

## **CHAPTER 4**

### **STUDIES ON SOLUTION PROPERTIES OF ACRYLAMIDE IN WATER -1,4-DIOXANE MIXTURES**

## 4.1 INTRODUCTION AND REVIEW OF PREVIOUS WORK

According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in first approximation only upon the volume concentration and the shapes of the suspended particles. By suitable application of such hydrodynamical considerations to solutions of long chain molecules, it is possible in a rough fashion to derive the Staudinger-Kraemer equation, denoting proportionality between specific or intrinsic viscosity and molecular weight [1]. It is an experimental fact, however, that the proportionality constant,  $K_m$ , is dependent not only upon the type of polymer concerned, but also upon the temperature and the nature of the solvent. The unperturbed dimension of a polymer chain is important in understanding the physical properties of the polymer both in solution as well as in the solid state. It is the dimension of the polymer chain where the volume exclusion due to long range segmental interaction is nullified by its interaction with a definite solvent ( $\theta$  solvent) [2]. The unperturbed dimension (UD) of a given polymer in a solvent does not depend on the nature of the solvent, as long as the solvent has no influence on the rotation of the chain segments [3, 4]. This is true in many cases, especially for nonpolar polymer-solvent pairs, but in the cases of polar polymer-polar solvent systems, the unperturbed dimension varies considerably with the nature of the solvent. Most of the polymeric materials are soluble only in a limited number of primary solvents, but they could be made soluble in all proportions in mixtures consisting of two or more solvents, which may be individually poor solvent for the polymers [5]. Several mixtures of nonsolvent are also known which produce good solvent systems or at least increase the solvency power of primary solvents [6]. Although some studies on the solution viscosity properties of polyacrylamide in water are available in the literature, similar studies in other solvents or cosolvent systems are surprisingly little [7-13]. The unperturbed dimension ( $K_\theta$ ) and the end-to-end dimension of polymer chain can be determined from the intrinsic viscosity measurement using the following equations [14,15]:

$$[\eta]_{\theta} = \Phi_0(r_0^2/M)^{3/2}M^{1/2}\alpha_n^3 = K_{\theta}M^{1/2}\alpha_n^3 \quad (32)$$

where  $\Phi_0$  is Flory's universal parameter ( $\Phi_0 = 2.5 \times 10^{23} \text{ mol}^{-1}$ ),  $M$  stands for molecular weight and  $r_0^2$  is the unperturbed mean square end- to-end distance. At theta temperature  $\alpha = \alpha_n = 1$ (where  $\alpha$  is molecular extension factor) and hence evaluation of  $K_{\theta}$  is possible from this equation. On the other hand, for evaluation of  $K_{\theta}$  from intrinsic viscosity at temperatures other than theta temperature, a number of equations have been proposed. These equations are shown below (where symbols have their usual meanings).

Fox and Flory (FF) equation [14]:

$$[\eta]^{2/3}/M^{1/3} = K_{\theta}^{2/3} + K_{\theta}^{5/3}C_T (M/[\eta]) \quad (33)$$

Kurata and Stockmayer(K-S) equation [15,16]:

$$[\eta]^{2/3}/M^{1/3} = K_{\theta}^{2/3} + 0.363\Phi B[g(\alpha_n) M^{2/3}/[\eta]]^{1/3} \quad (34)$$

Berry equation [17]:

$$([\eta]/M^{1/2})^{1/2} = K_{\theta}^{1/2} + 0.42K_{\theta}^{3/2}B(r_0^2/M)^{3/2}(M/[\eta]) \quad (35)$$

Burchard-Stockmayer and Fixman (B.S.F) equation [18,19]:

$$([\eta]/M)^{1/2} = K_{\theta} + 0.51\Phi BM^{1/2} \quad (36)$$

Inagaki-Suzuki-Kurata (ISK) equation [20]:

$$[\eta]^{4/5}/M^{2/5} = 0.786K_{\theta}^{4/5} + 0.454 K_{\theta}^{2/5} B^{2/3} \Phi^{2/3} M^{1/3} \quad (37)$$

Besides these, several other equations have also been reported [21-24]. According to the equations given above, the value of  $K_{\theta}$  is obtained from the intercepts on the ordinates of the plots of the quantity on the left-hand side

versus the function of  $M$  and  $[\eta]$  on the right hand side. Assuming Flory's limiting exponent and utilizing the first order perturbed results for the intrinsic viscosity and the friction coefficient ( $f$ ) of a flexible polymer Tanaka proposed [25]:

$$([\eta]/M)^{1/2} = K_{\theta}^{5/3} + 0.627\Phi_0^{5/3}(\langle R^2 \rangle_0/M)BM^{1/2} \quad (38)$$

and Bohdanecky derived the following equation [26]:

$$[\eta]/M^{1/2} = 0.80 K_{\theta} + 0.65 K_{\theta}K^{0.7}M^{0.35} \quad (39)$$

Qian and Rudin [27,28] described a method for predicting the thermodynamic properties of polymer solutions in which the radius of gyration ( $R_g$ ) is expressed as

$$R_g = 3[\eta]M/[9.3 \times 10^{24}(1+([\eta]-[\eta_0])(1-\exp(-C/C^*))/[\eta_0])]^{1/3} \quad (40)$$

where  $[\eta]$  and  $[\eta_0]$  are intrinsic viscosities in a given solvent and the same under  $\theta$  condition respectively and  $C$  is polymer concentration and  $C^*$  is the critical concentration (or overlap concentration) at which polymer molecules begin to overlap. This model was used for determining the unperturbed dimensions of polymethylmethacrylate with  $12.90 \times 10^6 < M_w < 23.84 \times 10^6$ . It is found that the calculated dimensions decrease with increasing polymer concentration upto a certain concentration; at higher concentrations the dimension remains constant for the same molecular weight and independent of the solvent type [29]. According to the literature, the relation put forwarded by Lenka and co-workers for the evaluation of the unperturbed dimensions (equation 41) has also been used for ultra high molecular weight polymers

$$6\langle S_0^2 \rangle^{1/2} = 2.204 \times 10^{-8}(M/C^*)^{1/3} \quad (41)$$

where  $C^*$  is the overlap point concentration of the polymer in number of solvents, obtained from viscometric data in the semi dilute concentration

regime where the macromolecular coils progressively contract and approach the unperturbed dimensions [30-32]. The unperturbed dimension of polystyrene and poly (2-vinylpyridine) have been measured by Dondos and Benoit [33] in solvent-precipitant mixtures of various compositions using the Stockmayer-Fixman representation. They obtained a linear relationship between  $K_\theta$  and  $\Delta G^E$  (the excess free enthalpy of mixing of the solvents) if, instead of using the bulk composition of the mixture, one introduces its "local" composition. This composition is calculated from the values of the preferential adsorption coefficient measured by light scattering.

In a resin solvent system, the change in temperature initiates conformational transition in polymer chains and the process of aggregation on precipitation was caused by such transitions [34-35]. Raju and Yaseen reported that the continuous decrease in limiting viscosity number of nylon-6 in m-cresol at temperatures ranging from 20° to 75°C was due to the contraction of the dimension of the polymer coil [36]. Quoting the view of other workers Haneczek and co-workers explained the partial helix-coil type polymer chain transition that occurs in polyamide-6 in solution. The results in higher value of limiting viscosity number of Nylon-6 in m-cresol at lower temperatures which in turn favours the dissolution, were also examined [37]. Chatfield reported that solvent power of an alcohol-ether mixture for nitrocellulose increases with lowering of temperature and at -50°C methyl alcohol alone became a solvent for cellulose ethers [38]. Recently Savas and Zuhail have determined the unperturbed dimension of anionically polymerized poly (p-tert-butyl-styrene) at various temperatures and found the theta temperature of the polymer to be of the order of 31.0° and 32.7°C in nitropropane and 2-octanol respectively [39]. Several other workers reported the conformational transition of polymers in solution with the change of temperature [40-41]. Coil dimension of polymethylmethacrylic acid in the cosolvent medium of CCl<sub>4</sub> and MeOH have been investigated by Maitra and co-worker [42]. They observed that the intrinsic viscosity exhibited a maximum for all fractions of polymers at a composition,  $\phi_{\text{MeOH}} = 0.33$  while the Huggins constant showed a minimum value at the same composition. The

experimental data for the solution properties of poly (N,N-dimethyl acrylamide) and poly (n-isopropylacrylamide) show that the hydrodynamic and configurational characteristics of these two polymers in methanol and water are different, showing a peculiar behaviour in water, which cannot be easily interpreted in terms of random coil structures. Chintore and co-workers found that the behaviour of poly (N-methylacrylamide) in aqueous solution was quite abnormal, as indicated by the values of second virial coefficients, lower than those measured in methanol solutions by the large difference of estimated unperturbed dimensions [43-44]. Therefore, the hypothesis was made that the solvation of N-substituted polyacrylamide by water would occur with large dipole interaction and/or hydrogen bonding with the structural units of the polymers in such a way as to give a large chain expansion with low chain flexibility, so that the polymer molecules could no more be treated as random coil in aqueous solutions. It has been pointed out that polyacrylamide, in which the lack of N-substitution increases the chances of intramolecular interactions has the highest unperturbed dimensions [45]. The aqueous solutions of polyacrylamide are suspected to contain fibrous aggregates of very high molecular weight. These aggregates were observed by electron microscopy and the disaggregation kinetics studied by viscometry [46-48]. This phenomenon is generally attributed to intermolecular hydrogen bonds and is evidenced by a significant decrease of viscosity with time. Boyadjian and co-workers have noticed differences of measured molecular weight by light scattering, according to the nature of the solvent and have concluded the presence of aggregates broken up by the effect of salt in pure water but not in formamide [49]. However, even for nonhydrolyzed polyacrylamide, there is a lack of reliable data in the literature concerning the chain conformation in salt-water solutions and its relation to intrinsic viscosity, particularly in the range of molecular weight of interest [50-51]. However, Francois and co-workers were successful in studying molecular weight dependence of radius of gyration, viscosity, sedimentation and diffusion on a set of fractions in the same range of molecular weight [52]. It has been shown recently that the unperturbed dimension of polyacrylamide could be determined by light scattering measurement in methanol-water system [53]. These authors concluded that the high value of the exponent (0.64) of the molecular weight dependence of

