

CHAPTER 6

Studies on solution properties of Poly (Vinyl Alcohol)
in water-acetone and water-tetra hydro furan
mixtures

6.1. Introduction and review of the previous work

Poly(vinyl alcohol) (PVA) has attracted much attention due to its excellent flexibility, transparency, toughness, and relatively low cost, especially in the era of high price petroleum. PVA has been widely used in different fields including textile sizing and is utilized as a finishing agent, an emulsifier, a photosensitive coating, and as an adhesive for paper, wood, textiles, and leather [1,2] In addition, it is a biologically friendly polymer because of its biodegradability and biocompatibility [3]. The unperturbed dimension (K_θ) of a polymer sample may be used to assess the viscosity expansion (α_n) of a flexible polymer chain [4,5]. This important parameter K_θ is conventionally determined by the solution-viscosity method at theta condition.

One of the most important methods utilizes Mark- Hownik-Sakurda (MHS) equation at theta condition (Equation 1)

$$[\eta]_\theta = K_\theta M^{1/2} \quad (1)$$

Where K_θ is the unperturbed dimension of the polymer which can be calculated from a number of graphical procedures based on the various theories of dilute polymer solution in non theta solvents.(as shown in Chapter 5)

Poly (vinyl alcohol) is an industrially important polymer, and this is shown by the fact that its production increases every year [6-10]. It exhibits a high degree of compatibility with inorganic salts [11], natural and synthetic resins, and other chemicals [12,13]. Small amount of PVA effectively stabilize emulsions [14], dispersions, and suspensions [15]. It also forms chemical complexes of practical importance [16]. The intrinsic viscosity $[\eta]$, which is a measure of the hydrodynamic size of the isolated molecules, and Huggin's constant K_H [17] which is a measure of their interactions with solvent, are both influenced by changes of solvent power[18] and temperature[19]. Besides theoretical interest, such measurements are also important for technical reasons such as the technique of polymer addition in motor oil recovery. Advances in the preparation of stereoregular polymers have stimulated the need to characterize their microtacticity and fine structure [20]. A

number of studies and experimental techniques were used to characterize the nature of polymers in different solvents, but there seems to be few systematic studies of the dilute solution properties in different solvents, and these are restricted to one or two temperatures.[21,22] As far as the polymers are concerned, the viscosity method can be successfully employed for the determination of the nature of the compound and their behavior in different solvents.

6.2 Exeperimental

High molecular weight Poly vinyl alcohol(Type-A) (average molecular weight 1.24×10^5), medium molecular weight Poly vinyl alcohol(Type-B) (average molecular weight 0.95×10^5) and low molecular weight Poly vinyl alcohol(Type-C) (average molecular weight 0.72×10^5) were purchased from Aldrich, Belgium, Across organics,USA and Fluka,Switzerland respectively. An Ubbelohde viscometer was used to mesure the relative viscosities of polymer solutions. The Viscometer was placed in thermostated water bath at appropriate temperature, controlled within the range of $\pm 0.1^\circ\text{C}$ and a digital stopwatch with accuracy ± 0.1 sec was used to measure flow time. The definitions of the important quantities and parameters are as follow:

$$\text{Specific viscosity, } \eta_{sp} = (t - t_0)/t_0 \quad (2)$$

$$\text{Reduced viscosity, } \eta_{red} = \eta_{sp}/C \quad (3)$$

$$\text{Intrinsic viscosity, } [\eta] = (\eta_{sp}/C)_{C \rightarrow 0} \quad (4)$$

and the Huggins equation is

$$\eta_{sp}/C = [\eta] + K_H [\eta]^2 C, \quad (5)$$

where K_H is the Huggins constant. In the above relations, the symbol $[\eta]$ refers to as 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.

6.2.1 Result and Discussion

6.2.2 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. In general, for a flexible polymer in poor solvent, the intrinsic viscosity increases with temperature, whereas in good solvent it decreases with temperature. In athermal solvent, however, viscosity is independent of temperature (As has been already mentioned in Chapter 5) [23]. The polymer chains are expanded most at the temperature at which intrinsic viscosity ($[\eta]$) is the maximum. The variation of $[\eta]$ in the water-acetone mixture of all three types of PVA at different temperatures and solution compositions are shown in Figure 6.1-6.3. The result shows with the increase in the amount of nonsolvent (acetone) up to a certain limit, intrinsic viscosity also increases for all types of Poly (vinyl alcohol). Intrinsic viscosity reaches its maximum value near $\Phi_{ACE} = 0.4$ (Φ being the relative volume composition in the mixture) for all types of Poly (vinyl alcohol). This indicates that energetically the most favorable solvent composition is same all types of PVA. It is found that for all the molecular weight fractions, the intrinsic viscosity attains the minimum near $\Phi_{ACE} = 0.3$, indicating energetically the most unfavorable solvent composition for the polymer. The lowest value of $[\eta]$ at $\Phi_{ACE} = 0.3$ indicates the maximum degree of intermolecular aggregation of the polymer at this solvent composition. The decrease in $[\eta]$ after a certain limit is explained by the decrease in unperturbed mean square end-to-end distance. Instead of giving a minimum with the variation of solution composition, the $[\eta]$ reaches a maximum for all the polymer fractions at $\Phi_{ACE} = 0.4$ due to most powerful co-solvent effect. On the

other hand, the variation of $[\eta]$ in the water-tetrahydrofuran (THF) mixture of all three types of Poly vinyl alcohol at different temperatures and solution compositions are shown in Figure 6.4-6.6. The result shows that with the increase in the THF (poor solvent) concentration, the intrinsic viscosity decreases due to the contraction of the dimensions of polymer coil as well as for the higher degree of intermolecular agglomeration. However, at high value of Φ_{THF} the $[\eta]$ value tends to increase again for preferential solvation of the polymer due to high co-solvent effect. It is found that for all the molecular weight fractions, the intrinsic viscosity attains the minimum near $\Phi_{\text{THF}} = 0.2$ indicating energetically most unfavorable solvent composition for the polymer. The $[\eta]$ reaches a maximum for all the polymer fractions at $\Phi_{\text{ACE}} = 0.3$ due to most powerful co-solvent effect. The decrease in $[\eta]$ after the maximum is explained by the decrease in unperturbed mean square end-to-end distance. Moreover the effect of temperature on $[\eta]$ is also important. In case of both the binary solvent mixtures (i.e. water-acetone mixture and water- THF mixture) with increasing temperature the value of $[\eta]$ decreases due to lowering of the rotational barrier of the polymer. This enhance the degree of rotation about a skeletal bond, forcing the molecular chains to be more compact.

