Permittivity and dipole moment of poly(vinyl pyrrolidone) in chloroform solutions

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Abstract

The electrical capacitance of poly(vinyl pyrrolidone), PVP of three different molecular weights (25K, 44K and 700K) in a chloroform solution were measured. The range of concentrations studied for the molecular masses 25K and 44K is (0.1-10w/v%) and that for the molecular mass 700K is (0.1 - 5.0w/v%). All the measurements of PVP solutions were carried out in a temperature range of 25 to 45°C and at 2.0MHz. The dielectric parameters such as static permittivity, increment

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of permittivity and dipole moment were calculated and their variation with concentration, temperature and molecular weight was discussed. It is found that the static permittivity, the increment of permittivity and the dipole moment of PVP solutions increase as the concentration and molecular weight of PVP increase but decrease as the temperature increases.

Key word: *poly(vinyl pyrrolidone), electrical capacitance, static permittivity, dipole moment.*

1. Introduction

Poly(vinyl pyrrolidone), PVP is a semi-crystalline synthetic polymer which forms a chain wound at random and very flexible in polar solvents. PVP is very soluble in polar solvents such as alcohol, so it is best to avoid phase separation in the reaction [1]. PVP has excellent characteristics such as high dielectric constant, dissolubility, stability, compatibility and strength PVP also has a unique characteristic in the way that it has unusual complexing and colloid properties. PVP has important uses in pharmaceuticals, cosmetics, beverages, detergents, soap and adhesives, etc. [1]. Studies of the reported dielectric properties of this polymer have been mainly limited to its aqueous solution in order to study the effect of polymer solutions in water [1-4], alcohol [1,3], the ethylene glycol oligomer (EGO) [5, 6], and chloroform [7,8] has been widely studied in the frequency range of 20Hz - 20GHz at 25°C. This article reports the static permittivity and the dipole moment of PVP in a chloroform solution for three different molecular weights (25K, 44K and 700K). The purpose of studying these dielectric parameters is to investigate the effect of concentration, temperature and molecular weight on dielectric behavior of the PVP.

2. Experimental Methods

2.1. Materials

Poly(vinyl pyrrolidone) PVP, three molecular weights (25K, 44K and 700K) was purchased from BDH Chemicals Limited Poole (England). Chloroform produced by Riedel deHaën, purity 96%. Cyclohexane, ethylene trichloride and chlorobenzene were used to calibrate the Dipolometer DM01. The PVP powder was dried under vacuum at 60°C before being used.

2.2. Preparation of solutions

PVP of molecular weights 25K, 44K and 700K solutions were prepared by dissolving the appropriate weights of PVP for 25K, 44K and 700K powder in a fixed volume (100ml) chloroform. To obtain homogeneous solutions the mixture were stirred by using a magnetic stirrer in the mixing process for 15minute. Due to the limited solubility of PVP in $CHCl_3$, the range of concentration of solutions for 25K and 44K were (0.1-10w/v%) while for that of 700K was (0.1– 5.0w/v%)

2.3. Methods

2.3.1. Dipolometer (DM01)

The electrical capacitance (C_s) measurements were carried out using a Wissenschaftlich-Technische-Werkstaetten Dipolmeter (DM01) at a constant frequency of 2.0MHz, using the cell type MFL1. The thermostat used was the WK6 colora messtechnik GMBH. The temperature was controlled up to ± 0.2°C. The instrument was calibrated using an analytical grade of cyclohexane and chlorobenzene, ethylene trichloride and carbontetra chloride. The observed values of permittivity

for the calibration process were in a good agreement with that of the literature.

The values of permittivity (ϵ`) obtained were calculated using the following equation:

$$\epsilon` = 1.566 + 0.0018\ C_s \tag{1}$$

Where, Cs is the electrical capacity of the materials tested.

The table below shows the values of both the permittivity and the electrical capacitance obtained using equation (1). These values were compared with that of the literature for all the materials mentioned above. As it can be seen there were a good agreement between the literature and the measured values ($< 0.3\%$).

