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INTRINSIC VISCOSITY-MOLECULAR WEIGHT RELATIONSHIP OF HIGH POLYMERS : A NEW EQUATION

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ABSTRACT—Based on Eyring's rate theory and the 'hole' theory of liquids the following equation, correlating the intrinsic viscosity, $[\eta]$ and molecular weight of polymers has been derived : $100\rho_0[\eta]=K_1M^{2/3}-\ln M+K_2$, where ρ_0 is the density of of the polymer at infinite dilution and K_1 and K_2 are constants. All existing data have been found to be in agreement with this equation. The modified Staudinger equation, $[\eta]=KM^a$, which is in common use, is shown to be a special case of this equation and cases are cited where the latter equation is found to be invalid, whereas the new equation is found adequate.

Critical tests based on differential $[\eta]$ in two solvents for the same polymer have been devised and it is conclusively demonstrated that the modified Staudinger equation leads to inconsistent results and is untenable, whereas the new equation is in conformity with experimental facts.

INTRODUCTION

Great interest has been shown during the past few years in the relationship between the intrinsic viscosity and molecular weight of high polymers. The modified Staudinger equation, $[\eta]=KM^a$, the modification being variously ascribed to Mark, Kuhn or Houwink, is extensively used. Of late, attempts (Brinkman, 1947 ; Debye *et al*, 1948 ; Kirkwood *et al*, 1948 ; Flory, 1949) to derive this equation from theoretical considerations have been made, but so far with not quite satisfactory results. However, recent theoretical development in the field of liquid viscosity based on Eyring's rate theory can be extended to the high polymer field to obtain in a simple manner a satisfactory equation correlating $[\eta]$ and M of high polymers.

Derivation of the New Equation—Based on Eyring's rate theory (Glasstone *et al*, 1947) and the void structure of liquids, Telang (1949) has recently deduced the following equation [eqn. (1)] for the absolute value of the viscosity of any liquid. This equation has the unique feature of not containing any arbitrary constant and has been found to give correct values of molecular weight of many liquids where standard data for all the terms are available.

$$\eta=\frac{hNb}{V^{2/3}(V-b)^{4/3}}\exp\left(\frac{1.091\,\gamma\,V^{2/3}N^{1/3}}{RT}\right) \qquad \dots \quad (1)$$

where h is Planck's constant, N is Avogadro number, b is van der Waals constant, V is molar volume and γ is surface tension.

If we put $b_{sp}M$ and $v_{sp}M$ for b and V respectively, the equation, after taking logarithm becomes

$$\ln\eta = \frac{1.091\,\gamma\, v_{sp}^{2/3} N^{1/3}}{RT} \cdot M^{2/3} - \ln M + \ln \frac{h\,N\,b_{sp}}{v_{sp}^{2/3}(v_{sp}-b_{sp})^{4/3}} \quad \ldots \quad (2)$$

$$\ln(\eta M) = k_1\,\gamma\,(v_{sp}M)^{2/3} + k_2 \quad \ldots \quad (3)$$

In order to use equation (2) we have to evaluate log viscosity of the polymer from data on solution viscosity. Considering a dilute high polymer solution as a mixture of two liquids, the solvent of viscosity η_s and a hypothetical high polymer liquid of viscosity η_p and assuming that the mixture law on volume fraction basis holds good for log viscosity of dilute solutions of high polymers, we have

$$\ln\eta = (1-\phi)\ln\eta_s + \phi\ln\eta_p \quad \ldots \quad (4)$$

where ϕ is the volume fraction of the polymer. If c is concentration in gms. per 100 cc and ρ_0 is the partial specific density of the polymer at infinite dilution, the above equation on proceeding to infinite dilution gives

$$\ln\eta_p = \left[\frac{1}{\phi}\ln\eta/\eta_s\right]_{\phi\to 0} + \ln\eta_s = 100\,\rho_0\left[\frac{1}{c}\ln\eta/\eta_s\right]_{c\to 0} + \ln\eta_s = 100\rho_0[\eta] + \ln\eta_s \quad \ldots \quad (5)$$

Substituting this value of log viscosity in equation (3), we obtain

$$100\,\rho_0[\eta] = k_1\,\gamma\,(v_{sp}M)^{2/3} - \ln M + k_2 - \ln\eta_s \quad \ldots \quad (6)$$

Since the surface tension and specific volume of ordinary homologous liquids are found to attain a limiting value at quite a low molecular weight region, we can reasonably expect the same polymer irrespective of molecular weight to have nearly the same value of γ and v_{sp} and so we can put the foregoing equation in the following simple forms.

$$100\,\rho_0[\eta] + \ln M = K_1[M]^{2/3} + K_2 \quad \ldots \quad (7)$$

$$[\eta] = 0.01\,v_{sp}K_1M^{2/3} - 0.023\,v_{sp}\log M + K_2' \quad \ldots \quad (8)$$

If $[\eta]$ is expressed in cc per gram and is designated by Z_η in conformity with the very recent German practice our equations (7) and (8) become

$$\rho_0 Z_\eta = K_1M^{2/3} - \ln M + K_2 \quad \ldots \quad (9)$$

$$Z_\eta = K_1 v_{sp}M^{2/3} - 2.303\,v_{sp}\log M + K_2' \quad \ldots \quad (10)$$

Equations (7) and its other forms, viz. (8), (9) and (10) are our final equations.

