SOME GENERAL RELATIONS ON THE VISCOSITY OF HOMOLOGOUS LIQUIDS

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(*Received for publication, November 8, 1952*)

ABSTRACT. From recent theoretical developments in the field of viscosity of liquids as explained from the hole theory of liquid structure, the following relations have been deduced

(1) In any homologous series, at constant temperature, the logarithm of the molecular viscosity ($\log \eta M$) is a linear function of the molar surface energy $\gamma(Mv_{sp})^{2/3}$. It is shown that the theoretical slope of this line is 0.17×10^{-2} and the observed slope for different homologous series is within a factor of two of this theoretical value.

(2) In any homologous series if the intercept of the Arrhenius plot (i e. $\log \eta$ *vs* $1/T$) is A, log molecular weight is in linear relation with A, the slope of the line being negative of unity, *i.e.* (*i*) $A=-\log M+\text{constant}$ or (*ii*) $M=K\eta\, 10^{-A}$

It is pointed out that the experimental results with methyl esters confirm the above equation, the observed slope being -1.01 and that the relation can evidently be utilised for determining molecular weight of liquids from viscosity measurements. There are too many exceptions to this equation which limits its utility but points to the soundness of the basic concept.

(3) In any homologous series, $\dfrac{\ln \eta}{K_E T_C}$ (where K_E=Eötvs constant $\simeq 2.1$ and T_c = critical temperature) plotted against $1/T$ would produce a system of parallel straight lines with a slope of near about unity.

(4) In any homologous series log molar viscosity plotted against reciprocal of absolute temperature would produce a system of straight lines which would all meet at near about the same point on the log molar viscosity axis The application of this relation to the establishment of chemical structure is obvious.

The above relations have been further simplified and applied in the case of high polymers.

All the above deductions have been found to be in conformity with the available experimental data.

Applying Eyring's rate theory considerations to the hole theory of liquid structure, Eyring *et al* (1941) gave the following equation for the viscosity of a liquid *viz.*,

$$(2\pi mkT)^{1/2}e^{\Delta\epsilon_f/kT} \qquad \ldots \quad (1)$$

where η= viscosity, λ_1= the distance between two layers of molecules in a liquid sliding past each other under the influence of an applied force, λ_3= the distance between two neighbouring molecules in the same direction, λ_2= the mean distance between two adjacent molecules in the moving layer in the direction at right angles to the direction of motion, v_h = the volume of a single hole, or increase in volume per equilibrium position, v = the volume inhabitated by a single molecule, v_s = the contribution of a single molecule to the volume of the unexpanded solid, m the mass of an individual molecule, k the Boltzmann constant, T the absolute temperature, and $\Delta\epsilon_f$ the activation energy required for a single molecule to flow into a hole that is available *in the absence of a shearing force.*

Telang (1949) has taken an important step forward by identifying the activation energy required to move the liquid molecules from one position to the next, *i.e.*, the activation energy for viscous flow as the free energy of formation of a surface (an idea which is somewhat similar to the concept of Frenkel (1946) that the activation energy required for the formation of a hole is proportional to the surface tension multiplied by the surface of the hole). From the above concept Telang has deduced the following equation (eqn. 2) for the viscosity of a liquid. This equation has the unique feature that it does not contain any arbitrary constant.

$$\eta = (hN/V^{2/3})(b/(v-b))^{1/3} \exp\left(1.091 N^{1/3}\gamma(M/D)^{2/3}/RT\right) \quad \dots \quad (2)$$

where η = is viscosity, V is molar volume, γ is surface tension, T is the absolute temperature, h is Planck's constant, N is the Avogadro number, R is the gas constont and b is the volume occupied by the molecules in the liquid state per mole (van der Waals constant) and D is density.

In order to test the validity of the above equation Telang has made a few calculations with data on a number of liquids with, on the whole, satisfactory results. This equation, however, instead of being applied to one liquid can be suitably modified as to be applicable to a homologous series, and such extension of this equation has been found to lead to some highly interesting results, which we shall investigate in this paper.

