CHAPTER 2

VISCOSITY STUDIES
INTRODUCTION

An extensive literature on the viscosity of solutions has appeared since the pioneering investigations of Poisuelle. After the introduction of the interionic attraction theory much of the interest has been evinced in the accurate determination and the theoretical interpretation of the viscosities of dilute salt solutions. In a very dilute salt solution the interstitial solvent between the cospheres of the solute ions is unmodified and has the same properties as it has in the pure state. Each ion in a solution is expected to contribute towards a change in the viscosity of the solvent. But electrostatic forces between the ions have to be taken into account in this regard. Grunession showed from his results that viscosity is not a linear function of the concentration in dilute solutions. In non-electrolytes it shows a linear function.

In general, we know that polymer solutions flow more slowly through a tube than do solvents alone under the same pressure. Molten polymers flow much more slowly than do their solutions. Since many operations in production and fabrications involve flow in pipes, between rolls, and through slots and stirring in vessels, it is well for us to
consider now some of the generalizations we can make regarding the effect of chemical and physical variables on flow properties.

Marked difference exists between the behaviour of viscosity of low molecular weight solution and polymer solution. In the former case, the molecular size of the solute and that of the solvent are comparable and the solute does not swell in volume in the process of dissolution, there is a free molecular mobility with respect to the solute without much increase in intermolecular friction. Hence, the viscosity of the solution is not very much different from that of the solvent. In the case of polymer solutions, however, the solute molecules, which are gigantic compared to the solvent molecules, swell considerably in volume during the process of dissolution. The giant size and the increased volume of the polymer molecules restrict its molecular mobility in the solution and increase the intermolecular friction. The polymer solution, therefore, is highly viscous. The states of solute molecules in low molecular weight and polymeric solutions are shown in Figs 2.1 and 2.2.
Fig. 2.1 Schematic representation of solute and solvent molecules present in dilute solutions of: (A) low molecular weight compounds and (B) polymers.

Fig. 2.2 Schematic details of dilute polymer solutions.
The viscosity of a dilute polymer solution depends on several factors, namely, the nature of the polymer and that of the solvent, their concentrations, the polymer molecular weight, the temperature and the shear rate (the effect of the shear rate has been neglected for simplicity).

At the molecular level, the viscosity of a polymer solution is a direct measure of the hydrodynamic volume of the polymer molecules. Hydrodynamic volume, is the apparent volume occupied by the expanded or swollen molecular coil along with the imbibed solvent and can be defined in terms of the expansion factor $\alpha$ and unperturbed end-to-end distance $\left(\bar{r}_o^2\right)^{1/2}$. It is known that $\alpha$ depends on the solvent nature and the factor $\left(\bar{r}_o^2\right)^{1/2}$ depends on the polymer molecular weight. It, therefore, follows that a polymer will exhibit a higher viscosity in a good solvent than in a poor solvent and that, in the same solvent, the viscosity will be directly proportional to the molecular weight.
Viscosity and Molecular Weight

Staudinger, during the early 1930s, used viscosity as a measure of the molecular weight of the polymer, to postulate his hypothesis about the long chain nature of polymer molecules. He proposed the relationship

\[ \eta_{sp} = K_s c M \] ........2.1.

Where \( K_s \) is a constant for a given polymer/solvent/temperature; \( c \) the concentration, \( M \) the molecular weight, and \( \eta_{sp} \) the specific viscosity denoting the increase of viscosity of a polymer solution over that of the pure solvent according to the relation

\[ \eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \] ........ 2.2.

Where \( \eta \) = viscosity of the polymer solution and \( \eta_o \) = viscosity of the solvent.

