

**CHAPTER - VI**

**SEDIMENTATION BEHAVIOUR OF POLYMER SOLUTIONS**

## 6.1 INTRODUCTION

There is considerable literature on the sedimentation behaviour of macromolecules in solution. Sedimentation in dilute solutions is widely used as a means of determining the size and shape of sedimenting particles. Interest in sedimentation in more concentrated solutions has been enhanced following the recent advances in the physics of polymers, such as scaling concepts (1). The results have been verified using advanced experimental techniques such as small angle neutron scattering and laser light scattering. The developments in this area have been extensively reviewed (2,3).

The approaches to the concentration dependence of the sedimentation coefficient (table 6.1) have not been uniformly successful. The porous plug model has been popular but it applies only to semidilute and concentrated solutions. The scaling laws have a firm theoretical basis, but the same limitation applies. Moreover, experimental tests of these laws have yielded conflicting results. Rudin's model (9) for the hydrodynamic radius combined with the hard sphere model predicts the sedimentation behaviour fairly well. None of these models give a satisfactory explanation for the dramatically different

Table 6.1

Summary of previous approaches to sedimentation

Theory	Remarks	Reference
1. Mean Field Theory	Applicable only to dilute solutions	4
2. $S = \frac{S_0}{1 + n\lambda v}$ $\lambda$ = constant, $n$ = no. of coils per unit volume $v$ = volume of coil	Applicable only to dilute suspensions of Gaussian coils.	5
3. Porous plug model $S$ is related to permeability by $K = \frac{\eta_0 S}{c \left(1 - \frac{\gamma_2}{\gamma_1}\right)}$	Applicable only to semidilute and concentrated solutions.	6
4. Scaling laws $S \propto C^{-0.5}$ (good solvents) $S \propto C^{-1.0}$ (theta solvents)	Applicable only to semidilute solutions.	7
5. $S$ is related to the mobility of solvent $\frac{S}{1-\phi} = \psi S_0' (\langle m \rangle)_{\text{intra}} + (1-\psi) S_0'' \langle m \rangle_{\text{inter}}$	Parameters of the theory are not well defined	8
6. Model for the hydrodynamic radius combined with the hard sphere model.	No adjustable parameters, fairly good agreement with experimental data, specially at low concentrations and molecular weights.	9

behaviour of the sedimentation coefficient in good and theta solvents in the neighbourhood of the overlap concentration.

It is well established that sedimentation in polymer solutions is governed by the mobility of the solvent (10). As we have seen in chapter 1, mobility-dependent transport properties are frequently explained in terms of free volume concepts. However, this approach to sedimentation has not as yet been attempted. We shall now devise such an approach and examine as to how such an approach could be successfully used.

## 6.2 THEORETICAL DEVELOPMENT

As sedimentation involves a movement of the sedimenting particles relative to the solvent molecules, it is equivalent if we consider the motion of the solvent molecules through the solution. The relationship between the sedimentation coefficient  $S$  and the mobility of the solvent  $m$  was shown by Elmgren (10) to be

$$S = M (1 - \bar{v} \rho_0) (1 - \phi) m \quad (6.2.1)$$

where  $M$ ,  $\bar{v}$  and  $\phi$  represent the molecular weight, partial specific volume and the volume fraction of the polymer, respectively, and  $\rho_0$  is the density of the solvent. Further, Elmgren (8) distinguished between

the mobility of the solvent through the polymer coils (the intra-coil mobility  $m_1$ ) and the mobility of the solvent in the solvent channels around the coil (the inter-coil mobility  $m_2$ ). The total sedimentation coefficient is composed of contributions from both kinds of mobility,

$$\frac{S}{1-\phi} = \psi S'_0 m_1 + (1-\psi) S''_0 m_2 \quad (6.2.2)$$

where  $S'_0$  and  $S''_0$  are the sedimentation coefficients in extremely dilute solutions of polymer segments and polymer coils, respectively, and  $\psi$  is the fraction of the solvent which exists within the polymer coils. To compute  $\psi$  it is necessary to know the volume occupied by the polymer coils in solution, since

$$\psi = \frac{\phi_p - \phi}{1 - \phi} \quad (6.2.3)$$

where  $\phi_p$  is the volume fraction of the swollen polymer coils in solution. We have already described in chapter II a model whereby  $\phi_p$  may be computed as a function of concentration

$$\phi_p = \frac{c [\eta]}{2.5 (1 + 0.765 c [\eta]) - \frac{1.91c}{\rho}} \quad (6.2.4)$$

where  $c$  is the concentration of the polymer in g/cc,  $\rho$  is its density and  $[\eta]$  is the intrinsic viscosity.

We consider that while it is important to distinguish between the two kinds of mobility, the distinction between  $S'_0$  and  $S''_0$  is unnecessary. Equation (7.2.2) therefore

$$\frac{S}{S_0(1-\phi)} = \frac{\phi_P - \phi}{1 - \phi} m_1 + \frac{1 - \phi_P}{1 - \phi} m_2 \quad (6.2.5)$$

Equation (6.2.5) implies that the contribution to sedimentation coefficient from intra-coil mobility is a maximum in dilute solutions where the polymer coils are most swollen, decreases through the semidilute concentration regime as the coils contract, and attains a low constant value in the concentrated regime.

The relationship between the mobility and the free volume was given by Cohen and Turnbull

$$m = A \exp \left( - \frac{B_s}{f} \right) \quad (6.2.6)$$

where  $B_s$  is a constant related to the size of the molecule or segment involved in sedimentation. The intra and inter-coil mobilities will therefore be related to the free volume within the coils and in the solvent channels, respectively.

$$m_1 = A \exp \left( - \frac{B_s}{f_1} \right) \quad (6.2.7)$$

$$m_2 = A \exp \left( - \frac{B_S}{f_2} \right) \quad (6.2.8)$$

As in chapter II, we consider that the free volume is less than the sum of the contributions of the polymer and the solvent by an amount proportional to the concentration of the polymer. The proportionality factor is  $\beta$ , the immobilization parameter. Within a polymer coil, the volume fraction of the polymer is

$\frac{\phi}{\phi_P}$ . Hence

$$f_1 = f_P \frac{\phi}{\phi_P} + f_S \left( 1 - \frac{\phi}{\phi_P} \right) - \beta_1 \frac{\phi}{\phi_P} \quad (6.2.9)$$

In the inter-coil regions, the free volume is

$$f_2 = f_S \phi_S - \beta_2 \phi_P \quad (6.2.10)$$

We have seen in chapter II that  $\beta$  changes from one concentration regime to another. Since the concentration of the polymer within a coil is likely to be considerably different from the overall concentration in the solution,  $\beta_1$  and  $\beta_2$  are likely to have different values.

Substitution of eqns. (6.2.7), (6.2.8), (6.2.9) and (6.2.10) into eqn. (6.2.5) yields

$$\frac{S}{S_0} = (\phi_P - \phi) \exp \left[ - \frac{(f_S - f_P + \beta_1) \frac{\phi}{\phi_P}}{f_S - (f_S - f_P + \beta_1) \frac{\phi}{\phi_P}} \cdot \frac{B_s}{f_S} \right] + (1 - \phi_P) \exp \left[ - \frac{(f_S + \beta_2) \phi_P}{f_S - (f_S + \beta_2) \phi_P} \cdot \frac{B_s}{f_S} \right] \quad (6.2.11)$$

Equation (6.2.11) is not in a form which can easily be used for analysis of experimental data. Moreover, there are three unknown parameters— $\beta_1$ ,  $\beta_2$  and  $B_s$ , which have to be determined in each concentration regime. This is clearly impossible. It is therefore necessary to simplify the model. This is done by considering the "average" mobility in the system which would depend on the "average" free volume

$$f = f_P \phi_P + f_S \phi_S - \beta \phi_P \quad (6.2.12)$$

Substitution of eqns. (6.2.6) and (6.2.12) into eqn. (6.2.1) yields

$$\frac{1}{\ln \frac{S}{S_0} \frac{(1-\phi)}{S}} = \frac{f_S}{B_s \left(1 + \frac{\beta - f_P}{f_S}\right) \phi_P} - \frac{f_S}{B_s} \quad (6.2.13)$$

A comparison with eqn. (6.2.11) shows that formulation of the model in terms of an average mobility and an average free volume is in effect equivalent to a neglect of the contribution of the intra-coil mobility to the sedimentation coefficient.



