VISCOSITY STUDIES ON POLY PROPYLENE GLYCOL AND ITS BLEND IN DIFFERENT SOLVENTS

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ABSTRACT

Viscosity studies were made with Poly Propylene Glycol of molecular weights 500, 1000, 2000 in 1,4 dioxane and isopropyl alcohol in the concentration range 0-1%, in the temperature range of 30-60 ° Celsius. The activation energy of flow shows a dip in 1,4 dioxane, whereas in isopropyl alcohol it shows a maximum at 1000 molecular weight. The effect of molecular weight observed in this study indicates that in PPG, molecular weight 1000 might be the transition state for the molecule from one shape to another shape. The K_eM value against molecular weight shows linear increase in isopropyl alcohol, but in 1,4 dioxane it shows nonlinear variation. This study shows the effect of molecular weight on the viscosity studies of PPG. The effect of concentration and that of the solvent are also seen. The behaviour of PPG in 1,4 dioxane is different from that in isopropyl alcohol. An attempt has been made to blend PPG of molecular weight 4000 with PEG 4000 and the compatibility nature of the blend is analysed through viscosity techniques and also through various interaction parameters. This study gives an idea regarding the solvent and molecular effect in PPG and also the compatibility nature of the blend.

1. INTRODUCTION

Viscometry is one of the simplest methods for studying the interactions and properties of polymer-polymer systems in solutions. Attractive interaction increases the viscosity of these systems. The temperature dependence of viscosity of polymer solutions was of great interest for a long time since Moore et al [1-4]. The Arhenius equation can be extended to dilute polymer solutions as for a pure liquid. Many researchers [5-6] have observed that the apparent activation energy of flow and the pre exponential term depend not only on the molecular weight and concentration but also on polymer chain stiffness and coil expansion. It has been reported that the difference between the activation energy for the solutions and for the solvent is much higher than for flexible chains.

Moore’s equation has been applied to poly (β-naphthyl methacrylate) dissolved in different solvents by Niezette et al [6]. They have also tried to express the pre exponential term in terms of the Mark-Houwink and Fox-Flory constants. Viscosity and ultrasonic studies on polyethylene glycol in benzene have been reported by Arumugam et al [7]. The conformational behaviour of PPG oligomers in various solvents has been reported by Sandell and Goring [8].

Polymer blending is one of the most commercially significant areas for the development of new polymer materials. The ultimate goal of polymer blending is a practical one of achieving commercially viable polymers through either unique properties or lower cost than some other means might provide. Poly propylene glycol, the simplest propylene oxide based polyol is a commonly used polymer for various applications. It finds its applications in hydraulic fluid, rubber lubricant, antifoam

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agents and so on. The advantage of using viscosity measurements for investigating polymer miscibility has been shown by many researchers [9-14].

In the present study, an attempt has been made to test Moore's equation for PPG of different molecular weight in different solvents and also to study the compatibility of PPG 4000 with PEG 4000 using viscosity technique.

2. MATERIALS AND METHODS

Polypropylene glycol (PPG) of molecular weight 500, 1000 and 2000 were obtained as gift from Manali Petro products, Chennai. Polymer solutions were prepared by dissolving these polymers in iso propyl alcohol and 1,4 dioxane to give concentrations 0.1, 0.25, 0.5, 0.75, and 1%. The viscosity studies were carried out in an Ubbelhode viscometer and the timings were measured accurately (0.01 s). The viscometer was kept in temperature controlled water bath (± 0.5° C) during the experiment. The density of the solutions was measured using gravimetric method.

2.1 BLEND PREPARATION

In the present study, PPG 4000 is blended with PEG 4000 in the solvents Isopropyl Alcohol and 1,4 Diaxone at 1% concentration. The compositions of the blend PPG 4000: PEG 4000 were in the following ratios 0:1, 0.2:0.8, 0.4:0.6, 0.5:0.5, 0.6:0.4, 0.8:0.2 and 1:0.

3. RESULTS AND DISCUSSION

Arhenius expression is valid for pure solvents and also for dilute polymer solutions.

