TABLE I

THE DENSITIES, AT 25°, OF SOLUTIONS OF THREE PROTEINS AND THEIR APPARENT OR PARTIAL SPECIFIC VOLUMES, $\phi = \bar{V}$

Protein	%	Density	$\phi = \bar{V}$
Ovalbumin	0	0.997074	0
	0.02945	0.997149	0.747
	.09707	.997319	.7493
	.14874	.997451	.7480
	.24300	.997691	.7478
	.24803	.997704	.7475
	.36045	.997990	.7477
	.50339	.998350	.7483
Bovine serum albumin	0	0.997074	0
	0.24543	0.997726	0.7346
	.42612	.998213	.7345
	.55264	.998586	.7335
	.55923	.998678	.7344
	.70535	.998969	.7334
	.82661	.999279	.7352
Bovine γ-globulin	0	1.018684	0
	0.06326	1.018855	0.7217
	.06818	1.018869	.7202
	.1390	1.019061	.7204
	.1544	1.019104	.7197
	.1762	1.019163	.7199
	.1992	1.019227	.7191
	.2609	1.019393	.7198
	.2949	1.019487	.7194

nents are to be kept constant. It can be readily shown that if ϕ does not vary with the solute concentration, as in the examples given above, $\bar{V}$ and ϕ have the same value. A comparison of our results with those of other workers is made in Table II. Pedersen's (1945) values are described as "tentative."

TABLE II

COMPARISON OF VALUES OF SPECIFIC VOLUMES OF PROTEINS OBTAINED BY DIFFERENT WORKERS

Protein	This paper (av.) 25°	Koenig[7] 20°	Pedersen[8] 20°	Svedberg and Pedersen[9] 20°
Ovalbumin (crystalline)	0.747$_9$	...	...	0.749
Bovine serum albumin (crystalline)	.734$_3$	0.730	0.736	...
Bovine γ-globulin	.720$_0$	.725	.732	...

In addition to the work of Lamb and Lee[10] and of Geffcken, Beckmann and Kruis[11] on the magnetic float method for determining densities, previously referred to in this series of papers, mention should be made of the interesting use of the method by Hall and collaborators.[12]

The authors are indebted to Elaine Lackman, and Grace Peters for aid in making the density measurements.

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(7) V. L. Koenig, *Arch. Biochem.*, **25**, 241 (1951).

(8) K. O. Pedersen, "Ultracentrifugal Studies on Serum and Serum Proteins," Almquist and Wiksells Boktryckeri A B, Uppsala, 1945.

(9) T. Svedberg and K. O. Pedersen, "Ultracentrifuge," Clarendon Press, Oxford, 1940.

(10) A. B. Lamb and F. E. Lee, THIS JOURNAL, **35**, 1666 (1913).

(11) W. Geffcken, C. Beckmann and A. Kruis, *Z. physik Chem.*, **B20**, 398 (1933).

(12) N. F. Hall and T. O. Jones, THIS JOURNAL, **58**, 1915 (1936); N. F. Hall and O. Alexander, *ibid.*, **62**, 3455 (1940).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Molecular Dimensions of Cellulose Triesters[1]

BY LEO MANDELKERN AND PAUL J. FLORY

RECEIVED DECEMBER 5, 1951

The unperturbed end-to-end dimension ratios $(\overline{r_0^2}/M)^{1/2}$ for two cellulose triesters, cellulose tributyrate and cellulose tricaprylate have been determined from intrinsic viscosity measurements in γ-phenylpropyl alcohol, in dimethylformamide and in a 3:1 mixture of dodecane and tetralin. The measurements were carried out in each case at the characteristic temperature Θ for ideal behavior of the polymer–solvent system. Several fractions of each polymer were used and the molecular weights were determined osmotically. $K = [\eta]_\theta/M^{1/2}$ is independent of M in accordance with previously published results, but not independent of temperature; for cellulose tributyrate K decreases rather strongly with increasing temperature. The values of $(\overline{r_0^2}/M)^{1/2}$ calculated from K indicate that these esters are only two to three times more extended than they would be if rotation about the interunit ether linkages were completely unhindered. Thus, there appears to be no basis for the alleged rod-like extension of the cellulose chain.