It can be seen from Eq. 2.1 that the specific viscosity is dependent on the concentration. In order to quantify a viscosity function of a polymer in a solvent, which will be independent of the concentration, the limiting value of
reduced viscosity \( (\eta_{sp} / C) \) or that of the inherent viscosity \( (\ln \eta_r / C) \) at infinite dilution is chosen and termed 'intrinsic viscosity' or 'limiting viscosity number'. \([\eta]\) :

\[
(\eta_{sp} / C)_{C=0} = [\eta] = (\ln \eta_r / C)_{C=0} \quad \ldots \ldots \quad 2.3.
\]

The term \([\eta]\) has been related to the two viscosity functions through the following two equations by Huggins and Kraemer, respectively:

\[
\frac{\eta_{sp}}{C} = [\eta] + K^1[\eta]^2C \quad \ldots \ldots \quad 2.4.
\]

\[
\frac{\ln \eta_r}{C} = [\eta] - K^{11}[\eta]^2C \quad \ldots \ldots \quad 2.5.
\]

Where \(K^1\) and \(K^{11}\) are constants for a given polymer/solvent/temperature system. For many linear flexible polymer systems, \(K^1\) often indicates the measure of the solvent power, the poor the solvent, the higher the values of \(K^1\). The value of \(K^1 + K^{11}\) has been shown to be 0.5.
It should be noted that \([\eta]\) is dependent on polymer/solvent/temperature and can be computed by measuring the viscosity of dilute solutions of the polymer in a given solvent at various concentrations \((C < 0.5 \text{ mol/dm}^3)\) and extrapolating the viscosity functions to zero concentration according to equations (2.4 and 2.5). Representative plots are shown in Fig. 2.3.

Staudinger's equation was subsequently replaced by the famous Mark-Houwink equation


Where 'K' and 'a' are constants for a given polymer/solvent/temperature system. The value of 'a' varies from 0.6 to 0.8 and becomes 0.5 in theta solvents, while the values of 'K' varies widely from one system to another. 'K' and 'a' values for some polymer/solvent systems are given in literature³.

Viscosity of concentrated polymer solutions

While the study of the viscosity behaviour of a dilute polymer solution is of significant theoretical importance, that of the flow behaviour of a concentrated polymer solution is of practical importance. Many
Fig. 2.3 Typical plots of viscosity data for computing intrinsic viscosity, $[\eta]$, according to Eqns. (2.4) and (2.5). The ordinate intercept gives $[\eta]$. 
industrial problems associated with adhesives, coatings, cast films and spun fibres cannot be fully appreciated without a proper knowledge of the properties of concentrated polymer solutions.

In a concentrated solution (>5% by weight), polymer molecules do not exist as isolated chain coils, but are interpenetrating and entangled with each other. Shear effects are, therefore, pronounced in the case of the viscosity behaviour of concentrated solutions. Any viscosity measurement will have to be made at different shear rates and extrapolated to zero shear so as to get the true picture of the solution behaviour.

The concentration dependence of viscosity of concentrated solutions is expressed by the equation

\[
\frac{\eta_{SP}}{C[\eta]} = \text{Exp} \left\{ \frac{K^1[\eta] C}{1-bC} \right\}
\]

(2.7)

where 'b' is a constant. The values of \(K^1\) and \([\eta]\) for a polymer-solvent system can be found out using Eq. 2.4.

Similarly, the viscosity as a function of Molecular weight and concentration can be expressed by the equation
\[ \eta = K^* \left[ \frac{C}{\alpha/\beta M} \right]^{3.4} \]  

Where \( K^* \) is a characteristic constant for a polymer-solvent system and is temperature dependent. Its value is roughly of the order of \( 2.0 \times 10^{-15} \) when \( C \) is expressed in g/ml and \( \eta \) in poise. The value of \( \alpha/\beta \) ranges from 1.38 to 1.85 with an average of 1.5.

In the present study the author has measured the densities and viscosities of poly(ethylene glycol) (Mol. wt. 6000) in water, water + Dimethyl sulfoxide (50%, v/v) and Dimethyl Sulfoxide at 30, 35, 40 & 45°C respectively. From these results calculated relative viscosity and reduced viscosities of these solutions and the results are analysed with the appropriate equations explained earlier.
Experimental Methods

Purification of Materials

The chemicals used in the present investigation were purified by the method given in literature.³

Poly(ethylene glycol) with molecular weight 6000 supplied by B.D.H. chemicals limited (Poole, England) was used without further purification.