According to Moore et al [4]

$$\eta = A\, e^{Q/RT} \qquad \text{-------- (1)}$$

where Q is the apparent activation energy of flow and A pre- exponential term with an activation entropy significance. The logarithm of this equation leads to a straight-line type.

$$\ln \eta = \ln A + (Q/R)\, 1/T \qquad \text{--------(2)}$$

Fig.1 shows the variations of log viscosity against inverse of temperature for PPG 500 in the temperature range of 30-60 ° C for Isopropyl alcohol and 1,4 Diaxone. The plots of PPG 1000 and 2000 are also similar to these plots for both the solvents. Generally a drastic change in the (ln η) viscosity indicates conformational transition of the polymer chain. The straight line indicates that the viscosity did not change in this temperature range (303-333k)[6]. In all the cases the ln η values increase with increase in the concentration and temperature.

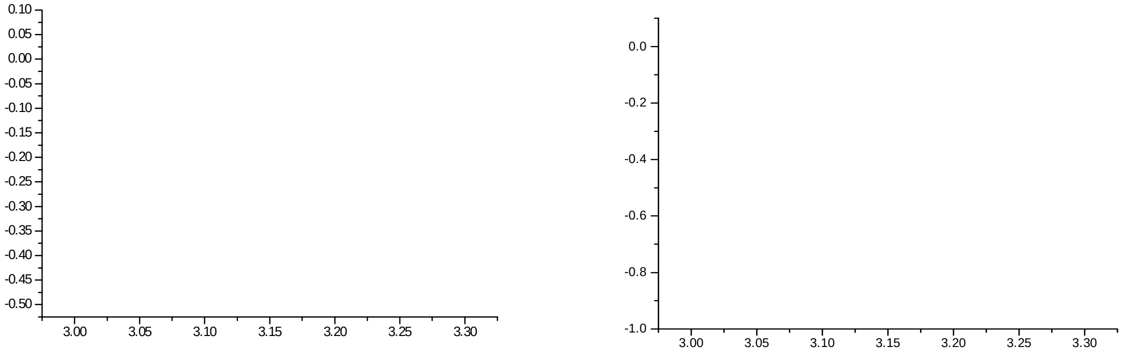

Fig1: Graph Between Log η And 1/ Temp for PPG 500 for (a)IPA and (b) 1,4 Diaxone

The slope of these curves gives the activation energy. The variation of Q with concentration C is given in Fig. 2.

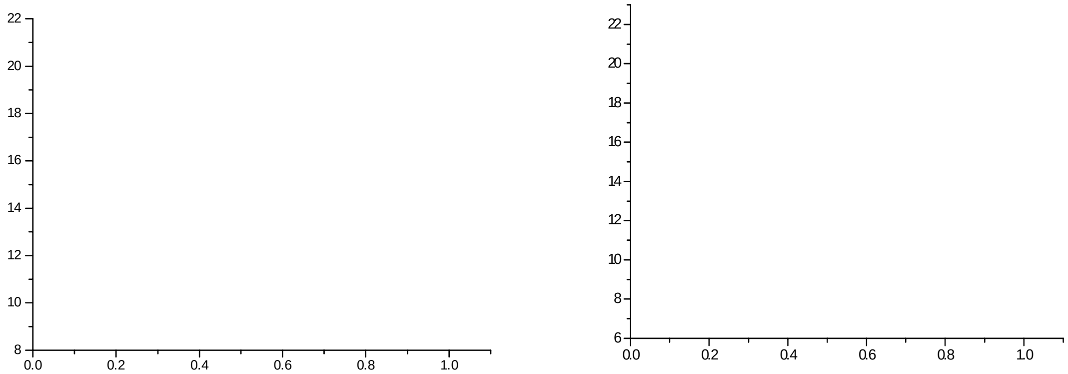

Fig 2 : Graph between Q and C

It can be seen from the Fig.2 that the variations fit into a straight line and the corresponding slope and intercept values are found out. The activation energy of flow, follows the equation

$$Q = Q_0 + K_e M c \quad \text{-----------} (3)$$

In this equation K_e is a constant, M is the molecular weight and C the concentration. Q_o is constant dependent on the polymer and its molecular weight. The effect of concentration was observed during plotting Q against concentration Fig.2 .