Introduction

Deduction of characteristic dimensions of linear polymer molecules from appropriate solution viscosity measurements has been demonstrated by a number of recent investigations.[2-4] The following relations are employed to interpret the intrinsic viscosity results

$$[\eta] = KM^{1/2}\alpha^3 \quad (1)$$

$$K = \Phi(\overline{r_0^2}/M)^{3/2} \quad (2)$$

$$\alpha^5 - \alpha^3 = 2\psi_1 C_M (1 - \Theta/T)M^{1/2} \quad (3)$$

where $(\overline{r_0^2})^{1/2}$ is the root-mean-square distance from beginning to end of the chain *in the absence of perturbations due to interactions between remotely connected segments.* The actual root-mean-square distance $(\overline{r^2})^{1/2}$ exceeds this unperturbed distance in a particular solvent at a given temperature by the factor α. K is a parameter characteristic of the polymer and of the temperature but independent of the solvent; since Φ appears to be a universal constant, the same for all polymers in all solvents

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(1) The work reported in this paper comprises a part of a program of research on the physical structure and properties of cellulose derivatives supported by the Allegany Ballistics Laboratory, Cumberland, Maryland, an establishment owned by the United States Navy and operated by the Hercules Powder Company under Contract NOrd 10431.

(2) T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1909 (1951).

(3) T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1915 (1951).

(4) H. L. Wagner and P. J. Flory, *ibid.*, **74**, 195 (1952).

at any temperature, the value of $\overline{r_0^2}$ can be obtained from an experimental determination of K. M is the molecular weight and Θ is the critical miscibility temperature for a polymer homolog of infinite molecular weight in a given solvent, *i.e.*, the consolute temperature for *liquid–liquid* phase separation at $M = \infty$. C_M is a constant calculable from $M/\overline{r_0^2}$, and ψ_1 is an entropy parameter characteristic of a given polymer–solvent pair.

The value of $\overline{r_0^2}$ may be obtained from the parameter K. For the most direct determination of K, the intrinsic viscosity is measured at the temperature $T = \Theta$ in a given poor solvent. From equation (3), $\alpha^3 = 1$ at $T = \Theta$, hence if M is known K may be calculated from $[\eta]$ according to equation (1). The change in K, and hence also in $\overline{r_0^2}$, with temperature may be established by measuring intrinsic viscosities in several poor solvents choosing temperature $T = \Theta$ in each case.

The successful application of these relationships to the interpretation of intrinsic viscosity–molecular weight–temperature data for polyisobutylene,[2] polystyrene,[3] natural rubber[4] and gutta percha[4] and to the assignment of average molecular dimensions of these polymers prompted the present investigation concerned with the application of these methods to the cellulose esters. The dimensions thus obtained are particularly important in view of their direct bearing on the question of the often postulated "stiffness" of the cellulosic chains.

Two organic acid triesters of cellulose were chosen for this study, cellulose tributyrate and the lower melting cellulose tricaprylate.

Experimental

Polymers and Fractionation.—Samples of completely esterified cellulose tributyrate and cellulose tricaprylate were used in this work.[5] The intrinsic viscosity in acetone at 30° was 2.03 for the former, and 0.69 for the latter in toluene at the same temperature. The fractionation of cellulose tributyrate was carried out at 30°, according to the procedure described previously,[6] by the addition of water to an acetone solution, containing initially about 1% of the polymer. The cellulose tricaprylate was fractionated at the same temperature by the addition of 95% ethanol to a 1% solution in methyl ethyl ketone. The amount of each fraction expressed as the per cent. of the whole polymer, its intrinsic viscosity at 30° (in toluene for cellulose tricaprylate, in methyl ethyl ketone for cellulose tributyrate) and its number average molecular weight, determined osmotically, are given in Table I.

Solvents.—All solvents used in osmotic, precipitation and viscosity measurements were carefully dried and distilled before use.

Determination of Molecular Weight.—The number average molecular weights of the fractions were determined osmotically using toluene solutions of the tributyrate, and methyl ethyl ketone solutions of the tricaprylate. The osmometers used were of the type designed by S. G. Weissberg and collaborators at the National Bureau of Standards and have been previously described.[4] Measurements were carried out at 30.000 ± 0.005°.

