

Evaluation of Poly (acrylates) and their Copolymer as Viscosity Modifiers

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Abstract

Homopolymers of decyl acrylate, dodecylacrylate and isodecylacrylate and copolymers of each of them with styrene were synthesized and characterized. Intrinsic viscosity and viscometric molecular weight of each of them were determined by using Huggins and Mark - Houwink equation respectively. Viscosity index improver (VII) properties were tested with additive doped base oil in terms of viscosity index (VI) of the base oil – additive blends. VI values of the additive doped base oils depend on the nature of mineral base oils used and the type and concentration of VI improvers.

Keywords: Viscosity index, base oils, blended oils, viscosity index improvers

Introduction

Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemicals that can improve or add performances of lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. One of the important types of additive is viscosity index improvers commonly known as viscosity modifier ¹.

Viscosity index improvers function by increasing the relative viscosity of oil more at high temperatures than at low temperatures²⁻⁴. Generally these result from the polymer changing its physical configuration with increasing temperature of the mixture. It is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase. In cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out and the interaction between these long molecules, having greater volume and the oil produces a proportionally greater thickening effect which in turn raises the viscosity

index (VI) of the oil. The viscosity index is an indicator of the change in viscosity as the temperature is changed. The higher the VI, the less the viscosity of an oil changes for a given temperature change.

Some of the polymers generally used commercially as VII, and known to possess certain inherent advantages and disadvantages in performance, are- i) Poly isobutylene (PIBs), ii) Hydro-generated Styrene –isoprene copolymers, iii) Olefin copolymers (OCP); e.g. Ethylene- propylene copolymer, IV) Esters of styrene- Maleic anhydride copolymers and v) Poly alkyl methacrylates (PMA).

In continuation of our activities towards the development of polymeric additives for lube oil⁵ recently we have synthesized some long chain poly acrylates, e.g. poly (decylacrylate), poly (dodecylacrylate), poly (isodecylacrylate) and also copolymer of each of them with styrene to see their applicability as VI improver. The polymers were characterized and evaluated in lube oil for their VII properties.

Material and Methods

Esterification and polymerization: Esterification of acrylic acid with different alcohols, purification of

the prepared esters and subsequent polymerization (homo and copolymerization) were carried out following the procedure as reported in our earlier publications^{6,7}.

Characterization: All the polymers were characterized on the basis of spectral analysis (IR, NMR), thermo gravimetric analysis (TGA) and by viscometric method as reported in our earlier paper⁸.

Determination of intrinsic viscosity and viscometric molecular weight: Intrinsic viscosity and viscometric molecular weight (Table 1) were determined by using the experimental viscosity of the polymer solutions in Huggins (eq.1) and Mark Houwink – Sukurda equation (eq.2) respectively⁶⁻⁸.

$$\text{Huggins (H)} \quad \frac{\eta_{sp}}{C} = [\eta]_h + k_h [\eta]_h^2 C \quad (1)$$

Where, C is mass concentration.

$\eta_{sp} = \eta_r - 1$, specific viscosity

$\eta_r = t/t_0$, relative viscosity or viscosity ratio (where t is time of flow of solution and t_0 is time of flow of pure solvent).

$[\eta]_h$ = intrinsic viscosity, respective to Huggins equation, k_h , Huggins coefficient

According to Mark Houwink – Sukurda (eq. 2), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (2)$$

Where, $[\eta]$, the intrinsic viscosity, can be calculate by using Huggins equation, parameter 'K' and 'a' depends on the type of polymer, solvent and temperature. For the viscosity – average molecular weight determination, the constants $K = 0.00387$ dl/g and $a = 0.725$ were employed in Mark Houwink – Sukurda relation^{7,8}.

Determination of viscosity index (VI): The prepared polymers were tested for their effectiveness as viscosity index improvers in two different base oils (BO1 and BO2) according to ASTM D-7042 method and also by using the method of viscosity index calculation reported in literasature⁹. In this

respect, the kinematic viscosities of the oil, doped with different concentrations of the tested additives were determined at 40°C and 100°C.

Different concentrations, ranging between 1-6% (wt/wt), were used to study the effect of concentration on VI of the lube oil.