Table 1 Electrical capacitance and permittivity values for some solvents at 35°C.

| Materials	$\epsilon`_{(lit)}$	$\epsilon`_{(mes)}$	C_s
Cyclohexane	1.999	2.006	241.53
Carbon Tetrachloride	2.208	2.204	350.15
Ethylene Trichloride	3.390	3.385	998.98
Chlorobenzene	5.451	5.453	213.99

3. Results and Discussion

3.1. Static permittivity (ε_o)

The electrical capacitance was measured for studied range of concentrations (0.1-10%) for 25K and 44K and (0.1-5.0%) for 700K of PVP in a chloroform solution at temperature ranged from 25°C to 45°C with intervals of 5°C. The maximum uncertainties observed were 0.3% for the electrical capacity. The results of the data obtained were discussed in terms of the effect of concentration, temperature and molecular weight on the general behavior of static permittivity, increment of permittivity and dipole moment. The values obtained from these measurements were used for the calculation of both the static permittivity (ε_o) and the dipole moment.

3.1.1. Concentration effect

The effect of concentration on static permittivity (ε_o) for the three molecular weights PVP, were illustrated in Figure (1). It shows a variation of ε_o as a function of the concentration of the three systems at 35^oC. As it can be seen the three molecular weights exhibit similar behavior. In other ward and as expected the static permittivity increasing as increase molecular weight. It can also be observed that the two lower molecular weights (25K and 44K) are approximately similar to each other while that of large molecular weight shows a dramatic increase of the static permittivity particularly at high concentration region. This may be due to the fact that increasing the concentration increases the number of polar solute molecules per unit volume, which probably lead to an increase of the values of the static permittivity. However, a similar phenomenon has been observed for PVP in THF and cyclohxanone solution at different concentrations[9].
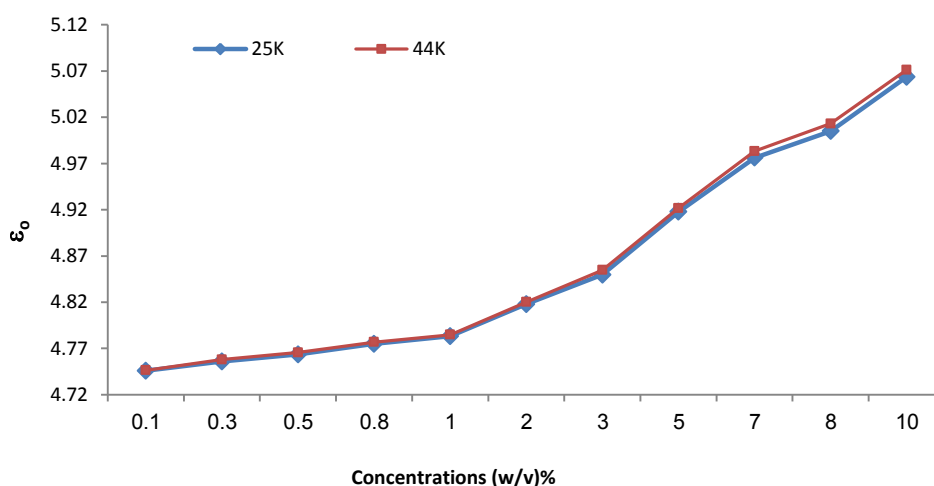
Figure 1 Concentration dependent on Static permittivity of PVP in chloroform solution at 35^oC for three different molecular weights..

3.1.2. Temperature effect

In order to compare the behavior of the three systems, the static permittivity was also plotted as a function of temperature for a selected concentration of 5.0% by way of example and represented in Figure (2). In this figure shows that the effect of temperature on the permittivity gradients ($\partial\varepsilon_o/\partial t$) for a higher molecular weight than the lowest one. However, generally the permittivity gradient decreases with increasing temperature. This may be due to the fact that the increase in temperature decreases the density of the solution, which leads to a decrease in the number of polar solute molecules per unit volume and reduces the interaction between molecules in the system[10].
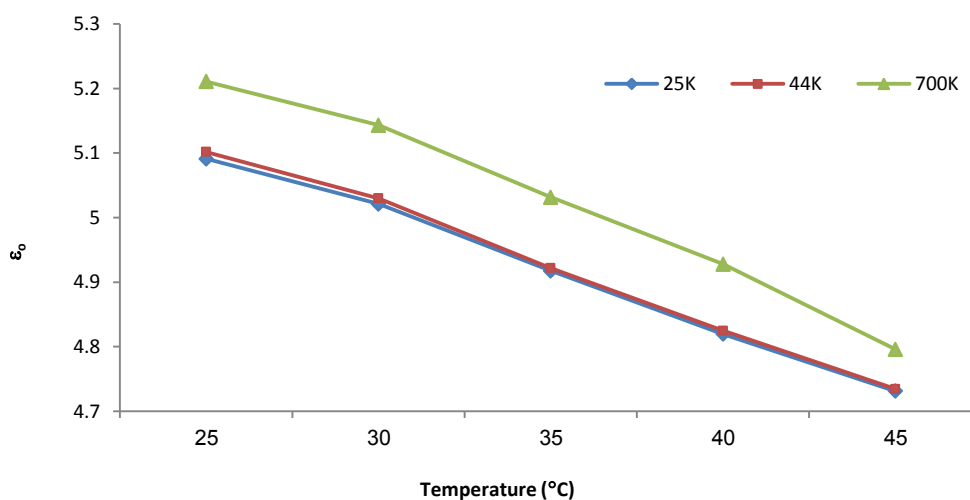