It is realised that our assumption of mixture law for log viscosity for polymer solutions [eqn (3)] is not beyond question, and no doubt, other types of mixture law (Partington, 1951) more in conformity with observations for mixtures, can be utilised and other equations similar in form to our equation

(7) can be deduced. We have, however, done this firstly in order to give our final equation a form containing $[\eta]$ on which extensive data are available and secondly, because it is known (Partington, 19 51; Houwink, 1950) that a similar relationship holds good for mixtures of small molecules. It may also be pointed out that equation (3) demands that specific viscosity should be linear in ϕ at low dilutions and we know that this is theoretically justified by the equations of Sakurda (1934), Simha (1940), Kuhn (1933) and others (Guth, et al 1938) in dilute solutions and this has also been found to be experimentally true.

EXPERIMENTAL TEST OF THE PROPOSED EQUATION

We need now examine how far the new equation along with its logical consequences is in agreement with experimental facts, to what extent it is useful for computation of molecular weight from viscosity data and in what respect it differs from the existing equation ; and further to devise some way of a critical assessment between the two.

Linear Relationship. A direct consequence of equation (7) is that a plot of 100 $\rho_0[\eta]+\ln M$ against $M^{2/3}$ should be linear. We have tested this relationship for a large number of polymers from available data and in all cases we have observed the plot to be linear. Some typical graphs are shown in figures 1 to 6 and the least square K_1 and K_2 values are collected in Table I. All references to the source of data used for these figures are given at the end of Table I.

In selecting our data we have taken molecular weight values up to about a million because we have felt that osmotic molecular weight for higher values of M are not very reliable owing to unavoidable experimental difficulties. It may also be pointed out that the value of ρ_0 need not be very accurate and hence if partial data are not available apparent data and even the density of the solid polymer would serve well for our equation, but the values of K_1 and K_2 necessarily depend on the chosen value of ρ_0, and accepting a given value of ρ_0 at a certain temperature allowance has to be made if the same solvent-polymer system is studied at a somewhat different temperature by assuming that ρ_0 changes with temperature in the usual manner for liquids.

Curve A of figure 1 shows the required plot for polyisobutylene in diisobutylene with the very precise data of Flory (1943) covering a molecular weight range of about 10^3 to 10^6, a more than hundred-fold increase in molecular weight. The plot is sensibly linear over the whole range. In the same graph is also shown a similar plot for the same polymer in cyclohexane (Krigbaum & Flory 1953) (curve B) and the plot is also found to be a good straight line.

TABLE I

K_1 and K_2 values of polymers

Polymer	Solvent	Temp. °C	ρ_0	Range of M	$K_1 \times 10^2$	K_2	Ref.
Polyethylene	Decalin	70°	0.875	395 − 33,700	7.782	4.045	a
Polyisobutylene	Di-isobutylene	20°	0.930	$8.7 \times 10^3 - 1.3 \times 10^6$	2.402	11.744	b,c
,,	Cyclohexane	30°	0.920	$38 \times 10^3 - 71 \times 10^4$	3.583	5.773	b
Polystyrene	Benzene	20° − 40°	1.037 − 1.055	$4. \times 10^3 - 1.4 \times 10^6$	2.862	7.397	d,e,f,g,h
,,	Toluene	20° − 30°	1.045 − 1.055	$830 - 1.1 \times 10^6$	2.460	7.819	g,h,i,j,k,l
Polymethyl methacrylate	Acetone	20°	1.180	$25 \times 10^3 - 3.2 \times 10^6$	1.679	−5.460	m
,,	Benzene	20°	1.180	$25 \times 10^3 - 3.2 \times 10^6$	2.634	−4.504	m
,,	Chloroform	20°	1.180	$25 \times 10^3 - 6.1 \times 10^5$	3.316	3.344	m
,,	Benzene	25°	1.180	$56 \times 10^3 - 4.1 \times 10^5$	2.852	4.998	n
Polymethyl acrylate	Benzene	35°	1.055	$46 \times 10^3 - 3.0 \times 10^5$	2.669	6.888	o
Cellulose acetate	Acetone	30°,40°	1.335	$25 \times 10^3 - 1.3 \times 10^5$	ca.32	ca.10	p
,,	,,	26.5°	1.344	$31 \times 10^3 - 3.6 \times 10^5$	ca.24	ca.−19	q
,,	,,	25°	1.345	$12 \times 10^3 - 1.2 \times 10^5$	ca.40	ca.−48	r
Benzyl Cellulose	Chloroform	35°	1.185	$1 \times 10^4 - 2.4 \times 10^4$	ca.15.5	ca.− 1	s
Triphenylmethyl methyl ethyl cellulose	Dimethyl formamide	35°	1.195	$3 \times 10^4 - 6 \times 10^4$	ca.11	ca.9.0	t

a. Ueberreiter, et al (1952) ; b. Flory (1943) ;
c. Krigbaum and Flory (1953) ; d. Krigbaum, et al (1952) ;
e. Kern and Rugenstein (1953) ; f. Bueche (1949) ;
g. Bawn, et al (1950) ; h. Bawn, et al (1950) ;
i. Goldberg et al (1947) ; j. Frank and Breitenbach, (1951) ;
k. Alfrey, et al (1943) ; l. Marzolph and Schulz (1954) ;
m. Schulz, et al (1953) ; n. Baxendale, et al (1946) ;
o Sen, Chatterjee and Palit (1952) ; p. Bartovics and Mark (1943) ,
q. Badgley and Mark (1947) ; r. Phillip and Bjork (1951) ;
s. Basu and Roy (1952) ; t. Roy Chowdhury (unpublished work from this laboratory).