radius of gyration was not related to a great expansion of macromolecular coil and the determination of unperturbed dimension by extrapolation of viscosity measurements in good solvent at  $M \rightarrow 0$  ( $M = \text{mol. wt.}$ ) should be possible and works of Okada and Yamaguchi provided such data [54-55]. Fundamental parameters of poly (2-acrylamido-2-methyl propane sulfonamide), which is soluble in water and formamide are obtained by light scattering, osmometry and viscometry in these good solvents by Gooda and Huglin and the data have been analyzed by extrapolation procedures to yield the unperturbed dimensions, steric factor and characteristic ratio [56]. There was good accord between the values of these parameters, obtained directly and those derived indirectly, the mean values being  $8.73 \times 10^{-9} \text{cm.g}^{1/2}.\text{mol}^{1/2}$ , 4.07 and 32 respectively. Bohdanecky and co-workers investigated the solutions of polyacrylamide fractions (molecular weight 3300-800,000) in water at  $25^\circ\text{C}$  and in a mixed theta solvent at  $20^\circ\text{C}$  by light scattering, sedimentation and viscometry [13]. Measurement in water gave the configuration characteristic ratio  $C_\alpha = 8.5$ . The fundamental parameters of polyacrylamide obtained previously by viscometry in good solvent and in  $\theta$  solvents have been analyzed by viscosity- molecular weight relationship procedures suggested by several workers (Newman [57] and Misra [12]). High value of excluded volume exponent, as was observed in some cases, once thought to be the result of great expansion of polyacrylamide in aqueous solution as mentioned earlier. This arose doubts on the applicability of the method of extrapolation of the viscosity data in determining unperturbed dimension of the polymer in water. Further study, however, confirmed that high value of exponent of molecular weight dependence of the radius of gyration was not due to great expansion of the macromolecular coil in water and it is now believed that determination of unperturbed dimension by extrapolating viscosity data in good solvents is possible as has already been mentioned [53].

Bera and co-worker have determined the unperturbed dimension of polyacrylamide in water-dimethylsulphoxide mixtures at  $30\text{-}50^\circ\text{C}$  by different methods of extrapolation and found a minimum value of unperturbed dimension at  $\phi_{\text{DMSO}} = 0.5$  [58]. Simionescu, Chee and co-workers performed

viscosity measurement on solutions of polyvinylchloride resin in various plasticizers to calculate polymer-solvent interaction parameter, using Flory equation pertaining to the linear expansion factor of the coiling in the solution [59-62]. This information was then used to estimate lower critical solution temperature. Kathmann and McCormick synthesized and studied the dilute and semi-dilute solution behaviour of the terpolymers of sodium acrylate, acrylamide and the zwitterionic 4-(2-acrylamido-2-methylpropane dimethyl ammonio) butanoate [63]. The authors observed polyelectrolyte behaviour of the terpolymer at pH 8.5 and the viscosity of the solution decreased in the presence of added electrolyte. Hocking and co-workers measured the progressive influence on the hydrodynamic volume and other properties contributed by incorporation of N,N dimethylacrylamide into a series of high molecular weight acrylamide copolymers [64]. Aqueous solution of these polymers showed little or no decrease of radius of gyration when low concentration of sodium chloride were added, in contrast to its effect on solutions of polyacrylamide itself. Shanks and Wu measured the viscosity of polyacrylamide dilute solutions in water with acetone, ethanol, dimethylformamide and ethylene glycol as cosolvent to study the conformation of polymer chains and the degree of polymer solvent interaction [65]. It was found that polymer chain conformation contracted as the acetone, ethanol and the DMF cosolvent composition ratio increased but there was no distinguishing difference of contraction in case of water-ethylene glycol compositions. Alorio and co-workers reported relationship between intrinsic viscosity and molecular weight for narrow molecular weight distribution of polyisoprene and polystyrene samples in  $\text{CCl}_4$  at  $25^\circ\text{C}$  [66]. Conclusions drawn from viscometry that  $\text{CCl}_4$  was a good solvent for both the polymers was also supported by the second virial coefficient from low-angle light scattering measurements. Azim and Huglin measured the intrinsic viscosities of different fractions of polystyrene (PS) at  $98.5^\circ\text{C}$  in the mixtures of methylcellulose (MC) and 1, 2, 3, 4-tetrahydronaphthalene over the whole range of solvent compositions [67]. The theta temperature of PS was measured as  $98.5^\circ\text{C}$  in MC. Solution viscosities of the copolymers and homopolymers of acrylamide were determined at 30, 40, and  $50^\circ\text{C}$  by Rakshit and co-workers [68]. The activation parameters of viscous flow, voluminosity,

and shape factor were also calculated. The average shape factor was observed to be nearly 2.5 for all the copolymer systems. Viscosity average molecular weights were calculated, and from the intramolecular expansion factor it was observed that copolymers were less flexible than that of homopolymers. The  $dn/dc$  values obtained from differential refractometry were in good agreement with those calculated theoretically. Rakshit and co-workers [69] also used the viscosity data to calculate the volume related parameter  $V_E$  of the polymer. Recently it has been used to determine the shape of protein and some other acrylate copolymers in solution.  $V_E$  is calculated by plotting  $Y$  against concentration  $C$ , where,

$$Y = (\eta_r^{1/2} - 1) / [C (1.35\eta_r^{1/2} - 0.1)], \quad (\eta_r \text{ is relative viscosity}) \quad (42)$$

From the plot,  $V_E$  is obtained as an intercept since

$$\text{Lt}_{C \rightarrow 0} Y = V_E. \quad (43)$$

The shape factor  $\gamma$  is calculated from the following relation [70]:

$$[\eta] = \gamma V_E. \quad (44)$$

The value of  $\gamma$  has been shown to be 2.5 for spherical particles [71]

In the present study, an Ubbelohde viscometer was used to measure the relative viscosities of polymer solutions (detail in experimental section 3.1.2).

The related definitions are as follow:

$$\text{Specific viscosity, } \eta_{sp} = (t - t_0)/t_0 \quad (45)$$

$$\text{Reduced viscosity, } \eta_{red} = \eta_{sp}/C \quad (46)$$

$$\text{Intrinsic viscosity, } [\eta] = (\eta_{sp}/C)_{C \rightarrow 0} \quad (47)$$

and the Huggins equation is  $\eta_{sp}/C = [\eta] + K_H [\eta]^2 C$ , (48)

where  $K_H$  is the Huggins constant. In the above relations, the symbol  $\eta$  refers to the viscosity of solution,  $t$  is the efflux time of the solution,  $t_0$  is the efflux time of solvent and  $C$  is the polymer concentration. For a linear relationship between  $\eta_{red}$  and  $C$ ,  $K_H [\eta]^2$  is the slope and  $[\eta]$  is the intercept.

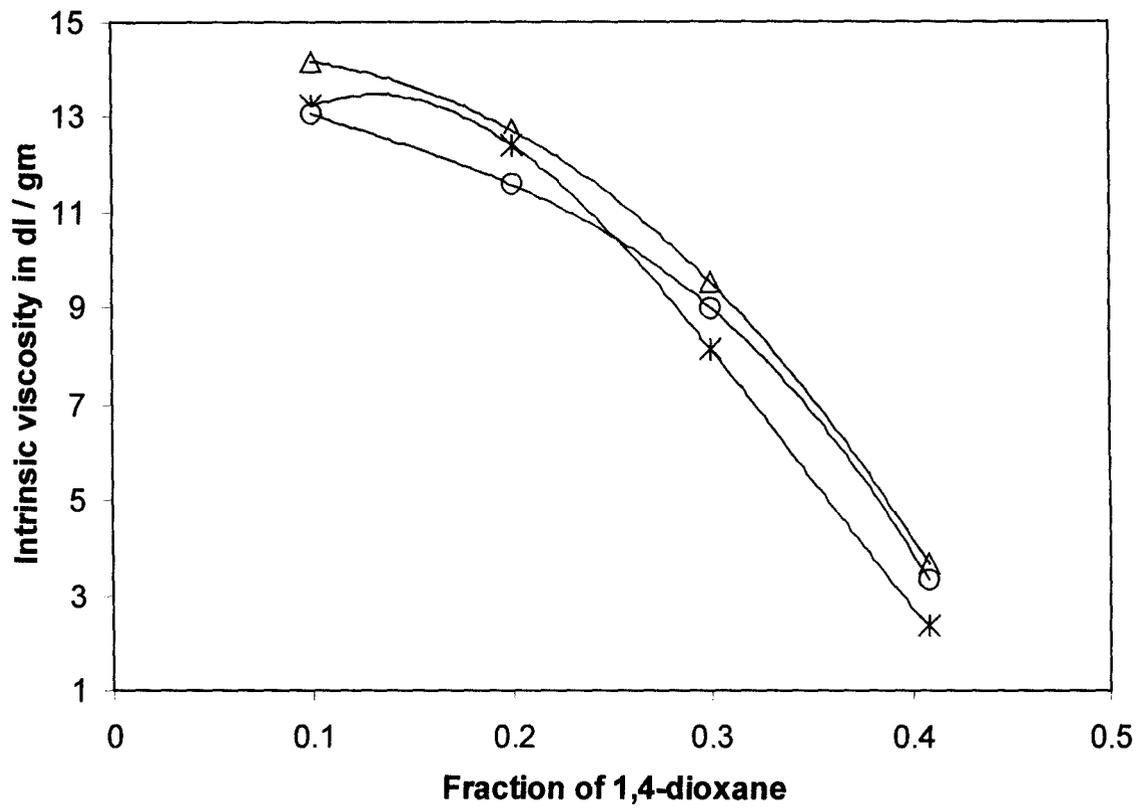
In the present section, the results of our investigation on unperturbed dimension, interaction parameter and related aspects of unhydrolyzed polyacrylamide in water-1,4-Dioxane mixtures have been described. The intrinsic viscosities of the polymer have been measured for different types of the polymer (viz., type-A, type-B, and type-C) in different compositions (water-1,4-Dioxane) of the cosolvent mixture at different temperatures. In the previous chapter, the technique by which the molecular weight of PAM in aqueous solution may be controlled by trapping the initiator component in the interlayer space of vermiculite is reported. This method has been adopted selectively to prepare polymers of varying molecular weights for the studies on solution property, presented in this section of the chapter. Low molecular weight polymers (viscosity average molecular weight  $2.3 \times 10^5$ , type-C) were prepared via redox polymerization of acrylamide monomer initiated by  $FeCl_3$  and thiourea redox system at  $50^\circ C$ . To obtain medium molecular weight polymers (viscosity average molecular weight  $1.6 \times 10^6$ , type-B), 0.4 M monomer and 0.06 M TU in aqueous suspension of ferric vermiculite (FeV) were used at  $60^\circ C$  temperature and at pH 1.98. Details are given in section 3.1 of this chapter. High molecular weight polymer (viscosity average molecular weight  $8.9 \times 10^6$ , type-A) was purchased from Acros Organics (Belgium). From the relation between  $[\eta]$  and  $M$ , the unperturbed dimension and molecular expansion factor have been measured. The Huggins constant value in each case was also determined in order to study the influence of cosolvent system on the aggregation of the polymer.

