

Viscometric Study of PEG-400 in Aqueous and Non Aqueous

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Abstract: *The increase in the viscosity with lower temperatures is particularly noticeable within super cooled water. The water cluster equilibrium shifts towards the more open structure as the temperature is lowered. This structure is formed by stronger hydrogen bonding. in turn this creates lager clusters and reduces the ease of movement (increase viscosity), so reducing the strength of the hydrogen bonding network, which is also partially responsible for the viscosity. This reduction in cohesiveness more than compensates for the reduce void volume. It is thus a direct consequence of the balance between hydrogen bonding effects and the Vander Waals dispersion forces in water; hydrogen bonding prevailing at lower temperature and pressure.*

Keywords: Polyethylene glycol (PEG), Triton X-100, Dimethylsulfoxide (DMSO), Potassium Chloride (KCl)

1. Introduction

The thermodynamic behavior of liquids, Physical properties and liquid mixtures are of great fundamental and practical importance. These properties provide information about molecular interactions as well as necessary data for various industrial applications. Polyethylene glycol (PEG) is a nontoxic, highly biodegradable polymer [1]. It is both a good proton Acceptor and proton donor, with ability to form strong inter and intra-molecular hydrogen bonds [PEG is also well known as a food additive and is used for various biomedical and biotechnical applications in aqueous solutions with biological macromolecules [2]. Polyethylene glycol is synthetic addition polymers prepared via an addition reaction of ethylene oxide and water in the presence of a 'catalyst. Several of the physico-chemical properties of the polyethylene glycols and thus the proposed specifications vary depending on the molecular weight of the particular polymer. Polyethylene glycols (PEGs) are a wide group of polymers of ethylene oxide very different from each other in their molecular weights and physico-chemical characteristics [3]. PEGs with a molecular weight below - 600 are clear, viscous liquids, while at a molecular weight of ~1000 PEGs appear as white waxy solids [4]. In general they are water soluble, stable, non-toxic compounds that do not hydrolyzed or deteriorate on storage [5]. The following formula applies: $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$ where n equals the average number of oxyethylene groups [6]. Polyethylene glycols (PEGs) are being used in many areas of research and technology [7]. They have important clinical uses due to their low toxicity [8]. They constitute the basis of many skin creams and laxatives. The unique ability of PEG to be soluble in both aqueous solutions and organic solvents makes it suitable for end group derivatization and chemical conjugation to biological molecules [9]. When

PEG is attached to a protein medication, it allows a slower clearance of the carried protein from the blood, thus a longer acting medicinal effect and a longer dosing interval, [10]. investigated strategies to increase the solubility of peptides in organic solvents by conjugating with PEG, PEG is also used in toothpastes as a dispersant, in lithium polymer cells as the separator and electrolyte solvent, in gas chromatography as a polar stationary phase, in wood preservation by replacing water in wooden objects, in the production of non-ionic surfactants by coupling with hydrophobic molecules [11]. Another interesting use of PEGs is in edible film preparation in which PEGs act as plasticizers [12]. In many edible film preparations and their application to food, PEGs of varying molecular weights have been used in our laboratories. The interaction of PEGs with water plays the major role in their uses in all the above applications [13]. Therefore, it is of importance to study and understand the aqueous solution behaviors of PEGs. The study of volumetric properties is one of the important tools in understanding solute-solvent interactions [14]. Assembly properties of polyethylene glycol (PEG) and water mixtures are widely used (i) to induce more or less marks gelation processes, (ii) to organize surface for elaboration of composite materials, and even (iii) as agents promoting crystallization [15]. The polymeric chain of any PEG is alternately hydrophilic and hydrophobic. It exhibits specific interactions with water leading, for example, to a helical structure that appears under certain conditions of temperature and temperature [16]. The rate of polymer dissolution thus depends on the surface area (particle size) of the polymer. The particle size of PLGA (as received from the supplier) was >500 um, The particle size could be reduced by cryogenic milling to 50 um. As the polymer and the viscosity of the resulting polymer solution [17]. Since PLGAs are water-insoluble, various organic biocompatible solvents, which have been in used in parenteral formulations, were evaluated for their ability to rapidly dissolve PLGA [18]. The properties of