Figure 2 Temperature dependent on Static permittivity of 5.0% PVP in chloroform solution for three different molecular weights.

3.1.3. Molecular weight effect

The dependence of the static permittivity (ε_o) on the molecular weight of PVP in a chloroform solution, for three selected concentrations

(0.3, 2.0 and 5.0%) and at a selected temperature of 35°C as example, is illustrated in Figure (3). It can be seen that the increase in molecular weight shows a fairly rapid increase in the static permittivity of the solution with molecular weight. This general increase in static permittivity with molecular weight may be due to the increase in polar side groups in the molecular chain of this polymer [10].
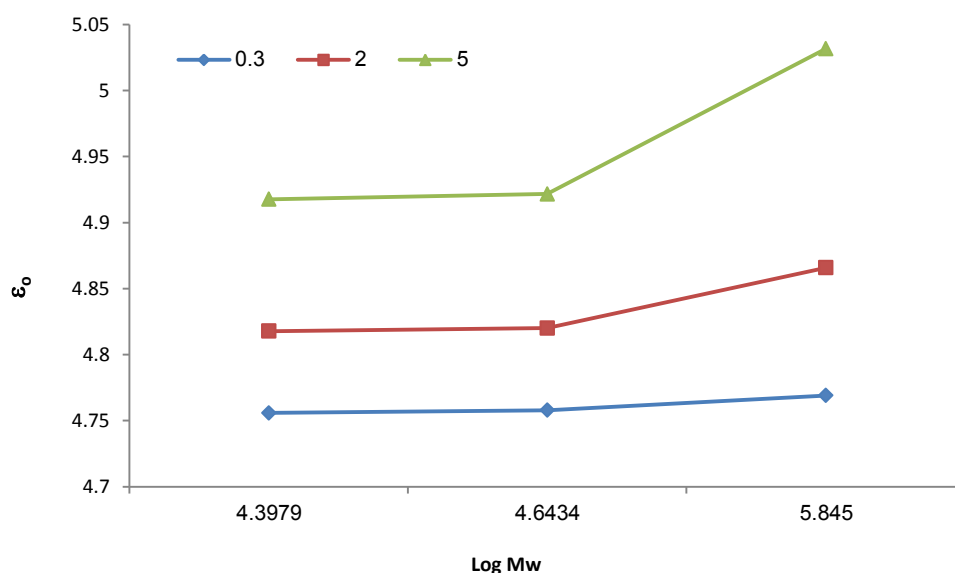

Figure 3 Molecular weight dependent on Static permittivity at three different concentrations PVP in chloroform solutions for three different concentrations at 35°C.

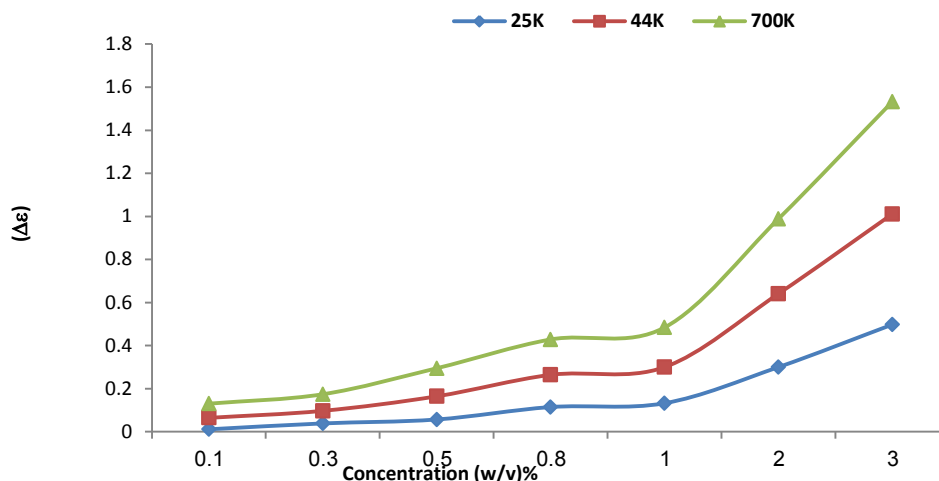### 3.2. Permittivity increment (Δε)