Dimethyl sulphoxide (Merck, proanalysis) was used after necessary purification.³

Mercury was first run in a fine stream through a long length of 5% nitric acid and the process was repeated for the second time and the sample was finally passed through a column of water. It was then dried by means of filter paper and run through a hardened filter paper with a pin hole at the apex of the cone. The dried sample was finally distilled twice under reduced pressure using Gallenkamp mercury distillation apparatus.
Deionised water (Permettite process) was distilled thrice. 0.5 gms of sodium hydroxide and 0.2 g of potassium permanganate was added to each litre of first and second distilled water. This alkaline solution was slowly distilled from an all pyrex glass vessel and the middle fraction was collected. The purity of the sample was checked by measuring the conductivity.

Density measurements

Density is determined by pycnometer method. Pycnometers of different design have been used for accurate measurements by several workers. In the present investigations, pycnometer of Parker and Parker type with minor modifications has been employed. The double stem pycnometer with a bulb of capacity 25 ml on one of the stems used in the studies is shown in the Fig. 2.4. The stems are made of pyrex glass tube of a bore of about 3 mm and bent to the sides making an obtuse angle at the bend. The vertical part of the stem containing the bulb is about 5 cm length and carries a mark in the middle to read the liquid level. A mark is also made on the second stem at about the same level to read the difference between the liquid levels in the two stems. The inclined part of each of the stem is 4 cm. The enlargement of the stem serves as
Fig. 2.4 Pycnometer
over flow cup where liquids are raised to temperatures above the room temperature. The open ends of the stems are closed by suitable teflon caps in order to prevent the loss of liquid due to evaporation.

The following procedure is adopted for filling the pycnometer and weighing.

Procedure

The well cleaned and dried pycnometer is weighed accurately with reference to another pycnometer of the same design, weight and surface area is hung to the hook of the pan containing the weights. The liquid is introduced into the weighed pycnometer with the help of a syringe without air bubbles, approximately upto the marks on the stems. The pycnometer is kept immersed vertically in a thermostatic bath maintained at the desired temperature with the ends of the stems closed with the caps for about half-an-hour. This permits the unfilled part of the stem to be drained completely and allows liquid vapour equilibrium to be established. The amount of the liquid at initial filling is adjusted to allow for expansion (or contraction) due to the difference in temperature between the bath and surroundings. The distance between the mark and the liquid meniscus in both the stems is determined
with the aid of a travelling microscope which reads with a precision of 0.002 cm. The pycnometer is then removed from the hook. After about 15 minutes, it is weighed. The reference pycnometer hung from the hook of the other pan is also subjected to the same treatment to eliminate the errors in weight due to moisture condensation on the surface of the pycnometer.

The volume of the pycnometer is calculated from the weight of the water filling the pycnometer up to the marks exactly. The weight of water at the required temperature filling the volume of pycnometer included between the marks is determined as described below.

The capillary used to prepare the stems is filled with mercury and the length of the mercury thread is measured with the help of the travelling microscope. The internal radius \( r \) of the capillary is calculated from the length of the mercury column. The uniformity of the bore of the tube is also checked by a similar procedure. The volume \( (dV) \) of water enclosed between the mark and the liquid meniscus is calculated by using the formula \( \pi r^2 h \) (where \( r \) is the radius of capillary, \( h \) is the distance between the mark and the meniscus). The difference between
the volume of water actually present in the pycnometer and the volume of water that fills exactly up to the mark at the required temperature gives the volume \( dV \) of water enclosed between the mark and the liquid meniscus. The weight \( dW \) of water, of this volume \( dV \), is calculated by multiplying \( dV \) with the density of water at that particular temperature (taken from literature). The mass \( W \) of water filling the pycnometer up to the marks is obtained by subtracting or adding \( dV \), as the case may be from or to the weight of water actually filling the pycnometer at the required temperature. The experiment is repeated till reproducible results with an accuracy of two in \( 10^4 \) parts is obtained. By dividing the weight \( W \) by the density of water at that particular temperature the volume of the pycnometer can be calculated.

