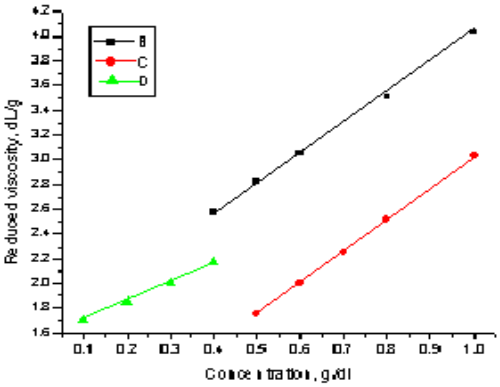

Fig. 3. The dependence reduced viscosity of concentration for solutions at 25^0C: B – Trichlorethylene, C – Chloroform, D – oil SAE 10W

The solvents used, their solubility parameters, the intrinsic viscosities obtained and Huggins and Schulz-Blascheke coefficients are given in Table 1.

Considering the intrinsic viscosities of the values it results that the good solvent is the carbon tetrachloride, followed by cyclohexane, trichloroethylene and the n-heptane, and the weasels is the chloroform. It explains the composition of the copolymer that has a non-polar structure.

If it calculates the constants Huggins it wile discover that the values are lower that 0.4 only for the two solvents, so the obtained of intrinsic viscosities of determined values for viscosities, a single concentration had been correct only for these solvents.

From table 1 it while find out that the intrinsic value of viscosities of the copolymer in oil SAE 10 W is very close to n n-heptane, it explains the fact that the oil is dominantly paraffin. Calculate ring the constants Huggins for n-heptane and oil it will see that the values are higher than 0.4, lout very close one

to another: 0.58 for n-heptane and 0.67 for the oil SAE 10W. It could appreciate that the even oil SAE 10 W is a good solvent for the copolymer ethylene-propylene.

Table 1.The solvents used, intrinsic viscosities, Huggins and Schulz-Blascheke coefficients for KELTAN 4200

Solvents	**[η], dl/g**	**k_H**	**k_{SB}**
n-Heptane	1.5739	0.5762	0.2772
Cyclohexane	2.2385	0.2763	0.1871
Benzene	0.6872	2.1313	0.3203
Toluene	0.7289	4.9010	0.7962
o-Xylene	1.2697	1.1184	0.3336
Methyl-ethyl-cetone	-	-	-
Cyclohexanone	-	-	-
Chloroform	0.4726	11.4369	0.4526
Ethane dichloride	-	-	-
Trichlorethylene	1.6174	0.9152	0.2229
Carbon tetrachloride	2.5962	0.2437	0.1290
Benzene chloride	0.6370	4.7955	0.6311
Ethyl acetate	-	-	-
Oil SAE 10W	1.5355	0.6690	0.4252

Sealing about solubility in different solvents it must been said that the copolymer INFINEUM SV 260 interact with methyl-ethyl-cetone and cyclohexanone and very little in ethyl acetate and ethane dichloride.

The dependence reduced viscosity of the copolymer concentration for used the solvents is represented in Figs. 4-6 for copolymer INFINEUM SV 260.

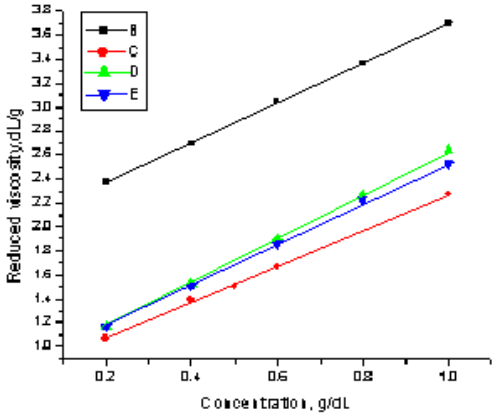

Figure 4. The dependence reduced viscosity of concentration for solutions at 25^0C:
B - Carbon tetrachloride, C – Benzene chloride, D – n-Heptane and E – o-Xylene

