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Viscometric properties of aqueous solutions of Poly (ethylene) glycols at 15^{0}C

***Rajendra Joshi and Narain Datt Kandpal**

Physical Chemical Laboratory, Department of Chemistry S.SJ., Campus Almora (U.K.), India

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ABSTRACT

*The viscosities of Poly (ethylene) glycols having molecular weight 200, 400, 2000 and 4000 have been determined with different composition in water at 15^{0}C. The experimental results of viscosity have been analyzed using Jone – Dole's equation. The viscosity coefficients have been obtained to through the light on the interaction resent in aqueous solutions of Poly ethylene glycols. The Poly (ethylene) glycols behave of structure maker in water. The value of Viscosity **B** coefficient increases with the increases in the molecular mass / chain length of ethylene glycols molecule. The structure making character of Poly (ethylene) Glycols follows the sequence PEG 4000 > PEG 2000> PEG 400 > PEG 200.*

Key words: Poly (ethylene) glycols, Jone – Dole's equation, Viscosity

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INTRODUCTION

Solvents play an important role in the preparation of chemicals and in their processing with applications. Most of the reactions to produce an intermediate or a chemical are generally carried out in solutions. In recent years the measurements of viscosity of liquids, liquids mixture and solutions have been used to study in Physico – Chemical behaviour. Physical properties of the liquids systems are play a momentous role in development of formulation and analysis of the different component [1]. The aqueous solutions of poly (ethylene) glycols have been found wide spared applications like separation of bimolecular mixtures [2] and Pharmaceuticals formulations [3]. A chemical and pharmaceutical application of PEG includes base materials of ointments, as anti – freezing agent as plasticizer, as a releasing agents for rubber, as a softener in antiseptic agent, scouring agent, sizing agent, dying auxiliary, etc., in textile industries as well as in metal, wood paper, resin, paint [4].

Poly (ethylene) glycol is a condensation polymer of ethylene oxide and water. It is soluble in water and in many organic solvents. The structural formula for n – degree of polymerization can be given as HO-(CH_2-CH_2O)-H. PEG and its derivative can be formed in linear or branch shape with different molecular mass having significant complexity and diversity. PEG compounds are also known as PEO / (Poly ethylene oxide) and POE (Poly oxy ethylene). Generally poly ethylene glycols molecular mess runs up to 20,000. In PEG both type of hydrogen bonding intra as well as inter molecular hydrogen bonds formation take place which enhance its solubility in water and main organic solvents [5].

There have been many recent studies on viscosities of Poly (ethylene) glycol in water and other solvents [6-15]. In acetonitrile and water PEG of molecular mess 8000 – 11000 the Jone – Dole's viscosity A and B coefficients have been obtained and the presence of solute – solvent interactions have been investigated [9]. The density, viscosity and ultrasonic velocity have been measured for aqueous solution of PEG of molecular mass 200 [16]. In separate studies it has been suggested that the formation of helices by PEG in water generates aggregates with hydrophobic domain [17-19]. However, these reports do not provide enough information on how different molecular mass structures of PEG form aggregates in water.

Therefore, the aim of resent studies was to measure the viscosity of aqueous solutions of two liquids PEG 200, 400 and two solid PEG 2000, 4000 in order to provide a better understanding towards the interactions and behaviour of PEGs in aqueous solutions.

MATERIALS AND METHODS

(A) Materials

All the polyethylene glycols namely PEG 200 (CDH), PEG 400 (CDH), PEG 2000 (MERCK), PEG 4000 (CDH), were used as received without further purification. The aqueous solutions were obtained by dissolving the desired amount of the sample in conductivity water (conductivity < 1.µS cm^{-1} at 25^{0}C).

(B)Methods

Viscosity Measurements

The Viscosities of the solutions were obtained with Ubbelohde viscometer (No. Z / 1645, Infosil make) by measuring flow time of fixed volume of the solution through capillary. The viscometer with the experimental liquid was immersed in a temperature controlled water bath. The Racer stop watch with accuracy of 0.1 sec was used. The viscosity of each solution was determined using the relation as given below.

$$\boldsymbol{\eta_2 = \eta_1 \frac{t_2}{t_1}\frac{\rho_2}{\rho_1}} \dots\dots\dots\dots\dots\dots\dots (\mathbf{1})$$

Where,

η_1, is the Viscosity of water

η_2, is the viscosity of experimental liquid

t_1, is the time of flow of water

t_2, is the time of flow of experimental water

ρ_1, is the density of water

ρ_2, is the density of the experimental liquid

The process was repeated for constant value of viscosity for each solution.