## 4.2 RESULTS AND DISCUSSION

### Intrinsic viscosity

The nature of interaction between liquids governs the solubility of a polymer in binary liquid mixtures. The changes in molecular dimension of the polymer in these systems are manifested in the varied molecular extension parameters and the unperturbed dimension due to the interaction with two component liquid mixtures. 1,4-Dioxane (DO) is a non-hydrogen bonded cyclic ether, miscible with water in all proportions and the boiling point of which (101.3°C) is close to that of water. The dipole moment of DO is close to zero (0.45D) and the dielectric constant is 2.2. The  $E_N^T$  values, which are values of an empirical parameter of solvent polarity, are remarkably decreased for aqueous mixtures of DO at about  $\phi_{DO}$  value of 0.2. Miscible solvents are mixed homogeneously, but solvents are not homogeneous at the microscopic level, as has been observed by X-ray diffraction and small angle neutron scattering measurements. Mixed solvents aggregate with similar molecules and form microscopic solvent clusters. The water structures persist in the mixture up to about 30 wt% DO and that beyond this the mixed solvent behaves like an ordinary liquid. Therefore, when a solute is dissolved in a mixed solvent, it is preferentially solvated by solvent molecules composing the mixed solvents. Viscosity vs. fraction of DO plot in mixed solvent shows that there is a maxima at around  $\phi_{DO} = 0.235$  (Figure 4.1-4.3).

In general for a flexible polymer in poor solvent, the intrinsic viscosity increases with rise in temperature, whereas in good solvent it decreases with temperature. In athermal solvent, however, it is independent of temperature [72]. The polymer chains are expanded most at the temperature at which  $[\eta]$  is maximum. The variation of  $[\eta]$  of all three types of polymer at different temperatures and solution compositions are shown in Figure 4.1-4.3. The result shows that with increasing the amount of nonsolvent (DO) up to a certain limit, intrinsic viscosity also increases for two types (B&C) of PAM. This variation is, however, distinguishable from the



**Figure 4.1:** Change in intrinsic viscosity with fraction of dioxane for PAM (Type A)  
△ 303K   ✖ 313K   ○ 323K

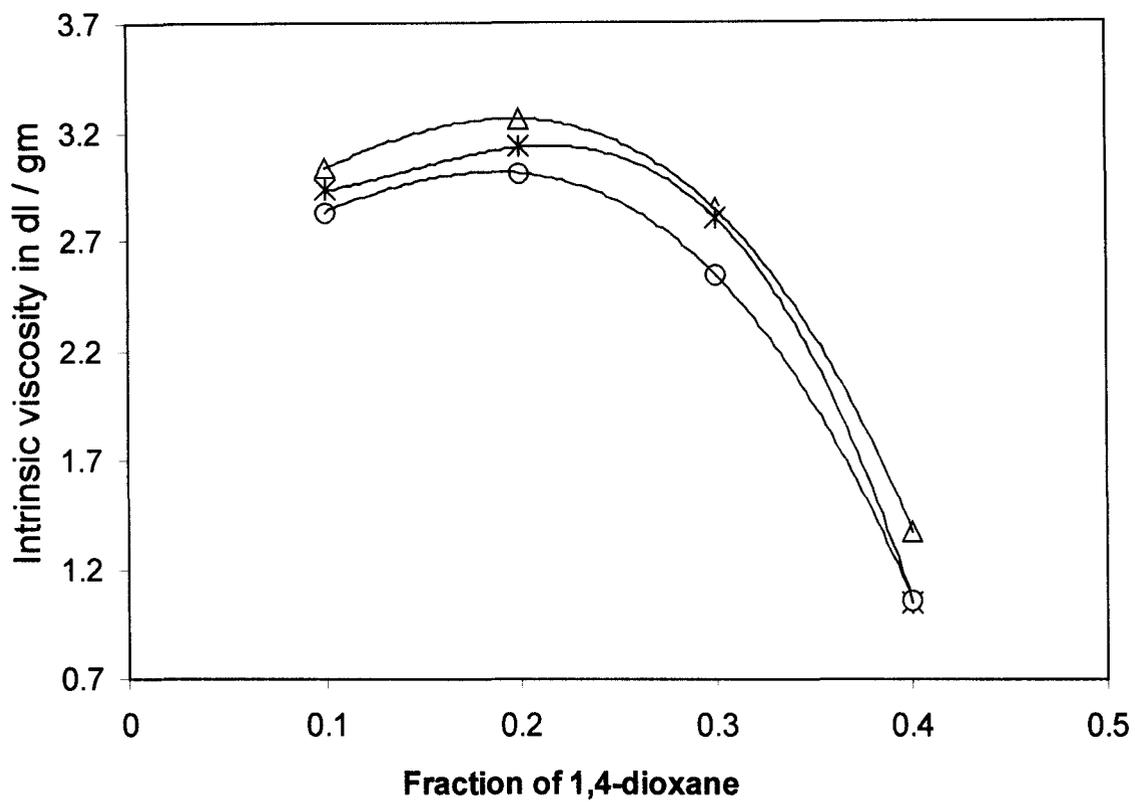
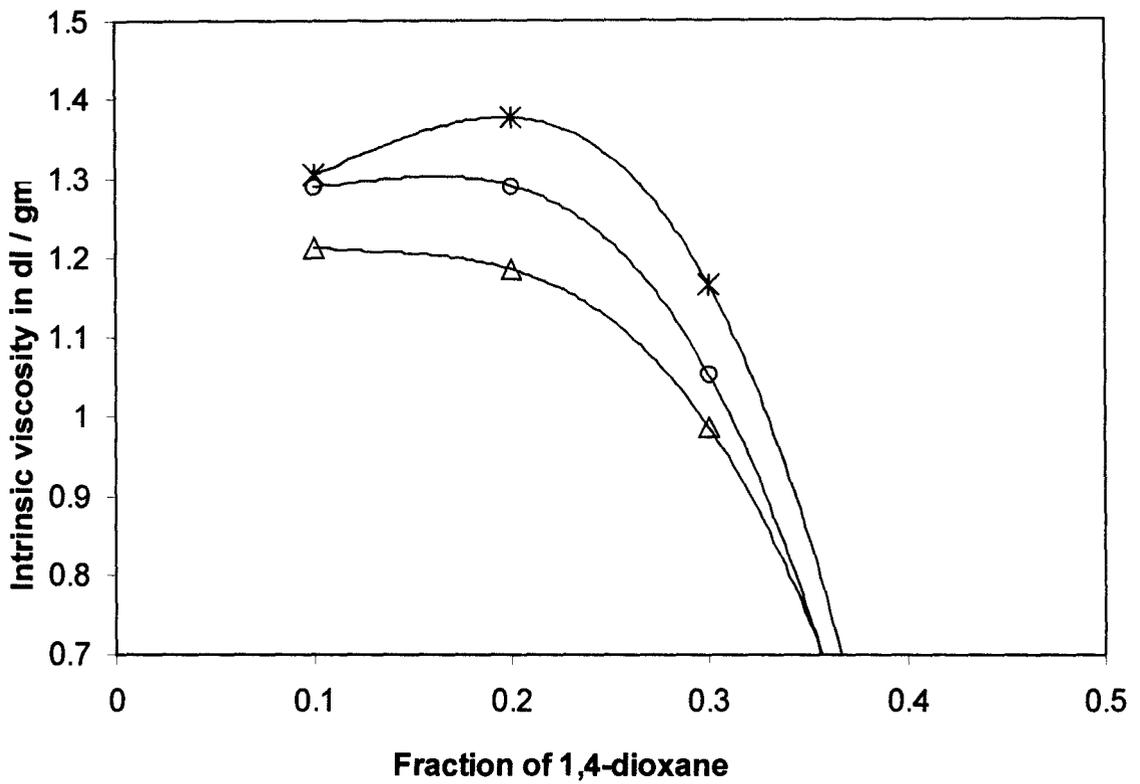


