Viscosities of Solutions of Polyvinyl Chloride

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Introduction

In connection with a study of the electrical properties of fractionated polyvinyl chloride,[1] the viscosity in solution was used as a measure of relative molecular weights.[2] The purpose of this paper is to present a systematic study of the viscosities of solutions of polyvinyl chloride, in which the effects of temperature, rate of shear, concentration, time and solvent were investigated. Vinyl chloride polymers prepared in different ways were investigated, and results on both fractionated and unfractionated samples are included.

It is convenient to use the relative viscosity η_r in discussing the viscosities of these solutions; this quantity is defined as the ratio of the viscosity of a solution η to that of the solvent η_0 at the same temperature. If $\ln \eta_r$ is plotted against concentration, a curve is obtained which approaches linearity at low concentrations. The limiting slope of this curve at zero concentration is $[\eta]$, the "intrinsic viscosity" introduced by Kraemer,[3] if concentrations are expressed in grams of solute per 100 cc. of solution. For linear polymers of high degree of polymerization, the intrinsic viscosity is proportional to molecular weight.[2-5]

In this paper, we shall express the concentration c in monomoles (Staudinger's "Grundmole") per liter, so that c equals the number of equivalents of monomeric units per liter, and is independent of degree of polymerization, branching or polydispersion. The logarithm of the relative viscosity approaches zero as the concentration approaches zero, but the ratio $(\ln \eta_r)/c$ approaches a constant limiting value. We define λ, the equivalent viscosity, as the ratio $(\ln \eta_r)/c$ because it measures the viscosity increment per equivalent of monomer. At low concentrations, λ is linear in concentration

$$\lambda = (\ln \eta_r)/c = \lambda_0 - \alpha c \qquad (1)$$

and λ_0, the limiting equivalent viscosity for zero concentration, is given by the intercept at $c = 0$ on the λ-c plot. Obviously, λ_0 is proportional to $[\eta]$.

We have found that the constant α of Eq. (1) is proportional to λ_0^2 for vinyl chloride polymers, permitting (1) to be rewritten in the form

$$\lambda = \lambda_0(1 - \beta\lambda_0 c) \qquad (2)$$

where *the constant β is independent of the molecular weight of the polyvinyl chloride.* In other words, *one determination of viscosity is sufficient to determine λ_0* and hence the molecular weight M, if the constant K in the Staudinger equation

$$\lambda_0 = KM \qquad (3)$$

is known. Furthermore, since $\lambda_0 c = K(Mc)$ is proportional to φ, the volume concentration of the solute, we conclude that (2) is the beginning of a power expansion of a function

$$\ln \eta_r = A\varphi f(\varphi) \qquad (4)$$

This empirical observation should help in the development of the theory of the viscosity of these solutions, in that it establishes the significant variables.

Finally, we present a preliminary value $K = 7 \times 10^{-5}$ for the constant of Eq. (3). This value is based on two ultracentrifuge runs and one diffusion experiment made by Dr. A. Rothen and Dr. T. Shedlovsky of the Rockefeller Institute. We take this opportunity to express our gratitude for their coöperation.

Experimental

Materials.—Two fractionated samples of polyviny chloride obtained from a commercial polymer (Polymer L-38) were used in the detailed study of experimental conditions. The high molecular weight fraction is designated as 7.1 and the fraction of lower molecular weight as A3.5. Details of their preparation have already been given.[1]

Data for a number of unfractionated polymers are also included. We are indebted to the B. F. Goodrich Company for the series I–VI, which were polymerized under different controlled conditions: (I) 33 g. of vinyl chloride and 66 g. of methyl alcohol were sealed in Pyrex tubes. The tubes were placed horizontally to half immersion in a waterbath at 25°, and exposed to the radiation from a Uviarc lamp for two days; average yield 35%. (II) Undiluted vinyl chloride was allowed to polymerize under the same conditions as I; average yield 18%. (III) 33 g. of vinyl chloride, 66 g. of methyl alcohol and 0.5 g. of benzoyl peroxide were sealed in glass tubes and tumbled end-over-end in a water-bath at 30° for four days; average yield 64%. (IV) 100 g. of vinyl chloride and 0.5 g. of benzoyl peroxide were polymerized under the same conditions as II;

(1) Fuoss, THIS JOURNAL, **63**, 2401 (1941).

