Dr. Muhanned A.R. Mohammed
Assist. Prof. in Chemical Engineering
Nahrain Unversity

Areej Jasim Mohammed

Former Post graduat student
Chemical Engineering Dept.
Nahrain Unversity

Effect of Type and Concentration of Different Water Soluble Polymer Solutions on Rheological Properties

Dr. Muhanned A.R. Mohammed and Areej Jasim Mohammed

Abstract

This research deals with experimental study of the effect of concentration of polymer solutions on rheological properties. All polymers studied in this work are water soluble, which are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol. The rheological properties of these polymer solutions was investigated using a Couette coaxial cylinder rotational viscometer (Fann model 35A), by measuring shear stresses versus shear rates (i.e. the flow curve). 55 experiments were performed with different polymer solutions concentrations at temperature 30 °C (±1 °C). It was found that as polymer concentration increased, the flow behavior index (n) decreased and the consistency index (k) increased. This behavior reflects the fact that as polymer concentration increases the solution become far from Newtonian fluid. Correlations were found which describe the effect of polymer concentration on n and k (for each polymer used in this study) and presented in a linear and exponential form respectively.

Key words: polymer, non-Newtonian fluids, Rheology.

1. Introduction

Rheology is the study of the deformation and flow of matter. Deformation is the relative displacement of points of a body. It can be divided into two types: flow and elasticity. Flow is irreversible deformation; when the stress is removed the material does not revert to its original form. This means that the work converted to heat. Elasticity is reversible deformation; the deformed body recovers its original shape, and the applied work is largely recoverable. Vescoelastic materials show both flow and elasticity [1].

Water Soluble Polymers

Polymers are large organic molecules compose of seed extracts (guar, starch), modified cellulose (CMC, HEC), biosynthetic gums (Xanthan), and synthetic polymers (PVA) [2].

Sodium Carboxymethyl Cellulose (CMC)

CMC is prepared by the reaction of cellulose with chloroacetic acid in the presence of sodium hydroxide. It is containing strong carboxyl groups which place it in the anionic polyelectrolyte category.CMC is mainly consumed in detergent, paint, textile, pulp and paper, ceramics and oil drilling industries [3].

Hydroxyethyl Cellulose (HEC)

HEC is prepared by reaction of alkali cellulose with ethylene oxide in the presence of isopropyl alcohol.

HEC is used in industry as dispersing agent, thickening, film-forming etc. In petroleum exploitation, it is used as stabilizer and thickening agent, lubricating agent for well drilling, completing and consolidating to give slurry a good fluidity and stability. Besides, it finds wide application in ink, textile dyeing, paper making, pharmaceuticals, food, agriculture etc [4].

XC Polymer (Xanthan gum)

XC polymer, also known as Xanthan gum, is an anionic polysaccharide derived from the fermentation of the plant bacteria Xanthamonas campestris. It is soluble in hot or cold water and gives visually hazy, neutral pH solution [4].

Xanthan gum is widely used as an effective stabilizer or a suitable thickener for various kinds of water-based systems. Its numerous area of application cover a broad range including food, pharmaceutical ,cosmetic, agricultural, textile, ceramic, and petroleum industries [5].

Polyvinyl Alcohol (PVA)

Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. PVA instated is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate group [6]. Some uses of PVA include [7]:
- Adhesive and thickener material in latex paints, paper coatings, shampoos and glue.
- Hoses, gaskets, pipe and gloves where its oil and solvent barrier properties are important.
- As an additive for strength to concrete and cements.

Polymer Solutions

Polymer solutions can be considered as liquid mixtures made of long macromolecular chains, and small, light molecules of solvent [2].

Dilute solutions are those in which each polymer chain is believed (or assumed) to be completely isolated from the other polymer chains, and forms a coil at equilibrium. When the concentration is increased polymer molecules begin to interact by becoming entangled. The concentration (known as the critical concentration) required for a solution to become entangled will decrease as the molecule becomes longer and occupies a larger equilibrium volume.

In response to a deformation, the polymer molecule itself can change both its shape and orientation. In dilute solutions, the rheology of the solution is dependent solely on the dynamics of an individual chain and the number of chains (i.e. the concentration) in the system. At higher concentrations in the entangled region, interactions between polymer molecules due to entanglements impact the rheology in a significant way [2].

The Power Law Model

The power law model is widely used as a model for non-Newtonian fluids.

$$\tau = k\dot{\gamma}^{n} \qquad \boxed{1}$$

where ; τ : is shear stress, $\dot{\gamma}$: is shear rate, n : is flow behavior index, and k : is consistency index.

The power law model holds many solutions and can describe Newtonian, shear-thinning, and shear-thickening behavior, depending on the power factor, n, also called the flow behavior index. For a Newtonian fluid, n=1 and the equation reduces to Newtonian model. If n is less than 1, the fluid is shear thinning; if it is greater than 1, the fluid is shear thickening. A test of whether the power law applies and a means to determining n is to plot the log shear stress vs the log shear rate. If the plot is linear the power low applies. The value of n, which is the slope of the line, can be used as a measure of the degree of shear thinning or shear thickening.

2. Experimental Work
Polymers Used

All polymers studied in this investigation are water soluble and used in industries as a rheology control additive (rheology modifiers). Five polymers were used in this study, these are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol, as follow:

Sets of Experiments

55 experiments were performed to study the rheological properties of the aqueous solutions of polymers used in this study. Experiments were performed at 30 °C (±1 °C). List of experiments is shown in Table (1).

Viscometer

The Fann viscometer model 35 is direct reading instrument which has six speeds: 600, 300, 200, 100, 6 and 3 rpm. It is a Couette coaxial cylinder rotational viscometer [9].

