Physico-Chemical Studies
on
Polymer Solutions

(I)   Studies on Solute – Solvent
        Interaction in Rubber Solutions
                    by Light Scattering.

(II)   A Theory of Viscosity of Long
         Chain Polymer Molecules in Dilute Solutions

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PART I

STUDIES ON SOLUTE-SOLVENT INTERACTION IN RUBBER SOLUTIONS BY LIGHT SCATTERING.

PART II

A THEORY OF VISCOSITY OF LONG CHAIN POLYMER MOLECULES IN DILUTE SOLUTION.

Acknowledgments

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PART   I

STUDIES ON SOLUTE-SOLVENT INTERACTION IN RUBBER SOLUTION BY LIGHT SCATTERING.

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I

High polymeric substances owe their unusual properties to the size and spatial configuration of their molecules, and in recent years, considerable attention has been paid to correlating their structural characteristics and solution properties. In general, the spatial configuration of high polymer molecules depends, inter alia, upon their monomeric structure and environmental conditions. Many changes in the physical properties of a polymer can be brought about by changing the environment.

The behaviour of polymeric substances towards solvents is very characteristic. Whereas low molecular weight substances dissolve in a suitable solvent to a well defined saturation limit, high polymeric substances first swell, imbibing liquid without themselves getting dispersed. In bad solvents the process stops here, while in good solvents polymers gradually lose form and ultimately get dissolved. According to the thermodynamic formulation, the process is related to a change in the Gibbs free energy of dilution ΔF_m. A polymer will be completely miscible with a liquid if ΔF_m is negative at all concentrations.

ΔF_m is related to the osmotic pressure of a solution by the well known equation

$$V_1 \pi = -N \left[\frac{\partial \Delta F_m}{\partial n_1} \right]_{T, P, n_2} \qquad (1)$$

where V_1 is the molar volume of the pure solvent, N the Avogadro Number and n_1 and n_2 the number of molecules of the solvent and the solute respectively in a given volume V.

Rewriting equation (I) as

$$V_1 \pi = -N \left[\frac{\partial \Delta F_m}{\partial V} \right]_{T, P, n_2} \left[\frac{\partial V}{\partial n_1} \right]_{T, P, n_2} \qquad (2)$$

we obtain .

$$\pi = -\left[\frac{\partial \Delta F_m}{\partial V} \right]_{T, P, n_2} , \qquad (3)$$

since

$$\left[\frac{\partial V}{\partial n_1} \right]_{T, P, n_2} = V_1 / N .$$

For an ideal solution,

$$\pi = \frac{n_2}{V} RT = RT \frac{C}{M} \qquad (4)$$

where C is the concentration in gms/ml, M the molecular weight of the solute, R the gas constant and T the absolute temperature.

It can be seen from equation (4) that π is
directly proportional to the number of solute particles in
a unit volume. Thus, by the measuring the osmotic pressure
of a solution at a given concentration both the molecular
weight and ΔF_m can be estimated. Equation (4) further
lays down the condition that for an ideal solution a plot
of π/c versus C should be a straight line with a zero
slope. Generally solutions of high polymeric substances
exhibit very low osmotic pressures and the plots of π/c
versus C do not show zero slopes except under specific
conditions. This indicates that polymeric substances
have high molecular weights, and their solutions show
a departure from ideality. This non-ideal behaviour is due
to the facts that the solute molecules occupy a large
volume in solution and that they interact with each other
and with their surroundings, thus violating the two of
the most important conditions for ideality. Therefore,
a knowledge of the volume requirements as well as the
nature and the magnitude of interaction of the polymer
molecules in solution is essential to understand their
non-ideal behaviour and other solution properties. In
what follows, we shall attempt to explain briefly the
origin and the consequences of this non-ideal behaviour.

II

The chemical formula of a polymer may be represented by (Monomeric unit)$_n$, where n has usually very high integral values. This type of structure is capable of acquiring a very large number of configurations in space by virtue of rotation around bonds of the main chain skeleton. A theoretical description of many properties of dilute polymer solutions requires/a knowledge of the average configurations of the polymer molecules, which is characterised by the mean-square end-to-end distance $\overline{r^2}$. W.Kuhn[54], and Guth and Mark[39] independently proposed that a chain consisting of Z flexibly-linked elements (segments) of length ℓ would have a configuration analogous to that of a three dimensional path of a freely diffusing particle which makes Z random jumps of length, ℓ. Accordingly, they calculated the probability W(r)(dr) that the two ends of a chain would be separated by a distance which lies in the range r and r + dr irrespective of direction and is given by

$$W(r)\, dr = \left[\beta/\pi^{1/2}\right]^{3} 4\pi\, r^{2}\, e^{-\beta^{2}r^{2}}\, dr, \qquad (5)$$

where

$$\beta = \left[\frac{3}{2 Z \ell^{2}}\right]^{1/2} \qquad (6)$$

From equations (5) and (6) $\overline{r^2}$ is found to be equal to $\ell Z^{1/2}$. In the case of real polymer chains, however, the problem of finding W(r) becomes difficult owing to the existence of potential barriers which

restrict free rotation around the bonds.   Kuhn[55,56]

showed that a reasonable statistical distribution of

displacement-lengths for such a chain as a whole will be

obtained if each element is replaced by a hypothetical

element of length ℓ' equal to the r.m.s. length of the actual

elements consisting of m bonds.   Thus the statistical

elements are both random in orientation and fixed in length,

and the problem is reduced to that of a freely-jointed

chain consisting of $Z'\left[=\frac{Z}{m}\right]$ elements of length ℓ'.

The form of the distribution of chain displacement lengths

in such a case would be approximately Gaussian, but the

value of β would be given by

$$\beta = \left[\frac{3}{2\,Z'\,\ell'^2}\right]^{1/2} \tag{7}$$

and

$$\overline{\pi^2} = \ell'^2\,Z' \tag{8}$$

$$= A\,\ell^2\,Z \tag{9}$$

where A is a constant for a given chain structure depending

upon bond angles, extent of any restricted rotation[2,57,71]

etc. Flory[28] pointed out that a treatment based on an

outright acceptance of a random walk model would be in error

since a freely diffusing particle is permitted to cross

its paths numerous times, whereas a configuration of a polymer

involving one or more crossovers is forbiddin because each

element excludes a volume from all other elements.   As a

result, the r.m.s. end-to-end distance would be increased

from its unperturbed value $(\overline{\mathfrak{R}_0^2})^{1/2}$ to $\alpha(\overline{\mathfrak{R}_0^2})^{1/2}$, α being

an expansion factor. As a result the volume pervaded by

a polymer chain would be considerably larger. Consequently,

even in dilute solutions there may be considerable over-lapping

of domains of the polymer molecules giving rise to

appreciable inter-and intra-molecular segment-segment

interaction. Since the segments of one molecule are

indistinguishable from those of another, the same parameters

would characterise the above interactions. The nature and

extent of these interactions, irrespective of the fact

that they belong to the same or different molecules, depend

on the solvent power of the medium i.e. on how effectively

the solvent molecules can separate them. Thus, the

problems of segment-segment and segment-solvent intereaction

are mutually dependent and therefore, the magnitude of the

volume excluded by a segment to other segments would depend

on the nature and extent of solute-solvent intereaction.

Consequently, the average value of $\overline{\mathfrak{R}^2}$ in any solvent will

depend upon the overall effect of the attractive and

repulsive forces operating between the segment-segment and

segment-solvent pairs. If the skeletal effects are isolated

the expansion factor α may be taken as a measure of

solute-solvent interaction. Flory[28] deduced an equation

relating α with various physical parameters of a polymer-

solvent system, namely

$$\alpha^5 - \alpha^3 = 2\, C_M \left[\psi_1 - \chi_1 \right] M^{1/2}, \tag{10}$$

where ψ_1 and χ_1 are entropy and heat parameters such that

$$\Delta \bar{S} = R \, \psi_1 \, v_2^2 \Big)$$

$$\text{and } \Delta \bar{H} = RT \, \chi_1 \, v_2^2 \Big) \tag{11}$$

v_2 being the volume fraction of a polymer in solution, $\Delta \bar{H}$ and $\Delta \bar{S}$ are partial molar heat and entropy of dilution respectively and C_M a constant for a particular polymer-solvent system. Equation (10) can be rewritten as

$$\alpha^5 - \alpha^3 = 2 \, C_M \, \psi_1 \left[1 - \theta/T \right] M^{1/2}, \tag{12}$$

where θ has the dimension of temperature. It can be seen that at $T = \theta$, $\alpha = 1$ and $\overline{r^2} = \overline{r_0^2}$ i.e. the molecular configurations are unperturbed by inter-or intra-molecular interactions. However, the skeletal effects would still be operative. For very dilute solutions, Flory[28], and Flory and Krigbaum[30] obtained an equation for excluded volume u in terms of χ_1 and ψ_1 :

$$u = 2 \left[\psi_1 - \chi_1 \right] \frac{\bar{v}^2}{V_1} \frac{M^2}{N^2} F(x),$$
where
$$\tag{13}$$

$$F(x) = 1 - \frac{x}{2! \, 2^{3/2}} + \frac{x^2}{3! \, 3^{3/2}} - \tag{14}$$

and
$$x = 4 \, C_M \, \psi_1 \left[1 - \theta/T \right] M^{1/2}/\alpha^3 \tag{15}$$

$$= 2 \left[\alpha^2 - 1 \right]$$

$\bar{v}$ being the specific volume of the polymer. Since, at $T = \theta$, $\alpha = 1$, $F(x)$ would be equal to unity and $u = 0$

: 8 :

Thus at θ temperature, the so-called 'Flory point', the polymer molecules would behave ideally since both the interactions and the excluded volume vanish.

In view of the importance of the intereference effects (excluded volume) in polymer solutions, several other attempts have been made to calculate an expression for u. Excellent reviews on the subject are available in the literature, (F.T.Wall and L.A.Hiller, Annual Review of Physical Chemistry, 1954 and Krigbaum, J.Chem.Phys. 23, 2113, 1955). In general, there are three views held regarding the dependence of excluded volume on the number of segments in a chain.

(a) $\overline{h^2}$ retains exactly the value it would have had if long range interference effects were absent [J.J.Hermans, Rec.Trav.Chim. 69, 220 (1950); H.Hadwiger, Makromol Chem.5, 148 (1950), and T.B.Grimley, Proc.Roy.Soc(London) A212, 339 (1952)]. This point of view has been shown to be incorrect by various workers.

(b) The value of $\overline{h^2}$ increases with the increase of Z, but it does not alter its proportionality constant. Thus the effects can be adequately represented by suitably altering the value of A in equation (9),[41,42,73] i.e.

$$\overline{h^2} = A \ell^2 Z$$

so that $\overline{h^2}/Z$ converges to a limiting value as Z tends to become infinite.

(c) $\overline{h^2}$ increases more rapidly than Z, i.e. $\overline{h^2}/Z$ diverges,[3,48,53,82] as Z tends to infinity.

The present state of affairs with respect to convergence or divergence of the ratio $\overline{h^2}/Z$ is still

unsettled. It may, however, be mentioned that the recent experimental results show better agreement with (c) and are consistent with Flory's treatment.

III

To demonstrate the consequences of volume exclusion, we can, following Flory,[29,30,32,51] deduce an expression for osmotic pressure for a polymer solution to show the resemblance of the non-ideal behaviour of a polymer solution with that of a non-ideal gas. For the sake of simplicity only first order deviations have been taken into account.

Consider a dilute solution of volume V containing n_2 identical polymer molecules and let u be the volume excluded per polymer molecule. For a very dilute solution, $n_2 u \ll V$, and there is no appreciable overlapping of the domains of any two molecules. The number of locations available for the centre of gravity of the first molecule introduced into the system would be proportional to V and for the second molecule to $(V-u)$, as the first molecule excludes a volume u. Likewise the number of locations available for the $i+1^{th}$ molecule would be proportional to $(V-iu)$. Thus the total number of arrangements for n_2 polymer molecules would be

$$Q = Constant \times \prod_{i=0}^{n_2-1} [V - iu]$$

(16)

and therefore, the entropy of mixing

$$\Delta S_m = k \log Q, \quad and$$

(17)

we get

$$\Delta F_m = -kT \log Q$$

$$= -kT \left[n_2 \log V - \frac{u}{V} \sum_{i=0}^{n_2-1} i \right] + constant$$

(18).

and hence

$$\pi = -\left[\frac{\partial \Delta F_m}{\partial V}\right] = kT\left[\frac{n_2}{V} - \left(\frac{n_2}{V}\right)^2 \frac{u}{2}\right] \qquad (19)$$

If $u = 0$ and $V = 1$ ml.,

$$\pi = n_2 kT = \frac{c}{M_n} RT$$

which is identical with equation (4), and thus $\left[\left(\frac{n_2}{V}\right)^2 \frac{u}{2}\right]$ represents the first order deviation from ideality. Equation (19) can be rewritten as

$$\frac{\pi}{c} = RT\left[\frac{1}{M_n} + A_2 c\right] = RT\left[A_1 + A_2 c\right] \qquad (20)$$

where $A_1 = 1/M_n$, M_n being the number average molecular weight and

$$A_2 = \frac{Nu}{2M_n^2} = \frac{\overline{u^2}}{V_1} Y_1 \left[1 - \theta/T\right] F_{(x)} \qquad (21)$$

Equation (20) shows clearly that so long as $u \neq 0$, a solution will not be ideal. Several other theoretical attempts to evaluate A_2 were made by Huggins[47], Flory[32] and Zimm[76]. A discussion on the merits and demerits of equation (21) and those deduced by Flory, Huggins, and Zimm will be given later. It may be stated, however, that equation (21) is actually a generalization as well as a refinement of the earlier equations and hence differs from them only in detail.

It is seen that osmotic pressure measurements
can help only in the evaluation of M_n and the second virial
coefficient A_2, but no information can be obtained about $\overline{n^2}$
required for the determination of the expansion factor α
Secondly, osmotic pressure, being inversely proportional
to molecular weight, decreases with increasing molecular
weight and is too small to be measured accurately for polymer
systems. This and other difficulties make the application
of the technique to polymer systems unsuitable. It is
therefore necessary to find an alternative method for
evaluating the three parameters M, A_2 and α .

IV

Measurement of the intensity of light scattered
by polymer solutions offers one such method, the fundamental
basis of which has been well established and excellent
reviews are available on the subject, (S.Bhagvantam,
"Scattering of Light and The Raman Effect", Published by
Andhra University, 1940., H.Mark ,"Chemical Architecture",
Interscience Publishers, New York. 1948., G.Oster,"Chemical
Reviews", 1948). Only a brief outline, therefore, will be
given on the development and application of the method to
the investigation of polymer solutions.

Einstein[20] pointed out that the scattering of
light by a condensed system is due to the existence of
thermal density fluctuations, as a consequence of which
the average refractivity also fluctuates in micro-space

and the system becomes optically nonhomogenous. Thus the intensity of light scattered may be regarded as proportional to the product of the magnitude of density fluctuations and their optical efficiency. If the solvent is made more nonhomogenous by the incorporation of solute molecules, there will be additional scattering of light due to fluctuations in concentration and the amount of this scattering can be used to ascertain the number of solute particles and thereby the molecular weight of a solute.

To evaluate the magnitude of the concentration fluctuations mentioned above, one can make use of equation(20).

Thus $d\pi/dc = RT\left[1/M_n + 2A_2 c \right]$

and $RT/d\pi/dc = \dfrac{M_n}{1+ 2A_2 M_n C}$ (22)

or $RT/d\pi/dc = \dfrac{m}{1+ 2A_2 M_n C}$

where m is the mass of a solute particle. The expression on the left represents the ratio of the thermal energy of a particle responsible for bringing about the local random density and concentration fluctuations, and the osmotic force per unit concentration which tends to restore the concentration to its average value. Without taking into account the effect of density fluctuations which can be subtracted out, equation (22) gives an equilibrium value of the magnitude of the local concentration fluctuations in a real solution. For an ideal system, where $A_2 = 0$, the expression on the right is equal to m, i.e. the mass of the particle. The presence of A_2 reduces this magnitude

by a factor, $\dfrac{1}{1+2A_2 M C_m}$ In view of the high

molecular weight of a polymer, the magnitude of concentration

fluctuations, and hence the intensity of scattered light,

will be high. Debye,[12,13] and Doty, Zimm and Mark[16]

deduced the following equation correlating M, A_2, C

and the excess turbidity τ_{90} at $90°$ due to solute molecules,

$$HC/\tau_{90} = 1/M_w + 2A_2 C \qquad (23)$$

where Mw is the weight-average molecular weight and H is

a constant for a particular polymer-solvent system and

is given by

$$H = \frac{32\pi^3}{3}\ \frac{1}{\lambda^4}\ \frac{1}{N}\ \left\{ n_0\ \frac{dn}{dc} \right\}^2$$

n_0 and n being the refractive indices of the pure solvent and

the solution respectively, and λ the wave-length of light.

