



Studying the rheological properties of poly(vinyl pyrrolidone) in chloroform solutions

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Abstract Three molecular weights (25k, 44k and 700k) of Poly(vinyl-pyrrolidone), PVP solutions in chloroform have been studied to conduct some of their rheological properties. In the temperature range of (25 - 45°C). Density and flow time parameters have been measured and used to calculate the viscosity parameter. The collected viscosity data suggests the ideal behaviour in the low concentrations of PVP solutions, due to the reduction of the interaction forces between molecules. However, the viscosity of higher concentrations is strongly affected by changing the molecular weight rather than the concentration itself. In addition, the density, flow time and viscosity parameters of 700K are more influenced by the temperature change, than the other two molecular weights.

Keywords: chloroform, flow time, PVP, and viscosity.

دراسة الخواص الانسيابية لمحاليل بولي فينيل بيرو ليدون في الكلوروفورم

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المخلص في هذا البحث تم دراسة الخواص الانسيابية لثلاثة اوزان جزئية من محاليل بولي فينيل بيرو ليدون (بي في بي) في الكلوروفورم لمدي درجات حرارة ٢٥-٤٥ درجة مئوية. تم قياس الكثافة وزمن التدفق واستخدامهما لحساب اللزوجة. المعلومات المتحصل عليها لمعامل اللزوجة تقترح سلوك مثالي في مدي التراكيز المنخفضة. ذلك يعود الي انخفاض القوي البينية لجزئيات البوليمر داخل المحلول. من ناحية أخرى قيم اللزوجة للتراكيز العالية تعتمد على تغيير الوزن الجزئي للبوليمر أكثر من اعتمادها علي تغيير التركيز. من الملاحظ أيضا أن قيم الكثافة وزمن التدفق واللزوجة للوزن الجزئي 700K تتأثر بتغيير درجة الحرارة بشكل اكبر من بقية الاوزان الجزئية. **الكلمات المفتاحية:** بي في بي، كلوروفورم، وقت التدفق، اللزوجة.

1. Introduction

The polymerization can be carried out in bulks, in solutions, and in suspensions. In view of its unique chemical and physical properties, Poly-vinyl pyrrolidone (PVP) has found significant uses in pharmaceuticals and cosmetics. The early use of PVP in medicine was as blood plasma volume expander during the Second World War, PVP is also used as blood storage. It forms complexes with a variety of toxic agents, thus it helps in eliminating toxic material in fresh plasma [1],[2]. In addition, PVP has been found useful in shampoos to improve foam stability, impart luster to the hair, and used as a backbone for grafting monomers in the production of synthetic fibers [3],[4]. It is employed, also in all types of paper manufacture [5].

Significantly, Poly-vinyl pyrrolidone (PVP) has used extensively due to its solubility in both aqueous and organic polar solvents [6],[7]. PVP is a semi-crystalline synthetic polymer that forms a randomly coiled and highly flexible chain in polar solvents. It is also nontoxic and has good biocompatibility. In addition, few polymers display a good performance as functional materials in a water-polymer interface [8],[9]. The mechanism of this process has not been known yet. It is

expected that it is related to the dynamics of the polymer in aqueous systems [9]. In addition to its water solubility, PVP is soluble in a very wide range of organic materials. These materials include hydrocarbons such as methylene dichloride and chloroform [10],[11]. Moreover, monohydric and polyhydric alcohols such as methanol, ethanol and ethyl glycol are well known solvents for this PVP [12],[13]. This polymer is also compatible with a variety of synthetic polymers. PVP has found several applications due to its solubility in a wide range of solvents.

This article is focused on the influences of concentration, temperature and molecular weight of PVP on its rheological properties in chloroform solutions.

2. Experimental section

2.1. Material

Three molecular weights 25k, 44k and 700k of poly vinylpyrrolidone (PVP) (BDH limited, England) are dried under vacuum at 60°C. Chloroform (Riedel- deHaën, with purity of 99 %) was used as a solvent.