This instrument is a form of concentric cylinder viscometer that enables the variation of shearing stress with shear rate to be observed.

Preparation of Polymer Solution
Preparation of CMC, HEC and XC polymer solutions

The method for preparing a sample of polymeric solution at a certain concentration was as follow:

A previously dried polymer powder was weighted to the nearest 0.001g using electronicbalance, and added to 500 ml ofdistilled water in the Hamilton beach cup.The polymer lightly sprinkled into the water and stirring continued for one hour to ensure completely polymer dissolution. The prepared solution was kept at rest at room temperature for 24 hr prior to conducting the rheology measurements.

Table (1) List of Experiments					
Exp.No.	Polymer	Conc.(g/l) (g/l)	Exp.No.	Polymer	Conc.(g/l) (g/l)
1	XC	4	29	CMC	48
2	XC	8	30	CMC	56
3	XC	12	31	CMC	64
4	XC	16	32	CMC	72
5	XC	20	33	CMC-2	4
6	XC	24	34	CMC-2	8
7	XC	32	35	CMC-2	12
8	XC	40	36	CMC-2	16
9	HEC	4	37	CMC-2	20
10	HEC	8	38	CMC-2	24
11	HEC	12	39	CMC-2	32
12	HEC	16	40	CMC-2	40
13	HEC	20	41	CMC-2	48
14	HEC	24	42	CMC-2	56
15	HEC	32	43	CMC-2	64
16	HEC	40	44	PVA	4
17	HEC	48	45	PVA	8
18	HEC	56	45	PVA	12
19	HEC	64	47	PVA	16
20	HEC	72	48	PVA	20
21	CMC	4	49	PVA	24
22	CMC	8	50	PVA	32
23	CMC	12	51	PVA	40
24	CMC	16	52	PVA	48
25	CMC	20	53	PVA	56
26	CMC	24	54	PVA	64
27	CMC	32	55	PVA	72

Preparation of PVA solution

There are two methods for preparing aqueous solution of polyvinyl alcohol, the conventional heating method and the microwave heating method.

The microwave oven method is the preferred method for preparing the PVA solution [6,10], so it was considered in this investigation as follow:

Dry PVA powder was weighted to the nearest 0.001g using electronic balance and added to 500 ml of distilled water in a Pyrex beaker with stirring. The beaker placed in a microwave oven and turned on high for three minutes. The prepared solution was kept at rest at room temperature for 24 hr prior to conducting the rheological measurements

Rheological Measurements

The procedure for measuring the rheological properties of polymer solutions, using the Fann viscometer model 35 was as follow: The sample cup was filled with polymer solution to the scribed line, and the rotor was immersed to the proper immersion depth.

The instrument was operated at 300 rpm for three minutes to equalize the temperature of the bob, rotor and polymer solution.

The instrument speed switched on to 600, 300, 200, 100, 6 and 3 rpm and the dial reading was recorded.

3. Results and Discussion

Sample of selected experimental results are presented in figures (1) to (5), which are a plot of shear stress versus shear rate. In each figure two curves were drawn, one at the lower polymer concentration used, and the other at the maximum polymer concentration which can be measured in the Fann viscometer instrument.

From these figures, one can notice that the shear stress increases with increasing shear rate in a non-linear shape. The curves are bending down which reflects pseudo-plastic behavior. As polymer concentration increases, the values of the shear stresses increased, since the polymer molecules begin to interact by becoming entangled.

Determination of Rheological Properties

To determine the values of the power law parameters, namely, flow behavior index (n) and consistency index (k), the shear stress versus shear rate are plotted on logarithmic scale.

Selected flow curves, for lower and upper polymer concentrations on logarithmic scale are shown in figures (6) to (10).

The power law index (n) is the slope of the line, while the power law consistency is the intercept of the line with shear rate equal to one.

The effects of polymer concentration on the flow behavior index (n) for all polymer solution used are shown in figure (11).

From this figure one can conclude that as the polymer concentration increased, n decreased. This behavior reflect the fact that as the polymer concentration increases the solution become more non-Newtonian, since the polymers act as a thickening agent due to the interaction between the polymer molecules.

Equations that describe the effect of polymer concentration on the flow behavior index can be presented in a linear form with correlation coefficients as shown in equations below:

$$n_{XC} = -0.02030\ C_{XC} + 0.8791 \quad R^2 = 0.9938 \quad \boxed{2}$$

$$n_{HEC} = -0.00240\ C_{HEC} + 0.6737 \quad R^2 = 0.8081 \quad \boxed{3}$$

$$n_{CMC1} = -0.0006\ C_{CMC1} + 0.7482 \quad R^2 = 0.1150 \quad \boxed{4}$$

$$n_{CMC2} = -0.0029\ C_{CMC2} + 0.7157 \quad R^2 = 0.8673 \quad \boxed{5}$$

$$n_{PVA} = -0.0009 C_{PVA} + 0.6964 \quad R^2 = 0.6165 \quad \boxed{6}$$

where ; R : is the correlation coefficient.