Equation (6.2.13) can be used to correlate the sedimentation behaviour in polymer solutions. The model now has two unknown parameters,  $B_s$  and  $\beta$ , which have to be determined by data fit. All other parameters appearing in eqns (6.2.13) and (6.2.4) can be experimentally determined ( $S$ ,  $S_0$ ,  $[\eta]$ ,  $c$  and  $\rho$ ) or can be obtained from the literature ( $f_s$  and  $f_p$ ).  $B_s$  and  $\beta$  are expected to be different in each concentration regime, analogous to the corresponding parameters for viscosity of polymer solutions.

### 6.3 COMPARISON WITH EXPERIMENTAL DATA.

In chapter II. the effect of a number of variables on the viscosity behaviour of polymer solutions was analysed. The sedimentation behaviour of polymer solutions has not been as extensively studied. The range of concentration investigated is not as wide and the data frequently show considerable scatter. In this section the data reported in the literature mainly in tabular form have been used for analysis. A summary of the systems analysed is given in table 6.2.

#### 6.3.1 Concentration Dependence of the Sedimentation Coefficient.

Roots and Nystrom (11) investigated the applicability of scaling concepts for the analysis of sedimentation

Table 6.2

## Summary of the Systems Analysed

System	Temperature (°C)	Concentration range (g/cc)	Molecular weight	Concentration regime	$B_s$	$\beta$	Regression coefficient	No. of data points	Reference
1. Polystyrene- toluene	25	0.0004-0.037	$4.48 \times 10^6$	II	0.7524	-0.0246	0.9829	5	11
		0.0005-0.040	$2.06 \times 10^7$	II	0.1484	0.1283	0.9751	6	
2. Polystyrene- toluene	25	0-0.10	$1.1 \times 10^5$	II	0.4485	0.0253	0.9901	3	12
		0-0.06	$3.9 \times 10^5$	II	1.1699	-0.0787	0.9977	10	
		0-0.03	$1.8 \times 10^6$	I	0.7629	0.0137	0.9953	5	
3. PMMA-toluene	25	0-0.056	$1.4 \times 10^6$	II	1.8082	-0.1076	0.9976	6	
				I	7.9945	-0.1808	0.9942	4	13
				II	1.2171	-0.0786	0.9645	4	
4. PTEMA-toluene	25	0-0.11	$1.35 \times 10^6$	III	0.3786	0.0503	0.9877	4	
				I	1.7307	-0.1059	0.9931	5	13
				II	0.4551	0.0448	0.9963	6	
5. Ficoll-water	25	0-0.13	$1.0 \times 10^6$	I	0.7688	-0.0221	0.9942	5	
		0-0.298	$4.0 \times 10^5$	II	0.5029	0.0327	0.9951	5	
				I,II	0.3976	0.0990	0.9955	10	14

Table 6.2 (contd.)

System	Temperature (°C)	Concentration range (g/cc)	Molecular weight	Concentration regime	$B_s$	$\beta$	Regression coefficient	No. of data points	Reference
6. Hydroxypropyl cellulose-water	25	0-0.09	$7.3 \times 10^4$	I	0.1307	0.3762	0.9945	3	15
				II	0.3699	0.0323	0.9909	8	
	30	0-0.09		I	0.4164	0.0104	0.9978	12	
	34			I	0.3279	0.0254	0.9845	11	
	37			I	0.1570	0.1373	0.9991	12	
7. Polystyrene- cyclopentane	20	0-0.27	$2.04 \times 10^4$	I	0.3172	0.1713	0.9876	7	18
				II	1.0950	-0.0539	0.9995	3	
		0-0.17	$1.1 \times 10^5$	I	0.2891	0.1113	0.9964	7	
				II	0.3212	0.1103	0.9930	4	
		0-0.11	$3.9 \times 10^5$	I	0.3617	0.0927	0.9906	7	
				II	0.6197	0.0116	0.9914	3	
8. Polystyrene- cyclopentane		0-0.08	$9.5 \times 10^6$	I	0.5723	0.0282	0.9958	5	
				II	1.1862	-0.0655	0.9998	3	
				III	0.5259	0.0433	0.9999	3	
	11	0-0.17	$1.1 \times 10^5$	I	0.0952	0.2803	0.9941	7	18
	15	"	"	II	0.1838	0.1567	0.9887	3	
	20	"	"	II	0.2409	0.1438	0.9912	6	
40		"	"	I	0.2891	0.1113	0.9964	7	
		"	"	II	0.3212	0.1103	0.9930	4	
		"	"	II	0.5929	0.0460	0.9989	5	

Table 6.2 (contd.)

System	Temperature (°C)	Concentration range (g/cc)	Molecular weight	Concentration regime	$B_s$	$\beta$	Regression coefficient	No. of data points	Reference
9. Polystyrene-cyclohexane	31	0-0.09	$3.92 \times 10^5$	I	0.1393	0.0736	0.9409	5	19
				II	0.1379	0.1995	0.9842	6	
	35	"	"	I	0.1136	0.2985	0.9904	6	
				II	0.3460	0.0909	0.9715	5	
	40	"	"	I	0.1945	0.1737	0.9990	7	
				II	0.3668	0.0884	0.9416	5	

data for the solutions of polystyrene in toluene. The transition from the dilute to the semidilute concentration regimes could be easily discerned and the concentration at which the transition occurred was in good agreement with the value predicted by the relationship  $c^* = \frac{1}{[\eta]}$ .

Figure 6.1 shows the results of analysis for this system. For polystyrene of molecular weight  $2.06 \times 10^7$ , the AFVS plot consists of a single straight line. This is to be expected since the concentration range investigated lies in the semidilute regime alone. On the other hand, for polystyrene of molecular weight of  $4.48 \times 10^6$ , the AFVS plot consists of two intersecting straight lines. The point of intersection corresponds to a transition from dilute<sup>(I)</sup> to semidilute regime (II). The concentration range investigated encompasses the entanglement concentration range as well. However, the transition from the semidilute unentangled (II) to semidilute entangled (III) regime is not apparent as only two data points lie in this range.