Membranes were prepared from wet regenerated cellulose film (Sylvania Type 300) by washing in water, followed by transfer successively to ethyl alcohol and then to the solvent used for the measurements. These membranes gave permeation rates (d $\log_{10} \Delta h/dt$, Δh in cm., t in hours) of 0.2–0.4 in methyl ethyl ketone, and 0.1–0.2 in toluene at 30°.

TABLE I

CELLULOSE TRIESTER FRACTIONS

Fraction	Whole polymer, %	Intrinsic viscosity[a]	$\overline{M}_n$
Cellulose tributyrate			
A-3	{10.2}	2.95	222,000[c] ± 5,000
A-3a[b]		2.85	210,000 ± 10,000
A-4	9.0	2.57	182,000 ± 5,000
A-5	6.6	2.30	170,000 ± 10,000
A-6	7.0	2.00	151,000 ± 6,000
A-8	9.0	1.58	109,000 ± 7,000
A-9	11.2	1.14	77,000[c] ± 6,000
Cellulose tricaprylate			
B-3	3.7	1.35	353,000 ± 15,000
B-4	6.0	1.25	320,000[c] ± 15,000
B-5	6.5	1.02	267,000 ± 10,000
B-7	12.0	0.868	170,000 ± 3,000
B-10	7.4	.531	99,000 ± 2,000
B-11	5.2	.451	81,000[c] ± 2,000

[a] Intrinsic viscosities of cellulose tributyrate were measured in methyl ethyl ketone at 30°, those of the tricaprylate in toluene at 30°. [b] Portion of fraction A-3 which was reused. [c] Interpolated or extrapolated from intrinsic viscosity measurements.

Most of the determinations were performed in duplicate. After each run the osmometer was filled with solvent and allowed to stand overnight before the next solution was introduced. The capillaries were carefully cleaned after each determination. Concentrations were chosen to give Δh values between 0.3 cm. and that height for which $(\pi/c)/(\pi/c)_0$ would be about three. Equilibrium was attained in about 24 hours; no significant changes were observed to occur after this time.

Precipitation Temperatures.—Procedures similar to those previously described[2-4] were used.

Viscosity Determination.—The solution viscosities were measured in Ubbelohde type viscometers employing techniques which have been described in detail elsewhere.[2,3] The measurements were not extrapolated to zero rate of shear, since the effect should be small (less than 1%) in the intrinsic viscosity range encountered.[7] Viscosities of a given solution were measured consecutively at different temperatures through the use of a series of constant temperature baths. Duplicate measurements on the same solution made before and after the higher temperature measurements invariably were in good agreement, hence there was no evidence of degradation *during the viscosity determinations*. Recovery of the fractions after the high temperature intrinsic viscosity measurements and subsequent viscosity measurement in good solvents, *e.g.*, in toluene at 30° for cellulose tricaprylate and in methyl ethyl ketone at 30° for cellulose tributyrate, indicated however that the cellulose tributyrate underwent degradation in the process of dissolving in the dodecane–tetralin mixture. The viscosity-average molecular weight of each fraction of this ester was reduced by about 20%; this is an upper limit to any actual degradation since heating was also involved in the recovery.

Viscosities were measured at concentrations so chosen in each instance as to give relative viscosities, η_r, in the range 1.1 to 1.6. Both the specific viscosity–concentration ratio η_{sp}/c and $(\ln \eta_r)/c$ were plotted against c. At sufficiently low concentration these plots may be represented by linear equations

$$\eta_{sp}/c = [\eta] + a_2c \tag{4}$$

$$(\ln \eta_r)/c = [\eta] - b_2c \tag{5}$$

with slopes a_2 and $-b_2$ which must necessarily be related according to the equation

$$(a_2 + b_2)/[\eta]^2 = 0.5 \tag{6}$$

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[5] We are indebted to Dr. C. J. Malm of the Eastman Kodak Company for making these samples available to us and for supplying us with the ester analyses.

[6] P. J. Flory, THIS JOURNAL, **65**, 375 (1943).

[7] T. G. Fox, Jr., J. C. Fox and P. J. Flory, *ibid.*, **73**, 1901 (1951).

which may be established by series expansion of ln η_r.[8] Accordingly the best pair of straight lines having a common intercept, and slopes fulfilling equation (6) were drawn through the points. The uncertainty of the extrapolation was no more than about ±1% unless otherwise indicated.

