

Study of Intrinsic Viscosity and Flow Activation Energy of Some Polymers in Different Solvents

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Abstract

The intrinsic viscosity has been studied for several polymers which are used in some industrial applications, such as polyisobutylene of types Oppanol B150, 200, and 250 with different molecular weights of 2.5, 4.1 and 5.9 million g/mole, respectively, which dissolved in crude and gas oil. In addition three types of additives brought from Al-Dura refinery, olefin copolymer (OCP), {viscoples-4-677, viscoplex-215496, and Lubrizol R 7077} which dissolved in crude oil, and the polymers which is soluble in water such as polyacrylamide with high molecular weight and xanthan gum with molecular weight 3.7 million g/mole where also studied. It was found that the intrinsic viscosity of polyisobutylene decrease as the temperature increase in crude and gas oil. The olefin copolymer (Viscoplex-4-677) showed the same behavior as polyisobutylene where it can be used as drag reduction agent. It was noted that neutral polymers as well as polyelectrolytes could be used as drag reduction agent.

Keywords

Intrinsic viscosity, Neutral polymers, Polyelectrolyte

Introduction

Intrinsic viscosity $[\eta]$ may be regarded as a measured of the specific hydrodynamic volume of dissolved polymer in at infinite dilution $C \rightarrow 0$ [1]. Intrinsic viscosity measured in specific solvent is related to molecular weight M , by the Mark – Houwink equation [2, 3].

$$[\eta] = KM^a \quad (1)$$

Where k and a are Mark-Houwink constant that depends upon the typed of polymer, solvent, and the temperature of the viscosity determinations [2]. The unit of intrinsic viscosity is inverse concentration [4].

A plot of the $\log [\eta]$ vs. $\log M_w$ usually gives a straight line, the slope of this line is the

" a " value and the intercept is equal to the log of the " k " value as shown in Fig.1 [2].

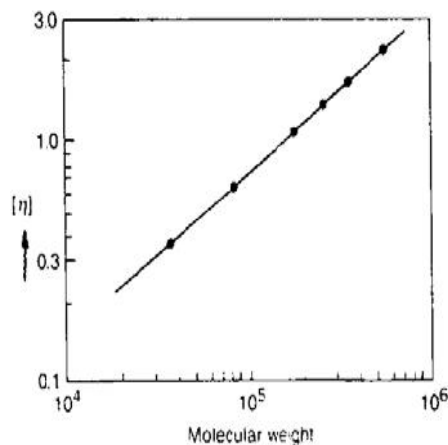


Fig.1 Logarithmic Plot of $[\eta]$ vs. M (Schematic) [2].

The slope contains information about the shape of molecules:

- $a = 1/2$ (for flexible polymer chain in "ideal" solvent).
- $0.5 < a < 0.8$ (for flexible polymer chain in "good" solvent).
- $a > 0.8$ (for "stiff" chain) [4].

The viscosity of a polymer solution (η) is higher than that (η_0) of the pure solvent at a specified temperature and the increase in medium viscosity on dissolving the polymer in the solvent is a function of both molecular weight and concentration of the polymer solute.

If the polymer solution is very dilute, then the viscosities of the solvent and the solution at a given temperature would be proportional to their flow times in a given capillary viscometer such that the relative viscosity η_r expressed by the ratio (η / η_0) would be given by the flow time ratio (t / t_0), where t_0 is the flow time of a given volume of the solvent and t is the flow time of the same volume of solution respectively. The parameter

called specific viscosity, y_{sp} as defined by $y_{sp} = (\eta - \eta_0) / \eta_0 = (t - t_0) / t_0$, where specific viscosity per concentration equal to reduced viscosity, and intrinsic viscosity is: [5]

$$[\eta] = \lim_{c \rightarrow 0} y_{red} \quad 2$$

The term of $[\eta]$ has been related to the three viscosity function through the following three equations by Huggins, Kraemer, and Schulz-Blaschke respectively: [6, 7]

$$\frac{y_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad 3$$

$$\frac{(\ln y_{rel})}{c} = [\eta] - k''[\eta]^2 c \quad 4$$

$$\frac{y_{sp}}{c} = [\eta] + k'''[\eta] y_{sp} \quad 5$$

Where k' , k'' and k''' are constants for a given polymer-solvent-temperature systems [8]. The value of k' is usually in range $0.3 < k' < 0.4$ and increases as solvent power decreases [6].