Table 6.2 shows that  $B_s$  values for this system in the dilute regime could not be determined as the intercept of the AFVS plot was positive. This indicates that eqn. (6.2.13) underestimates the sedimentation coefficient, and that the error is most serious in the dilute regime. This is consistent with the fact that an error is introduced in eqn. (6.2.13) due to the

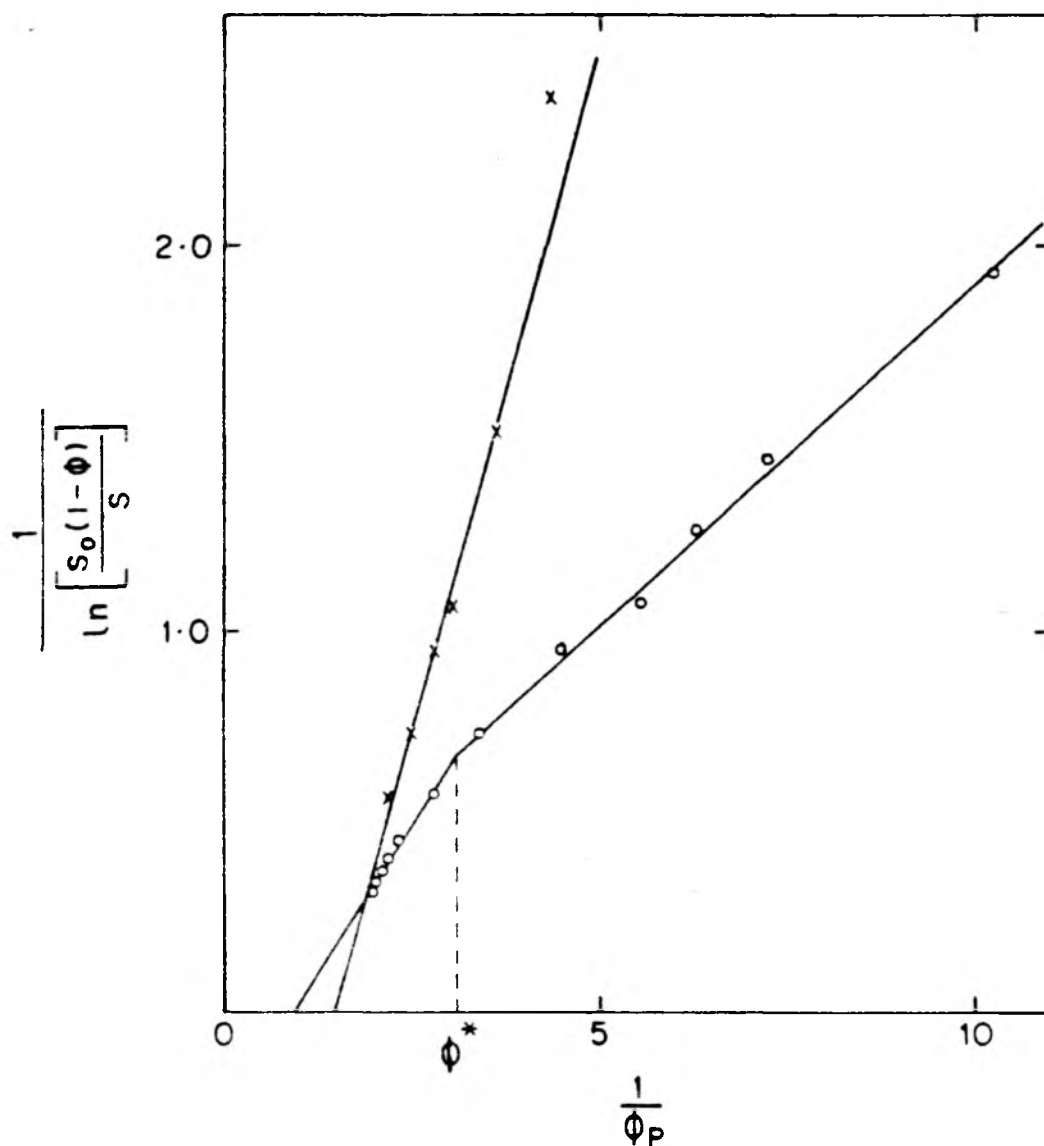


FIG.6-1: AFVS PLOTS FOR THE SYSTEM POLYSTYRENE-TOLUENE. SYMBOLS: o -  $MW = 4.48 \times 10^6$ ; x -  $MW = 2.06 \times 10^7$ . (REF. 11)

neglect of the contribution of the intra-coil mobility, which has the largest magnitude in the dilute regime.

Analysis of data reported by Nystrom et al (12) for solutions of polystyrenes of molecular weights  $1.1 \times 10^5$  and  $3.9 \times 10^5$  in toluene also clearly indicates a transition from regime I to regime II (Fig. 6.2). The transition in each case occurs at a concentration  $c^* = \frac{1}{[\eta]}$ . Again,  $B_s$  in the dilute regime could not be determined for the reasons mentioned above. For polystyrene of molecular weight  $1.8 \times 10^6$ , no meaningful parameters could be obtained due to the anomalous behaviour reported by Nystrom et al.

The concentration dependence of sedimentation coefficient of polymethylmethacrylate (PMMA) in dilute and semidilute solutions in toluene was reported by Nystrom et al (13). From the AFVS plot for this system shown in Fig. 6.3, two transitions, viz. from regime I to II and from regime II to III are evident. The value of  $B_s$  decreases with each transition, which is similar to the trends in  $B_\eta$  in the case of viscosity behaviour of polymer solutions. The negative values of  $\beta$  in dilute and semidilute regimes are again an indication that eqn. (6.2.13) underestimates the diffusion coefficient, specially in the lower concentration ranges.