To eliminate the observed permittivity of the solvent over that of the solution, the permittivity increment using equation (2):

$$\Delta\varepsilon = \varepsilon_{o\,(solution)} - \varepsilon_{o\,(solvent}$$ **(2)**

3.2.1. Concentration effect

The permittivity increment values were plotted as a function of the concentration, of the concentration range (0.1-3.0%) and at the

temperature of 35°C, and illustrated in Figure (4). As it can be seen, the solutions of the three molecular weights exhibits the same behavior of the permittivity increment. The behavior might be reflecting that all the solutions of the three molecular weights studied have the same intermolecular interaction.
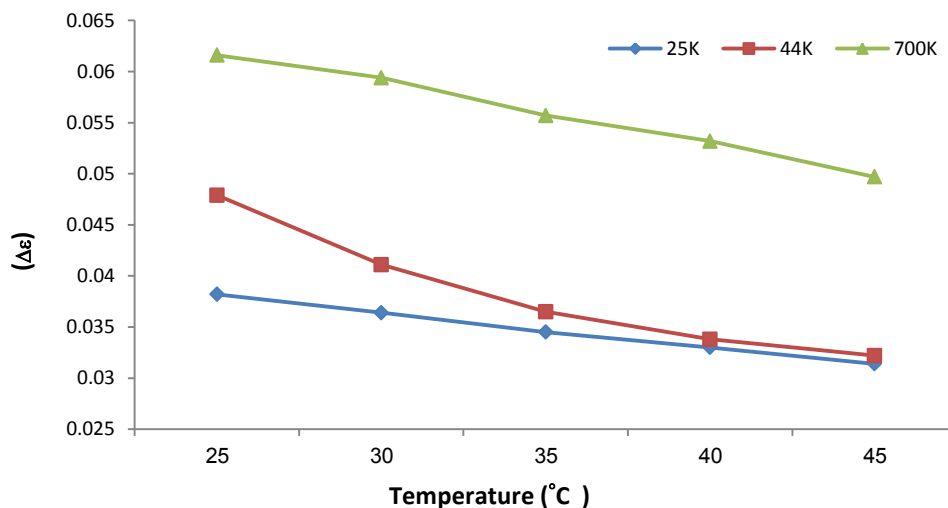

Figure 4 Concentration dependent on Permittivity increment of PVP in chloroform solution at 35°C for three different molecular weights

3.2.2. Temperature effect

The permittivity increment $(\Delta\varepsilon)$ as a function of the temperature range $(25 - 45^{o}C)$, at 0.3% selected, is illustrated in Figure (5). It can be seen, (as expected), $\Delta\varepsilon$ decreases with increasing temperature for three different molecular weights. This can be explained in terms of increasing temperature causes decreasing in density of the solution which in turn decrease in intermolecular interaction

Figure 5 Temperature dependent on Permittivity increment of 0.8**% PVP in chloroform solution for three molecular weights.**

3.2.3. Molecular weight Effect

The dependence of $\Delta\varepsilon$ for the molecular weight of PVP for the three different selected concentrations (0.5, 2.0 and 5.0%) at 35°C, were illustrated in Figure (6). It can be seen from this figure that there is a significant dependence of $\Delta\varepsilon$ on molecular weight in the two different concentrations, where $\Delta\varepsilon$ increases with increasing molecular weight. This reflects the differences in polarity of the three molecular weights [10].
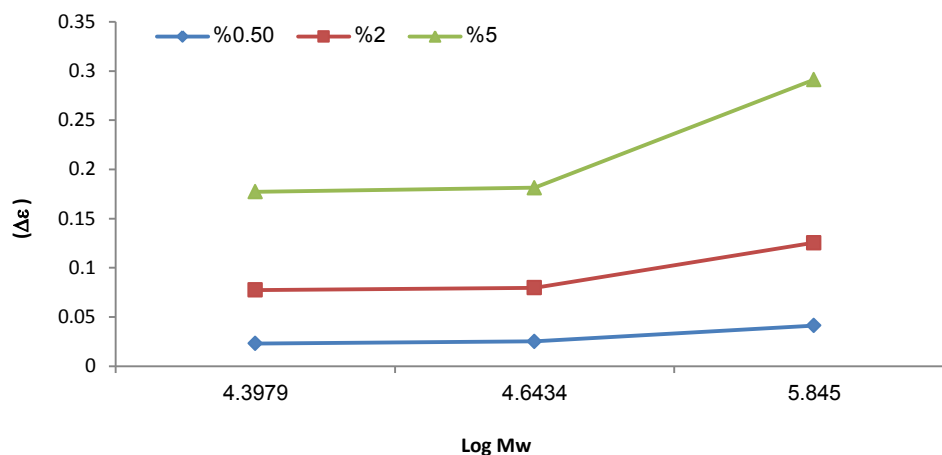
Figure 6 Molecular weight dependent on Permittivity increment of PVP in chloroform solutions for three different concentrations at 35°C.