Viscosity of a homologous series. If we put $b_{sp}M$ and $v_{sp}M$ for b and V respectively in eqn (2), the equation after taking logarithm becomes,

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

It can be safely assumed with a fair degree of approximation that though b and V will vary considerably with increase in molecular weight, b_{sp} and v_{sp} would vary only slightly from member to member in a homologous series; particularly, the last term in eqn (3), which involves log of ratio of these terms, would change very little from member to member. Hence, for the same homologous series at constant temperature we may write equation (3) in the following form,

$$\ln(\eta M) = \frac{1.091 N^{1/3}}{RT} \cdot \gamma v_{sp}^{2/3} M^{2/3} + k_2' \quad \dots \quad (4)$$

$$\log(\eta M) = \frac{1.108}{2.303T} \cdot \gamma v_{sp}^{2/3} M^{2/3} + k_2 \quad \dots \quad (4a)$$

$$\log(\eta M) = k_1 \gamma v_{\kappa p}^{2/3} M^{2/3} + k_2 \qquad \ldots \quad (4b)$$

$$\text{At } 20^\circ\text{C} \ \ln(\eta M) = 0.38 \times 10^{-2} \gamma (M v_{\kappa p})^{2/3} + k_2' \qquad \ldots \quad (5)$$

$$\text{or, } \log(\eta M) = 0.165 \times 10^{-2} \gamma (M v_{\kappa p})^{2/3} + k_2 \qquad \ldots \quad (6)$$

Hence, we should expect that in a homologous series, log (ηM) when plotted against $\gamma v_{\kappa p}^{2/3} M^{2/3}$ would yield a straight line. Calling ηM as molar viscosity we may say that *in any homologous series the logarithm of the molar viscosity increases linearly with the molar surface energy*, the relative rate of increase being roughly one sixth of one per cent at near about room temperature. It would be of interest to test the above relation with available experimental data.

In figure 1, we have made such plots for C_7 to C_{12} straight chain alkanes, the alcohols, the four lowest methyl esters, and the four lowest ethyl esters. It is surprising, considering the assumptions involved in deriving the equation,

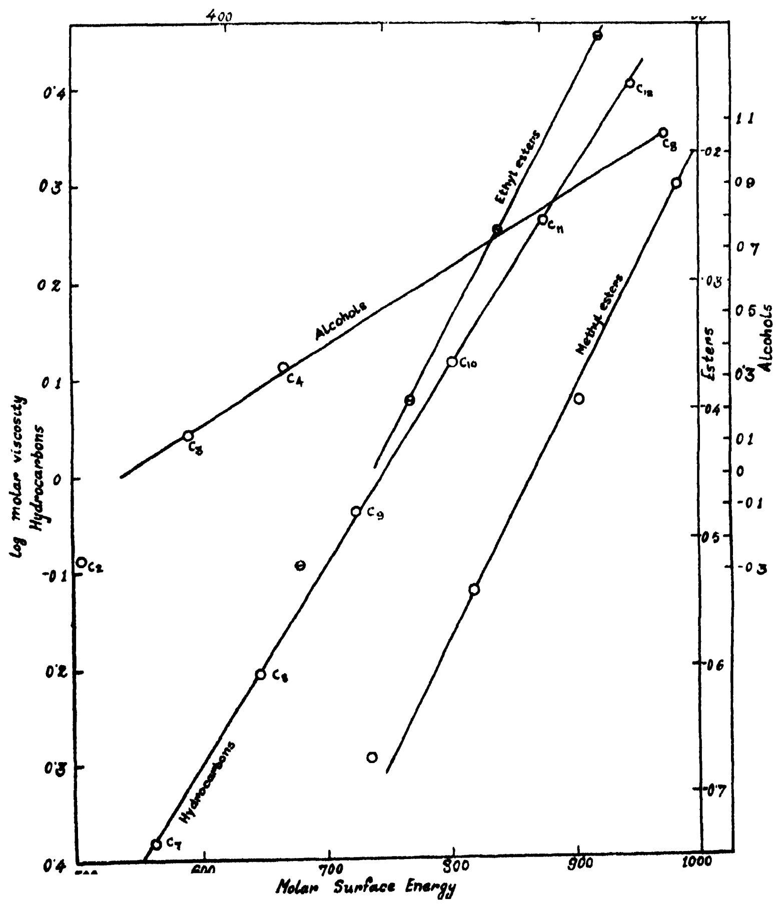

FIG. 1

Log molar. viscosity against molar surface energy of homologous liquids. Lower scales of abcissare for hydrocarbons, and alcohols, the scale for the alcohols having been displaced 170 units to the right. Top scale is for esters, the scale for methyl esters is displaced 100 units to the right.]

that the points (except for methyl alcohol, formates and ethyl alcohol) fall on excellent straight lines. This is more striking in consideration of the fact that the above plot is highly sensitive to slight errors in γ on which however, the published data are probably not of as high order of accuracy as those on the other quantities. So we conclude that the general features of equation (4), particularly the statement made in the previous para (in italics) are confirmed by experimental data.