From the above equations and from figure (11) it can be noticed that n for XC polymer is more effected by concentration than other polymer used in this study. While PVA and CMC (type 1) is less effected than other. and it can be concluded that, in the range of polymer concentrations used in this study, n affected by concentration in the order:

$$n_{XC} > n_{CMC2} > n_{HEC} > n_{CMC1} > n_{PVA}$$

The effects of polymer concentration on the consistency index (k) for all polymer solutions used are shown in figure (12).
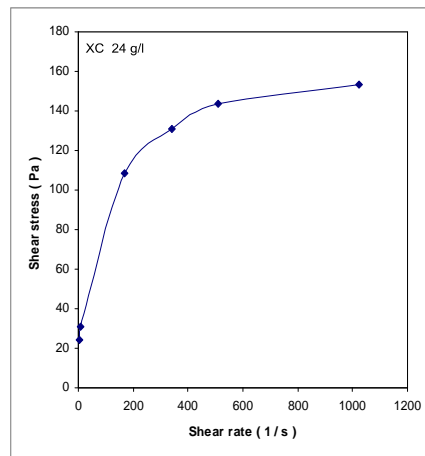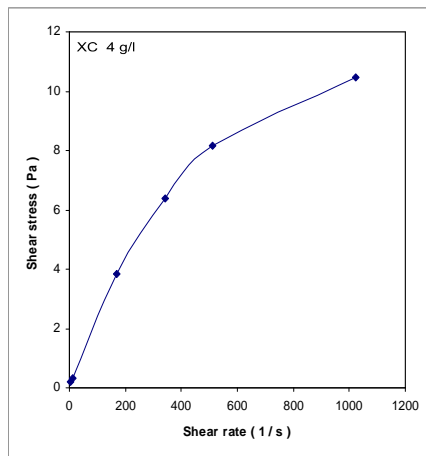
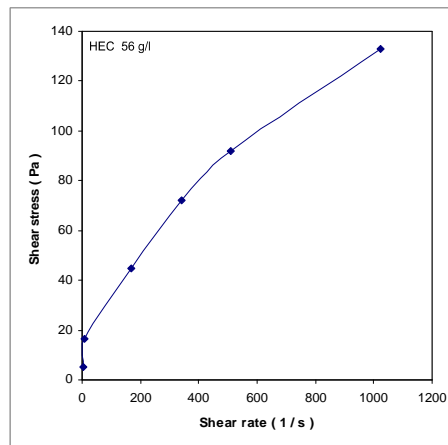**Figure (1) Flow curves for XC polymer solution at concentrations 4 and 24 g/l.**

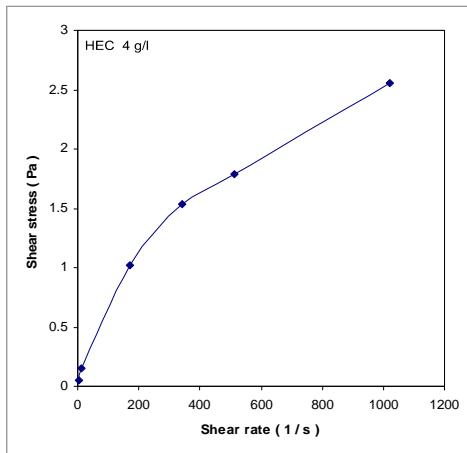
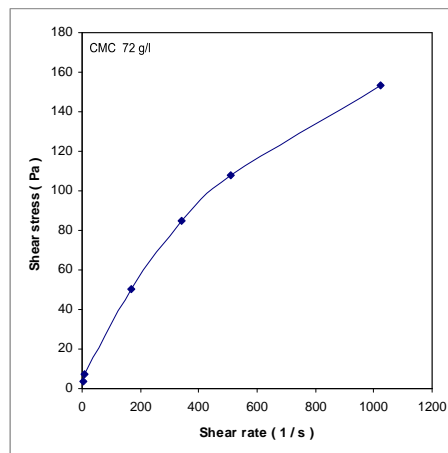**Figure (2) Flow curves for HEC solution at concentrations 4 and 56 g/l.**