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water-polyethylene glycol (PEG 400) solutions vary with the PEG content. The highest acidity and conductivity values were observed in 20% PEG 400 solutions. Oxygen solubility in such solutions decreased as the PEG 400 content increased [19]. Adsorption of PEG 400, estimated by EQCM, varied with the PEG 400 concentration, also reaching a maximum in 20% PEG 400 solutions, with the weight of the adsorbed layer reaching 3.5 cm. Polyethylene glycol (PEG) is an important industrial solvent, which may be used in the cleaning of exhaust air and gas streams from industrial production plants because of its favorable properties, such as low vapor pressure, low toxicity, high chemical stability, and low melting point [20]. The main advantage of PEG is also high solubility and desorption capability for SO₂, which lead to lower energy requirements for absorption and regeneration processes [21].

2. Experimental Work

The experimental part of this dissertation has been discussed in detail under the following headings:

Materials:

Water:

Ordinary tap water (2000 mL) of conductivity in the range $3\text{-}5 \times 10^{-6} \text{ Scm}^{-1}$ at 25°C was distilled twice in the presence of alkaline KMnO₄. The distillation was carried out through a 750 mm long vertical fractionating column. The middle fraction of the double distilled water of conductivity $1\text{-}4 \times 10^{-7} \text{ Scm}^{-1}$ and pH in the range 6.8-7.0 all at 25°C was collected for use in all experiments.

Triton X-100 (C₁₄H₂₂O (C₂H₄O)_n) is a nonionic surfactant that has a hydrophilic polyethylene oxide chain (on average it has 9.5 ethylene oxide units) and an aromatic hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4- (1, 1, 3, 3-tetramethylbutyl)-phenyl group. It is closely related to IGEPAL CA-630 or erstwhile Nonidet P-40, which might differ from it mainly in having slightly shorter ethylene oxide units. Thus Triton X-100 is slightly more hydrophilic Triton X detergents are distantly related to Pluronic range of detergents marketed by BASF. The pluronics are triblock copolymers of ethylene oxide and propylene oxide with the ethylene oxide segments being more hydrophilic than the propylene oxide.

Dimethylsulfoxide (DMSO):

Dimethylsulfoxide (DMSO) is the organosulfur compound with the formula (CH₃)₂SO. It is a common organic solvent that has been used widely in biological studies and as a drug carrier across cell membranes. Due to two lone pairs on its oxygen atom, DMSO can interact with water forming strong hydrogen bonds. A single DMSO molecule is thought to form hydrogen bonds with as many as four water molecules simultaneously. In addition, the two methyl groups provide a non-polar attribute to the molecule causing effects of hydrophobic hydration and hydrophobic association of DMSO molecules. This

combination of polar and non-polar characteristics makes DMSO and its aqueous solutions an important solvent in organic chemistry and fine chemical industries [50]. Its molecular weight is 78.13 g mol⁻¹. Its boiling pt. ranges from 189-192°C and melting pt. ranges from 18-19°C. Its dipole moment is 3.96D. DMSO was used as solvent of AR grade and supplied by Sisco Research Lab. Pvt. Ltd.

Potassium Chloride (KCl):

Potassium Chloride (KCl) was required for the determination of cell constant of the conductivity cell. It was of AR grade and was recrystallized twice from double distilled water. Initially, the salt was dried at 60 – 80°C in vacuum, and then ground and again dried for 2 – 3 days at 280 – 300°C in the presence of P₂O₅. The purified sample was stored in vacuum desiccator in the presence of P₂O₅ and allowed to attain the room temperature before use.

Instrumentation:

Thermostat:

A high precision water thermostat of capacity ~ 30L fitted with a digital temperature controlled device was used for conductance. It was supplied by popular traders. The temperature of the thermostat was maintained within ± 0.1°C over the entire temperature range studied i.e., 25 - 45°C. However, the temperature of the bath was continuously monitored with the help of a 1/100°C calibrated thermometer.