The term $\left[n_0\ dn/dc \right]^2$ represents the optical efficiency

due to the fluctuations. Equation (23) is deduced on the

assumption that the scattering particles have dimensions

less than 1/15 of the wave-length of light in solution.

If this condition is not fulfilled, the light scattered from

two portions of the same macromolecule will interfere,

and the radiation envelope becomes asymmetric. Doty and

Steiner,[19] Zimm,[77,80,81] and Zimm, Stein and Doty[78] have deduced

modified expressions which take into account the

interference of light due to particle size. An expression

due to Zimm takes the form

$$\frac{KC}{\tau} = \frac{1}{M_w\ P(\theta)} + 2A_2 C + \cdots \qquad (24)$$

where θ is the angle of observation of scattered light, K a constant equal to $3H/16\pi$ and

$$P(\theta) = \frac{2}{x^2}\left[e^{-x} - (1-x)\right],$$

(25)

where

$$x = \frac{8\pi^2}{3\lambda^2}\,\overline{r^2}\,m_0^2\,\sin^2\theta/2$$

For small values of x, $P_{(\theta)}^{-1} = 1 + x/3$ and

(26)

$$\frac{Kc}{I_{[\theta,c]}} = \frac{1+x/3}{M_w} + 2A_2c$$

(27)

If a plot of $Kc/I_{[\theta,c]}$ vs. $(kc + \sin^2\theta/2)$ is made,

at $\theta = 0$, the slope of the curve is $2A_2/K$;

at $C = 0$, the slope of the curve is $x/3\,M_w\,\sin^2\theta/2$

and at $\theta = 0$ and $C = 0$, the intercept is equal to $1/M_w$

Therefore, from a single plot, one obtains the values of M, $\overline{r^2}$ and A_2.

A simpler method of evaluation of $\overline{r^2}$ is based on the measurement of the intensities of scattered light at two angles symmetrical about 90°, and the ratio of the two intensities when extrapolated to zero concentration, the so-called dissymmetry ratio, is represented as

$$\left[I_\theta / I_{[180-\theta]}\right]_{c \to 0} = [Z]$$

The intrinsic dissymmetry $[Z]$ is a measure of the particle size. Doty and Steiner[19] have tabulated the values of D/λ and $1/P(90)$ for various values of $[Z]$ for spheres, rods and random coils. (Figs. 2 and 3)

Equation (25) is deduced on the assumption that a chain molecule can be regarded as made up of a series of emitters, the polarizability of each emitter being independent of direction. In general, the polarizability of an individual emitter depends on direction and is a tensor. Due to this anisotropy, the scattered light consists also of a weak horizontal component. Depending upon the state of polarization of the incident light, we have V_u, H_u, V_v, V_h, H_v and H_h components of the scattered light. The capitals represent the components of the scattered light, namely, vertical or horizontal, and the subscripts refer to the state of polarization of the incident light, namely, unpolarized, vertically or horizontally polarized. Since Vv is the only component which is related to the mass of the particle, the turbidity as observed should be suitably corrected to take only the Vv component into account.

In contrast to Vv, the Hv $[= V_h$ according to the Theorem of reciprocity] component of the scattered light depends upon the number and the intrinsic anisotropy of segments at a given concentration, and as pointed out by Doty,[17] and Zimm, Stein and Doty,[78] independent of molecular weight. If the size of the segments in a solution is changed,

the anisotropy and hence the magnitude of Hv or Vh will
be altered.   In good solvents, where a polymer molecule is
expanded due to volume exclusion, the average size of the
segments would be bigger as compared with their unperturbed
state and there would be fewer solute-solute contacts.
As a result Hv/C would remain unaltered by a change in
concentration C.   In poor solvents, on the other hand, due
to increased inter- and intra-molecular contacts with
increasing concentration, the segment size would be slightly
shortened and its anisotropy would be decreased correspondingly
This would result in a diminution of the values of Hv/C
compared with those in good solvents, and also the
magnitude of Hv/C would decrease with increasing concentration.
Doty and Stein,[18] and Bhatnagar and Biswas,[4] attempted to
utilize depolarization properties of scattered light for an
evaluation of polymer-solvent interaction.   They measured
the depolarization ratios ρ_v and ρ_h

$$\text{given by,} \quad \rho_v = \frac{Hv}{Vv} \quad \text{and} \quad \rho_h = \frac{Hh}{Vh}$$

and furnished an indirect confirmation of the above
reasoning, but no attempts were made to compare the deductions
arrived at with those obtained from the measurements of
A_2 and α .

In what follows, an attempt will be made to
compare the experimentally observed values of A_2 with
those calculated and the various attempts made to test
equation (12) experimentally will be indicated.

V

According to the theories proposed by Flory[24,26], and Huggins[45,46] based on the lattice model for polymer solutions, the value of A_2, as given by the general equations[59,79]

$$\Pi/c = RT\left[\frac{1}{M_n} + A_2c + A_3c^2 + \cdots\right]$$

(28)

and

$$\frac{Hc}{\tau_{qo}} = \frac{1}{M_w} + 2A_2c + A_3'c^2 + \cdots$$

(29)

should be a constant for a given polymer-solvent pair, independent of molecular weight and unaffected by the heterogeneity of the molecular weights. However, studies on various polymer-solvent systems made by Outer, Carr and Zimm[64], Flory and collaborators[31,35,52] and other continental workers[5,10,63,68] have, on the contrary, definitely established that A_2 decreases with increase in molecular weight and increases with molecular heterogeneity at a fixed average/molecular weight. As explained by Flory[27], the failure of the earlier theory is due to the fact that, in their development, it was assumed that there is a uniform distribution of segments in solution, an assumption which is correct only at fairly high concentrations. However, in deducing equation (21) for A_2, no such assumption has been made and the dependence of A_2 on molecular weight is shown, though a quantitative agreement is still lacking. This is attributed primarily to a defect in the function F(x) given by equation (14). F(x) is sensitive to molecular heterogeneity and changes to

$$y = \sum_{i} \sum_{J} \omega_i \, \omega_J \, F \, (\chi_{iJ}), \qquad (30)$$

where ω_i and ω_J are the weight fractions of the polymer species i and J respectively and $[\chi_{iJ}]$ is given by[30]

$$\frac{[\chi_{iJ}]}{[M_i \, M_J]} = \left[\frac{2 \left(\frac{\chi_{ii}}{M_i^2} \right)^{2/3} \left(\frac{\chi_{JJ}}{M_J^2} \right)^{2/3}}{\left(\frac{\chi_{ii}}{M_i^2} \right)^{2/3} + \left(\frac{\chi_{JJ}}{M_J^2} \right)^{2/3}} \right]^{3/2} \qquad (31)$$

Thus the modified expression for A_2 is given by

$$A_2 = \frac{\bar{v}^2}{V_1} \left[\psi_1 - \chi_1 \right] y . \qquad (32)$$

The trend of the experimentally observed values of A_2 agrees with that predicted by equation (32).[52]

From the foregoing discussion it is clear that, for a quantitative estimation of A_2 , polymer fractions should be either very sharp or of known molecular weight distribution. Otherwise, only a qualitative approach to the problem of solute-solvent interaction is possible. On the other hand H_v/c data seem to be independent of the molecular weight and its distribution, and hence, if their interpretation is properly developed, valuable information regarding the interaction of a polymer with its environment may be revealed.

VI

Besides light scattering and osmotic pressure measurements, measurements of the swelling of a polymer and of the viscosity of a polymer solution are used for the estimation of solute-solvent interaction. Swelling measuremer are qualitative in nature. Viscosity measurements, however, are easy to carry out and of great interest, since much information on excluded volume has been obtained from them. This method has been dealt with in greater detail in the second part of the thesis. Mention, however, mav be made of some important equations, proposed by Flory and his collaborators,[11, 31,33,34,36,58,74] which relate the intrinsic viscosity with M, viz.:

$$[\eta] = K_0 \alpha^3 M^{1/2} = K_0 M^{1/2 + \alpha'} \tag{33}$$

$$= \phi \frac{(\overline{r^2})^{3/2}}{M} \tag{34}$$

where K_0 and ϕ are constants and

$$\alpha' = \frac{d \log \alpha^3}{d \log M} \tag{35}$$

Equation (33) predicts that at $T = \theta$, when $\alpha = 1$,

$$[\eta]_{T=\theta} = K_0 M^{1/2}. \tag{36}$$

i.e. the intrinsic viscosity would be directly proportional to $M^{\frac{1}{2}}$. Equation (36) is of great importance, since its validity is a direct proof of the excluded volume theory. It has been shown that the results obtained from studies on polyisobutylene,[33] polystyrene,[11,33] natural rubber,[74] gutta percha,[74] cellulose tributyrate,[58] cellulose tricaprylate[58] and polydimethylsiloxanes[31] systems satisfy equation (36).

Since the light scattering method provides scope for the direct determination of the parameters M, A_2 and α in different polymer-solvent systems, this technique has been used in the present studies.

VII

Almost all the solution properties of rubber depend upon the electronic configuration of the functional groups as well as the spatial configuration of the molecule in the medium. One can influence to varying extents the reactivity of the functional groups of rubber by changing the solvent. For example, the rate of halogenation or the adhesive properties of rubber solutions may be altered with the change of the solvent media. Hecht, Coles and Keeler[40] have shown that adhesion is dependent on the specific viscosity of a polymer in solution.

Considering its great importance, the light scattering data on rubber are fragmentary.[9,15,38,72]

Bywater and Johnson[9] studied several fractions of rubber by
light scattering, viscosity, osmometry etc. These studies,
however, were confined to only two solvents, namely,
chloroform and hexane, and thus afforded little information
regarding the rubber-solvent interaction. Moreover, the
deductions made by these investigators about the state of
rubber molecules in solution are not convincing. The rest
of the work[15,38,72] reported is actually a study on
depolarization ratios, using rubber as a solute. From
their studies of f_h , f_v and f_u , Gehman and Field[38] showed
that rubber molecules are quite large and have a liquid-like
structure in solution, but they made no attempt to compare
the molecular configurations of rubber in different solvents.

The present studies were undertaken to examine the
behaviour of rubber in a number of solvents such as carbon
tetrachloride, chloroform, trichloroethylene, 1,2,dichloroethane
2,2,4-trimethyl pentane (iso-octane), tetrahydrofuran,
cyclohexane, cyclohexanone and mixtures of these two and
evaluate the solution properties in the above systems as
revealed by light scattering measurements.

Recently Streeter and Boyer[70] measured viscosities
of very dilute solutions of polystyrene and reported that in
the range of very low concentrations the linear relation
between η_{sp}/c vs C breaks down. The values of η_{sp}/c
decrease with decreasing concentration, reach a minimum and
then increase. Kapadia[49,50] instead of observing only one
minimum, obtained several humps in the plot of η_{sp}/c vs C
for natural and chlorinated rubber solutions. In tetrahydrofura
this phenomenon was reported to be very pronounced (private

the above phenomenon.

(a) In dilute solution, polymer molecules may undergo a change in size and shape[70], of

(b) the effect may be due to adsorption of polymer molecules on the wall of the capillary of the viscometer thereby decreasing its radius. This effect would alter the viscosity in the range of very dilute solutions. To test the first hypothesis repeated dissymmetry measurements on rubber-tetrahydrofuran system were performed in the range of very low concentrations. The data did not reveal any significant change in the particle size. This is also in conformity with similar studies made by Frank[37] on polystyrene solutions.

In the present investigation, molecular weights and particle sizes were determined by measuring the turbidities at 90° and dissymmetry at 60° and 120° respectively. The measurements of Vu, Hu, Vv and Hv components were made in separate sets of experiments. Since only Hv and Vv components are of interest in the evaluation of solute-solvent interaction, only their values will be presented in what follows.

II

E_X_P_E_R_I_M_E_N_T_A_L

Purification of rubber: Commercial latex was diluted to about 15% dry rubber content and deproteinised by adding sodium hydroxide in an amount equivalent to 2% on the weight of latex[62], which was then heated to 55°C for five hours with slow stirring. The latex was cooled and allowed to separate into two layers. The serum was removed and the concentrated latex was diluted to 10% solids and coagulated with 1% acetic acid. The coagulum was washed repeatedly with distilled water. The water was squeezed out and coagulum dried in vacuum at 50°C for about 48 hours.

Extraction of sol-rubber: Sol-rubber was extracted by means of petroleum ether (40°-60° fraction) in a soxhlet extractor for about 96 hours. The solution containing the "sol" portion was concentrated and stored in a nitrogen atmosphere in dark.

Purification of solvents: All the solvents used in the experiments were purified by standard methods as given in "Experiments in Organic Chemistry" by L.F.Fieser. Each solvent was distilled in a fractionating column after purification and only the middle fraction collected. Just before use, each solvent was redistilled in an all glass pyrex distilling apparatus.

Preparation of the solutions of sol-rubber in various solvents: The sol-rubber concentrate in petroleum ether was diluted with the desired solvent and the solution concentrated to an extent

that it did not completely dry up. This process of concentration followed by dilution by the solvent and reconcentration was repeated six times to remove the last traces of petroleum-ether, not allowing the solute to get dry and interact with the atmospheric oxygen. Finally a stock solution of sol-rubber in the desired solvent was prepared and its concentration determined by evaporation of three 5 c.c. samples under vacuum at $50^{o}C$. for 24 hours. The stock solution was filtered through a sintered glass filter till no suspended particle could be detected. Other concentrations were made by adding a known volume of the stock solution to a known volume of the solvent in the light scattering cell. As a check the final concentration was determined by evaporating 5 c.c. of the solution under vacuum. After the preparation of the stock solution no care was taken to avoid its contact with air, but the light scattering studies were made as quickly as possible.

In the case of solutions in cyclohexanone, cyclohexane and their mixtures, each concentration was separately prepared and stored in the dark. Each solution was filtered repeatedly in a dissymmetry cell till no visible suspension could be observed in the solution.

Light scattering cells: In the case of other solvents, a 100 ml. centrifuge tube with a spout was used for turbidity and dissymmetry measurements. Out of 20 scratchless tubes selected out of 100, only five gave symmetrical scattering envelope for benzene. A dull black wooden adapter was designed to hold these tubes, similar to the one used by
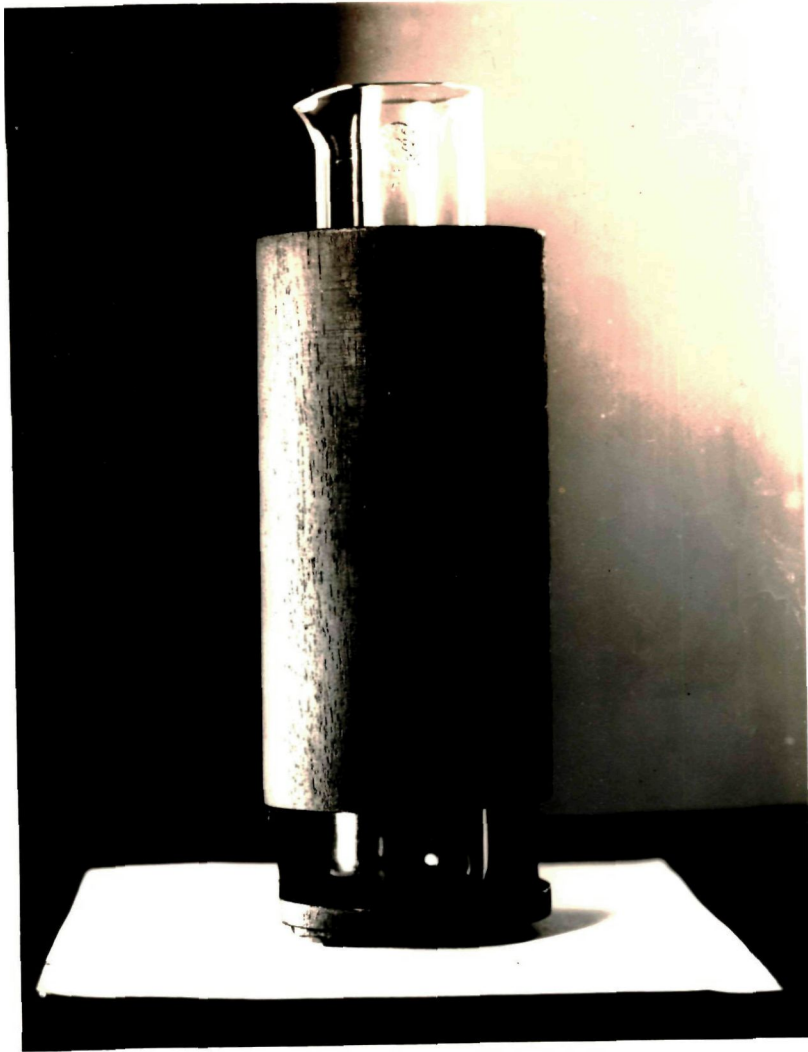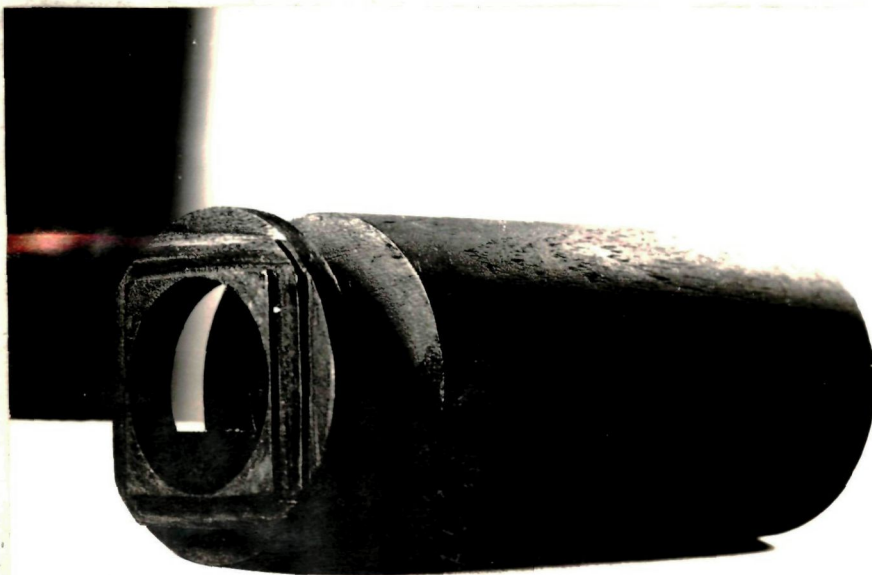
FIGURE 1a

