

## **CHAPTER - 5**

**STUDIES ON SOLUTION PROPERTIES OF POLYACRYLAMIDE  
IN WATER - DIMETHYL SULPHOXIDE MIXTURE.**

## 5.1 INTRODUCTION AND REVIEW OF PREVIOUS WORK

In the treatment of the properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of chain elements, or segments, about the centre of gravity. The average distribution of segments for a chain polymer molecule is approximately Gaussian<sup>280</sup>, its breadth depends on the molecular chain length and on the thermodynamic interaction between polymer segments and solvent. 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.<sup>281</sup> 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. A relationship between intermolecular and intramolecular agglomeration tendency is established. Solutions of polystyrene, rubber and cellulose acetate in the solvent-non solvent systems were investigated by Alfrey and co-workers.<sup>281</sup> They observed that the specific viscosity of a dilute solution of polystyrene or rubber is strongly dependent upon the nature of solvent, the specific viscosity is high in a good solvent and low in a poor solvent or a solvent-non solvent mixture. This has been interpreted as being due to changes in mean molecular shape. The specific viscosities of cellulose acetate solutions are not so sensitive to the nature of solvent. Besides this, the extrapolated specific viscosity at the limit of solubility is in the same range for several different solvent-non solvent systems. The effect of temperature upon intrinsic viscosity should depend strongly upon the nature of solvent. Alfrey and co-workers also noted that the effect of a temperature increase is to lower the specific viscosity of rubber or polystyrene solutions in a good solvent, but to increase the specific viscosity in a mixture of solvent and non-solvent. Unperturbed dimensions of

flexible linear macromolecules can be obtained from intrinsic viscosity-molecular weight data in any solvent, good or poor, if (as is almost always true) the hydrodynamic draining effect is negligible and if an estimate can be made of the viscosity expansion factor  $\alpha_n$ , defined by<sup>282</sup>

$$[\eta] = K_0 M^{1/2} \alpha_n^3 \quad (54)$$

In principle, this can be done graphically from the relation alone if a reliable expression is available for the dependence of  $\alpha_n$  on  $M$ . In particular, it has been shown from theoretical considerations that the intrinsic viscosity should depend on the molecular weight  $M$ , temperature  $T$  and solvent type in accordance with the relationships,<sup>283-285</sup>

$$\alpha^5 - \alpha^5 = 2 \psi_1 C_M (1 - \theta/T) M^{1/2} \quad (55)$$

where  $\theta = k_1 T / \psi_1$

$$K_0 = \phi_0 \left( r_0^2 / M \right)^{3/2} \quad (56)$$

$$C_M = 27 (2^{5/2} / \pi^{3/2} N) (\bar{v}^2 / v_1) (M / r_0^2)^{3/2} \\ = 1.4238 \times 10^{-24} (v^2/v_1) (\theta_0 / K_0) \quad (57)$$

where  $\psi_1$  is entropy parameter,  $k_1$  is the enthalpy parameter,  $\theta$  is the temperature and  $K_0$  is the unperturbed dimension of the polymer;  $\phi_0$  is the Flory's universal constant. Here,  $\bar{v}$  is the partial specific volume of the polymer and  $v_1$  is the molar volume of the solvent.

Intrinsic viscosities of polyisobutylene fractions ( $M=1.8 \times 10^5$  to  $1.88 \times 10^6$ ) and polystyrene fractions ( $M = 7.0 \times 10^4$  to  $1.27 \times 10^7$ ) have been determined in various pure solvents and in several solvent mixtures at several temperatures by Fox and Flory<sup>286,287</sup>. They observed that the parameter  $K_0$  in

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*K and k in this chapter are different from those used in chapter 3.*

the equation (54), is same in different solvents but decreases somewhat with temperature ( $1.08 \times 10^{-3}$  at  $24^\circ$  to  $0.91 \times 10^{-3}$  at  $105^\circ$  for polyisobutylene and  $8.0 \times 10^{-4}$  at  $34^\circ$  to  $7.3 \times 10^{-4}$  at  $70^\circ$  for polystyrene). The root-mean square end-to-end distance  $(r_0^2)^{1/2}$ , unperturbed by intramolecular interactions (other than hindrance to free rotation) for a polyisobutylene molecule and polystyrene molecule with  $M=10^6$  has been calculated to be  $795\text{\AA}$  and  $730\text{\AA}$  at  $25^\circ\text{C}$  respectively. The solution properties of poly (methyl acrylate) in various solvents by light scattering, osmometry, and viscosity techniques have been investigated by many workers.<sup>288-300</sup> Many empirical and semi empirical methods for the estimation of  $K_\theta$  from viscometric measurements in good solvents have recently been proposed.<sup>301-314</sup>

The viscosity behaviour of poly (methyl methacrylate) in four solvents was studied within the temperature range of  $25^\circ$  to  $60^\circ\text{C}$  and the thermodynamic parameters were evaluated and discussed using Fox-Flory,<sup>285</sup> Burchard Stockmayer-Fixman,<sup>315, 316</sup> Kurata-Stockmayer<sup>317,318</sup> and Berry<sup>319</sup> equations by Lenka and co-workers.<sup>320</sup> On the other hand, for evaluation of  $K_\theta$  from  $[\eta]$  at  $T > 0$  (in good solvent), a number of equations relating  $[\eta]$  and  $M$  through  $K_\theta$  (after eliminating linear expansion factor ( $\alpha$ ), hydrodynamic expansion factor ( $\alpha_n$ ), lattice co-ordination number ( $z$ ) etc.) have been suggested. These equations are shown below (where symbols have their usual meanings). Fox and Flory equation<sup>285</sup>:

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + K_\theta^{5/3} C_T (M/[\eta]) \quad (58)$$

Kurata-Stockmayer (K-S) equation<sup>317,318</sup>:

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363 \phi B [g(\alpha_n) M^{2/3} / [\eta]^{1/3}] \quad (59)$$

Burchard-Stockmayer and Fixman (B.S.F) equation<sup>315,316</sup>

$$[\eta]/M^{1/2} = K_\theta + 0.51\phi BM^{1/2} \quad (60)$$

Berry equation<sup>319</sup>:

$$([\eta]/M^{1/2})^{1/2} = K_0^{1/2} + 0.42 K_0^{3/2} B (\bar{r}_0^2/M)^{3/2} (M/[\eta]) \quad (61)$$

According to these equations, the value of  $K_0$  may be obtained from the intercepts on the ordinates of the plots of the quantity on the left hand side versus a function of  $M$  and  $[\eta]$  on the right hand side. The unperturbed dimensions for polymethylacrylate, polyethylacrylate, polybutylacrylate, polyacrylonitrile, and polyvinyl pyrrolidine have been calculated by Lenka and co-workers<sup>321</sup> using an expression relating to the cross-over point concentration,  $C_x$ , of the polymer in a number of solvents with the unperturbed dimension of polymer molecule  $(\bar{r}_0^2)^{1/2}$ . Assuming Flory's limiting exponent and utilizing the first-order perturbation results for the intrinsic viscosity  $[\eta]$  and the friction coefficient ( $f$ ) of a flexible polymer, Tanaka proposed<sup>322</sup>:

$$([\eta] / M^{1/2})^{5/3} = K_0^{5/3} + 0.627 \phi_0^{5/3} (< R^2 >_0 / M) BM^{1/2} \quad (62)$$

and Bohdanecky derived the following equation<sup>330</sup>:

$$[\eta]/M^{1/2} = 0.80 K_0 + 0.65 K_0 K^{0.7} M^{0.35} \quad (63)$$

The unperturbed dimensions of polystyrene and poly (2-vinylpyridine) have been measured in solvent-precipitant mixtures of various compositions using the Stockmayer-Fixman representation by Dondos and Benoit<sup>323</sup>. They obtained a linear relationship between  $K_0$  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<sup>282</sup> and the process of aggregation

on precipitation is caused by such transitions.<sup>324</sup> 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 dimensions of the polymer coil.<sup>325</sup> Quoting the view of other workers they explained that a partial helix-coil type polymer chain transition occurs in polyamide-6 in solution and results in higher value of limiting viscosity number of nylon-6 in m-cresol at lower temperatures which in turn favours the dissolution.<sup>326</sup> They also observed that limiting viscosity number of Nylon-6 in phenol increase with temperature and the system attained a state of optimum dissolution at 55°C and further increase in temperature and had adverse effect. Chatfield reports that solvent power of an alcohol-ether mixture for nitrocellulose increases with lowering of temperature and at -50°C, methyl alcohol alone becomes a solvent for cellulose ethers.<sup>327</sup> Recently, Savas and Zuhai have determined the unperturbed dimensions of anionically polymerized poly (p-tert-butyl-styrene) at various temperatures and found the θ-temperature of the polymer of the order of 31°C and 32.7°C in 1-nitropropane and 2-octanol respectively.<sup>328</sup> Several other workers reported the conformational transition of polymers in solution with change in temperature.<sup>310,329</sup> Coil dimensions of poly (methylacrylate) in the cosolvent medium of CCl<sub>4</sub> and MeOH have been investigated by Maitra and Nandi.<sup>331</sup> They observed that the intrinsic viscosity exhibited a maximum for all fractions of polymer at a composition,  $\phi_{\text{CH}_3\text{OH}}$  (volume fraction of methanol) = 0.33 and also Huggins constant showed a minimum at the same composition. The unperturbed dimension ( $K_0$ ) exhibited a maximum and molecular extension parameter  $\alpha_n$ , showed a minimum at  $\phi_{\text{CH}_3\text{OH}} = 0.33$ . The experimental data for the solution properties of poly (N,N-dimethylacrylamide) and poly (N-isopropylacrylamide) show that the hydrodynamic and configurational characteristics of these two N-substituted polyacrylamide, in methanol and water are different, showing a peculiar behaviour in water, which cannot be easily interpreted in terms of random coil molecules.<sup>332,333</sup> Also, the unperturbed dimensions estimated from data in good solvents are found to depend more on the lateral substituent structure