Experimental Procedure

The density of PEG 400 was determined by using specific gravity bottle. The concentration of PEG 400 in the range of [0-4.0 wt %] was made in the aqueous medium as well as aqueous rich mixtures of DMSO [wt %] at 20-30°C. With the help of density and flow time of polymer solution, viscosity of different composition and its variation with temperature was reported in appendices I, II.

Various sources of errors and factors affecting the reproducibility are discussed as follows:

(a) Fluctuation of temperature: Density is a function of temperature and it changes to a large extent with small change in temperature. So even a small fluctuation in temperature of thermostat will cause a large change in density. This error has been avoided by placing the glass cell in a water bath where the temperature fluctuations are always controlled within ± 0.01°C.

(b) Evaporation of solution: A small change in the level of solution in the cell introduces a major error in the reproducibility of the weight of float in the solution. The solution can evaporate and this was avoided by having a bakelite top with a hole in it and the level of the solution just before and after taking the weight of float was checked and no change has been observed.

(c) **Improper suspension of float:** A significant error is caused in weight of float, if the float slightly touches the sides of the cell or if the suspension thread touches the sides of lid. This has been avoided by careful suspension.

(d) **Entrapped air bubbles:** Solution in the cell is stirred in order to avoid error due to the air bubbles attached to the float.

(e) **Solvent and solute purity:** The error due to these impurities was minimized by using AnalaR grade chemicals and conductivity water for making the solutions.

3. Result and Discussion

The increase in the viscosity with lower temperatures is particularly noticeable within super cooled water. The water cluster equilibrium shifts towards the more open structure as the temperature is lowered. This structure is formed by stronger hydrogen bonding. In turn this creates larger clusters and reduces the ease of movement (increase viscosity), so reducing the strength of the hydrogen bonding network, which is also partially responsible for the viscosity.

This reduction in cohesiveness more than compensates for the reduce void volume. It is thus a direct consequence of the balance between hydrogen bonding effects and the Vander Waals dispersion forces in water; hydrogen bonding prevailing at lower temperature and pressure.

The addition of water to the dope showed interesting viscosity (η) behaviour. The presence of a small amount of water to the dope showed interesting viscosity and consequently increases its tendency to flow. When increasing the water content beyond 5% by weight, the viscosity (η) value shows an increasing trend, especially its low temperature (20°C). In the dope, there are two kinds of changes, molecular coil contractions intermolecular aggregation. The evolution of viscosity (η) could be

attributed to the competitive processes of both changes. On the one hand, some shrinkage of molecular coil would reduce viscosity. On the other hand, intermolecular aggregation would increase viscosity (η) and promote gelation. The interactions in the dope consist of; intermolecular interaction, the interaction between molecule chains and DMSO, the interaction between DMSO, Triton x 100 and Water

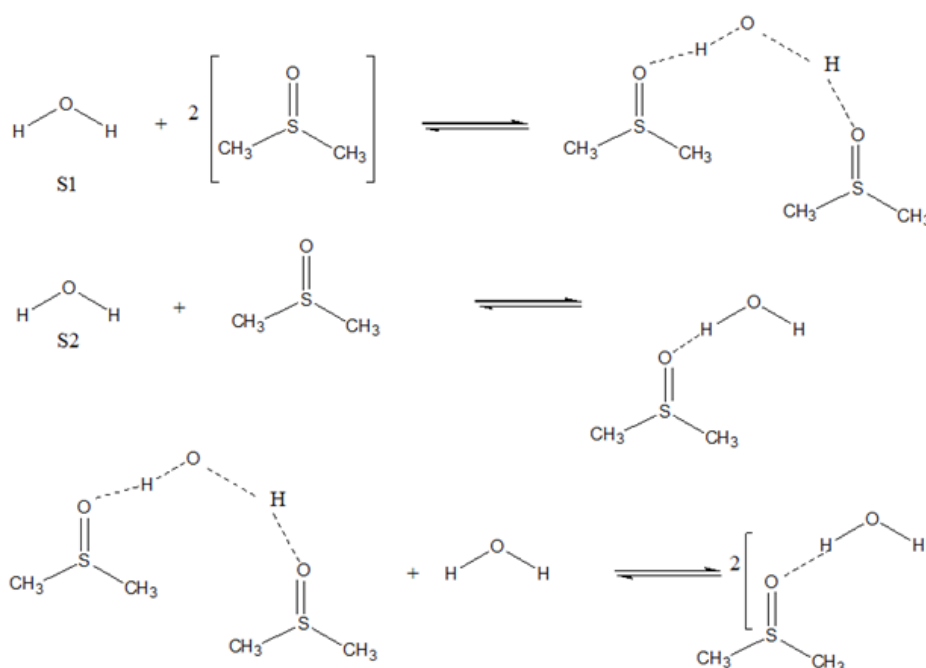
The addition of water will decrease the interaction between molecule chain and DMSO, increase the intermolecular interaction. The decrease of the interaction between molecular chains and DMSO leads to the molecular coil contraction, the increase of the intermolecular interaction leads to intermolecular aggregation. We suggest the molecular coils contraction is dominant when the water content is to 5% by weight, so the viscosity (η) often copolymer solution with water is lower than that without water, However, the intermolecular aggregation would be dominant with the increase of the water content, so the viscosity (η) increase rapidly when the water content is greater than 5% by weight.