(2) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

(3) Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

(4) Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939).

(5) Flory and Stickney, *ibid.*, **62**, 3032 (1940).

average yield 32%. The reaction was interrupted at this point, in order to obtain a powdered polymer, rather than the hard, horny lumps which appear when the reaction is allowed to approach completion. (V) The same reaction mixture as for III was polymerized in Pyrex tubes at 60°; average yield 67%. (VI) 100 g. of vinyl chloride and 0.5 g. of benzoyl peroxide were kept at 60° in a lead container until the reaction was 39% complete. The vinyl chloride used in preparing samples I–VI contained a trace of water.

Samples VII and VIII were polymers of high molecular weight (XS168 and A807) which the Dow Chemical Company kindly gave us.

The solvents used in the viscosity determinations were purified by distillation; the middle fraction, about 60%, was retained. Cyclohexanone and methyl amyl ketone were distilled at atmospheric pressure; nitrobenzene, mesityl oxide and chlorobenzene were distilled at reduced pressure. Solvent viscosity, which varied slightly (ca. 0.1%) for different batches, was checked frequently.

Apparatus.—Viscosities were measured in Bingham[6] type viscometers. Four viscometers in all were used, each having a flow volume of about 4 cc. and capillary length of 10 cm. Viscometers 50 and 80 had capillaries with radii of about 0.01 cm. as calculated from time of flow of water. For viscometers 1 and 2 the capillary radii were about 0.014 cm., measured by plug gages before the viscometers were built.

Viscosities were calculated using the formula

$$\eta = Cpt - c'\rho/t \qquad (5)$$

where η is the viscosity in poises, p is the driving pressure in centimeters of water at 25°, t is the time of flow in seconds, ρ is the density of the liquid measured and C and c' are constants of the viscometer. The constants were obtained for each viscometer by measuring the time of flow of water at a series of pressures, using Bingham's[7] data for the viscosity of water at 20° (viscometers 1 and 2) and at 40° (viscometers 50 and 80). Knibbs[8] method was used for the determination of the kinetic energy constant c'. It might be pointed out that the relative viscosity, in which we are primarily interested, is practically independent of viscometer constants as long as the kinetic energy correction is small. The kinetic energy term was always less than 1% and usually less than 0.5%.

Between runs, the viscometers were cleaned with successive rinses of solvent, alcohol, and ether; then dried with air which had been filtered through lambs' wool. All solutions and wash liquids which entered the viscometers were filtered through sintered glass. Occasionally (about once a week) the viscometers were filled with chrome-sulfuric cleaning solution and allowed to stand for a day.

The pressure system comprised a steel tank of about 40 liters capacity (packed in excelsior to lag the effects of changes in room temperature), a water manometer reading from 60 to 150 cm., air filters of lambs' wool and a stopcock system for controlling the direction of flow.

Times of flow were measured (to 0.02 second) with an electric timer (Precision Scientific Co.), and were always

kept greater than four hundred seconds, except in some of the higher pressure calibration runs.

The constant temperature oil-bath consisted of a large unsilvered Dewar flask, fitted with a motor stirrer, cooling coil, toluene–mercury thermo-regulator and thyratron controlled heating coil. Temperatures were held constant to ±0.02°.

Solutions.—In order to eliminate the difficulty in weighing due to static charges, the polymers were pressed into pills. A pill was then weighed and placed in a weighed, ground-glass capped Erlenmeyer flask containing a stirring rod. After crushing the pill with the rod, which was left in the flask, solvent was added. The mixture was placed in an oven (at 110° ± 5°) and stirred by occasional gentle shaking until the polymer dissolved. After cooling, the flask was weighed back. Concentrations were calculated in terms of monomoles of polyvinyl chloride per liter of solution. In calculating volume of solution from weight, it was assumed that the density of the solution was the same as that of the solvent. The densities at 25° of cyclohexanone (0.9412), nitrobenzene (1.198) and chlorobenzene (1.101) were calculated from "I. C. T." formulas. The density of methyl amyl ketone (0.8127) was interpolated from the data of R. H. Cole.[9] Measurements were made of the density of mesityl oxide at 25° (0.8500), 35° (0.8406) and 45° (0.8312).