Results and Discussion

Table 1 presents intrinsic viscosity and viscometric molecular weight. Intrinsic viscosity and molecular weight of the copolymers are always found higher than the respective homopolymers.

The base oil properties are tabulated in table 2. The prepared polymers were tested for their effectiveness as viscosity index improvers for base oil (BO1 and BO2) according to ASTM D-2270. In this respect, the kinematic viscosities of the oil doped with different concentrations of the tested additives were determined at 40°C and 100°C. The concentrations were ranging from 1% to 6%, which is used to study the effect of the additives concentration on VI of lube oil.

It is clear from the VI data tabulated in table 3 to table 14 and the plots of VI vs concentration (Figure 1 and Figure 2), that irrespective of the type of polymer (homo or copolymer) and nature of the base oil, VI values increases with the increase in additive concentration in the base oils studied. A critical observation of the VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. It is also observed that branching in the carbon chain of the alcohol deteriorates its performance when used as a VII in the lube oil. Thus the chain length and its arrangements play a significant role when added in the lube oil to act as a VI. A possible explanation may be, as the temperature is raised, the lube oil viscosity gets decreased and as a result of that the polymer molecules get expanded due to the increase in the salvation power and the size of the micelle. This increase in micelle size counterbalanced the reduction of the viscosity of the lube oil and hence,

decreases the change of viscosity with temperature of the mixture¹⁰⁻¹¹. The increase in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution and thus exerting greater thickening effect and so as to VI properties.

Conclusion

Irrespective of the polymers (homo and copolymer) and nature of the base oils, VI values increases with the increase in additive concentration in the base oils studied.

VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. Again, branching in the carbon chain of the alcohol deteriorates the performance of the acrylate when used as a VI improver in the lube oil. Thus, the chain length and its arrangements in the polymer of a viscosity modifier play a significant role when added in the lube oil to act as a VI improver.

Acknowledgement

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Table-1: Intrinsic viscosity and viscometric molecular weight of prepared polymer. S-1 poly(decylacrylate), S-2 poly(dodecylacrylate), S-3 poly(isodecylacrylate), S-4 copolymer of decylacrylate with styrene, S-5 copolymer of dodecylacrylate with styrene and S-6 copolymer of isodecylacrylate with styrene

Samples	$[\eta]_h$	M_h
S-1	4.34	16051
S-2	4.059	14,672
S-3	3.774	13,270
S-4	2.677	8255
S-5	2.621	8,026
S-6	2.737	8,520

Table-2: Base oil properties

Base oil properties	Base oils	
	BO1	BO2
Viscosity at 40 ⁰ C in cSt	7.202	23.609
Viscosity at 100 ⁰ C in cSt	1.872	3.951
Cloud point, ⁰ C	-8	-10
Pour point, ⁰ C	-3	-6

Table-3: VI values for poly (decyl acrylate) (S-1) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at 100 ⁰ C	VI
0	7.202	1.872	87.00
1	7.262	1.891	90.48
2	7.298	1.901	91.93
3	7.345	1.914	93.66
4	7.403	1.928	95.08
5	7.440	1.946	98.98
6	7.479	1.962	101.95

Table-4: VI values for poly (decyl acrylate) (S-1) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at 100 ⁰ C	VI
0	23.609	3.951	81.68
1	23.982	4.032	85.09
2	24.070	4.080	88.41
3	24.125	4.099	89.30
4	24.232	4.157	92.80
5	24.303	4.189	94.80
6	24.393	4.248	98.15

Table-5: VI values for poly (isodecyl acrylate) (S-2) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.302	1.903	92.51
2	7.340	1.915	94.52
3	7.382	1.925	95.36
4	7.424	1.945	99.52
5	7.460	1.959	101.95
6	7.502	1.975	104.58

Table-6: VI values for poly (isodecyl acrylate) (S-2) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	24.026	4.060	87.21
2	24.083	4.087	88.71
3	24.156	4.116	90.48
4	24.248	4.164	93.38
5	24.335	4.223	96.77
6	24.402	4.284	100.34

Table-7: VI values for poly (dodecylacrylate) (S-3) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.357	1.918	94.52
2	7.422	1.938	97.60
3	7.474	1.953	99.52
4	7.546	1.977	103.00
5	7.603	1.993	104.58
6	7.682	2.022	108.68