than on its dimensions. Chintore and co-workers found that behaviour of poly (N-methylacrylamide) molecules in aqueous solution was quite abnormal, as indicated by the values of the second virial coefficients, lower than those measured in methanol solutions by the large difference of estimated unperturbed dimensions.<sup>332,333</sup> Therefore, the hypothesis was made that the solvation of N-substituted poly acrylamides 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 coils in aqueous solutions. It has been pointed out that polyacrylamide, in which the lack of N-substituents increases the chances of intramolecular interactions, has the highest unperturbed dimensions.<sup>334</sup> The aqueous solutions of polyacrylamides are suspected to contain fibrous aggregates of very high molecular weight. These aggregates were observed by electronic microscopy<sup>335</sup> and the disaggregation kinetics studied by viscometry.<sup>336,337</sup> This phenomenon is generally attributed to intermolecular hydrogen bonds and is evidenced by an important decrease of viscosity with time. Boyadjian and co-workers have noticed differences of measured molecular weight by light scattering, according to the nature of solvent and have concluded the presence of aggregates broken up by the effect of salts in pure water but not in formamide.<sup>338</sup> However, even for non-hydrolysed 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 weights of interest.<sup>339,240</sup> However, Francois and Sarazin 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.<sup>214</sup> It has been shown recently that, the unperturbed dimensions of polyacrylamide could be determined by light scattering measurements in methanol-water system.<sup>340</sup> These authors concluded that the high value of the exponent (0.64) of the molecular weight dependence of the radius of gyration was not related to a great expansion of the macro molecular coil, and the determination of the unperturbed dimensions by extrapolation of viscosity

measurements in good solvents at  $M \rightarrow 0$  should be possible and works of Okada and Yamaguchi provide such determinations.<sup>341,342</sup> 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<sup>343</sup> and has been analysed by extrapolation procedures to yield the unperturbed dimensions ( $r^2/M_w$ )<sup>1/2</sup>, steric factor ( $\sigma$ ) and characteristic ratio ( $C_\alpha$ ). There was good accord between the values of ( $r^2/M_w$ )<sup>1/2</sup>,  $\sigma$  and  $C_\alpha$  thereby obtained directly and those derived indirectly, the mean values being  $8.73 \times 10^{-9}$  cm<sup>2</sup>/mol<sup>1/2</sup>, 4.07 and 32 respectively. Bohdanecky and Petrus and co-workers investigated the solution of 9 polyacrylamide fractions (molecular weight 3300-800,000) in water at 25°C and in a mixed θ solvent (3.2 volume, H<sub>2</sub>O-MeOH) at 20°C by light scattering, sedimentation and viscometry.<sup>344</sup> Measurements in water gave the configuration character ratio  $C_\alpha = 8.5$ .

The fundamental parameters of the polyacrylamide obtained previously by viscometry in good solvent i.e. water and in a θ solvents have been analysed by viscosity molecular weight relationship procedures suggested by several workers (Scholtan<sup>339</sup>, Newman<sup>345</sup> and Misra<sup>346</sup>). 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 above<sup>214,340</sup>. 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 the high value of the exponent of molecular weight dependence of the radius of gyration was not due to a great expansion of the macromolecular coil in water and it is now believed that determination of the unperturbed dimension by extrapolating viscosity data in good solvents is possible.<sup>340</sup> Although some studies on the solution viscosity properties of acrylamide in water are available in the literature, similar studies in other solvents or cosolvent systems are surprisingly little.<sup>340,344</sup> In a binary liquid mixture, it is the interaction between the liquids that governs

the solubility of a polymer in the mixture. Expansion of coil are also occurred due to two main reasons. (I) variation of molecular extension factor ( $\alpha_n$ ) and (II) change of the unperturbed dimension of the polymer due to interactions of two component liquids.<sup>347,348</sup> In the present chapter, the results of our investigation on unperturbed dimension, interaction parameter and related aspects of unhydrolyzed polyacrylamide in water-DMSO mixtures have been described. The intrinsic viscosities  $[\eta]$  of the polymer have been measured for different molecular weight fractions of the polymer and also in different compositions (water/DMSO) of the cosolvent mixture. From the  $[\eta] - M$  relation, the unperturbed dimension( $K_0$ ) and molecular extension factor ( $\alpha_n$ ) 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 polymer.<sup>331</sup> While DMSO is a poor solvent for PAM, water-DMSO mixture acts as a cosolvent in all proportions. In the previous chapters, we have reported the technique by which the molecular weight of the polyacrylamide in aqueous solution may be controlled by trapping the initiator component in the interlayer space of montmorillonite. This method has been adopted selectively to prepare polymers of varying molecular weights for the solution property studies as presented in this chapter.

## 5.2 EXPERIMENTAL

### Polymerization

PAM was synthesized from acrylamide monomer (AM) by redox polymerization technique. The polymerization technique of AM, initiated by Ferric-montmorillonite (FeM) - thiourea (TU) redox system has been discussed in Chapter 3 (section 3.2). To obtain high molecular weight polymers for the present study, a similar technique has been adopted using 0.4 M monomer and 0.04 thiourea in aqueous suspension of 0.50% FeM (W/V) in the temperature range between 70°C and 50°C (already discussed in Chapter 3,

section 3.4.3). Low molecular weight polymers were obtained via polymerization of AM monomers initiated by  $1.5 \times 10^{-3}$  M  $\text{FeCl}_3$  and 0.04M TU redox system at 50°C in absence of montmorillonite( already discussed in Chapter 3, section 3.3.3). The molecular weights (determined from intrinsic viscosity measurements in water at 30°C) of the polymers used in the present study are listed in Table-30.

### Viscosity Measurements

The intrinsic viscosities  $[\eta]$  of the polymers in aqueous solutions were determined by an Ubbelohde viscometer, placed at appropriate temperature in a thermostat, measuring specific viscosities ( $\eta_{sp}$ ) and using the Huggin's equation for extrapolation :

$$\eta_{sp}/C = [\eta] + K [\eta]^2 C \quad (64)$$

where C is the concentration of the polymer solution. Molecular weights of the polymer were calculated from the intrinsic viscosity data (already mentioned in section 3.3.3 and 3.4.3). The  $[\eta]$  values of the polymer in various water-DMSO compositions (prepared by volume) were also measured in a similar way.

**Table-30**

Molecular weights of polyacrylamides

Polyacrylamide types	$M_v \times 10^5$
High Molecular weight (HM)	12.55
Medium Molecular weight (MM)	8.44
Low Molecular weight (LM)	1.33

### 5.3 RESULTS AND DISCUSSION

Nature of the interaction between the liquids governs the solubility of a polymer in a binary liquid mixture. The changes in the molecular dimensions of the polymers in these systems are manifested in the varied molecular extension parameter ( $\alpha_n$ ) and the unperturbed dimensions due to the interaction with two component liquid.<sup>347,348</sup> The changes in intrinsic viscosities [ $\eta$ ] of various molecular weight fractions of PAM at 30°C and different solution compositions are shown in Figure 59. With increasing DMSO (poor solvent) concentration, the intrinsic viscosity decreases due to contraction of the dimensions of the polymer coil as well as for the degree of intermolecular agglomeration. However, at high value of  $\phi_{\text{DMSO}}$  ( $\phi$  being the relative volume composition in the mixture), the [ $\eta$ ] value tends to increase again for preferential solvation of the polymer due to high cosolvent effect. It is found that for all the molecular weight fractions, the intrinsic viscosity attains the minimum near  $\phi_{\text{DMSO}}$  value between 0.6-0.7 indicating energetically most unfavourable solvent composition for the polymer. The lowest value of [ $\eta$ ] around  $\phi_{\text{DMSO}} = 0.6 - 0.7$  indicates the maximum degree of intermolecular aggregation of the polymers at this solvent composition. Similar nature of the variation of [ $\eta$ ] on solvent composition is also observed at 40°C temperature (Figure 60). Such changes of the [ $\eta$ ] value as a function of solvent composition clearly indicates the flexibility of the PAM molecules in the present solvent systems also. On the other hand, at 50°C temperature the nature of the curves is changed dramatically (Figure 61). Instead of giving a minimum with the variation of solution composition, the [ $\eta$ ] reaches a maximum near  $\phi_{\text{DMSO}} = 0.3$ , for all the polymer fractions. The maximum intrinsic viscosities for all polymer fractions at this solvent composition indicate preferential solvation of the polymers due to most powerful cosolvent effect.<sup>331</sup> The effect of temperature upon [ $\eta$ ] should depend strongly upon the nature of the solvent. In a binary solvent composition where cosolvancy factor is poorer, an increase of temperature should increase the relative importance of entropy factors over energetic factors, and results in

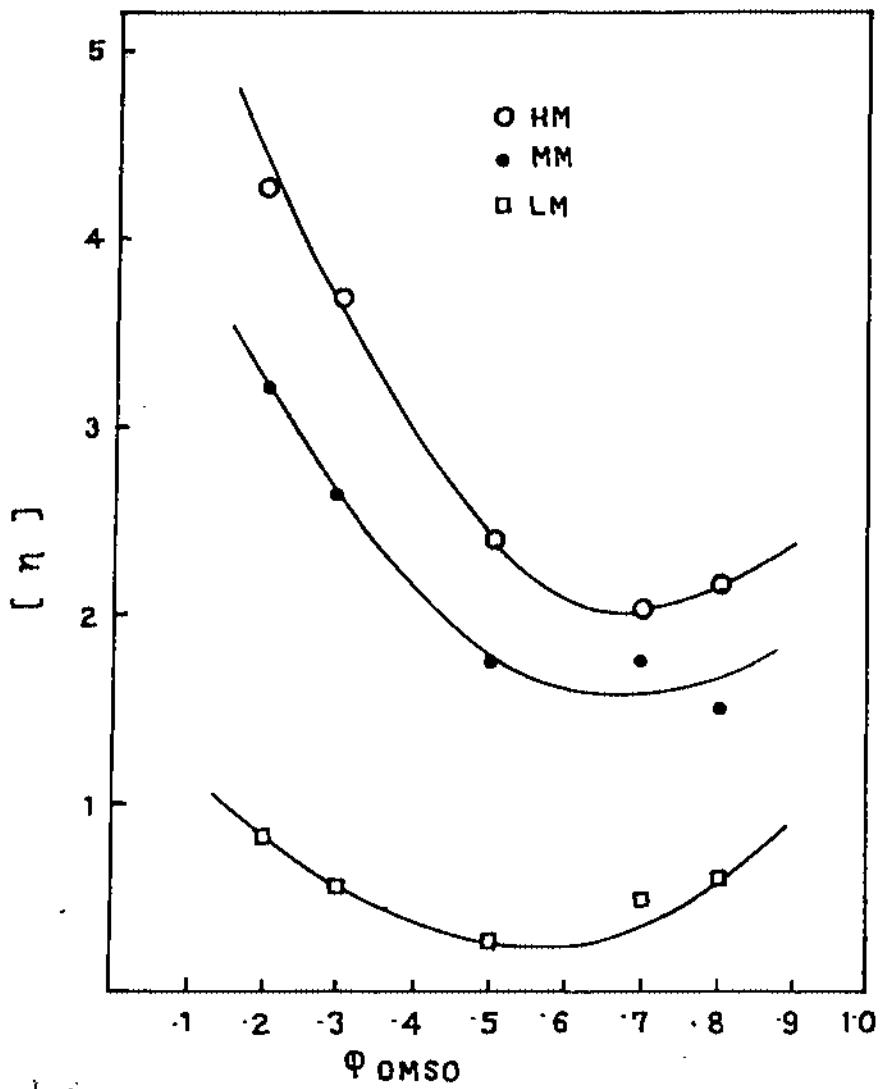


Fig.59 Plot of intrinsic viscosity of PAM fractions at 30°C versus volume fraction of DMSO.