Figure 4.2: Change in intrinsic viscosity with fraction of dioxane for PAM (Type B)

△ 303K \* 313K ○ 323K



**Figure 4.3:** Change in intrinsic viscosity with fraction of dioxane for PAM (Type C)

$\Delta$  303K  $\times$  313K  $\circ$  323K

variation observed in case of a pure solvent system. Intrinsic viscosity reaches its maximum value near  $\phi_{DO} = 0.2$  for the polymers of type-B and type-C. This indicates that energetically the most favourable solvent composition is same for two different types of PAM. The decrease in  $[\eta]$  after the maximum is explained by the decrease in unperturbed mean square end-to-end distance. At a higher co-solvency condition, the energetic weighting factor favours the extended configuration of the polymer molecules. For type-A PAM, however, there is no maxima in the plot of  $[\eta]$  vs.  $\phi_{DO}$ . The  $[\eta]$  for type-A PAM is found to decrease with an increase in the DO content in the solvent mixtures. The result may be attributed to the lack of co-solvency effect of this PAM due to very high molecular weight. Moreover the effect of temperature on  $[\eta]$  is also different from that of other two PAM's. An Increase in the temperature of a polymer solution generates two antagonistic effects [73, 74]. This is apparent in case of type-A PAM at higher concentration of DO. Firstly, an increase in temperature generally leads to an increase in the solubility and this result in uncoiling of the polymer chain leading to an increase in intrinsic viscosity with temperature. Secondly, an increase in temperature may lower the rotational barrier, thereby enhancing the degree of rotation about a skeletal bond, forcing the molecular chains to assume more compact coiled configuration. This leads to decrease in intrinsic viscosity with increase in temperature.

The cosolvency and the intermolecular interaction of polymers are also manifested in the Huggins constant values when the composition of the solvent is varied.  $K_H$  values are used to predict the degree of interaction between polymer and the solvent. The sign of  $K_H$  is also often taken as a measure of the type of interaction in the polymer chain. The general positive nature of the  $K_H$  values and their increase with ionic strength of the medium indicate enhanced interunit attractive interactions. Values of Huggins constant are presented in Table 4.1. The  $K_H$  values are calculated from the least square slopes of equation 48. It is observed that  $K_H$  values are maximum at the solvent composition,  $\phi_{DO} = 0.3$  for all the types of polymers and it increases with an increase in the molecular weight of the polymer indicating higher

tendency of intermolecular aggregation for higher molecular weight fractions of the polymers.  $K_H$  is the smallest and negative at  $\phi_{DO} = 0.4$  and under this condition, DO pulls the distance between polymer molecules closer to make polymer side chains twisted around each other. This action makes polymer main chain wind around polymer side chain and agglomerate.

### Unperturbed dimension (UD)

The UD of a polymer chain is the dimension where volume exclusion due to long-range segmental interaction is nullified by its interaction with a definite solvent (theta solvent) [21]. UD is the end-to-end distance of the polymer chain under theta condition and can be determined from intrinsic viscosity measurement at this condition using the equation 32. But, under non-theta conditions various equations are employed to derive  $K_\theta$  of PAM in different water-DO mixtures. The value of  $K_\theta$  obtained from three different methods of measurements viz., BSF, I-S-K and Berry agree well with each other except in a few compositions of the solvents. The results are summarized in Table 4.2. The BSF plots for PAM fractions for various cosolvent compositions at 30°C, 40°C and 50°C are shown in Figures 4.4-4.15. It is apparent that at  $\phi_{DO} = 0.4$ , the polymer has the lowest unperturbed dimension and this result is in general true for all the adopted methods for  $K_\theta$  calculation. Above the  $\phi_{DO}$  value of 0.4 the cosolvency of the system is lost and the polymer is precipitated out from the solution. At  $\phi_{DO} = 0.2$ , the polymer shows highest  $K_\theta$  for all the methods of calculation. The effect of temperature is interesting. With an increase in temperature,  $r_0^2$  and hence  $K_\theta$ , decrease due to greater freedom of rotation around the skeletal bonds [21]. However, such a temperature dependence of  $K_\theta$  can be attributed not only to the change in flexibility of macromolecular chain but also to the specific polymer solvent interaction [34]. The effect may also be correlated to the cohesive energy density of the polymer and the solvent [33].

### Temperature coefficient of unperturbed dimension (K')

The effect of temperature on UD can be attributed to the change in flexibility of a macromolecular chain as well as to polymer solvent interactions. Some solvents at certain temperatures hinder internal rotations in macromolecules due to favourable interactions, which lead to expanded uncoiled conformation of the polymer. Previous workers attributed this variation in UD to the specific solvent effect resulting from hydrogen bonding or other polar interactions [68]. In the case of mixed solvents, preferential adsorption leads to similar observations and the effects are correlated to cohesive energy density of the polymer and the solvent. Unperturbed dimension ( $K_\theta$ ) is related to statistical parameter ( $r_o^2$ ) and unperturbed mean square end-to-end distance by Flory equation as follows:

$$K_\theta = \phi_o [r_o^2/M_w]^{3/2} \quad (49)$$

On differentiating equation 49 with respect to T, the temperature coefficient of unperturbed dimension may be obtained.

$$d\ln K_\theta/dT = 3/2[d\ln(r_o^2)/dT] = K' \quad (50)$$

Here  $K'$ , the temperature coefficient of unperturbed dimension, provides information regarding the configuration dependent properties of polymer chain and energies of bond conformation in the molecule [75].

From the Table 4.3 it is seen that the value of  $K'$  changes with solvent composition. Depending upon the composition of polymer-solvent system,  $K'$  assumes positive, zero or negative value. The negative values of  $K'$  for these systems indicate that the PAM molecules have more compact and high energy configuration in these solvent mixtures. Due to the above reasons, the configurationally dependent properties of PAM molecular chain and the energetic of bond configuration in water-DO mixtures were adversely affected at higher temperatures.

### Molecular extension factor ( $\alpha_n$ )

The molecular extension factor ( $\alpha_n$ ), which represents the effect of long-range interaction, can be described as an osmotic swelling of the chain by the solvent-polymer interaction.

$\alpha_n$  has been calculated from the relation given below[42]:

$$\alpha_n^3 = [\eta]/K_\theta M_v^{1/2}, \quad (51)$$

where  $K_\theta$  has been taken from the BSF plot.

The actual end-to-end distance,  $\alpha_n K_\theta$ , of the polymer molecule is also computed, which is shown in Table 4.4. It is observed that  $\alpha_n K_\theta$  attains its lowest value at  $\phi_{DO} = 0.4$ . It attains its highest value at  $\phi_{DO} = 0.2$  for all fractions of the polymer.

### Chain rigidity

The characteristic ratio ( $C_\alpha$ ), which serves as a measure of short-range interactions such as bond angle restrictions and steric hindrances, are also influenced by the torques exerted on the chain by solvent molecules. This effect is, however, small in many cases. The characteristic ratio ( $C_\alpha$ ) is a parameter that compares the unperturbed mean square end-to-end distance to the dimension of the chain if each segment was freely jointed. Steric factor ( $\sigma$ ) the characteristic ratio ( $C_\alpha$ ) and  $[\langle r_o^2 \rangle / M]^{1/2}$  are calculated in the usual manner from the following equations [76].

$$\sigma = [\langle r^2 \rangle_o / M]^{1/2} / [\langle r^2 \rangle_{of} / M]^{1/2} \quad (52)$$

$$[\langle r^2 \rangle_{of} / M]^{1/2} = [\langle r^2 \rangle_{of} / N]^{1/2} [1/M_o]^{1/2} \quad (53)$$

$$C_\alpha = [K_\theta / \Phi_o]^{2/3} (M_o / 2L^2) \quad (54)$$

Where  $\langle r^2 \rangle_{of}$  is the unperturbed mean square end-to-end distance for a freely rotating chain,  $N$  is the degree of polymerization,  $M_o$  is the molecular weight of the monomer unit and  $L$  is the backbone bond length ( $L = 0.154\text{nm}$ ). For vinyl polymers the value of  $[\langle r^2 \rangle_{of}/N]^{1/2} = 3.08 \times 10^{-8} \text{ cm}$  [77]. The computed values of  $\sigma$ ,  $C_\alpha$ , and  $[r_o^2/M]^{1/2}$  for PAM at different solvent compositions and temperatures are given in the Table 4.5. Cowie observed that the range of the values of  $\sigma$  normally encountered, is about 1.5 to 2.5. In a previous study with water-DMSO mixtures the values of  $\sigma$  were found to be within 1.07 to 2.36 [78]. In the present study it ranged between 1.74 and 2.89. The  $\sigma$  values are found to decrease initially with  $\phi_{DO}$  and then increase giving rise to the highest value at  $\phi_{DO} = 0.4$  indicating the highest rigidity of the polymer at this solvent composition.  $C_\alpha$  values indicate that short range interactions are maximum at  $\phi_{DO} = 0.2$ . The  $C_\alpha$  value decreases at higher  $\phi$ 's and reaches its minimum at  $\phi_{DO} = 0.4$ .

### Volume related parameter ( $V_E$ )

Volume related parameter ( $V_E$ ) is obtained from the intercept of the straight line of plot of  $Y$  vs. concentration as shown in the Figure 4.16 according to the equation no 42. The volume related parameter is a function of temperature and a measure of volume of the solvated polymer molecules. Computed data of  $V_E$  and  $\gamma$  are shown in Table 4.6. The table shows that as the temperature increases the solvation of polymer molecule decreases and hence  $V_E$  decreases. This is true in most of the cases except for the polymer of type-A. It is to be noted that as the molecular weight decreases the solvated volume becomes smaller. A poor solvent system leads to the less solvation of the polymer molecules, and hence the nature of variation of  $V_E$  is almost similar to the nature of variation of  $[\eta]$  with  $\phi_{DO}$ . The shape factor  $\gamma$  gives an idea about the shape of the polymer molecules in solution [79]. Ideally it is 2.5 for spherical particles. Rakshit and co-workers suggested the conformation of hydrolyzed PAM to be other than spherical ( $\gamma = 2.5\text{-}8.7$ ) [80]. It is interesting to note that  $\gamma$  values of unhydrolyzed PAM in the present study are very close to 2.5 and are not affected by solvent, molecular weight and the temperature of the system. This indicates that unhydrolyzed PAM molecules have spherical structures in solution.