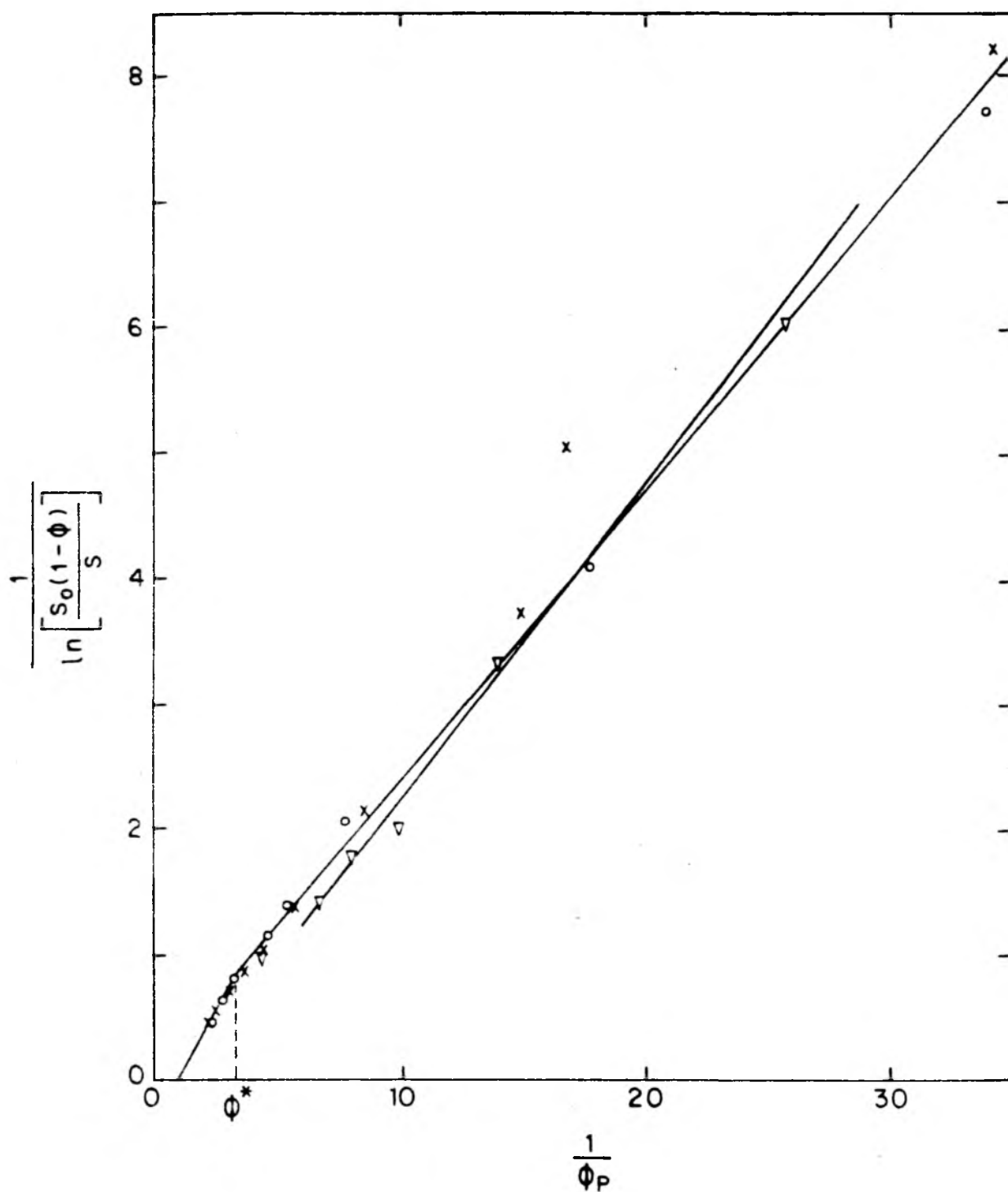


FIG.6-2 : AFVS PLOTS FOR THE SYSTEM POLYSTYRENE-TOLUENE. SYMBOL :  $\circ$  - MW =  $1.1 \times 10^5$ ;  $\times$  - MW =  $3.9 \times 10^5$ ;  $\nabla$  - MW =  $1.8 \times 10^6$ . (REF. 12)



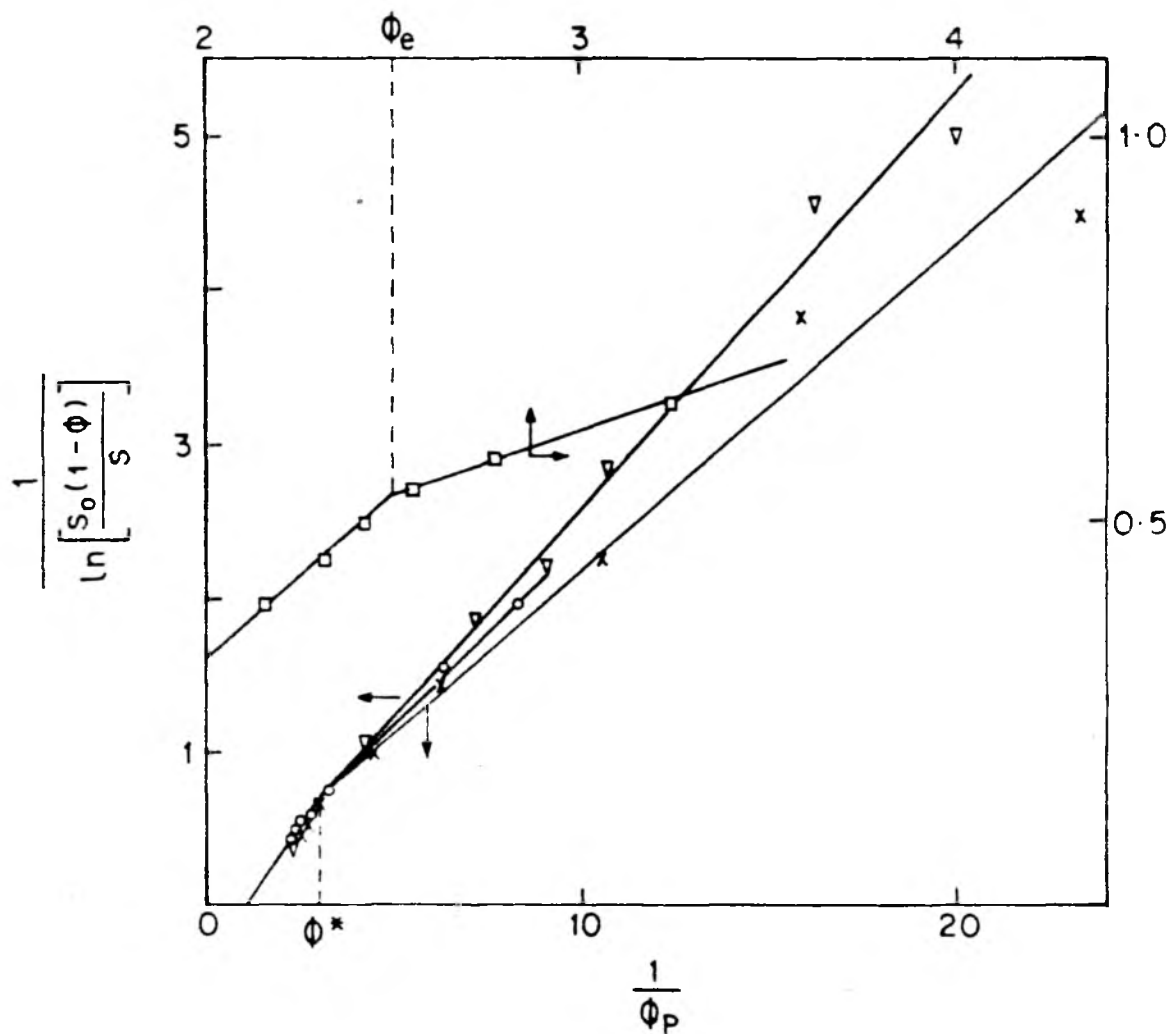


FIG.6-3: CONCENTRATION DEPENDENCE OF SEDIMENTATION COEFFICIENT FOR THE SYSTEM PMMA-TOLUENE,  $MW = 1.4 \times 10^6$  (o); PTEMA-TOLUENE,  $MW = 1.0 \times 10^6$  (x); PTEMA-TOLUENE,  $MW = 1.35 \times 10^6$  (∇). (REF.13)

So far we have considered sedimentation in solutions of flexible polymer molecules in good solvents. In such systems  $B_s$  has been shown to increase as there is a transition from one concentration regime to another. This is because in the semidilute regime the chain dimensions are smaller than in the dilute regime, and in the entangled regime a smaller part of the macromolecule takes part in process than in the unentangled regime. In the case of stiff molecules which do not assume random coil configurations in dilute solutions, a different behaviour may be expected.

Sundelof and Nystrom (14) determined the concentration dependence of sedimentation in aqueous solutions of Ficoll. An AFVS plot of the data is shown in Fig. 6.4. The data cover a concentration range upto 0.298 g/cc, which encompasses the dilute and semidilute concentration regimes. However, the data over the entire concentration regime may be represented by a single straight line. Ficoll being a stiff-chain molecule, not much change in the dimensions of the molecule is likely to take place when overlap between molecular domains becomes imminent. The values of  $B_s$  and  $\beta$  (table 6.2) are reasonable. Equation (6.2.13) is expected to be accurate in this case, since the contribution of the intra-coil mobility is absent.