Results and Discussion

Variation of Viscosity with Rate of Flow.— The viscosity of the solutions measured increased with increasing time of flow.[3,10] Each solution was therefore measured at several pressures in the range 60 to 150 cm. Viscosities were plotted against pressure and the resulting straight line was extrapolated to $p = 0$. The extrapolated value was used for all subsequent calculations. If expressed on a percentage basis, the decrease of viscosity with increasing pressure is approximately the same for different solvents and different polymers, but increases with concentration, as is shown in Fig. 1, where we have plotted $100\ \Delta\eta/\eta\Delta p$, the percentage change of viscosity per centimeter water head, against concentration. The line given is the average of measurements in viscometers 1 and 2 on many solutions and, within the experimental error (which is rather large due to the fact that the effect is small), seems to hold for all solutions measured in these viscometers at 25°. For a given viscometer, or series of similar viscometers, a plot similar to Fig. 1 can be made, from which it is possible to interpolate corrections for change of viscosity with rate of shear which will be of ample accuracy. Once having "calibrated" a viscometer in this manner, the

(6) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 76.

(7) Ref. 6, p. 340.

(8) Ref. 6, p. 18.

(9) R. H. Cole, *J. Chem. Phys.*, **9**, 251 (1941).

(10) Mark, *J. Appl. Phys.*, **12**, 41 (1941).

time-consuming task of measuring each solution at several pressures can be eliminated.
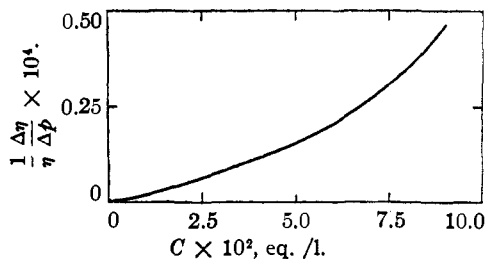

Fig. 1.—Correction function for rate of shear in capillary viscometer.

Viscosity in Various Solvents.—The fractionated sample 7.1 was used in comparing different solvents. The experimental results are shown in Fig. 2, where $\lambda = (\ln \eta_r)/c$ is plotted against c. It will be seen that all of the points conform with Eq. (1); the radius of each circle in the figure corresponds to an error of 0.1% in relative viscosity. The constants of the equation are given in Table I. For polymer A3.5 in cyclohexanone, we found

$$\lambda = 1.95 - 0.56 \, c$$

It will be noted that the variation of λ_0 from solvent to solvent is not very large; the solvents listed are, however, somewhat similar.

Table I

Polymer 7.1 in Various Solvents at 25°

Solvent	$100\eta_0$	λ_0	α
Cyclohexanone	2.000	7.19	6.3
Nitrobenzene	1.843	6.07	3.3
Mesityl oxide	0.574	6.77	6.7
Methyl amyl ketone	0.746	6.71	4.2

Huggins[11] has derived a theoretical formula connecting λ_0 and n, the number of units in a randomly kinked linear polymer. His equation, for the case of tetrahedral bond angles, low concentration and low velocity gradient, reduces to

$$\lambda_0 = 5.88 \times 10^{20} l^2 a n \qquad (6)$$

If we let $l = 1.54 \times 10^{-8}$, the C–C distance in paraffin hydrocarbons and use, say, one Ångström unit for a, the equivalent radius of the chain link, we find $n = 5000$ using the round value $\lambda_0 = 7$. This corresponds to a polymerization degree of 2500 (two carbon atoms per monomer unit) and a molecular weight of 156,000. Considering the uncertainties in the dimensions and the crudity of the model assumed above for $(CH_2CHCl)_n$, this figure is in excellent agreement with the ultra-

(11) Huggins. *J. Phys. Chem.*, **43**, 455 (1939).