FIGURE 1b

Figure 2

L/λ' VS. Z for polydisperse coils $Z = \dfrac{I60}{I120}$
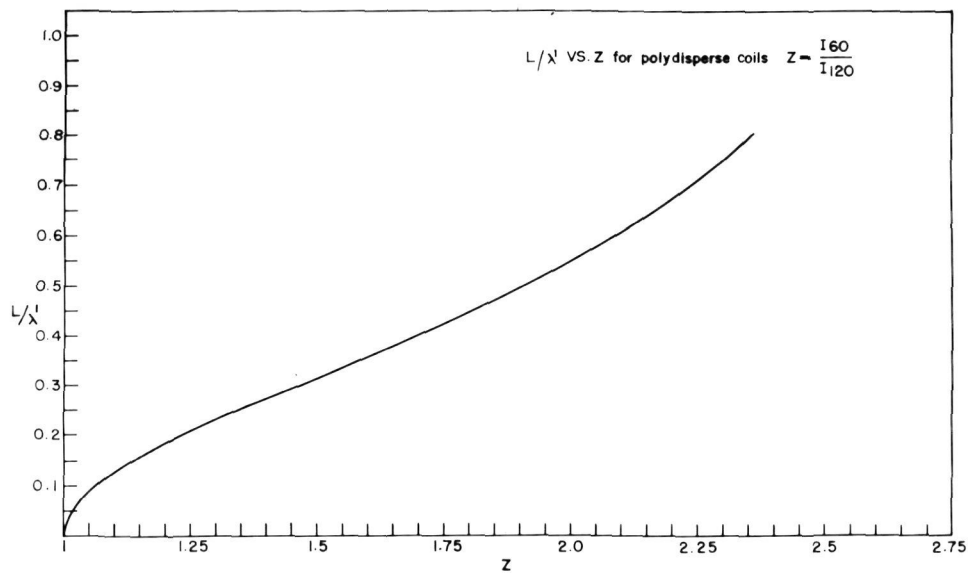
Figure 3
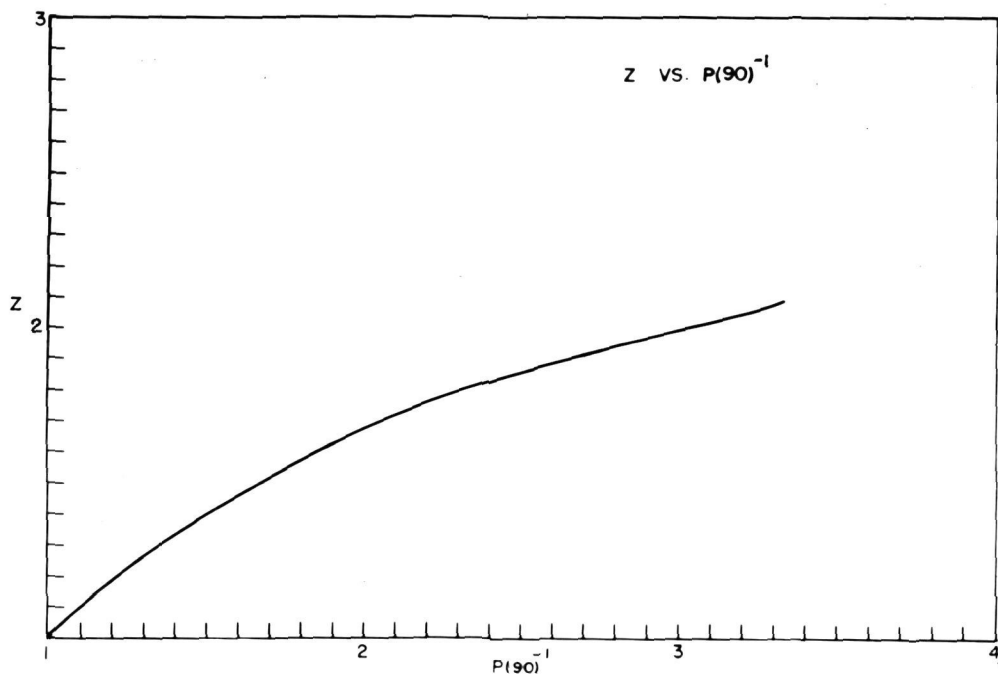
Boedtker and Doty[6] (Photograph I). Due to the geometry
of the adapter, it was possible only to measure intensities
in the range of 60° to 120° without introducing back
scattering from the cell wall. The advantage in using
these jointless cells is the ease with which they can be
cleaned. The use of such a cell was found necessary due to
two reasons, *viz.*, the non-availability of the usual dissymmetry
cells at the time and the time-taken for cleaning the square
or dissymmetry cells was found to be almost prohibitive.
The depolarization measurements for the rubber solutions
were made in a standard square cell.

Refractive indices: Refractive indices at various wave
lengths of all the solvents were obtained from
"International critical tables" and the values for
$\lambda = 4360\overset{\circ}{A}$ were interpolated from the available
data. No temperature corrections were applied; since
after corrections in turbidity for refraction effects, m_s^2
term cancels out in the expression for HC/τ_{90}. However,
this inaccuracy would affect the absolute values of τ as
well as those of Hv component.

Refractive index Increments: To evaluate $\frac{dn}{dc}$ for the
rubber solutions, the modified Glasstone-Dale equation was
employed as suggested by Outer, Carr and Zimm[64] and later used
by Boedtker and Doty[6], *i.e.*

$$\frac{dn}{dc} = R_2 - \frac{d_1}{d_2} R_1 \; , $$

$$R_1 = \frac{n_1 - 1}{d_1} \quad and \quad R_2 = \frac{n_2 - 1}{d_2} \tag{37}$$

where subscript 1 and 2 refers to solvent and polymer

respectively, d is the density and R_1 and R_2 are supposed to

be constants independent of the temperature or state of

aggregation. n_2 was evaluated by measuring dn/dc

for rubber in chloroform at $25^\circ C$ by means of Rayleigh

Interference Refractometer.   The observed value of 0.108

at $\lambda = 4360 \text{\AA}$ is in good agreement with that obtained by

Bywater and Johnson[9] e.g. 0.105 at $\lambda = 5460 \text{\AA}$.   The

necessity of using equation (37) arose due to the fact that

for rubber solutions a dependence of $\frac{dn}{dc}$ on C was observed

for most of the solvents used.   This may be due to rapid

oxidation of rubber, thereby preventing reproducible

observations.   The experimentally observed value of $\frac{dn}{dc}$

was obtained for concentration of about 1%, a region in which

$\frac{dn}{dc}$ was found to be a linear function of concentration.

The values of n_0 , $\frac{dn}{dc}$ and H for rubber and various solvents

and solvent mixtures are given in Table I.

TABLE I.

Solvent	n^0 at 4360 $\text{\AA}$	dn/dc	$H \times 10^6$
Chloroform	1.45288	0.108	3.705
Carbon tetrachloride	1.47516	0.0838	2.299
Dichloroethane	1.45215	0.1084	3.729
Trichloroethylene	1.4777[D]	0.0791	2.056
Tetrahydrofuran	1.40762	0.1247	4.637
Iso-öctane	1.3916	0.1421	5.884
Cyclohexanone	1.4634	0.0962	2.982
Cyclohexane	1.4412	0.1202	4.516
Rubber	1.5525		

Calibration of the Light Scattering photometer: Light

scattering studies were made by using B-S light scattering

photometer[8] supplied by Phøoenix Precision Instrument Co.,

Philadelphia, U.S.A.   Molecular weight of a purified sample

of sodium lauryl sulphate (S.L.S.) was determined using a

cylindrical cell.   The reported value[65] of S.L.S. in water

using the Debye plot is 23,000.   The value obtained by

three separate sets of experiments using vertically

polarized light was found to be 22,700, which is in good

agreement with the reported value.   This indicates that

under the experimental conditions, the excess scattering

by solute needs no other correction except the one used

for a square cell.   The calibration for these cells has

also been done before, using a standard polystyrene fraction

supplied with the instrument.   The molecular weight of

the sample determined at the wavelengths 4360 $\overset{o}{A}$ and 5460 $\overset{o}{A}$

was found to be the same.   However, it was observed that

the slopes of HC/γ vs.   C curves at the two wavelengths

were different, the value of the slope i.e. A_2, being less

for the blue wavelength by a factor of 0·735   .

The experimentally observed values of A_2 have been divided

by this factor to obtain the correct values of A_2 for

the various systems.

***

FIGURE 4

I. Chloroform
ii Carbon tetrachloride
iii Trichloro ethylene
iV Ethylene dichloride
V Tetrahydrofuran
Vi Iso-Octane

$HC/\gamma \times 10^6$

$C \times 10^4$ gm /c.c.
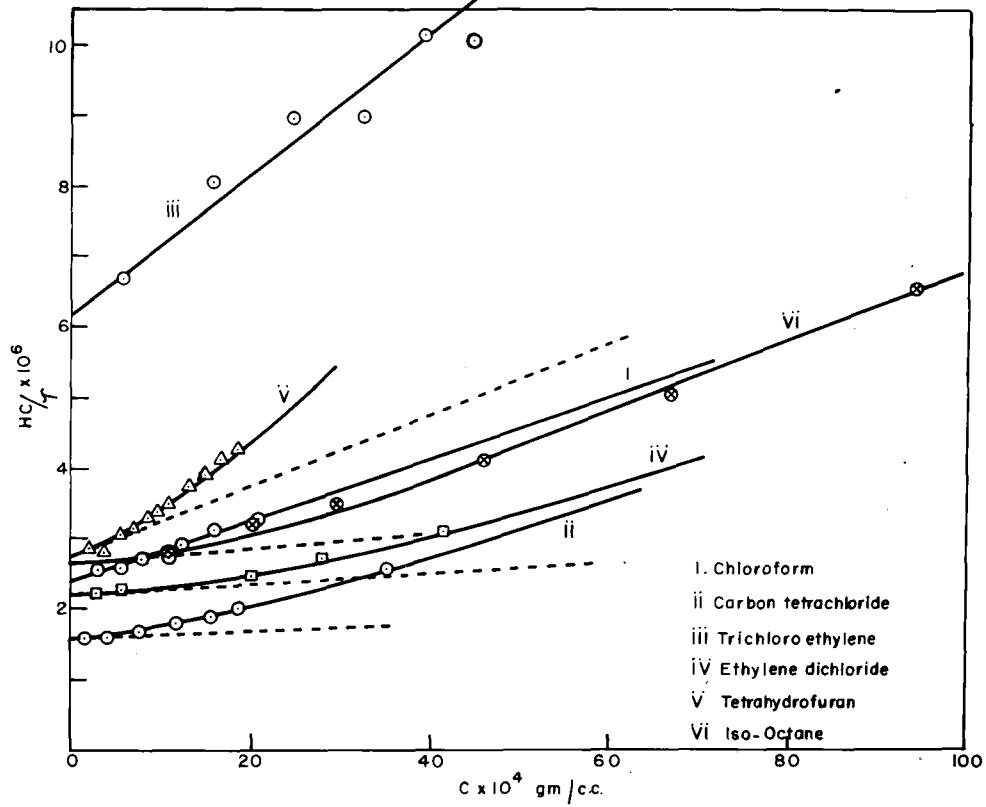
Figure 5
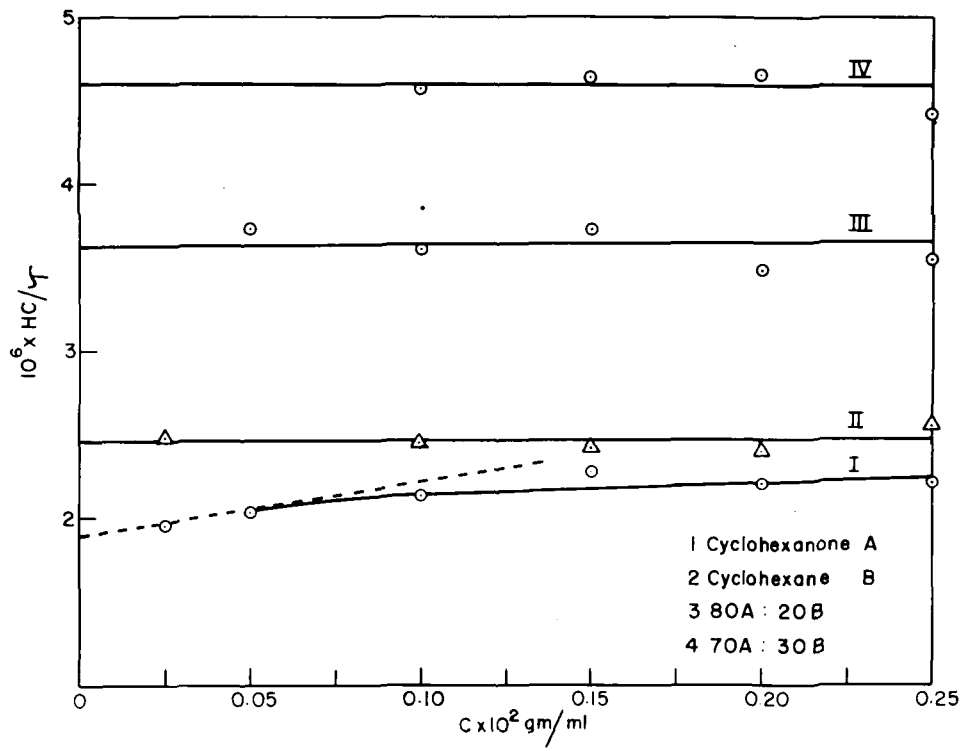
TABLE II.

Solvent	$[HC/T] \; x10^6$ $C = 0$	$[Z]$	$1/p(90)$	$Mx10^{-5}$ Corr.for diss.	$A_2 \; x \; 10^4$
Chloroform	2.425	1.6	1.855	7.65	5.276
Carbon tetrachloride	1.575	1.92	2.34	15.6	0
Dichloroethane	2.2	1.55	1.76	8.0	0
Trichloroethylene	6.4	1.28	1.325	2.55	14.14
Tetrahydrofuran	2.75	1.3	1.355	4.92	6.61
Iso-octane	2.65	1.39	1.49	5.62	0
Cyclohexanone (A)	1.9	2.32	2.26	11.9	4.35
Cyclohexane (B)	2.46	1.82	1.66	6.74	0
80A:20B	2.62	1.80	1.64	6.26	0
70A:30B	4.6	1.62	1.46	3.17	0

- -

TABLE III

Solvent	$[Z]$	r/λ'	λ'	$(\bar{r}^2)^{1/2}$
Chloroform	1.6	0.36	3000	1080
Carbon tetrachloride	1.92	0.51	2955	1507
Ethylene dichloride	1.55	0.335	3002	1005
Trichloroethylene	1.28	0.22	2950	650
Tetrahydrofuran	1.3	0.2325	3097	720
Iso-octane	1.39	0.27	3133	846
Cyclohexanone (A)	2.32	0.44	2979	1310
Cyclohexane (B)	1.82	0.322	3025	974
80A:20B	1.80	0.32	2987.5	956
70A:20B	1.62	0.265	2988.6	792

TABLE IV.