Some of polymers are polyelectrolyte. Polyelectrolytes are polymers whose repeating unit bears an electrolyte group. These groups dissociate in aqueous solutions, making the polymers charged [9,10], other terms Polyelectrolyte are polymers that fall apart in polar solvent for examples polyacrylic acid Put in water and the acid hydrogens split off with the water molecules and form H_3O^+ ions, as in Fig.2 [11]:

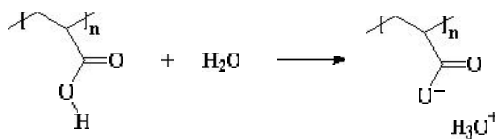


Fig.2 The polyacrylic acid in sodium salts [11].

From Fig.2, the polymer is left with bunch of negative charged groups; all those negative charges are going to repel each other.

Aim Of Work

1- Estimation of the intrinsic viscosity for different polymers which are used in previous literature either as drag reduction agent or viscosity index improver in crude oil and other solvents.

2- From the intrinsic viscosity, The Mark-Houwink parameters were calculated for different molecular weights for polyisobutylene in crude and gas oil.

Experimental Work

Preparation of Polymer Solution

The dissolving of polymers was carried out in a magnetic stirrer, of type Heidolph, MR 3000, made in Germany, at room temperature. The method of dilute solution preparation takes 1 gram of polymer per 100 ml (w/v) of solvent in a conical flask. The magnetic stirrer was started at a speed of 500 rpm and increase continuously. Then, the homogeneous solution was diluted to different concentrations such as (0.5, 0.4, 0.3, 0.2, and 0.1g) per 100 ml of solvent (w/v) by the same magnetic stirrer for 30 sec.

Calculations

1- The times of the solvent (t_0) and solution (t) was measured by using capillary viscometer as shown in fig.3.

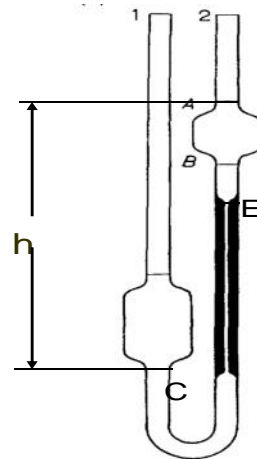


Fig.3 Ubbelohde Capillary Viscometer

2- The relative viscosity was measured

$$\text{from } y_{rel} = \frac{t}{t_0}.$$

3- The specific viscosity was calculated

$$\text{from } y_{sp} = \frac{t - t_0}{t_0}.$$

4- The reduced viscosity was also calculated

$$y_{red} = \frac{y_{sp}}{c}.$$

5- The $y_{red} = \frac{y_{sp}}{c}$ was plotted with each

concentration to get intrinsic viscosity $[\eta]$ as shown in fig.4

Results And Discussions

The experiments were performed to determine the intrinsic viscosity $[\eta]$, Huggins constant for different polymers and Mark-Houwink constant for polyisobutylene in crude and gas oil.

Polyisobutylene, Oppanol B 150, 200 and 250 were dissolved in crude oil; and the effect of concentration on reduced viscosity is represented graphically for two temperatures (40 and 100°C) as shown in Fig.5 and 6 respectively.