The co-solvency and the intermolecular interaction of polymers are also manifested in the Huggins constant (K_H) 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 value of the K_H values and their increment with the medium composition indicate enhanced interunit attractive interactions. Values of Huggins constant are presented in Table 6.1 and 6.2 for water- acetone mixture and for water-THF mixture respectively. The K_H values are calculated from the least square slopes of equation (5). It is observed that K_H values are maximum at the $\Phi_{\text{ACE}} = 0.1$ for water- acetone mixture and also at the $\Phi_{\text{THF}} = 0.1$ for the water- THF mixture respectively for all the types of polymers, indicating higher tendency of intermolecular aggregation at this composition of the solvent. K_H is the smallest for $\Phi_{\text{ACE}} = 0.4$ and for $\Phi_{\text{THF}} = 0.3$

under this condition, the nonsolvents pull the distance between polymer molecules closer to make polymer side chains twisted around each other. This action makes polymer main chain winds around polymer side chain and agglomerates.

6.2.3 Unperturbed dimension (UD)

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 volume exclusion due to long range segmental interaction is nullified by its interaction with a definite solvent (θ) [24, 25]. 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. In the present study, BSF equation under non-theta condition [26] has been used to derive K_θ (UD) of PVA in different water- acetone mixtures and water- THF mixtures respectively. The results are summarized in Table 6.3 for water- acetone mixtures and in Table 6.4 for water- THF mixtures respectively. Some of the BSF plots are shown (Chapter 5) in figures 6.7- 6.9 for water-acetone mixtures and in figures 6.10-6.12 for water- THF mixtures respectively. Plots are essentially linear. The value of K_θ obtained from various methods of measurements viz. BSF, ISK and Berry agree well with each other except for a few composition conditions of the solvents. It is apparent that at $\Phi_{ACE}=0.4$ and $\Phi_{THF}=0.1$ polymer have the lowest unperturbed dimension (this result is in general true for all the adopted methods for K_θ calculation). Strong attraction of two solvents (water- acetone mixtures at $\Phi_{ACE}=0.4$), causes the Poly (vinyl alcohol)s to have the lowest value of unperturbed chain. On the other hand, . It is observed that at $\Phi_{ACE}=0.2$ and $\Phi_{THF}=0.4$, the polymer have the highest unperturbed dimension (this result is in general true for all for all the methods which are mentioned for K_θ calculation) which indicates that above $\Phi_{ACE}=0.2$ water - acetone mixtures have the same co-solvency effect as was found at the $\Phi_{THF}=0.4$ in the water - THF mixtures. The effect of temperature is interesting. With an increase in temperature, r_0^2 and hence K_θ , increase due to greater bindness of rotation around the skeletal bonds. However, such a

temperature dependence of K_θ can be attributed not only to the change in flexibility of macromolecular chain but also to the specific polymer solvent interaction [27]. The effect may also be correlated to the cohesive energy density of the polymer and the solvent.

6.2.4 Molecular extension factor (α_n)

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

α_n has been calculated from the relation given below

$$\alpha_n^3 = [\eta]/K_\theta M_v^{1/2} \quad (6)$$

where K_θ 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 6.5 for water - acetone mixtures and in Table 6.6 for water - THF mixtures. It is observed that $\alpha_n K_\theta$ do not attain a definite lowest value at any fraction for water - acetone mixture but at $\Phi_{\text{THF}} = 0.1$ (water - THF mixtures) it is minimum. However, α_n value is the highest at the above composition. The intermolecular interaction is probably responsible for the high value of α_n at that ($\Phi_{\text{THF}} = 0.1$) composition for the solvent mixtures (water - THF mixtures). The molecular weight dependency of α_n is probably clear from the Table 6.5 and 6.6. α_n generally increases with increase in molecular weight of the polymer. As the molecular weight of the polymer increases, the number of segmental interaction of the polymer molecules with the solvent molecule increases, resulting in a large value of α_n .