Table-8: VI values for poly (dodecyl acrylate) (S-3) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	24.070	4.097	89.59
2	24.147	4.149	93.09

3	24.236	4.217	97.32
4	24.311	4.270	100.34
5	24.371	4.310	102.48
6	24.419	4.338	103.80

Table-9: VI values for copolymer of DA+ styrene (S-4) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.246	1.882	88.11
2	7.310	1.900	90.77
3	7.385	1.914	91.35
4	7.451	1.932	93.66
5	7.529	1.952	95.93
6	7.610	1.972	98.15

Table-10: VI values for copolymer of DA+ styrene (S-4) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.899	4.017	84.78
2	23.986	4.054	86.91
3	24.092	4.092	89.00
4	24.159	4.125	91.06
5	24.267	4.174	93.95
6	24.357	4.214	95.93

Table-11: VI values for copolymer of IDA+ styrene (S-5) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.284	1.893	89.89
2	7.334	1.905	91.35
3	7.410	1.923	93.09
4	7.498	1.949	96.77

5	7.606	1.976	99.52
6	7.673	1.991	100.61

Table-12: VI values for copolymer of IDA+ styrene (S-5) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.949	4.040	86.00
2	24.020	4.067	87.81
3	24.084	4.088	89.00
4	24.158	4.124	91.06
5	24.234	4.166	93.66
6	24.342	4.214	96.21

Table-13: VI values for copolymer of DDA+ styrene (S-6) in BO1 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.339	1.906	91.35
2	7.422	1.925	93.09
3	7.510	1.951	96.77
4	7.608	1.965	95.93
5	7.684	1.992	100.34
6	7.738	2.014	104.06

Table-14: VI values for copolymer of DDA + styrene (S-6) in BO2 oil

Solution Conc. (wt %)	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.987	4.050	86.61
2	24.080	4.087	88.71
3	24.171	4.128	91.35
4	24.250	4.165	93.38
5	24.364	4.215	95.93
6	24.478	4.275	99.25