In figure 2 are shown such plots for a few cellulose derivatives including a plot of cellulose acetate based on the data of Badgley and Mark (1947). It is of interest to note that though the conventional log[η] versus log$M$ plot has been found by these authors to be curved in this case, our plot gives a very good straight line. We have, of course, omitted the two points for the two highest molecular weight fractions as the authors themselves have twice

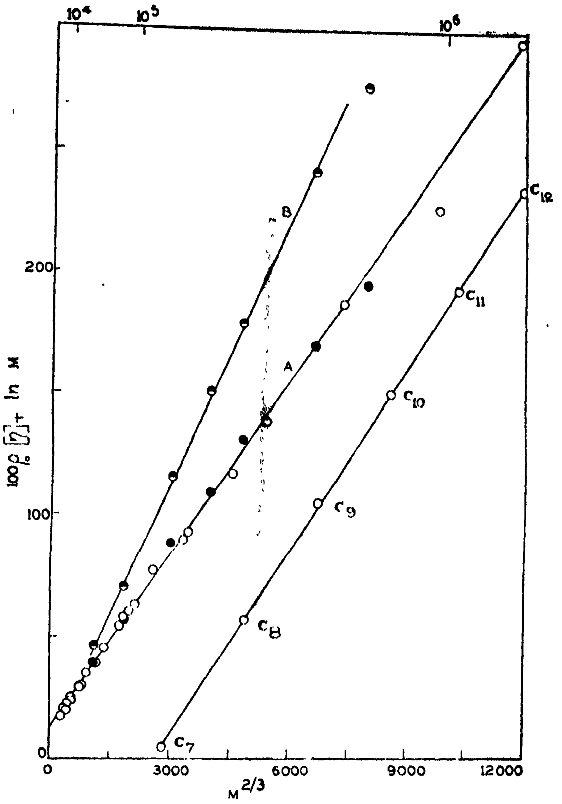

FIG. 1. Viscosity molecular weight plot for polyisobutylene. Curve A in di-isobutylene (open circles, ref: Flory, 1943; dark circles, ref : Krigbaum and Flory (1953). Curve B in cyclohexane, ref: *ibid*; $C\text{-}\log(\eta M)$ *Vs.* $\gamma(M_{v,p}{}^{2/3})$ for straight chain alkanes in arbitary units.

expressed uncertainty about them. This linearity, when the conventional $\log[\eta] - \log M$ plot fails, is not due to any insensitivity of our plot as compared to the conventional plot as would be discussed at length later on. In fact, our plot would be shown to be more sensitive than the conventional plot over a larger range of molecular weight. Similar plots have also been made in figure 2 for cellulose acetate based on other data, and a few other cellulose derivatives, e.g. triphenyl-methyl methyl ethyl cellulose in dimethyl formamide and benzyl cellulose in chloroform, etc., and all the curves are found to be linear in agreement with our equation.

We want to draw special attention to figure 3 wherein we have plotted the precise data of Ueberreiter, Orthmann and Sorge (1952) for polyethylene. They have not only determined M and $[\eta]$ values for four fractions but have also obtained data for a highly pure hydrocarbon, $C_{28}H_{58}$. They themselves find that their $\log[\eta] - \log M$ plot is wide off the point for the pure hydrocarbon. Their $\log[\eta] - \log M$ plot showing this departure has been also reproduced in figure 3. However, our plot passes through all the five points which conclusively proves that our equation is valid over

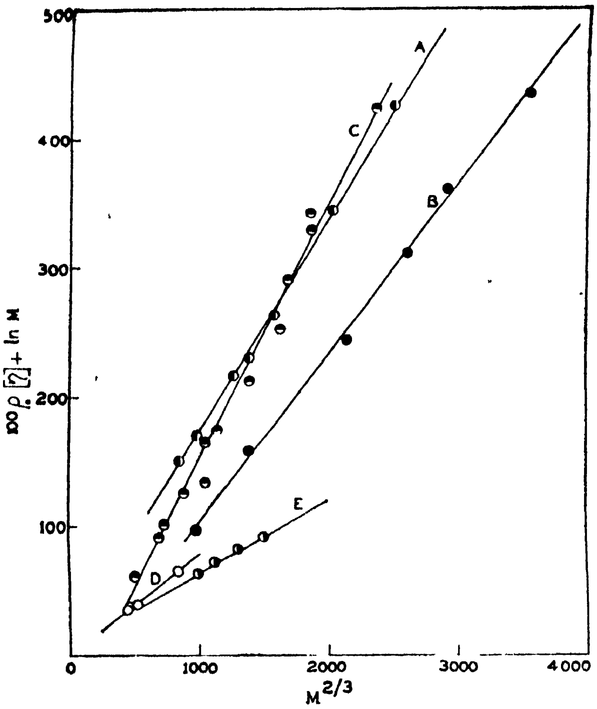

FIG. 2. Viscosity-molecular weight plot of cellulose derivatives. Curves A (Bartovics and Mark, 1943), B (Badgley and Mark, 1947) and C (Phillip and Bjork, 1951) are for cellulose acetate in acetone; D (Basu and Ray, 1952) for benzyl cellulose in chloroform and E (Roy Chowdhury) for triphenylmethyl-methyl-ethyl cellulose in dimethyl formamide.