In the determination of the density of any liquid first the pycnometer is filled with the liquid such that the liquid meniscus is as close as possible to the mark on the pycnometer.

The pycnometer with the liquid is kept immersed in the thermostat at the required temperature for sufficient time such that the level of the liquid is constant in both
the limbs. The height of the liquid level above or below the reference mark as the case may be is measured with the travelling microscope. The weight \( W \) of the liquid in the pycnometer is determined by the procedure similar to that described earlier.

**Viscosity Measurements**

Viscosity measurements are made with an Ostwald type Viscometer (Fig 2.5) with a flow time of 260 sec for water at \( 40^\circ \text{C} \). The viscometer was first thoroughly cleaned with chromic acid followed by distilled water and dried. A definite quantity of water, say 10 ml depending upon the capacity of the bulb, \( A \) was pipetted out into the bulb, \( B \), of the viscometer and was immersed in the thermostat. After the attainment of equilibrium, the liquid was drawn up by suction into the bulb \( A \), with the help of a rubber tube attached at the end \( C \) till the liquid level is above the mark \( a \). The liquid was then allowed to drain and the flow time \( t_2 \) taken by the water to pass from \( a \) to \( b \) was noted by means of the stop watch which could read 1/10 sec. The viscometer was cleaned, dried and the same volume of the liquid under investigation was taken into the bulb \( B \) and the process repeated as before to determine the flow time \( t_1 \).
Fig. 2.5
Ostwald Viscometer
The viscosity of the test liquid was calculated by using the equation,

$$\eta_1/\eta_2 = \frac{d_1}{d_2} \frac{t_1}{t_2}$$

Where

- $\eta_1$ = viscosity of the test liquid
- $d_1$ = density of the test liquid
- $t_1$ = flow time of the test liquid
- $\eta_2$ = viscosity of the reference liquid (water)
- $d_2$ = density of the reference liquid
- $t_2$ = flow time of the reference liquid.

At least eight determinations were made for each liquid and the difference of any two readings did not exceed 0.2 sec. The reported viscosity data are reproducible within ± 0.3%.
RESULTS AND DISCUSSION

The viscosities, relative viscosities and reduced viscosities of PEG (Mol. wt. 6000) in water, water + DMSO (50%, v/v) and pure DMSO are determined at temperatures 30, 35, 40 and 45°C and the results are tabulated in Tables 2.1-2.3.

Figs 2.6-2.8 illustrates the variation of viscosity with concentration of the polymer in water, water + DMSO and DMSO at the above said temperatures, respectively. The viscosity shows linear variation in the lower range of concentration (C < 0.02 m) of PEG in the three solvents. When the concentration of PEG is higher the linearity is not maintained. This is expected because the difference between the absolute viscosity of the solvent and PEG is very large. So at higher concentrations of PEG, the viscosity of solution rises sharply. The viscosity of the solution is high due to the increase in hydrogen bonding of the solvents. The hydrogen bonding capacity between solute and solvent is in the following order:

\[ \text{PEG-Water} > \text{PEG - (water+DMSO)} > \text{PEG - DMSO} \]
Fig. 2.6: Variation of Viscosity ($\eta$) with concentration (C) for PEG in $H_2O$. 

Fig. 2.6: Variation of Viscosity ($\eta$) with concentration (C) for PEG in $H_2O$. 