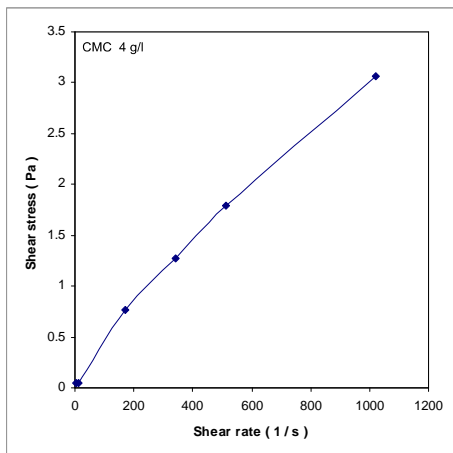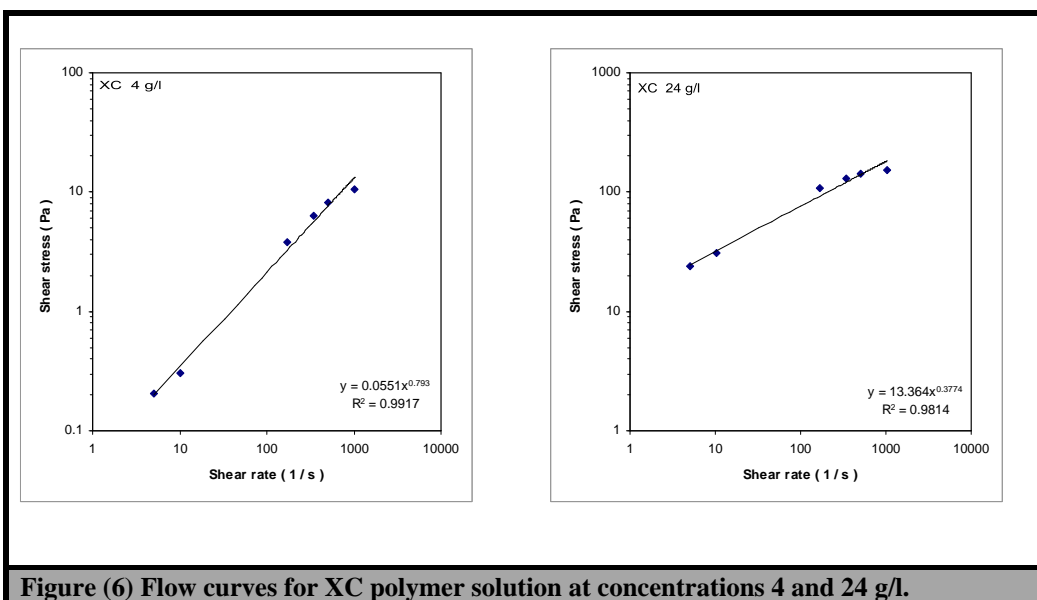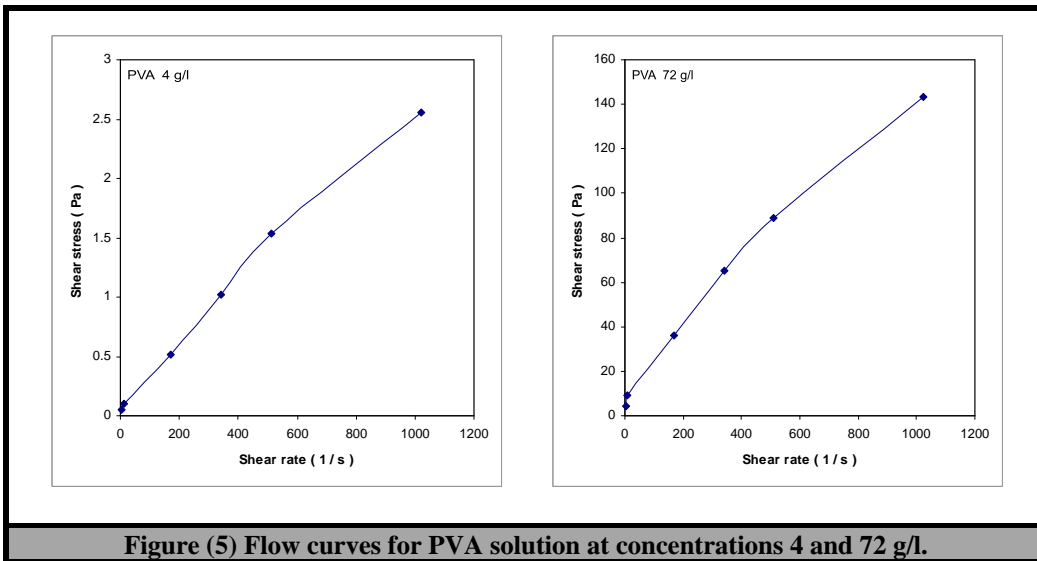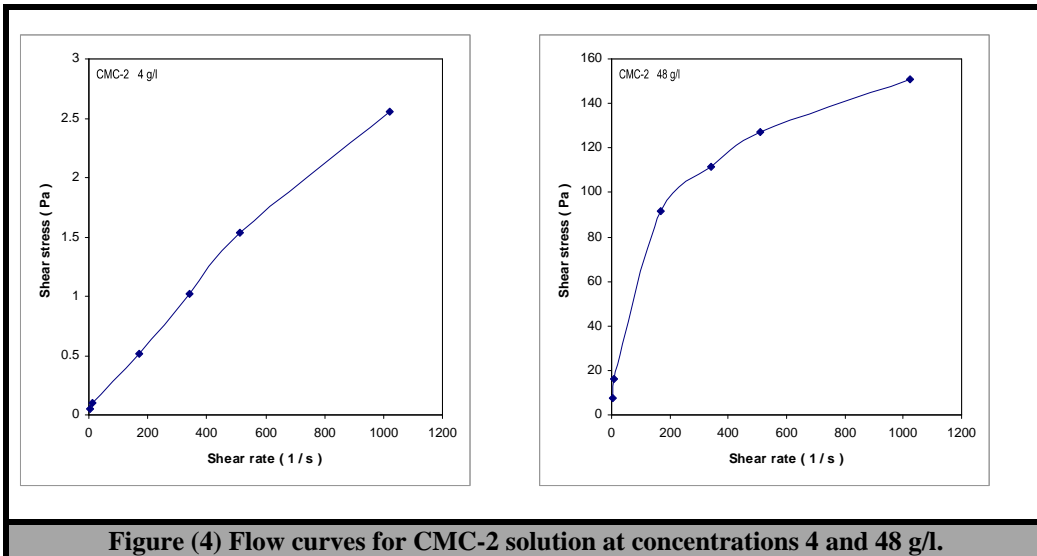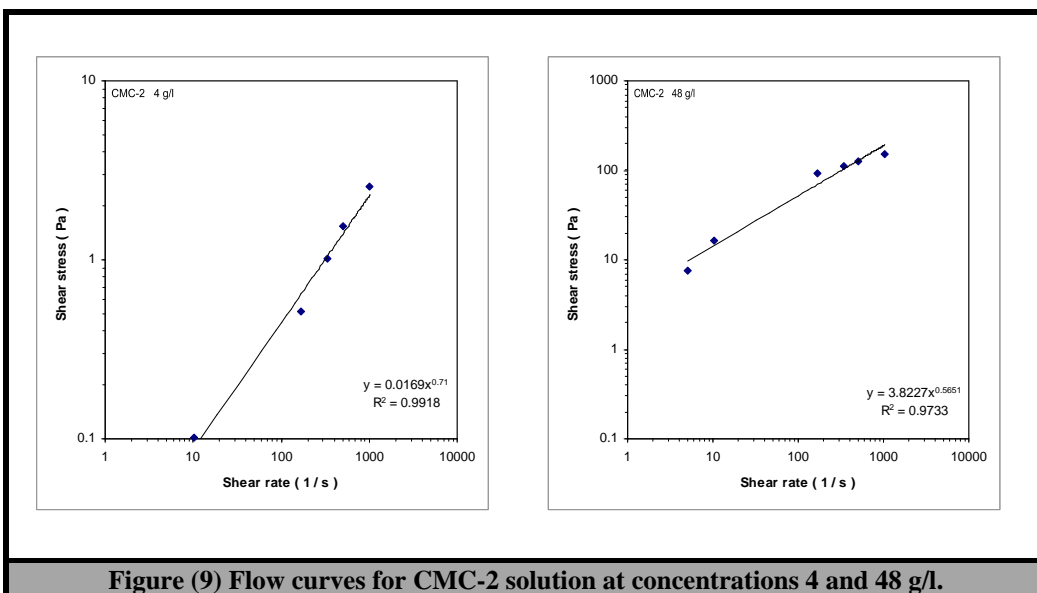