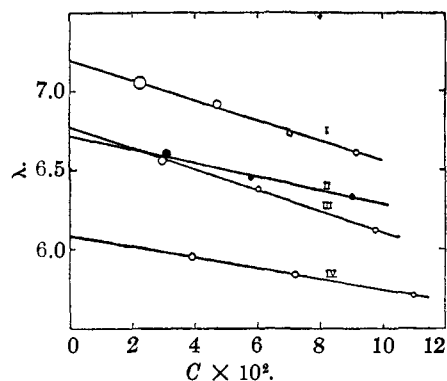centrifuge and diffusion data which will be presented later.

Fig. 2.—Viscosities of PViCl No. 7.1 in cyclohexanone .(I), methylamyl ketone (II), mesityl oxide (III) and nitrobenzene (IV).

Stability of Solution.—In general, the viscosities of solvents and solutions remained essentially constant with time. For example, solutions of A3.5 and 7.1 in cyclohexanone were allowed to stand for about sixty days, with occasional measurement. Weights were checked to assure that no change in concentration by evaporation had occurred. The viscosity decreased at a rate of about 0.01% per day. A solution of 7.1 in methyl amyl ketone, allowed to stand forty days, showed an *increase* in viscosity of $0.01_5\%$ per day.

It is of interest to note that a methyl amyl ketone solution of a commercial polymer (Dow 105) which had *not* been dissolved and reprecipitated showed a much greater change with time. In this solution, the viscosity increased at an original rate of about 0.2% per day. After 140 days the viscosity had increased by 10% and was still increasing, although at a much slower rate than initially. If we assume that the "as received" polymer consisted of "clumps" which slowly break up, untangle and elongate, we have an explanation for this abnormally large change with time. In the case of the fractionated polymers, where the effect was much smaller (or absent) it seems evident that the dissolving and re-precipitating allowed this "unclumping" to occur before the viscometric solutions were made up.

Mesityl oxide was not entirely satisfactory as a solvent, due to the fact that the solvent viscosity increased about 0.25% per day. Solution viscosities were of course corrected for this change.

Methyl amyl ketone although suitable for most of the polymers considered in this paper, is unsatisfactory as a general solvent for polyvinyl chlo-

ride because polymers of higher molecular weight are insoluble in it.

An attempt was made to include chlorobenzene in the list of solvents studied, but the solutions were highly unstable, the viscosity decreasing as much as 2% in one day. Since the value of solvent viscosity (0.757 cps. at 25°) agrees well with other experimenters' results,[5,12] we must conclude that there is some unexplained interaction between polyvinyl chloride and chlorobenzene, because Flory and Stickney find it a satisfactory solvent for decamethylene adipate esters. After correcting as well as possible for the very rapid change with time, we get a limiting equivalent viscosity of about 3.5. The disparity between 3.5 and the λ_0 values of Table I, if real, suggests that λ_0 does depend on the structure of the solvent. More data are needed before any general conclusions may be drawn.

After considering the solvents investigated with respect to solvent power, ease of purification, consistency of results and stability of solutions, we believe that cyclohexanone is the most satisfactory solvent for general viscometric work on solutions of polyvinyl chloride.
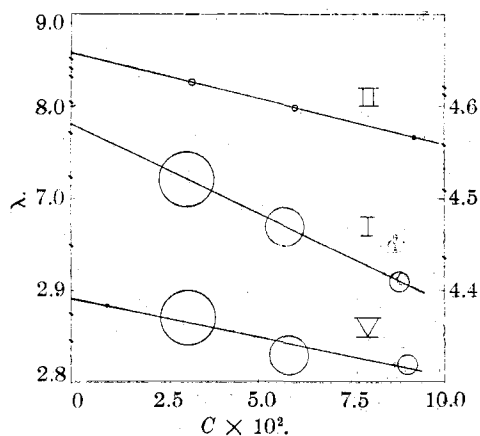

Fig. 3.—Dependence of λ on C: ordinates for II, upper left; for I, right; for V, lower left.