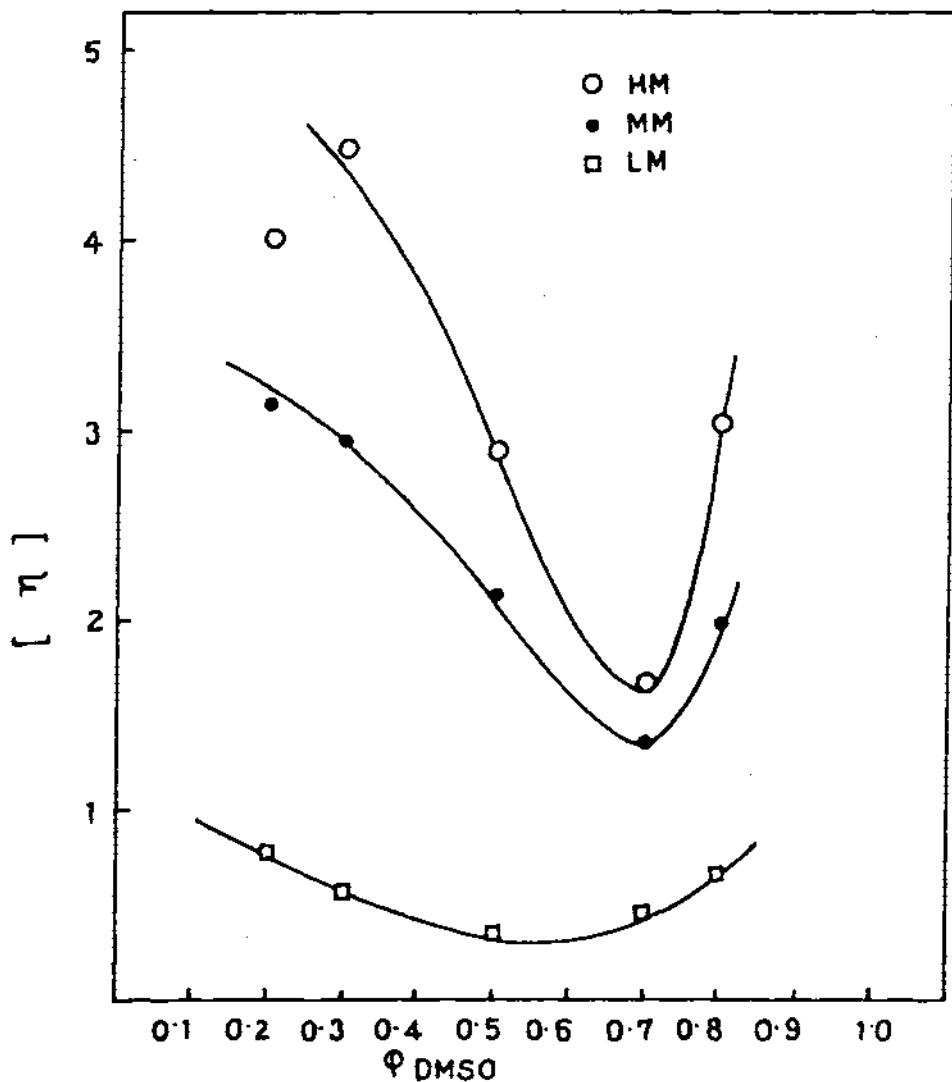


Fig. 60 Plot of intrinsic viscosity of PAM fractions at 40°C versus volume fraction of DMSO.

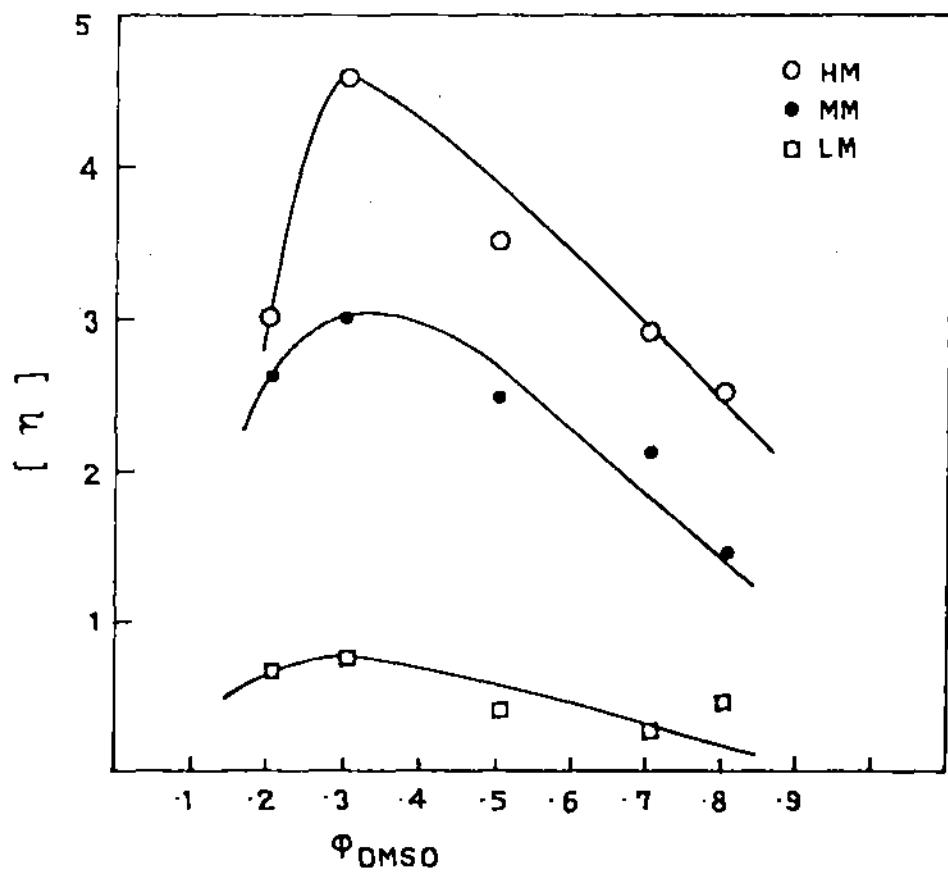


Fig. 61 Plot of intrinsic viscosity of PAM fractions at 50°C versus volume fraction of DMSO.

an uncurling of the molecule.<sup>281</sup> The uncurled configurations will be favoured due to long chain molecule being surrounded by solvated hull which tends to prevent polymer-polymer contacts. In such a solvent, a temperature increase should result in an increase of  $[\eta]$ . On the other hand, at higher cosolvency condition, the energetic weighting factors favour the more extended configuration; here an increase in temperature should diminish the  $[\eta]$  value. As a result, above maxima in  $[\eta]$  versus  $\phi_{\text{DMSO}}$  plots are observed at high temperature for all types of the polymer studied. The cosolvency and the intermolecular interaction of polymers are also manifested in the Huggins constant values when the composition of the solvent system were varied. Plots of Huggins constant as a function of solvent composition are shown in Figures 62-64. The Huggins constants ( $K$ ) are calculated from the least square slopes of equation (64). It is observed that there is a maximum at solvent composition  $\phi_{\text{DMSO}} = 0.7$  for medium and high molecular weight polymers. This shows that cosolvent effect is apparent above  $\phi_{\text{DMSO}}$  value of 0.7. However, at 50°C temperature, although a maximum is obtained at  $\phi_{\text{DMSO}} \sim 0.7$ , the small value of  $K$  indicate better cosolvency at this temperature for MM and HM samples. For LM fraction, very high values of  $K$  indicate strong aggregation of polymer molecules at all the temperatures studied. Figure 65 shows a plot of Huggins constant against  $\log M_v$  for three different solvent compositions (upto  $\phi_{\text{DMSO}} = 0.5$ ). All the curves show a decrease in the Huggins constant value with the increase in molecular weight indicating higher tendency of intermolecular aggregation for smaller fractions of the polymers in poor cosolvent conditions.

### **Unperturbed Dimension**

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

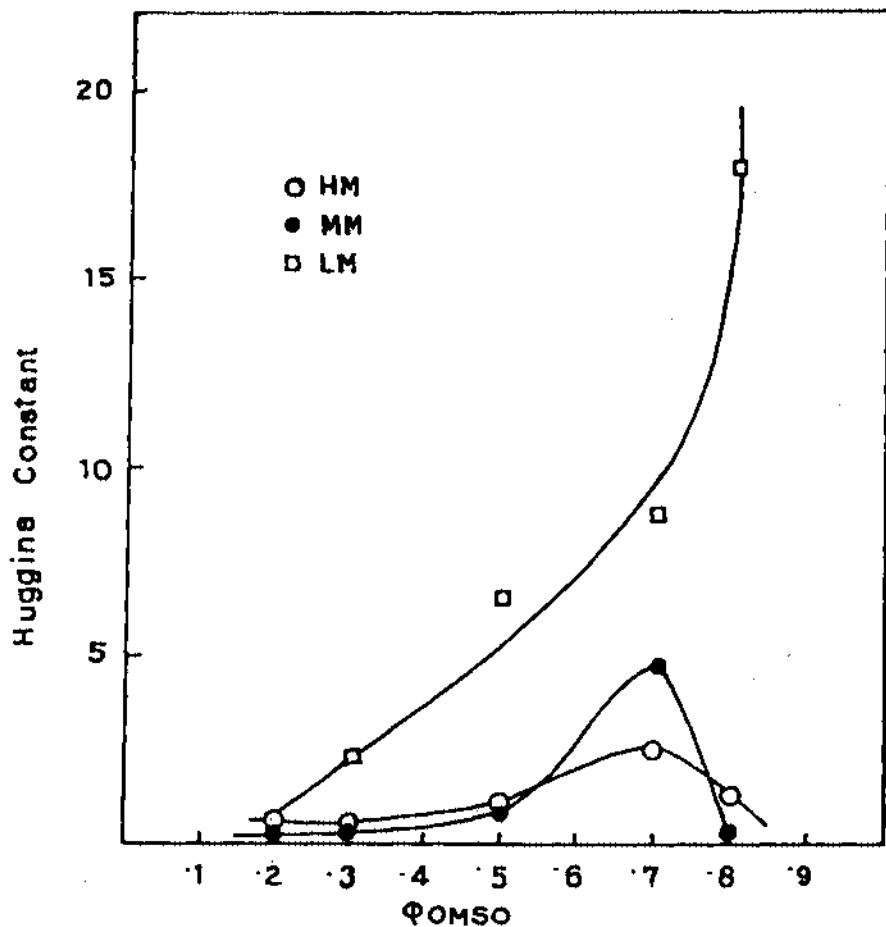


Fig. 62 Plot of Huggins constant of PAM fractions at 30°C versus volume fraction of DMSO.