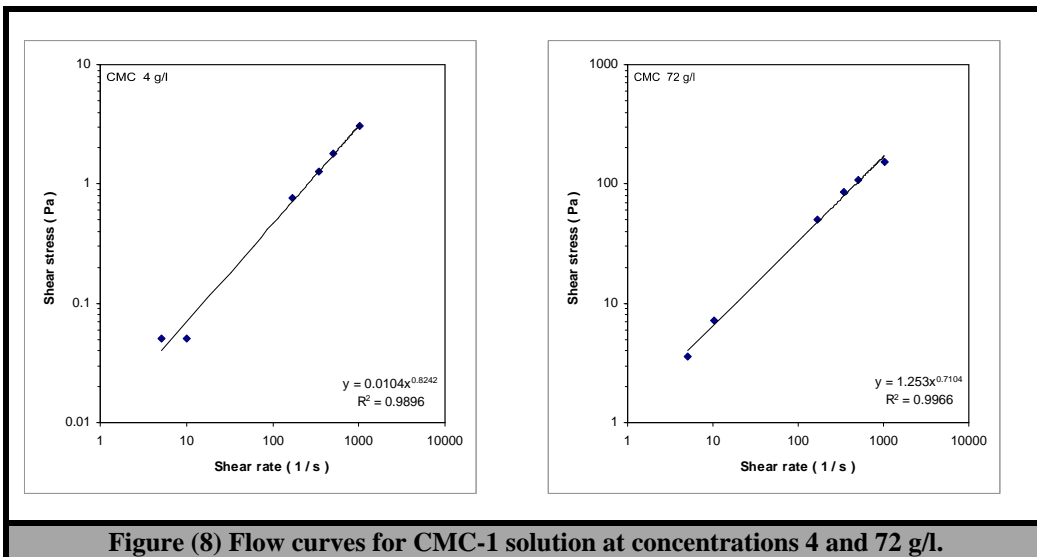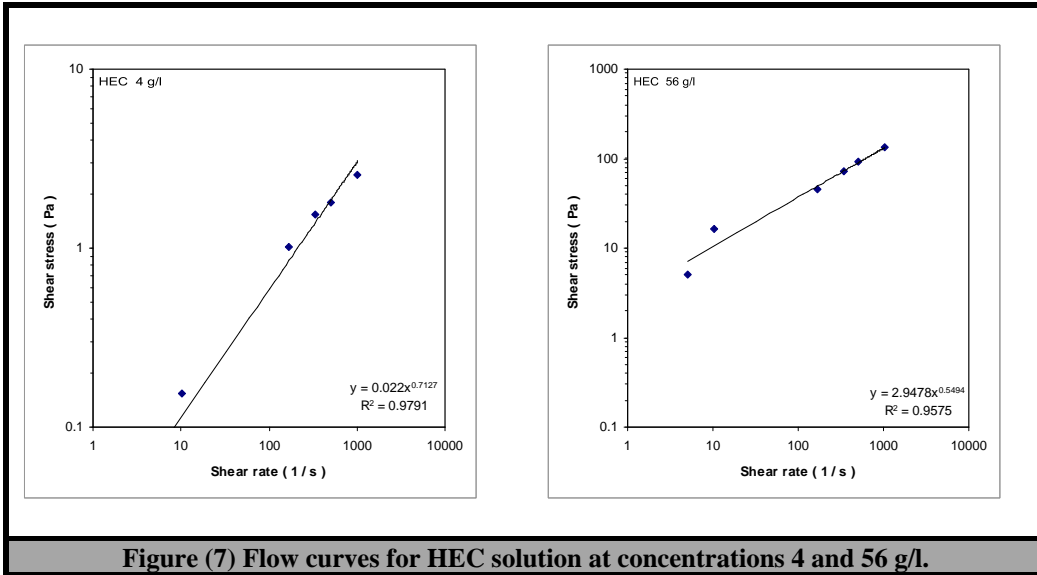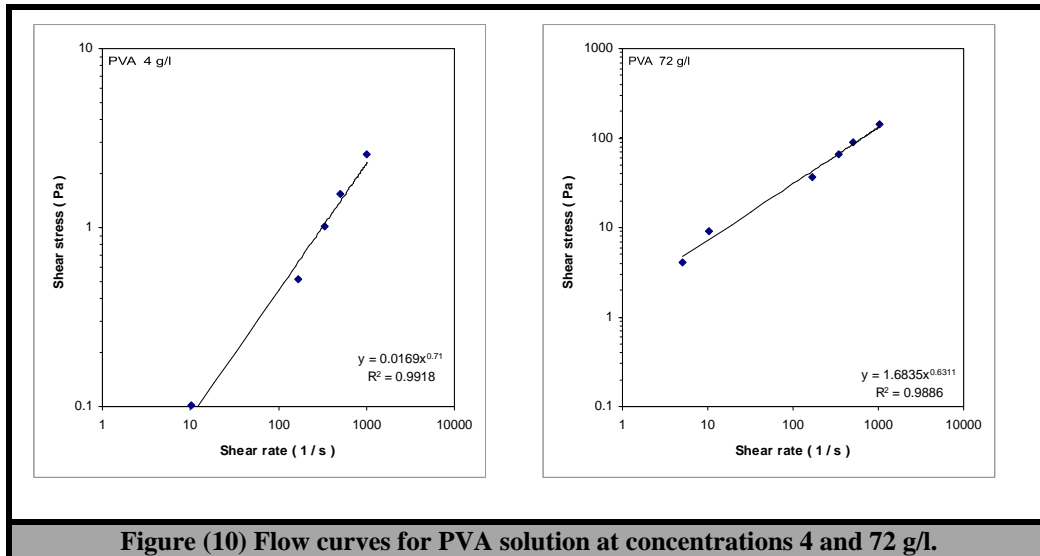**Figure (3) Flow curves for CMC-1 solution at concentrations 4 and 72 g/l.**