**Table 4.1**

Huggins constant of different fractions of PAM at different temperature and various solvent compositions

Temp. in °C	$\Phi_{DO}$	Polymer		
		Type-A $K_H$	Type-B $K_H$	Type-C $K_H$
30	0.1	2.75	1.82	1.19
	0.2	4.35	1.85	0.92
	0.3	8.04	1.99	1.75
	0.4	-0.23	-0.06	-0.35
40	0.1	2.06	1.62	1.02
	0.2	4.44	1.31	1.10
	0.3	8.10	2.00	0.69
	0.4	-0.28	-0.04	-0.05
50	0.1	1.46	1.66	0.95
	0.2	3.87	1.84	0.77
	0.3	4.75	2.29	1.82
	0.4	-0.09	-0.16	-0.007

**Table 4.2**

Unperturbed Dimension of PAM in various solvent compositions at different temperatures and methods

Temp. in °C	$\phi_{DO}$	$K_0 \times 10 \text{ ( cm}^3 \text{g}^{-3/2} \text{ mol}^{1/2} \text{)}$		
		B-S-F	I-S-K	BERRY
30	0.1	1.68	1.27	1.67
	0.2	1.86	1.49	1.83
	0.3	1.70	1.45	1.68
	0.4	0.75	0.63	0.73
40	0.1	1.91	1.57	1.92
	0.2	2.25	1.97	2.25
	0.3	2.05	1.87	2.03
	0.4	0.69	0.66	0.69
50	0.1	1.84	1.51	1.91
	0.2	2.13	1.88	2.13
	0.3	1.78	1.59	1.78
	0.4	0.50	0.38	0.48

**Table 4.3**

Temperature co-efficients of Unperturbed Dimension in various solvent compositions

$\phi_{DO}$	$K' \text{ (degree}^{-1} \text{)}$
0.1	-0.0033
0.2	-0.0038
0.3	-0.0066
0.4	-0.0196

**Table 4.4**

Molecular extension factor and coil dimensions of PAM at different temperatures in various solvent compositions

Temp. in °C	$\phi_{DO}$	Polymer					
		Type-A		Type-B		Type-C	
		$\alpha_n$	$\alpha_n \times K_{\theta} \times 10$	$\alpha_n$	$\alpha_n \times K_{\theta} \times 10$	$\alpha_n$	$\alpha_n \times K_{\theta} \times 10$
30	0.1	1.41	2.37	1.12	1.88	1.14	1.91
	0.2	1.31	2.44	1.11	2.06	1.09	2.03
	0.3	1.23	2.09	1.09	1.85	1.06	1.80
	0.4	1.19	0.89	1.13	0.85	1.00	0.75
40	0.1	1.32	2.52	1.06	2.02	1.12	2.14
	0.2	1.22	2.75	1.04	2.34	1.08	2.43
	0.3	1.20	2.46	1.02	2.09	1.05	2.15
	0.4	1.04	0.72	1.06	0.73	0.99	0.68
50	0.1	1.33	2.44	1.06	1.95	1.13	2.08
	0.2	1.22	2.59	1.04	2.21	1.08	2.30
	0.3	1.19	2.12	1.04	1.85	1.06	1.88
	0.4	1.30	0.65	1.18	0.59	1.04	0.52

**Table 4.5**

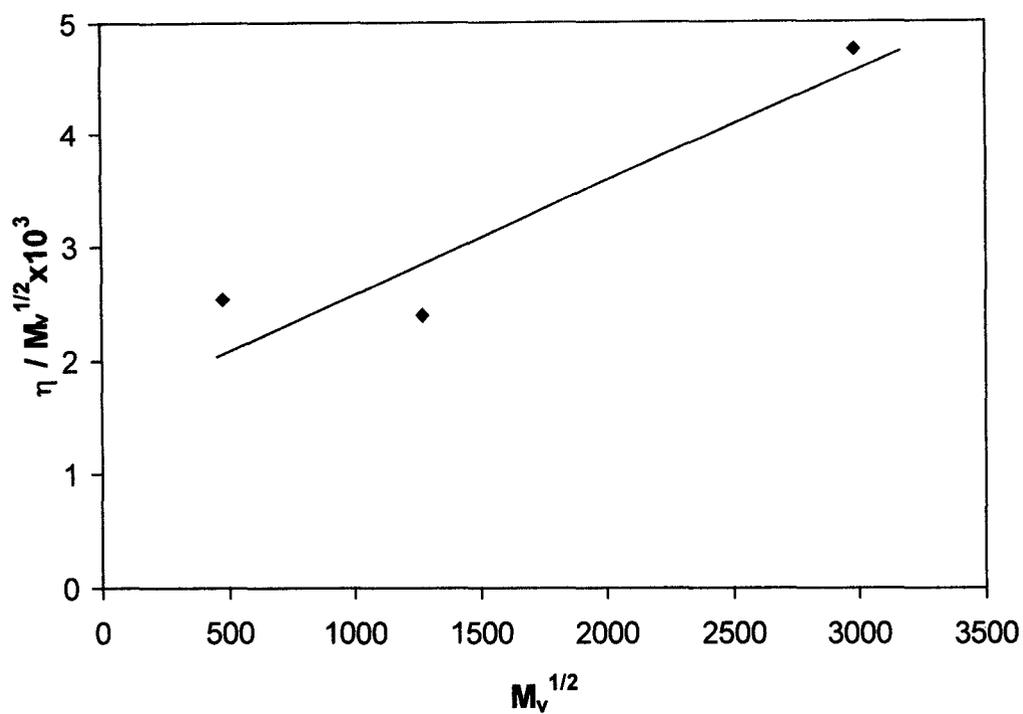
Steric Factor, Characteristic Ratio and Unperturbed Dimension (in  $\text{cm.g}^{-1/2}$   $\text{mol}^{1/2}$ ) of PAM as a function of DO fraction and temperature

Temp. in °C	$\Phi_{\text{DO}}$	$r_0^2/M^{1/2} \times 10^9$	$C_\alpha$	$\sigma$
30	0.1	2.00	9.25	1.82
	0.2	2.09	10.12	1.74
	0.3	2.03	9.53	1.80
	0.4	1.43	4.75	2.55
40	0.1	1.98	9.10	1.84
	0.2	2.07	9.97	1.76
	0.3	2.02	9.46	1.80
	0.4	1.45	4.83	2.52
50	0.1	1.96	8.85	1.86
	0.2	2.04	9.61	1.78
	0.3	1.94	8.72	1.88
	0.4	1.26	3.66	2.89

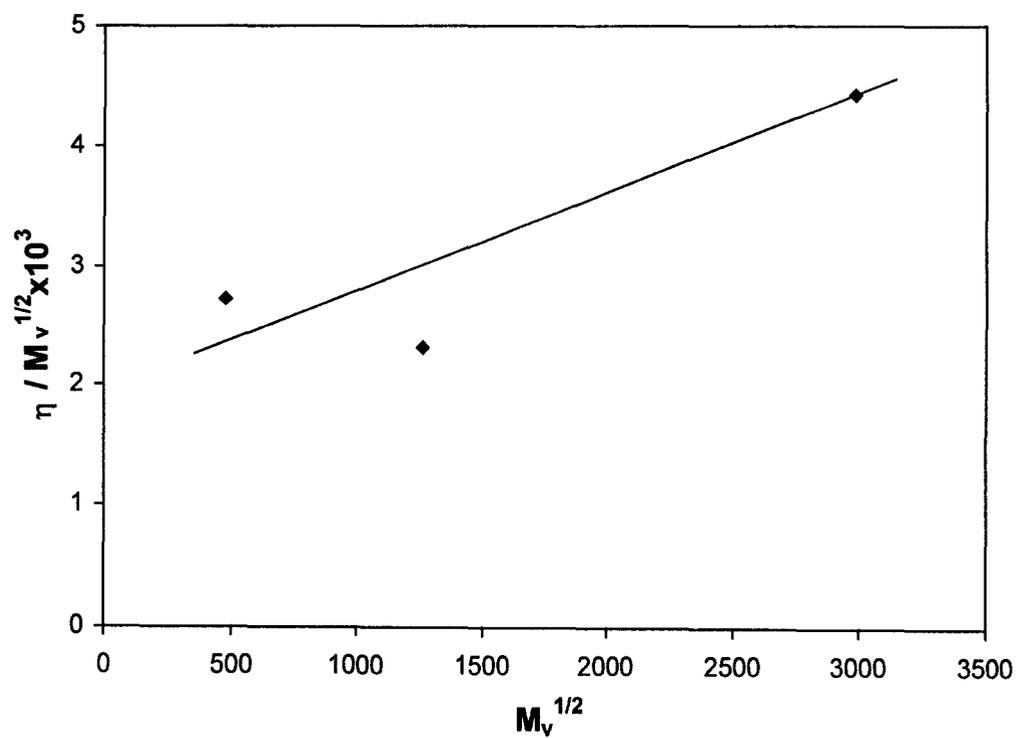
**Table 4.6**

Volume related Parameter and Shape Factor values of PAM in different solvent compositions and temperature