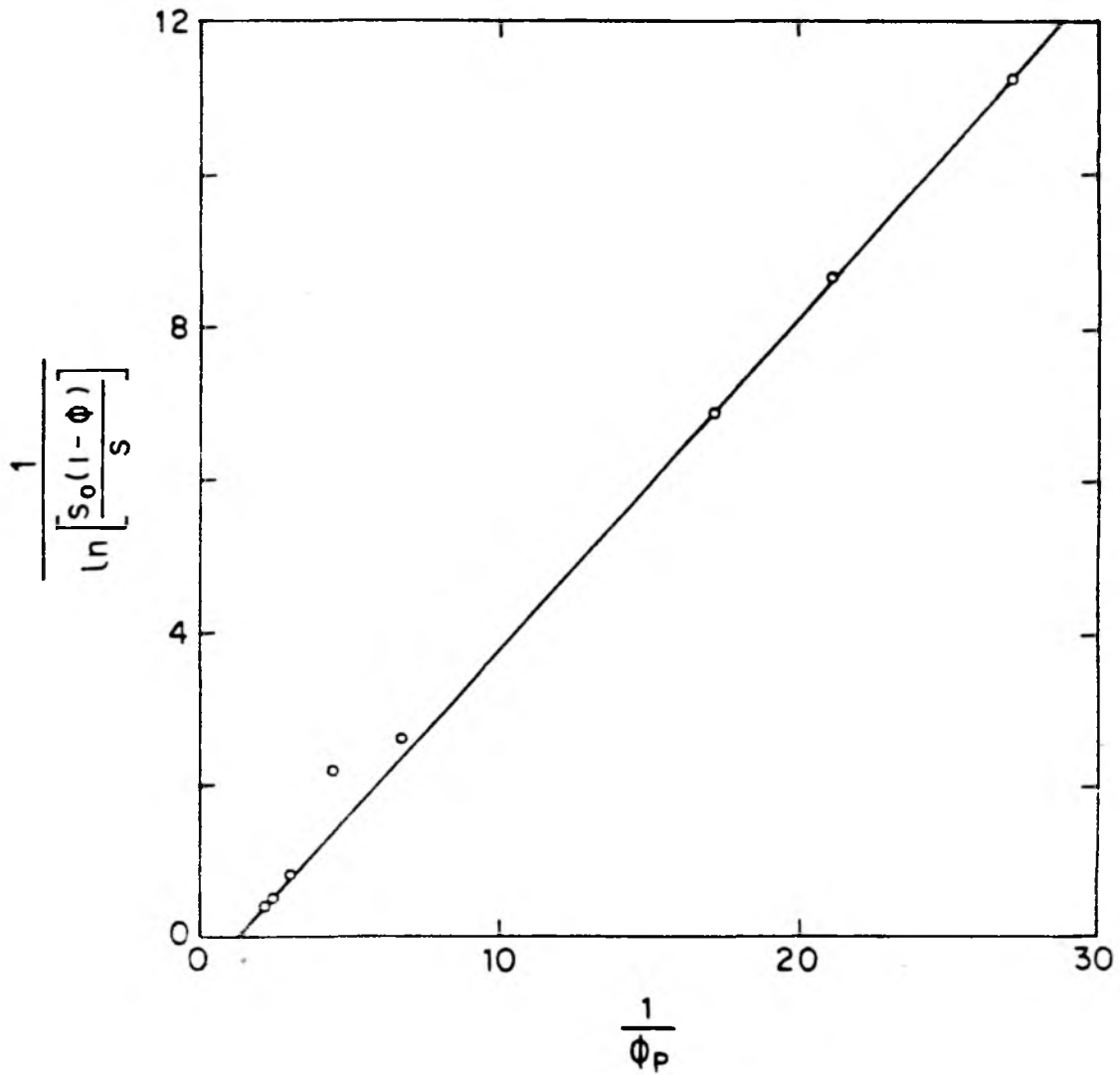


FIG.6.4 : CONCENTRATION DEPENDENCE OF SEDIMENTATION COEFFICIENT IN AQUEOUS SOLUTIONS OF FICOLL. (REF.14)

Figure 6.5 shows that the data for the system hydroxypropyl cellulose - water (15) lie along two straight lines intersecting at the critical concentration  $c^*$ . The value of  $B_s$  obtained below  $c^*$  is lower than above it, and the value of  $\beta$  is much higher in the lower concentration regime. This observation is contrary to our earlier observations in the case of flexible polymers. It may be noted here the Sundelof and Nystrom (15) also noted that a plot of  $\frac{S}{S_0}$  against the hydrodynamically normalised concentration was convex to the concentration axis, in contrast to the behaviour of flexible polymers for which this plot was concave to the concentration axis. Hydroxypropyl cellulose is a stiff-chain polymer with an extended conformation and water is a comparatively poor solvent for it at  $25^\circ\text{C}$ . Consequently when the overlap concentration is approached, there is not much contraction of the molecules. On the contrary, polymer-polymer linkages may be formed to some extent, leading to a higher value of  $B_s$ . Secondly, the system is one with a lower consolute temperature, a situation which is encountered when mixing is exothermic and the excess entropy of mixing has a large negative value. That is, there are regions in the solution which have a considerable degree of order (16). This ordered structure probably breaks down when the concentration of the polymer is

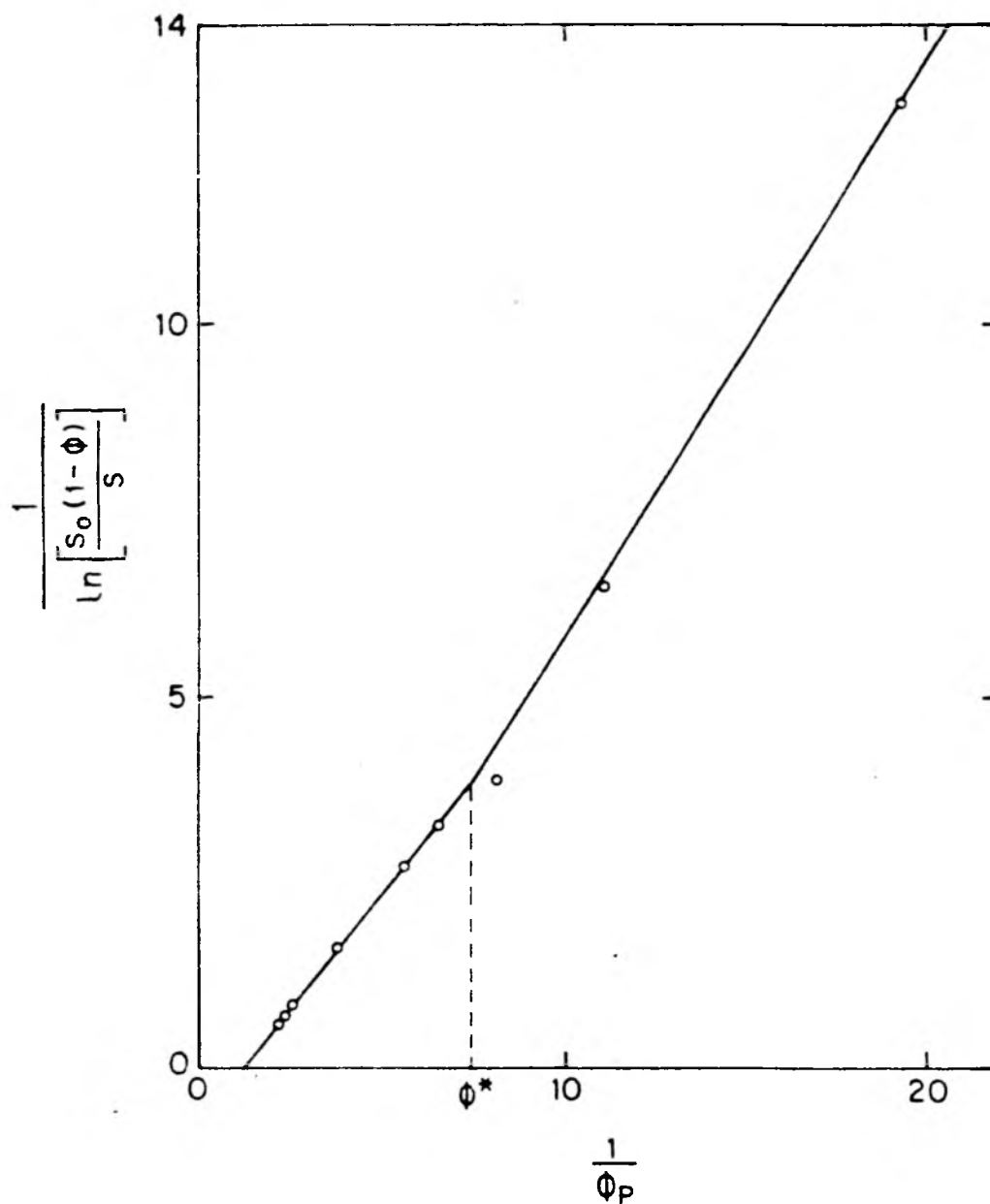


FIG. 6.5 : AFVS PLOT FOR AQUEOUS SOLUTIONS OF HYDROXYPROPYL CELLULOSE AT 25°C (REF.15)

high enough for the molecular domains to overlap. In terms of our model, this would mean a smaller degree of immobilisation, and hence a smaller value of  $\beta$ .