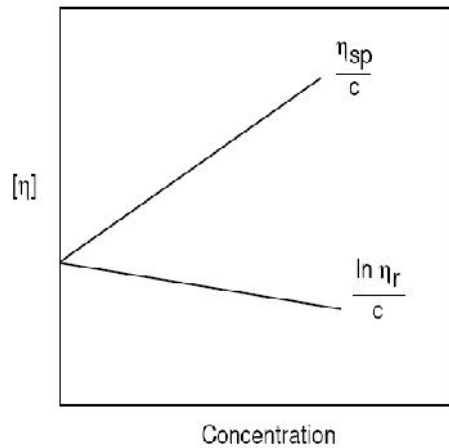


Fig.4 $\frac{\eta_{sp}}{c}$ or $\frac{\ln \eta_r}{c}$ versus Concentration

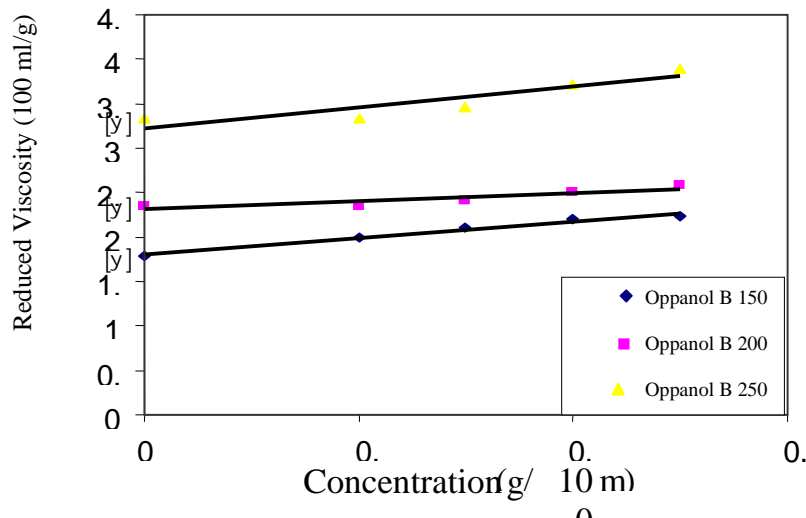


Fig. 5 Reduced Viscosity Versus Concentration for Different Oppanol B in Crude Oil at Temperature 40°C.

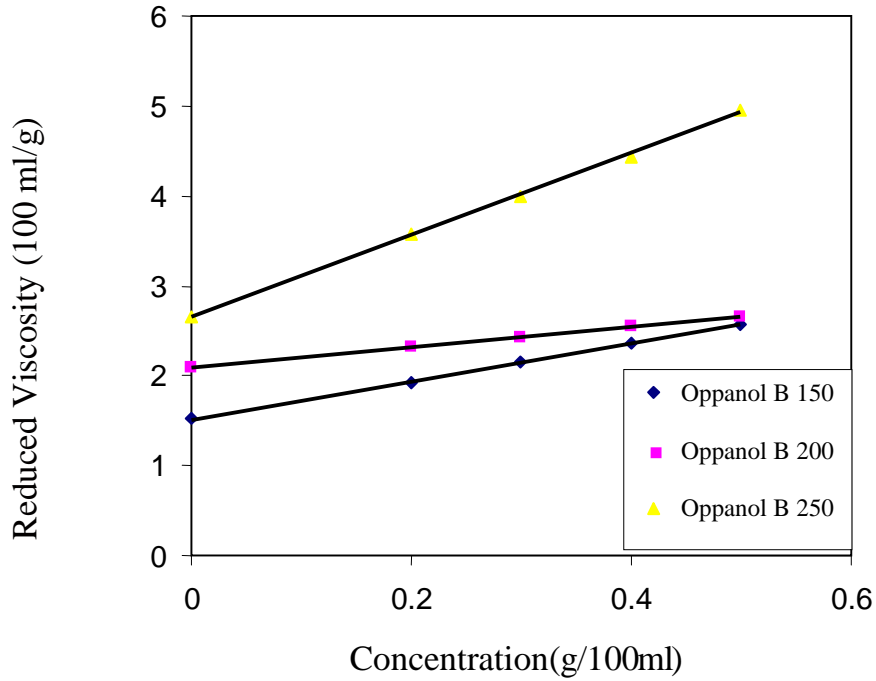


Fig. 6 Reduced Viscosity Versus Concentration for Different Oppanol B in Crude Oil at Temperature 100°C.

Also other plots are obtained for different Oppanol B in gas oil at two temperatures (40 and 100°C).

By using eq.3, and reduced viscosity equal to $\frac{y_{sp}}{c}$, the relation of reduced viscosity against concentration, usually gives a straight line, the

slope of this line is equal to $k'[\eta]^2$ and intercept equals to $[\eta]$, so that Huggin's constant K' can estimated with known $[\eta]$ [2,24], the intrinsic viscosities and Huggins constants for polyisobutylene in crude and gas oil illustrated in tables 1, 2, 3 and 4 respectively

Temperature (°C)	Intrinsic Viscosity(ml/g)		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	178	218	290
100	152	209	265

Table 2 Huggins Constant of Crude Oil with Different Oppanol B at Temperature (40 and 100°C).

