

## Viscosity-Concentration Relationships in Solutions of High Polymers

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### INTRODUCTION

The first rigorous hydrodynamic analysis of the viscosity of colloidal solutions was that of Einstein<sup>1</sup> in 1906, and he expressed his conclusions in the equation

$$(\eta - \eta_0)/\eta_0 = \eta_{sp} = 2.5V_f \quad (1)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and pure solvent, respectively, and  $V_f$  is the volume fraction of solute, which is directly proportional to the concentration  $c$  of solute in grams per 100 cc. of solvent. Thus:

$$\eta_{sp} = (2.5/100 d_{solute})c \quad (2)$$

where  $d_{solute}$  is the density of the solute. From eq. (2) it follows that the quantity  $\eta_{sp}/c$ , known as the viscosity number, is independent of concentration and equal to  $2.5 \times 10^{-2}/d$ . This is so because in the theoretical treatment the interactions between solute molecules, as well as their shapes, were neglected.

This assumption is certainly not valid in solutions of high polymers, and the quantity  $\eta_{sp}/c$  is found to vary with concentration. This simple equation of Einstein was modified by Guth and Gold<sup>2</sup> to take account of solute-solute interaction. The resulting equation was applicable to higher concentrations than the linear equation of Einstein, but was still inadequate for high polymer systems, partly on account of the assumption of spherical shape involved. It has since been found that the variation of viscosity with concentration for solutions of high polymers can best be represented by the type of equation proposed by Huggins:<sup>3</sup>

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (3)$$

where  $[\eta] = (\eta_{sp}/c)_{\lim c \rightarrow 0}$  and  $k'$  is known as the Huggins constant.

For linear polymers in good solvents,  $k'$  has been found to take values between 0.3 and 0.4. The limiting value of  $\eta_{sp}/c$  at  $c = 0$ , designated  $[\eta]$ ,

is of special interest to the polymer scientist, since it is a characteristic of the polymer which, in many cases, can be related in straightforward fashion to the viscosity-average molecular weight  $\bar{M}_v$ . Very often  $[\eta] = K\bar{M}_v^\alpha$  where  $K$  and  $\alpha$  are constants for a given homologous series of polymer and solvent. Once values for  $K$  and  $\alpha$  have been established, a measurement of  $[\eta]$  in the same solvent will lead to a value of  $\bar{M}_v$ .

The method usually adopted for determination of  $[\eta]$  is to measure  $\eta_{sp}$  at a series of decreasing values of  $c$  and extrapolate the plot of  $\eta_{sp}/c$  against  $c$  to infinite dilution. This is a laborious process in itself, and many attempts<sup>4-10</sup> have been made to find a formula which will lead to a value of  $[\eta]$  from a single determination of  $\eta_{sp}$ , preferably at a high concentration where experimental accuracy is greatest.

In this paper a number of polymer solutions which are known to have very different Huggins constants are considered, and the precision with which  $[\eta]$  can be derived from a single determination of  $\eta_{sp}$  by use of different forms of the relationship between  $[\eta]$ ,  $\eta_{sp}$ , and  $c$  is evaluated.

### EXPERIMENTAL

Viscosity measurements were made in a Ubbelohde suspended-level viscometer at a temperature of  $25 \pm 0.02^\circ\text{C}$ . Flow times were measured to 0.1 sec. In the first instance, measurements were made in the dilute region up to  $c = 0.13$  g./100 cc. of solvent, and were then extended to concentrations of about 4 g./100 cc. wherever possible.

### RESULTS

Results of measurements in the dilute region are shown in Figure 1 and those for the more concentrated region in Figure 2. Values for the Huggins constant  $k'$  are calculated on the basis of the Huggins equation:  $\eta_{sp}/c = [\eta] + k'[\eta]^2c$ ; these are shown in Table I.

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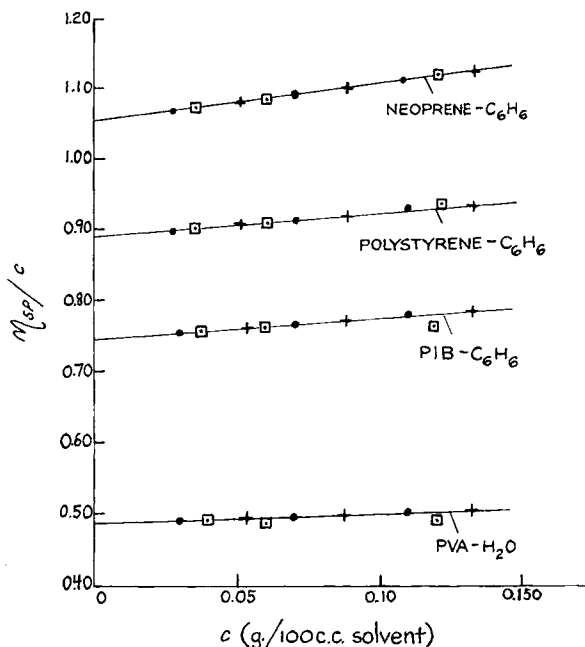


Fig. 1. Plots of  $\eta_{sp}/c$  vs.  $c$  for various systems: (+) experimental values; (●) values according to the equation,  $\eta = \eta_0 e^{[\eta]c}$ ; (□) values according to the equation,  $\eta_{sp} = [\eta]c + 0.5[\eta]^2c$ .