Solvent	$M \times 10^{-5}$ Corr. for Dep.	$(\overline{r_0^2})^{1/2}$	$(\overline{r^2})^{1/2}$	$\propto$	$M/\overline{r^2}$
Chloroform	6.7	979	1080	1.11	577
Carbon tetrachloride	14.3	1457	1507	1.03	659
1,2,Dichloroethane	7.66	1048	1005 ∓ 50	0.96	758
Trichloroethylene	2.31	575	650 ∓ 10	1.13	547
Tetrahydrofuran	4.77	826	720	0.87	921
Iso-octane	5.47	879	846 ∓ 20	0.96	763
Cyclohexanone	9.28	1155	1310	1.13	539
Cyclohexane	6.59	972	974	1.0	694

- -

RESULTS AND DISCUSSION

(1) Molecular weight of Sol-Rubber:-

The molecular weights obtained by light scattering of a single sample of sol-rubber in various solvents used exhibit a six-fold variation (230,000 to 1,480,000, vide table IV). Such a large variation is unexpected as the molecular weight of the same polymer fraction in different solvents should not differ to this extent if the polymer is molecularly dispersed. However, a similar variation was also observed by Bywater and Johnson[9] for a rubber fraction in chloroform and hexane, the molecular weights being 450,000 and 910,000 respectively. There are two possible explanations for this phenomenon, viz., the rubber molecules may aggregate to different extents in the solvents, or they might have undergone degradation in solution due to some reasons. Bywater and Johnson[9] explained the difference in molecular weights on the assumption that the rubber molecules were aggregated in hexane. They further observed that the intrinsic viscosities of the rubber fractions were always higher in chloroform than in hexane, although they should be higher in the medium in which the rubber molecules are aggregated. They have not accounted satisfactorily for these apparently contradictory observations.

Rubber in pure state has a marked susceptibility to undergo photochemical and oxidative breakdown reactions and it will be shown that the above mentioned discrepancy can be satisfactorily explained on the basis of degradation of rubber.

It has been shown by Bateman[1] that, on irradiation of rubber with light, two processes do occur:

(1) chain scission and (ii) the activation of H in 1, 3 and
5 positions with its subsequent removal or substitution. As
will be seen presently the probability of the former is
greater than that of the latter.

$$-\overset{1}{C}H_2-\overset{2}{C}\overset{\overset{3}{C}H_3}{=}\overset{4}{C}H-\overset{5}{C}H_2-\overset{*}{C}H_2-\overset{CH_3}{C}=CH-CH_2-$$

$$\longrightarrow ISOPRENE\ LINK.$$

$$*\ \alpha\text{-METHYLENE GROUP}$$

Bateman[1] has shown that the active spectral region
for rubber extends upto 3650 A^o. The light quanta
corresponding to wavelengths 2800 A^o and 3650 A^o can raise the
molecular energy by about 100 and 78 K cal.per gm. mol.
respectively. These are of the order of the dissociation
energies of normal C-H and C-C bonds. Further, Bolland and Orr[7]
have pointed out that whenever there is scission of an isoprene
link, the heat of fission is reduced from 78 to 43 k. cal.per gm.
mol. due to the appearance of two allyl radicals. Similarly,
whenever there is dissociation of any of the 1, 3 and 5 C-H
bonds, the heat of fission is reduced from 98 to 79 k.cal.
per gm. mol due to the appearance of one allyl radical.
This shows that the chance of chain scission is greater than
that of dissociation of the C-H bond, as less energy is
required for the former process. Farmer[21,22,23] and Dogadkin[14]
have similarly explained the susceptibility of rubber to
oxidation due to the highly reactive nature of α -methylene
sites.

During photo-irradiation or oxidation, the free
radicals produced tend to recombine and regenerate polyisoprene
(in the case of oxidation, oxidised polyisoprene). This product

can be linear or branched. The nature and extent of such
reactions is dependent upon environmental conditions. In
chlorinated solvents, moreover, work done in this laboratory[66,67]
has shown that photo-halogenation of rubber is also possible
and may be followed by the removal of hydrochloric acid
and degradation.

It seems quite likely, therefore, that degradation
and branching of rubber molecules will take place during the
period of preparation of rubber solutions, and subsequent
light scattering and viscometric measurements. As a
result a sharp fraction of rubber will become molecularly
heterogeneous. To illustrate the susceptibility of rubber
to degradation, experiments performed by us may be mentioned.
We found that a freshly prepared solution of rubber in benzene
showed appreciable excess scattering of light. The same
solution, however, did not show any such excess scattering
after one year even though it was kept in the dark and in a
nitrogen atmosphere. This definitely indicated that the
rubber molecules had undergone degradation to a very large
extent during this period. It can be seen from table (IV)
that the molecular weight in carbon-tetrachloride is about twice
that in chloroform; that in 1,2, dichloroethane (ethylene
dichloride) is about three times that in trichloroethylene.
These two pairs of solvents do not differ in their dielectric
dispersive powers to an extent to effect such disparities in
the states of aggregation of rubber molecules and hence the
molecular weights, as have been observed. However, they do
differ in their susceptibilities to photosensitization, which
would affect their ability to degrade rubber molecules to
different extents.

From the above, it is apparent, that, although sol-fraction is used in this investigation, some amount of branched product may be produced during the period in which the rubber is transferred to the particular solvent and studies made on it. In the present study, there seems to be no appreciable net-work or branched chain formation, since $M/\bar{r^2}$ is fairly constant in most of the solvents, thus indicating that the molecules retain their random coil characteristics. In the case of rubber - tetrahydrofuran, however, the possibility of branching cannot be ruled out as the value $M/\bar{r^2}$ in this particular case is about 920, whereas in others it averages 650. This also will be discussed later.

The apparently contradictory observations made by Bywater and Johnson[9], viz., the higher intrinsic viscosities exhibited by rubber fractions in chloroform as compared to hexane, can be reconciled on the basis of expansion of rubber molecules in the two media and the use of Flory-Fox equations[33,36],

$$[\eta] = K_0 \alpha^3 M^{1/2} = \phi \frac{(\bar{r^2})^{3/2}}{M} \tag{33}$$

Knowing the values of α and M in different solvents; the values of the intrinsic viscosity can be calculated and compared as Ko is a characteristic of a polymer and independent of solvents. Unfortunately the value of α for rubber in hexane is not available. However, we may assume that the solution properties of rubber in hexane and iso-octane to be the same, so that α may be taken to be 0.96 as compared to 1.11 in chloroform. This will give $[\eta]$ to be equal to 916 Ko $\left[= (1\cdot11)^3 \times (450,000)^{1/2} \cdot K_0\right]$ in chloroform and 878 Ko $\left[= (0.96)^3 \times (910,000)^{1/2} \cdot K_0\right]$ in hexane It may, therefore, be concluded that the variations in molecular weights of rubber dissolved in different solvents are largely

due to degradation to varying extents: aggregation in solution as assumed by Bywater and Johnson[9] may not be appreciable.

2. **Evaluation of** $\left[\overline{r_o^2}/M\right]^{1/2}$:- In order to obtain the value of the expansion factor α , it is essential that the value of the parameter $\left[\overline{r_o^2}/M\right]^{1/2}$ be known for a partiéular polymer. It can be conveniently determined by performing the experiments at the 'Flory point' of a particular system at which $\alpha = 1$ and $A_2 = 0$. An interesting feature noticeable in Figure (5) is the zero slope of HC/γ **vs.** C curves fár rubber-cyclohexane and rubber-cyclohexane-cyclohexanone systems. This indicates that there is no interaction between rubber and cyclohexane at room temperature (about 298-300°K). This fact can be conveniently utilized to evaluate $\left[\overline{r_o^2}/M\right]^{1/2}$ for rubber and when its value is known, values of α and

$$C_M = \left(\frac{2\cdot 7}{2^{5/2}}\, \pi^{3/2}\right)\left(\overline{\upsilon^2}/V_1 N\right)\left(M/\overline{r_o^2}\right)^{3/2}$$

for the various systems can be evaluated. The values of the former are presented in table (IV) and of the latter in Table (VI) for the various systems studied on the basis of $\left[\overline{r_o^2}/M\right]^{1/2} =$ 1.195 Å, computed from the present data. This is higher than that found by Wagner and Flory[74] (0.83 Å) from viscosity data obtained at $\theta = 287.5°$K. in methyl n-propyl ketone. However, the value 0.83 Å is higher than the theoretical value computed by Wall[75], assuming free rotation, on purely statistical grounds from the following equation:

$$\frac{\overline{r_o^2}}{Z} = \rho^2 \left\{\frac{1 + \cos^2\alpha}{4\,(1 - \cos^2\alpha\,\cos 2\beta)}\right\} + \rho\sigma \left\{\frac{\cos\beta\,(1 + \cos\alpha + \cos^2\alpha}{1 - \cos^2\alpha\,\cos 2\beta}\right.$$

$$\left. + \sigma^2 \left\{\frac{(3 + 2\cos 2\beta) + 4\cos\alpha\,(1 + \cos 2\beta) + \cos^2\alpha\,(2 + 3\cos 2\beta)}{4\,(1 - \cos^2\alpha\,\cos 2\beta)}\right\}\right. \quad (38)$$

where Z is the number of links, ρ and σ, the double and single carbon-carbon bond lengths, α, the angle which a single bond makes with the extension of the adjacent single bond and β, the angle which a single bond makes with the extension of the adjacent double bond. Substituting $\rho = 1.34$ $\overset{o}{A}$, $\sigma = 1.54$ $\overset{o}{A}$, $\alpha = 68^{o}$ 30' and $\beta = 55^{o}$ 40' obtained from electron diffraction studies of small molecules (by Pauling and Brockway and co-workers[75a]), Wall[75] obtained $\left[\overline{r_0^2}/M\right]^{1/2} = 0.485$ $\overset{o}{A}$. It is easy so see that higher values would be obtained in practice, since the assumption regarding free rotation is not valid due to local steric hinderences. Moreover, the incidence of such hindrances will be greater in the more compact cis-structure (natural-rubber) than in trans-structure (gutta-percha). This is found to be true from viscosity data obtained by Wagner and Flory[74].

The higher value obtained in the present investigation is hardly surprising since the quality of the sample and experimental techniques were quite different from those employed by Wagner and Flory. Foreign impurities in the form of proteins or anti-oxidants were eliminated as far as possible, the deproteinisation of the rubber sample being thoroughly carried out. Moreover, only the sol-fraction with respect to petroleum ether (40-60°C) was employed. Wagner and Flory[74], on the other hand, used acetone-extracted rubber which normally contains impurities in the form of proteins and also the gel-fraction, the amount of the latter varying from 40-60% in freshly prepared crepe-rubber. Gel-rubber is regarded as highly-branched polyisoprene for which a smaller value of $\left[\overline{r_0^2}/M\right]^{1/2}$ is expected. Although it cannot be claimed emphatically that the sample of rubber used by us was completely free

from branched chains, it is more likely to have had few
branched-chain molecules and a predominant number of linear
chain molecules.

Another reason for the disagreement is that the
value of 0.83 $\overset{o}{A}$ for $\left[\overline{r_o^2}/M\right]^{1/2}$ was obtained by Wagner and
Flory on the assumption that the Flory-Fox constant $\phi = 2.1$ x
10^{21} at the 'Flory point' for rubber in methyl n-propyl ketone.
Although the most frequently observed value of ϕ
for various systems is about 2.1 x 10^{21}, certain variations
are known. In the case of branched polymers ϕ is
expected to be different from the generally accepted value and
hence the calculated value of $\left[\overline{r_o^2}/M\right]^{1/2}$ would be in error.
In view of these facts, the higher value obtained by us
appears to be reasonable.

3. Variation of A_2 and α :-

Taking the value of $\left[\overline{r_o^2}/M\right]^{1/2}$ to be 1.195 $\overset{o}{A}$,
the values of α are calculated and presented in Table(IV)
for the various systems investigated. On the basis of
A_2 and α , the systems can be broadly classified into two
categories, viz., the systems for which $\alpha > 1$ and $A_2 > 0$
and the systems for which $\alpha \leq 1$ and $A_2 \simeq 0$.
In the former class, are rubber dissolved in cyclohexanone,
trichloroethylene, chloroform and carbon-tetrachloride and,
in the latter, rubber dissolved in cyclohexane, mixtures of
cyclohexane and cyclohexanone, 1,2 dichloroethane and iso-octane

In the case of rubber in tetrahydrofuran,
$\alpha > 1$, but $A_2 > 0$.

4. Solute-solvent interaction and cohesive energy density:-

We shall now discuss the interaction of rubber with various solvents used in the present investigation. It was pointed out in the introduction that,

$$A_2 = \frac{\overline{v^2}}{V_1} \left[Y_1 - \chi_1 \right] Y,$$
(32)

$$\alpha^5 - \alpha^3 = 2C_M \left[Y_1 - \chi_1 \right] M^{\frac{1}{2}} = 2C_M Y_1 \left[1 - \theta/T \right] M^{\frac{1}{2}},$$
(12)

$$Y = \sum_i \sum_j W_i \, W_j \, F(X_{ij}),$$
(30)

$$F_{(x)} = 1 - \frac{X}{2! \, 2^{3/2}} + \frac{X}{3! \, 3^{3/2}} - \cdots \cdots,$$
(14)

$$X = 2 \left[\alpha^2 - 1 \right].$$
(15)

AND

$$\left[\frac{X_{ij}}{M_i M_j} \right] = \left[\frac{2 \left(\frac{X_{ii}}{M_i^2} \right)^{2/3} \cdot \left(\frac{X_{jj}}{M_j^2} \right)^{2/3}}{\left(\frac{X_{ii}}{M_i^2} \right)^{2/3} + \left(\frac{X_{jj}}{M_j^2} \right)^{2/3}} \right]$$
(31)

since the values, of W_1, W_J, X_{11}, X_{jj}, M_1, and M_j are not

known, a quantitative discussion on the significance of observed values of A_2 and α is not possible. However, a semi-quantitative approach to the problem can be made, as is shown in the following:

From the equation (32) and (12), it can be seen that the parameters which characterise the solute-solvent intereaction are Y_1 and X_1 given by

$$\Delta \bar{S} = R\, Y_1\, \upsilon_2^2 \left.\begin{array}{c} \\ \end{array}\right\}$$

$$\text{and} \quad \Delta \bar{H} = RT\, X_1 \upsilon_2^2 \left.\begin{array}{c} \\ \end{array}\right\} \tag{11}$$

where υ_2 is the volume fraction of the polymer in solution and $\Delta \bar{S}$ and $\Delta \bar{H}$ are the partial molar entropy and heat of dilution. So long as $\upsilon_2 \neq 0$, $\Delta \bar{S} \neq 0$ and therefore $Y_1 \neq 0$. But the same does not hold for $\Delta \bar{H}$, the value of which, depending upon X_1, can be positive, negative or zero. As was pointed out in the introduction, the parameters Y_1 and X_1 are obtained by generalizing the corresponding parameters obtained on lattice model treatment of polymer solution, Y_1 replacing the term $1/2$, and X_1, the term χ_1. The expression for X_1 as obtained by Flory[32], is

$$X_1 = \frac{Z \Delta W_{12}\, V_1}{V_2\, RT} \tag{39}$$

where Z is the lattice co-ordination number, V_1 and V_2, the molar volumes of the solvent and the segment respectively,

$$\Delta w_{12} = W_{12} - \tfrac{1}{2}\left[W_{11} + W_{22}\right] \tag{40}$$

W_{11}, W_{22} and W_{12} being the energies associated with solvent-solvent, segment-segment and solvent-segment pair contacts respectively. Equation (40) is actually the well known van Laar expression for the two-component system. Hildebrand[43,44] relates W to the term $(E/V)^{\frac{1}{2}}$, being the energy of vaporization per mℓ. of a component, which has been taken as a measure of the "internal pressure" and $(E/V)^{\frac{1}{2}}$ designated as δ has been called the "solubility parameter"; E is equal to (L -RT), V the molar volume and L the latent heat of vaporization. The term W_{12} has been assumed by van Laar and later by Hildebrand to be the geometric mean of the terms W_{11} and W_{22}. Thus, one obtains

$$\chi_1 \propto \chi_1 = \frac{Z}{RT} \cdot \frac{V_1}{V_2}\,(\delta_1 - \delta_2)^2$$

$$\text{or} \qquad \chi_1 = \chi_0 \cdot \frac{V_1}{RT}\,(\delta_1 - \delta_2)^2 \left.\right\} \tag{41}$$

where χ_0 is a variable depending, inter-alia, upon Z and V_2. In the original equation deduced by Hildebrand χ_0 has been assumed to be unity. It is the uncertainity in the value of χ_0 which restricts the exploitation of equation (41). However, it can be seen that, irrespective of the value of χ_0, whenever $\delta_1 = \delta_2$, χ_1, is zero, i.e. $\Delta\bar{H} = 0$. When $\Delta\bar{H} = 0$, the δ for the polymer and solvent must be equal and thus the value of δ_2 can be easily obtained.