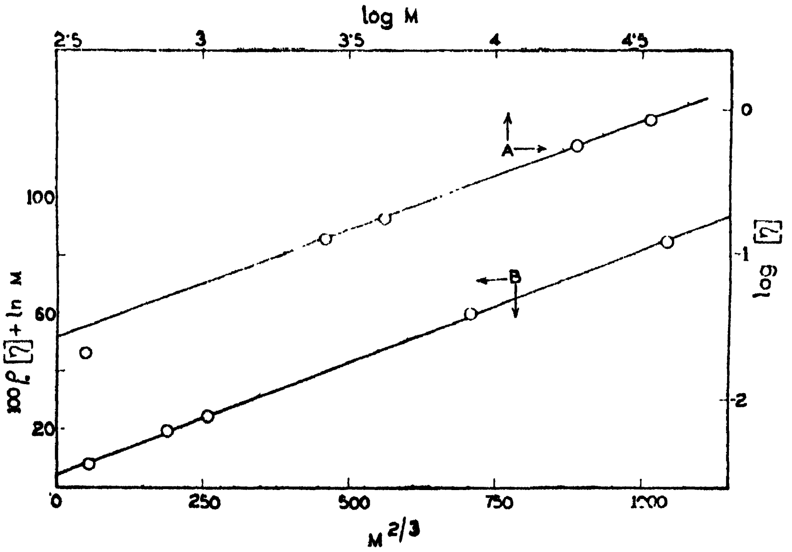

Fig. 3. Intrinsic viscosity-molecular weight relationship of polyethylene. Curve A is log[η] *vs.* log$M$ plot. Curve B is according to the new equation $100\rho_0[\eta]+\ln M$ *vs.* $M^{2/3}$. Data taken from Ueberreiter, *et. al.* (1952).

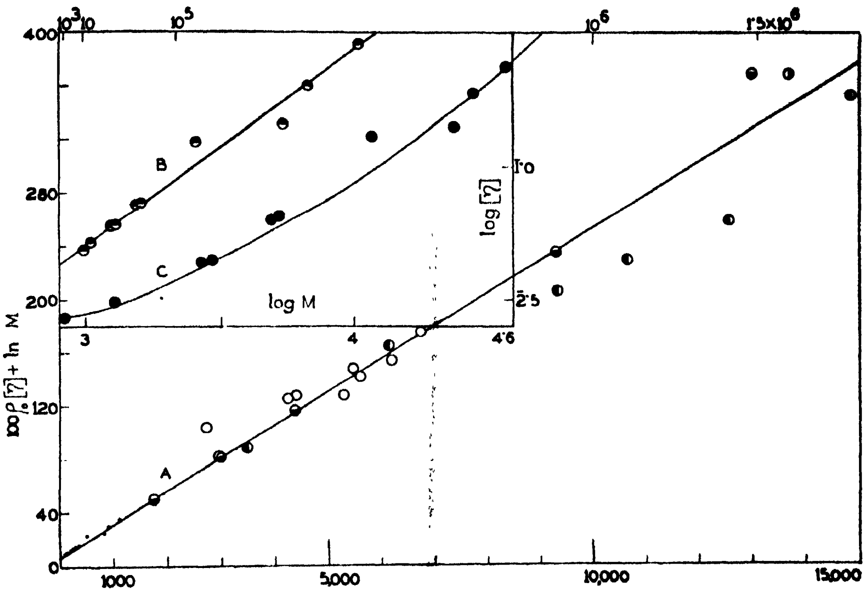

FIG. 4. Viscosity-molecular weight plot of polystyrene in toluene. Shaded circles are for Marzolph and Schulz (1954), lower half shaded circles for Bawn, et.al (1950), left half shaded circles for Alfrey et,al (1943), right half shaded circles for Bawn, Grimley and Wajid (1950), Unshaded circles for Frank, et.al (1951). Inset curve B shows the lowest data (Marzolph, et al, 1951) in a magnified plot, ordinate 6 times and abscissa 4 times magnified. Inset curve C is the conventional log $[\eta]$-log M plot of the same data.

a much wider range than that covered by the modified Staudinger equation. To demonstrate this point more clearly we have compared in Table II the calculated $[\eta]$ values from our least square equation with the experimental ones. It would be seen that the agreement is excellent in all cases and is certainly within the limits of experimental error of $[\eta]$. Similar comparison has also been made on the basis of modified Staudinger equation and it is clearly seen that the agreement is in no way better for the four fractions and is rather poor for the pure hydrocarbon.

It may be pointed out here that though ln$M$ term in the ordinate is generally rather small in comparison with $100\rho_0[\eta]$, and its variation is comparatively very small in the usual high molecular weight range, it is comparatively quite a large term in the low molecular weight range as in the above case of polyethylenes. In fact, for the lowest point the ln M-term is more than three times the corresponding value of $100\,\rho_0[\eta]$, whereas for the highest point the former is only some twelve per cent of the latter. This demonstrates the reality of this term. Though the reality of the 'ln M' term is thus demonstrated, in very many cases particularly for systems with comparatively high values of K_1 and over a narrow range and high values of molecular weight, it can be easily shown from our equation that $[\eta]$ would be practically linear with $M^{2/3}$ within the limits of our experimental accuracy of determining M. We have verified this by graphical

TABLE II

Comparison of the experimental and theoretical values for the intrinsic viscosity of polyethylene

M	New equation $100\,\rho_0\,[\eta]=7.782\times10^{-2}\,M^{2/3}-\ln M+4.045$ $[\eta]$			Modified Staudinger equation $[\eta]=3.873\times10^{-4}\,M^{0.738}$ $[\eta]$		
	Observed	Calculated	Difference	Observed	Calculated	Difference
33,700	0.850	0.855	+0.005	0.850	0.848	−0.002
18,960	0.574	0.571	−0.003	0.574	0.557	−0.017
4,200	0.180	0.182	+0.002	0.180	0.183	+0.003
2,620	0.130	0.125	−0.005	0.130	0.129	−0.001
395	0.021	0.026	+0.005	0.021	0.032	+0.011

plotting in many cases specially for cellulose derivatives whose K_1 values are unusually high.

