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## Solution Viscosity of Linear Flexible High Polymers and Viscosity Interaction Parameter

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### ABSTRACT

Several methods based on the Huggins equation are available for studying the behavior of linear flexible high polymers in the Newtonian region of concentrated solutions. The work of Simha and Zakin has attracted our attention to further investigation since it suffers from limitations in the type of solvent and the molecular weight range of the polymer suggested for study. It was observed that a suitable modification of the Huggins equation would widen the scope of the original method. An alternative method for determining the incipient concentration  $c_0$ , where the intermolecular attraction and the repulsion just balance each other, is also suggested.

### INTRODUCTION

Simha and Zakin [1] reported that the viscosity behavior of high polymers in the Newtonian region of concentrated solutions could satisfactorily be explained by the expression  $\eta_{sp}/[\eta]c$  vs  $c/c_0$ , where  $c_0$ , equal to  $1.08/[\eta]$ , is the incipient concentration [2] derived from the molecular dimension at infinite dilution. Such an expression is superior to others arrived at by different approaches [3, 4]. The

method, although interesting, suffers from the drawback of being limited only to theta ( $\theta$ ) or good solvents and for polymers with molecular weights above  $5 \times 10^4$ . We applied this to the polymers studied by these authors (PS, PMMA, and SMMA), but in solvents other than those suggested by them [1]. A similar relationship, applicable over a wide range of concentrations, was suggested by Martin [5], but discussion of this falls beyond the scope of the present communication.

With a view to widening the scope of the expression of Simha and Zakin, the study has been extended to other polymers as well. An attempt has also been made to calculate  $c_0$  from the Huggins equation by extending the plot of  $\eta_{sp}/c$  vs  $c$  into the nonlinear region.

## EXPERIMENTAL RESULTS

### Determination of $[\eta]$ and $c_0$

Viscosities of solutions of styrene-acrylonitrile copolymer (SAN, prepared in our laboratory, having an ACN content of 26% by weight) in butanone (MEK) in the concentration range from 0.2 to 3.5 g/dL were determined at 30°C with an Ubbelohde viscometer. The intrinsic viscosity  $[\eta]$  of the sample was determined by the usual extrapolation procedure, and the concentration at which the slope of  $\eta_{sp}/c$  vs  $c$  changes was taken to be  $c_0$  (Fig. 1).

Further, the aforementioned SAN sample was fractionated into eight fractions following a procedure described elsewhere [6]. Four of these fractions of different molecular weights were selected for the present study. Besides these fractions, one sample of polystyrene (Styron 666 of Polychemicals Ltd., India) was similarly treated for the determination of  $[\eta]$  and  $c_0$ . The values thus obtained at 30°C in butanone and in toluene and those of the unfractionated SAN sample are given in Table 1.

### Relationship between $\eta_{sp}/[\eta]c$ and $c/c_0$

The first seven polymer-solvent systems shown in Table 2 were chosen for a study of the above relationship. The values of  $[\eta]$  and  $\eta_{sp}/c$  (corresponding to  $c$ ) for samples of different molecular weights in each system were either determined experimentally or taken from the literature [7, 8]. In the case of PS-toluene and PS-MEK systems where direct values of  $\eta_{sp}/c$  corresponding to  $c$  were not available, these were calculated from the slope  $S$  of  $\eta_{sp}/c$  vs  $c$  and  $[\eta]$  values