3.3. Dipole moment (μ)

The dipole moment (μ) for the three different molecular weights at the studied concentrations and temperatures was evaluated using equation (3) [11]. The static permittivities (ε_1) and (ε_{12}) for solvent and solution respectively, were used in this equation

$$<\mu^2> = 9000 \ kT/4\pi NC \ [(2\varepsilon_1 + n_2{}^2) \ (\varepsilon_1 - \varepsilon_{12})/\varepsilon_1 \ (2\varepsilon_1 + \varepsilon_{12}) \ (n_2{}^2 - 2)^2] \qquad (3)$$

Where, k refers to Boltzmann's constant, T refers to absolute temperature, N refers to Avogadro's number, C refers to concentration in mol / dm^3 and n_2 refers to refractive index of the polymer solution.

3.3.1. Concentration effect

The values of dipole moment (μ) were plotted versus the concentration of the studied solutions of the three molecular weights at 35°C. The plot is to examine the effect of the change in concentration on the dipole moment. Such variation is shown in Figure (7). It was clear

from this Figure that the dipole moments increase with dilution for concentrations below (1.0%) particularly for solution of molecular weight 700K.
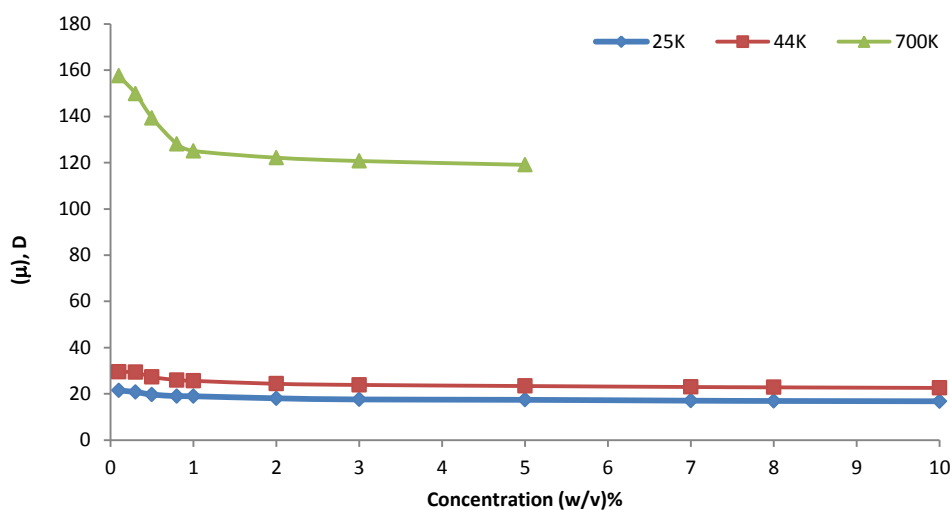
Figure 7 Concentration dependent on Dipole moment of PVP in chloroform solutions for three different molecular weights at 35°C.