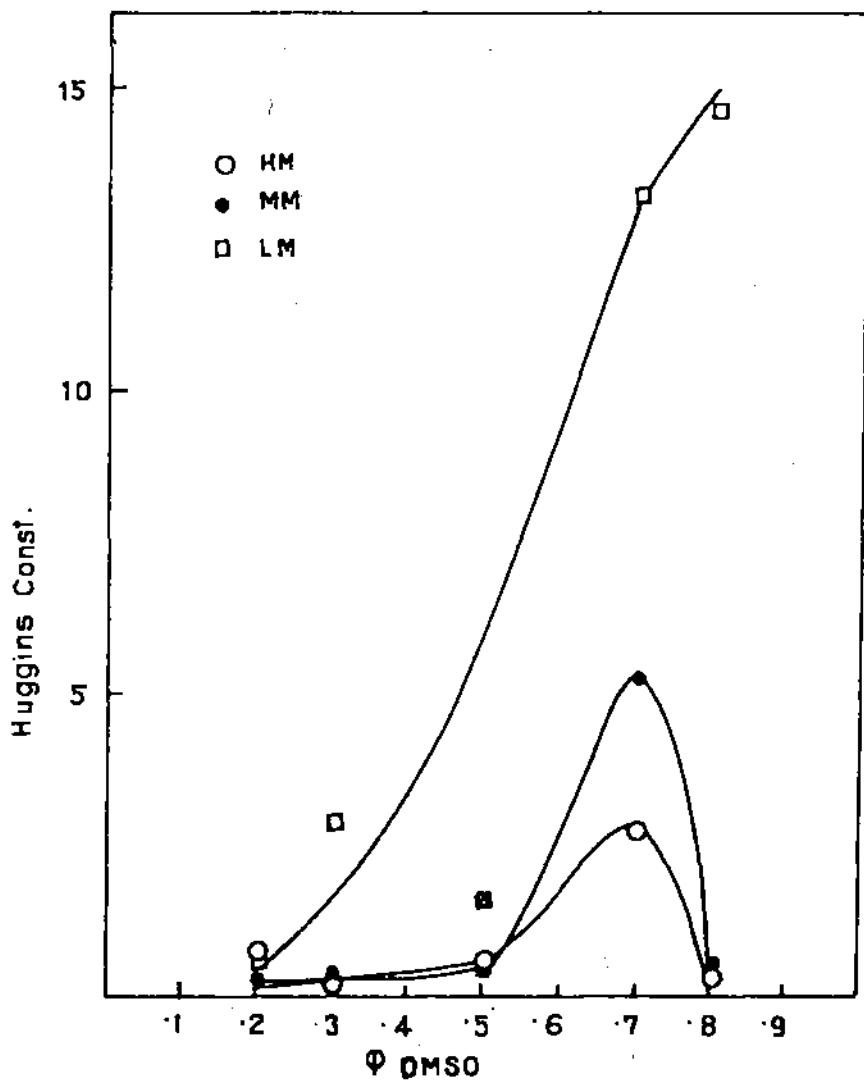


Fig. 63 Plot of Huggins constant of PAM fractions at 40°C versus volume fraction of DMSO.

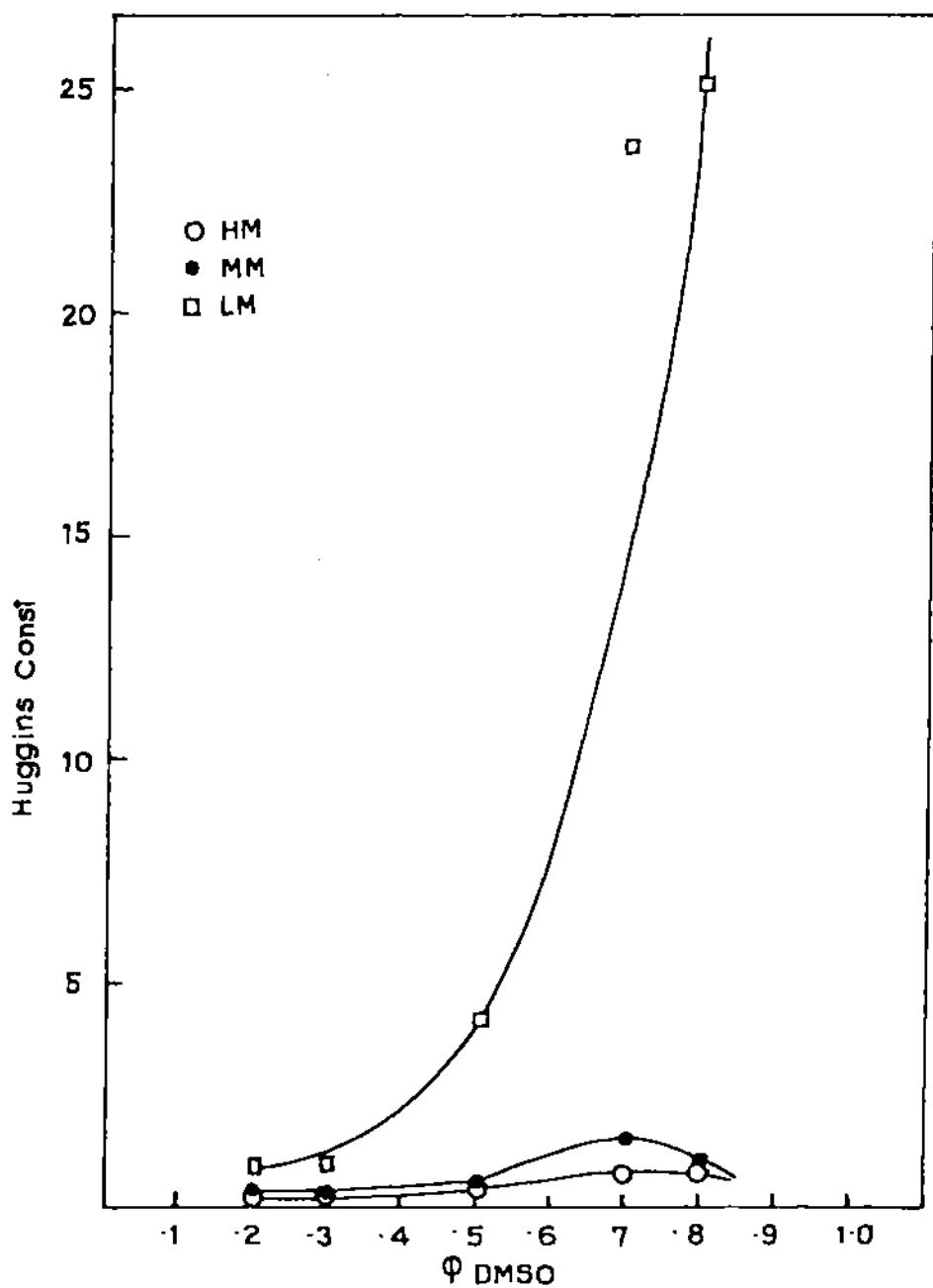


Fig. 64 Plot of Huggins constant of PAM fractions at 50°C versus volume fraction of DMSO.

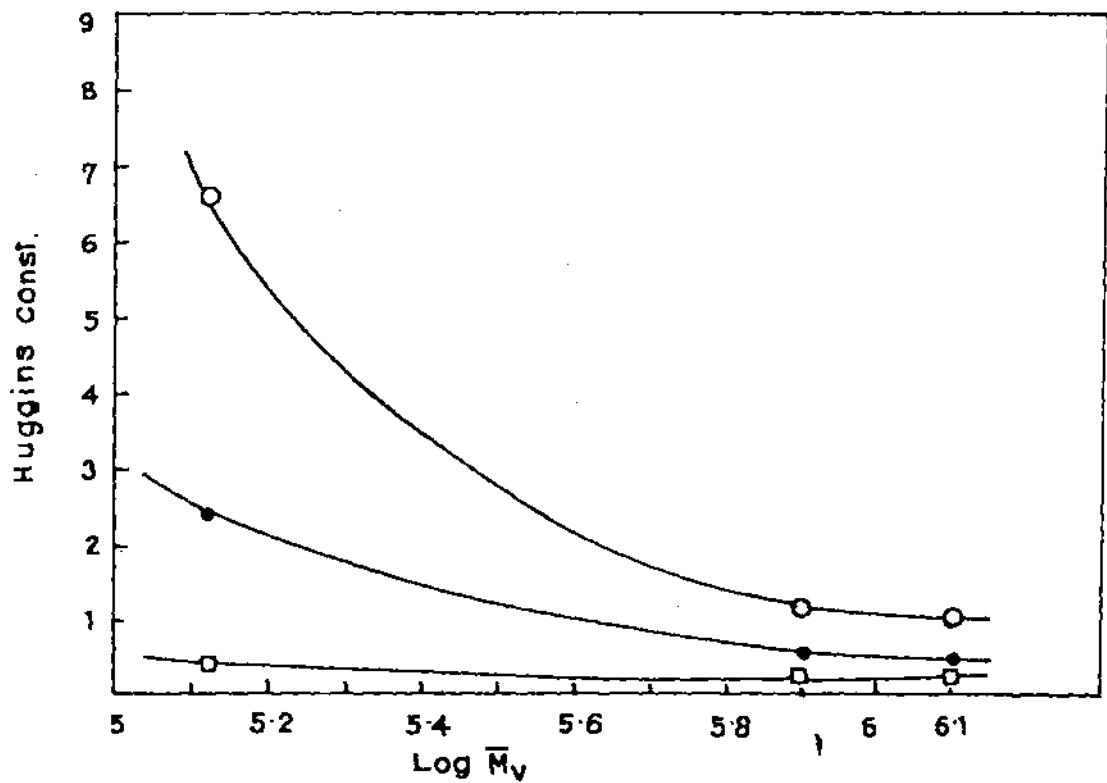


Fig. 65 Plot of Huggins constant versus log(molecular weight)  
at different solvent composition at 30°C.  $\phi_{DMSO} = 0.5$   
(○), 0.3 (●), 0.2 (□).