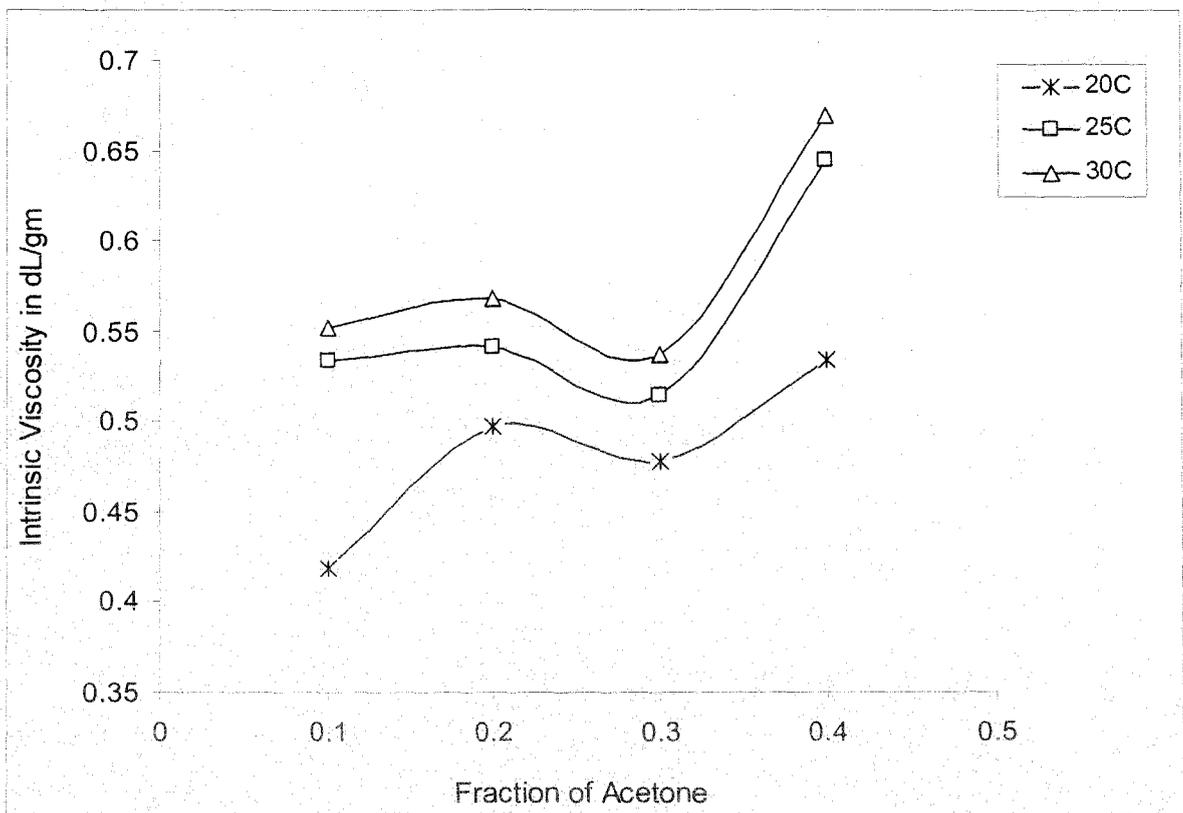


Figure 6.1: Change in intrinsic viscosity with fraction of acetone for PVA of (Type-A.)

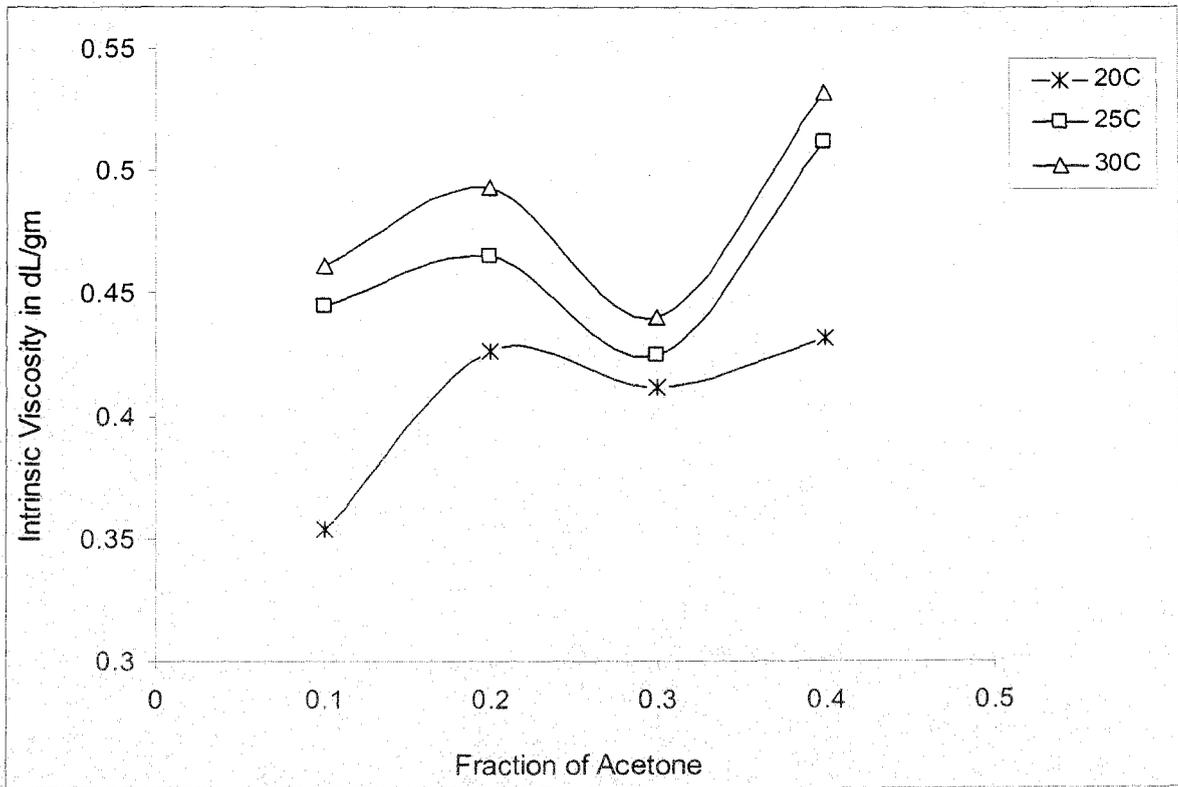


Figure 6.2: Change in intrinsic viscosity with fraction of acetone for PVA of (Type-B)