The variations in the intercepts of ln η Vs 1/T plots, which are the A values, i.e. the pre exponential term. The equation that fit the values is given by

$$A= A_0 \; e \, (K_\beta \; M^\beta \; c \;) \quad \text{----------}(4)$$

However, the variations of for PPG does not seem to follow the above equation as poly (β - naphthyl methacrylate).

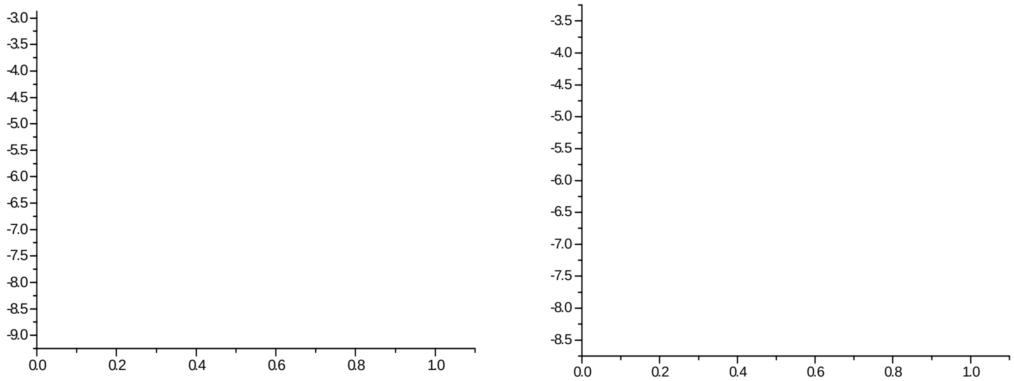

Fig 3: Graph between intercept log A and concentration C

The variation of A with concentration and molecular weight is given in Fig. 3. The ln A against concentration curves show that the general trend is a straight line and of the form

$$A = A_0 + K_\gamma M^\gamma c \qquad \text{---------(5)}$$

In contrast to ploy (β-naphthyl methacrylate) [6] PPG shows decreasing trend with increase in concentration and molecular weight as can be seen from Fig.3.

If the graph is drawn between activation energy Q and concentration C , according to eqn (2), we can get the value of Q_o from the intercept and the slope will give the value of KeM. The general trend seems to be the same, though the values are different in both the graphs. It can be observed that the activation energy of flow is greater for molecular weights 1000 and 2000 than that of the solvent . According to Niezette [6], such a behaviour is for flexible chain polymers. Sandell and Goring [8] have reported that the polypropylene chain was flexible and could be bent into a flat, compact coil at chain lengths as short as five repeating units. However, they have reported the disk-coil configuration as most suitable for aqueous PPG solutions only. In organic solvents the conformation of the oligomer chain would depend on the nature of the solute-solvent Van der Waals forces and also on the solute-solute interactions. It has been reported by Sandell and Goring that for molecular weights greater than 500, PPG in benzene assumes a random coil configuration. Meyerhoff et al [15] have suggested that at low molecular weights the configurations changes from random coil to rotation ellipsoid shape. From fig.4&5, we understand that the behaviour of PPG is different below and above 1000. So we can infer that in poly propylene glycols, molecular weight 1000 may be the transition state for the change of behaviour which is clearly observed from both the solvents in general and in 1,4 diaxone in specific. Graph between K_eM and molecular weight M shows that for Isopropyl alcohol, the value of K_eM increases with M and vice versa for 1,4 Diaxone which is shown below.