The discrepancy in the case of methyl alcohol and formates is expected from the wellknown fact that the first member of a homologous series does not generally fall in line with the higher members in many properties and almost always behaves in an exceptional way. The case of ethyl alchol, however is a real exception.

From equation (6) we should expect that the slope of the above plots should be 0.16×10^{-2}. Our observed slopes are 0.21×10^{-2}, 0.24×10^{-2}, 0.23×10^{-2} and 0.24×10^{-2} in the case of alkanes, the ethyl esters, the methyl esters and the alcohols respectively. It is gratifying to note that the observed slopes are of the right order and quite close to our expected value. We ascribe this slight numerical discrepancy to the assumptions made in the derivation of equation (2) that the molecules are spherical in shape and the activation energy of viscous flow is equal to the molar surface energy. The latter assumption cannot be entirely true as the potential inside a liquid is higher than that at the surface and so, the coefficient in eqn (4) should contain a parameter to take care of these factors and it appears from our calculations that this parameter generally lies within a factor of two or so. So we rewrite equation (4) as

$$\ln \eta M = \frac{1.108p}{T} . \gamma(v_{bp}M)^{2/3} + k_2' \qquad \ldots \quad (6)$$

$$\text{or,} \quad \log \eta M = k_1[\gamma(v_{bp}M)^{2/p}] + k_2 \qquad \ldots \quad (7)$$

where p is a parameter which generally lies between 1 and 2 and depends on the shape or packing possibility of the molecule and also on the strength of the field inside a liquid. It is of interest to note from figure 1 in this connection that the observed slope k_1 is lowest for the hydrocarbons and increases in the order hydrocarbons < methyl esters < ethyl esters < alcohols. This may indicate that the more polar the liquid type is the higher will be the value of p *i.e.*, higher will be k_1.

We have thus arrived at a method of calculating the molecular weight of any member of a homologous series from density, surface tension and viscosity data if k_1 and k_2 of eqn (7) are already known from experiments on a few other members of the same homologus series. Such calculations of molecular weight of substances represented in figure 1 are shown in Table I. It would be seen that the calculated molecular weights are in good agreement with the theoretical values.

TABLE I

Calculation of Molecular weight from viscosity, surface tension and density data (20° C)

Substance	$k_1 \times 10^2$	k_2	Molecular weight	
			Theoretical	Calculated from eqn (7)
n-alkanes				
(C_7) Heptane	0.2065	−1.5451	100.2	99.2
(C_8) Octane			114.2	113.7
(C_9) Nonane			128.2	129.3
(C_{10}) Decane			142.3	142.5
(C_{11}) Undecane			156.3	156.5
(C_{12}) Dodecane			170.3	169.5
Ethyl esters				
Acetate	0.2377	−1.6218	88.1	87.8
Propionate			102.1	102.9
Butyrate			116.1	116.0
Methyl esters				
Acetate	0.2431	−1.6575	74.1	75.1
Propionate			88.1	86.9
Butyrate			102.1	102.13
Alcohols				
n-Propyl alcohol	0.2436	−0.8883	60.1	58.1
n-Butyl alcohol			74.1	76.1
n-Octyl alcohol			130.2	130.0

Effect of temperature. By using Eötvos equation $\gamma(M/D)^{2/3}=K_E(T_C-T)$ where K_E is the Eötvos contant and T_C is the critical temperature we can easily put equation (4) in the following from,

$$\ln \eta = \frac{1.11 K_E T_C}{T} - 1.11 K_E - \ln M + k_2' \qquad \ldots \quad (8)$$

This equation, except for the ln M term, has already been deduced by Telang combining his equation [Equation (2)] with Eötvos equation. This equation immediately leads to a number of very interesting conclusions when applied to a homologous series. It is thus apparent that if we plot $\frac{2.303}{K_E T_C}$ log η against $1/T$ for members of the same homologus series, we shall get a system of parallel straight lines with a slope of the order 1.1. That this is true is shown in figure 2 for a number of esters. Conversely, by determininig the slope of the log η versus $1/T$ plot (to be called Arrhenius plot in this paper) we can obtain the critical temperature of a liquid by dividing the slope by $\frac{k_1 K_E}{2.303}$ Thus, we have been able to obtain theoretically an expression for the slope of the Arrhenius plot. Thomas (1946), taking up a suggestion by Prasad (1933), has already shown that the Arrhenius slope of viscosity is proportional to critical temperature and equation (8) further shows that the slope is also proportional to K_E in any homologous series. The restriction to a homologous series comes from the fact that the slopes of the straight lines in figure 2 are not exactly equal to 1.11 but has been found to have nearly equal values for all members of a homologous series. Hence, it is advisable to write equation (8) in the following from where k_1 is a constant whose value is of the order of unity.