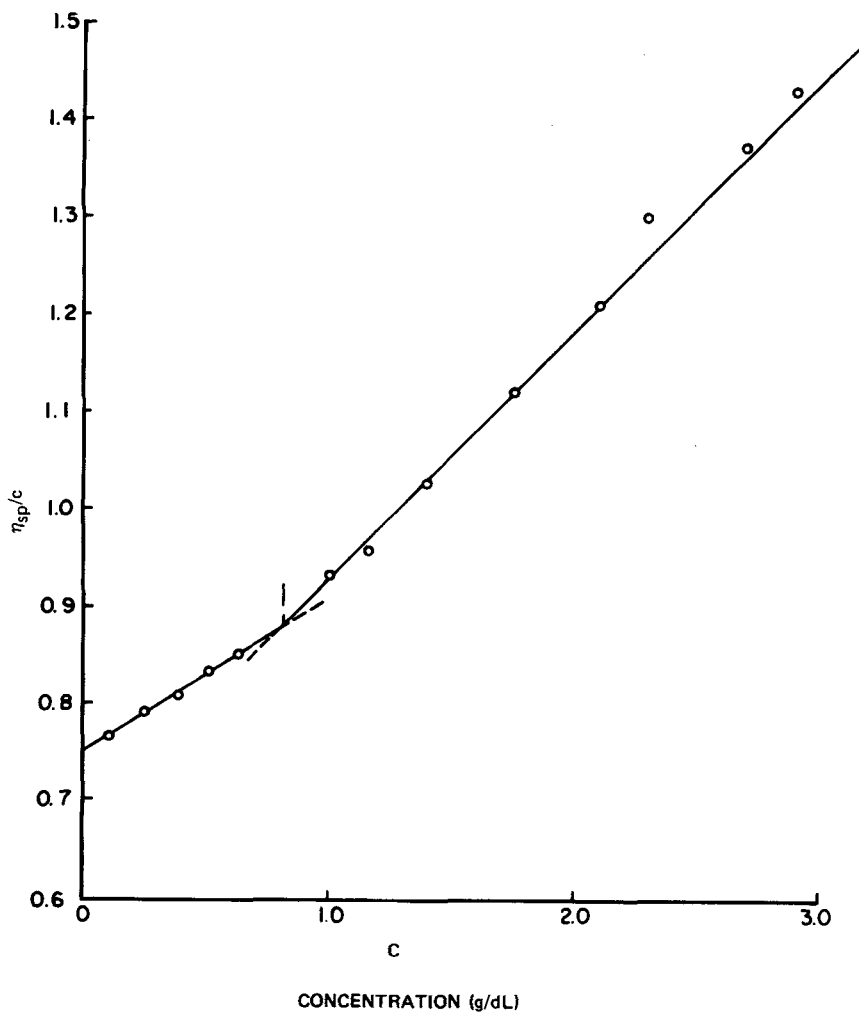


FIG. 1.  $\eta_{sp}/c$  vs  $c$  for SAN in MEK at 30°C.

reported in the literature following the Huggins equation. In all these systems the solvents used were non- $\theta$ -solvents, and the molecular weights (except for CA) were over  $5 \times 10^4$ .

The values of  $c_0$  for all the systems were calculated from the relationship  $c_0 = 1.08/[\eta]$ .

It was observed that none of the systems studied gave a straight line

TABLE 1. Data on  $[\eta]$  and  $C_0$  for Samples of PS and SAN

Sample	$[\eta]$ , dL/g	$C_0$ , g/dL	$[\eta]C_0$
SAN (unfractionated)	0.75	0.82	0.615
PS (unfractionated)	0.79	0.78	0.616
SAN (Fraction I)	1.4	0.44	0.616
SAN (Fraction II)	0.835	0.74	0.618
SAN (Fraction III)	0.68	0.93	0.632
SAN (Fraction IV)	0.53	1.16	0.615

TABLE 2. Values of  $K'$  and  $\alpha'$  for  $S = K'[\eta]^{\alpha'}$  for Different Polymer-Solvent Systems

Systems	T, °C	$K'$	$\alpha'$
1. PS-toluene	30	0.4290	1.8627
2. PS-MEK	40	0.5418	2.3614
3. PMMA-benzene	30	0.2719	2.1647
4. PMMA-MEK	30	0.8933	2.1754
5. SAN-MEK	30	0.5310	1.7282
6. SMMA-MEK	25	0.5333	1.5882
7. CA-acetone	25	0.6129	2.3031
8. PIB-benzene	30	0.4561	1.9497
9. PS-benzene	30	0.3800	1.9997

plot of  $\eta_{sp}/[\eta]c$  vs  $c/c_0$  for all points irrespective of the value of  $[\eta]$ . Only the CA-acetone system gave a smooth curve instead of a straight line.

Figure 2 describes the plots of  $S$  vs  $[\eta]^2$  for PIB-benzene and PS-benzene [9] in addition to the aforementioned systems.