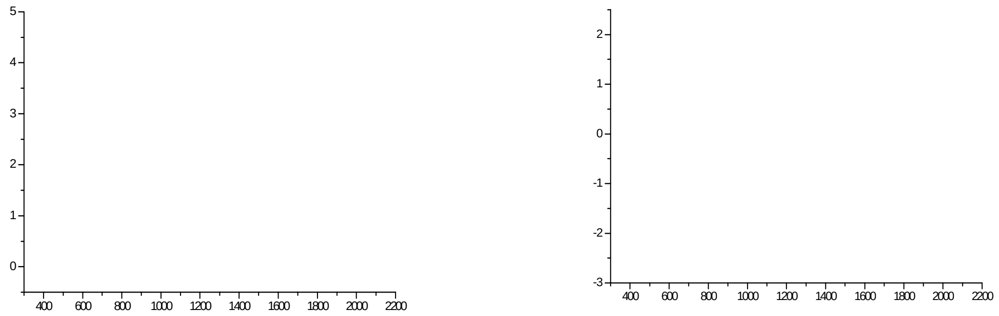

Fig 4. Graph Between KeM and Molecular Weight M

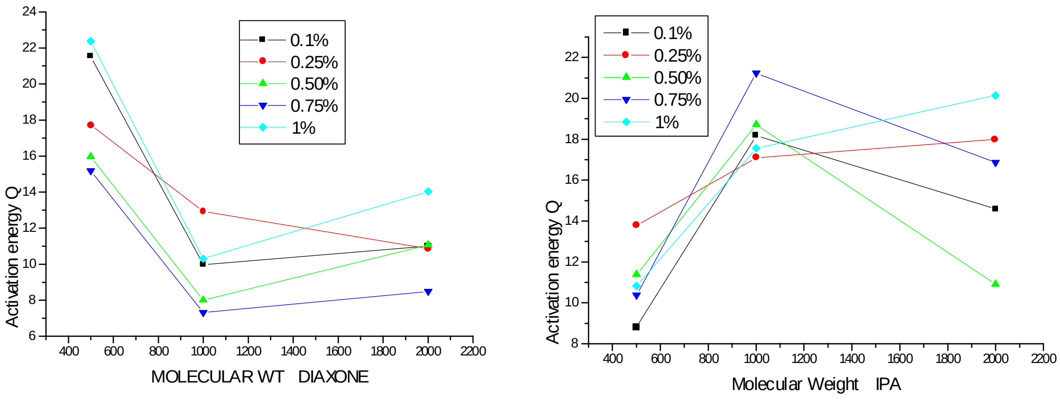

Fig 5. Graph Between Activation Energy Q and Molecular Weight M

4. BLENDS

When two or more polymers are intimately mixed in a single continuous solid product, the composition is generally referred to as a polymer blend or polyblend. Singh and Singh [16] have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Varadharajulu [17] carried out ultrasonic and viscometric investigation of cellulose acetate / PMMA blends in solution and reported that the immiscible blend shows an S-type behaviour. Sun et al [18] have suggested viscometric method to study polymer-polymer miscibility. The viscosity study (Fig.6) shows that the blend is incompatible. Viscosity method is simple and it offers very useful information about the relationship between dilute solution properties and bulk structure of the polymer blend. The basic idea of using viscosity as a parameter for compatibility determination of polymer blends lies in the fact that in solution the repulsive interaction may cause shrinkage of polymer coils resulting in a viscosity of the polymer mixture that is lower than the value calculated from viscosities of the pure components on the assumption of the additive law.

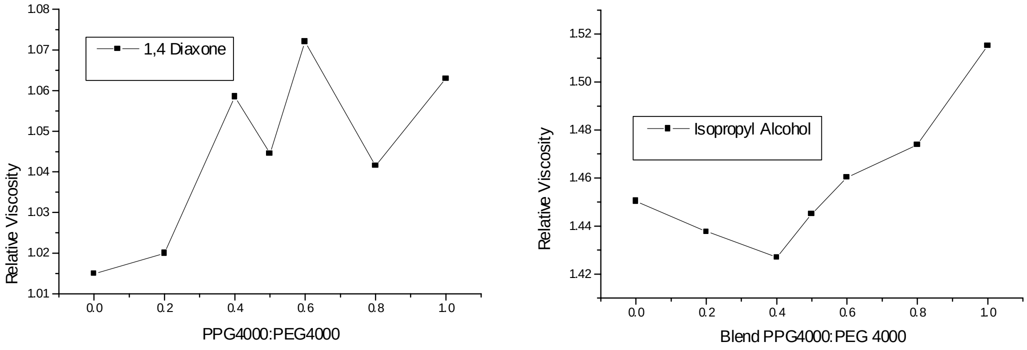

Fig 6: Variation of Viscosity against blend composition

The viscosity measurements may indicate the miscibility of a polymer blend. Das and Banerjee [19] have used a few empirical and semi empirical equations for predicting the miscibility of polymer blends based on viscosity viz., the additive rule, log additive rule, and free volume additive rule.
Three significantly different behaviour patterns may be observed in the blends. In a compatible blend, where the rheology is an ideal mixing of the two components, which is very rare. The other two are the blends having viscosity of the blends higher or lower than their components. For miscible blends a number of empirical and semi empirical equations predicting the viscosity of polymer blends have been proposed with varying degrees of success.