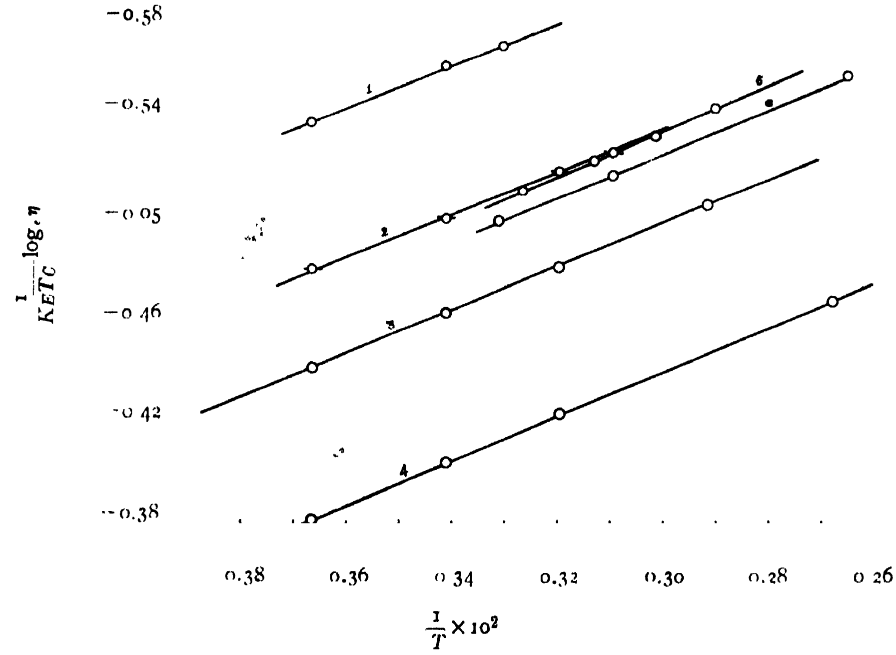

FIG. 2

$\frac{1}{K_E T_C}$ ln η against $1/T$ for esters ; (1) methyl formate (2) methyl acetate (3) methyl propionate (4) methyl butyrate (5) ethyl acetate (6) ethyl propionate (for (5) and (6) the odinates have been displaced upwards by 0.1 unit)

$$\log \eta = \frac{k_1 K_E T_C}{T} - k_1 K_E - \log M + k_2 \qquad \ldots \quad (8a)$$

It should be remarked, however, that the slopes of the above straight lines (figure 2) are not exactly the same, the values being in the range 0.82 ± 0.02. It should also be noted that this value is somewhat lower than the theoretical slope 1.11. This discrepancy is partly due to causes as explained in the previous section and partly due to the approximate nature of Eötvos equation which we have taken help of in its derivation.

An interesting modification of equation (8) is to write it in the from

$$\log(\eta M) = k_1 K_B T_0 \cdot \frac{1}{T} - (k_1 K_B - k_2) \qquad (9)$$

We should hence expect that if we plot log (ηM) against $1/T$ we should obtain for all members of the same homologous series a system of straight lines which would meet at near about the same point on the log ηM axis. This is shown for a few typical homologues in figure 3. The application of