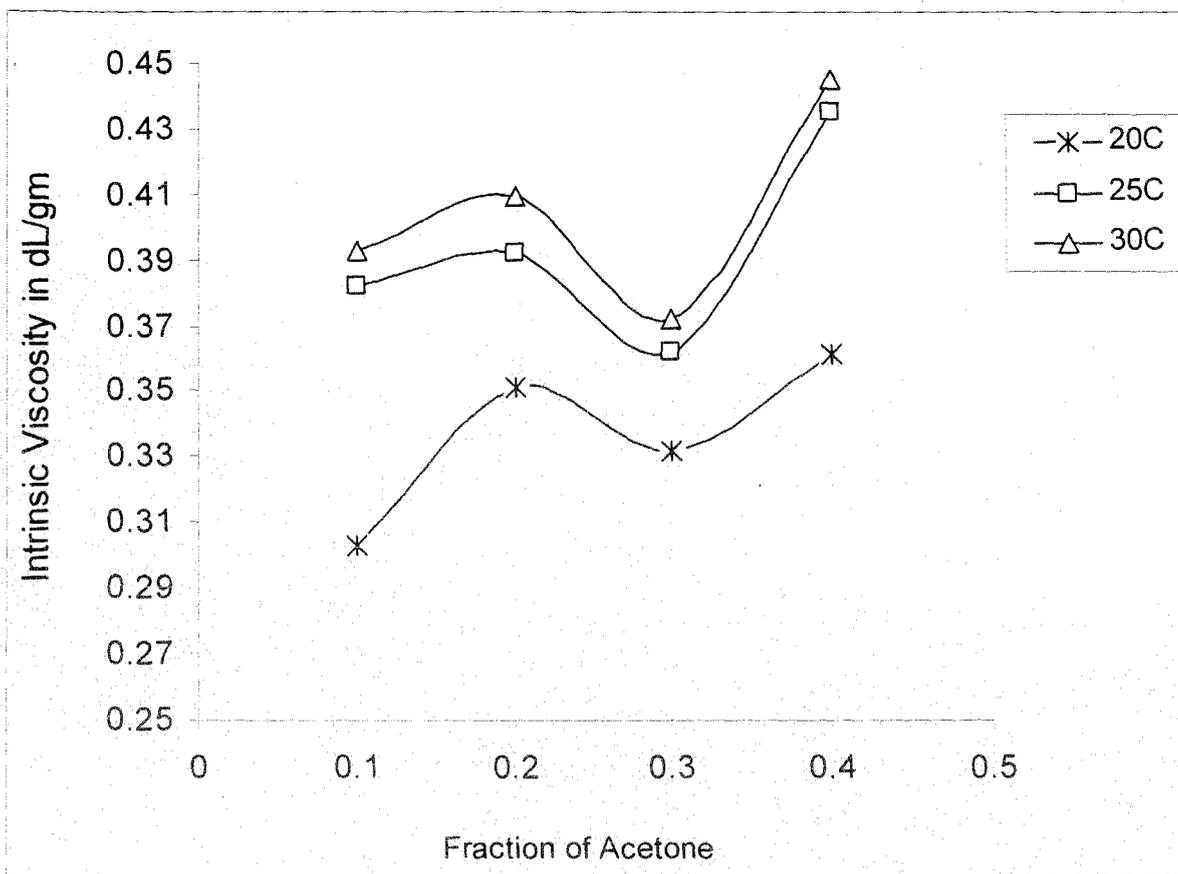


Figure 6.3: Change in intrinsic viscosity with fraction of acetone for PVA of (Type-C)

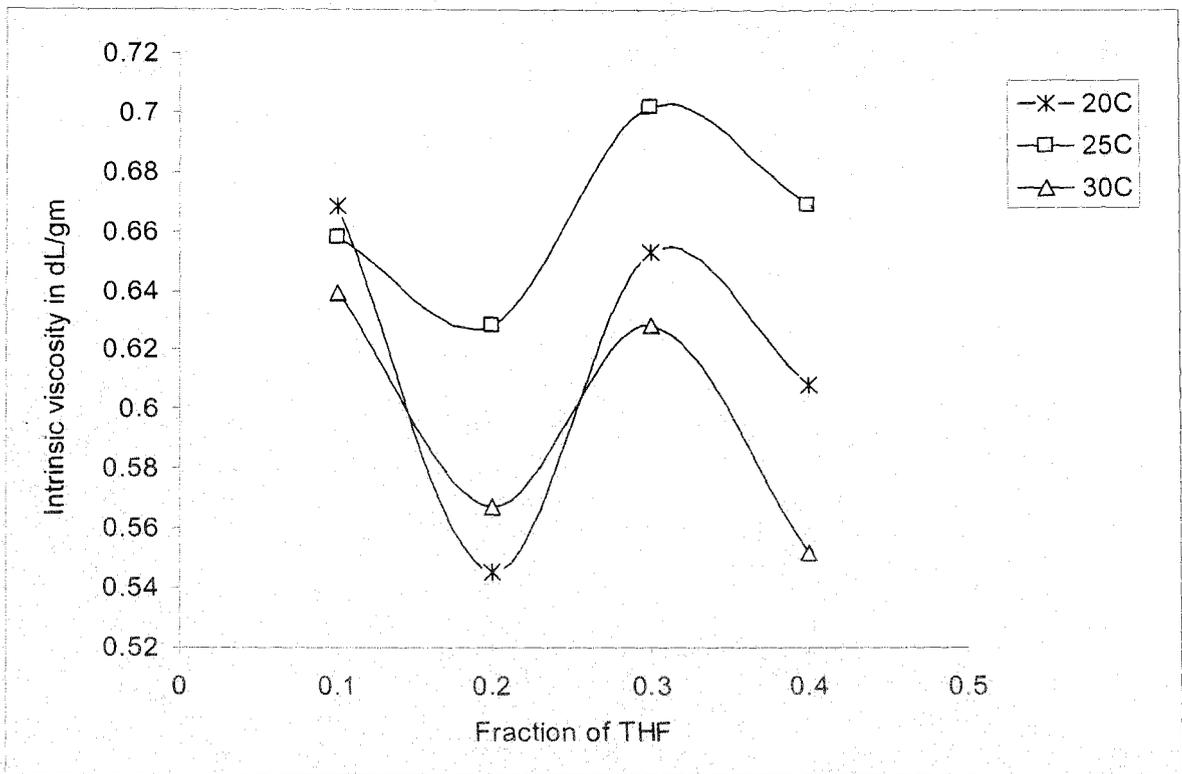


Figure 6.4: Change in intrinsic viscosity with fraction of THF for PVA of (Type-A)