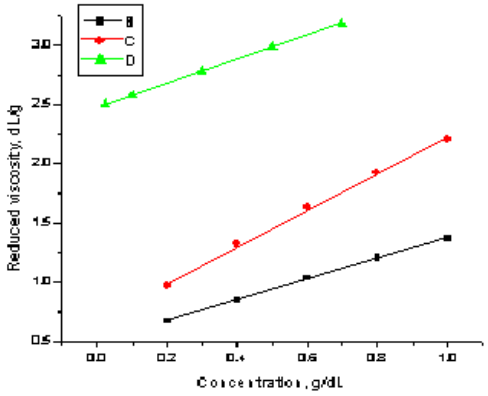

Figure 5. The dependence reduced viscosity of concentration for solutions at 25^0C:
B – Benzene, C – toluene, D – cyclohexane

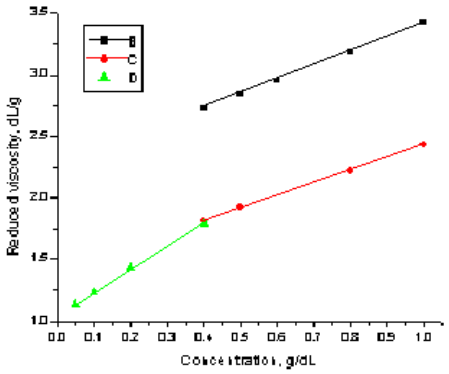

Figure 6. The dependence reduced viscosity of concentration for solutions at 25^0C:
B – Triclorethylene, C – Chloroform, D – oil SAE 10W

The solvents used, their solubility parameters, the intrinsic viscosities obtained and Huggins and Schulz-Blascheke coefficients for INFINEUM SV 206 are given in Table 2.

Table 2.The solvents used, intrinsic viscosities, Huggins and Schulz-Blascheke coefficients for INFINEUM SV 260

Solvents	**[η], dl/g**	**k_H**	**k_{SB}**
n-Heptane	0.7903	2.9574	0.5352
Cyclohexane	2.4767	0.1659	0.1267
Benzene	0.4923	3.6391	0.8761
Toluene	0.6836	3.2910	0.6259
o-Xylene	0.8309	2.4681	0.5175
Methyl-ethyl-cetone	-	-	-
Cyclohexanone	-	-	-
Chloroform	1.4131	0.5077	0.2277
Ethane dichloride	-	-	-
Trichloroethylene	2.2608	0.2263	0.1228
Carbon tetrachloride	2.0413	0.3965	0.1817
Benzene chloride	0.7777	2.4630	0.5288
Ethyl acetate	-	-	-
Oil SAE 10W	1.8733	0.2980	0.8755

The values obtained from intrinsic viscosities you jump to conclusion that the good solvent for this copolymer is cyclohexanone, followed by trichloroethylene, carbon tetrachloride and oil SAE 10 W and the lowest is benzene. The Huggins, constants calculated from intrinsic viscosity values resulted from the extrapolation of reduced viscosities to zero concentration of the copolymer have lower values than 0.4 for all four solvents. This means that the oil SAE 10W is a good solvent for INFINEUM SV 260.

3. CONCLUSIONS

The both copolymers do no dissolve in solvents as methyl-ethyl-cetone, cyclohexanone, ethane dichloride or ethyl acetate as expected for non-polar polymers [12].

The values of intrinsic viscosities show that the oil SAE 10 W is a good solvent for the copolymer ethylene-propylene ([η] = 1.53 dL/g, Huggins constant is 0.67) and a very good solvent for the copolymer hydrogenated poly(isoprene-co-styrene) ([η] = 1.87 dL/g, Huggins constants is 0.30), so you can obtain concentrated solutions with appreciated viscosity, specially for the last copolymer.

INFINEUM SV 260 has the highest intrinsic viscosity in cyclohexane, followed by trichloroethylene and carbon tetrachloride and the lowest value in benzene; KELTAN 4200 has the highest intrinsic viscosity in carbon tetrachloride, followed by cyclohexane and the lowest one in chloroform.

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