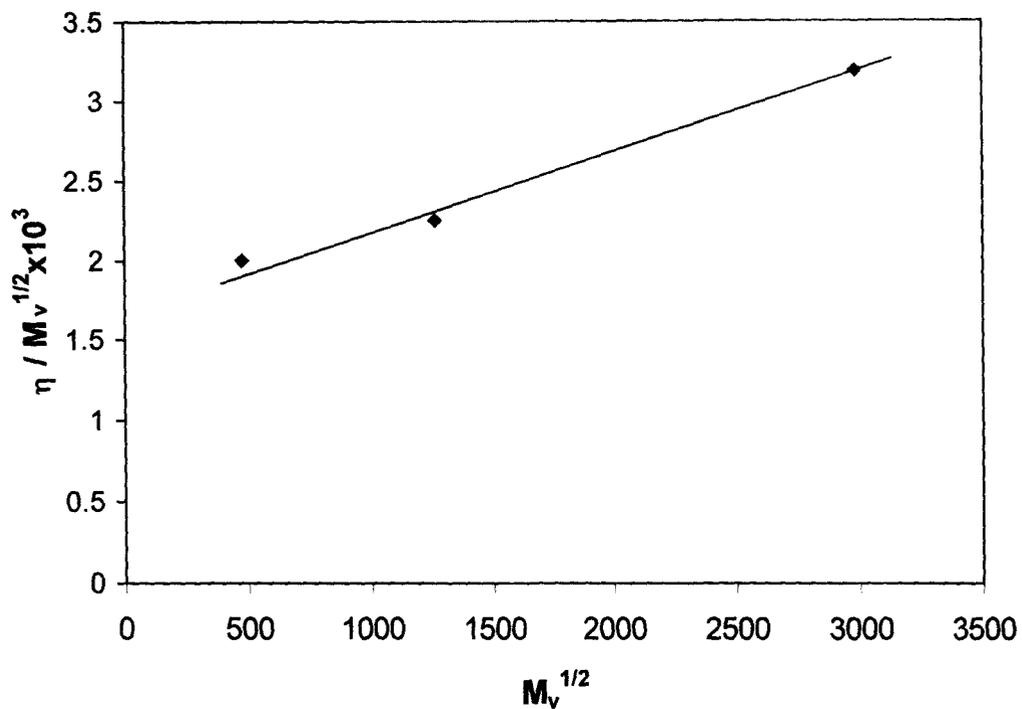
Temp. in °C	$\Phi_{DO}$	Polumer					
		Type-A		Type-B		Type-C	
		$V_E$	$\gamma$	$V_E$	$\gamma$	$V_E$	$\gamma$
30	0.1	3.84	3.68	1.47	2.48	0.39	1.96
	0.2	4.31	2.95	2.37	1.53	0.56	2.54
	0.3	4.08	2.34	1.40	2.52	0.60	2.84
	0.4	2.74	0.86	1.11	2.48	0.59	3.06
40	0.1	4.02	3.28	1.17	2.30	0.40	2.12
	0.2	4.68	2.64	1.56	1.87	0.53	2.58
	0.3	4.38	2.09	1.40	2.51	0.58	2.88
	0.4	2.36	0.84	1.04	2.24	0.64	3.06
50	0.1	3.71	3.51	1.36	2.37	0.32	2.53
	0.2	4.04	2.87	1.15	2.20	0.46	2.81
	0.3	3.64	2.46	1.17	2.37	0.48	2.88
	0.4	2.23	0.80	1.03	2.32	0.56	2.73



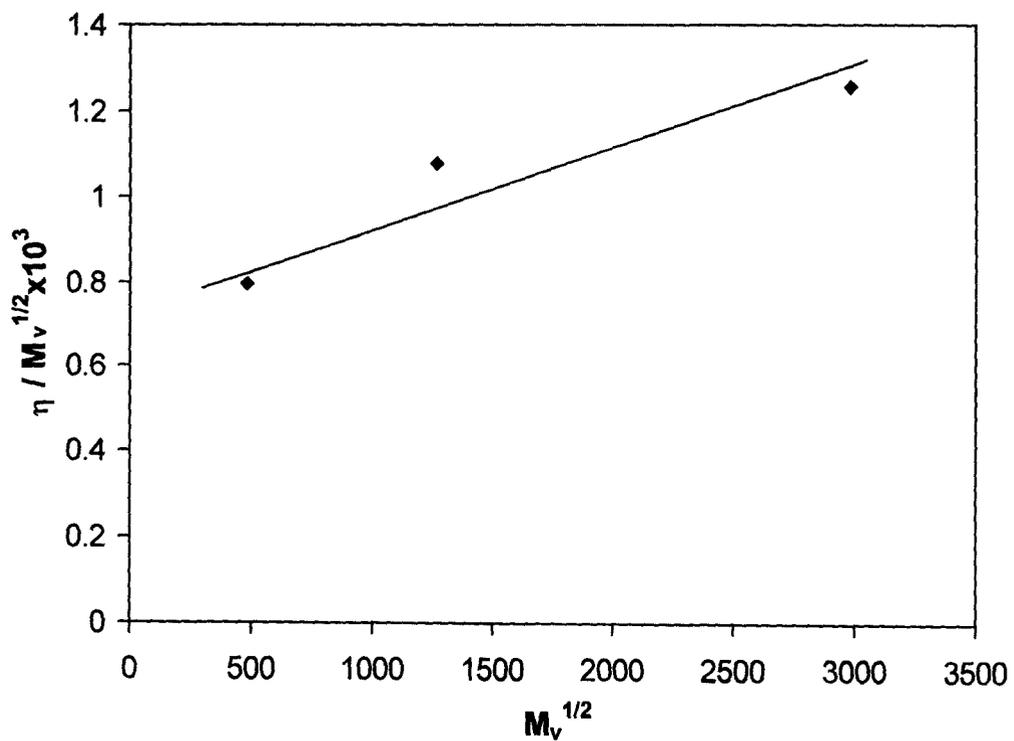
**Figure 4.4:** BSF plot at 30°C:  $\phi_{DO} = 0.1$



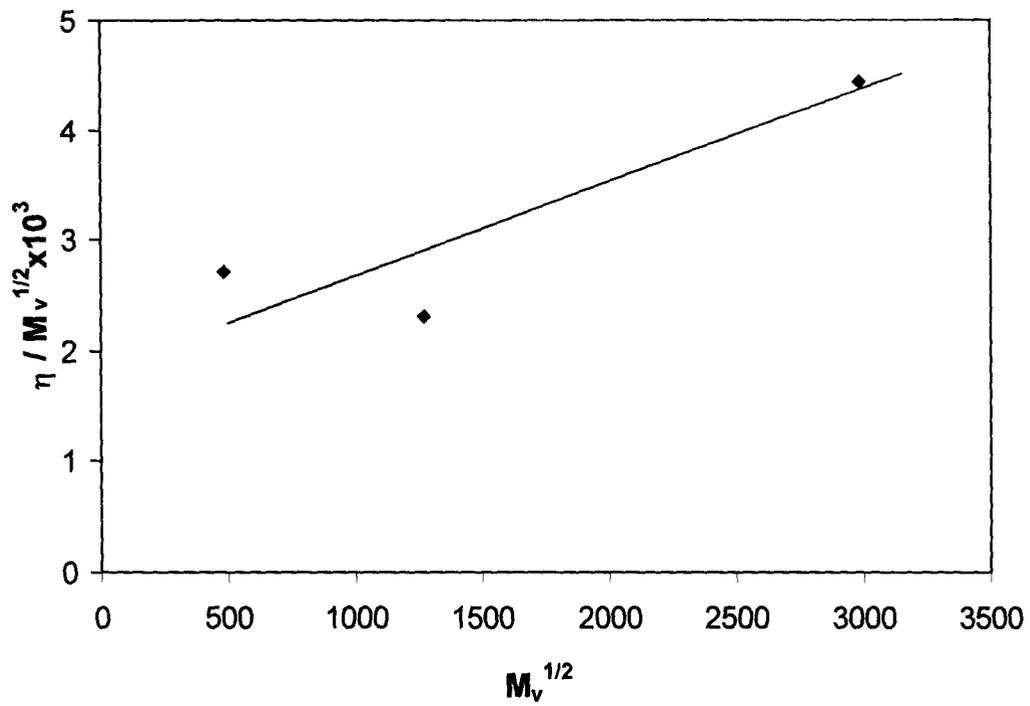
**Figure 4.5:** BSF plot at 30°C:  $\phi_{DO} = 0.2$



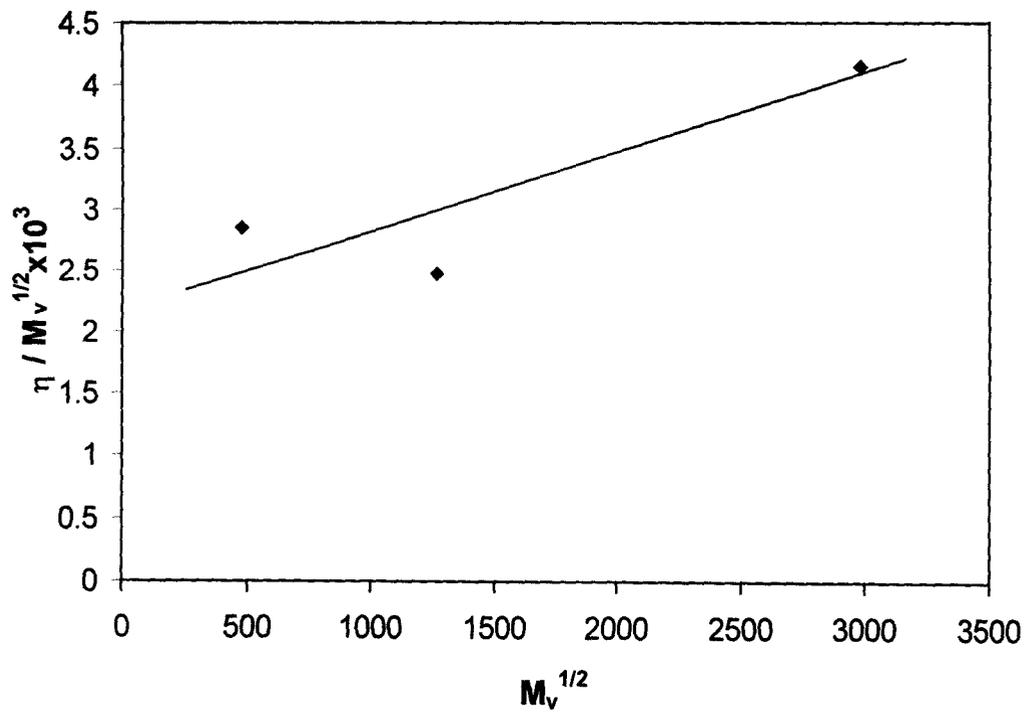
**Figure 4.6:** BSF plot at 30°C:  $\phi_{DO} = 0.3$