Results

Determination of Θ.—Thermodynamic theories[9] of binary polymer solutions indicate that the critical consolute temperature for a fraction of given molecular weight below which two stable liquid phases may coexist should depend on the molecular weight according to the relation

$$T_c = \Theta(1 - b/M)^{1/2} \qquad (7)$$

where b is a constant. The value of T_c for each polymer fraction was determined by locating the maximum in the plot of the precipitation temperature of the solution T_p against the concentration of polymer. Θ for a given polymer in a particular solvent was then obtained as the intercept of the linear plot of T_c against $M^{-1/2}$. For polymers such as the triesters of cellulose which are capable of crystallizing in the temperature range of interest, precautions are necessary to distinguish between crystallization of the polymer in dilute solution and the separation into two liquid phases, since *the critical miscibility temperature Θ that we require is that for liquid–liquid equilibrium.* If the polymer which separates is crystalline, the observed separation temperatures should increase monotonically with concentration; only if the precipitated phase consists of a liquid solution is a maximum observed. In this way liquid–liquid precipitation may be distinguished from crystalline separation. The factors which determine whether under a given set of conditions liquid–liquid separation or crystallization will occur have been discussed in detail recently.[10,11] The plots of T_p against concentration, shown in Fig. 1 for one of the fractions of cellulose tricaprylate in γ-phenylpropyl alcohol and in dimethylformamide, indicate occurrence of liquid–liquid separation. The plots of the consolute temperatures T_c against $M^{-1/2}$ shown in Fig. 2 for fractions of cellulose tricaprylate in dimethylformamide and in γ-phenylpropyl alcohol are linear in accordance with equation (7). From the intercepts, Θ = 413(±1)°K. for the former solvent and Θ = 321(±2)°K. for the latter. As will be evident below, these uncertainties in the values of Θ are of little consequence insofar as the present investigation is concerned.

No single solvent giving liquid–liquid type separation of cellulose tributyrate was found. Investigation of various mixed solvents led to adoption of a 75–25 mixture by volume of dodecane and tetralin from which precipitation appeared to occur without development of crystallinity, in the vicinity of 100–115°. However, the problem of deducing the temperature corresponding to Θ for a binary system (which must correspond to the temperature at which the second virial coefficient in the osmotic expansion is zero) is complicated for a three component system.

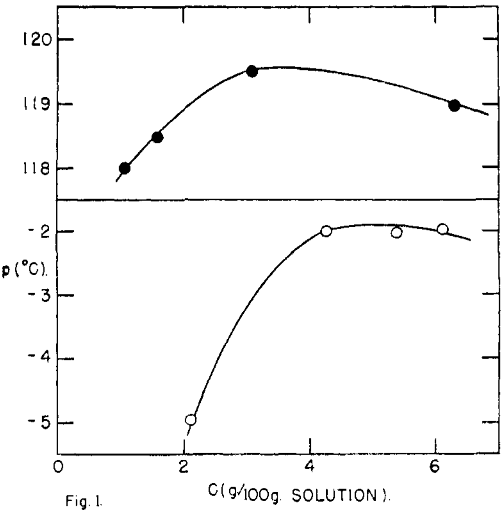

Fig. 1

Fig. 1.—Dependence of the precipitation temperature T_p on polymer concentration: ●, cellulose tricaprylate (fraction B-7) in dimethylformamide; ○, cellulose tricaprylate (fraction B-10) in γ-phenylpropyl alcohol.

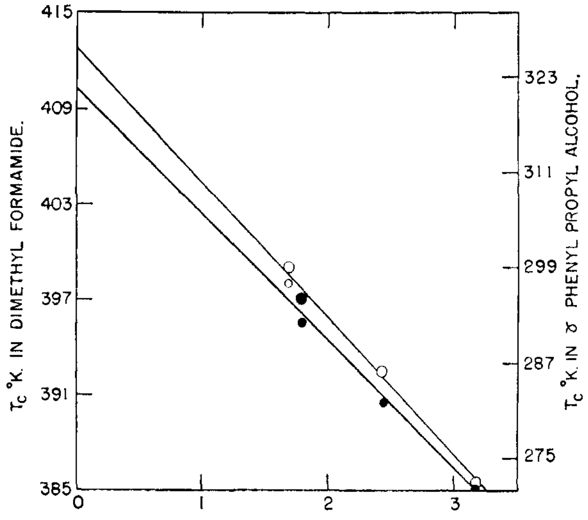

Fig. 2

Fig. 2.—Dependence of the critical precipitation temperature T_c on the reciprocal of the square root of the molecular weight: ●, cellulose tricaprylate in γ-phenylpropyl alcohol; ○, cellulose tricaprylate in dimethylformamide.