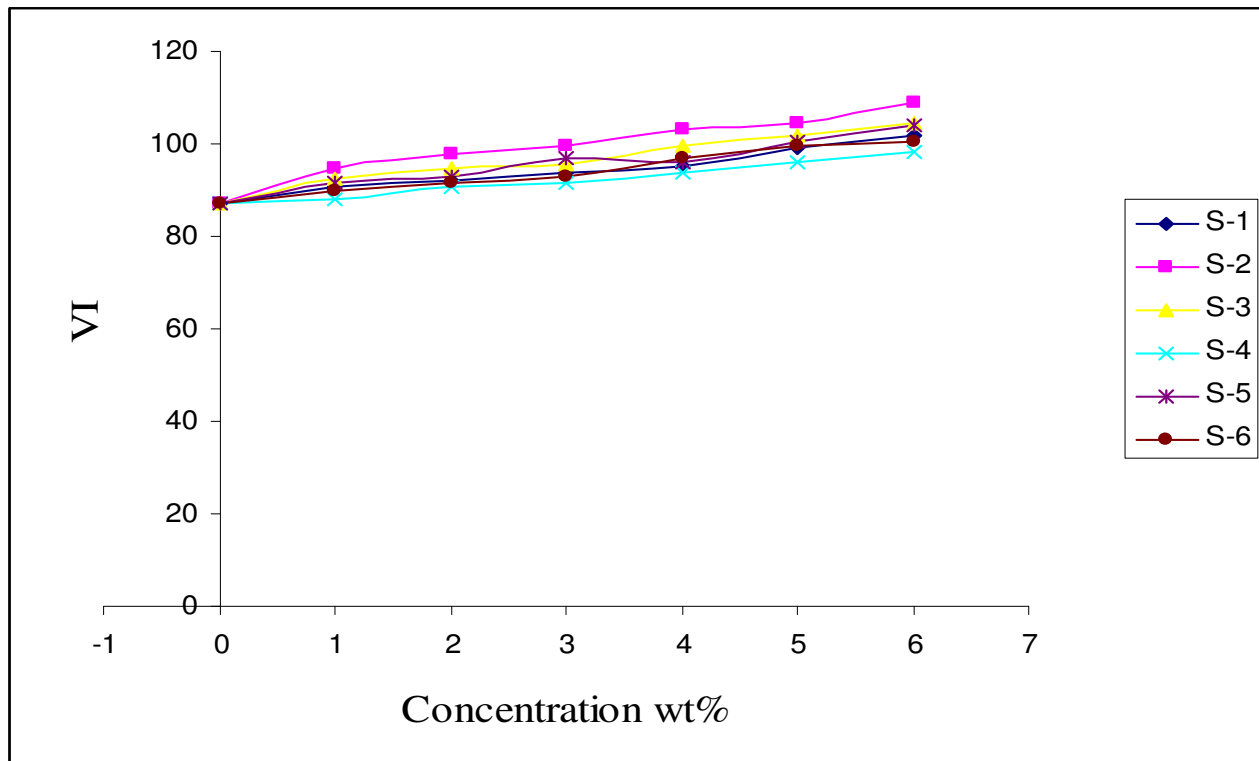


Figure-1: Plot of Viscosity Index (VI) vs polymer concentration in BO1 base oil, where S-1 Poly(decyl acrylate), S-2 Poly(isodecyl acrylate), S-3 Poly(dodecyl acrylate), S-4 copolymer of DA+ styrene, S-5 copolymer of IDA+ styrene, S-6 copolymer of DDA+ styrene

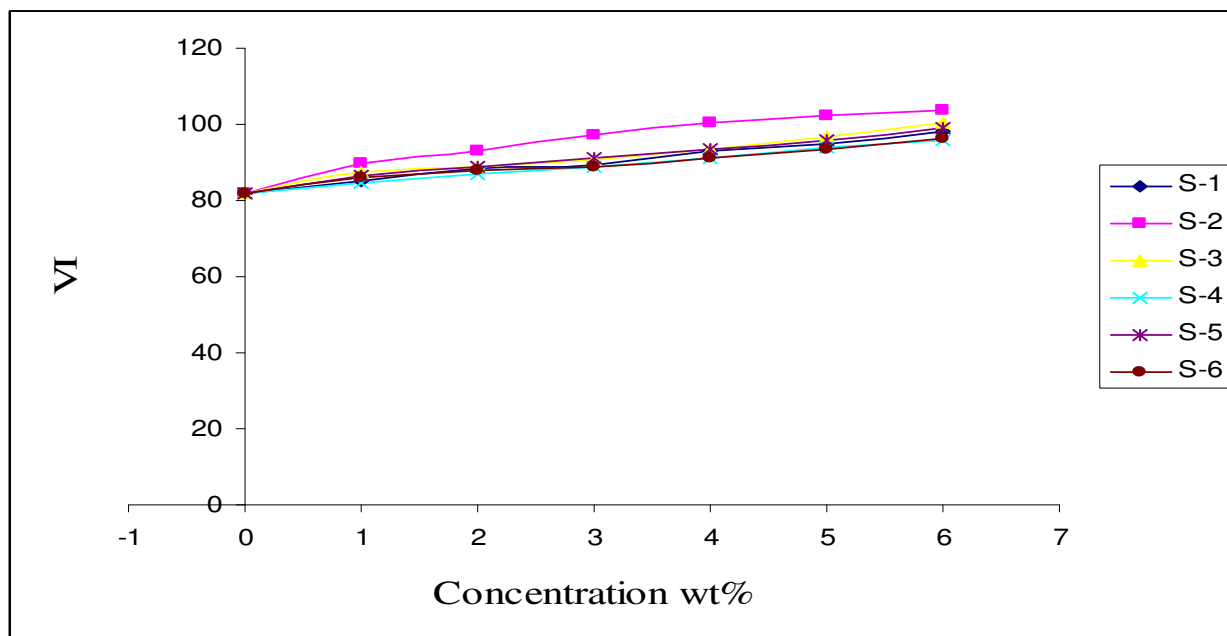


Figure-2: Plot of Viscosity Index (VI) vs polymer concentration in BO2 base oil, where S-1 Poly(decyl acrylate), S-2 Poly(isodecyl acrylate), S-3 Poly(dodecyl acrylate), S-4 copolymer of DA+ styrene, S-5 copolymer of IDA+ styrene, S-6 copolymer of DDA+ styrene