Data for polystyrene in toluene have been plotted in figure 4. Curve A is for viscosity data in toluene taken from different sources covering a wide range of molecular weight from below 10^3 to beyond 10^6. It would be seen that the data upto $M \simeq 10^6$ fall on practically the same straight line. The conventional $\log[\eta]-\log M$ plot of these data has been given by Marzolph and Schulz (1954) and they have found that the lowest points considerably deviate from a straight line, the slope falling off at a low range of molecular weight. This falling off at the low range has been shown in the inset curve C in the same figure along with our plot of the same data on a larger scale. Our plot is found to be linear, whereas the $\log[\eta]-\log M$ plot is seen to have a continually decreasing slope in this range. As would be seen later this decrease of slope is a necessary consequence of our equation in this case.

In figure 5 we have plotted the data for polystyrene in benzene from various authors according to our equation along with the conventional $\log[\eta]-\log M$ plot. It would be seen that the $\log[\eta]-\log M$ plot scatters very much more than our plot and in fact, the points from different authors show varied slopes and can hardly be accommodated on the same line, whereas the fit is much better with our equation at least upto a million molecular weight. However, for polystyrenes prepared at not too high temperatures we recommend use of our equation in toluene at 20°C, as the latter solvent shows greater consistency.

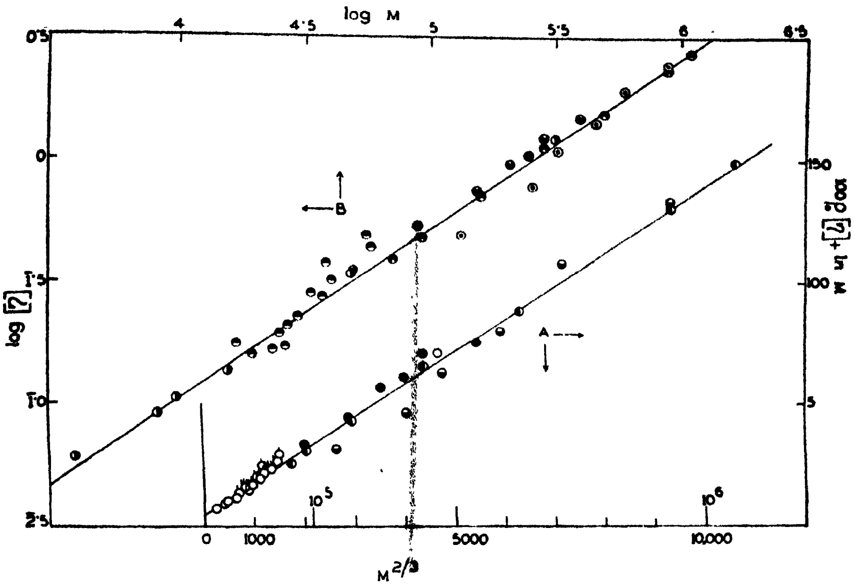

FIG. 5. Viscosity-molecular weight plot of polystyrene in benzene; Curve A is according to the new equation, curve B is the conventional log [η]-log *M* plot. Data from Krigbaum et.al. (1952), Kern and Rugenstein (1953), Bueche (1949), Bawn, et.al (1950), Bawn, et.al. (1950).

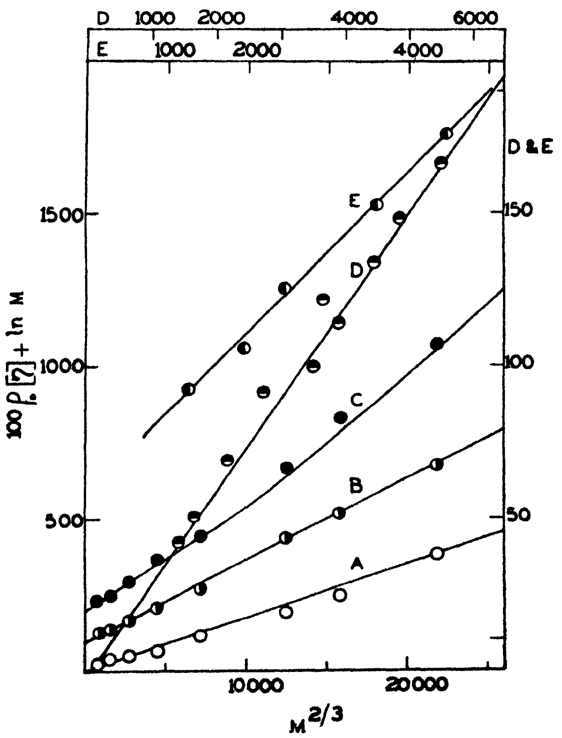

FIG. 6. Viscosity-molecular weight plot of polyacrylates according to the new equation. Curves A, B and C are for polymethyl methacrylates in acetone, benzene and chloroform respectively. Data from Baxendale, et. al (1946). Curve E for polymethyl acrylate (data from Sen, et. al., 1952).

In figure 6 we have plotted some recent data on acrylates and the plots in all cases except for methyl methacrylate in chloroform are found to be good straight lines in agreement with our equation. Our equation shows a definite rising tendency in chloroform for molecular weight of a few millions and onward, where the intrinsic viscosity is inordinately high. Such intrinsic viscosity values may not be useful for our equation as they are known to be strongly affected by shear gradient and this along with the uncertainty in molecular weight determination in this very high range may contribute to this deviation from our equation.

Sensitivity and Computational Error.