Scott[12] has shown that for a mixture of solvent and non-solvent having equal molar volumes, the second virial coefficient will vanish for a polymer of any molecular weight if the solvent–non-solvent ratio corresponds to that of the plait point for infinite molecular weight at the same temperature. This plait point occurs on the solvent–non-solvent axis (*i.e.*, where the polymer concentration is zero) of the ternary phase diagram. Tompa[13] has shown by a generalization of Scott's treatment that the

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[8] These expressions are more general than those originally given by Huggins, THIS JOURNAL, **64**, 2716 (1942), where $a_2 = k_1[\eta]^2$ is assumed, k_1 being a constant for any homologous series. Values of k_1 calculated from our data occur in the usual range from 0.2 to 0.4, with a few exceptions. No trend with molecular weight is evident. We have not, however, assumed constancy of k_1 in making the extrapolations.

[9] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[10] P. J. Flory, L. Mandelkern and H. K. Hall, THIS JOURNAL, **73**, 2532 (1951).

[11] L. Mandelkern and P. J. Flory, *ibid.*, **73**, 3206 (1951).

[12] R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).

[13] H. Tompa, private communication.

above deductions apply also to the general case of unequal molar volumes of solvent and non-solvent. Hence, for a ternary system the problem is that of determining a plait point for the polymer homolog of infinite molecular weight. If the temperature is specified, one must seek the solvent–non-solvent ratio corresponding to the occurrence at that temperature of the plait point for infinite molecular weight.[14] Conversely, the solvent–non-solvent ratio may be specified, in which case the problem resolves itself into determining the temperature at which the required plait point occurs.

Calculations of ternary phase diagrams for the system composed of solvent, non-solvent and amorphous polymer have been carried out by Scott[12] and by Tompa.[15] The essential features of the isothermal phase diagrams for several polymer fractions in the high molecular weight range are illustrated in Fig. 3. The circles are plait points at this temperature for the respective molecular weights; the dotted line represents the locus of compositions for which the solvent–non-solvent ratio remains the same.

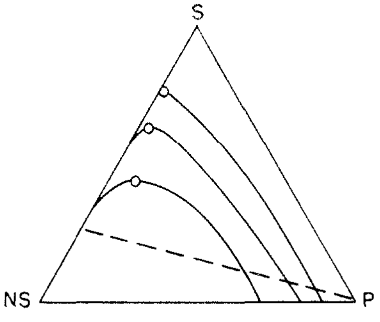

Fig. 3

Fig. 3.—Schematic ternary phase diagram for different molecular weight fraction at constant temperature. Circles are plait points. The dotted line represents a locus of compositions for which the solvent–non-solvent ratio is the same.

In order to obtain the temperature of the plait point for infinite molecular weight at the chosen solvent–non-solvent ratio, precipitation temperatures were measured at a series of polymer concentrations on each of several fractions differing in molecular weight. The precipitation temperatures for each concentration were plotted against $M^{-1/2}$ and the resulting straight line was extrapolated to infinite molecular weight as shown in Fig. 4. This type of plot was chosen by analogy to binary systems; at present there is no theoretical justification for it to be linear in a ternary system.

The precipitation temperatures at infinite molecular weight for each concentration were then extrapolated to infinite dilution to obtain the required temperature Θ. This procedure gives 395 ± 1°K. for the plait point for infinite molecular weight in the 75:25 by volume mixture of dodecane and toluene.