Otherwise it is difficult to determine it as both L and V_2 for a segment of a polymer are not known.

To illustrate the influence of X_o on X_1 , values of the latter have been calculated, using equation (41) for various polystyrene-solvent systems and compared with the experimentally observed values.

In the case of the methyl ethyl ketone - polystyrene system, it has been assumed by Fox and Flory[36] that $\Delta \bar{H} = 0$, on the basis of visco-metric measurements. Schick, Doty and Zimm[82a] also have found from osmotic pressure measurements that $\Delta \bar{H}$ is very small. Thus it may be assumed that δ_2 for polystyrene is very nearly the same as that for methyl ethyl ketone, viz. 9.3. Assuming $\delta_2 = 9.3$ and $X_o = 1$, the following values of X_1 are obtained.

TABLE V

Solvent	δ at T 298°K	v_1 at T 298°K	θ	X_1 Calc.	Obs.
p-dioxane	10	85.7	198	0.071	0.07
Benzene	9.15	89.58	100	0.003	0.03
Ethylacetate	8.6	97.88	222	0.08	0.02
Toluene	8.9	106.8	160	0.029	0.06
Cyclohexane	8.2	109	307	0.223	0.134
Polystyrene	9.3	(115) (monomer)			

It is seen in the last two columns of table (V) that, except in the case of p-dioxane, the agreement between the calculated and the observed values of X_1 tends to improve as the value of V_1 approaches that of the monomer Vm. This point:

to the fact that, amongst other things, χ_0 is a function of the
term $(Vm - V_1)^2$, the exact nature of which is not yet known.
The good agreement found in the case of p-dioxane seems to
be fortuitous.

A qualitative estimate of the solvent power can
be made on the basis of δ_s provided certain restrictions
are observed. For example, whenever two solvents have the
same molar volumes, that for which $(\delta_1 - \delta_2)^2$
is smaller, will be a better solvent. Similarly, a polymer
for which $(\delta_1 - \delta_2)^2$ is the same in two different
media, that for which $(Vm - V_1)^2$ is less, will show a better
solvent power.

On the basis of the above reasoning, we can also
discuss the solvent powers of the various media used for
dissolving rubber in the present investigation. The
value of δ_2 for rubber can be evaluated from the fact that
Meyer, Wolff and Boissonnas[60] have observed that $\Delta \bar{H} = 0$
for the rubber-toluene system, and, on the basis of their data,
Wagner and Flory[74] have assumed $\theta \simeq 0°K$ for the same system.
This means that δ_s for rubber and toluene are equal,
namely 8.9. This value is higher than those given by Gee[44a]
and Scott and Magat[44a] which are 8.3 and 7.89 respectively.
These values were obtained from swelling data on raw rubber or
from the direct measurements of heat of dilution at
concentrations of the order of 1 - 10% wt/volume. Neither of
the above procedures is likely to give accurate results and
hence the disagreement is hardly surprising. We shall assume
the value of δ_2 as 8.9 to be more reliable.

In table (VI), the value of $[\psi_1 - \chi_1]$ and C_M have been

computed from the observed values of α and M

and the values of X_1 have been calculated using equation

(41) as before with $X_o = 1$. In the last column are given the

values of Ψ_1 , which have been obtained by subtracting the

respective values of X_1 from those of $[\Psi_1 - X_1]$.

TABLE VI

δ At T 298 K^o

Solvent	δ	V	c_M	$[\Psi_1 - X_1]$	X_1	Ψ_1
Chloroform	9.3	80.5	0.0123	0.0155	0.0218	0.0373
Trichloro-ethylene	9.2	90.3	0.0110	0.376	0.0137	0.3897
Cyclohexanone	9.9	104.4	0.0095	0.218	0.177	0.395
Carbontetra chloride	8.6	96.9	0.0103	0.0026	0.0147	0.0173
Cyclohexane	8.2	109	0.0091	0	0.0905	0.0905
Iso-octane	6.85	166	0.006	-0.0079	1.18	1.1721
1,2 dichloro-ethane	9.8	79.2	0.0126	-0.0032	0.1085	0.1053
Tetrahydrofuran	9.3	81.1	0.0123	-	-	-
Isoprene	8.9	101	00	--	--	--

For rubber-cyclohexane, since $\Lambda_2 = 0$, $\Psi_1 = X_1 = 0.09$.

This value compares well with that of 0.085 obtained by Wagner

and Flory for rubber-methyl n-propyl ketone at $\Theta = 287.5^o K$.

In these studies, we find that, whenever V_1

and V_m are very dissimilar, the values of X_1

are unusually high, indicating a poor solvent power.

Hildebrand[44a] has suggested on empirical grounds the

following condition of miscibility of a polymer and a solvent.

$$(\delta_2 - 1 \cdot 1) < \delta_1 < (\delta_2 + 1 \cdot 1) \qquad (42)$$

On the basis of this empirical rule, tetrahyfrofuran should be a good solvent for rubber, whereas a value of $\alpha = 0.87$ suggests that, of all the solvents used, it is the poorest. Tetrahydrofuran is found to form peroxide with atmospheric oxygen readily, and it is probable that rubber dissolved in this medium undergoes oxidative degradation as well as branching, and the value of $M/\bar{r^2}$ for this system, which is about 920 and the highest in the series, bears out this assumption. It would, therefore, be incorrect to assume

$$\left[\overline{r_0^2}/M\right]^{1/2} = \quad 1.195 \, A^\circ \text{ for the system rubber-}$$

tetrahydrofuran. By using the smaller value i.e. 0.83, obtained by Wagner and Flory[74] for a mixture of gel and sol-rubber, it is found that $\alpha = 1.253$, and hence a positive slope observed in HC/τ vs. C plot is justifiable. Moreover, one does not violate equation (42). That this assumption about degradation and branching is justifiable is also demonstrated by the fact that the viscosity of rubber in this solvent decreases with time more rapidly than in the other solvents. (Private communication from late Dr.Pande, Plstics & Polymer Division, N.C.L.). In view of this labile nature, this particular system will not be discussed later.

In the present series, the effect of molar volume of solvents on rubber-solvent interaction can be easily illustrated by comparing the solvent power for rubber of chloroform, 1,2-dichloro-ethane, trichloroethylene,
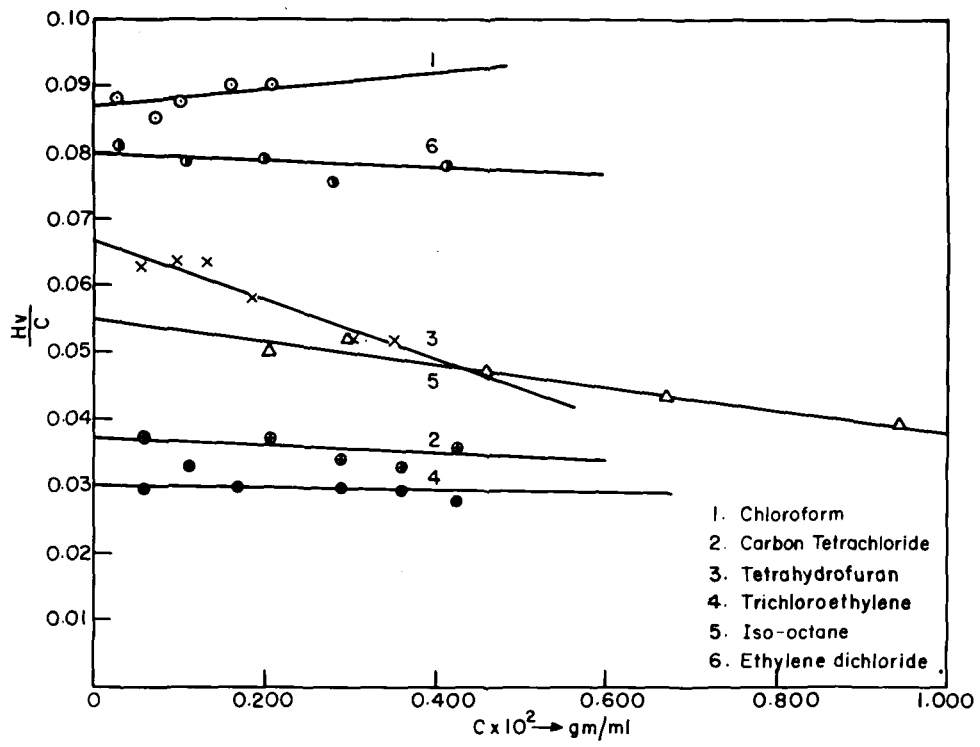
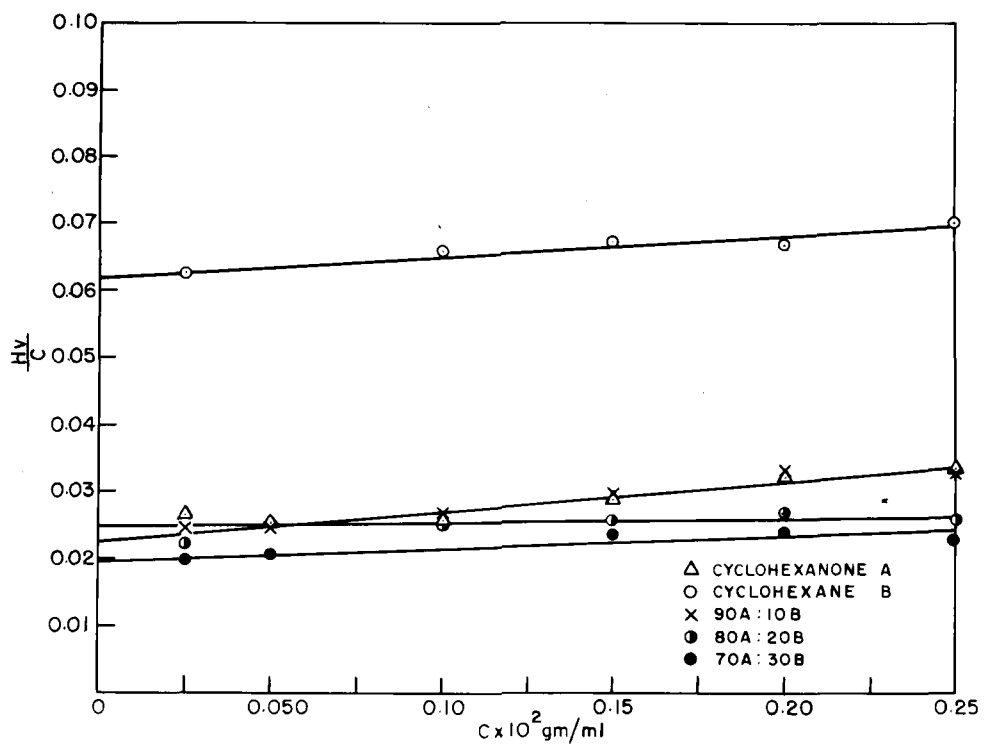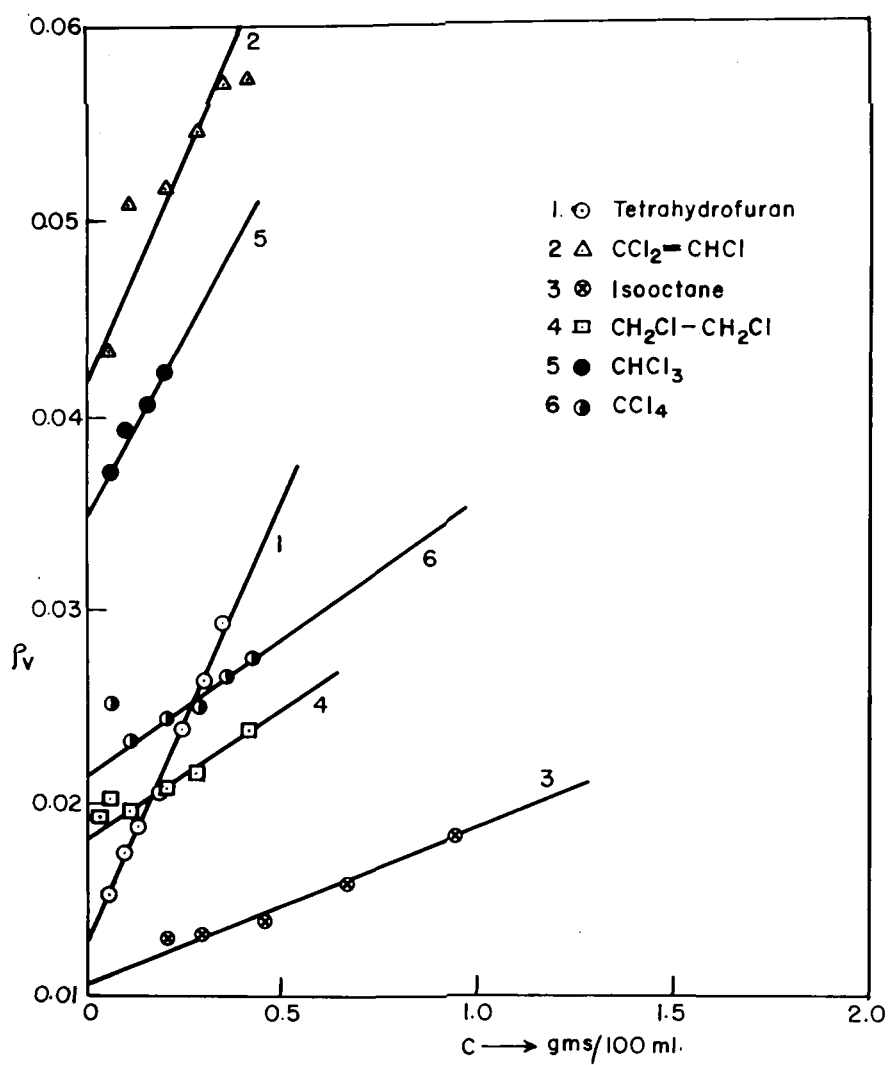Figure 6

Figure 7

Figure 8

Figure 8

cyclohexanone and iso-octane. For comparing the solvent power of chloroform with that of 1,2-dichloroethane, one finds that although the molar volumes of the two are nearly the same, the former is a better solvent, since $[\delta_1 - \delta_2]^2 =$ 0.16 for the former system and 0.81 for the latter. Similarly, trichloroethylene is a better solvent than chloroform, even though the δs for the two solvents are nearly the same, since the molar volume of the former is nearer to Vm than that of the latter. In the case of cyclohexanone, where $[\delta_1 - \delta_2]^2 = 1$, its solvent power, which compares with that of trichloroethylene, is due to the fact that $V_1 \simeq$ Vm. Iso-octane, of which neither nor molar volume is comparable, is a poor solvent for rubber. Thus, from a proper understanding of the solubility parameters and molar volumes of the polymer and the solvent respectively, it is possible to make a qualitative estimate of the solvent power. The discrepancies observed by earlier workers can be attributed to the unsatisfactory experimental conditions employed by them and to the imperfect understanding of the problem of solute-solvent interaction, which owing to the pioneering work of Flory and his collaborators have now become more comprehensible.

Variation of Hv/c. vs. C:

In figures (6) and (7) are represented the observed variation of Hv/C. vs.C. It is seen that the negative values of the slopes for the various systems are in the order tetrahydrofuran > Iso-octane > 1,2-dichloroethane > carbon-tetrachloride > trichloroethylene. In the cases of chloroform, cyclohexanone and cyclohexane the slopes unexpectedly are positive. Actually the slopes should be zero

for good solvents and negative for bad, the magnitude of negativeness increasing with poorness of the solvent. There may be two reasons for the discrepancy viz. the relative and possibly quite appreciable inaccuracy of the data at low concentration, and multiple scattering. The data presented in figure (7) were obtained using a dissymmetry cell, which has a rather complicated geometry[61]. It is therefore likely that multiply-scattered light might also have contributed to the observed Hv component. Since multiple scattering increases with concentration, slight positive slope is understandable.

In figure 8 are presented the observed variations of ρv with C for the various systems. The values of the intercepts i.e. $(\rho_v)_{c \to 0}$ have been used to correct the values of molecular weights for the depolarization effect. As ρv is related to the anisotropy through Hv component and to the mass of a particle thorough Vv component, it is difficult to analyse the observed data at present.

Thus, it is seen that one can obtain a qualitative measure of solvent power from a study of the slopes of the Hv/C vs. c. curves alone, although it does not give as deep an insight into the nature and extent of solute-solvent interaction as does a study of the parameters α and $[\gamma_1 - x_1]$ On the basis of both the depolarization and $[\gamma_1 - x_1]$ data, one can assign the following order to the relative solvent power for the media used to dissolve rubber viz. trichloroethylene $\geq$ cyclohexanone $>$ chloroform $>$ carbon-tetrachloride $>$ cyclohexane $>$ 1,2-dichloroethane $>$ iso-öctane.

: 44 :

SUMMARY AND CONCLUSIONS.