Effect of Temperature.—The viscosity of methyl amyl ketone was measured at various temperatures in the range 25 to 80°. The solvent viscosity decreases 1.2% per 1° (calculated between 25 and 45°). A plot of log η vs. $1/T$ is linear and gives $Q = 2.36$ kcal. (25–80°). For cyclohexanone, in the range 25–55°, $Q = 3.40$ kcal.; the viscosity decreases 1.8% per 1° between 25 and 45°.

(12) Meyer and Mylius. Z. physik. Chem., **95**. 366 (1920), η at 25°, 0.756 (interpolated).

The variation of solution viscosity with temperature was studied for two solutions of 7.1 and one solution of A3.5, all in cyclohexanone. Measurements were made at 25 and 45°. Due to change in density, there is a slight change in concentration with temperature. The results are summarized in Table II.

TABLE II

TEMPERATURE DEPENDENCE OF VISCOSITY

Polymer	t, °C.	$c \times 10^2$	100η	$100 \Delta\eta/\eta\Delta T$	λ
A3.5	25	8.33	2.346	−1.9%	1.88
A3.5	45	8.18	1.613		1.79
7.1	25	9.18	3.680	−2.0%	6.61
7.1	45	9.01	2.467		6.34
7.1	25	2.25	2.340	−1.8%	7.02
7.1	45	2.21	1.610		6.56

A glance at the table shows that to a first approximation the change in the viscosity of the solutions is the same as that in the solvent alone. A slight decrease of equivalent viscosity with increasing temperature of the order of 0.2–0.3% per degree is observed.

Viscosity of Different Polymers in Cyclohexanone at 25°.—In Table III is given a summary of the data for the unfractionated polymers, and in Fig. 3 λ–c plots for several examples are shown. The circles are drawn to correspond to 0.1% error in relative viscosity; the ordinate scale for I and V is much magnified compared to that of Fig. 2. The relative viscosities (η/η_0) range from 1.092 to 2.023; that is, depending on concentration and polymer, viscosity increases from about 10 to 100% were observed. A description of each sample, using obvious abbreviations, is given at the head of each group of data.

TABLE III

VISCOSITIES OF DIFFERENT POLYMERS IN CYCLOHEXANONE AT 25°

$100c$	η_r	λ	$100c$	η_r	λ
I.	30°, U. V., 2:1 MeOH		IV.	30°, Bz$_2$O$_2$	
3.06	1.149	4.52	3.12	1.278	7.68
5.70	1.290	4.47	5.81	1.555	7.60
8.78	1.473	4.41	8.94	1.927	7.34
II.	30°, U. V.		V.	60°, Bz$_2$O$_2$, 2:1 MeOH	
3.20	1.303	8.26	3.12	1.094	2.87
5.98	1.612	7.98	5.83	1.179	2.83
9.18	2.023	7.67	9.00	1.289	2.82
III.	30°, Bz$_2$O$_2$, 2:1 MeOH		VI.	60°, Bz$_2$O$_2$	
2.79	1.125	4.21	3.05	1.092	2.89
5.70	1.267	4.13	5.82	1.181	2.85
9.00	1.435	4.01	9.04	1.295	2.85

If we assume equal degrees of branching for these polymers, some interesting conclusions

about the polymerization reaction can be drawn. The low temperature polymerization in the pure polymer gives the longest chains, regardless of whether the chain reaction is initiated by ultra-violet or peroxide catalyst. If the monomer is diluted with an inert solvent, some of the chains terminate on solvent molecules by a deactivating mechanism, and the molecular weight is cut to about one-half. At the higher temperature, one would expect shorter chains on the average, because more chains would be growing per unit time than at the lower temperature and the competition for monomer would be greater. We do find a lower equivalent viscosity, but both diluted and undiluted vinyl chloride give about the same result. But the two reactions were stopped at different stages of completion, and VI was carried out in lead instead of glass as were the others, so no direct comparison is possible. Also the high temperature reaction is probably complicated by branching much more than the lower, and it is emphatically unsafe to argue relative molecular weights from equivalent viscosities of compounds of different structures.