Temperature (°C)	Huggins constant(K')		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	0.224	0.22	0.24
100	0.9	0.26	0.42

Table 3 Intrinsic Viscosity of Gas oil with different Oppanol B at Temperature (40 and 100°C).

Temperature (°C)	Intrinsic Viscosity(ml/g)		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	320	421	541
100	230	303	340

Table 4 Huggins constant of Gas oil with different Oppanol B at temperature (40 and 100°C)

Temperature (°C)	Huggins constant(K')		
	Oppanol B 150	Oppanol B 200	Oppanol B 250
40	0.34	0.8	0.9
100	0.94	1.80	4.3

Fig. (5 and 6) show that the polyisobutylene (PIB) behaves as neutral polymers in crude oil. Neutral polymers have the property that reduced viscosity increase with increasing of polymer concentration [12], because of the structure of PIB may be does not contain a carboxyl group [13]. When the polymer behaves as polyelectrolyte, reduced viscosity increase with decreasing polymer concentration, which is usually observed in aqueous solution, occurs because the carboxyl group on the polymer chain can ionize in the polar solvent and the effective electrostatic repulsion makes this polymer chain highly extended [14], and also show the hydrodynamic volume $[\eta]$ of PIB in crude oil decreases with increasing the

temperature, the interaction of PIB in crude oil becomes an unfavorable with increasing temperature due to decreasing of solvent power of crude oil, which suggest that PIB coil tend to shrink at higher temperature, and also show the behavior of PIB in crude oil which has similar behavior of PIB in gas oil, this result agreed with previous literature for PIB in cyclohexane and carbon tetrachloride [12, 15, 16].

By using eq.1, $[\eta] = KM^a$, a plot of the log vs. log M for PIB in crude and gas oil at a temperature of 40°C. Our results compared for PIB in crude and gas oil with other solvent in previous literature [8, 17], as shown in table 5

Table 5 Mark-Houwink parameters for polyisobutylene in Crude and Gas oil and Compared with other solvent in previous literature [8, 17]				
Polymer	Solvent	Temperature/ C	k (cm ³ /g)	a
Polyisobutylene	Benzene	30	0.061	0.56
	Toluene	30	0.02	0.67
	Cyclohexane	30	0.0276	0.69
	Carbon tetrachloride	30	0.029	0.68
	Crude oil	40	0.0442	0.558
	Gas oil	40	0.0415	0.6

Table 3 show that the intrinsic viscosity of PIB in gas oil is higher than that in crude oil as shown in table1 at the same temperature, this is because the difference in Mark-Houwink parameter (K and a) in crude and gas oil as shown in table 5.

In addition three types of additives brought from Al-Dura refinery, olefin copolymer (OCP), {viscoples-4-677, viscoplex-215496, and Lubrizol R 7077} which dissolved in crude oil; the effect of changing the concentration on reduced viscosity is represented graphically for two temperatures (40 and 100°C) in Fig.7 to 9.

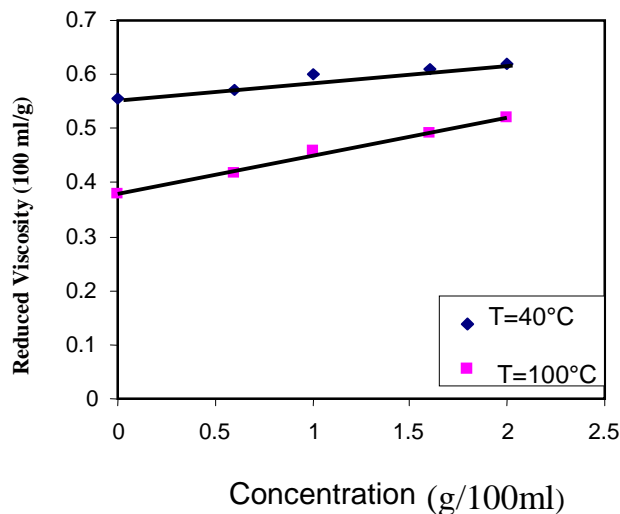


Fig. 7 Reduced Viscosities Versus concentration for OCP (Viscoplex-4-677) in crude oil at temperature 40 and 100°C.