Figure (4) Flow curves for CMC-2 solution at concentrations 4 and 48 g/l.

Figure (5) Flow curves for PVA solution at concentrations 4 and 72 g/l.

Figure (6) Flow curves for XC polymer solution at concentrations 4 and 24 g/l.

Figure (7) Flow curves for HEC solution at concentrations 4 and 56 g/l.

Figure (8) Flow curves for CMC-1 solution at concentrations 4 and 72 g/l.

Figure (9) Flow curves for CMC-2 solution at concentrations 4 and 48 g/l.

Figure (10) Flow curves for PVA solution at concentrations 4 and 72 g/l.

From this figure one can conclude that as the polymer concentration increased, k increased. This behavior reflect the fact that as the polymer concentration increases the solution become more thicker.

Equations that describe the effect of polymer concentration on the power law consistency can be presented in an exponent form with correlation coefficients as shown in equations below:

$$k_{XC} = 0.0243\ e^{0.2743\ C} \qquad R^2 = 0.9837 \qquad \boxed{7}$$

$$k_{HEC} = 0.0310\ e^{0.0845\ C} \qquad R^2 = 0.9581 \qquad \boxed{8}$$

$$k_{CMC1} = 0.0119\ e^{0.0674\ C} \qquad R^2 = 0.9776 \qquad \boxed{9}$$

$$k_{CMC2} = 0.0101\ e^{0.1316\ C} \qquad R^2 = 0.9805 \qquad \boxed{10}$$

$$k_{PVA} = 0.0149\ e^{0.0672\ C} \qquad R^2 = 0.9883 \qquad \boxed{11}$$

where ; C: is the concentration of the polymer used.

Also from the above equations and from figure (12) it can be noticed that k for XC polymer is more effected by concentration than other polymer used in this study. And it can be concluded that, in the range of polymer concentrations used in this study, k affected by concentration in the order:

$$k_{XC} > k_{CMC2} > k_{HEC} > k_{PVA} > k_{CMC1}$$

4. Conclusions

1. All polymer solutions used in this work (XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol) behave as shear-thinning fluid, in which the viscosity decreases as the shear rate increases, or the shear stress increases as shear rate increases.

2. As polymer concentration increased, the flow behavior index (n) decreased. This behavior reflects the fact that as polymer concentration increases the solution become far from Newtonian behavior, since the molecules of polymer interact to become entangled. The XC polymer is more effected by concentration than other polymers used in this study.

3. Correlations were found, which describe the effect of polymer concentration on the flow behavior index (n) for each polymer used in this study.

4. As the polymer concentration is increased, the consistency index (k) is increased. This behavior reflects the fact that as the polymer concentration increases the solution become thicker, since the polymers act as thickening agents. The XC polymer is more effected by concentration than other polymers used in this study.