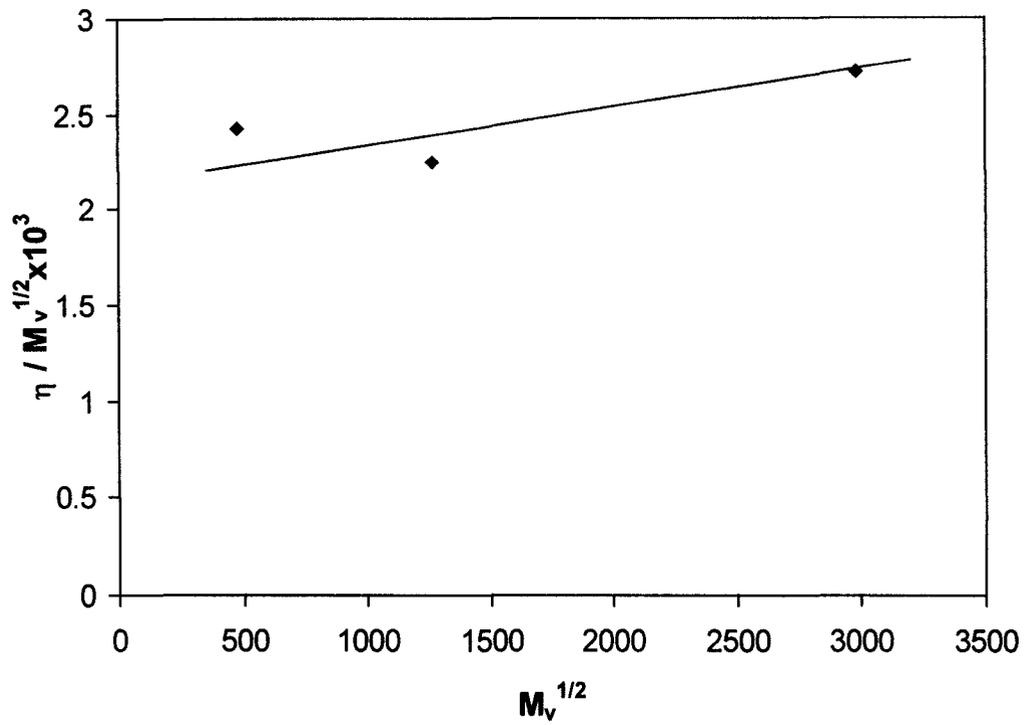
**Figure 4.7:** BSF plot at 30°C:  $\phi_{DO} = 0.4$



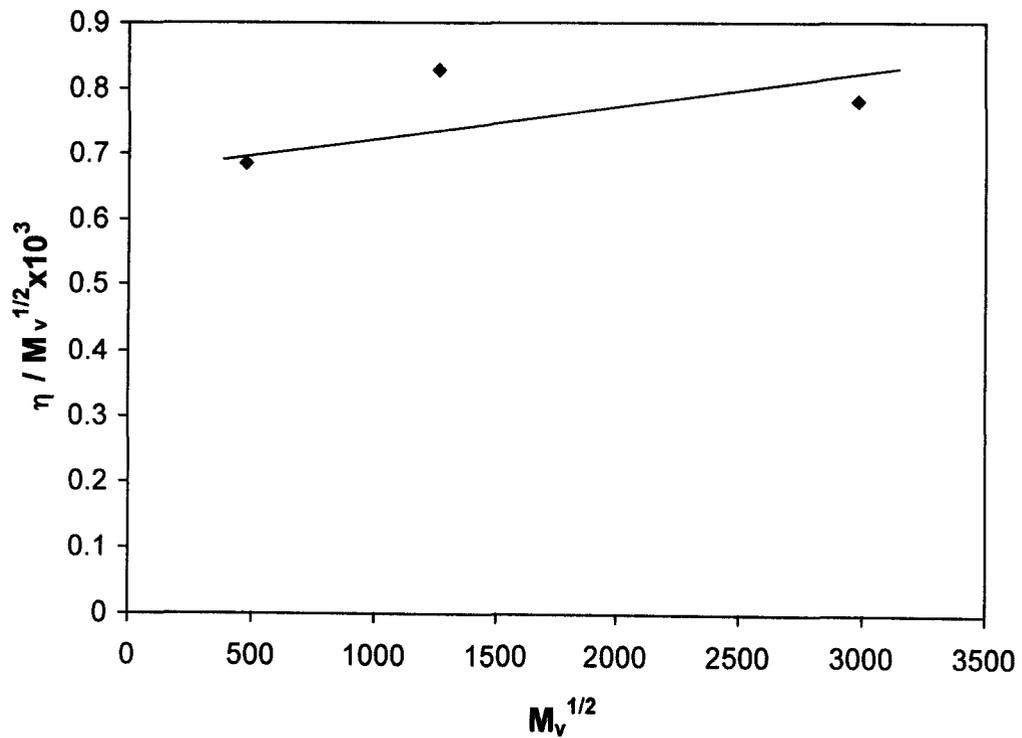
**Figure 4.8:** BSF plot at 40°C:  $\phi_{DO} = 0.1$



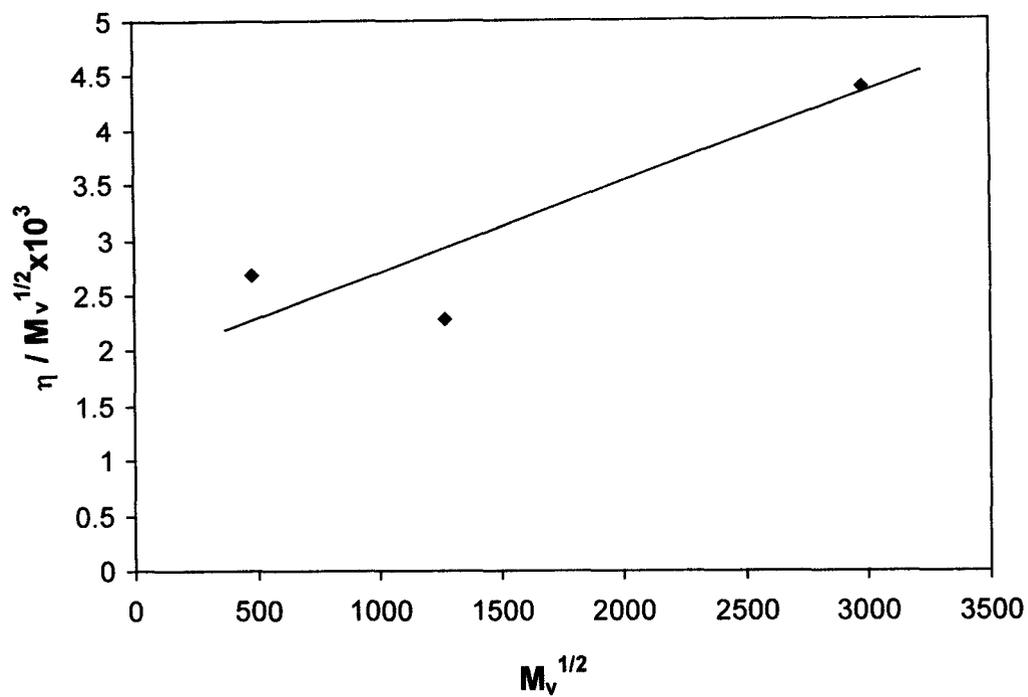
**Figure 4.9:** BSF plot at 40°C:  $\phi_{DO} = 0.2$