- $30^\circ C$ 
- $35^\circ C$ 
- $40^\circ C$ 
- $45^\circ C$
Fig. 2.7: Variation of viscosity ($\eta$) with concentration (C) for PEG in $\text{H}_2\text{O} + \text{DMSO (50\%, v/v)}$ Mixture.
Fig. 2.8: Variation of Viscosity ($\eta$) with concentration (C) for PEG in DMSO.
Table 2.1.
Viscosity data of PEG in Water at different temperatures

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Table 2.2

Viscosity data of PEG in Water + DMSO (50%, v/v) at different temperatures

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<th>Concentration (mol dm(^{-3}))</th>
<th>Density (g/cm(^3))</th>
<th>Viscosity (Cp)</th>
<th>Relative Viscosity ((\eta_{rel}))</th>
<th>Reduced Viscosity ((\eta_{sp}/c))</th>
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\(30^\circ C\)

| 0.004 | 1.0695 | 3.13 | 1.51 | 127.60 |
| 0.008 | 1.0703 | 4.33 | 2.09 | 135.89 |
| 0.012 | 1.0750 | 5.88 | 2.82 | 151.52 |
| 0.016 | 1.0757 | 6.38 | 3.25 | 128.58 |
| 0.020 | 1.0787 | 9.78 | 4.68 | 183.84 |
| 0.024 | 1.0818 | 12.55 | 5.98 | 207.58 |
| 0.028 | 1.0826 | 15.95 | 7.60 | 235.67 |
| 0.032 | 1.0842 | 19.54 | 9.29 | 259.15 |
| 0.036 | 1.0862 | 23.89 | 11.34 | 287.35 |
| 0.040 | 1.0898 | 28.90 | 13.67 | 316.83 |

\(35^\circ C\)

| 0.004 | 1.0659 | 3.07 | 1.55 | 137.11 |
| 0.008 | 1.0677 | 4.15 | 2.09 | 136.38 |
| 0.012 | 1.0713 | 5.59 | 2.80 | 150.31 |
| 0.016 | 1.0735 | 5.76 | 3.20 | 117.64 |
| 0.020 | 1.0754 | 9.34 | 4.67 | 184.43 |
| 0.024 | 1.0757 | 11.71 | 5.85 | 202.08 |
| 0.028 | 1.0797 | 14.82 | 7.37 | 227.65 |
| 0.032 | 1.0815 | 18.57 | 9.22 | 257.02 |
| 0.036 | 1.0819 | 21.66 | 10.76 | 271.05 |
| 0.040 | 1.0840 | 27.10 | 13.43 | 310.79 |

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Table 2.3

Viscosity data of PEG in DMSO at different temperatures

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<th>Density (g/cm(^3))</th>
<th>Viscosity (Cp)</th>
<th>Reduced Viscosity ((\eta_{rel}))</th>
<th>Reduced Viscosity ((\eta_{sp}/C))</th>
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<th>Concentration (mol dm⁻³)</th>
<th>Density (g/cm³)</th>
<th>Viscosity (Cp)</th>
<th>Relative Viscosity (η_{rel})</th>
<th>Reduced Viscosity (η_{sp}/C)</th>
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Because of this reason, the observed viscosity values is also in the same order. Hence it is expected that the hydrogen bonding between polymer and the solvent is responsible for increase in viscosity by causing the increase in radius of gyration overriding other solvent effects. A similar observation was made by Bagchi et al.\textsuperscript{5} from the ultrasonic and viscosity studies of ISRO POLYOL in various solvents. In the present study it is also clear that in each system the viscosity decreases with increase in temperature. Figs 2.9 - 2.11, illustrates how the relative viscosities (efflux times of solutions/efflux time of the pure solvent) can change for solutions of PEG as a function of polymer concentration, 'C' (mol/dm\textsuperscript{3}) in water, water + DMSO and pure DMSO at 30, 35, 40 and 45°C respectively.