It might be surmised that in our equation M is much less sensitive to $[\eta]$ in comparison with the modifiied Staudinger equation. This is, however, not so, as can be seen from the calculations in Table II. This can, however, be theoretically demonstrated as below. By differentiating equation (7) with respect to $[\eta]$ and M, we can obtain the following equations:

$$d \ln [\eta] = d \ln M \times \tfrac{2}{3}\left(\frac{K_1 M^{2/3} - 1.5}{K_1 M^{2/3} + K_2 - \ln M} \right) \qquad \dots \quad (11)$$

$$\frac{\partial \ln \eta}{\partial \ln M} = \tfrac{2}{3}\nu \text{, where } \nu = \frac{K_1 M^{2/3} - 1.5}{K_1 M^{2/3} + K_2 - \ln M} \qquad \dots \quad (12)$$

Hence, the calculated percentage accuracy of M is $3/2 \times 1/\nu$ times the percentage accuracy of $[\eta]$. As would be shown in a later section ν is very near to unity in the usual experimental range for most polymers and so the uncertainty of M is 1.5 times the uncertainty of $[\eta]$. This sensitivity compares very well with the value $1/\alpha$ which is the value of the above sensitivity for the modified Staudinger equation.

Though we have demonstrated above that the error in M for a given error in $[\eta]$ would be nearly the same in both the equations, there is, however, a very large source of error in the modified Staudinger equation. In the latter equation M is highly sensitive to α and it can be easily shown by proper differentiation of the modified Staudinger equation that for a given value of $[\eta]$, the calculated value of M would have an accuracy of $\ln M$ times that of α. Since α can be relied upon to an accuracy of about one per cent (generally the uncertainty is higher) we can never expect to calculate M at about 10^5 to an accuracy better than about 12 per cent.

The situation, however, is quite different with the new equation as M has no such disproportionate sensitivity with respect to the constants K_1 and K_2. It is easily shown that our calculated value of M in the useful region, *viz*, 10^4 to 10^6, is generally of the order of, and very often better than, the accuracy of K_1 and K_2. Further, the computed value of M becomes increasingly precise with increase in molecular weight, whereas the accuracy decreases with increase in molecular weight in the case of the modified Staudinger equation. This is the reason why a difference of even half a million in molecular weight in the million range would not appear very much off the line in a $\log[\eta]-\log M$ plot, whereas it would be sharply brought out in our plot. It is no doubt true that equal difference does not also get equal weightage in our plot, but the M-values are certainly more widely spaced in our plot than in the conventional $\log[\eta]-\log M$ plot.

Deduction of Modified Staudinger Equation.

It is easy to see that under certain conditions particularly at high values M our equation reduces to the modified Staudinger equation. Thus, from equation (12) as written below

$$\frac{d\log[\eta]}{d\log M}=\frac{2}{3}\left\{\frac{K_1M^{2/3}-1.5}{K_1M^{2/3}+K_2-\ln M}\right\}=\frac{2}{3}\nu$$

it is easy to see that for high values of M, ν tends to unity and so our equation reduces to the modified Staudinger equation with the exponent $\alpha=2/3$. That the exponent α tends to be $2/3$ has already been noted by many previous workers (Carter, *et al*, 1946).

This is equivalent to neglecting the second and the third term on the right hand side of equation (8) as shown below,

$$[\eta]=K_1'M^{2/3}-\frac{0.023}{\rho_0}\log M+K'_2$$

$$[\eta]=K_1'M^{2/3}\approx KM^{\alpha} \qquad \dots \quad (13)$$

We can, however, go one step further by calculating the order of the values of K_1' which is equal to the Staudinger constant, since our expression for K_1' does not contain any arbitrary constant. This we can do by putting $\gamma=20$ and $\rho=0.9$ in the expression for K_1' [equation (2)] which are fairly representative values for nonpolar compounds when we obtain $K_1'=9\times10^{-4}$. We have thus arrived at a theoretical interpretation of the interesting observation that the modified Staudinger constant K is generally of the order of 10^{-4}.

Numerical Values of K_1 and K_2

Since our equation does not contain any adjustable parameter we can roughly compute the values of K_1 and K_2 and check if the experimental values are of the expected order. Taking the usual values as above, K_1 comes out to be near about 9×10^{-2} i.e. of the order of 10^{-2} for all high polymers. Table I shows how nicely this theoretical expectation is fulfilled by experimental data.

An instructive case of how K_1 in our equation always comes in the theoretically expected range whereas K of modified Staudinger equation shows a wide scatter can be studied from the data of Alfrey, Bartovics and Mark (1943). Their K-values for three samples of polystyrene prepared at 60°, 120° and 180°C are 1.6×10^{-2}, 6.6×10^{-3} and 4×10^{-4} respectively, thus showing a variation of about forty times. Our K_1 values, however, are 2.3×10^{-2}, 3.7×10^{-2} and 3.6×10^{-2}, an extreme variation of merely 1.6 times in excellent corroboration of our theoretical expectation.

The calculation of K_2 requires a knowledge of the free volume per gram. We can write K_2 in the following form

$$K_2 = \ln h\, N + \tfrac{2}{3} \ln b_{sp}/v_{sp} + \tfrac{1}{3} \ln b_{sp}/\varphi_{sp} + \ln 1/\varphi_{sp} - \ln \eta_s \qquad \dots \quad (14)$$

where φ_{sp} is the free volume in cc per gram. Making the very drastic approximation that $b_{sp} \simeq v_{sp} \simeq 1$, we have to a first approximation

$$K_2 = \ln h\, N - \tfrac{4}{3} \ln \phi_{sp} - \ln \eta_s \qquad \dots \quad (15)$$

Taking that about one per cent is void inside liquids under usual conditions we get $K_2 \simeq 4$. Thus we find that K_2 has to be a small number whose value would be of the order of unity. This expectation is fairly confirmed experimentally as is seen from Table I. It seems from general consideration of our equation and the experimental figures that K_1 is related to the shape of the molecule and K_2 is related to compactness of packing inside the solvent, the K_1 values increasing with the stiffness and consequent approach to a rod shape of the chain molecule, and the K_2 values decreasing with increasing branching of the chain. However, this is only conjectural and a thorough understanding of the significance of these constants has to await further theoretical development in this line.