### 6.3.2 Effect of Branching

In order to investigate the effect of the degree of branching on the sedimentation behaviour, Nystrom et al (13) compared the sedimentation behaviour of polymethylmethacrylate (PMMA) and poly(triphenylmethoxyethyl)methacrylate (PTEMA) in toluene. The points of intersection in the AFVS plot of PTEMA-toluene systems (Fig. 6.3) correspond to a transition from dilute to semidilute unentangled concentration regime. A comparison of  $B_s$  values for PMMA and PTEMA shows that in dilute as well as semidilute regimes,  $B_s$  for the linear PMMA molecules is larger than for the branched PTEMA molecule. Branched molecules have a smaller hydrodynamic value than linear ones as is evident from the values of the corresponding intrinsic viscosities. The order of values of  $B_s$  is consistent with this observation.

### 6.3.3 Effect of Nature of Solvent

The concentration dependence of the sedimentation coefficient also depends on the nature of the solvent. The difference in the expected trends in the model parameters in good and poor solvents has been explained

in chapter II. To summarise,  $B_s$  in good solvents assumes a smaller value in regime II than in regime I, while the value of  $\beta$  is higher in regime II. Similar changes accompany transitions to higher concentration regimes. In theta solvents on the other hand,  $B_s$  in regime II is higher than in regime I, while  $\beta$  has a smaller value. This is because the polymer coils in theta solvent have their unsolvated dimensions even in dilute solutions, so that no contraction in coil size can be expected in the semidilute regime. Moreover, while in dilute solution the polymer molecules may be regarded as individual coils, aggregation takes place at higher concentrations, which is reflected in the value of the Huggin's constant (17). The transitions to higher concentration regimes are expected to be similar to those in good solvents.

At temperatures below the theta temperature, where polymer-polymer interactions are more favourable than polymer-solvent interactions, there will be some coil expansion in the semidilute regime, and also a considerable degree of aggregation. The above mentioned trends in the model parameters will therefore be even more pronounced.

As the quality of the solvent improves, there is a change-over from behaviour typical of a poor

solvent to that typical of a good solvent. The change in the slope of the AFVS plot at  $c^*$  changes from negative to positive. At some intermediate temperature, probably slightly above the theta temperature, the data could be expected to fall on a single straight line over dilute and semidilute ranges. These considerations are illustrated with the following example.

Nystrom et al (15) investigated sedimentation in the system hydroxypropyl cellulose-water at three temperatures close to the theta temperature. Water becomes a better solvent for hydroxypropyl cellulose as temperature is decreased below  $40^{\circ}\text{C}$ . The AFVS plots are shown in Fig. 6.6. As temperature increases,  $B_s$  decreases, which is consistent with the decreasing coil dimensions as the thermodynamic quality of the solvent deteriorates. Simultaneously  $\beta$  increases, reflecting increasing association between polymer molecules.

Nystrom and Roots (18) provided sedimentation data for polystyrene in cyclopentane at the theta temperature ( $20^{\circ}\text{C}$ ) for various molecular weights. The AFVS plots for two of the samples are shown in Fig. 6.7. The values of  $B_s$  and  $\beta$  listed in table 6.2 show the expected trends. It may be recalled here that these



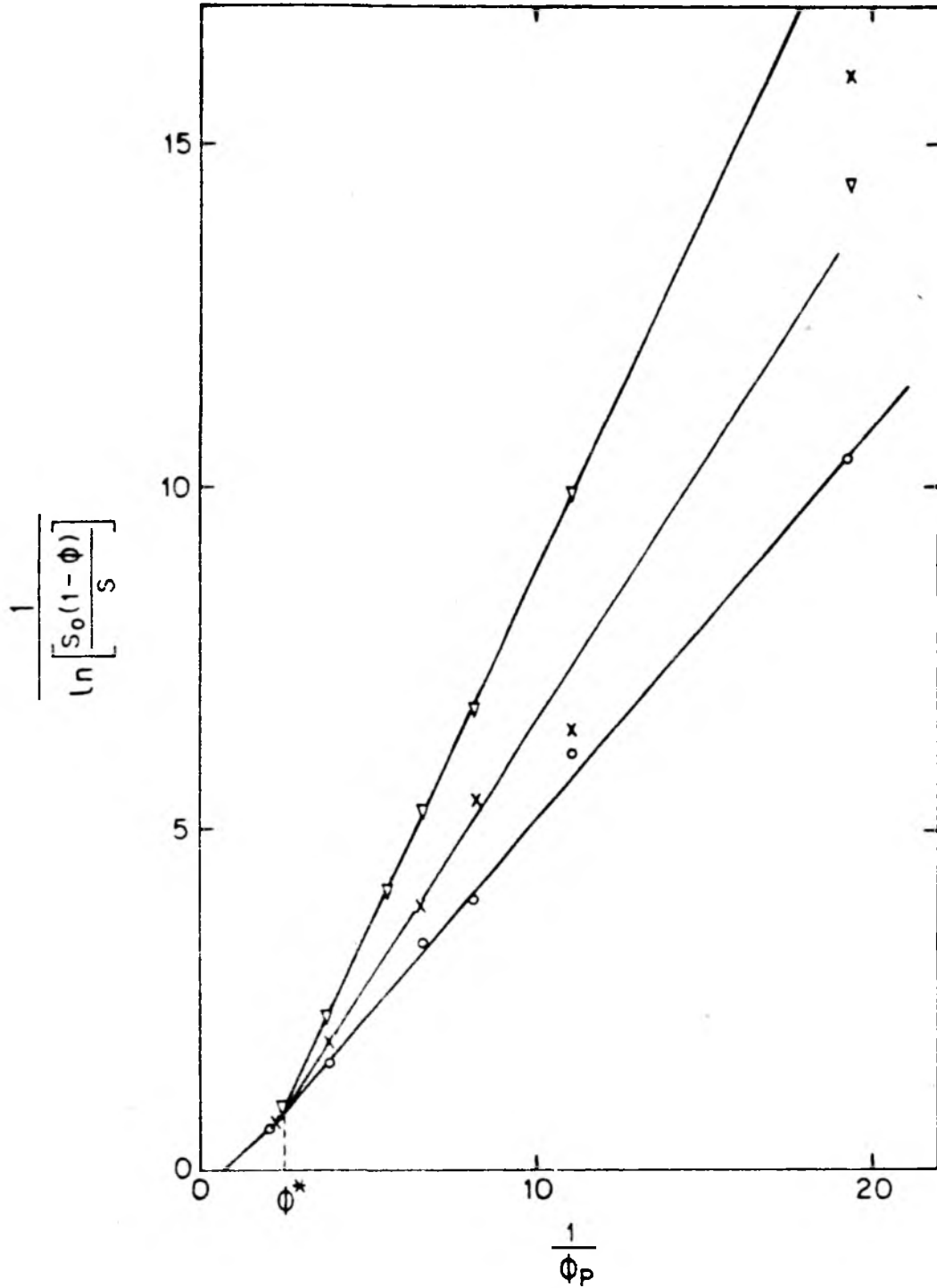


FIG. 6.6: AFVS PLOTS FOR THE SYSTEM HYDROXYPROPYL CELLULOSE-WATER AT 30°C ( $\circ$ ); 34°C ( $\times$ ) AND 37°C ( $\nabla$ ). (REF. 15)