RESULTS AND DISCUSSION

For all the poly ethylene glycols namely PEG – 200, 400, 2000 and 4000 and the values of η/η_0 at different concentration in aqueous solutions were observed. The variation of η/η_0 values of aqueous solutions of varying amount of PEGs of different molecular masses have been summarized in **Table 1**. The viscosity data for all the solutes at different concentration has been utilized for the determination of interaction parameter in aqueous solution. The interaction parameters were obtained with the help of Jone – Dole's equation given by **Equation 2.**

$$\boldsymbol{\frac{\left(\frac{\eta}{\eta_0} - 1\right)}{\sqrt{C}} = A + B\sqrt{C}} \dots\dots\dots (\mathbf{2})$$

Where, A and B are the coefficients for the ion – ion and ion – solvent interaction respectively and C is the molar concentration. The values of B were obtained from the linear plots between $\sqrt{C}$ and $\eta/\eta_0 - 1 / \sqrt{C}$. These plots are given in **Figure 1**. The values of 'A' and 'B' coefficients calculated from the intercepts and slop for all the PEGs liquids and solids are given in **Table 2**.

Appraisal of the values of coefficients 'B' for all the PEGs are positive in aqueous solutions their by suggesting the presence of strong solute – solvent interactions in solution. Further the values of 'B' tend to become large with the molecular mass of solute which indicates that the strength of solute – solvent interactions increased with the molecular mass / chain length of the polymers. The 'B' values for all the ethylene glycols indicates that these polymer acts as structure – maker in water. The structure making character of polymers follows the sequence-

PEG 4000 > PEG 2000> PEG 400 > PEG 200

The structure making character of polymers in water as observed in the study is in good agreement with the earlier report on polyethylene glycol 20,000 [9]. In this report measurements of the viscosity have been taken in dilute solution up to the concentration 1.5×10^{-3} mol dm^{-3} (3% weight) at 25^{0}C. In this concentration region 'B' coefficient value was found to be lower than the values obtained for polymers (PEG's) of lower molecular mass at temperature 15^{0}C in higher concentration region used in the study.

The value of 'A', obtained from all the polymers are negative. However no significance could be attributed to these results since such negative values are expected for non electrolytes as solute which is a measure of ion – ion interactions. The coefficient 'A' is expected to be positive for strong electrolytes and zero for non electrolytes [20]. Hence A√C term in Equation 1 can be reduced in **Equation 3**

$$\frac{\eta}{\eta_0} - 1 = BC \dots\dots\dots (3)$$

A plot η/η_0 verses concentration should be linear having slop value equals to B coefficient. In case of non electrolytes the applicability of **Equation 3** has been considered [21]. The Experimental data were used to examine how far the experimental results of the viscosity agree with **Equation 3** applicable for non electrolyte / polymer molecules. Therefore, $\eta/\eta_0 - 1$ were plotted against different concentration of poly (ethylene) glycols given in **Figure 2.** It is evident from **Figure 2** that all these plots show the linearity > 0.9. The values of gradient 'B' obtained for different polymers are given in **Table 2** with values of 'B' coefficients obtained from Jone – Dole equation. The linearity of the plots is in conformity with the assumption that the value of A√C can be taken negligible for non electrolytes.