Slope of the log [η]-log M curve According to our equation the slope of log [η]-log M curve is given by equation (12) as below.

$$\text{Slope} = \tfrac{2}{3} \left\{ \frac{K_1 M^{2/3} - 1.5}{K_1 M^{2/3} - \ln M + K_2} \right\} = \tfrac{2}{3} \nu$$

It can be easily shown that for the usual values of K_1 and K_2, ν tends to unity as M approaches 10^5 and higher, and therefore the log [η]-log$M$ slope is near about 2/3 in this region. It is further to be noted that our expression for the slope is quite insensitive to a change of M in this usual range of M and this explains the observed approximate linearity of the log[η]-log M curve over this range.

An examination of the variation of ν with change of K_1 and K_2 and M leads to a clear understanding of the observed behaviour of log [η]-log M curve. From figure 3 it is seen that the log [η]-log M line passes quite high above the point for the lowest molecular weight polyethylene ($C_{28}H_{58}$) which shows that at nearabout this region the log [η]-log M curve has a decidedly higher slope. The behaviour of polystyrene, however, is just the opposite as can be easily seen from the figure given by Marzolph and Schulz (1954) who have collected much available data, and find that the log [η]-log M curve has a continuously decreasing slope with lowering of molecular weight (figure 4, curve C).

The above behaviour is easily understood from figure 7 wherein we have plotted ν against log M for polystyrene and polyethylene, the data for K_1 and K_2 being taken from Table I. A value of $\nu = 1$ means that the log [η]-log M

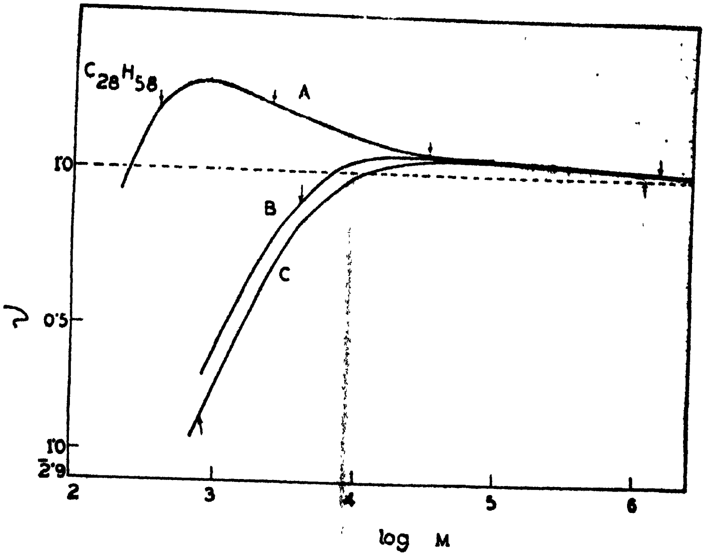

FIG. 7. Theoretical variation according to the new equation of slope of log [η]-log *M* plot with molecular weight. Curve A for polyethylene in decalin, B for polystyrene in benzene, C for polystyrene in toluene. The arrow heads mark range of molecular weights.

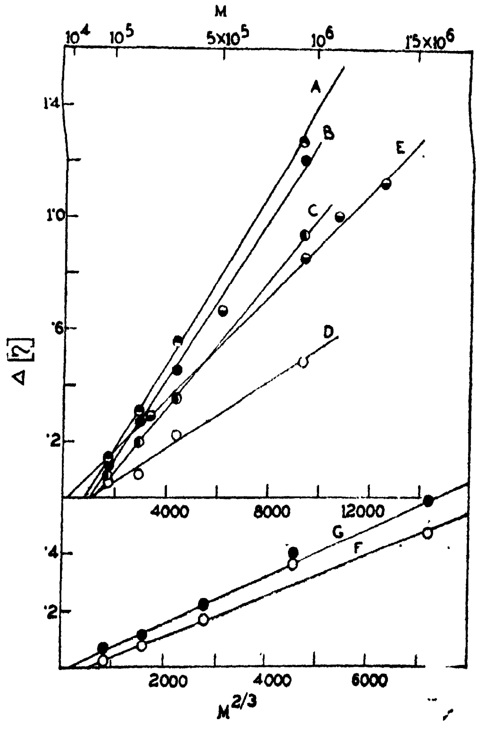

FIG. 8. Differetial intrinisic viscosity-molecular weight plot of polystyrene, A: Benzene-M.E K., B—toluene-toluene 50: heptane 50 ; C toluene-toluene 80: methanol 20, D—benzene: ethylbenzene, E—toluene-M.E K. Data from Bawn, et. al (1950), Bawn et.al (1950) Goldberg, et. al, (1947); and of polymethyl methacrylate F—acetone : benzene; G—chloroform : acetone. Data from Schnlz et. al, (1953).

curve has a slope of 2/3. On the graph for polyethylene we have indicated by dots the experimental points studied by Ueberreiter and coworkers(1952) and similarly we have marked off the regions of study for polystyrene by arrows.