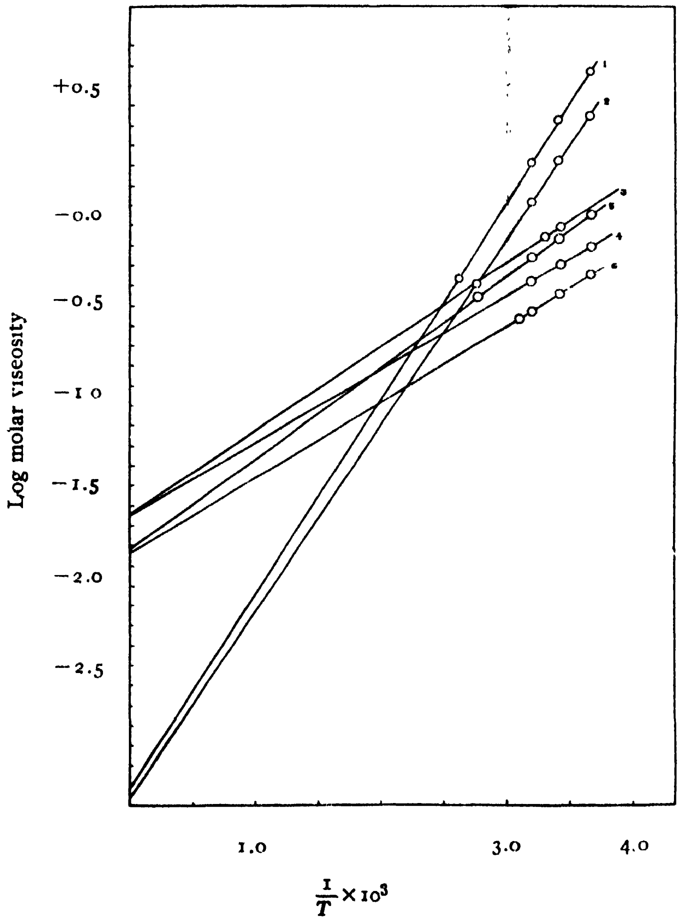

FIG. 3

Log molar viscosity against reciprocal of absolute temperature for various types of compounds. (1) Butyl alcohol (2) Propyl alcohol (3) Octane (4) Heptane (5) Ethyl propionate (6) Methyl acetate.

this relation for confirmation of the chemical structure of any unknown liquid is obvious. It is relevant to point out that instead of the usual plot of log η anainst $1/T$, it is more convenient for comparative purpose to plot log ηM against $1/T$ as almost all liquids can be easily accommodated on the same graph.

Determination of molecular weight. We have already pointed out in Table I how molecular weight can be calculated from viscosity, surface tension and density data at one temperature. Eqn (8) promises to provide another method from measurements of temperature variation of viscosity. It is easy to see that the intercept of the log η versus $1/T$ plot *i.e.* the intercept of the Arrhenius plot, A is given by the equation,

$$A = -1.11K_E - \log M + k_2 \qquad \ldots \quad (10)$$

or,

$$A = -k_1K_E - \log M + k_2 \qquad \ldots \quad (11)$$

or,

$$M \simeq K_\eta 10^A \qquad \ldots \quad (12)$$

where k_1 has a value near about unity and K_η is a constant for the same homologous series.

If the above equation is true we should expect that for any homologous series, the Arrhenius intercept, A would be a linear function of log M and the slope of this straight line would be negative of unity. Figure 4 illustrates the above relation for the methyl esters. The intercepts were obtained by the least square method. The points (except the first member) fall remarkably well on a straight line and its slope is -1.01 *i.e.* practically the same as the theoretical slope of negative of unity.

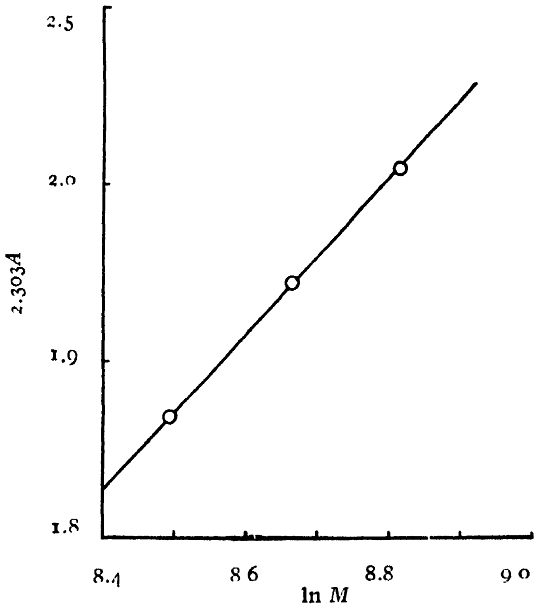

Fig. 4

A versus log M plot for methyl acetate, propionate and butyrate
Expected linear relationship between the Arrhenius intercept of viscosity and log molecular weight for members of the same homologous series (methyl acetate, propionate and butyrate.

This behaviour of methyl esters as shown in figure 4 is, however, exceptional rather than being the rule with any homologous series. Most series show quite irregular behaviour with the intercept A as already observed by Andrade (1934), Thomas (1946) and others. Such failure of equation (10) or for that matter equation (8) is owing to the fact that Eövtos equation used in its derivation is only an approximate one and that k_2 is not a strictly temperature independent constant. The agreement, however, is not fortuitous but shows the basic correctness of the underlying concept.