3.3.2. Temperature effect

The estimated values of the dipole moments (μ) were plotted as a function of temperature, for PVP in chloroform for a selected concentration (0.8%). This concentration was applied for three molecular weights (25K, 44K and 700K) and shown in Figure (8). It clear that the graphs of dipole moment for the three solutions shows a plateau. This behavior reflects that the intermolecular are the same within the three entities.
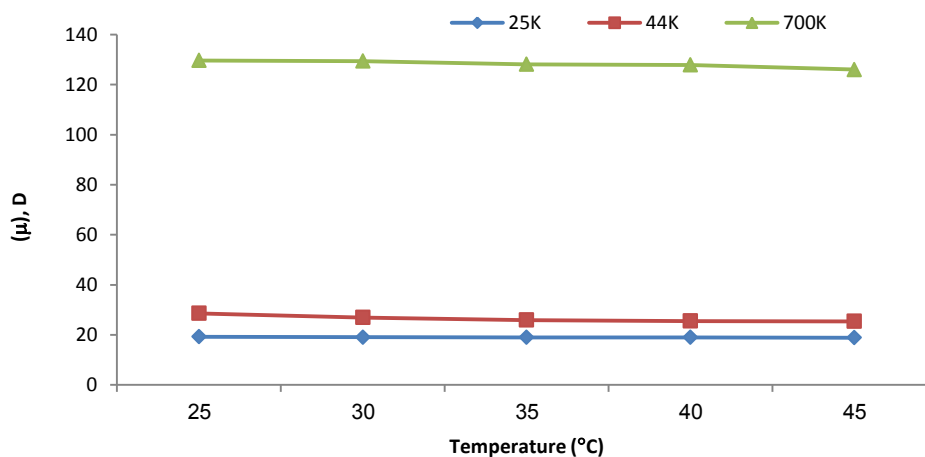
Figure 8 Temperature dependent on Dipole moment of 0.8% PVP in chloroform solutions for three different molecular weights.

3.3.3. Molecular weight Effect

The dependence of the dipole moment on the molecular weight of PVP in a chloroform solution, for three selected concentrations (0.1, 1.0 and 5.0%) at 35°C, is illustrated in Figure (9). As it can be seen, dramatic increase of the moment dipole with increasing molecular weight. This might be reflected the increasing of intermolecular interaction by the increasing of the molecular weight. The same behavior was reported for poly (vinyl acetate), PVA in a toluene solution [12] at (-18°C), poly (butylisocyanate), PBTC in benzene at 22.5°C [13] and poly (γ-benzyl-L-glutamate) in cis-ethylene dichloride [14].
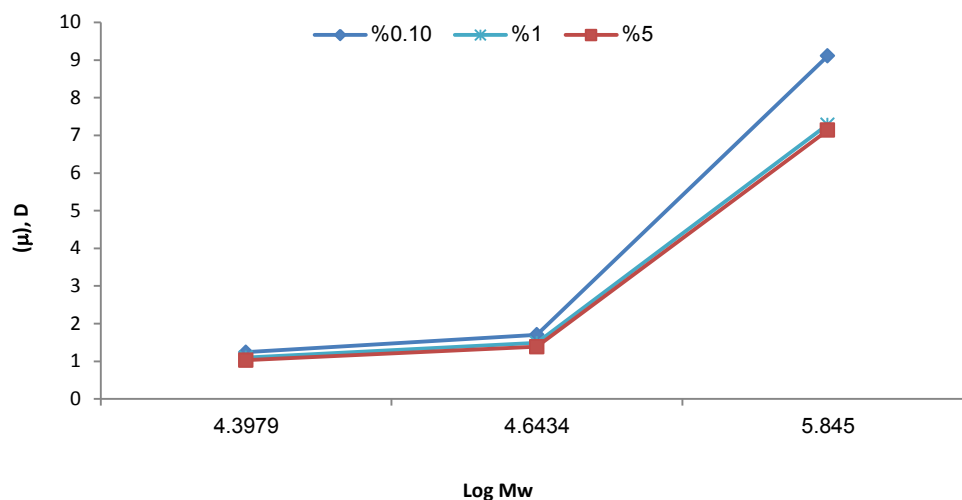
Figure 9 Molecular weight dependent on Dipole moment of PVP in chloroform solutions for three different concentrations at 35°C.

4. Conclusion

The dielectric properties caused by local segmental movement of PVP have been observed in solutions with a chloroform solvent and with static permittivities between 4.5 and 5.2 and with a dipole moment between 16 and 157 Debye, (1 Debye = 3.33564×10^{-30} C · m) for three different systems. The dielectric parameters of polymer solutions for PVP with different concentrations of solutions, different temperatures and different molecular weights were studied. These polymer solutions show a continuous change in their dielectric parameters (static permittivity, permittivity increment and dipole moment) due to the increase in PVP concentration, increase in temperature and increase in molecular weight which have led to the improvement of these properties. On the other hand, the increase in temperature leads to a decrease in the static permittivity, the increment of permittivity and the dipole moment of the solution.

Acknowledgements

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