with a definite solvent ( $\theta$  solvent).<sup>282</sup> The unperturbed dimension ( $K_0$ ) is the end-to-end dimension of polymer chain under  $\theta$  conditions and can be determined from the intrinsic viscosity measurement at this condition.

$$[\eta]_\theta = \phi_0 (\bar{r}_0^2 / M)^{3/2} M^{1/2} = K_0 M^{1/2} \quad (65)$$

where  $\phi_0$  is the Flory's universal constant ( $2.5 \times 10^{23}$  mole<sup>-1</sup>),  $M$  stands for molecular weight and  $\bar{r}_0^2$  is the mean square unperturbed dimension. However, in the present study, the Burchard-Stockmayer – Fixman equation (60) has been used for deriving  $K_0$  of PAM in various water – DMSO mixtures under non  $\theta$  conditions.<sup>315,316</sup> The BSF plots for PAM fractions at various cosolvent compositions at 30°C are shown in Figures 66-67. The  $K_0$  values obtained by plotting  $[\eta]/M^{1/2}$  against  $M^{1/2}$  from the equation (60) in different cosolvent compositions

$$[\eta] / M^{1/2} = K_0 + 0.51B\phi_0 M^{1/2} \quad (60)$$

( $B$  being the polymer-solvent interaction free energy parameter) are compared with those obtained from other methods of measurement, viz., Kurta-Stockmayer (KS)<sup>317,318</sup>, Fox-Flory (FF)<sup>285</sup>, Berry (Be)<sup>319</sup>, Tanaka(T)<sup>322</sup> and Bohdanecky(Bo)<sup>330</sup> methods. The results are summarized in Table 31. The values obtained by different methods agree well with each other except in a few composition conditions of the solvent. From the Table 2, it is apparent that at  $\phi_{DMSO} = 0.5$  i.e., at the same volume ratio of water and DMSO in the mixture, strong attraction of two solvents, causes the polymers to have the lowest value of unperturbed chain. This observation is independent of the method of measurement with certain exceptions. Effect of temperature is rather interesting. The BSF plots for PAM fractions at various cosolvent compositions at 40°C and 50°C are shown in Figures 68-71. With an increase in temperature,  $\bar{r}_0^2$  and hence  $K_0$ , are decreased due to greater freedom to rotation around the skeletal

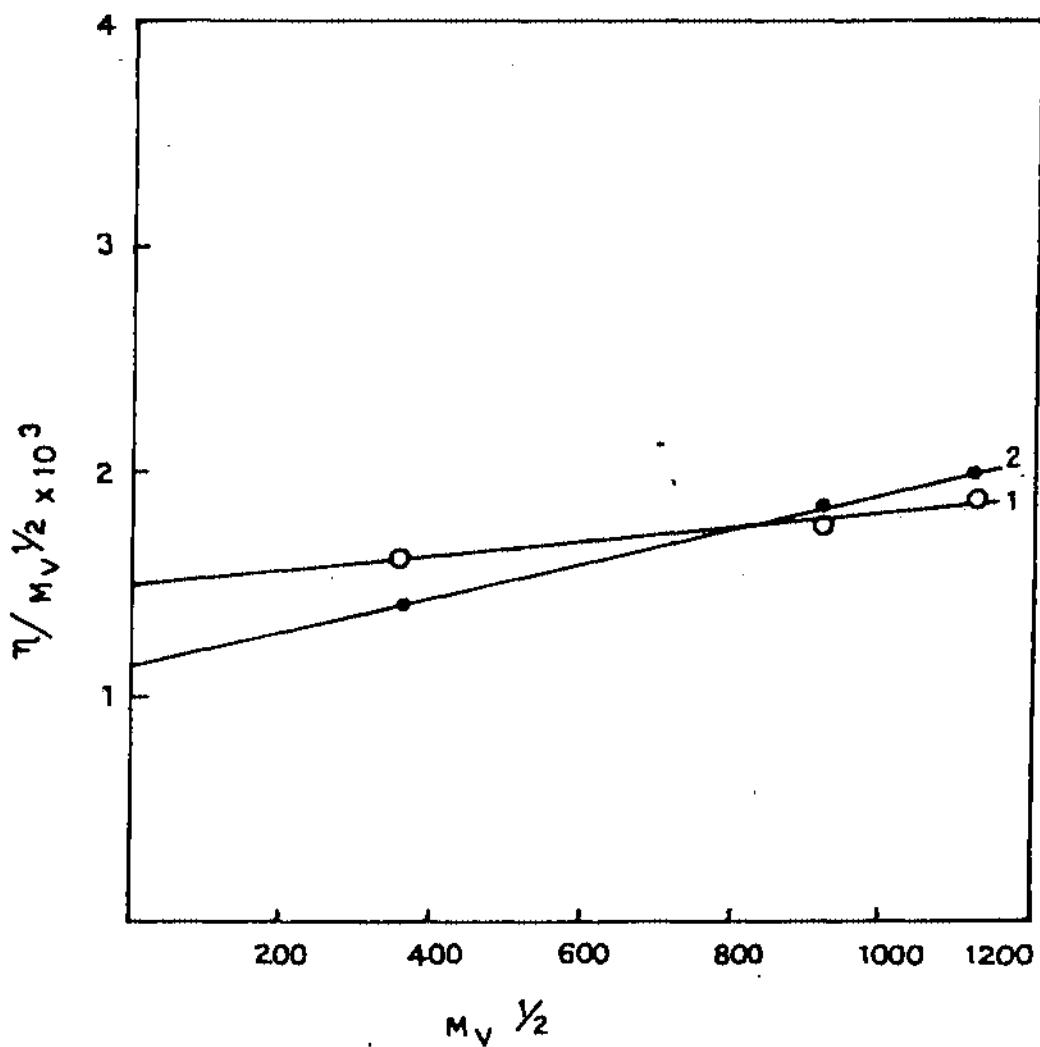


Fig. 66 BSF plots for PAM fractions at various cosolvent compositions at 30°C:  $\phi_{\text{DMSO}} = 0.20(1)$ ;  $\phi_{\text{DMSO}} = 0.30(2)$ .

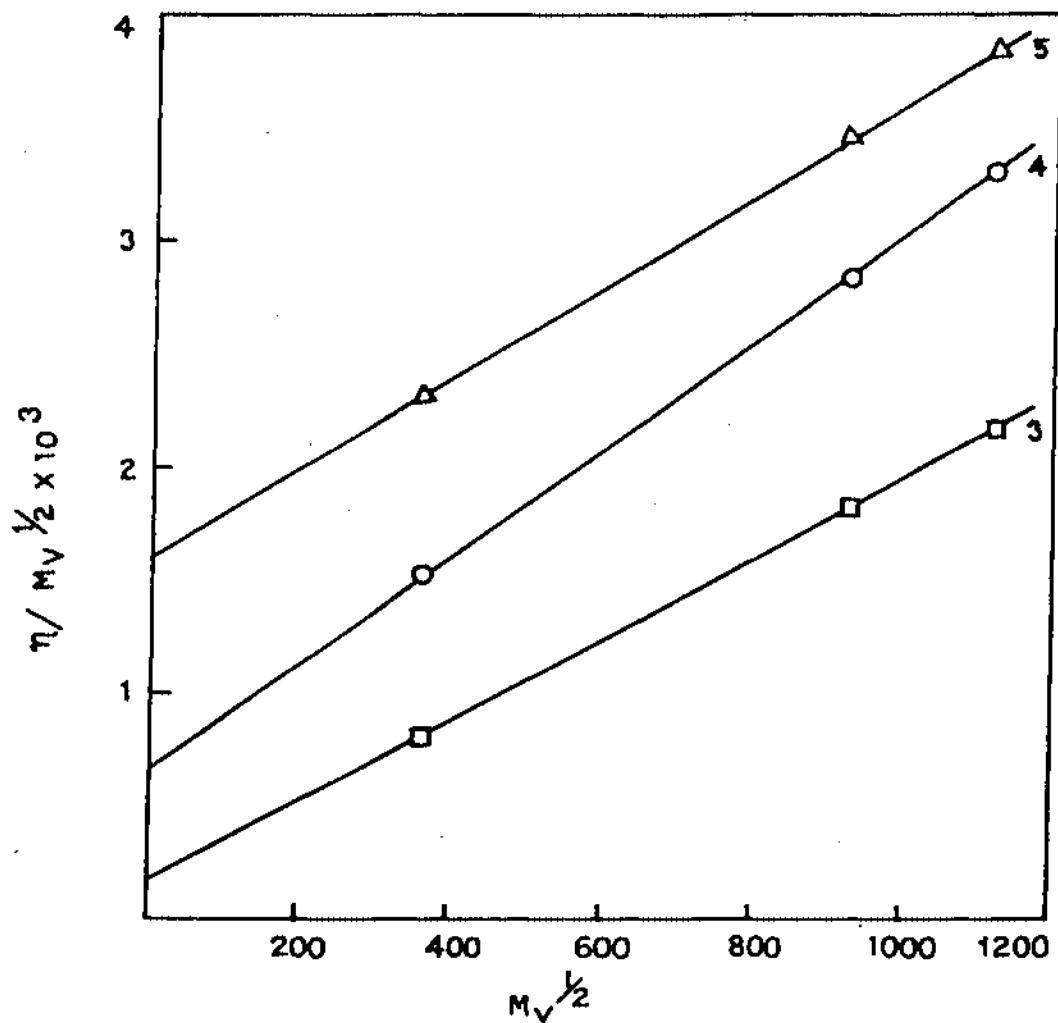


Fig. 67 BSF plots for PAM fractions at various cosolvent compositions at 30°C:  $\varphi_{\text{DMSO}} = 0.50(3)$ ;  $\varphi_{\text{DMSO}} = 0.70(4)$ ;  $\varphi_{\text{DMSO}} = 0.80(5)$ .