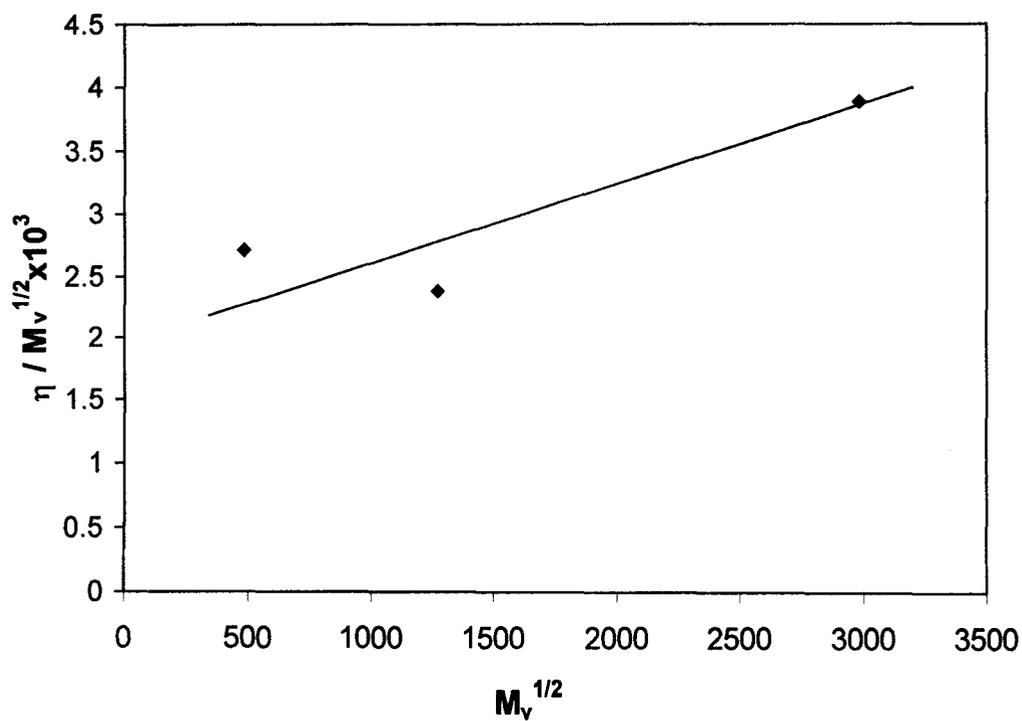
**Figure 4.10:** BSF plot at 40°C:  $\phi_{DO} = 0.3$



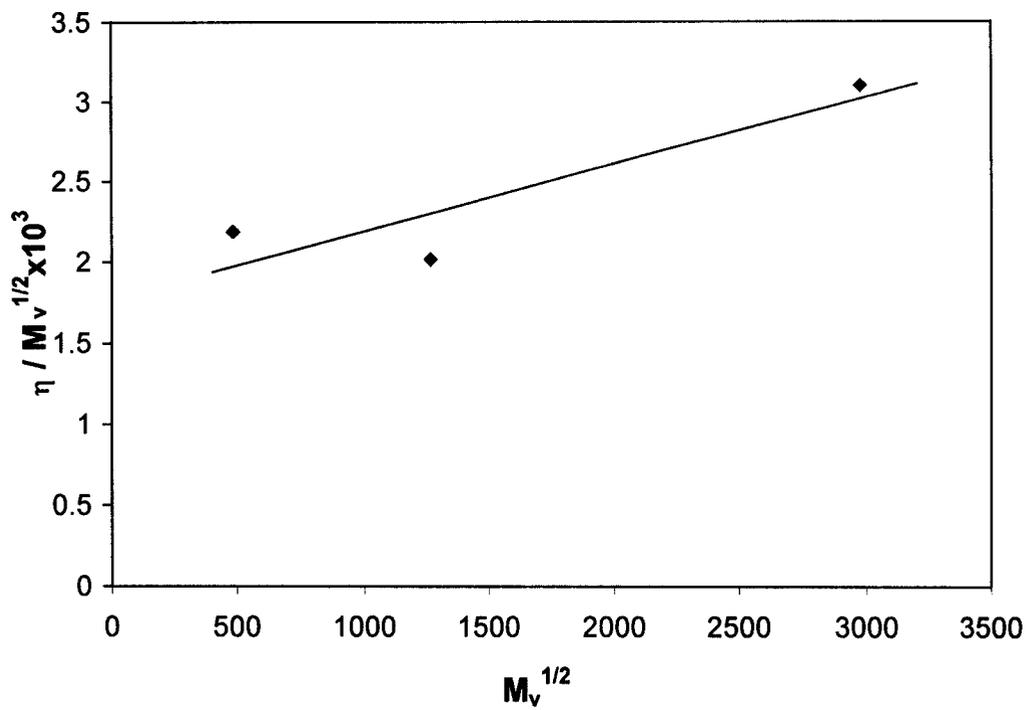
**Figure 4.11:** BSF plot at 40°C:  $\phi_{DO} = 0.4$



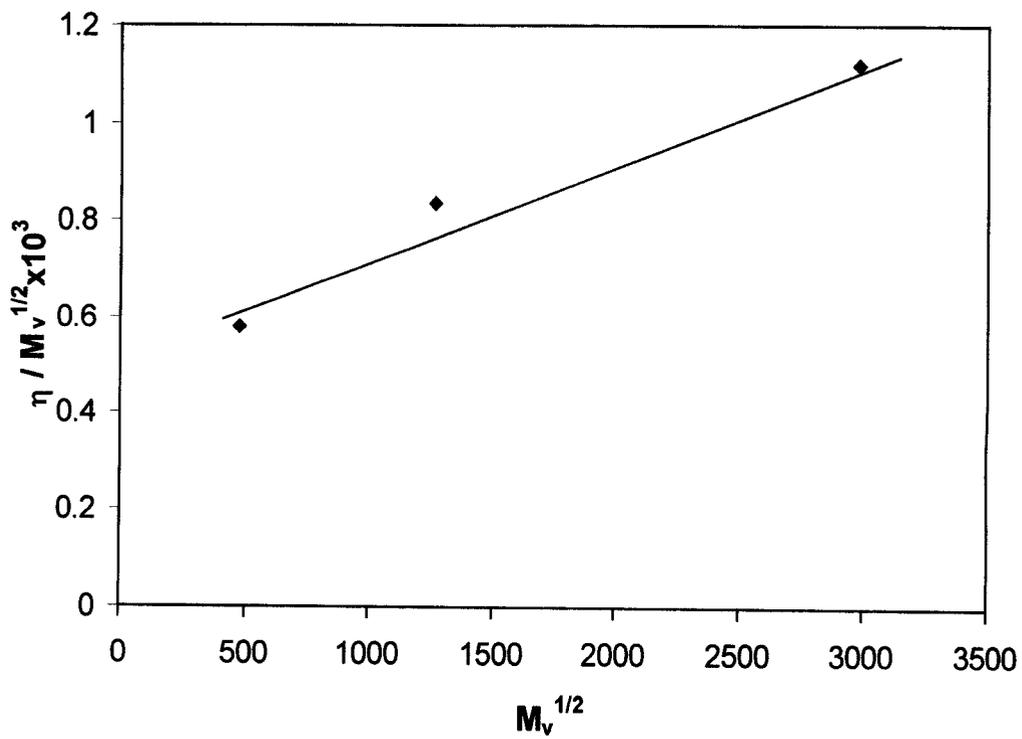
**Figure 4.12:** BSF plot at 50°C:  $\phi_{DO} = 0.1$



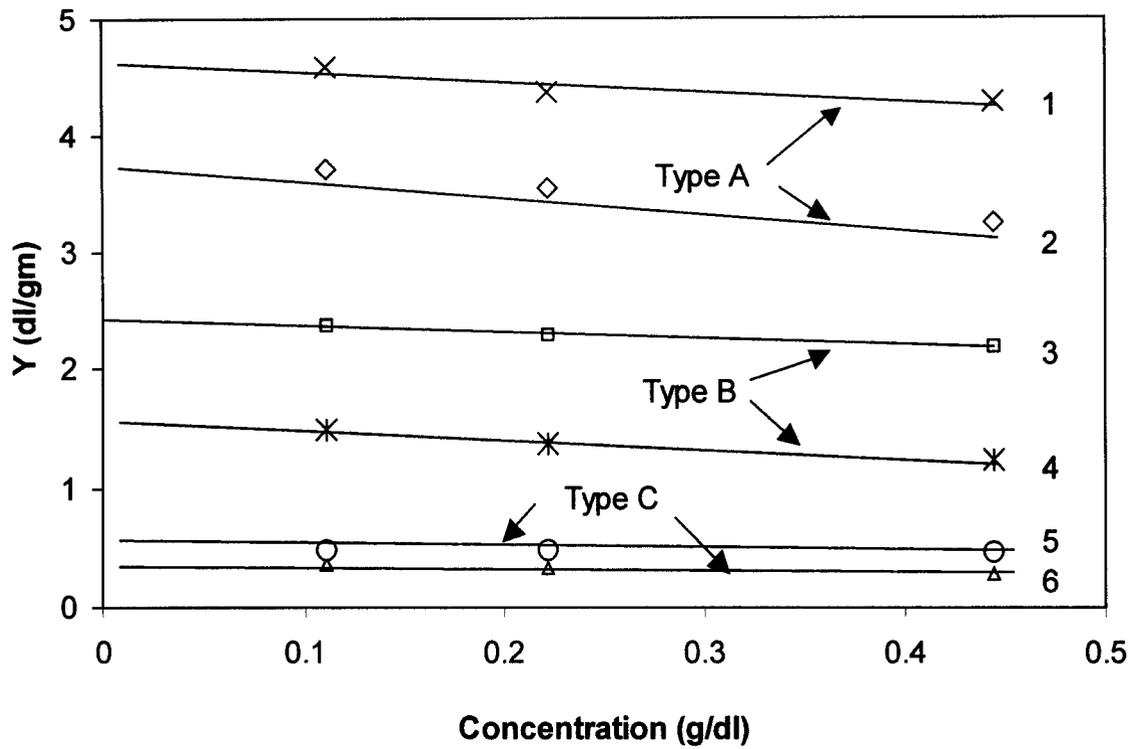
**Figure 4.13:** BSF plot at 50°C:  $\phi_{DO} = 0.2$



**Figure 4.14:** BSF plot at  $50^\circ\text{C}$ :  $\phi_{\text{DO}} = 0.3$



**Figure 4.15:** BSF plot at  $50^\circ\text{C}$ :  $\phi_{\text{DO}} = 0.4$



**Figure 4.16:** Plot of Y versus concentration for different types of PAM:  
 $\phi_{DO} = 0.1$  (2,3, and 6),  $\phi_{DO} = 0.2$  (1,4 and 5),  $30^{\circ}\text{C}$  = (2,3 and 6),  $40^{\circ}\text{C}$  = (1,4 and 5)

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