By Poiseuille's equation

$$Q = \pi Pr^4 / 8l\eta$$

$$\text{viscosity } (\eta) = \eta_1 / \eta_2 = hd_1gt_1 / hd_2gt_2 = d_1t_1 / d_2t_2$$

The change of efflux time denotes the change of viscosity. There is maximum viscosity with increasing of water content. The increase of the viscosity is due to the increase of the intermolecular interaction that is derived from H-bonding between DMSO and water. the complex equilibriums (S2) and (S3) will be present with the increase of water content. The viscosity (η) increase with the increase of water content due to the formation of H-bonding between the two solvent. Moreover, the viscosity decreases when the water content is greater than 65 mol% where the formation of H-bonding achieves saturation.



The intrinsic viscosity (η) of polymer solution is usually studied under extremely dilute conditions where the polymer chains are separated by large distances and the interaction between them is reduced to a minimum. Therefore, the intrinsic viscosity (η) the polymer was studied by the variation of the water content from 0 to 9.2% by weight. There was large drop in viscosity (η) of the copolymer containing water. Water associate and the solvent is reduced by adding water. The resulting polymer chain contraction causes the decrease of (η). However, viscosity (η) increases when the water content was greater than 5% by weight. This phenomenon is due to the competitive processes of molecular chains contraction and intermolecular aggregation. The interaction in the polymer solution brings on these competitive processes. The interaction of polymer molecular chains, DMSO and water in dope is the reason of these competitive processes, and change of viscosity (η) is the macroscopic exhibition for these competitive processes.

It has been observed from that the viscosity of polymer in aqueous solution shows a significant difference with comparison to the viscosity of polymer in aqueous rich mixture of DMSO. This is due to the hydrophobic interaction and intermolecular interaction. As we increase the concentration of DMSO, the viscosity of solution goes on increasing due to increase in intermolecular interaction between the polymer chain As the interaction between the molecular chain increases, contraction of chain take place. Due to which viscosity increase. The viscosity of solution also goes on increasing with decrease in temperature. This is due to increase in increase in hydrogen bonding. Due to which size of cluster increase and mobility of polymer get reduces. Water in small content result in decrease in viscosity and as water is added, due to decrease in the interaction between DMSO and water leads to molecular aggregation result into increase in viscosity of polymer solution.