An Empirical Viscosity Equation.—After a number of data had been collected, a parallelism between λ_0 and α of Eq. (1) was noted. In Table IV is given a summary of the results for a number of polymers in cyclohexanone at $25°$, where the constants given are for the equation

$$\lambda = \lambda_0(1 - \gamma c) \tag{7}$$

TABLE IV

VISCOSITY CONSTANTS FOR DIFFERENT POLYMERS

Polymer	λ_0	γ	Polymer	λ_0	γ
I	4.58	0.41	VI	2.90	0.21
II	8.57	1.14	VII	10.48	1.43
III	4.30	0.71	VIII	24.4	3.4
IV	8.13	1.09	7.1	7.19	0.88
V	2.89	0.28	A3.5	1.95	0.29

It will be seen that γ increases as λ_0 increases and, as is shown in Fig. 4, the increase is linear within the experimental error. This result shows that we may write (1) in the form

$$\lambda = \lambda_0(1 - \beta\lambda_0 c) \tag{2}$$

where $\beta = 0.14$ is a constant, *independent of the molecular weight of the polyvinyl chloride.*

This result has considerable practical significance, because it means that λ_0 can be determined by a single viscosity determination, and the tedious work of making measurements at a series of concentrations and extrapolating the results to zero concentration is eliminated. For low con-
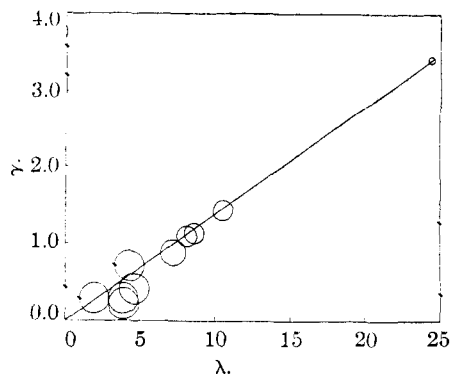

Fig. 4.—Derivation of constant coefficient in viscosity equation.

centrations (less than about 5 g. of polymer per liter), the quadratic is most simply solved by successive approximations. To first approximation

$$\lambda_0' = \lambda/(1 - \beta\lambda c) \tag{8}$$

and to second approximation

$$\lambda_0'' = \lambda/(1 - \beta\lambda_0'c) \tag{9}$$

This scheme is rapidly convergent for the range of variables considered here.

Since λ_0 is proportional to molecular weight, $c\lambda_0$ is proportional to φ, the volume fraction of solute. If we rewrite (2) in terms of φ, we find the simple form

$$\ln \eta_r = k\varphi(1 - k'\varphi) \tag{10}$$

which suggests that (10) is the beginning of a power expansion of $\ln \eta_r$ in terms of φ. Einstein[13] in 1906 used volume concentration in his theoretical treatment of viscosity of suspensions, arguing that it was the relative volume of suspended particles rather than their number, which was the fundamental independent variable. Since $\ln \eta_r$ in general shows less curvature than $(\eta_r - 1)$ against concentration, the general viscosity formula for solutes of high molecular weight is therefore probably of the form

$$\ln \eta_r = A\varphi f(\varphi)$$

Absolute Molecular Weights.—A solution of polymer 7.1 in methyl amyl ketone containing 0.0759 monomole per kilogram (0.475 wt. %) was investigated in the ultracentrifuge and in the diffusion apparatus at the Rockefeller Institute in New York. In Fig. 5a is given a plot of X_m against $1/\sqrt{t}$ (time in hours), where X_m is the height of the peak in the schlieren patterns[14] obtained in the diffusion experiment. From the slope of this line and the area under the schlieren