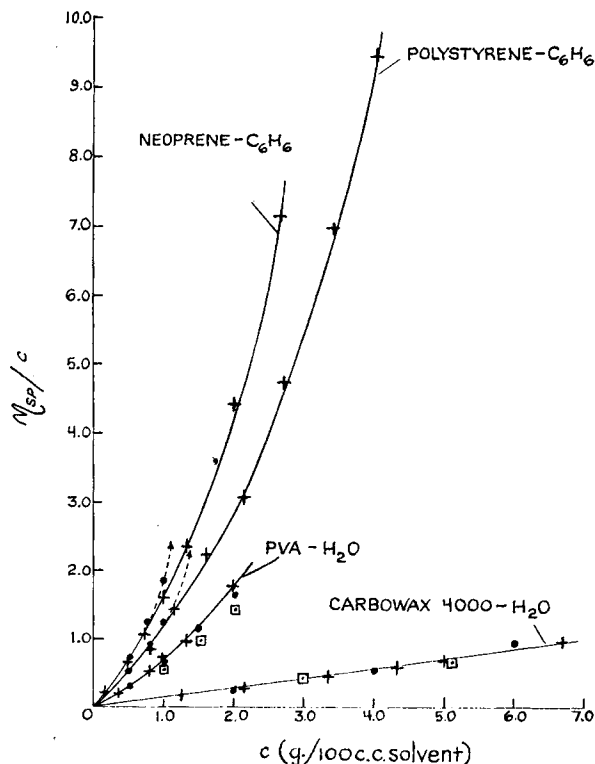


Fig. 2. Plots of  $\eta_{sp}/c$  vs.  $c$  for various systems: (+) experimental values; (●) values according to the equation,  $\eta = \eta_0 e^{[\eta]c}$ ; (□) values according to the equation,  $\eta_{sp} = [\eta]c + 0.5[\eta]^2c$ .

TABLE I

System	Huggins constant $k'$	$[\eta]$ experimental
Neoprene-benzene	0.50	1.05 <sub>2</sub>
Polystyrene-benzene	0.39	0.89
Polyisobutylene-benzene	0.59	0.74 <sub>6</sub>
Polyvinyl alcohol-water	0.65	0.48 <sub>7</sub>
Polymethyl methacrylate-benzene	0.53	2.61
Polyethylene glycol-water	0.44	0.10 <sub>8</sub>

## DISCUSSION

First, the results obtained in dilute solution (Fig. 1) show the measure of agreement between the experimental results, those calculated from the exponential equation  $\eta = \eta_0 e^{[\eta]c}$ , and those from a Huggins-type equation for which  $k'$  is assumed to be 0.5. This Huggins equation corresponds, in fact, to the first two terms of the expanded exponential. It will be seen that, regardless of the fact that the actual Huggins constant varies from 0.39 for polystyrene to 0.65 for polyvinyl alcohol, the error introduced in  $[\eta]$  by assuming a value of 0.5 for  $k'$  is small at these concentrations. If the exponential expression is used the errors are even less, and the error in all cases considered is less than 1%. The experimental error at these concentrations is also of the order of 1%; for example, in the case of polyisobutylene in benzene at a concentration of 0.0532 g./100 cc. ( $t - t_0$ ) (flow time) is 7.0 seconds, and at a concentration of 0.1331 g./100 cc. ( $t - t_0$ ) is 16.75 sec. The quantity ( $t - t_0$ ) is known to within 0.1, and hence at a concentration of 0.0532 g./100 cc., the error in  $\eta_{sp}$  is one part in 70, falling to one part in 167 at a concentration of 0.1331 g./100 cc. Introducing the limits of error into the plot of  $\eta_{sp}/c$  against  $c$  shows that the extrapolated value of  $[\eta]$  quoted in Table I is accurate to 1%.

We can conclude, therefore, that although  $k' = 0.5$  may be far from the true value for the Huggins constant, its use does not introduce appreciable errors into the value of  $[\eta]$  obtained from the equation  $\eta_{sp}/c = [\eta] + 0.5[\eta]^2c$  at concentrations below 0.13 g./100 cc. The exponential equation,  $\eta = \eta_0 e^{[\eta]c}$  seems to provide an even closer approximation to the experimental results and is well suited to the determination of  $[\eta]$  from a single measurement of  $\eta_{sp}$ . Values of  $[\eta]$ , as calculated from the exponential equation for representative concentration below 0.15 g./100 cc., are shown in Table II. It will be seen that the difference between