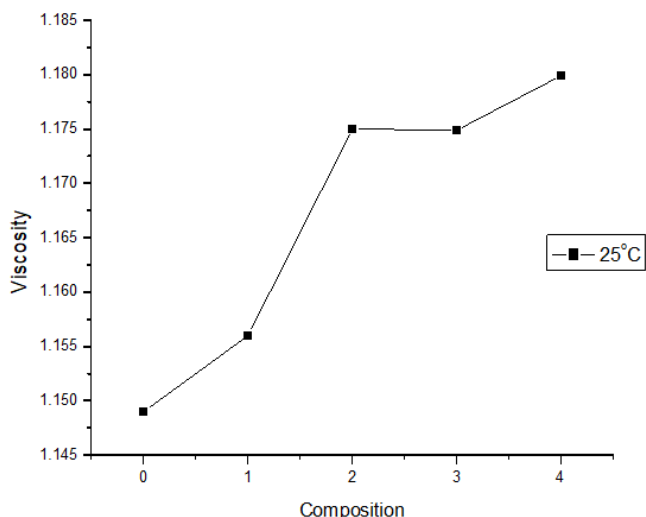


Figure 1: Plot between viscosity versus polymer (1.0, 2.0, 3.0 wt %) at 25°C

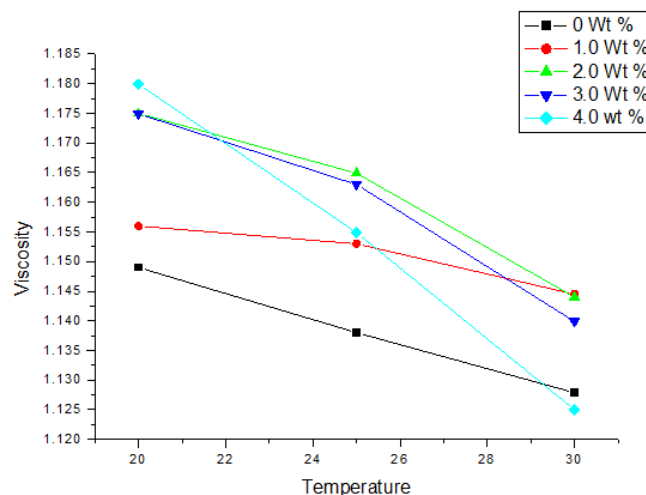


Figure 2: plot of variation of viscosity with temperature at 25°C having composition of PEG-400 (0, 1.0, 2.0, 3.0 and 4.0)

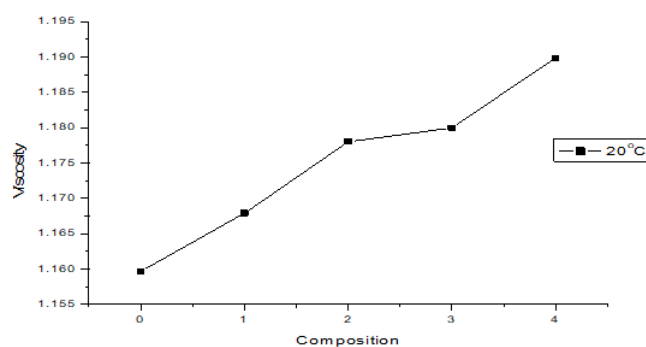


Figure 3: Plot between viscosity versus different composition of PEG-400 in aqueous rich mixture of DMSO-Triton X-100 at 20°C.

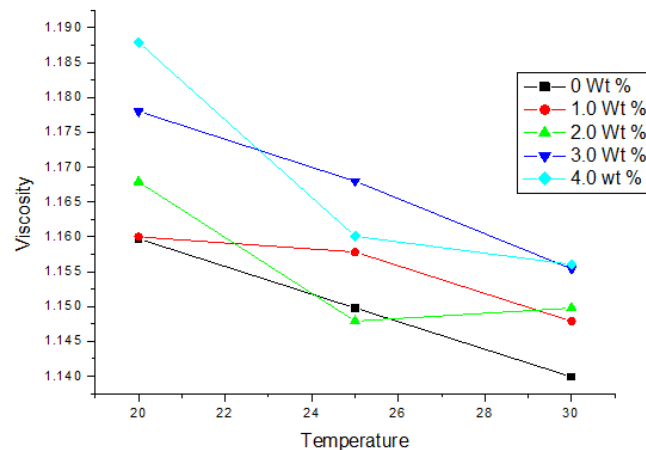


Figure 4: Plot between viscosity versus Temperature in aqueous rich mixtures of (PEG-DMSO-Triton X-100) at 25°C sss

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