The viscosity values of η/η_0 of a polymer solutions at constant temperature are directly proportional to the molar concentration (C) and given by Straundinger **Equation 4** [22, 24, 25].

$$\frac{\eta - \eta_0}{\eta_0} = knCn \dots\dots\dots (4)$$

k, is a constant for a given solute in a given solvent, C, is the molar concentration of monomer, and n is the number of monomers in the polymer. The relative viscosity values are given in **Table 1**. The values of gradient 'kn' obtained for all the PEGs are given in **Table 2.** From **Equation 3 and 4** it is clear that the 'kn' values are equal to viscosity 'B' coefficient. Poly (ethylene) glycols are the polymer of monomeric unit of ethylene oxide having molecular mass 44. If we consider these molecular masses for calculating the number of monomer units present in PEGs, the numbers of monomers have been calculated. The obtain values of 'n' are also given in **Table 2** for each PEG. The characteristic constant 'k' has been determined by using the value of 'n' and experimental value of 'B'. The values of 'k' are different for liquid PEGs and solid PEGs whereas the 'k' values are equal for liquids and solids separately. The values of 'B' coefficient obtained from both the plots as recorded in **Table 2** have same magnitude, which satisfies our experimental results for all the PEGs. The experimental values obtained are also in agreement with the applicability of all the **Equation 2, 3 and 4**.

From the values reported in **Table 1**, it is observed that the viscosity of the aqueous solutions of PEGs increases in the concentration of solute. Appraisal of the **Figure 1** reveal that the values of 'A' are 0.03, 0.068, 0.52 and 0.65 for PEGs 200, 400, 2000 and 4000 respectively with negative sign. All these values are negligible or nearly zero which supports the conclusion drawn in the study that the value of A√C is negligible for non – electrolytes as also reported in literature [20]. This is also supported by the values of 'A' obtained which is measure of ion – ion interactions, are absent in aqueous polymer solutions. The positive value of 'B' for all the PEGs indicates that the solutes have structure maker effect on water in concentration range used in the study. The values of 'B' indicates that the presence of solute – solvent interactions. The interactions increased with the molecular mass of Poly (ethylene) glycol molecule. In aqueous solutions the Poly (ethylene) glycol molecules can self associated into aggregates due to their amphiphilic nature. Generally such characteristic can exist in dilute solutions because the repulsion hydrophobic interactions between $-CH_2$ groups and the water molecules are more effective for low molecular masses at low concentration. The experimental evidences for Poly (ethylene) glycol aggregates in water have been reported in literature [17]. In our study such aggregations have not observed in the concentration region but the aggregation can be assumed in the lower concentration region. The higher concentration region it favourable for hydrogen bonding of PEGs which leads to the poor contribution to the hydrophobic interactions. The structure maker character also supports the hydrogen bond formation between the solute and water. The hydrodynamic volumes have also calculated using the relation given by **Equation 5** [21].

$$B = 0.0025V_h \dots\dots\dots (5)$$

Where, 'V_h' is hydrodynamic volume. The values of 'V_h' have been calculated for each PEG and listed in **Table 2**. It is clear that the hydrodynamic volume also increases with increase in molecular mass. A plot between molecular mass of PEG and 'V_h' values is given in **Figure 3**. It indicates that variation of 'V_h' at lower molecular masses have more linear nature in comparison to higher molecular masses. These observations justify the phase change from liquid to solid as taken in study.

Table 1: Variation of η/η_0 and densities of aqueous solutions of PEGs with Concentration at 288K

PEG	S. NO.	CONC. mol.dm^{-3}	Density g.cm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	η/η_0-1	$\frac{\left(\frac{\eta}{\eta_0}-1\right)}{\sqrt{C}}$
200	1	0.0496	0.9922	0.2227	0.0595	0.26717
	2	0.2501	1.0006	0.5001	0.2471	0.49420
	3	0.5043	1.0086	0.7101	0.5669	0.79833
	4	0.7596	1.0128	0.8715	0.9098	1.04394
	5	1.0246	1.0246	1.0122	1.2687	1.25340
	6	1.2927	1.0342	1.1369	1.8366	1.61544
400	1	0.0254	1.0174	0.1593	0.0637	0.3998
	2	0.128	1.0242	0.3578	0.2802	0.7833
	3	0.258	1.0322	0.5079	0.6405	1.2607
	4	0.3902	1.0404	0.6245	1.125	1.8013
	5	0.5249	1.0498	0.7244	1.534	2.1183
	6	0.6612	1.058	0.8131	1.9095	2.3484
2000	1	0.0050	1.0068	0.0707	0.200	2.8288
	2	0.02524	1.0096	0.1519	0.838	5.5168
	3	0.0510	1.0200	0.2258	1.815	8.038
	4	0.0770	1.0272	0.2774	2.998	10.8074
	5	0.1032	1.0318	0.3212	4.453	13.8593
	6	0.1303	1.0424	0.3609	6.981	19.3433
4000	1	0.025	1.0116	0.05	0.3	6
	2	0.127	1.0156	0.1126	1	8.881
	3	0.256	1.0248	0.16	2.36	14.75
	4	0.385	1.0264	0.1962	4.25	21.6616
	5	0.517	1.0346	0.2273	7.42	32.6441