2.2. Measurements

2.2.1. Density Measurements

The density of solutions was measured using a clean dry density bottle, with the volume of 25ml,

at a controlled temperature. The following equation 1, was used to calculate the density [14]

$$D^{\circ}t_{(liq)} = (W_{Liq}/W_{water}) D^{\circ}t_{water} (1 + 2.4 \times 10^{-2})(t_{water} - t_{liq}) + (1.2 \times 10^{-5}) (1 - W_{Liq}/W_{water}) \quad (1)$$

where; $D^{\circ}t_{(liq)}$ is the density of PVP solution, W_{Liq} is the weight of density bottle fill with PVP solution, W_{water} is the weight of density bottle filled with water, $D^{\circ}t_{(water)}$ is the density of water, $t_{(liq)}$ is the temperature in °C for the liquid, $t_{(water)}$ is the temperature of water.

2.2.2. Flow time Measurements

Measuring flow time of the polymer solution is usually studied by comparing the flow time (t) required for specified volume of the polymer solution to flow through a capillary tube to the corresponding flow time (t_0) of the solvent. Usually, two types of viscometers are used for this purpose, Ostwald-Fenske, and Ubbelohde. For this project, Ostwald - Fenske viscometer has been used to measure the viscosity. The flow time is kept greater than 100 sec in order to minimize the kinetic energy correction during the measurement and the time was recorded using stop-watch type Hanhart-Profile-2 (made in Germany). The temperature was maintained within $\pm 0.2^{\circ}C$ using the thermostat (CT1450/2) of SCHOTT GERATE, (made in Germany).

2.2.3. Viscosity Calculations

The viscosity has been determined using the equation 2 [15]

$$\eta = K * d * t \quad (2)$$

where; η is the viscosity in c.p, K is constant, t is the flow time in second, and d is the density g/cm^3 .

3. Results and Discussions

Data analysis and results have been discussed by looking at the general behavior of the rheological properties through measuring the density and flow time and calculating some other rheological properties such as viscosity, relative viscosity, specific viscosity and intrinsic viscosity of PVP in chloroform solutions as a function of concentration, temperature and molecular weight for all systems.

3.1. Density

The density of different concentrations of PVP solutions with molecular weights of 25k, 44k and 700k in chloroform at different temperatures were estimated using equation 1. The data has been listed in tables 3.1, 3.2 and 3.3 respectively. It is obvious that the density decreases with increasing the temperature for the individual molecular weight. Moreover, there is a slight increase in the density with increasing the molecular weight at a constant temperature.

Table (3.1): Density (g/cm^3) of PVP (Mw = 25k) in chloroform solutions.

Conc/ (w/v)%	25°C	30°C	35°C	40°C	45°C
0.1	1.514	1.507	1.489	1.489	1.464
0.3	1.514	1.505	1.489	1.487	1.464
0.5	1.513	1.504	1.489	1.486	1.463
0.8	1.511	1.503	1.488	1.482	1.462
1.0	1.510	1.502	1.488	1.478	1.461
2.0	1.508	1.502	1.486	1.474	1.460

3.0	1.507	1.501	1.484	1.473	1.459
5.0	1.507	1.496	1.483	1.473	1.459
7.0	1.504	1.493	1.480	1.469	1.444
8.0	1.501	1.491	1.478	1.468	1.443
10.0	1.499	1.484	1.477	1.466	1.442

Table (3.2): Density (g/cm^3) of PVP (Mw = 44k) in chloroform solutions.