The intrinsic viscosity, [\eta] and Huggin's constant K, were obtained from the Huggin's equation\textsuperscript{6},

\frac{\eta_{sp}}{C} = [\eta] + K[\eta]^2C \hspace{1cm} \text{2.10.}

Where \(\eta_{sp}\) is the specific viscosity (the relative increment solution viscosity over that of the solvent); \(\eta_{sp}/C\), the reduced viscosity; [\eta], the intrinsic viscosity, and C, the polymer concentration.
Fig. 2.9 Variation of relative viscosity ($\eta_{rel}$) with concentration (C) for EIG in $\text{H}_2\text{O}$.
Fig. 2.10: Variation of relative viscosity ($\eta_{rel}$) with concentration (C) for PEG in $H_2O + DMSO$ (50%, V/V) Mixture.
Fig. 2.11: Variation of relative Viscosity ($\eta_{rel}$) with concentration ($C$) for PEG in DMSO.
The intrinsic viscosities were obtained by extrapolating plots $\eta_{sp} / C$ versus $C$ to infinite dilution (see Fig. 2.12 as an example); while Huggin's constants 'K' were calculated from the slope of the plots (Table 2.4).

The Figs. 2.9 - 2.11 also indicate that the relative viscosity of polymer solution increases with concentration of polymer in all the three systems at different temperatures. These figures also reveal that the relative viscosities of polymer solution, decreases with increasing temperature.

From the above figures (2.6 - 2.11) it can be concluded that the viscosity of polymer solutions vary in the following order for the systems studied at any temperature

Water > Water + DMSO > DMSO

Intrinsic viscosity data used to calculate the equivalent hydrodynamic volume $V_e$, a measure of the size of a polymer molecule at infinite dilution where polymer coils behave essentially like hard spheres and do not interpenetrate\(^7,\)\(^8\). The following equation was used to obtain $V_e$: \[ V_e = \frac{kT}{6\pi\eta_0} \]
Fig. 2.12: Variation of reduced Viscosity ($\eta_{sp}/C$) with concentration (C) for PEG in DMSO at 40°C.
Table 2.4
Intrinsic viscosity $[\eta]$, Huggins Constant 'K', and Equivalent Hydrodynamic Volume 'Ve' of PEG in water, water + DMSO (50%, v/v) and DMSO at different temperatures.

<table>
<thead>
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<th>System</th>
<th>Temperature $^\circ$C</th>
<th>Intrinsic viscosity $[\eta]$</th>
<th>K</th>
<th>Hydrodynamic Volume $Ve \times 10^{19}$ (Cm$^3$/molecule)</th>
</tr>
</thead>
<tbody>
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<td>0.67</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>35</td>
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<td>45</td>
<td>160.0</td>
<td>0.14</td>
<td>6.4</td>
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<tr>
<td>PEG in water + DMSO (50%, v/v)</td>
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<tr>
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<td>95.0</td>
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<td>45</td>
<td>107.5</td>
<td>0.28</td>
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<tr>
<td>PEG in DMSO</td>
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<td>30.0</td>
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<td>45</td>
<td>50.0</td>
<td>2.50</td>
<td>2.0</td>
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</table>
\[ V_e = M[\eta] \nu N \quad \ldots \ldots \ 2.11. \]

where \( M \) is the molecular weight; \( N \), Avagadro's number; and \( \nu \), a shape factor - for spheres, \( 'v' \) is equal to 2.5.

Equivalent hydrodynamic volumes for the PEG in water, water + DMSO, and DMSO are given in Table 2.4. The values increase with increasing temperature. The larger the value obtained for PEG in water compared to water + DMSO and DMSO indicate that water is a good solvent compared to DMSO.

Dependence of Intrinsic Viscosity on Temperature

Papers discussing the dependence of molecular characteristics of water soluble non-ionic polymers are not numerous. The results of numerous theoretical works show that the intrinsic viscosity-temperature relation can be very complex\(^{10}\). Reasons for the viscosity variation with increasing temperature can be different, viz., ordering of segments and solvent molecules,\(^{11}\) dissolutions of macromolecules, conformational changes\(^{12}\) and helix-coil transactions.\(^{13}\)
REFERENCES