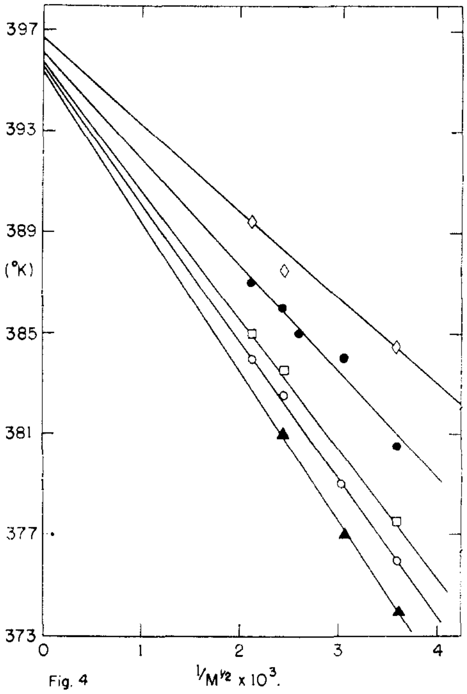

Fig. 4

Fig. 4.—Dependence of the precipitation temperature of cellulose tributyrate fractions in (75) dodecane–(25) tetralin mixture on molecular weight and on polymer concentration. Concentrations in g. polymer/100 g. solution: ▲, 0.16; ○, 0.25; □, 0.50; ●, 1.00; ◇, 2.00.

Molecular Weights.—The number average molecular weights were obtained from the osmotic pressures (π), measured in each case at a series of concentrations (c) by means of the extrapolation method recently described,[16] which is based on the theoretical expression of the form

$$\log [(\pi/c)/(\pi/c)_0] = \log (1 + \Gamma_2 c + 5/8\, \Gamma_2^2 c^2) \quad (8)$$

Experimental values of log (π/c) were plotted against log c and this plot was fitted to the theoretical graph of the right-hand member of equation (8) against log ($\Gamma_2 c$). Log $(\pi/c)_0$ was obtained by comparison of the ordinate scales of the theoretical

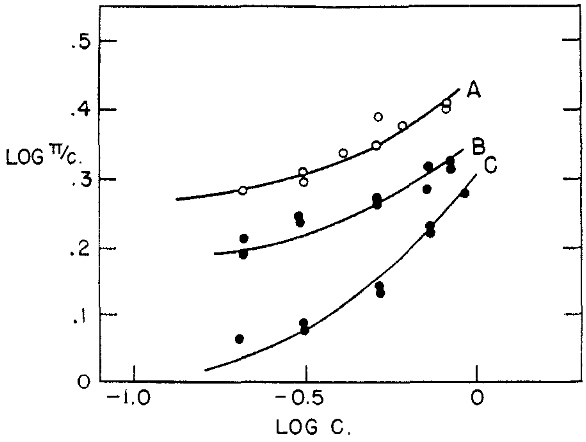

Fig. 5

Fig. 5.—Examples of osmotic pressure results. Points represent experimental data; the line represents the "best fit" line calculated from equation (8): A, cellulose tributyrate fraction A-6; B, cellulose tricaprylate fraction B-7; C, cellulose tricaprylate fraction B-5.

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(14) Unpublished data by A. R. Shultz show that the required plait point can be found by this method.

(15) H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).

(16) T. G. Fox, Jr., P. J. Flory and A. M. Bueche, THIS JOURNAL, **73**, 265 (1951).

and experimental plots. This procedure is illustrated in Fig. 5 for three of the fractions; the points are experimental values and the lines represent the theoretical curve. The average uncertainty in the molecular weight calculated from $(\pi/c)_0 = RT/M$ is about ±4%. The molecular weights so obtained are listed in Table I. The indicated "extrapolated" molecular weights were obtained from a log–log plot of intrinsic viscosity against M, the intrinsic viscosity being measured in good solvents—toluene for cellulose tricaprylate and methyl ethyl ketone for cellulose tributyrate.

Intrinsic viscosities of fractions of cellulose tricaprylate were determined in γ-phenylpropyl alcohol and in dimethylformamide at several temperatures in the vicinity of their critical miscibility temperatures; the results are reported in Table II. Included in this table are the intrinsic viscosities of several fractions of cellulose tributyrate in the mixture of 75% dodecane–25% tetralin at temperatures in the vicinity of the critical temperature. Intrinsic viscosities of the highest fraction in tributyrin at several temperatures also are given.