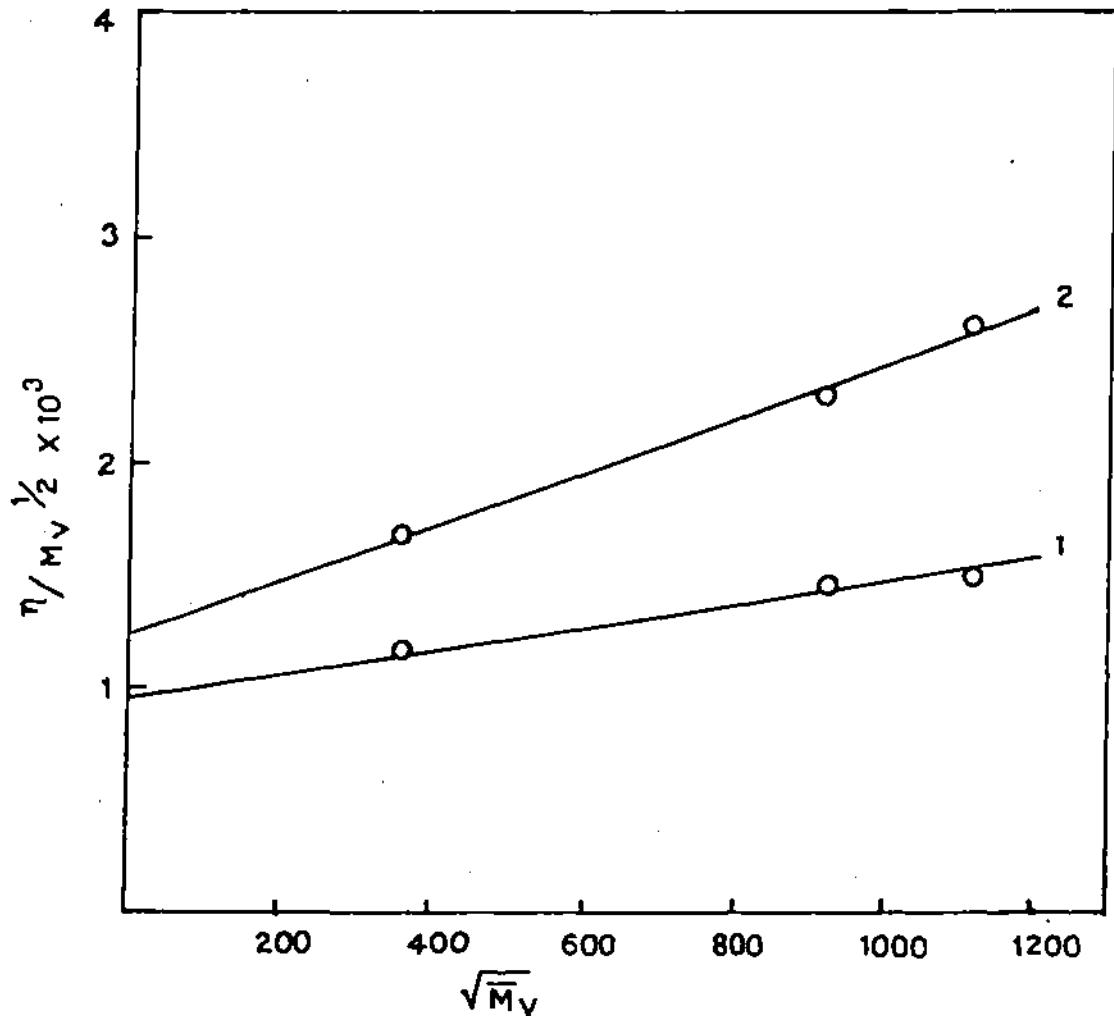


Fig. 68 BSF plots for PAM fractions at various cosolvent compositions at 40°C:  $\varphi_{OMSO} = 0.20(1)$ ;  $\varphi_{OMSO} = 0.30(2)$ .

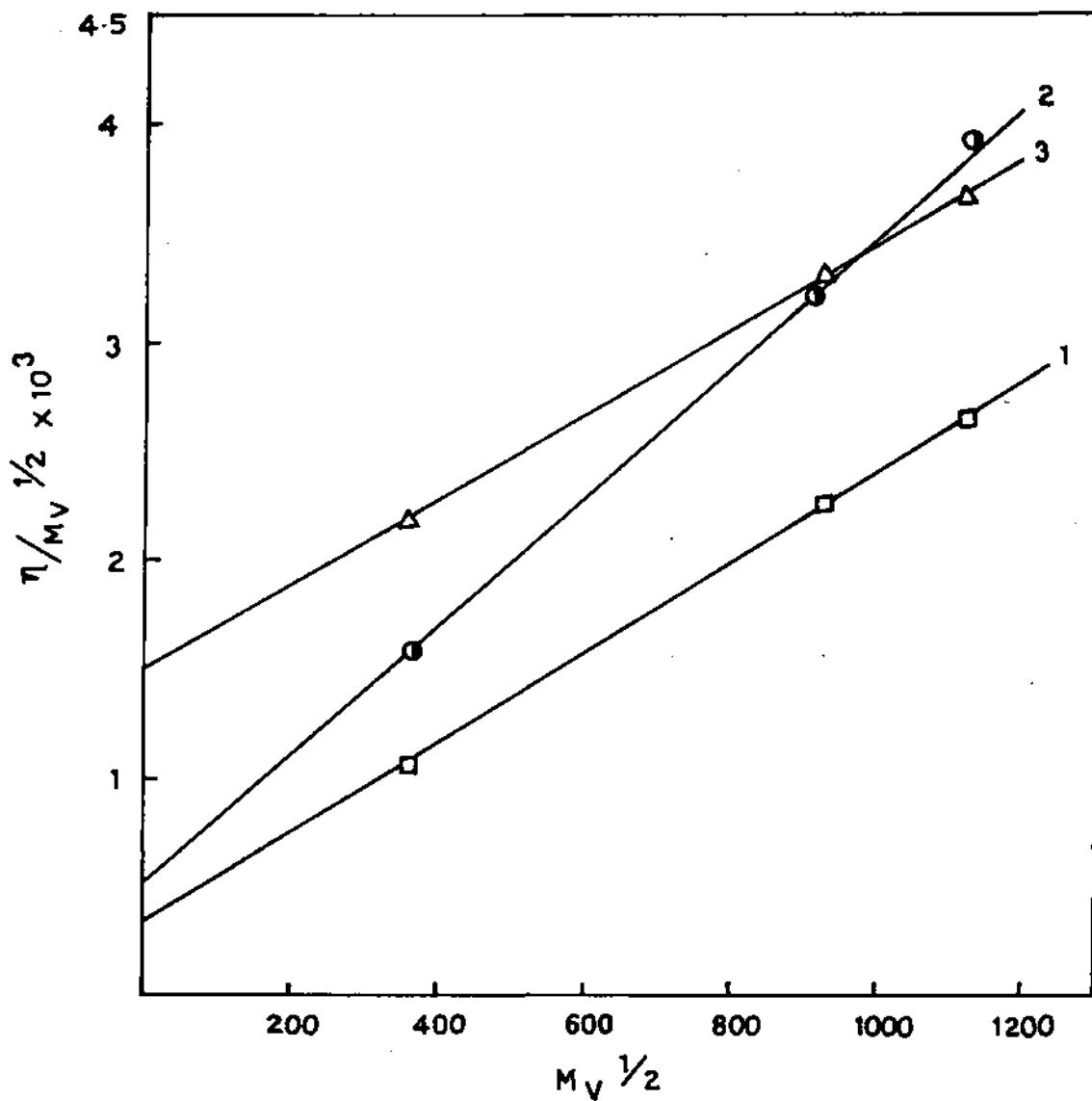


Fig. 69 BSF plots for PAM fractions at various cosolvent compositions at 40°C:  $\phi_{DMSO} = 0.50(1)$ ;  $\phi_{DMSO} = 0.70(2)$ ;  $\phi_{DMSO} = 0.80(3)$ .

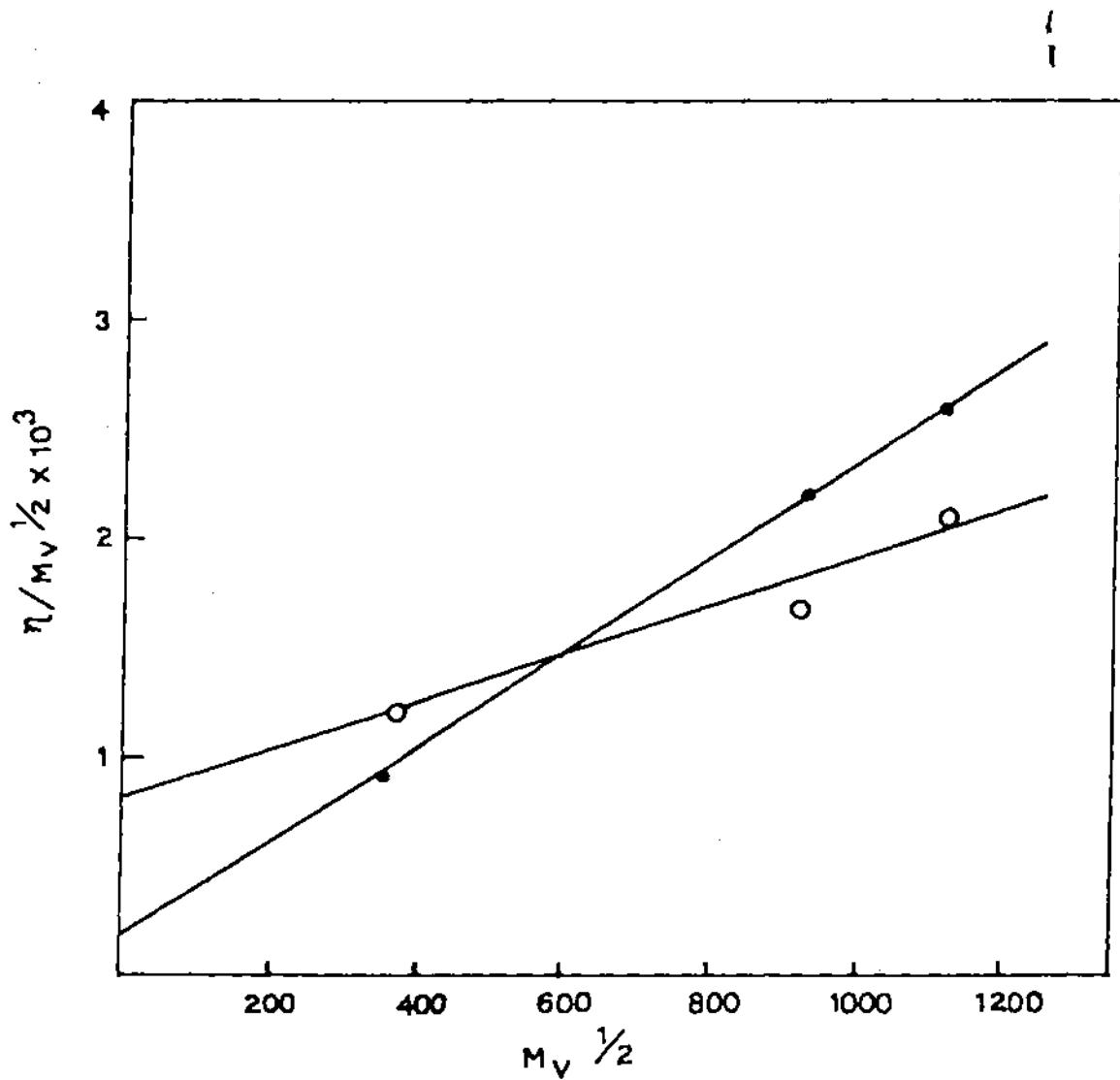


Fig. 70 BSF plots for PAM fractions at various cosolvent compositions at 50°C:  $\varphi_{\text{DMSO}} = 0.20(1)$ ;  $\varphi_{\text{DMSO}} = 0.30(2)$ .