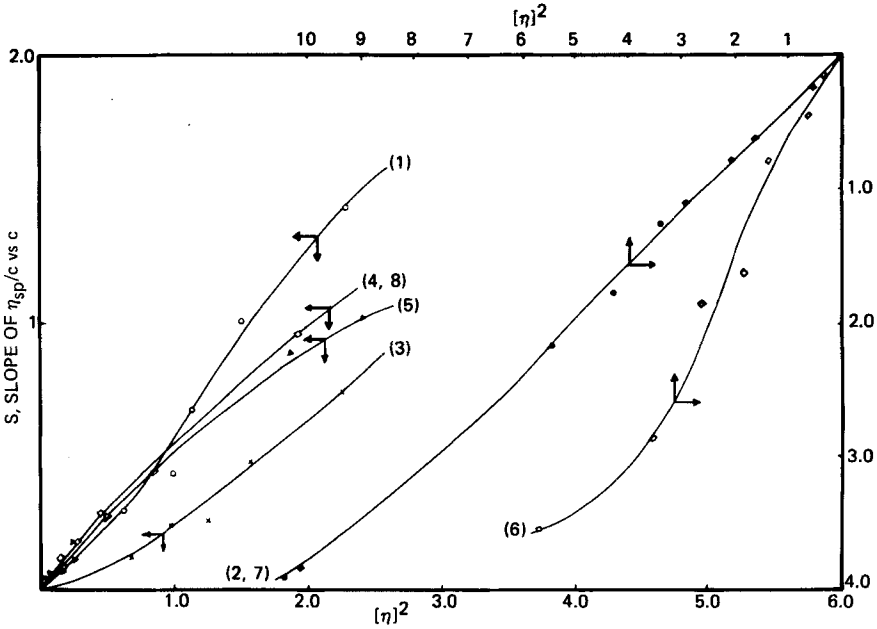


FIG. 2.  $S$  (slope of  $\eta_{sp}/c$  vs  $c$ ) vs  $[\eta]^2$ . Curves (1) PS/MEK/40.3°C, (2) PS/toluene/30°C, (3) PMMA/benzene/30°C, (4) PMMA/MEK/25°C, (5) PIB/benzene/25°C, (6) CA/acetone/25°C, (7) PS/benzene/30°C, and (8) SAN/MEK/25°C.

DISCUSSION

According to the Huggins equation:

$$\eta_{sp}/c = [\eta] + Sc$$

where  $S = K' [\eta]^2$  and  $K'$  is a Huggins constant, or

$$\eta_{sp}/c = [\eta] + K' [\eta]^2 c \tag{1}$$

Dividing Eq. (1) by  $[\eta]$ ,

$$\eta_{sp}/[\eta]c = 1 + K' [\eta] c \tag{2}$$

Substituting  $[\eta] = 1.08/c_0$  on the right-hand side of Eq. (2),

$$\eta_{sp}/[\eta]c = 1 + K' 1.08/c_0c \quad (3)$$

In Eqs. (2) and (3), if  $K'$  is constant for a particular polymer-solvent system, plots of  $\eta_{sp}/[\eta]c$  vs  $[\eta]c$  or  $c/c_0$  should be straight lines, irrespective of the value of  $[\eta]$ .

In each of the systems studied, with the exception of CA-acetone, the intercept on the ordinate of the plot  $\eta_{sp}/[\eta]c$  vs  $c/c_0$  was found to be equal to 1, but the slope was different for different values of  $[\eta]$ . In the case of the CA-acetone system, although the molecular weights were below  $5 \times 10^4$ , a smooth curve instead of a straight line was obtained, indicating that the behavior was not farther from that predicted by Simha and Zakin. Our experience with various systems and the fact that a slight variation in  $K'$  may not appreciably affect the value of  $[\eta]$  led us to believe that the power of  $[\eta]$  in the Huggins equation, namely  $S = K'[\eta]^2$ , need not necessarily be 2; this derives support from the observations of other workers as well [10-14]. A slight variation in the power of  $[\eta]$  in the equation  $S = K'[\eta]^2$  would appreciably affect the abscissas of Eqs. (2) and (3). We have tried to determine this variation in the power of  $[\eta]$  for the systems under consideration.

The expression for the slope in the Huggins equation may now be rewritten as

$$S = K'[\eta]^{\alpha'} \quad (4)$$

The values of  $K'$  and  $\alpha'$  in Eq. (4) were obtained by least-square fit of the  $S$  and  $[\eta]$  data for each system (Table 2). The values of  $\alpha'$  vary from 2 by  $\pm 20\%$ . A variation in the power of  $[\eta]$  in the equation  $S = K'[\eta]^2$  was also observed in  $S$  vs  $[\eta]^2$  plots (Fig. 2).

A plot of  $\eta_{sp}/[\eta]c$  vs  $[\eta]^{\alpha'-1}c$  (modification of Eq. 2) was found to be linear irrespective of the value of  $[\eta]$  for all systems except CA-acetone. In this particular case the points were scattered, but lay on a smooth curve when plotted according to Simha and Zakin.

From the foregoing discussion on systems other than CA-acetone, it is concluded that the work of Simha and Zakin can be extended to all types of solvents, once the power of  $[\eta]$  in the Huggins equation has been established. As pointed out by these authors, it is possible to determine the viscosity at any concentration in the region under study for a sample in any solvent from a single curve, provided  $[\eta]$  is known.

Further, the product of  $[\eta]$  and  $c_0$  was found to be almost constant (Table 1), indicating that  $c_0$  is proportional to  $1/[\eta]$ . The

value of the proportionality constant was very close to what Simha and Zakin derived from molecular dimensions. These authors further observed that for linear flexible high polymers at a certain temperature and concentration, the inter- and intramolecular repulsions and attractions balance each other and the molecules behave as if they were in an unperturbed state. Our studies suggest that the point at which the slope of  $\eta_{sp}/c$  vs  $c$  changes probably represents that state. Thus, it is possible to determine the unperturbed dimension in non- $\theta$ -solvents merely from a plot of  $\eta_{sp}/c$  vs  $c$ . Work along these lines will be the subject of a future communication.

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