5. Correlations were found, which describe the effect of polymer concentration on the consistency index (k) for each polymer used in this study.
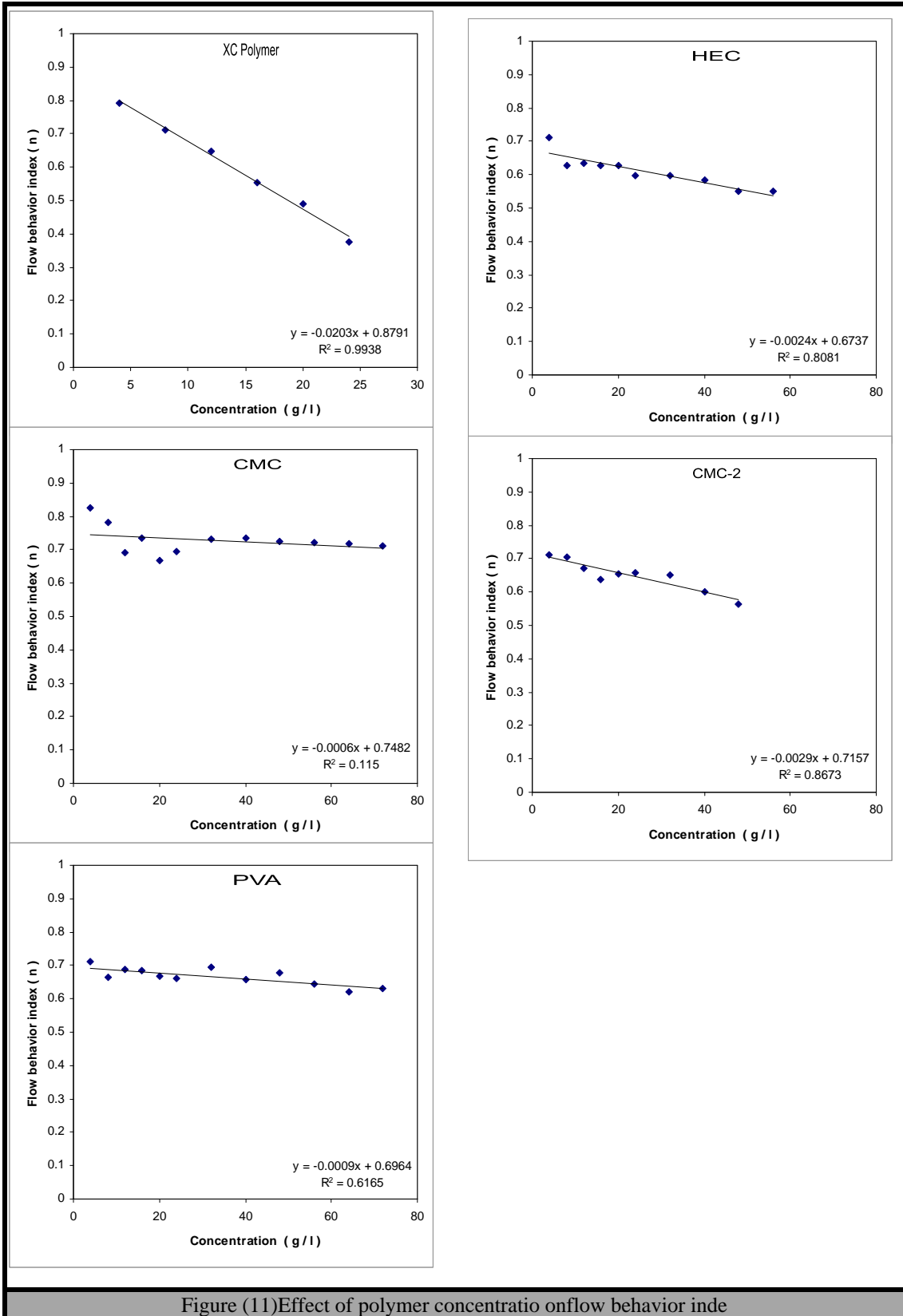
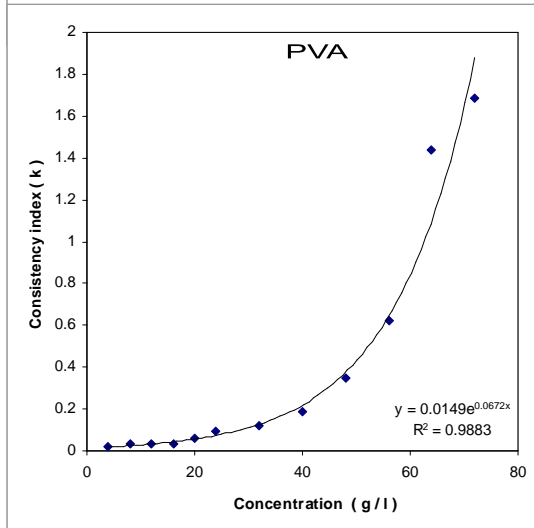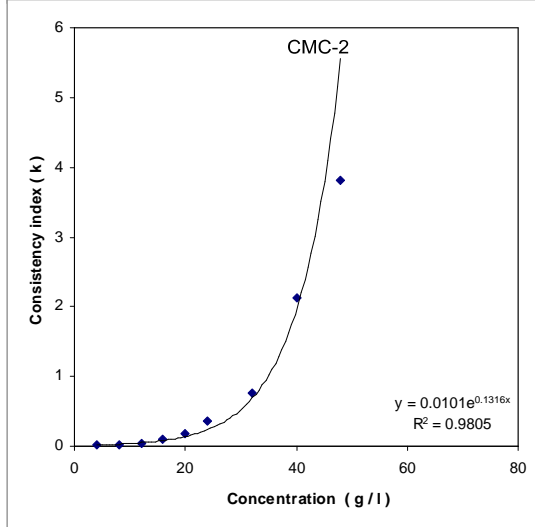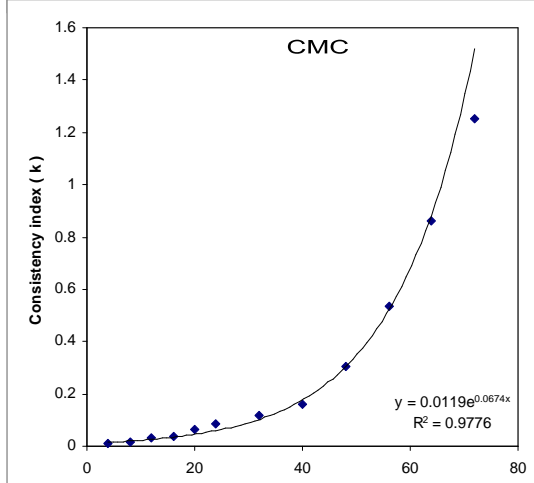Figure (11)Effect of polymer concentratio onflow behavior inde