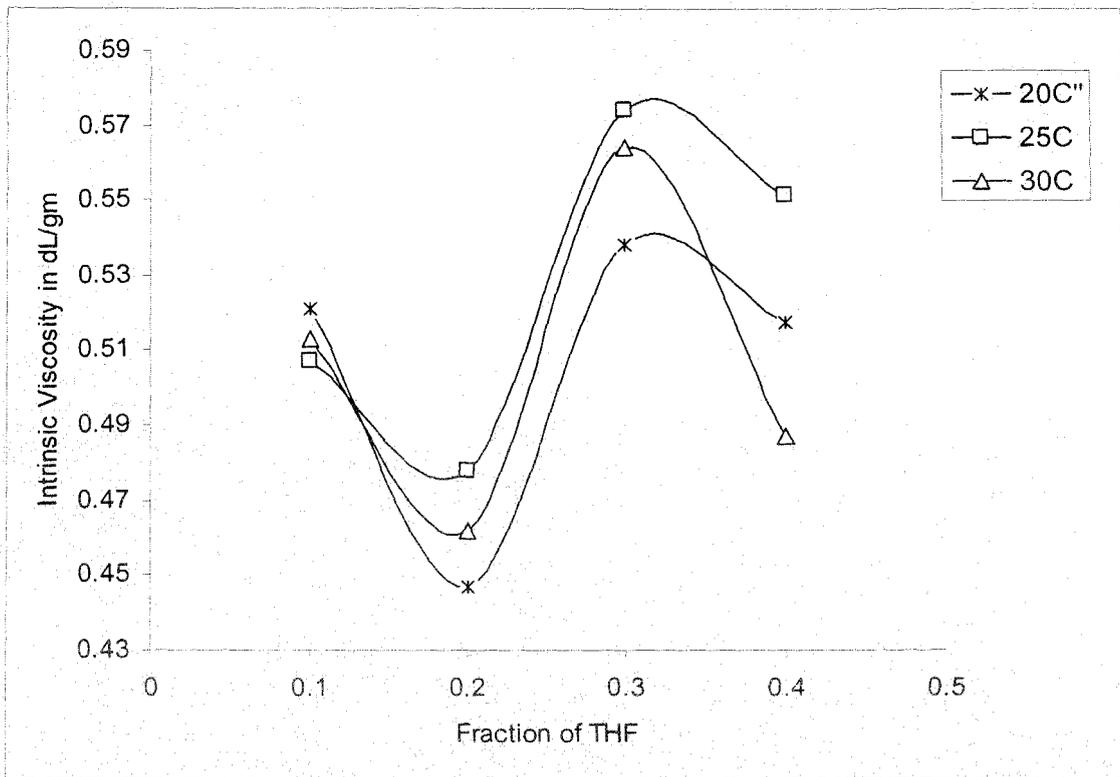


Figure 6.5: Change in intrinsic viscosity with fraction of THF for PVA of (Type-B)

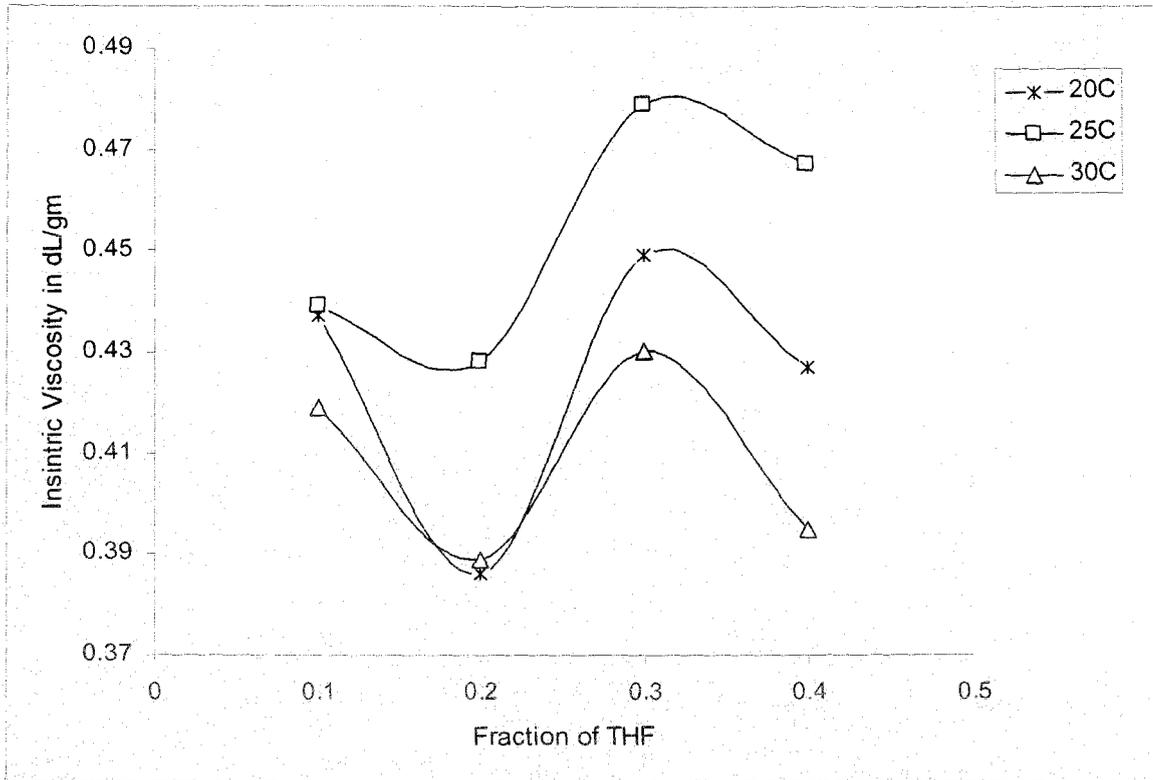


Figure 6.6: Change in intrinsic viscosity with fraction of THF for PVA of (Type-C)