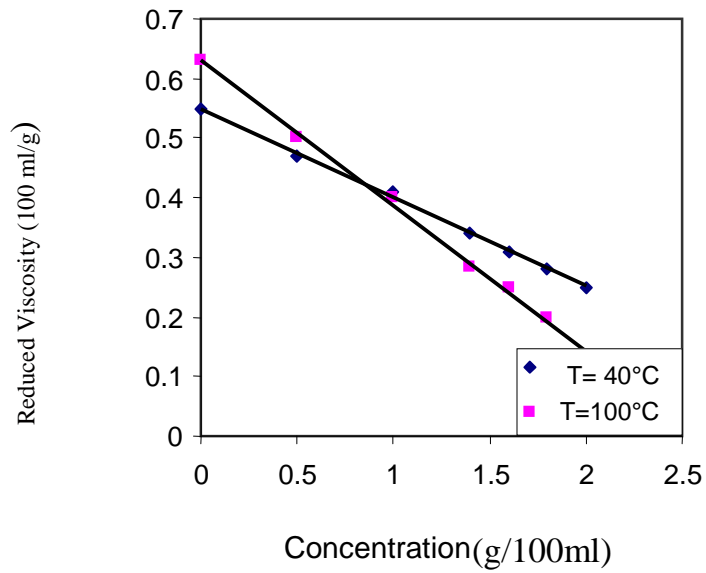


Fig. 8 Reduced Viscosities Versus concentration for OCP (Viscoplex-215496) in crude oil at Temperature 40 and 100° C.

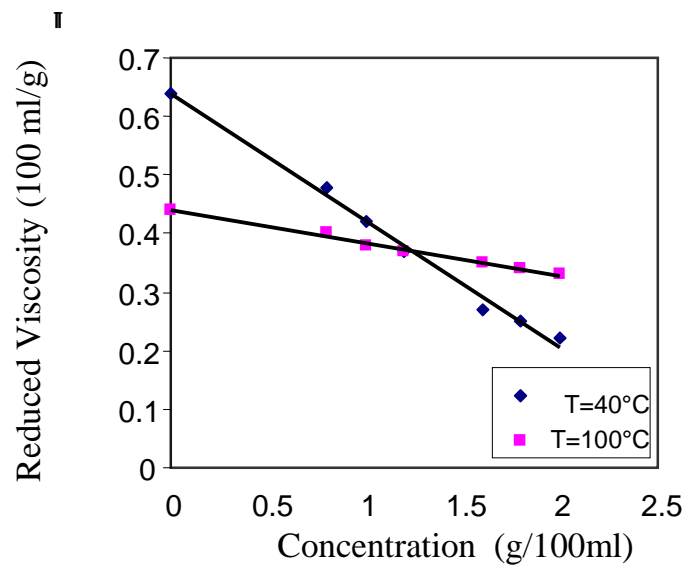


Fig. 9 Reduced viscosities versus concentration for OCP (Lubrizol R7077) in crude oil at Temperature 40 and 100° C.

By using eq.3, reduced viscosity equals to $\frac{y_{sp}}{c}$,

from fig. (7 to 9) the relation of reduced viscosity against concentration, the intrinsic viscosities and

Huggins constants illustrated in tables 6 and 7 respectively

Table 6 Intrinsic Viscosity of Crude Oil with Different OCP at Temperature (40 and 100°C).			
Temperature (°C)	Intrinsic Viscosity(ml/g)		
	Viscoplex-4-677	Viscoplex215496	Lubrizol R7077
40	55.7	55	64
100	37.9	63.3	43.9

Table 7 Huggins constant of Crude Oil with Different OCP at Temperature (40 and 100°C).			
Temperature (°C)	Huggins constant (K')		
	Viscoplex-4-677	Viscoplex215496	Lubrizol R7077
40	0.351	0.49	0.61
100	0.44	0.54	0.47

Fig.(7 to 9) show two types of olefin copolymers (OCP), the first type is (Viscoplex-4-677), which behaves as neutral polymers, neutral polymers have the property that reduced viscosity increase with increasing concentration, the second types are (Viscoplex-215496, Lubrizol R7077), which behaves as polyelectrolyte, where the reduced viscosity increases with decreasing concentration. The behavior of OCP as neutral and polyelectrolyte is not known, because the structure of OCP is unknown.