Conc (w/v)%	25°C	30°C	35°C	40°C	45°C
0.1	1.515	1.508	1.502	1.489	1.465
0.3	1.515	1.505	1.501	1.487	1.464
0.5	1.513	1.505	1.501	1.486	1.463
0.8	1.513	1.505	1.498	1.482	1.462
1.0	1.511	1.504	1.497	1.479	1.462
2.0	1.508	1.503	1.490	1.475	1.461
3.0	1.508	1.502	1.484	1.474	1.460
5.0	1.507	1.496	1.483	1.473	1.459
7.0	1.505	1.496	1.481	1.471	1.457
8.0	1.502	1.495	1.479	1.469	1.455
10.0	1.499	1.484	1.478	1.466	1.452

Table (3.3): Density (g/cm^3) of PVP (Mw = 700k) in chloroform solutions.

Conc (w/v)%	25°C	30°C	35°C	40°C	45°C
0.1	1.517	1.508	1.502	1.489	1.477
0.3	1.516	1.506	1.502	1.488	1.474
0.5	1.514	1.506	1.501	1.486	1.469
0.8	1.513	1.505	1.498	1.484	1.469
1.0	1.513	1.504	1.498	1.484	1.468
2.0	1.510	1.504	1.491	1.481	1.467
3.0	1.509	1.501	1.486	1.479	1.466
5.0	1.507	1.497	1.483	1.473	1.463

3.2. Flow time

The flow time of different concentrations of PVP solutions of molecular weights of 25k, 44k and 700k in chloroform has been measured in a range of temperatures (25-45°C) (tables 3.4, 3.5, and 3.6). There have been noticed that the flow time has increased with increasing the concentration for each molecular weight at constant temperature. Moreover, it is decreased when the temperature is increased for each molecular weight which indicates that the kinetic energy between molecules could be the most responsible factor affecting the flow time values. At higher temperatures molecules move faster and the mobility of molecules is greater thus, flow time is less.

Table (3.4): Flow time (sec) of PVP (Mw = 25k) in chloroform solutions.

Conc. (w/v)%	25°C	30°C	35°C	40°C	45°C
0.1	118.1	105.9	102.4	101.5	100.7
0.3	119.6	116.4	113.5	102.9	101.8
0.5	120.6	119.6	115.3	114.4	113.9
0.8	128.9	124.3	117.2	116.3	115.6
1.0	142.1	127.8	119.8	118.2	116.9
2.0	165.9	158.1	141.9	139.6	122.6
3.0	210.5	184.5	172.6	168.0	165.3
5.0	299.9	289.0	283.5	280.2	231.1
7.0	361.4	358.8	352.3	346.1	341.9
8.0	410.5	407.1	391.9	388.8	371.4
10.0	812.1	749.0	646.3	548.7	544.8

Table (3.5): Flow time (sec) of PVP (Mw = 44k) in chloroform solutions.

Conc (w/v)%	25°C	30°C	35°C	40°C	45°C
0.1	126.8	122.0	115.2	114.4	113.6
0.3	143.5	125.8	117.7	116.0	115.0
0.5	144.0	133.7	128.8	119.0	117.7
0.8	145.3	137.6	133.9	132.4	130.6
1.0	148.9	142.6	140.1	133.4	132.5
2.0	205.9	201.9	195.9	191.0	182.1
3.0	213.1	203.6	199.7	196.7	193.6
5.0	320.3	299.4	289.7	287.2	254.2
7.0	670.0	620.3	595.4	559.7	550.5
8.0	874.2	695.8	607.0	598.1	590.9
10.0	983.8	949.9	826.5	805.0	728.8

Table (3.6): Flow time (sec) of PVP (Mw = 700k) in chloroform solutions.

Conc (w/v)%	25 °C	30 °C	35 °C	40 °C	45 °C
0.1	140.1	137.1	133.2	132.7	129.2
0.3	211.0	202.1	184.7	172.1	140.2
0.5	270.6	261.7	256.2	253.4	251.8
0.8	371.7	364.9	353.2	338.5	324.5
1.0	534.5	524.3	469.0	440.0	421.3
2.0	666.7	593.1	585.0	550.3	525.8
3.0	863.0	636.5	621.1	600.5	577.5
5.0	10490	10214	9802	8762	7566

3.3. Viscosity

The viscosity of different concentrations of PVP solutions with molecular weights of 25k, 44k and 700k in chloroform at different temperatures were calculated using equation 2. The influences of concentration, temperature and molecular weight on the viscosity have been extensively studied in this part of the article.