It is easily seen from the trend in the value of ν in the above graph that for polystyrene the slope has to remain constant at nearabout 2/3 in the usual experimental range, and has to fall off continuously in the low molecular weight region. It is to be pointed out that though the slope of the log $[\eta]$-log M line falls off in the low molecular weight region it is sensibly a straight line in our plot as expected. We, therefore, consider it unnecessary to invoke the concept of chain branching to explain the change of slope as has been done by Marzolph and Schulz (1954).

Equally evident is the reason why the lowest experimental point for polyethylene is below the curve and the slope there has to be high. The lowest experimental point happens to fall on a high value of ν and so has to be below the line. Further in the region investigated ν has an average value 1.13 and so the log $[\eta]$-log M slope should be $0.66 \times 1.19 = 0.736$ in agreement with the observed slope of 0.738.

Effect of a Change of Solvent on $[\eta]$. If $[\eta]_1$ and $[\eta]_2$ be the intrinsic viscosities of a polymer in two different solvents, it can be easily shown on the basis of our equation that they are related by the equation.

$$\rho_1[\eta]_1 - \rho_2[\eta]_2 = a'M^{2/3} + b' \qquad \ldots \quad (16)$$

where a' and b' are constants given by $100a' = (K_1)_1 - (K_1)_2$ and $100b' = (K_2)_1 - (K_2)_2$. Since $\rho_1 \simeq \rho_2$, the above equation becomes

$$\Delta[\eta] = [\eta]_1 - [\eta]_2 = aM^{2/3} + b$$

where a is equal to a'/ρ. Thus we obtain the interesting result that the difference in viscosity is a linear function of $M^{2/3}$. That this is true is shown in figure 8 for polymethyl methacrylate and polystyrene in a number of solvent pairs. The usually quoted relation which directly follows from the modified Staudinger's equation that $\log[\eta]_1$, is linear in $\log[\eta]_2$ is also expected to be approximately true from our equation in the usual experimental range as can be easily seen by a calculation of $\partial \log[\eta]_1 / \partial \log[\eta]_2$ from our equation (9) being equal to ν_1/ν_2.

A Critical Test between the two Equations—A critical test can be easily devised between the proposed equation and the modified Staudinger equation, success or failure of which can decide one way or the other. We write below our foregoing equation and also its counterpart based on the modified Staudinger equation.

New equation :— $$\Delta[\eta] = [\eta]_1 - [\eta]_2 = aM^{2/3} + b \qquad \ldots \quad (17)$$

Modified Staudinger equation :—

$$\Delta[\eta] = [\eta]_1 - [\eta]_2 = M^{2/3}\{K_1 M^{\alpha_1 - 2/3} - K_2 M^{\alpha_2 - 2/3}\} \qquad \ldots \quad (18)$$

It can be easily seen that $\Delta[\eta]$ has to vanish absolutely at $M = 0$, according to equation (18) whereas our equation expects a very small but not necessarily zero value. The fact that both the equations cease to have a meaning long before M approaches zero is immaterial for the present purpose, and the extrapolated line has to pass through the origin in a $\Delta[\eta]$ versus $M^{2/3}$(or for that matter any positive power of M) plot if equation (18) is valid. That this is not so is clearly seen from curves A and B of figure 8. In fact, some of these lines meet the $M^{2/3}$-axis at quite a high value of M, *viz.* $M >$ 50,000. This conclusively shows that there are inconsistencies in the modified Staudinger equation and so it cannot claim to be a true description of facts. At least, the algebraic form of the modified Staudinger equation is formally inadequate.

It is possible to design another subtle critical test based on equation (18). It is evident that since α is very near to 0.66 for most polymers, the quantity in bracket on the right hand side of equation (18) is simply $K_1 - K_2$ for low values of M and so the equation becomes

$$\Delta[\eta] \simeq M^{2/3}(K_1 - K_2) \qquad \ldots \quad (19)$$

Thus, for such cases we should expect the slope of the $\Delta[\eta]$ versus $M^{2/3}$ line to be equal to $(K_1 - K_2)$. Frequently we observe not only a discrepancy with the above equation (19) but a positive slope is obtained where we should expect a negative slope.

Thus we cannot escape the conclusion that either the modified Staudinger equation is insufficient or that the K and α values are inconsistent. There is, however, no such difficulty with our equation as can be seen from the form of our equation. We feel that if the modified Staudinger equation is to be retained and has to serve any useful purpose, the above inconsistencies have to be removed, which seems to be an almost impossible task within the limits of two adjustable parameters.

Low Molecular Weight Liquids. Another important point in favour of the present equation is that this equation is not only true for polymers but the basic equation viz. equation 3, has been shown by the present author (Palit, 1952) to be very accurately followed by homologous liquids of low molecular weight. This is illustrated for hydrocarbons in figure 1 (curve C) where $\log(\eta M)$ is found to be accurately linear with $\gamma v_{sp}^{2/3} M^{2/3}$ from C_5 to C_{12} alkanes with almost the theoretical slope in agreement with our equation (2). Other deductions from equation (2) have also been found (Palit, *loc. cit*) to be experimentally valid.

CONCLUSIONS

It is hence concluded that the proposed equation is in quantitative agreement with known facts, covers a wider range of molecular weight, is as sensitive as, if not more than, the current equation, answers satisfactorily the differential viscosity test, and has a theoretical background. Even considered as an empirical equation it scores over the modified Staudinger equation on many counts. The latter equation has also been demonstrated to be formally inadequate from differential viscosity studies in two solvents. It is hoped that the proposed equation would be used in preference to the purely empirical modified Staudinger equation now in use in consideration of the above points.

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