(13) Einstein, *Ann. Physik*, (4) **19**, 289 (1906).
(14) Longsworth, *Annals N. Y. Acad. Sci.*, **41**, 267 (1941).
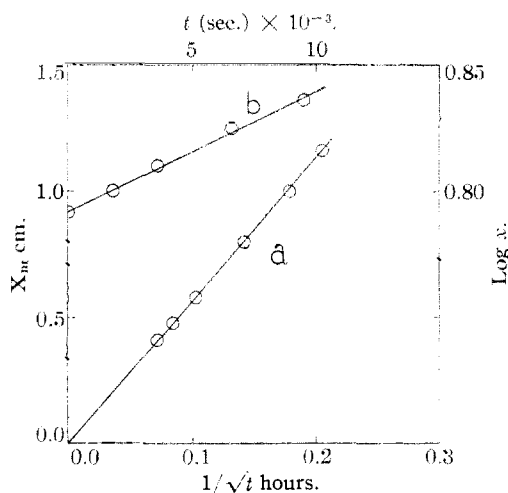
Fig. 5.—Test plots for centrifuge (b) and diffusion (a) runs.

curve, the diffusion constant D is found to be 1.74 $\times$ 10^{-7}. The temperature was 20°. In Fig. 5b, the test plot for the ultracentrifuge[15] run is shown, where log x is the distance from the center of rotation to the sedimentation boundary. The speed was 57,600 r. p. m. The sedimentation constant at 23.2° for the main component of 7.1 was found to be 3.19 $\times$ 10^{-13}. In order to determine the effect of concentration, a second run was made at one-half the above concentration. A value of $S = 3.28 \times 10^{-13}$ was found at 19.4°. Correcting the two values to 20°, using the known viscosity and density coefficients of the solvent, we obtain $S(c_1) = 3.05 \times 10^{-13}$ and $S(c_1/2) = 3.30 \times 10^{-13}$. The friction ratio calculated from the sedimentation and diffusion constants is 3.5, which corresponds to an axis ratio of the order of 100:1 for the ellipsoid which would be hydrodynamically equivalent to the polyvinyl chloride molecule.

If we assume that the ratio of sedimentation and diffusion constants is independent of concentration, we may calculate the molecular weight, M, from the relationship[16]

$$M = RTS/D(1 - v\rho) \qquad (11)$$

where v is specific volume of the solute and ρ is the density of the solvent. We find for polymer 7.1, using $D_{20} = 1.74 \times 10^{-7}$ and $S_{20} = 3.05 \times 10^{-13}$,

(15) Bauer and Pickels in T. Svedberg. "The Ultracentrifuge." Oxford. 1939.
(16) For a review containing an excellent summary of these methods, see Oncley, *Annals N. Y. Acad. Sci.*, 41, 121 (1941).

$M = 102,000$. In cyclohexanone at 25° we found $\lambda_0 = 7.19$. Combining these results, we have finally

$$\lambda_0/M = 7 \times 10^{-5} \qquad (12)$$

as a preliminary value for the Staudinger constant for vinyl chloride polymers. Further work will, of course, be necessary before a more precise value can be given; this should include absolute determinations on samples from different sources, fractionated using different temperatures and combinations of solvents. Tentatively, Eq. (12) may be used to calculate weight-average molecular weights of polyvinyl chloride, subject to the assumption that they have the same structure as the polymer used in our present work.

Summary

1. The viscosities of a number of polyvinyl chloride samples, fractionated and polydisperse, were studied as a function of concentration, temperature, rate of shear and solvent.

2. The equivalent viscosity is a linear function of concentration. It does not vary much among the solvents nitrobenzene, mesityl oxide, cyclohexanone and methyl amyl ketone, and decreases only slightly with increasing temperature.

3. The absolute viscosity of solutions of polyvinyl chloride decreases with increasing pressure; this effect must be eliminated by extrapolation to zero pressure or by an empirical correction formula.

4. An empirical formula is derived which permits determination of the limiting equivalent viscosity λ_0 for zero concentration from a single viscosity measurement at a finite concentration of polyvinyl chloride.

5. A fractionated sample which has an equivalent viscosity of 7.2 in cyclohexanone at 25° was found to have a molecular weight of 102,000, based on values of 3.05×10^{-13} for the sedimentation constant at 20° and of 1.74×10^{-7} for the diffusion constant at 20° in 0.475% solution in methyl amyl ketone. Assuming the validity of the Staudinger equation, these data give the preliminary result $\lambda_0 = 7 \times 10^{-5} M$ for vinyl chloride polymers.