3.3.1. Concentration effects on viscosity

Figure 3.1, 3.2, 3.3 show the relationship between the viscosity and the concentration of the 25K, 44K and 700K PVP solutions respectively. It is obvious that the viscosity rapidly increases as the concentration is increased above 3.0% solution for 25K and 44K. However, the increase of the viscosity of 700K solutions is consistent through all concentrations. The result reflects the magnitude of the interaction forces between the polymer molecules in the lower molecular weights solutions. The steady relationship at low concentrations below the 3.0% solution suggests an ideal behaviour, due to the reduction in the interaction forces between the molecules comparing to that in the high concentrations [16].

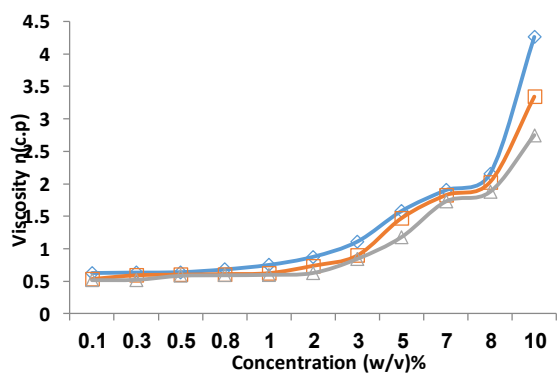


Figure (3.1): The variation of viscosity with concentration of PVP (Mw = 25k) in chloroform solutions at 25°C (blue), 35°C (red), 45°C (green).

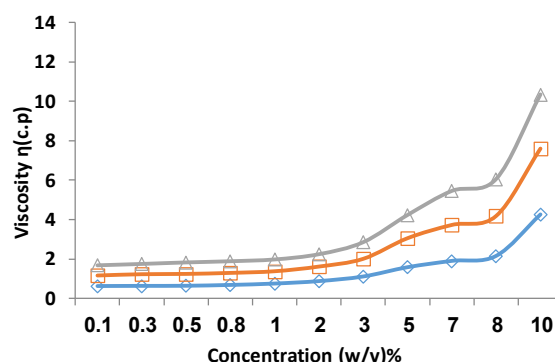


Figure (3.2): The variation of viscosity with concentration of PVP (Mw = 44 k) in chloroform solutions at 25°C (blue), 35°C (red), 45°C (green).

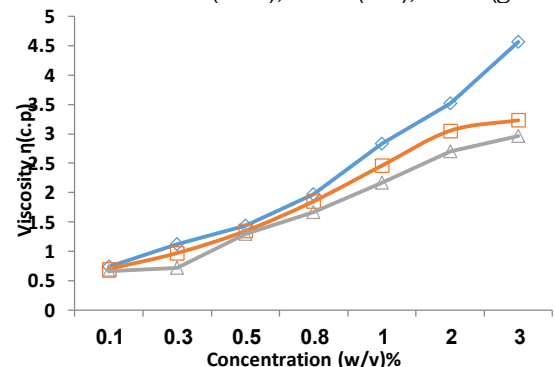


Figure (3.3): The variation of viscosity with concentration of PVP (Mw = 700 k) in chloroform solutions at 25°C (blue), 35°C (red), 45°C (green).