1.   In the present studies, a six-fold variation in molecular weight has been observed for the same sample of purified sol-rubber in different solvents. These observations, as well as those by Bywater and Johnson, have been explained on the basis that purified rubber readily undergoes oxidative and photo-chemical degradation reactions and as a result, its original average molecular weight and chain length changed to different extents in the solvents used. The molecular weights as obtained are the weight-average molecular weights at the time of observation.

2.   No quantitative comparison of the solvent power of the different solvents used could be made because of the difference in molecular weight heterogeneity. However, use has been made of parameters, such as Flory's expansion factor α , the second virial coefficient A_2 and the slopes of the curves of Hv/C vs. C plots for qualitative comparison. In rubber-cyclohexane system, where $A_2 = 0$, a value of $\left[\overline{r_0^2}/M\right]^{1/2} = 1.195 \, A^{\circ}$ has been obtained for rubber, which is about 1.44 times higher than the value obtained by Wagner and Flory[74]. The lower value has been ascribed to the presence of gel-fraction (40-60%) in their sample, which consists of highly branched-chain product.

Taking $\left[\overline{r_o^2}/M\right]^{1/2} = 1.195 \ A^o$,

values of α , C_M and $\left[\Psi_1 - \chi_1\right]$ have been calculated

for the various systems.

Since $\chi_1 = 0$ for the rubber-toluene system,

the value of the "solubility parameter" or cohesive

energy density (δ_2) for rubber has been taken as

equal to that of toluene, viz., 8.9. Using equation (41)

and $\chi_0 = 1$, values of χ_1 for the various systems have been

evaluated. For rubber-cyclohexane, $\Psi_1 = \chi_1 = 0.0905$,

which is in good agreement with the reported value

of 0.085 for the rubber-methyl n-propyl ketone system at

its Flory point.

Values of χ_1 for polystyrene in five

solvents have been computed theoretically and compared

with the experimentally observed values of Fox and Flory.

It was found that the agreement tends to become better

as the value of V_1 approached that of V_m. It

has been suggested that χ_0 is a function of $(V_1 - V_m)^2$,

amongst other things. The solvent powers of

cyclohexanone, trichloro-ethylene, carbon-tetrachloride,

1,2-dichloroethane (ethylene dichloride) and iso-öctane

have been explained on the basis of ($\delta_2 - \delta_1$)^2

and $(V_1 - V_m)^2$.

3. For the rubber-tetrahydrofuran system,

$M/\overline{r^2}$ is the highest, which may be due to the degradation

of rubber followed by branching. Further, α is found to be equal to 0.87 and at the same time $A_2 > 0$. This could be explained on the grounds that, at least for this system $\left[\overline{r_o^2}/M\right]^{\frac{1}{2}}$ is lower than 1.195 A^o.

4   These studies confirm by direct measurements the suggestion put forth by Doty that the slopes of Hv/C <u>vs</u>. C curves can be utilized to evaluate the solute-solvent interaction easily even in polydisperse systems, since H_v component does not depend upon molecular weight but only on the number of segments per ml., whereas A_2 is dependent upon molecular weight. It has been found that unless multiple-scattering is checked by using solutions of low concentrations and a cell of simple geometry, unexpected positive slopes are obtained in the Hv/C <u>vs</u>. C curves, and the results become less reliable.

5   On the basis of our observations, the relative solvent powers of the various media for rubber used here are in the order, cyclohexanone $\geq$ trichloroethylene $>$ chloroform $>$ carbon tetrachloride $>$ cyclohexane 1,2 dichloroethane $>$ Iso-octane.

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VISCOSITY OF LONG CHAIN POLYMER MOLECULES IN DILUTE SOLUTION

I_N_T_R_O_D_U_C_T_I_O_N.

I

Long chain polymer molecules in solution increase the viscosity of the solvent to an extent which has/related, $_\wedge^{been}$ inter-alia, to their molecular weight. It is true that the longer the chain, the higher the viscosity of a given weight concentration of polymer in a given homologous series. In other words, the intrinsic viscosity, i.e. the capacity of a polymer to enhance the viscosity, increases with molecular weight and, in fact, it was at first supposed to be directly proportional to the molecular weight M. Thus the intrinsic viscosity

$$[\eta] = KM \, , \qquad\qquad (I)$$

where

$$[\eta] = \left\{ \frac{\eta_r - 1}{C} \right\}_{C \to 0} = \left\{ \eta_{sp}/C \right\}_{C \to 0} \qquad (2a)$$

$$= \left\{ \frac{\log \eta_r}{C} \right\}_{C \to 0} = \left\{ \frac{\log [1 + \eta_{sp}]}{C} \right\}_{C \to 0} \qquad (2b)$$

where η_r is the relative viscosity, i.e. the ratio of the viscosities of solution and solvent, η_{sp} is the specific viscosity, C the concentration in grams per 100 c.c. and K is a constant.

Equation (1) is called the Staudinger's[44],[45]
law, which experiment has shown to be valid for polymers
of low molecular weight upto about few thousands. At
higher molecular weights the law breaks down.

Two empirical modifications of Staudinger's law
have been proposed,[15],[18],[27],[38] the one equates

$$[\eta] \quad \text{to} \quad KM + a \, , \qquad (3)$$

the other to

$$KM^{\alpha} \qquad (4)$$

The latter equation in particular was found to apply to
several varieties of polymer over quite wide ranges of
molecular weight. The constant 'a' appearing in this
equation has the limiting values of 0.5 and 2.

The intrinsic viscosity $[\eta]$ has the dimensions of
specific volume, and the large values of $[\eta]$ for polymers
indicate that these molecules occupy a large volume in
solution. This is hardly surprising, as a single polymer
molecule in dilute solution is subject to the osmotic action
of the surrounding solvent. This action tends to swell the
molecule to a larger average size than it would assume due to
a random spatial distribution of its segments.

Thus frictional characteristics of polymer molecules
in dilute solution, as manifested in solution viscosities,
sedimentation velocities and diffusion rates, therefore,
depend directly on the volume encompassed by the polymer chain.

there are two types of theoretical calculations for the
intrinsic viscosity of dilute polymer solutions based upon,

(a) the "Free draining model"[6,23,28,32,35]   and

(b) the "Equivalent sphere model"[4,7,31,33].

The first of these assumes that the polymer molecule does
not distort the flow lines in the solvent and that the
solvent flows freely through the polymer molecule.
Calculations based on this model predict that the
frictional coefficient should increase with the first power of
the molecular weight and that the intrinsic viscosity should
increase with M raised to a power a little greater than unity.
Experimental evidence, however, indicates an increase with a
power of 0.5 to 0.6 for both quantities.   Because of the
unrealistic nature of the assumptions made, this discrepancy
is not surprising.

The second type of theoretical calculation of
dilute solution viscosities recognizes that the flow lines
of the solvent may be distorted by the presence of the
polymer molecule because the solvent trapped in the coiled-up
molecule would normally move almost in unison with the
polymer segments as if the solvent were bound to the polymer.
In the extreme limit, such a calculation leads to an
expression for the viscosity of hard spheres impenetrable
to solvent molecules (Einstein's equation).

The resulting equations can be expressed
mathematically as,

$$[\eta] = \phi' \frac{r^3}{M_1}$$

with r = root mean square end-to-end distance and M_1

the mass of the polymer molecule, ϕ' being a

dimensionless constant having values 0.0057, 0.015 and

0.006 in the treatments given by Kuhn and Kuhn[36] and Debye[7],

and Kirkwood and Riseman[31] respectively. The value of ϕ'

is found to be of the order of 10^{21}, if M_1 is replaced

by the molecular weight M of the polymer. Flory and

Fox[19] have shown that for various polymers the value of ϕ'

is of the order of 2×10^{21}. These theories, however,

do not take into account the effect of the temperature and

solvent on the polymer molecules in solution. The values

of ϕ' as obtained experimentally by Fox and Flory[19]

show a small but definite sensitivity to temperature and the

solvent power.

In addition to the above mentioned hydrodynamic

treatments of the theory of viscosity of dilute polymer

solutions, attempts have also been made to treat the problem

on the basis of the "Theory of rate processes". This

theory gives a better physical picture. The first[37]

treatment is more or less empirical in nature. Palit[40]

has recently deduced an expression which relates $[\eta]$ with

the two-thirds power of molecular weight, assuming the polymer
(i.e. the solvent and monomer)
solution to be a mixture of two liquids, an assumption which

makes the treatment subject to objections. Ree and Eyring[10]

have recently deduced a generalised viscosity formula which

describes the variation of viscosity with the rate of shear.

However, in this otherwise critical treatment no attempt has

been made to correlate the viscosity with the molecular weight of the polymer or its root-mean-square end-to-end distance, quantities which are of first interest to the physical chemist.

In applying equations (4) and (5), a prior knowledge of the intrinsic viscosity $[\eta]$ is necessary, which in turn entails a knowledge of the variation of viscosity with concentration. To date, few theoretical attempts have been made to establish a relation between the two parameters. However, several workers[1,2,3,5,14,21,24,26,29,39,42.] have proposed empirical equations of which that due to Martin[39] represents the viscosity-concentration relationship upto a concentration of 5%. It can be expressed mathematically as

$$\frac{\eta_{sp}}{c} = \left[\frac{\eta_{sp}}{c}\right]_{c\to o} exp.\left[k_M \left\{ \frac{\eta_{sp}}{c} \right\}_{c\to o} c\right] \tag{6}$$

A special case of this equation is the relation proposed by Huggins[29], viz.

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \tag{7a}$$

$$or \quad \frac{\log \eta_r}{c} = [\eta] - k''[\eta]^2 c \tag{7b}$$

It is obvious that k' and k" will be related to each other. It has been shown[11,22] that k' and k" determined experimentally obey the relationship $k' + k'' = \frac{1}{2}$, (8) irrespective of the system and temperature. It has also been shown by Fox and Flory[16] that k' and k" are constants

characteristic of the given solvent-polymer pair and

independent of the molecular weight of the latter.   On

the other hand Wagner[46] has pointed out in his studies on

polyvinyl acetates that k" is essentially zero up to

intrinsic viscosities of about 0.4 (molecular weight 38,000),

above which the slope becomes increasingly negative up to

viscosities of about 2.0.   It should be noted, however, that

the data obtained by Fox and Flory were extrapolated for zero

rate of shear, whereas this was not done by Wagner. This is

of interest, as it points to a possible relation between the

rate of shear (as experienced by the polymer molecule) and

the molecular weight, and indicates the desirability of

extrapolating the data to zero rate of shear.

In spite of the several attempts made to correlate

the viscosity of polymer solution with the characteristic

properties of the polymer molecule, the method remains more

or less empirical in nature.   A prior knowledge of K and 'a'

occurring in equation (4) is necessary, which involves the

determination of molecular weight and particle size by an

absolute method such as light scattering.   In the

treatment given below, an attempt has been made to deduce

equations (4), (5), (7a), (7b) and (8), assuming an

"equivalent sphere model" on the basis of the "theory of

rate processes", and the present treatment reconciles the

apparently contradictory observations of Fox and Flory[16], and

Wagner[46].   It has further been pointed out that the number of

unknown parameters in the viscosity equations can be reduced and

the method be made an absolute one for the determination of the

molecular weight of the polymers.

II

STATEMENT OF THE PROBLEM

In a polymer solution which is so dilute that there is no interaction between the solute molecules, there are regions where the segment density of the polymer is high as compared to the average, the regions in between being completely filled by solvent molecules. Debye[7] has, however, pointed out that the density is maximum around the centre of gravity of the polymer molecule and that with increasing distance it decreases gradually, the shape of the density function $\rho(r)$ resembling the Gaussian probability curve. He has not, however, made use of this distribution in his treatment of the viscosity of high polymer solutions.

If the movement of a solvent molecule parallel to the direction of an applied stress is regarded as equivalent to crossing an energy barrier, then each successful jump of such a molecule will contribute towards the fluidity of the system. The number of such jumps depends on the stress and temperature of the system. However, when one considers the regions which are pervaded by polymer chains, the situation alters. The solvent molecules occupying the volume pervaded by polymer molecules may be classified into three categories:

(a) Those which flow freely like the other free solvent molecules. Such molecules exist just inside the periphery of space pervaded by the polymer chain, where $\rho(r)$ is fairly small.

(b) Those which move with the polymer chain only,
as if they were associated with it. Such molecules exist
near the centre of gravity of the polymer chain, where
$\rho(r)$ is large.

(c) Those which are not completely free, nor move
with the chain, and occupy an intermediate space, where
$\rho(r)$ has intermediate values.

As compared with the solvent, the movement of the
polymer chain itself as a whole in the direction of the flow
depends upon two factors: (a) the frequency of successful
jumps of any segment which would depend only on the stress,
temperature and the energy of activation; and (b) the
probability that all the segments of the chain have a net
coordinated movement in the forward direction. This would
depend upon the volume pervaded by the chain molecule, as
compared to its actual volume and would be independent of
the parameters such as stress, temperature and the energy
of activation, as suggested by Kauzmann and Eyring[30].
The various types of flow mechanism operative in the system
obviously make it difficult to treat the problem with
mathematical rigour; and even then the resulting equations
will contain several unknown constants and parameters, thereby
making them unsuitable for experimental verification. An
alternative approach which has been followed in the present
treatment is the use of some simplifying assumptions the
nature of which is such as not to make the treatment
unrealistic.

III

ASSUMPTIONS AND THE DEFINITION OF THE SYSTEM.

Consider a monodisperse polymer solution of concentration c gm /cc. and divide 1 c.c. of this solution into equivalent cells, so that each cell (of volume $1/n$ c.c.) represents on an average the volume occupied by a solvent molecule plus its free volume. Further, let p be the number of statistical segments in each polymer molecule and, assuming that each segment replaces only one solvent molecule in the cell space, the number of cells occupied by each polymer molecule would be p . If the polymer molecule is completely flexible the segments would have a random distribution, and the volume encompassed would be $\frac{4\pi}{3} R^3$, where R is the radius of the sphere circumscribing the volume pervaded by the polymer chain. It has been pointed out in the previous section that within this sphere of radius R, there are three types of flow mechanism in operation. In the outer regions of the sphere, the solvent flows unhampered, i.e. without distortion of the flow lines. Inside the sphere, the flow lines are more and more distorted due to the increasing influence of the polymer molecule, and near the central regions solvent molecules and polymer segments flow as a unit. An 'equivalent sphere' of radius Re is defined for each polymer molecule in which all the solvent molecules present are assumed to flow as a unit with the polymer molecule, the rest of the solvent molecules outside this flowing freely. This gives the volume due to a single polymer molecule with its entrapped solvent which behaves differently from the free solvent molecules. It has been

pointed out by Debye[7], that it is this volume which
determines the intrinsic viscosity of the polymer solution
rather than the molecular weight of the polymer. Re is
related to the root mean square distance $(\overline{s^2})^{1/2}$ of an
element from the centre of gravity of the polymer molecule.
The density ρ of the segments of a polymer molecule
obeys the Gaussian distribution, given by

$$\rho = \rho_o \, e^{-\beta^2 r^2} , \qquad\qquad (9)$$

with the normalising condition

$$\int_o^\infty 4\pi r^2 \rho \, dr = M ,$$

giving

$$\rho_o = \frac{M_1 \beta^3}{\pi^{3/2}} ,$$

where, ρ_o = density at the centre of the sphere, $\beta =$
a constant, and M_1 = mass of the polymer molecule in gm.

Equation (9) has a point of inflection determined
by the condition $\dfrac{\partial^2 \rho}{\partial r^2} = 0$, which gives $r^2 = \frac{1}{2\beta^2}$.
At this point the rate of variation of density is maximum,
and this is conveniently taken as the radius of the sphere
which is impenetrable. To take into account the contribution
due to the partially hampered solvent flow, i.e. the
contribution from the outer regions of the molecules, the
radius Re will have to be greater than the distance of the
point of inflection, and will be less than, say $(\overline{s^2})^{1/2}$,
the root mean square distance of the segments from the centre

of gravity of the polymer molecule. The r.m.s. distance is given by

$$\bar{S}^2 = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r^4 e^{-\beta^2 r^2} \sin\theta \cdot d\theta \cdot d\phi \cdot dr}{\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r^2 e^{-\beta^2 r^2} \sin\theta \cdot d\theta \cdot d\phi \cdot dr} \qquad (10)$$

$$= \frac{3}{2\beta^2} \quad . \quad Thus, \frac{3}{2\beta^2} > Re^2 > \frac{1}{2\beta^2} \qquad (11)$$

We take the mean of the two extremes as a possible value of Re, i.e.

$$Re^2 = \frac{1}{\beta^2} = \frac{2}{3}\bar{S}^2 .$$

This equates Re to the radius of gyration $(\bar{S}_1^2)^{1/2}$, a term often loosely employed for the r.m.s. distance, and given by

$$\bar{S}_1^2 = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r^4 e^{-\beta^2 r^2} \sin^3\theta \cdot d\theta \cdot d\phi \cdot dr}{\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r^2 e^{-\beta^2 r^2} \sin\theta \cdot d\theta \cdot d\phi \cdot dr} = \frac{1}{\beta^2} \qquad (12)$$

Since it is well known that

$$\bar{S}^2 = \frac{\bar{r}^2}{6} = \frac{\alpha^2 c'^2 Z}{6} \qquad (13)$$

α being Flory's[17] factor.

where $(\overline{r^2})^{1/2}$ is the r.m.s. end-to-end distance, Z the

number of links in the polymer chain, and C^1 a constant

characteristic of a given polymer chain structure, for the

volume of the equivalent sphere, the following expression

is obtained:

$$\frac{4\pi}{3}Re^3 = \frac{4\pi}{3}\left[\frac{2}{3}\,\overline{S^2}\right]^{3/2} = \frac{4\pi}{3}\left[\frac{2}{3}\cdot\frac{1}{6}\,\overline{r^2}\right]^{3/2} = 0.155(\overline{r^2})^{3/2}$$

$$= 0.155\,\alpha^3 C'^3 Z^{3/2} \times 10^{-24}\ c.c. \tag{14}$$

$$\left[\text{where},\ \alpha^2 = \overline{r^2}/\overline{r_0^2}\right]$$

Let $\quad p' = \dfrac{4\pi}{3}\cdot Re^3\big/\dfrac{1}{n}$,

where p^1 represents the number of cells occupied by the

'equivalent sphere' substituted for the polymer molecule.