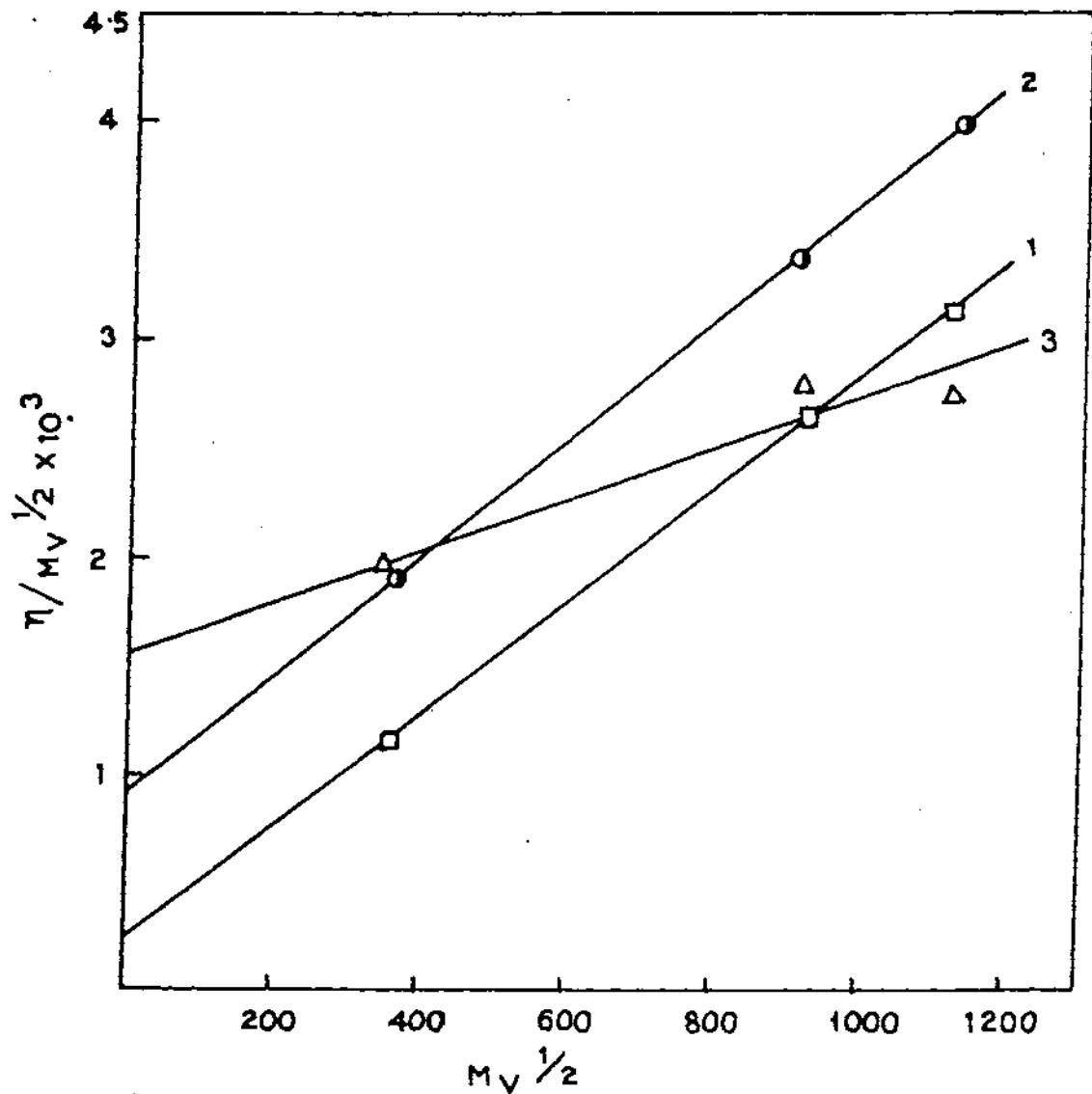


Fig. 71 BSF plots for PAM fractions at various cosolvent compositions at 50°C:  $\phi_{\text{DMSO}} = 0.50(1)$ ;  $\phi_{\text{DMSO}} = 0.70(2)$ ;  $\phi_{\text{DMSO}} = 0.80(3)$ .

bonds.<sup>282</sup> Such a temperature dependence of unperturbed dimension can be attributed not only to the change in flexibility of macromolecular chains but also to the specific polymer-solvent interaction<sup>349</sup>. The effect may also be correlated to the cohesive energy density of the polymer and the solvent.<sup>323</sup>

### Temperature coefficient of unperturbed dimension

$K_0$  is related to the statistical parameters ( $\bar{r}_0^2$ ) and the unperturbed mean square end-to-end distance by the Flory's Equation (56)

$$K_0 = \phi_o [\bar{r}_0^2 / M]^{3/2} \quad (56)$$

On differentiating equation (56) with respect to T, the temperature coefficient of unperturbed dimension may be obtained

$$(d \ln K_0 / dT) = 3/2 [\{d \ln (\bar{r}_0^2)\} / dT] = K^l \quad (66)$$

Here  $K^l$ , the temperature coefficient of  $K_0$ , provides information regarding the configuration dependent properties of polymer chain and energies of bond conformations in the molecule.<sup>350</sup> The plots are shown in Figures 72-73 In water - DMSO composition of 2:8,  $K^l$  is found to be 0.046 degree<sup>-1</sup> for acrylamide polymer (Table-32). The value of the temperature co-efficient increases upto 3:7 mixture of the solvent, indicating again that the solvency power increases with the increase in temperature upto above solvent composition.<sup>351</sup> This further shows that the acrylamide polymer molecule expands more in the later solvent composition and reveals the presence of low energy configuration in this solvent mixtures at high temperature. On the otherhand, at 5:5 and 7:3 compositions, the  $K^l$  value is negative. The negative coefficient value indicates more compact structure and the existence of high energy configuration of the polymer in these

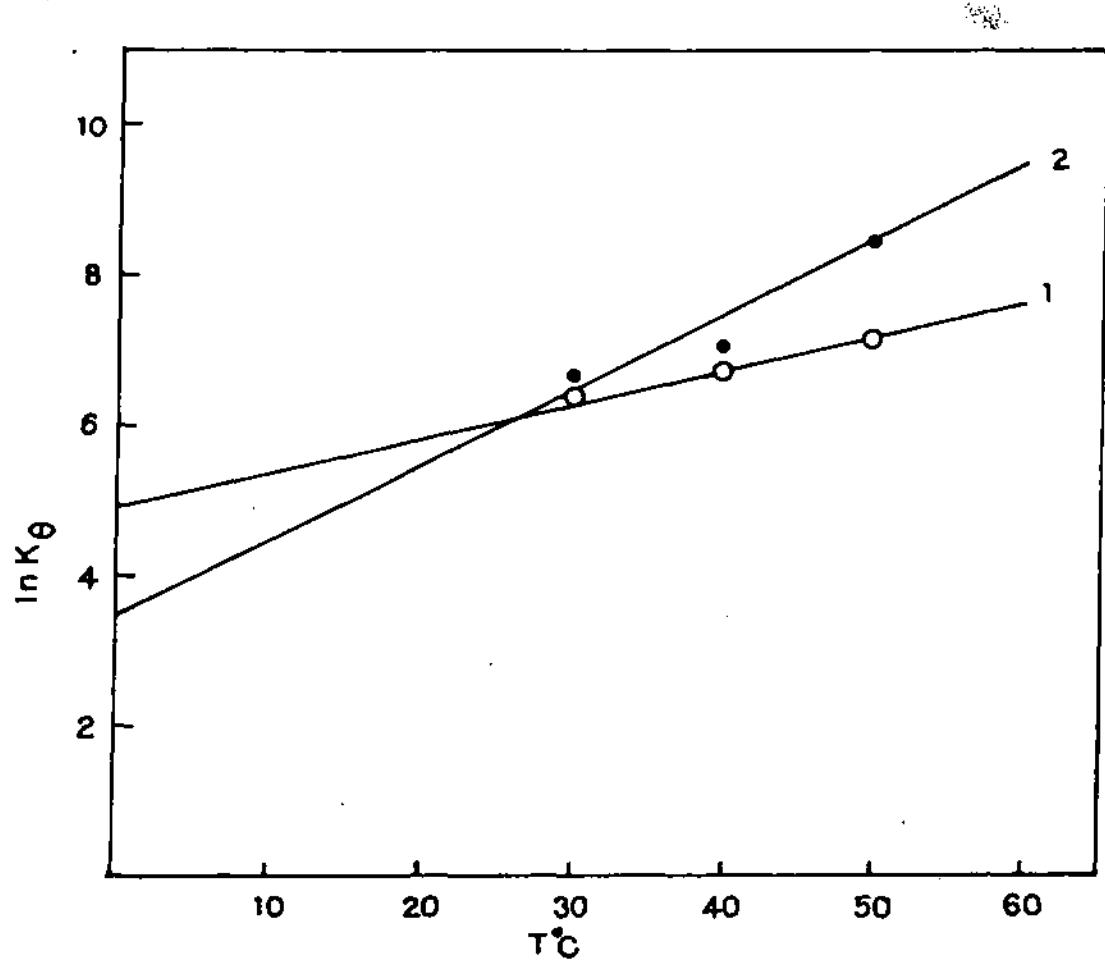


Fig. 72 Dependence of  $\ln K_\theta$  on temperature for PAM fractions  
at various cosolvent compositions:  $\phi_{\text{DMSO}} = 0.20(1)$ ;  
 $\phi_{\text{DMSO}} = 0.30(2)$ .