Table 2: Parameters of Staurding and Jon – Dole's equation for the PEGs at 288K in aqueous solutions

S.No	Plot→	η/η_0-1 verses C	$\frac{\left(\frac{\eta}{\eta_0}-1\right)}{\sqrt{C}}$ verses$\sqrt{C}$	n	k	V_h x 10^3 (dm^{3}mol^{-1})
	PEGs ↓	B/kn (dm^{3}mol^{-1})	B/kn (dm^{3}mol^{-1})			
1.	200	1.40	1.43	4	0.35(*0.31)	0.56
2.	400	2.99	3.14	9	0.33	1.20
3.	2000	52.13	52.69	45	1.16	2.08
4.	6000	141.9	143.0	90	1.56	56.4

*B = kn, in all the PEGs, * For n = 4.54*

Figure 1

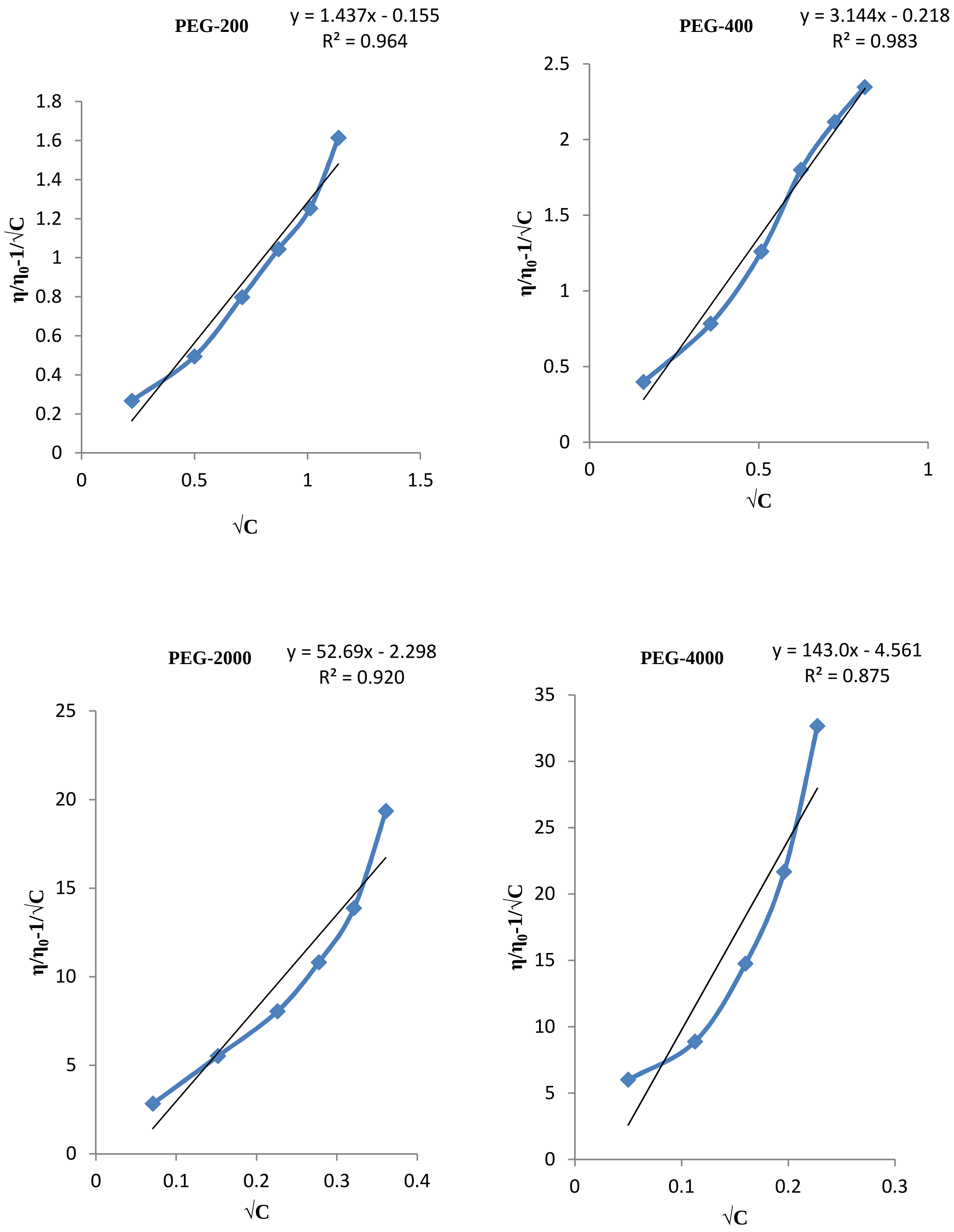

PEG-200
y = 1.437x - 0.155
R² = 0.964
η/η0-1/√C
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
0.5
1
1.5
√C
PEG-400
y = 3.144x - 0.218
R² = 0.983
η/η0-1/√C
0
0.5
1
1.5
2
2.5
0
0.5
1
√C
PEG-2000
y = 52.69x - 2.298
R² = 0.920
η/η0-1/√C
0
5
10
15
20
25
0
0.1
0.2
0.3
0.4
√C
PEG-4000
y = 143.0x - 4.561
R² = 0.875
η/η0-1/√C
0
5
10
15
20
25
30
35
0
0.1
0.2
0.3
√C