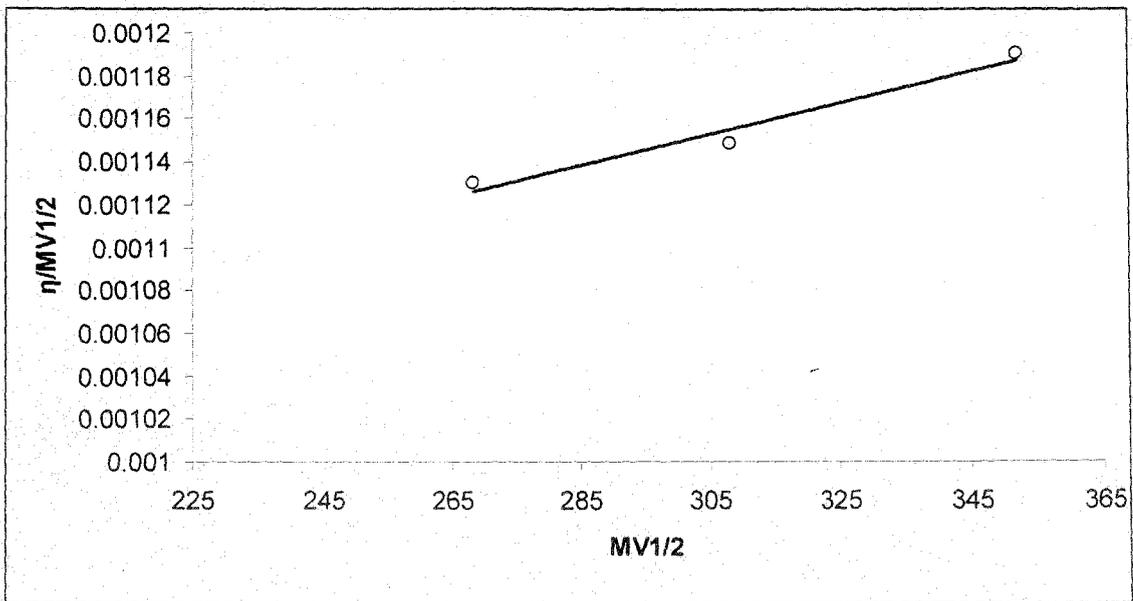


Figure 6.7: BSF plot at 20°C : $\Phi_{ACE} = 0.1$ for PVA

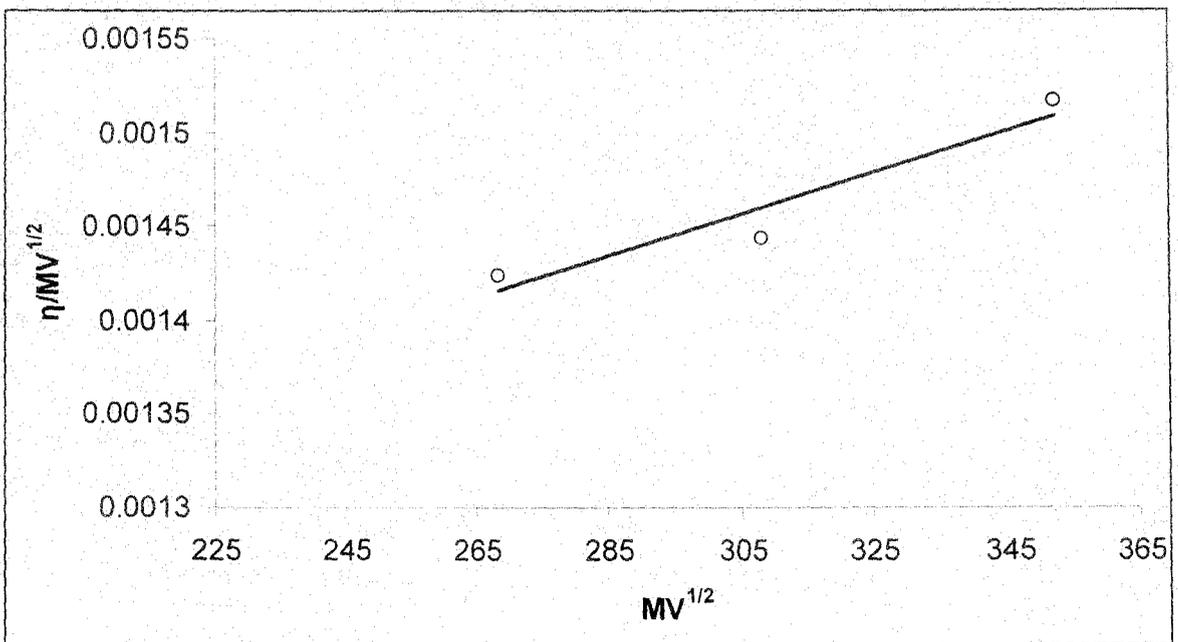


Figure 6.8: BSF plot at 25°C : $\Phi_{ACE} = 0.1$ for PVA

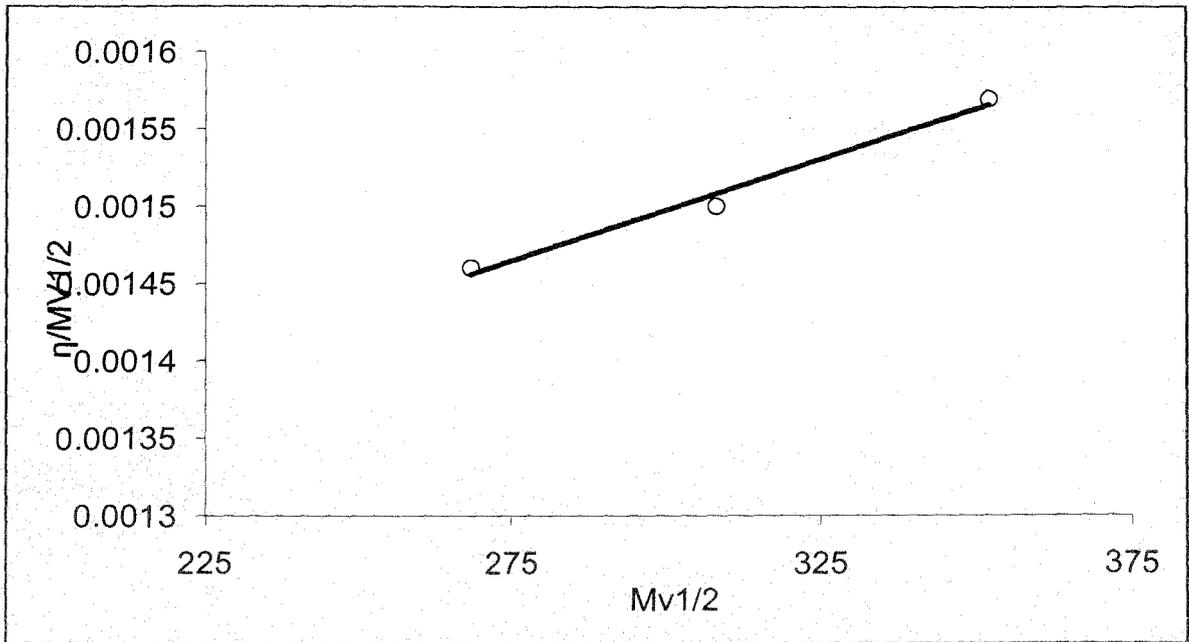


Figure 6.9: BSF plot at 30°C : $\Phi_{ACE} = 0.1$ for PVA

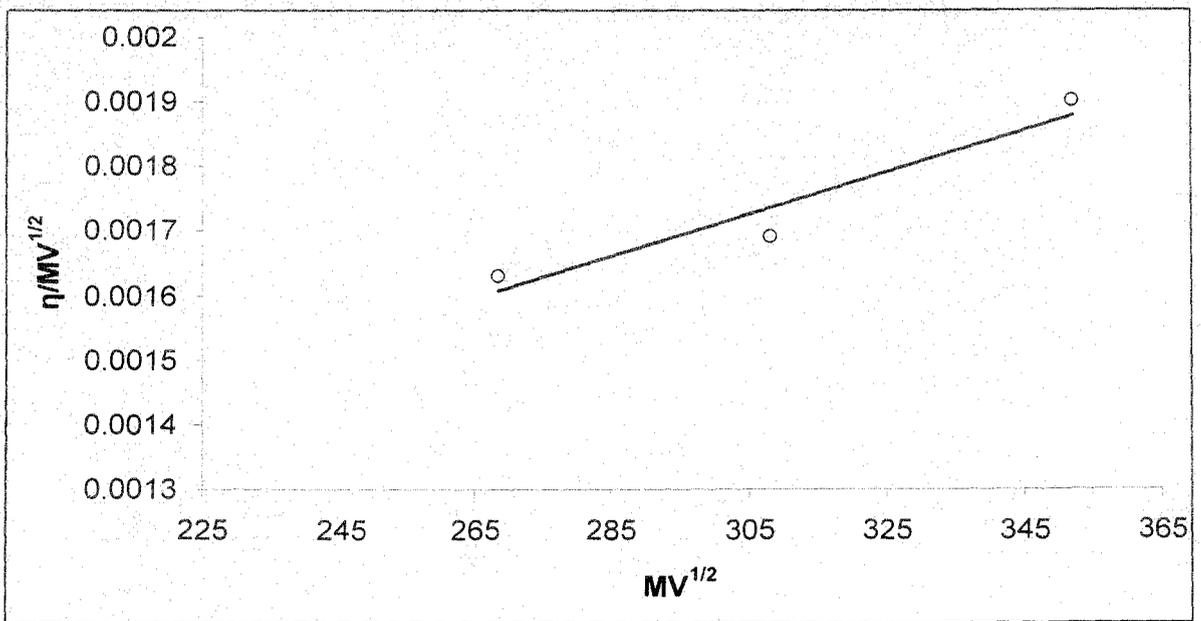


Figure 6.10: BSF plot at 20°C : $\Phi_{THF} = 0.1$ for PVA

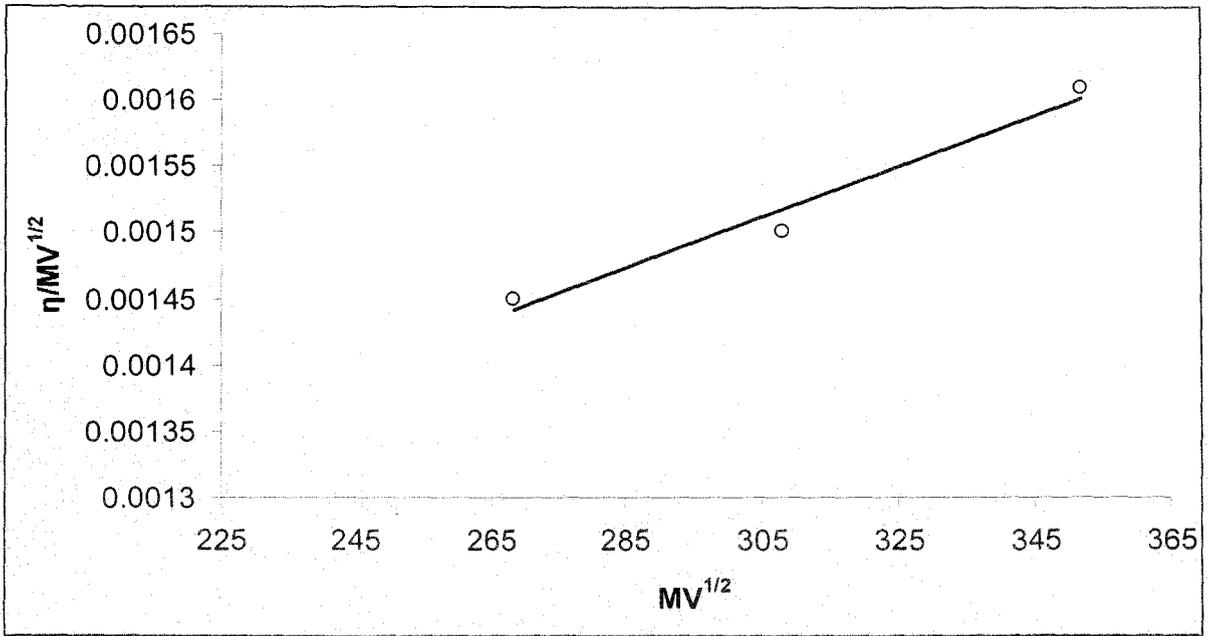


Figure 6.11:BSF plot at 25°C : $\Phi_{THF} = 0.1$ for PVA

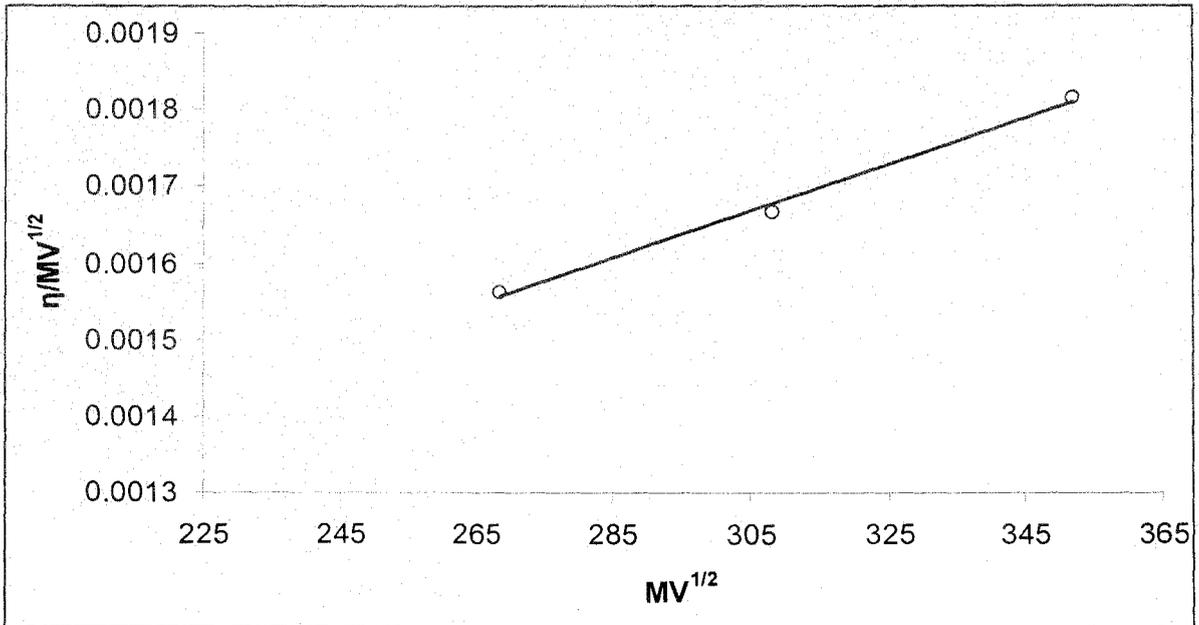


Figure 6.12 :BSF plot at 30°C: $\Phi_{THF} = 0.1$ for PVA

Table 6.1

Huggins constant of different fractions of Poly Vinyl Alcohol at different temperature and various solvent compositions(water-acetone)..				
Temp. in °C	$\Phi_{E.E}$	Poly Vinyl Alcohol		
		Type-A. K_H	Type-B. K_H	Type-C. K_H
20	0.1	0.594	0.638	0.645
	0.2	0.518	0.537	0.583
	0.3	0.453	0.478	0.514
	0.4	0.373	0.392	0.416
25	0.1	0.626	0.697	0.736
	0.2	0.598	0.562	0.674
	0.3	0.498	0.534	0.578
	0.4	0.422	0.475	0.517
30	0.1	0.783	0.734	0.796
	0.2	0.629	0.684	0.737
	0.3	0.573	0.622	0.684
	0.4	0.482	0.542	0.438

Table 6.2

Huggins constant of different fractions of Poly Vinyl Alcohol at different temperature and various solvent Compositions(water-THF).				
Temp. in °C	Φ_{THF}	Poly Vinyl Alcohol		
		Type-A K_H	Type-B K_H	Type-C K_H
20	0.1	0.414	0.398	0.341
	0.2	0.374	0.352	0.297
	0.3	0.239	0.193	0.174
	0.4	0.297	0.287	0.256
25	0.1	0.578	0.483	0.437
	0.2	0.426	0.386	0.227
	0.3	0.278	0.232	0.437
	0.4	0.284	0.252	0.238