Equation (12) can be easily tested for ordinary liquids. Such a test is shown in Table II with data for methyl esters where equation (10) has been found to be valid. It would be seen that the calculated value of the constant K_η remains essentially constant as we go up the series and this establishes equation (12). This equation undoubtedly provides a simple method of determining molecular weight from viscosity data only, provided a table of K_η values is available.

TABLE II

Determination of molecular weight from Arrhenius intercept with the help of eqn. (12)

Substance	A	log M	log $K\eta = -A + \log M$	$M = K\eta 10^{-A}$	
				Calculated	Theoretical
Methyl acetate	−3.6880	1.8697	1.8183	74.08	74.08
Methyl propionate	−3.7607	1.9450	1.8157	87.84	88.10
Methyl butyrate	−3.8269	2.0092	1.8179	102.3	102.13

mean = 1.8170 $K\eta = 10^{-1.8170}$

It should be pointed out, however, that equation (12) is only an approximate one and its validity depends on two assumptions *viz.*, (*i*) k_2 is exactly the same for all members and (*ii*) K_E values are equal for all members of the homologous series. Even any slight deviation from the above conditions would produce large discrepancy in the calculated values of M. Hence, the equation is not very suitable for use with ordinary liquids and the case of methyl esters as given in Table II is rather exceptional than usual. Most probably nonpolar hydrocarbons and also high polymers would strictly conform to this equation and correct values of their molecular weights would be obtainable from temperature coefficient of viscosity. Only further work, now in progress in this laboratory, can decide the matter.

Application to high polymers. A series of high polymers of the same structure, for example, polystyrenes of different molecular weights, forms something akin to a homologous series where eqution (3) finds an ideal application and admits of further simplification. This would be thoroughly discussed in a separate publication but we can write the final eqution for such case forthwith as below

$$100\rho_0[\eta] = K_p M^{2/3} - \ln M + k_2 \qquad \cdots \quad (13)$$

where ρ_0 is the density of the solvent and $[\eta]$ the intrinsic viscosity of the polymer. We have found that almost all published data show that $\{100\rho_0[\eta]$

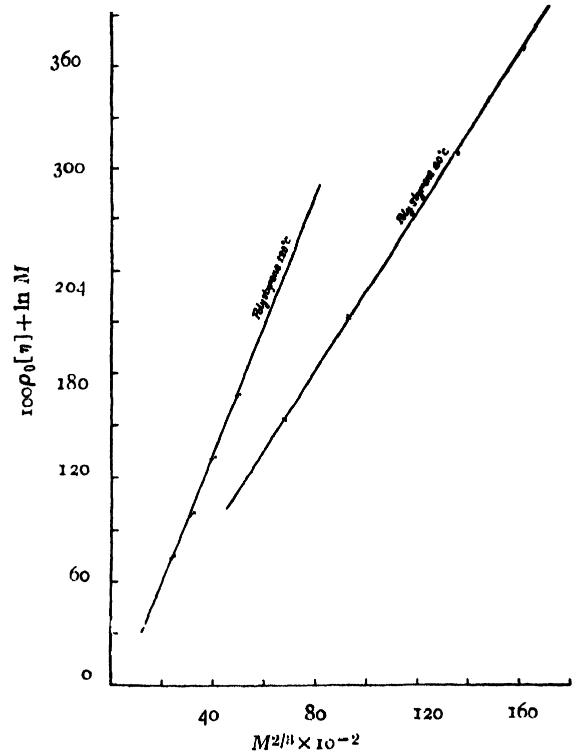

FIG. 5

A plot of $100\rho_0[\eta]+\ln M$ versus $M^{2/3}$ for fractions derived from two samples of polystyrenes prepared at 60°C and 120°C respectively (Data from T. Alfery, A. Bartovics, and H. Mark, J. Amer. Chem. Soc., **16**, 2319 (1643)

$+\ln M\}$ when plotted against $M^{2/3}$ give straight lines with a slope of the right order as expected from theory. figure 5 is a typical illustration for two samples of polystyrenes.

We, however, like to point here that though polymers being solids often of ill-defined melting points, have to be of necessity inevstigated in solution, we can probably apply equation (11) or (12) to their solutions and thus determine their molecular weight from temperature coefficient of the viscosity of their solutions in a suitable solvent. Experiments are in progress in this laboratory to investigate the possibility of such an application.

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