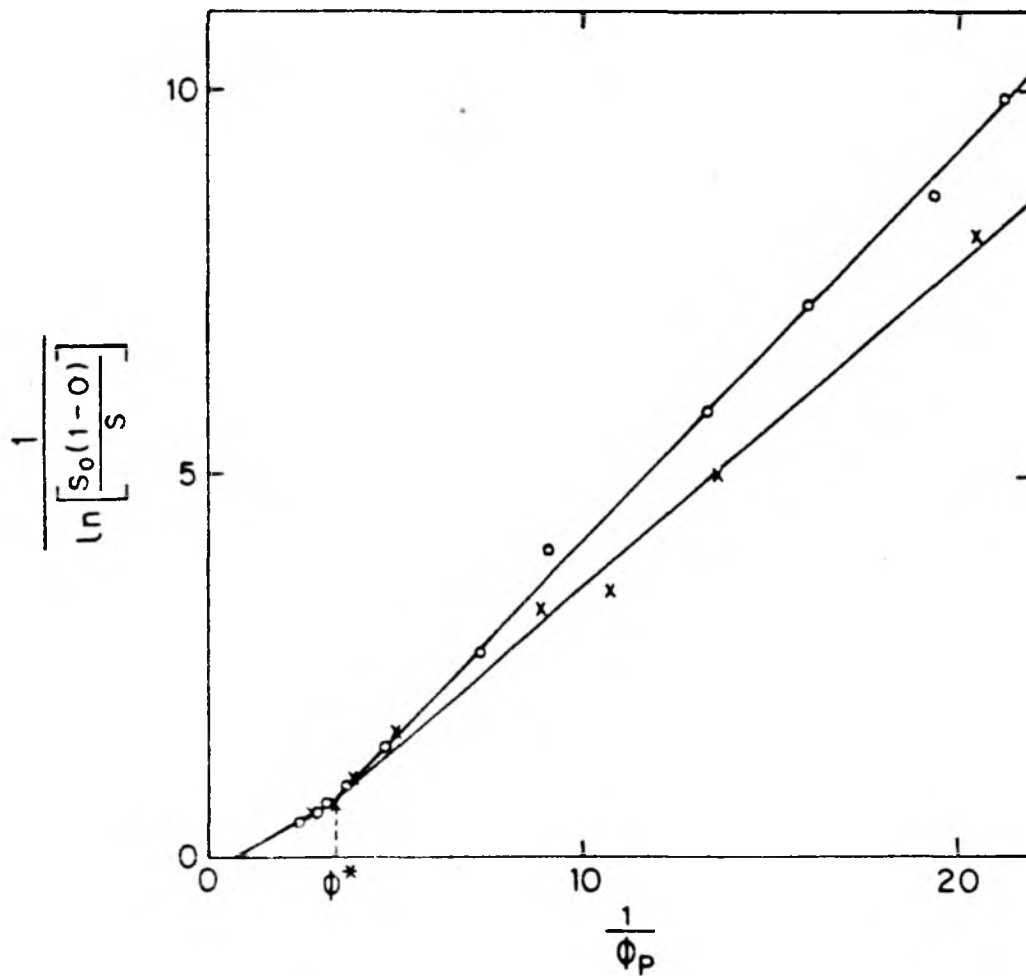


FIG.6.7: AFVS PLOTS FOR THE SYSTEM POLYSTYRENE-CYCLOPENTANE AT THETA TEMPERATURE. MW =  $1.1 \times 10^5$  (o) AND  $3.9 \times 10^5$  (x) (REF.18)

trends were also observed for the parameters derived from the viscosity data for polymer solutions in theta solvents (section 2.5.5). It may be noted that the model parameters for this system have reasonable values for the most part. The negative values of  $\beta$  obtained in two cases (see table 6.2) are probably because of the fact that data have been evaluated from only three data points and are inaccurate. The approximate model represented by eqn. (6.2.13) is more accurate for theta systems than for good solvent systems because in the former case the polymer coils are less extended, the intra-coil mobility term is less important and is more nearly a constant.

Nystrom and Roots (18) also studied the effect of temperature on the sedimentation behaviour for the system polystyrene-cyclopentane in the neighbourhood of the theta temperature. The AFVS plots are shown in Fig. 6.8. It is clear that with increasing temperature as the quality of the solvent improves, the change in the AFVS plot at  $c^*$  becomes positive instead of negative.  $B_s$  increases with increasing temperature both below and above  $c^*$  due to increasing coil size.  $\beta$  in the semidilute regime decreases with improvement in solvent quality due to breaking up of aggregates, while  $\beta$  in the dilute