TABLE II

System	Calculated values of $[\eta]$ deduced from measured viscosity at various concentrations			Extrapolated value of $[\eta]$
	$c = 0.05$	$c = 0.10$	$c = 0.15$	
Neoprene-benzene	1.05 <sub>4</sub>	1.04 <sub>9</sub>	1.04 <sub>9</sub>	1.05
Polystyrene-benzene	0.88 <sub>4</sub>	0.88 <sub>4</sub>	0.88	0.88 <sub>9</sub>
Polyisobutylene-benzene	0.74 <sub>3</sub>	0.74 <sub>7</sub>	0.74 <sub>7</sub>	0.74 <sub>5</sub>
Polyvinyl alcohol-water	0.48 <sub>3</sub>	0.48 <sub>8</sub>	0.49 <sub>2</sub>	0.48 <sub>7</sub>
Polymethyl methacrylate-benzene	2.62	2.62	2.59	2.61

the experimental and calculated values of  $[\eta]$  is less than 1% in all cases, i.e., it is of the same order as the experimental error.

For the higher concentration region, Figure 2 shows the agreement obtainable with the same two equations. Up to a concentration of 1.0 g./100 cc. the exponential equation still applies fairly well, but thereafter very large deviations occur.

### CONCLUSIONS

For concentrations below 0.13 g./100 cc. of solvent, an exponential expression,  $\eta = \eta_0 e^{[\eta]c}$ , has proved a valid relationship between viscosity and concentration for all the polymer-solvent systems studied. The first two terms of the expanded form of this equation are equivalent to the Huggins equation having a value of  $k'$  of 0.5, and this latter is also found to give a fairly good representation of the experimental results in this dilute region. If as appears likely from the results so far obtained, the exponential expression is generally applicable to within 1% at these concentrations, it will provide a powerful means of establishing relationships between intrinsic viscosity and molecular weight for given homologous series of polymers. In addition, when such a relationship has been established, it will allow of an estimation of the molecular weight of any sample from a single determination of  $\eta_{sp}$  within these concentration limits.

We are indebted to Professor A. Charlesby for his stimulating comments.

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### Synopsis

Measurements of the viscosities of a number of polymer-solvent systems have shown that an exponential expression,  $\eta = \eta_0 e^{[\eta]c}$ , is applicable in the concentration range up to  $c = 0.13$  g./100 cc. of solvent to within the precision of the experimental measurements. This exponential equation lends itself readily to the determination of the intrinsic viscosity  $[\eta]$  from a single determination of  $\eta/\eta_0$  and is therefore of great use in determining molecular weights of high polymers from a Houwink-type expression. At higher concentrations, departures from the exponential equation occur, but agreement remains reasonably good up to a concentration of 1 g./100 cc. of solvent. The experimental results are compared with those predicted by the exponential expression and with those expected from a Huggins-type equation in which  $k' = 0.5$ , which corresponds to the first two terms of the expanded form of the exponential.

### Résumé

Des mesures viscosimétriques sur plusieurs systèmes polymère-solvant ont montré qu'une expression exponentielle  $\eta = \eta_0 e^{[\eta]c}$  est applicable dans un domaine de concentration jusque  $c = 0.13$  g./100 ml. de solvant dans la limite de précision des mesures expérimentales. Cette équation exponentielle conduit elle-même rapidement à la détermination de la viscosité intrinsèque  $[\eta]$  à partir d'une simple détermination de  $\eta/\eta_0$  et est de ce fait d'un grand emploi dans la détermination des poids moléculaires des hauts polymères à partir d'une expression du type Houwink. Aux concentrations plus élevées, on observe des écarts à l'équation exponentielle, et ceux attendus à partir d'une équation du type Huggins dans laquelle  $k' = 0.5$ , et qui correspond aux deux premiers termes de l'exponentielle développée.

### Zusammenfassung

Die Messung der Viskosität einer Anzahl von Polymer-Lösungsmittelsystemen hat gezeigt, dass eine exponentielle Beziehung,  $\eta = \eta_0 e^{[\eta]c}$ , im Konzentrationsbereich bis hinauf zu  $c = 0,13$  g./100 cm<sup>3</sup> Lösungsmittel innerhalb der Versuchsgenauigkeit anwendbar ist. Die Exponentialgleichung ermöglicht in einfacher Weise die Bestimmung der Viskositätszahl  $[\eta]$  aus einer Einzelbestimmung von  $\eta/\eta_0$  und ist daher für die Bestimmung von Molekulargewichten von Hochpolymeren mittels eines Ausdrucks vom Houwink-Typ von grossem Wert. Bei höheren Konzentrationen treten Abweichungen von der Exponentialgleichung auf, es bleibt aber die Übereinstimmung bis hinauf zu einer Konzentration von 1 g./100 cm<sup>3</sup> Lösungsmittel hinreichend gut. Es wird ein Vergleich zwischen den experimentellen Ergebnissen, den nach dem Exponentialausdruck zu erwartenden und den sich aus einer Gleichung vom Huggins-Type mit  $k' = 0,5$  ergebenden, was den beiden ersten Termen des in einer Reihe entwickelten Exponentialausdrucks entspricht, angestellt.

Received October 14, 1959