Fig.7 shows that the OCP (Viscoplex-4-677) dissolved in crude oil behaves as polyisobutylene, show that the intrinsic viscosity decreases with increasing the temperature, so that this behavior of (Viscoplex-4-677) can be used in crude oil as drag reduction agent like polyisobutylene.

And the polymers which is soluble in water such as polyacrylamide at high molecular weight and xanthan gum at molecular weight 3.7 million g/mole; the effect of changing the concentration on reduced viscosity is represented graphically for temperatures 40°C as shown in Fig. 10 and 11.

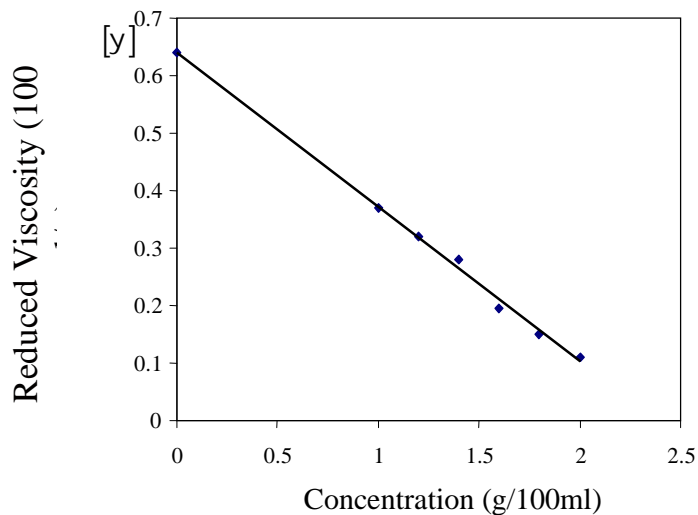


Fig. 10 Reduced Viscosities versus concentration for XG in water at Temperature 40°C.

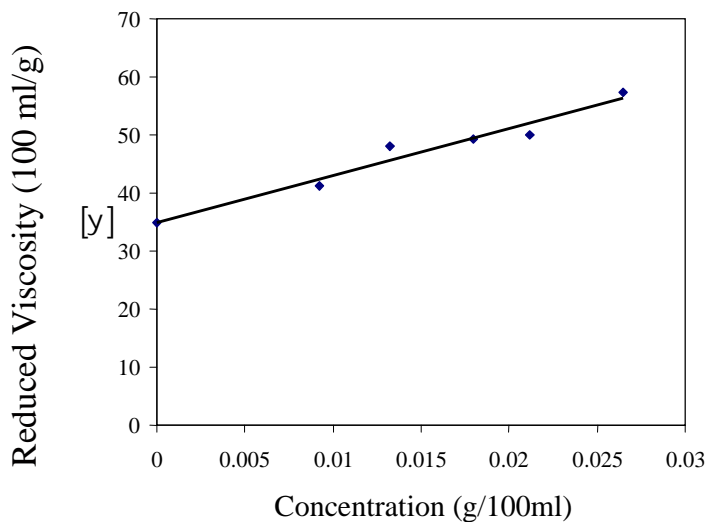


Fig.11 Reduced Viscosities Versus concentration for PAM in water at temperature 40°C.