30	0.1	0.473	0.422	0.419
	0.2	0.369	0.338	0.317
	0.3	0.234	0.221	0.216
	0.4	0.254	0.236	0.214

Table 6.3

Unperturbed Dimension of Poly vinyl Alcohol in water -acetone mixtures at different temperatures determined by different methods.

Temp. in °C	Φ_{ACE}	$K_g \times 10^4 (\text{mol}^{1/2} \text{g}^{-3/2} \cdot \text{dL})$		
		BSF	BERRY	ISK
20	0.1	9.306	7.800	9.963
	0.2	9.886	9.078	11.134
	0.3	8.702	7.775	9.250
	0.4	7.862	5.470	7.400
25	0.1	11.200	10.608	13.042
	0.2	12.200	11.833	14.835
	0.3	9.847	8.946	10.971
	0.4	9.296	7.403	8.703
30	0.1	11.300	10.517	13.000
	0.2	12.500	12.159	14.964
	0.3	9.313	10.654	9.804
	0.4	8.641	5.317	7.402

Table 6.4

Unperturbed Dimension of Poly Vinyl Alcohol in water -tetra hydro furan mixtures at different temperatures determined by different methods.

Temp. in °C	Φ_{THF}	$K_g \times 10^4 (\text{mol}^{1/2} \text{g}^{-3/2} \cdot \text{dL})$		
		BSF	BERRY	ISK
20	0.1	7.395	4.397	10.890
	0.2	10.700	10.182	12.164
	0.3	10.900	8.538	11.093
	0.4	11.700	10.407	12.916
25	0.1	8.456	8.928	7.327
	0.2	9.316	12.702	9.093
	0.3	11.100	8.237	10.930
	0.4	12.200	10.641	13.169
30	0.1	7.432	2.595	5.750
	0.2	9.237	7.349	9.330
	0.3	10.900	13.169	10.930
	0.4	11.900	11.999	13.975

Table 6.5

Molecular extension factor and coil dimensions of Poly Vinyl Alcohol at different temperature in various solvent composition (water- acetone).

Temp. in °C	Φ_{ACE}	Poly Vinyl Alcohol					
		Type-A		Type-B		Type-C	
		α_n	$\alpha_n \times K_{\theta} \times 10^4$	α_n	$\alpha_n \times K_{\theta} \times 10^4$	α_n	$\alpha_n \times K_{\theta} \times 10^4$