The additive rule of mixture is given by

$$\eta_b = W1 * \eta 1 + W2 * \eta 2 \qquad \text{--------------}(6)$$

$$\log \eta_b = W1 * \log \eta 1 + W2 * \log \eta 2 \qquad \text{--------------}(7)$$

$$1 / (\log \eta_b) = W1 * (1/\log \eta 1) + W2 * (1/ \log \eta 2) \qquad \text{--------------}(8)$$

where η_b is the viscosity of the blend , $\eta 1$, $\eta 2$ that of the components and W1, W2 the weight fractions of the components.

Utracki and Kamal [20] have described the complexity of the viscosity composition behaviour of polymer blends. Using rheological data, they are divided into three categories depending on the deviation from log additive rule ie) 1] positively deviating 2] negatively deviating 3] positively - negatively deviating. The negative deviation of the log additive rule in the case of immiscible blends was reported by Plochocki [21].

From fig.7, we could observe that the experimental values are negatively deviating and they are closer to log additive values, which refers negative interaction, which in turn causes the macromolecules to shrink. This shows that the blend is immiscible.

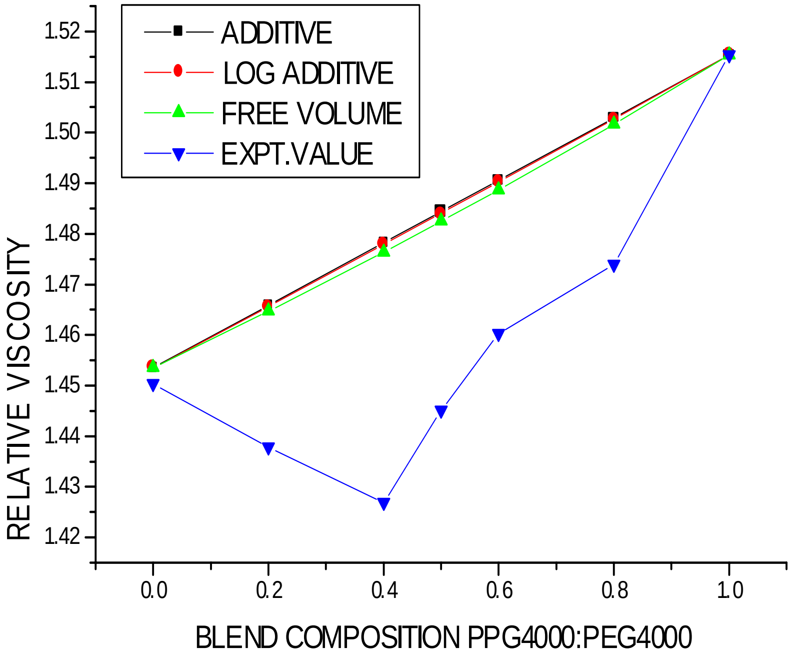

Fig 7: Variation of Viscosity against blend composition-Additive rule

5. CONCLUSION

The effect of concentration on the activation energy of flow was calculated for PPG 500, 1000 and 2000. It was observed that the activation energy of flow is greater for molecular weight 1000 and 2000 than that of 500 in the case pf IPL and vice versa in Diaxone**.** The effect of molecular weight was analysed from the graph between KeM and molecular weight (M), which indicated that for lower concentration, the value of KeM decreases with M and vice versa for higher concentration[diaxone]and it is linear with IPL. This showed that in PPG, molecular weight 1000 might be the transition state for the molecule from one shape to another shape. The miscibility nature of the blend PPG 4000:PEG 4000 was analysed through viscosity studies and other techniques. The blend showed immiscibility.

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