3.3.2. Temperature effects on viscosity

In order to compare the dependence of the viscosity of 25K, 44K and 700K solutions on the temperature, figures 3.4 and 3.5 were plotted for two concentrations 0.3% and 3%. As can be seen from these figures, data fall in straight-line relaxation i.e. η is linearly decreases with increasing temperature. This is more pronounced in the higher molecular weight than the lower ones, where the viscosity has not highly affected by changing the temperature. This is consistent with flow time outcomes and may be due to the fact that increasing temperature causes a decrease in the density of the solution, which reduces the number of the polar solute molecules per unit volume. Thus, that influences the interaction between molecules to be reduced too, and reflects a decrease in the viscosity [16].

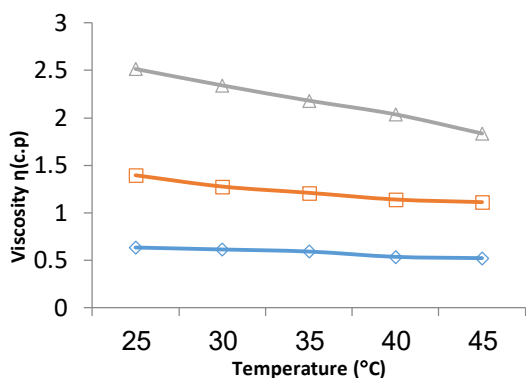


Figure (3.4) The variation of viscosity with the temperature for 0.3% of 25K (blue), 44K (red) 700K (green) PVP in chloroform solution.

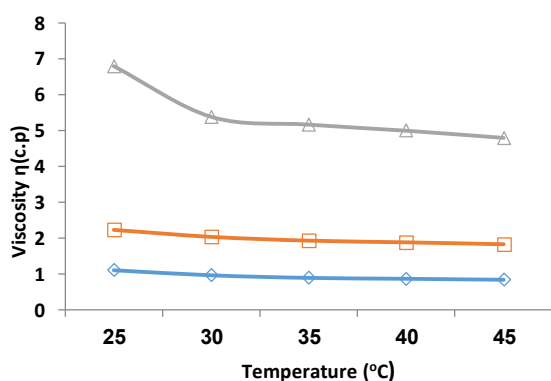


Figure (3.5): The variation of viscosity with the temperature for 3.0% of 25K (blue), 44K (red) 700K (green) PVP in chloroform solution.

3.3.2. Molecular weight effects on viscosity

In , the highest molecular weight (700K) is the one that more changeable and that is compatible to the results in figures 3.1, 3.2 and 3.3. A linear relationship can be observed in figure 3.6 which explains that the dependence on molecular weight is more pronounced in the high concentration region than in the low concentrations one.

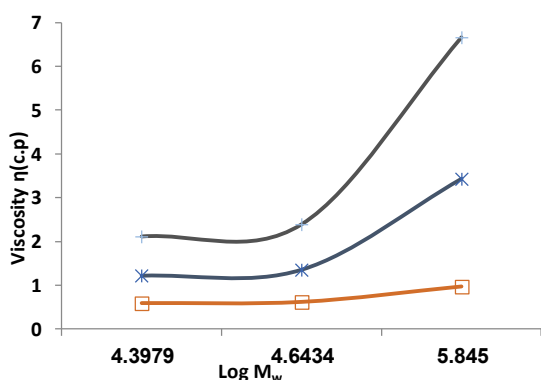


Figure (3.6): The variation of viscosity with molecular weight of 0.3% (red), 1% (blue) and 3% (green) PVP in chloroform solutions at 35 °C.

Conclusion

The density, flow time and viscosity parameters have been estimated for different concentrations of three molecular weights of PVP including 25K, 44K and 700K in chloroform solutions. The study shows a strong relationship between the

intermolecular forces of PVP molecules and their rheological properties which is compatible to the literature [17],[18],[19]. These properties have also been studied in terms of changing the temperature and the solution concentration. The collected data could be used further in order to estimate more related parameters, such as the relative, and intrinsic viscosities. The outcomes will provide a complemented overview of the behaviour of PVP molecules in chloroform solutions.

Abbreviations and Acronyms

PVP :Poly(vinyl-pyrrolidone),

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