The difference between p^1 and p gives the

number of solvent molecules which can be considered as

trapped and moving with the polymer molecule as a unit

during its flow. If N_1 and N_2 are the number of molecules

of the polymer and the solvent per c.c. respectively, then

the total number of cells occupied by the polymer per c.c.

is given by pN_1 and those occupied by the solvent are N_2;

then

$$pN_1 + N_2 = n$$

We define $\quad \dfrac{p'N_1}{n} = x_1\quad$ and $\quad \dfrac{N_2 - (p'-p)N_1}{n} = x_2$,

so that $\quad x_1 + x_2 = 1$.

x_1 and x_2 being the volume fractions of the swollen polymer
and the free solvent respectively.   If we are dealing with
fairly dilute solutions, then $N_2 \gg (p'-p)$ and $\frac{N_2}{n} \backsimeq x_2$.
If M_1 and Mo are the mass and the mass per link of the
polymer molecule respectively then $M_1 = MoZ$. Expressing
X_1 in terms of concentration.

$$X_1 = \frac{p'N_1}{n} \cdot \frac{M_1}{M_1} = \frac{p'}{nM_1} \quad X \qquad \text{mass of the polymer per c.c.}$$

$$= \frac{p'c}{nM_1} \qquad \text{which gives}$$

$$X_1 = 0.155 (\overline{r^2})^{3/2} \cdot \frac{nc}{nM_1} \tag{15}$$

If the mass is replaced by the molecular weight M of the
polymer,

$$X_1 = 0.155 (\overline{r^2})^{3/2} \frac{cN}{M} = 9.33 \times 10^{22} \propto^3 (\overline{r_0^2})^{3/2} \frac{c}{M} \tag{16}$$

$$= 9.33 \times 10^{22} c'^3 \propto^3 z^{3/2} \frac{c}{M}$$

$$= 9.33 \times 10^{22} \propto^3 c'^3 \frac{M^{3/2}}{M_0^{3/2}} \cdot \frac{c}{M}$$

$$= BC \propto^3 M^{1/2} \tag{16a}$$

where N is Avogadro's number and $\propto$ is Flory's
perturbation factor.

STANDARD FREE ENERGY OF ACTIVATION FOR FLOW OF A POLYMER SOLUTION.

In a system as defined in Section III, one observes that although a segment and a solvent molecule can replace each other in the cell space, their energies of activation for crossing the potential barrier to enter an adjacent cell in the direction of flow, will not be the same. For liquid mixtures, the following equation has been used by Powell, Roseveare and Eyring[41].

$$\cdot F_{Av} = X_1 E_1 + X_2 E_2 - \frac{\Delta F_m}{2.45} \tag{17}$$

where E_1, E_2 and F_{AV} are the standard free energies of activation for the two components and the average value for the mixture respectively; ΔF_m is the excess free energy of mixing, representing the departure from Raoult's law. Equation (17), however, can be applied only in those case where the molar volumes of the two components are nearly the same. We extend the use of this equation for polymer solutions, assuming the equality of the molar volumes of the polymer segment and the solvent. In the present treatment ϵ_1, ϵ_2 and $X_1 \cdot \epsilon_{12}$ represent the molar standard free energies of activation for a segment and the solvent molecule and the contribution due to non-ideality of the mixture respectively. The equation (17) is thus modified to give

$$E = X_1 \epsilon_1 + X_2 \epsilon_2 - X_1 \epsilon_{12} \tag{18}$$

Equation (18) assumes that all the segments of a polymer molecule have the same average value for the energy of activation at the same temperature. Even with this simplifying assumption, it would be difficult to fix any value for $\in_1$, as the average size of the segment would change from solvent to solvent for the same polymer. A simple method of evaluation of E from the experimental data, however, suggests itself on inspection of the final set of equations and will be discussed later.

THE PROBABILITY OF CO-ORDINATED MOVEMENT OF 'Z' LINKS:

It has been pointed out (equation 14) that the volume of the equivalent space encompassed by the Z links is equal to $0.155 c'^3 \propto^3 z^{3/2} \times 10^{-24}$ c.c. , while the chain itself occupies a volume, say, $V_2 = 20 Z \times 10^{-24}$ c.c. (for a methylene chain, V_2 being higher for others). Of the total volume enclosed by the freely, twisting chain containing p segments, the portion V_1 equal to $\left[\dfrac{0.155 c'^3 \propto^3 z^{3/2}}{p} \right]$ is available for each segment. In order that movement may be successful the segment must be located within some definite region of the volume V_2 that the molecule would occupy after moving under the action of a shear force. The probability of failure is the probability that the segment will be in the portion V_1 of the total space $V_1 + V_2$ in which it might be and this is given by

$$\frac{V_1}{V_1 + V_2} \approx \frac{V_1}{V_2} = \frac{0.155 c'^3 \propto^3 z^{3/2}}{20 Z p} = \frac{0.00775 c'^3 \propto^3 z^{1/2}}{p}$$

Therefore, the probability of success that all p segments
will move independently and successively, each having a
probability of success $\left[1 - \dfrac{0.00775\, c'^{3} \alpha^{3} z^{1/2}}{p}\right]$
is given by

$$W(p) = \left[1 - \frac{0.00775\, c'^{3}\alpha^{3} z^{1/2}}{p}\right]^{p} \simeq e^{-0.00775\, c'^{3}\alpha^{3} z^{1/2}} \qquad (19)$$

which shows that the probability decreases with increasing
chain length. For example, one may calculate $W(p)$ for a
chain of 6400 isoprene units for natural (cis) rubber.
Wall[47] has shown that for cis-rubber $C' = 2.01\,\overset{o}{A}$ which
when substituted in equation (19) gives

$$W(p) = e^{-10.76} \approx 0.000045, \quad \text{assuming } \alpha = 1$$
$$z = 6400 \times 4$$

In other words, for a rubber chain consisting of 25600 links,
only 45 in every 100,000 sets of jumps of the individual
segments contribute towards the fluidity of the polymer
molecule. This explains qualitatively the decrease in
fluidity or increase in the viscosity of the polymer molecule
with the degree of polymerisation.

IV

EXPRESSION FOR THE FLUIDITY OF A POLYMER SOLUTION

The flow of a fluid takes place with a definite
velocity under a given set of conditions, and therefore the
problem of fluidity can be treated on the basis of the
"Theory of Rate Processes"[9,12,13,25]   For the purpose of
the present treatment, the motion of one layer with respect

to another may be assumed to involve the passage of a cell
from one equilibrium position to another in the same layer
and the process may be pictured as the passage of a unitary
cell across a potential-energy barrier. Let λ be
the distance between two equilibrium positions in the
direction of motion; the distance between neighbouring cells
in the same direction being λ_3 . The latter is not
necessarily equal to λ , but it may be so approximately.
Finally, the mean distance between two adjacent cells in
the moving layer in the direction at right angles to the
direction of motion is λ_2 . It may be assumed that the
potential-energy barrier is a symmetrical one, so that the
distance between the initial equilibrium position and the
top of the barrier (activated state) is $\lambda/2$. The applied
force acting on a free cell in the direction of motion is
$f \lambda_2 \lambda_3$, since $\lambda_2 \lambda_3$ is the effective area per cell.
However, when one considers the regions pervaded by flexible
macromolecules it is observed that due to linking between
the adjacent cells, the area $\lambda_2 \lambda_3$ behaves as if it is
resisting shear on an area larger than itself. The magnitude
of such an apparent area would depend on the degree of
polymerization and the flexibility of the chain. For
want of an exact expression we assume that each cell offers
the same resistance to the flow and that the average applied
force per cell in the polymer region is represented by
$\beta' f \lambda_2 \lambda_3$, where β' is a dimensionless constant.
The value of β' would depend not only on the chain
structure and length of the polymer but on the concentration
of the solution also, if one is dealing with very high

concentrations.

The specific rate of flow in the direction of the applied force f, for the cells pervaded by polymer chains is given by[20],

$$K_{f_1} = K \, e^{f\beta' \lambda \lambda_2 \lambda_3/2kT} \cdot W(p) \qquad (20a)$$

W(p) being given by equation (19), and for free cells in solution is given by,

$$K_{f_2} = K \, e^{f \lambda \lambda_2 \lambda_3/2kT} , \qquad (21a)$$

where $K = \dfrac{kT}{h} \, e^{-E/RT}$, k is Boltzmann's constant, h Planck's constant, T the absolute temperature, R the gas constant and E is given by equation (18).

Similarly , the rates of flow in the direction opposite to that of the applied force are given by,

$$K_{b_1} = K \, e^{-\beta' f \lambda \lambda_2 \lambda_3/2kT} \cdot W(p) \qquad (20b)$$

and

$$K_{b_2} = K \, e^{-f \lambda \lambda_2 \lambda_3/2kT} \qquad (21b)$$

The fluidity of a system is given by[20]

$$\phi = \lambda \left[K_f - K_b \right] / \lambda_1 f ,$$

where $\lambda_1 =$ distance between adjacent sliding layers.

Thus we obtain for fluidities ϕ_1 and ϕ_2 of the polymer type cells and the free solvent type cells, the following expressions:

$$\phi_1 = 2 \frac{\lambda}{\lambda_1} \cdot \frac{kT}{hf} e^{-E/RT} \cdot W_{(p)} \; sinh \; \beta' \gamma \qquad (23)$$

and

$$\phi_2 = 2 \frac{\lambda}{\lambda_1} \cdot \frac{kT}{hf} e^{-E/RT} \; sinh \; \gamma , \qquad (24)$$

where $\quad \gamma = f \lambda \lambda_2 \lambda_3 / 2kT.$

Since we have assumed an average value E/N [Equation (18)] for the activation energy of a cell, irrespective of the fact that it may be occupied by a solvent molecule or a segment to cross the potential-energy barrier, we can make use of the simple expression for the fluidity applicable to liquid mixtures to evaluate the fluidity ϕ_{12} of a polymer solution, . $i.e.$

$$\phi_{12} = X_1 \phi_1 + X_2 \phi_2 , \qquad (25)$$

giving
$$\phi_{12} = \phi_2 \left[X_1 W_{(p)} \frac{sinh \; \beta' \gamma}{sinh \; \gamma} + X_2 \right] \qquad (26)$$

Putting $\quad X_1 = 0 \quad$ and $\quad X_2 = 1 \quad$ in equation (26), we obtain for the fluidity of the pure solvent, with the help of equation (18),

$$\phi_2' = 2 \frac{\lambda}{\lambda_1} \cdot \frac{kT}{hf} e^{-\epsilon_2/RT} \; sinh \; \gamma . \qquad (27)$$

The relative fluidity $\phi_r = \phi_{12}/\phi_2'$, which gives

$$\phi_r = e^{-x_1[\epsilon_1 - \epsilon_2 - \epsilon_{12}]/RT}\left[x_1 W_{(p)}\frac{\sinh \beta' Y}{\sinh Y} + x_2\right] \qquad (28)$$

$$= e^{-x_1 Y/RT} x_2\left[\frac{x_1}{x_2} W_{(p)} F_{(Y)} + 1\right] ,$$

where $Y = \epsilon_1 - \epsilon_2 - \epsilon_{12}$, and $F_{(Y)} = \dfrac{\sinh \beta' Y}{\sinh Y}$

Now, if $\dfrac{x_1}{x_2} W_{(p)}\dfrac{\sinh \beta' Y}{\sinh Y} \ll 1$, which will be shown to be true, as $f \rightarrow 0$,

$$\eta_r = 1/\phi_r = \frac{e^{x_1 Y/RT}}{x_2}\left[1 - \frac{x_1}{x_2} W_{(p)} F_{(Y)}\right] \qquad (29)$$

and since $x_2 = 1 - x_1$, therefore $1/_{1-x_1} \simeq 1 + x_1$ and

$$\eta_r = [1 + x_1]\left[1 - x_1\{1 + x_1\} W_{(p)} F_{(Y)}\right] e^{x_1 Y/RT}$$

Since $x_1 \ll 1$, higher power terms in x_1 can be neglected, yielding finally,

$$\eta_r = e^{x_1 Y/RT}\left[1 + x_1\{1 - W_{(p)} F_{(Y)}\}\right] , \qquad (30)$$

with $x_1 = BC \propto^3 M^{1/2}$, $W_{(p)} = e^{-0.00775 \propto^3 c^{13} z^{1/2}}$

and $F_{(Y)} = \dfrac{\sinh \beta' Y}{\sinh Y}$, with $Y = \dfrac{f \lambda_1 \lambda_2 \lambda_3}{2kT}$

A_P_P_L_I_C_A_T_I_O_N_S.

The general applicability and validity of equation (30) will now be considered.

Expression for $\log \eta_r / c$ **and k"** :- Making use of equation (30), one can deduce the expressions most commonly used in the evaluation of the intrinsic viscosity in the following way:

$$\log \eta_r = X_1 Y/RT + \log \left[1 + X_1 \left\{ 1 - W_{(p)} F_{(Y)} \right\} \right]$$

$$= X_1 Y/RT + X_1 \left[1 - W_{(p)} F_{(Y)} \right] - \frac{X_1^2}{2} \left[1 - W_{(p)} F_{(Y)} \right]^2 + \cdots \cdots$$

$$= X_1 \left[Y/RT + 1 - W_{(p)} F_{(Y)} \right] - \frac{X_1^2}{2} \left[1 - W_{(p)} F_{(Y)} \right]^2 \qquad (31)$$

Substituting the value of X_1 from (16) or (16 a), one obtains

$$\frac{\log \eta_r}{C} = B \propto^3 M^{1/2} \left[Y/RT + 1 - W_{(p)} F_{(Y)} \right]$$

$$- \left[B \propto^3 M^{1/2} \right]^2 \cdot \frac{C}{2} \left[1 - W_{(p)} F_{(Y)} \right]^2$$

$$= [\eta] - k''[\eta]^2 c \qquad (32)$$

where

$$[\eta] = 9 \cdot 33 \times 10^{22} \propto^3 (\bar{r_o^2})^{3/2} \cdot \frac{1}{M} \left[Y/RT + 1 - W_{(p)} F_{(Y)} \right] \qquad (33)$$

and
$$k'' = \frac{\left[1 - W_{(p)} F_{(Y)} \right]^2}{2 \left[Y/RT + 1 - W_{(p)} F_{(Y)} \right]^2} \qquad (34)$$

Expressions for η_{sp}/c **and k'** : Equation (3) can be rewritten after expanding the exponential into a series;

$$\eta_r = \left[1 + \frac{X_1 Y}{RT} + \frac{1}{2!}\left(\frac{X_1 Y}{RT}\right)^2\right]\left[1 + X_1\left\{1 - W(p)\,F(Y)\right\}\right]$$

$$= 1 + X_1\left[Y/RT + 1 - W(p)\,F(Y)\right] + X_1^2\left(\frac{Y}{RT}\right)\left[\frac{Y}{2RT} + 1 - W(p)\,F(Y)\right]$$

or

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \qquad\qquad (35)$$

where $[\eta]$ is given by equation (33) and

$$k' = \frac{Y/RT\left[Y/2RT + 1 - W(p)\,F(Y)\right]}{\left[Y/RT + 1 - W(p)\,F(Y)\right]^2} \qquad\qquad (36)$$

Relation between k' and k": To deduce equation (8) in a general way, let $Y/RT = a$ and $\left[1 - W(p)\,F(Y)\right] = b$,

then $k' = \dfrac{a\left[\frac{a}{2} + b\right]}{[a+b]^2}$ and $k'' = \dfrac{b^2}{2[a+b]^2}$

and $k' + k'' = \dfrac{a^2 + 2ab + b^2}{2[a+b]^2} = \dfrac{1}{2}$,

in agreement with equation (8). It may be mentioned, however, that equation (8) is a mathematical necessity.