Fig.(10 and 11) show the concentration effect on the reduced viscosity for polymers dissolved in water, where the polyacrylamide(PAM) behaves as neutral polymer as reduced viscosity increases with increasing the polymer concentration, although water is polar solvent but the polymer behaves as polyelectrolyte must contain a carboxyl group, such as polyacrylic acid dissolved in water as shown in fig.2[11], and polyelectrolyte depends also on the solution pH, counter ion concentration, or ionic strength[18], partially hydrolyzed polyacrylamide by copolymerization of acrylamide and sodium acrylate can behave as polyelectrolyte as shown in previous literature [14].The chemical structure of partially

hydrolyzed polyacrylamide is as shown in fig.12 [14]:

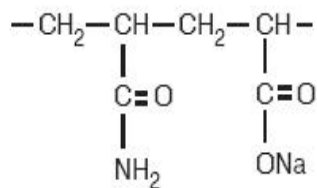
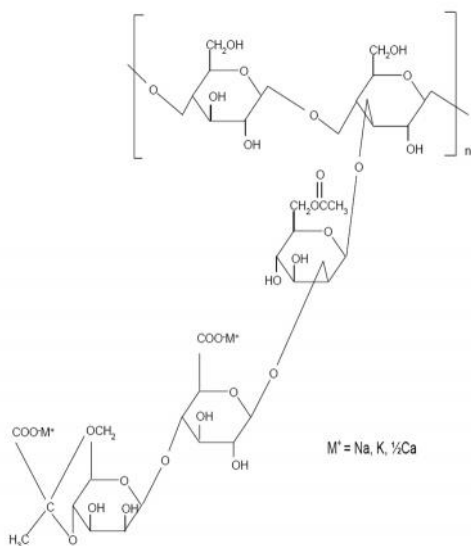


Fig.12 The chemical structure of partially hydrolyzed polyacrylamide [14].

u Xanthan gum (XG) behaves as polyelectrolyte as reduced viscosity increases with decreasing the

polymer concentration because it may contains a carboxyl group as shown below [19]



And water is polar solvent, then the carboxyl group when dissolved in water will have negative charges, and the repulsion forces between ionized carboxyl groups which makes XG chain highly extended [14].

Xanthan Gum used as drag reduction agent as in the previous works [20, 21, and 22], this polymer behaves as polyelectrolyte and it is good as drag reduction agent because the polymer chain will be extended and also simulate the department of linear random-coiling macromolecules in solution, this indicates a possible relationship between the mechanisms of drag reduction produced by these additives [23].

By using eq.3, and reduced viscosity equals to $\frac{y_{sp}}{c}$, fig. (10 and 11) show the relation of reduced viscosity against concentration, the intrinsic viscosities and Huggins constants illustrated in table 8

Table 8 Intrinsic Viscosity and Huggin constant for xanthan gum and polyacrylamide at temperature 40°C

Temperature 40 (°C)	Xanthan gum	polyacrylamide
Intrinsic Viscosity(ml/g)	64	349
Huggins constant (K')	0.17	0.74

Conclusion

Several conclusions have been extracted from the present work:

- 1- Reduced viscosity increases with increasing the concentration of polyisobutylene in crude and gas oil where the polyisobutylene in crude and gas oil behaves as neutral polymer.
- 2- Intrinsic viscosity of polyisobutylene in crude and gas oil decreases with increasing the temperature.
- 3- k and a (Mark-Houwink constants) was determined for polyisobutylene in crude and gas oil at temperature 40°C, and this has not been mentioned in the literature and could be used for unknown M.WT of the same system at 40°C.

4- Intrinsic viscosity of different molecular weight of polyisobutylene in gas oil is higher than that in crude oil at temperature 40°C.

5- When OCP (Viscoplex-4-677, Viscoplex-215496, and Lubrizol R 7077) have been dissolved in crude oil, it shows that there are two types of OCP, the first type is (Viscoplex-4-677), where its reduced viscosity increases with increasing of concentration which behaves as neutral polymer, the second types is (Viscoplex-215496, Lubrizol R7077), where the reduced viscosity increases with decreasing the concentration where it is behave as polyelectrolyte.

6- When OCP (Viscoplex-4-677) has been dissolved in crude oil, it behaves as polyisobutylene in crude oil where the intrinsic viscosity decreases with increasing of

temperature, so that this type of OCP can be used in crude oil as drag reduction agent like polyisobutylene.

7- Poluisobutylene, Xanthan gum and Polyacrylamide used as drag reduction agent, show that xanthan gum behaves as polyelectrolyte where the reduced viscosity of xanthan gum increases as concentration of xanthan gum decreases, but the reduced viscosities of polyisobutylene and polyacrylamide increase as the concentration of polymers increases and they behave as neutral polymer.

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