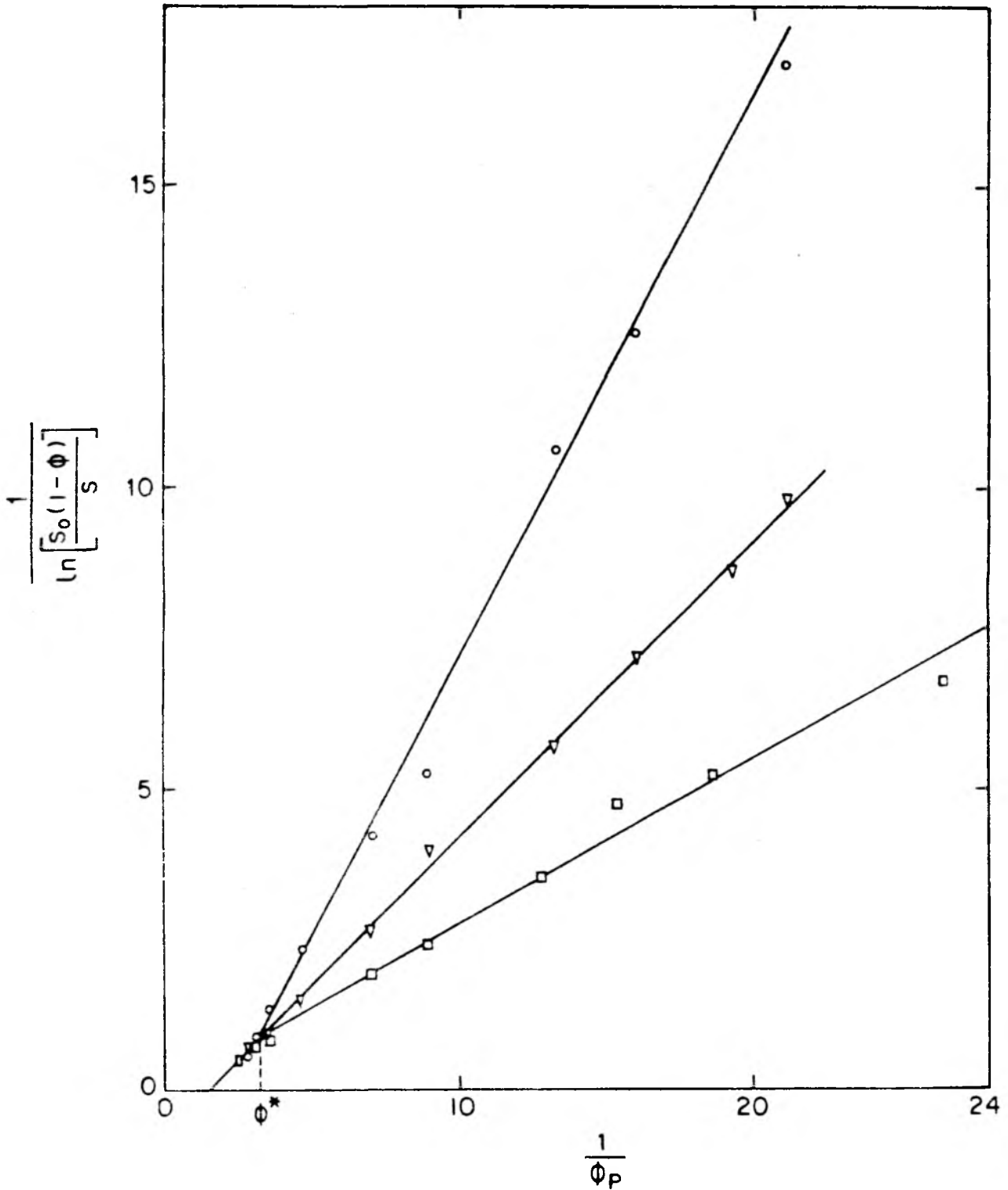


FIG.6.8: EFFECT OF TEMPERATURE ON AFVS PLOTS FOR THE SYSTEM POLYSTYRENE - CYCLOPENTANE. MW =  $1.1 \times 10^5$ . SYMBOLS: (o)  $11^\circ\text{C}$ , ( $\nabla$ )  $20^\circ\text{C}$ , ( $\square$ )  $40^\circ\text{C}$ . (REF.18)

regime decreases due to the increasingly open molecular conformation leading to a smaller degree of immobilization.

Another illustration of this effect is provided by the system polystyrene-cyclohexane (19) for which sedimentation coefficients have been reported at three temperatures close to the theta temperature ( $34^{\circ}\text{C}$ ).

Fig. 6.9 shows the same trends as described above in the semidilute regime. In the dilute regime,  $B_s$  has a larger value at  $31^{\circ}\text{C}$  than at  $35^{\circ}\text{C}$ . This is because at  $31^{\circ}\text{C}$ , which is close to the consolute temperature ( $27^{\circ}\text{C}$ ), some aggregation takes place even in dilute solutions.

It is thus clear that the AFVS model can adequately interpret the effect of the nature of the solvent as the temperature changes in the vicinity of the theta solvent. Phenomena such as aggregation and coil expansion are reflected in the values of  $B_s$  and  $\beta$ .

#### 6.4 CONCLUSIONS

The precise model presented here (eqn.(6.2.11)) for the sedimentation behaviour in polymer solutions could not be used because it involves more unknown parameters than could be evaluated from the data. An approximate model developed instead errs by neglecting the contribution of intra-coil mobility to sedimentation

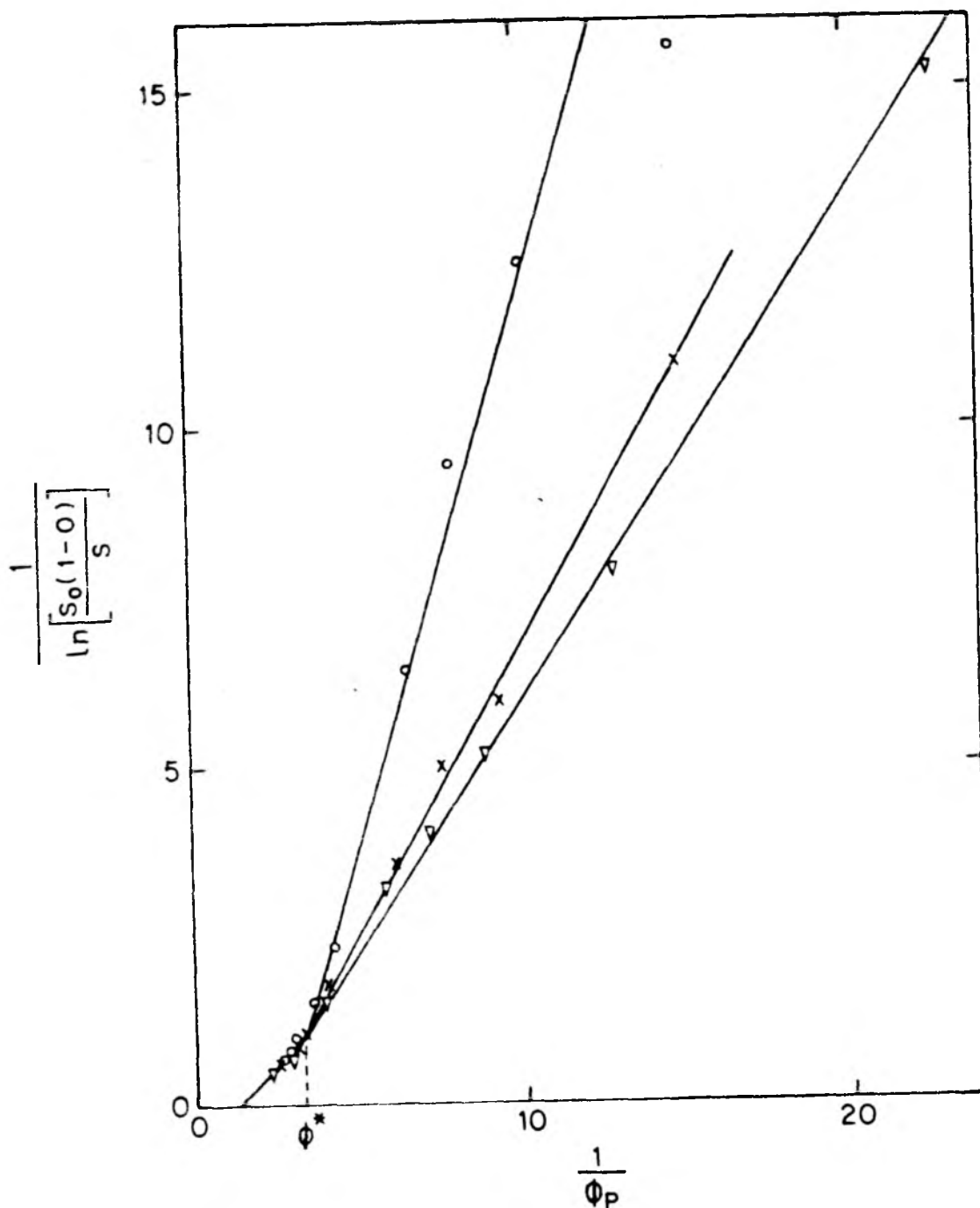


FIG. 6.9: EFFECT OF TEMPERATURE ON AFVS PLOTS FOR THE SYSTEM POLYSTYRENE-CYCLOHEXANE. MW =  $3.92 \times 10^5$ . SYMBOLS: (o) 31°C, (x) 35°C, ( $\nabla$ ) 40°C. (REF. 19)

coefficient. This error is most serious in the case of flexible polymer-good solvent systems. For stiff-chain polymers in good solvents and flexible polymers in poor solvents where the intra-coil mobility is less important, the approximate model is adequate. The model can account for the qualitative differences in the sedimentation behaviour of polymers in good and poor solvents.

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