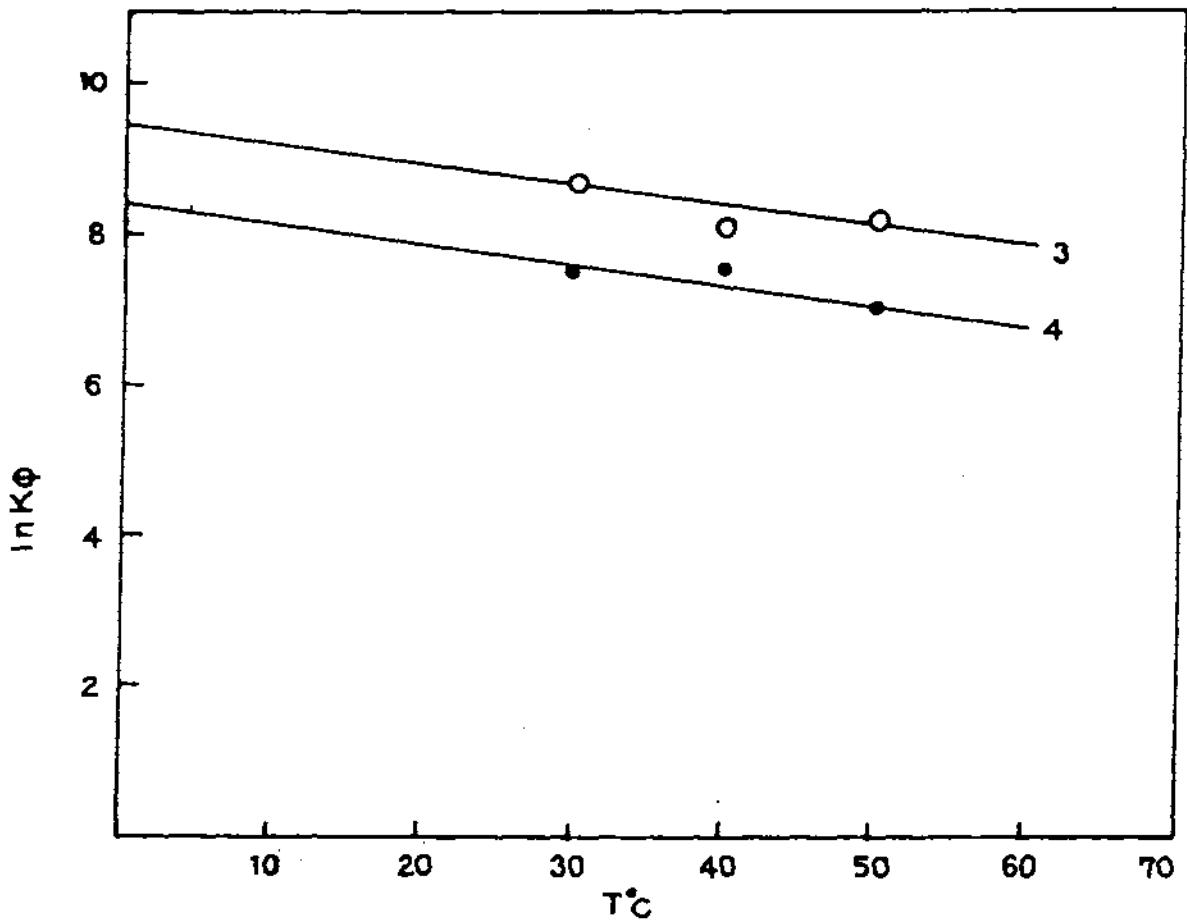


Fig. 73 Dependence of  $\ln K_\phi$  on temperature for PAM fractions at various cosolvent compositions:  $\varphi_{\text{DMSO}} = 0.50(3)$ ;  $\varphi_{\text{DMSO}} = 0.70(4)$ .

compositions of the solvent.<sup>352</sup> However, at 8:2 composition, K<sup>t</sup> again assumes a positive value showing better cosolvency of the mixture.

**Table – 31**

Unperturbed dimension of PAM in water + DMSO mixtures at different temperatures determined by different methods.

Temp. °C	$\phi_{\text{DMSO}}$	$K_0 \times 10 (\text{cm}^3 \text{g}^{-3/2} \text{mole}^{1/2})$					
		BSF <sup>a</sup>	KS <sup>b</sup>	T <sup>c</sup>	Bo <sup>d</sup>	FF <sup>e</sup>	Be <sup>f</sup>
30	0.2	1.500	1.480	1.446	1.500	1.440	1.440
	0.3	1.125	1.115	0.910	1.120	1.114	1.123
	0.5	0.150	0.116	0.110	0.125	0.107	0.086
	0.7	0.650	0.649	0.490	0.375	0.196	0.225
	0.8	1.600	1.570	1.430	1.312	1.250	1.370
40	0.2	1.25	1.240	1.070	1.125	1.174	1.123
	0.3	0.95	0.960	0.954	0.968	0.960	0.945
	0.5	0.35	0.327	0.287	0.187	0.290	0.256
	0.7	0.50	0.465	0.435	0.312	0.164	0.100
	0.8	1.50	1.483	1.300	1.281	1.253	1.225
50	0.2	0.825	0.818	0.435	0.812	0.801	0.730
	0.3	0.200	0.125	0.110	0.125	0.098	0.095
	0.5	0.250	0.241	0.165	0.125	0.218	0.170
	0.7	0.925	0.925	0.807	0.688	0.512	0.484
	0.8	1.550	1.525	1.375	1.343	1.525	1.520

<sup>a</sup> Burchard – Stockmayer – Fixman, <sup>b</sup> Kurata – Stockmayer,

<sup>c</sup> Tanaka, <sup>d</sup> Bohdanecky, <sup>e</sup> Fox-Flory, <sup>f</sup> Berry.

**Table – 32**

Temperature co-efficients ( $K^l$ ) of unperturbed dimension at different DMSO compositions.

$\phi_{\text{DMSO}}$	$K^l \text{ (degree}^{-1}\text{)}$
0.2	0.0460
0.3	0.0947
0.5	-0.0300
0.7	-0.0280
0.8	0.0320

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

The molecular extension factor ( $\alpha_n$ ) has been calculated from the relation<sup>331</sup>:

$$\alpha_n^3 = [\eta] / K_0 M^{1/2} \quad (54)$$

using  $K_0$  from the BSF plot. The actual end-to-end distance,  $\alpha_n K_0$ , of polymer molecule is also computed, which are shown in Table 33. It is observed that at  $\phi_{\text{DMSO}} = 0.5$ ,  $\alpha_n K_0$  attains the lowest value for all the molecular weight fractions of the polymer. However,  $\alpha_n$  value is the highest at the above composition. The intermolecular interaction is probably responsible for the high value of  $\alpha_n$  at  $\phi_{\text{DMSO}} = 0.5$  because of the small value of the unperturbed dimension at this composition. The molecular weight dependency of  $\alpha_n$  is also clear from the table ;  $\alpha_n$  increases with the increase in molecular weight of the polymer. As the molecular weight of the polymer increases, the number of segmental interactions of the polymer molecule with solvent molecule increases, resulting in a larger value of  $\alpha_n$ .

## Chain rigidity

The structural parameters of PAM, viz., the steric factor  $\sigma$  and the characteristic ratio  $C_\infty$  are also calculated in the usual manner from the following equations<sup>29</sup>:

$$\sigma = [\langle r^2 \rangle_o / M]^{1/2} \text{ of} / [\langle r^2 \rangle_{of} / M]^{1/2} \quad (67)$$

$$[\langle r^2 \rangle_{of} / M]^{1/2} = [\langle r^2 \rangle_{of} / N]^{1/2} [1/M_o]^{1/2} \quad (68)$$

$$C_\infty = (K_0 / \phi_o)^{2/3} (M_o / 2L^2) \quad (69)$$

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 ( $L = 0.154$  nm). For vinyl polymers the value of  $(\langle r^2 \rangle_{of} / N)^{1/2} = 3.08 \times 10^{-8}$  cm (Ref. 353). The computed values of  $C_\infty$ ,  $\sigma$  and  $(r^2)_o / M)^{1/2}$  for PAM at different solvent compositions and temperatures are shown in Table 34. Cowie<sup>354</sup> observed that the range of values of  $\sigma$  normally encountered is about 1.5 – 2.5 (Ref. 354). In the present study also the value of  $\sigma$  falls within the above range and it decreases with  $\phi_{DMSO}$  initially and, then increases giving rise to the lowest value at  $\phi_{DMSO} = 0.5$ . This indicates again that the most rigid structure of the polymer exists at the above solvent composition.

**Table-33**

Molecular extension factor and coil dimensions of PAM at different temperatures and water + DMSO mixtures.

Temp. °C	$\phi_{\text{DMSO}}$	LM		MM		HM	
		$\alpha_n$	$\alpha_n K_e \times 10$	$\alpha_n$	$\alpha_n K_e \times 10$	$\alpha_n$	$\alpha_n K_e \times 10$
30	0.2	1.031	1.546	1.026	1.539	1.085	1.628
	0.3	1.053	1.185	1.192	1.340	1.176	1.323
	0.5	1.723	0.258	2.332	0.350	2.426	0.364
	0.7	1.330	0.865	1.640	1.070	1.720	1.117
	0.8	1.133	1.813	1.299	2.080	1.339	2.142
40	0.2	1.114	1.392	1.203	1.503	1.296	1.620
	0.3	1.091	1.036	1.170	1.112	1.169	1.110
	0.5	1.438	0.503	1.890	0.661	1.948	0.682
	0.7	1.470	0.735	1.858	0.929	2.000	1.001
	0.8	1.130	1.695	1.313	1.970	1.338	2.008
50	0.2	1.143	0.943	1.235	1.020	1.393	1.150
	0.3	1.580	0.316	2.250	0.450	2.347	0.470
	0.5	1.663	0.416	2.216	0.554	2.327	0.582
	0.7	1.293	1.196	1.522	1.408	1.650	1.526
	0.8	1.074	1.664	1.222	1.894	1.200	1.860

**Table – 34**

Unperturbed dimension, steric factor ( $\sigma$ ), characteristic ratio ( $C_\infty$ ) as functions of  $\phi_{\text{DMSO}}$  and temperature.

Temp. °C	$\phi_{\text{DMSO}}$	$[<r^2>_0/M]^{1/2} \times 10^9$ (cm.g <sup>-1/2</sup> mole <sup>1/2</sup> )	$C_\infty$	$\sigma^a$
30	0.2	8.43	8.85	2.31
	0.3	7.66	7.30	2.10
	0.5	3.91	1.89	1.07
	0.7	6.38	5.05	1.75
	0.8	8.62	9.24	2.36
40	0.2	7.94	7.83	2.17
	0.3	7.24	6.52	1.98
	0.5	5.19	3.34	1.42
	0.7	5.85	4.24	1.60
	0.8	8.43	8.85	2.31
50	0.2	6.91	5.93	1.89
	0.3	4.31	2.30	1.62
	0.5	4.64	2.67	1.27
	0.7	7.18	6.40	1.97
	0.8	8.52	9.01	2.33

<sup>a</sup> value of  $[r^2]_0/M]^{1/2}$  has been taken as  $3.65 \times 10^{-9}$  cm.g<sup>-1/2</sup> mole<sup>1/2</sup>