Figure 2

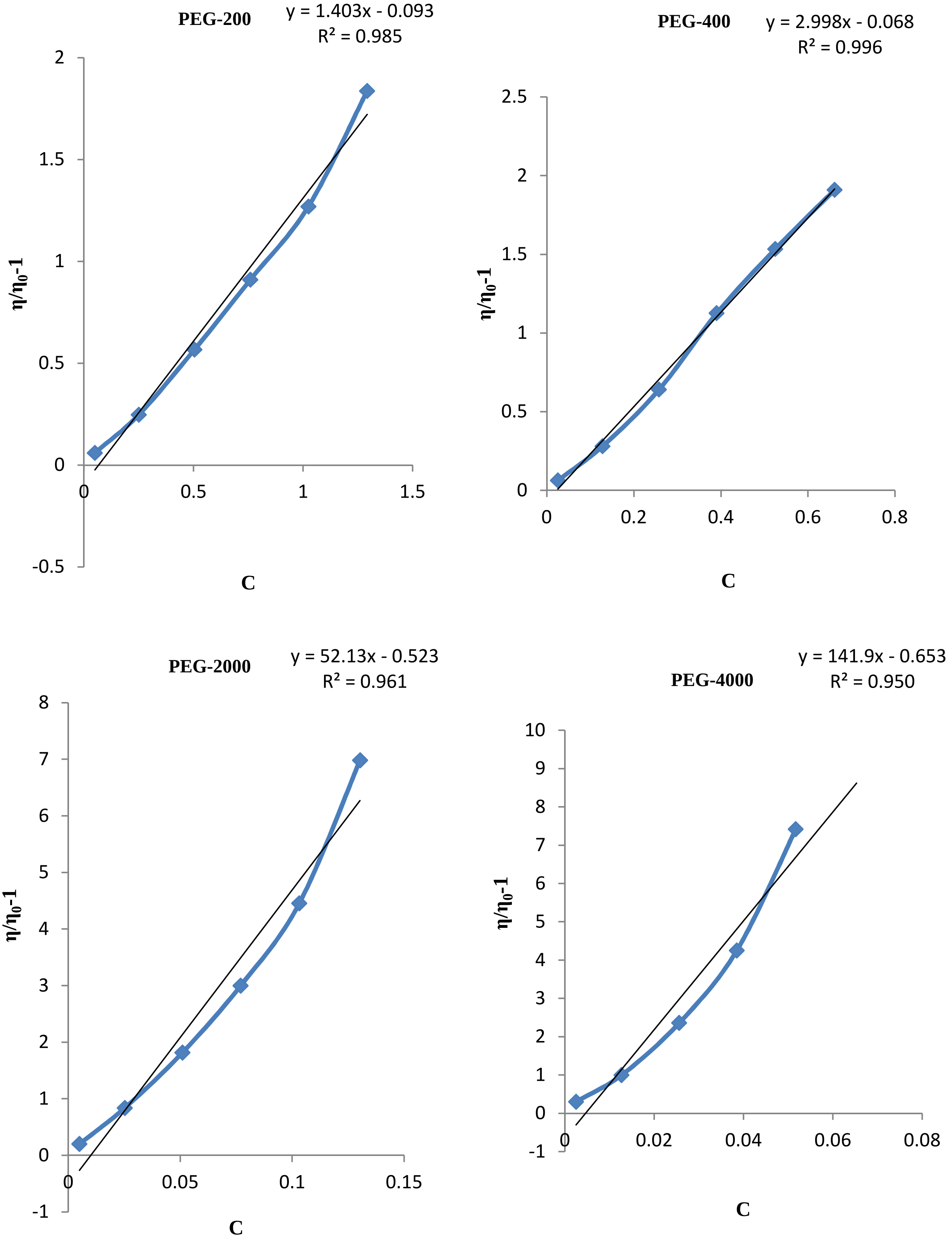
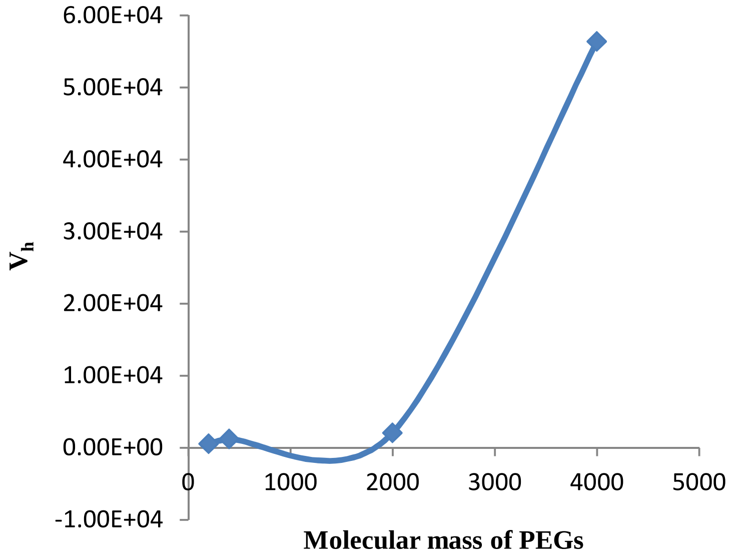

PEG-200
y = 1.403x - 0.093
R² = 0.985
η/η₀-1
2
1.5
1
0.5
0
-0.5
0
0.5
1
1.5
C
PEG-400
y = 2.998x - 0.068
R² = 0.996
η/η₀-1
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
C
PEG-2000
y = 52.13x - 0.523
R² = 0.961
η/η₀-1
8
7
6
5
4
3
2
1
0
-1
0
0.05
0.1
0.15
C
PEG-4000
y = 141.9x - 0.653
R² = 0.950
η/η₀-1
10
9
8
7
6
5
4
3
2
1
0
-1
0
0.02
0.04
0.06
0.08
C

Figure 3



CONCLUSION

In the study from analysis of experimental observation, it is concluded that there is association between Poly (ethylene) glycol and water molecules because of hydrogen bonding. It also shows that the molecular mass of the polymer and the concentration can influence the magnitude and nature of inter molecular interactions. All the PEGs act as structure maker in aqueous solutions and results are in agreement for both the classes of PEGs liquids and solids. The study is useful for production and uses of polymers in different industries like pharmaceuticals, textile, cosmetics, surfactants etc. The aqueous solutions of Poly (ethylene) glycols have application as green solvents to develop compounds of biological or medicinal interest to synthetic Chemists [23] and hence the results obtained in the study are useful in the preparation of green solvents for particular reactants as a model.

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