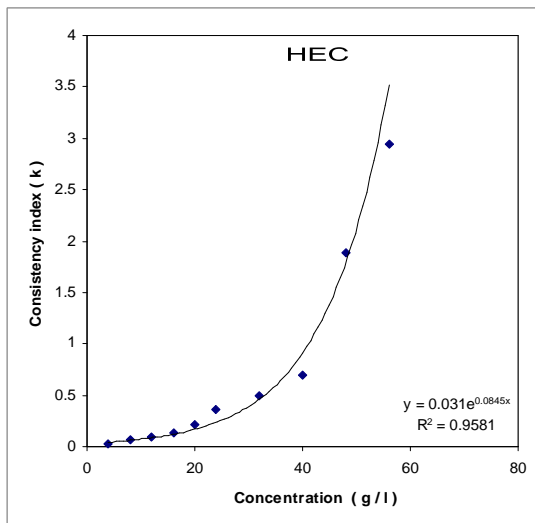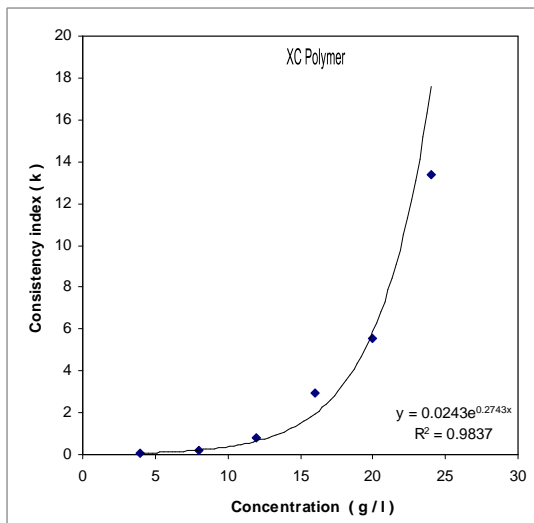**Figure (12)Effect of polymer concentrationon consistency index.**

5. NOMENCLATUR

Symbol	Meaning	Unit
k	Consistency index	-
n	Flow behavior index	-

Greek letters	Meaning	Unit
$\dot{\gamma}$	Shear rate	s^{-1}
η	Viscosity	Pa. s
η_{∞}	Newtonian limiting viscosity	Pa.s
τ	Shear stress	Pa
τ_m	Shear stress at mean viscosity	Pa
τ_o	Yield stress	Pa

Abbreviations

CMC	Carboxymethyl Cellulose
PVA	Polyvinyl Alcohol
HEC	Hydroxyethyl Cellulose
XC	Xanthamonas Campestris

6. References

1. Kirk-Othemer, "Encyclopedia of chemical technology", 4th edition, Vol.21, John Wiley and sons (1998).
2. Gowariker, V.R.,Viswanathan, N.V. and Sreedhar, J., "Polymer science", John Wiley and sons (1986).
AQUALON Sodium Carboxymethyl cellulose", Hercules Incorporated (1999).
http://www.herc.com/aqualon/product_data/brochures/250_10.pdf
3. Vanderbilt Company, Inc., "Rheology control additive".
   http://www.rtvanderbilt.com/wwwprd/No920CD.pdf
4. Vanderbilt Company, Inc., "Rheology control additive".
http://www.rtvanderbilt.com/wwwprd/No920CD.pdf
2. Xanthan Gum.
http://en.wikipedia.org/wiki/Xanthan_gum
3. Katz, D.A. "Polyvinyl alcohol slime", (2005).
http://www.chymist.com/PVA%20Slime.pdf

4. Polyvinyl Alcohol.
http://en.wikipedia.org/wiki/Polyvinyl_alcohol
5. Chhabra, R.P. and Richardson, " Non-Newtonian flow in the process industries", Elsevier Publishing Ltd. (1999).
6. Fann Viscometer, Model 35A Manual.
http://www.expotechusa.com/manuals/fann/35496.pdf
7. Flinn Scientific Inc., "Preparation of polyvinyl alcohol" (2003).
http://www.flinnsci.com
8. Mohammed, M. AR. and Mohammed, A.J, "Effect of concentration of water-soluble polymer solutions on rheological properties.", M.Sc. thesis, Nahrain University (2008).

تأثير نوع و تركيز المحاليل المائية لبوليمرات مختلفة على الخواص الريولوجية

أريج جاسم محمد

ماجستير هندسة كيمياوية

قسم الهندسة الكيمياوية / جامعة النهرين

د. مهند عبد الرزاق محمد

أستاذ مساعد

قسم الهندسة الكيمياوية / جامعة النهرين

هذا البحث يهتم بدراسة الخواص الريولوجية للمحاليل المائية للبوليمرات. البوليمرات المستخدمة في البحث هي : XC – بوليمر ، كاربوكسي مثيل سيليلوز (نوعين) ، هايدروكسي مثيل سيليلوز ، بولي فنيل الكحول.

تم دراسة الخواص الريولوجية باستخدام جهاز (Fann VG-35A) وذلك بقياس اجهاد القص (shear stress) المصاحب لكل معدل قص (shear rate) . تم اجراء ٥٥ تجربة بتراكيز مختلفة وعند درجة حرارة ٣٠ °م (± ١ °م).

من خلال النتائج العملية وجد بانه كلما زاد تركيز البوليمر في المحلول فان دليل سلوك الجريان n يقل ، و هذا التصرف يعكس الحقيقة بانه كلما زاد تركيز البوليمر فان المحلول يتجه اكثر نحو المحاليل اللانيوتينية. تم ايجاد المعدلات الرياضية التي تبين تاثير التركيز على n (معادلة لكل بوليمر مستخدم).

كذلك من خلال النتائج العملية وجد بانه كلما زاد تركيز البوليمر في المحلول فان دليل التماسك k يزداد ، و هذا التصرف يعكس الحقيقة بانه كلما زاد تركيز البوليمر فان المحلول يصبح اكثر سمكاً و لزوجة. تم ايجاد المعادلات الرياضية التي تبين تاثير التركيز على k (معادلة لكل بوليمر مستخدم).