20	0.1	1.085	10.101	1.073	9.982	1.067	9.925
	0.2	1.126	11.132	1.118	11.054	1.098	10.853
	0.3	1.160	10.092	1.153	10.033	1.124	9.785
	0.4	1.245	9.787	1.213	9.532	1.196	9.404
25	0.1	1.106	12.390	1.088	12.189	1.082	12.132
	0.2	1.079	13.175	1.073	13.095	1.061	12.955
	0.3	1.140	11.228	1.119	11.017	1.110	10.936
	0.4	1.253	11.648	1.213	11.281	1.203	11.189
30	0.1	1.115	12.603	1.041	11.764	1.090	12.320
	0.2	1.089	13.609	1.020	12.751	1.068	13.354
	0.3	1.179	10.973	1.090	10.253	1.141	10.636
	0.4	1.300	11.236	1.186	10.155	1.242	10.738

Table 6.6

Molecular extension factor and coil dimensions of Poly Vinyl Alcohol at different temperature in various solvent composition (water- tetra hydro furan).

Temp. in °C	Φ_{THF}	Poly Vinyl Alcohol					
		Type-A		Type-B.		Type-C	
		α_n	$\alpha_n \times K_{\theta} \times 10^4$	α_n	$\alpha_n \times K_{\theta} \times 10^4$	α_n	$\alpha_n \times K_{\theta} \times 10^4$
20	0.1	1.369	10.123	1.317	9.741	1.301	9.621
	0.2	1.098	12.844	1.107	11.841	1.104	11.809
	0.3	1.194	13.012	1.17	12.752	1.154	12.574
	0.4	1.139	13.321	1.128	13.193	1.108	12.963
25	0.1	1.303	11.014	1.248	10.556	1.246	10.537
	0.2	1.242	11.567	1.185	11.041	1.196	11.145
	0.3	1.216	13.492	1.188	13.190	1.172	13.005
	0.4	1.159	14.141	1.136	13.857	1.126	13.734
30	0.1	1.347	10.008	1.308	9.723	1.281	9.518
	0.2	1.198	11.223	1.170	10.959	1.157	10.837
	0.3	1.178	12.844	1.188	12.955	1.137	12.394
	0.4	1.096	13.045	1.099	13.079	1.073	12.774

6.3 Reference

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