TABLE II

INTRINSIC VISCOSITIES OF CELLULOSE TRIESTERS

Cellulose tricaprylate

In γ-phenylpropyl alcohol				In dimethylformamide			
	Fraction				Fraction		
T, °C.	B-4	B-7	B-11	T, °C.	B-4	B-7	B-10
32	0.86 ± 0.01	0.598	0.735	130	0.600	0.492	0.365
42	.81 ± .01	.544	.505	138	.599	.480	.360
52	.735	.505	.356				

Cellulose tributyrate

In 75% dodecane-25% tetralin				In tributyrin	
	Fraction				Fraction
T, °C.	A-3a	A-4	A-8	T, °C.	A-3a
120	0.370	0.353 ± 0.03	0.286	0	3.55 ± 0.05
140	.415	.400	.304	45	2.33
				90	1.43
				130	1.11

The temperature dependences of the intrinsic viscosities for these cellulose esters present a sharp contrast to those observed for other polymers. Ordinarily the temperature coefficient is strongly positive in poor solvents at temperatures near Θ, and very small in good solvents.[2,3] The intrinsic viscosity of the tributyrate in tributyrin, a good solvent, decreases rapidly with temperature. Similar behavior has been observed for cellulose and other derivatives in good solvents,[17,18] which suggests that it is characteristic of cellulose chains. The cellulose tributyrate and tricaprylate have small temperature coefficients in poor solvents (Table II), and they are actually negative for the latter. These observations indicate an abnormally large decrease in K for most cellulosics with increasing temperature, as will be discussed further below.

Discussion

Determination of K.—Values of K were computed from the molecular weights M and the intrinsic viscosities interpolated to the temperature $T = \Theta$ for each poor solvent–polymer system. Results for cellulose tricaprylate at two temperatures and for cellulose tributyrate at a single temperature are recorded in Table III.

TABLE III

UNPERTURBED MOLECULAR CONFIGURATION PARAMETERS FOR CELLULOSE TRIESTERS

Cellulose tricaprylate

		$(\overline{r_0^2}/M)^{1/2} \times 10^{11}$		
T = 321°K.: M	$K \times 10^3$	Calcd. from K	Calcd. free rot.	Ratio
320,000	1.35 ± 0.06			
170,000	1.25 ± .02			
81,000	1.27 ± .02			
Av.:	1.29 ± .04	850	366	2.3
T = 413°K.:				
320,000	1.07 ± 0.03			
170,000	1.17 ± .02			
99,000	1.14 ± .02			
Av.:	1.13 ± .02	810	366	2.2

Cellulose tributyrate

T = 395°K.:				
210,000	0.82 ± 0.02			
182,000	.84 ± .02			
109,000	.86 ± .02			
Av.:	.84 ± .02	735	408	1.8

Cellulose tributyrate

	M = 210,000	$(\overline{r_0^2}/M)^{1/2} \times 10^{11}$		
T, °K.	$K \times 10^3$	Calcd. from K	Calcd. free rot.	Ratio
273	5.10 ± 0.2	1350	408	3.30
318	2.74 ± .1	1090	408	2.67
363	1.27 ± .05	845	408	2.07
403	.82 ± .03	730	408	1.80

The change in K with temperature may be obtained alternatively from the intrinsic viscosity–temperature coefficient in an athermal solvent ($\Theta = 0$°K.). For this case equations (1) and (3) can be combined to give

$$\alpha^2 - 1 = a/[\eta] \tag{9}$$

where $a = 2\psi_1 C_M K M$ should be independent of temperature,[19] since C_M contains the reciprocal of the temperature-dependent factor $(\overline{r_0^2}/M)$ occurring in K. Thus, from intrinsic viscosity measurements in an athermal solvent at the temperature at which K is known, the constant a can be determined. From intrinsic viscosity measurements at other temperatures, $\alpha^2 - 1$ may then be computed from equation (9). Knowing α, K may be deduced at this temperature using equation (1).

Previously published studies[11] of the depression of the melting point of cellulose tributyrate by tributyrin indicate that it is an athermal solvent, hence a suitable one with which to determine the temperature dependence of K. The values of K thus determined at different temperatures are included in Table III.

The indicated uncertainties in the values of K given in this table are calculated from the errors in the molecular weights and in the values of Θ. For both cellulose tributyrate and cellulose tricaprylate, the values obtained for K are independent of M within experimental error. Even the

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(17) D. A. Clibbins and A. Geake, *J. Textile Inst.*, **19**, T 77 (1928).