Deduction of Eirich - Riseman Relationship:- Another relationship which follows as a corollary to the present treatment is that due to Eirich and Riseman[8], which states that

$$k'[\eta]^2 = \alpha' + \sigma[\eta] \qquad\qquad (37)$$

Substituting the values of $[\eta]$ and k' from (33) and (36), and putting

$$H = 9 \cdot 33 \times 10^{22} \propto^3 / M \cdot (\overline{r_o^2})^{3/2} \tag{38}$$

$$k'[\eta]^2 = \frac{H^2 [a+b]^2 \cdot a [a/2 + b]}{[a+b]^2}$$

$$= aH [a+b - \frac{a}{2}] H ,$$

$$= Ha[\eta] - \frac{(aH)^2}{2} = \sigma [\eta] - \propto' , \tag{39}$$

since $H[a+b] = [\eta]$

Streeter and Boyer[43] experimentally verified equation (37) and Heller[22] obtained the value 0.53 and -0.12 for the slope and the intercept respectively for a sample of polystyrene (mol.wt. 370,000). It is seen from equation (39) that, assuming the value of σ to be 0.53, the value obtained for $\propto'$ is - 0.14, which, taking into account the possible errors involved in the determination of the slope and intercept, is in good agreement with the experimentally observed values.

Evaluation of $[Y/RT + 1]$: According to equation (34),

$$k'' = \frac{[1 - W(p) F(Y)]^2}{2[Y/RT + 1 - W(p) F(Y)]^2} .$$

It was found from equation (19), that the value of $W(p)$ for a natural rubber fraction with 6400 isoprene units is approximately 0.000045. For higher values of Z and other

stiffer chains $(c' > 2.01)$, the value of $W(p)$ would be still smaller. Further we have

$$F_{(Y)} = \frac{\sinh \beta' Y}{\sinh Y} , \qquad Y = f \frac{\lambda \lambda_2 \lambda_3}{2kT} ,$$

which has the property

$$F_{(Y)} = \beta'$$
$$Y \rightarrow 0$$
$$i.e. \ f \rightarrow 0$$

i.e. at zero rate of shear, $F_{(Y)}$ is equal to β' . It has already been pointed out that β' is a complicated function of Z, c' and of the concentration C also (at very high concentrations). Even if we assume that $\beta' \simeq Z$ i.e. the unit area behaves as if the whole chain were resisting shear, the value of

$$W_{(p)} F_{(Y)} \ll 1 \qquad \text{when } f \rightarrow 0$$

At higher concentrations where the coupling between the chains begins and becomes increasingly important, β' may increase so much that the above condition no longer holds. This probably explains why the viscosity of polymer solutions at low concentrations is shear independent i.e. k" is independent of $F(Y)$, and is increasingly dependent as concentration increases. For dilute solutions, however, where

$$W_{(p)} F_{(Y)} \ll 1 , \quad f \rightarrow 0$$

we can approximate

$$k'' = \frac{1}{2[\gamma/RT + 1]^2} \quad \text{or} \quad [\gamma/RT + 1] = \left(\frac{1}{2k''}\right)^{1/2} \tag{40}$$

This is an important relation as it gives the value of $[\gamma/RT + 1]$ from the actual experimental data.

Evaluation of ϕ and K: One can make use of equation (40) in the evaluation of the important parameters such as and K.   Generally, one observes that the value of k'' lies between 0.1 and 0.2 for good solvents indicating that the value of $[\gamma/RT + 1]$ varies from 2.23 to 1.58. Substituting these values as upper and lower limits in equation (33), one obtains

$$\left[\eta\right]_{\substack{f \to 0 \\ k''=0.2}} = 9.33 \times 10^{22} \times 1.58 \frac{(\overline{r^2})^{3/2}}{M} \tag{41a}$$

$$= 1.47 \times 10^{23} \frac{(\overline{r^2})^{3/2}}{M}$$

and

$$\left[\eta\right]_{\substack{f \to 0 \\ k''=0.1}} = 2.08 \times 10^{23} \frac{(\overline{r^2})^{3/2}}{M}, \tag{41b}$$

where $\left[\eta\right]_{f \to 0}$ is expressed in c.c./gm.   Converting these values into the practical unit e.g. decilitres/gm., 1.47 x 10^{21} and 2.08 x 10^{21} are obtained for the minimum and maximum values of ϕ .   This is in good agreement with Flory's data, where ϕ is found to be of the order 2.1 x 10^{21}.   However, it should be remembered that the value of ϕ varies from 1.39 to 3.9 x 10^{21} as found in the literature, depending upon the solvent and the temperature.

This is easily explained on the basis of the present treatment where it is shown that ϕ is a function of both the solvent, i.e. of γ and of the temperature.

Equation (33) can also be written as ($[\eta]$ in decilitres/gm.)

$$[\eta]_{f \to 0} = 9.33 \times 10^{22} \alpha^3 C'^3 / M_0^{3/2} \; M^{1/2} [\gamma/RT + 1]$$
$$= K \alpha^3 M^{1/2}, \tag{42}$$

which can be shown to be equivalent to equation (4), *i.e.*

$$[\eta] = KM^{\alpha} = KM^{1/2 + \alpha'}, \quad \{1 > \alpha > 1/2\}$$

Since Flory and Fox[17] have shown that $\alpha = \dfrac{d \log \alpha^3}{d \log M}$, α being given by Flory's equation

$$\alpha^5 - \alpha^3 = 2 C_M \psi_1 [1 - \theta/T] M^{1/2} \tag{43}$$

Equation (43) indicates that at $T = \theta$, $\alpha = 1$ and $\epsilon_{12} = 0$, giving

$$[\eta]_{\substack{f \to 0 \\ T = \theta}} = K_0 M^{1/2} \tag{44}$$

To illustrate the utility of equation (44), let us take an example.

For polyisobutylene[16,19] solution in benzene

$$\theta = 297\,^\circ K, \quad k'' \text{ at } 298\,^\circ K = 0.03, \quad i.e. \left[\frac{\gamma}{RT} + 1\right] = 4.08,$$

$$c' = 2.97 \times 10^{-8} \, cm. \quad ^{(16)}$$

and the average value of
M_0 for $-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 -$ is 28,

i.e. $M_0^{3/2} = 148.1$. Substituting these values
in equation (44) one obtains, $K_0 = 6.73 \times 10^{-4}$

The value of K_0 for this particular system at $T = \theta$
is 10.7 x 10^{-4} as given by Fox and Flory[16]. This suggests
that at $T = \theta$, the approximation $R_e = \left[\frac{2}{3}\,\overline{s^2}\right]^{1/2}$
is not correct. Let us put the other extreme value, viz.

$R_e = \left(\overline{s^2}\right)^{1/2}$. This would increase the value
of Ko by a factor of $\left(\frac{3}{2}\right)^{3/2} = 1.84$, giving $K_0 = 12.4 \times 10^{-4}$

This is in good agreement with the observed value, taking
into account the fact that near θ , k" becomes very
sensitive to temperature and we have used the value of k"
obtained at 298°K instead of 297°K, and also the
uncertainties in the evaluation of k". This incidentally
also points out that in bad solvents, where $\propto = 1$ and $R_e = \left(\overline{s^2}\right)^{1/2}$,
K is definitely different at θ than at any other
temperature as $\epsilon_{/2} = 0$ at $T = \theta$. This treatment
would have made it possible to evaluate M directly from the
viscosity measurements, were it not for the unfortunate fact
that for most good solvent-polymer systems θ is rather
low and in bad solvent at $T = \theta$, k'' has a positive value.
This abnormal behaviour, which cannot be explained on the
present treatment, prohibits the use of equation (44), in the

case of bad solvents, for the evaluation of M, under the •

conditions $T = \theta$ and $f = 0$ and hence an alternative method of

evaluating $\left[\frac{\gamma}{RT} + 1\right]$ is necessary.

An alternative for the evaluation of $\frac{\gamma}{R}$: Equation (33)

gives the value of

$$\left[\eta\right]_f = H\left[\frac{\gamma}{RT} + 1 - F(Y) W(p)\right] \qquad (33)$$

whereas, the value of $\left[\eta\right]_{f \to 0}$ as given by equation (42) is

$$\left[\eta\right]_{f \to 0} = H\left[\frac{\gamma}{RT} + 1\right] \qquad (42')$$

Equations (33) and (42) can be combined to give,

$$\left[\eta\right]_f = \left[\eta\right]_{f \to 0} \left[1 - \frac{W(p)\, F(Y)}{\left[\frac{\gamma}{RT} + 1\right]}\right] \qquad (45)$$

$$\text{where} \quad Y = \frac{f \lambda \lambda_2 \lambda_3}{2kT} = \frac{f\upsilon}{2kT}$$

If $\beta'Y > 1$, which is necessary if the flow is non-Newtonian,

and $Y < 1$, then one obtains

$$F(Y) = \frac{\sinh \beta'Y}{\sinh Y} = \frac{e^{\beta'Y}}{2Y} = \frac{e^{\beta' f \upsilon/2kT}}{2 f \upsilon/2kT}$$

Substituting the value of F(Y) in equation (45) and

rearranging, it gives

$$P = \frac{\left[\eta\right]_{f \to 0} - \left[\eta\right]_f}{\left[\eta\right]_{f \to 0}} = \frac{kT}{\upsilon} \cdot \frac{W(p)}{\left[\frac{\gamma}{RT} + 1\right]} \, e^{\beta' f \upsilon/2kT}$$

$$\text{or} \quad \log P = \log \frac{W(p)\, kT}{\left[\frac{\gamma}{RT} + 1\right]\upsilon} + \beta'\frac{f\upsilon}{2kT} \qquad (46)$$

A plot of the experimentally observed values of log P versus f will give $\log W_{(p)} kT / \vartheta [\gamma/_{RT} + 1]$ and $\beta' \vartheta /_{2kT}$ as the intercept and slope respectively.

Defining, $J = W_{(p)} \beta' /_2 [\gamma/_{RT} + 1]$

$$= [\text{Antilog of the intercept}] \cdot [\text{slope}]$$

one gets

$$\frac{1}{J} = \frac{2}{W_{(p)}\beta'} [\gamma/_{RT} + 1] \tag{47}$$

A second plot of $1/_J$ versus $1/_T$ would yield

$$\text{slope} = \frac{\gamma}{R} \cdot \frac{2}{W_{(p)}\beta'} \tag{48}$$

$$\text{and intercept} = \frac{2}{W_{(p)}\beta'}$$

giving $\quad \frac{\gamma}{R} = \quad$ slope/intercept.

Thus, the present treatment helps in the evaluation of K and ϕ from the concentration or the shear and temperature dependence of the viscosity of high polymer solutions. It also makes the technique an absolute method for the determination of molecular weight of polymers under certain restricted conditions of temperature and shear rate and therefore, has a definite advantage over the various hydrodynami treatments.

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SUMMARY AND CONCLUSIONS

1.   An expression for the relative viscosity η_r of dilute polymer solutions has been deduced on the basis of the "Theory of Rate Processes". The equation helps in making the technique of viscosity measurements an absolute method for the determination of molecular weights of polymers. It relates η_r to the concentration C.gms/ml., the temperature T, the shear rate f, the energies of activation for flow of a polymer segment and a solvent molecule and the probability $W_{(p)}$ of the co-ordinated movement of p segments in the direction of flow. Thus,

$$\eta_r = e^{X_1 \gamma /RT} \left[1 + X_1 \left\{ 1 - W_{(p)} F_{(\gamma)} \right\} \right]$$

with $\quad X_1 = 9 \cdot 33 \times 10^{22} \alpha^3 (\bar{r}_0^2)^{3/2} \dfrac{c}{M}$, $\quad W_{(p)} = e^{-0 \cdot 00775 \, c^3 \alpha^3 z^{1/2}}$,

and $\quad F_{(\gamma)} = \dfrac{\sinh \beta' \gamma}{\sinh \gamma}$ $\quad$ with $\quad \gamma = f \dfrac{\lambda \lambda_2 \lambda_3}{2kT}$

      The equation is based on the following assumptions.

      (a) The solution is dilute so that there are no intermolecular entanglements between the molecules. The polymer molecules are thus randomly distributed and flow individually.

      (b) The polymer molecules have random coil characteristics. The density of polymer in space has been assumed to be given by $\rho_{(r)} = \rho_0 e^{-\beta^2 r^2}$, where r is the

the distance from the centre of gravity of a polymer molecule.

(c) The solvent molecules in the solution have been divided into three categories, namely, those which flow freely, those which flow as if they were bound to the polymer coil and those which exhibit intermediate characteristics. The freely flowing solvent molecules contribute individually to the fluidity. The solvent molecules bound with the polymer chain contribute in a manner as if they were a part of the polymer chain. The contribution to fluidity of such molecules as well as that of the polymer chains themselves is very small, since only a small fraction of the total number of jumps of such polymer-bound solvent units contribute towards the fluidity of the solution. The magnitude of this fluidity is determined by the probability $W(p)$, that all the segments of a polymer chain have a net co-ordinated movement in the forward direction.

(d) The volume of a randomly coiled polymer chain which determines the intrinsic viscosity of a polymer solution has been assumed to be equal to that of an "Equivalent sphere" with a radius $R_e = \left[\frac{2}{3} \bar{S^2} \right]^{1/2}$,

where $\left[\bar{S^2} \right]^{1/2}$ is the root mean square distance of the segments from the centre of gravity of a polymer molecule.

(e) The average standard free energy of activation for a unit of flow of either species has been assumed to be given by

$$E = x_1 \epsilon_1 + x_2 \epsilon_2 - x_1 \epsilon_{12}$$

where x and ϵ refer to the volume fraction and the standard free energy of activation for flow of the species 1 (polymer segment) and 2 (solvent molecule) respectively and $x_1 \epsilon_{12}$ is the contribution due to the non-ideality of the mixture.

(f) It has been assumed that the segments of a polymer chain each having an area $\lambda_2 \lambda_3$ on which the shearing stress acts, behave as if they are resisting shear on a much larger (β' times larger) area than their own or that of a solvent molecule. No assumption has been made regarding the magnitude of β' except that for a nòn-entangled chain its value does not exceed that of the number of links in the chain i.e. Z.

2(a) Several practical applications of the expression for η_r have been given. Thus, theoretical expressions have been obtained for the hitherto empirical constants k' and k" in the series:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c + \cdots$$

and

$$\frac{\log \eta_r}{c} = [\eta] - k''[\eta]^2 c + \cdots$$

where

$$[\eta] = 9.33 \times 10^{22} \frac{(\overline{r^2})^{3/2}}{M} \left[Y/RT + 1 - W(\phi) F(Y) \right],$$

$$k' = \frac{Y/RT \left[Y/RT + 1 - W(\phi) F(Y) \right]}{\left[Y/RT + 1 - W(\phi) F(Y) \right]^2}$$

and

$$k'' = \frac{[1 - W_{(p)} F_{(\gamma)}]^2}{2 [\gamma/RT + 1 - W_{(p)} F_{(\gamma)}]^2}$$

It has been shown that at $T = \Theta$ and as $f \to 0$

$$[\eta]_{\substack{f \to 0 \\ T = \Theta}} = 9.33 \times 10^{22} \left(\frac{1}{2k}\right)^{1/2} \left(\frac{\overline{r_0^2}}{M}\right)^{3/2}$$

$$= K_0 M^{1/2}$$

Thus suggesting an independent method for the evaluation of the Flory-Fox constants ϕ and K_0. This helps in making the technique of viscosity an absolute method for the determination of molecular weights of the polymers.

(b)   It can be easily shown that

$$k'[\eta]^2 = \sigma [\eta] - \sigma^2/2 \quad,$$

where $\sigma = 9.33 \times 10^{22} \frac{\alpha^3}{M} (\overline{r_0^2})^{3/2} \frac{\gamma}{RT}$,

thereby deducing the Eirich-Riseman relationship and correlating its slope and intercept.

(c) Since at very low concentration k'' tends to become positive due to hitherto unknown reasons, its value cannot be exploited to evaluate γ. An alternate method of its evaluation has been suggested by making use of the shear dependence of the intrinsic viscosity $[\eta]$.

In conclusion, it can be said that the present treatment successfully explains the behaviour of certain empirically observed constants such as ϕ , K , σ and α' . It also furnishes a theoretical back-ground to the constants k' and k" and reveals their importance in making the method an absolute one for molecular weight determination. As regards the weak points of the treatment, mention may be made of the unexplained nature and magnitude of β' , an arbitrary assumption about the value of the radius of an equivalent sphere. Further no attempt has been made to specify the type of averages to be used while using molecularly polydisperse polymer chains.

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