(18) E. O. Kraemer, in "The Chemistry of Large Molecules," edited by R. E. Burk and O. Grummitt, Interscience Publishers, Inc., New York, N. Y., 1943, p. 84.

(19) P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

lowest molecular weight fraction of cellulose tricaprylate having a degree of polymerization of only 150 shows no change. This is in accord with the previously reported results for the polyisoprenes,[4] polyisobutylene[2] and polystyrene.[3]

As was pointed out earlier, the dissolution of cellulose tributyrate in the mixture of dodecane-tetralin was accompanied by degradation. The values of K computed from the viscosity average molecular weights calculated from intrinsic viscosities in methyl ethyl ketone after degradation were slightly higher than those listed above; they were also independent of M.

Polymer Dimensions.—Differences in K for a polymer at different temperatures, or for different polymers, merely reflect differences in $(\overline{r_0^2}/M)$, since Φ in equation (2) should be a universal constant which is the same for any polymer in any solvent at any temperature. The universality of Φ is indicated by the *asymptotic* form of the Kirkwood-Riseman[20] equation for intrinsic viscosity.[21] Furthermore, since for a given polymer at a given temperature K is observed experimentally to be independent of the solvent, the contribution of the molecule as a whole to the intrinsic viscosity must be independent of the nature of the solvent, hence independent of the magnitude of the frictional interaction between a chain element and the solvent medium. This being true, it should be unaffected by the nature of the chain element as well. It follows that Φ should be the same for all systems.

The empirical value of Φ, obtained from determination of $\sqrt{\overline{r^2}}$ by the light scattering dissymmetry method, in conjunction with the intrinsic viscosity measured in the same solvent at the same temperature and for the same molecular weight, is 2.1×10^{21}.[1,22] Using this value of Φ, the quantities $(\overline{r_0^2}/M)^{1/2}$ given in the third column of Table III are obtained from the corresponding K's using equation (1). The units given represent the root-mean-square *unperturbed* end-to-end distance measured in ångström units for a polymer of molecular weight 10^6. The mean-square end-to-end distance $\overline{r_{0f}^2}$ calculated assuming free rotation about the ether linkages of the chain is

$$\overline{r_{0f}^2} = 62.4x \qquad (10)$$

where x is the number of glucose units in the chain.[23] This formula should be valid for any of the derivatives of cellulose, as well as for cellulose itself, and is based on dimensions of the cellulose unit given by Hermans,[24] and an oxygen valence angle of 110°. Values of $(\overline{r_{0f}^2}/M)^{1/2} \times 10^{11}$ calculated according to equation (10) are given in the fourth column of Table III. The last column gives the ratio of the root-mean-square unperturbed end-to-end distance (calculated from K) to that calculated assuming free rotation.

At a temperature far above Θ, *i.e.*, in a good solvent medium, $\sqrt{\overline{r^2}}$ exceeds the unperturbed distance $\sqrt{\overline{r_0^2}}$ by the factor α, which may be calculated from the intrinsic viscosity provided K is known.

Table IV gives the values of α, and of $\sqrt{\overline{r^2}}$ in good solvents. The ratio of $\sqrt{\overline{r^2}}$ to $\sqrt{\overline{r_{0f}^2}}$ calculated for free rotation is given in the last column.

TABLE IV

MOLECULAR CONFIGURATION PARAMETERS OF CELLULOSE TRIESTERS IN GOOD SOLVENTS

M	α	$(\overline{r^2})^{1/2}$	Ratio
Cellulose tributyrate in methyl ethyl ketone at 30°			
222,000	1.22	670	3.5
170,000	1.17	567	3.4
109,000	1.10	430	3.2
77,000	1.06	347	3.1
Cellulose tricaprylate in toluene at 30°			
353,000	1.20	610	3.0
267,000	1.15	509	2.9
170,000	1.17	415	2.9
81,000	1.07	266	2.8

If *completely extended*, cellulose tributyrate of molecular weight 10^6 would have a length of 14,000 Å. Since this is of the order of ten to twenty times the observed $\sqrt{\overline{r_0^2}}$, the flexible chain model, rather than the often suggested stiff rod, is appropriate for the cellulose esters. The ratios $\sqrt{\overline{r_0^2}}/\sqrt{\overline{r_{0f}^2}}$ for these esters range from 3.3 to 1.8; for polystyrene at 34° this ratio has been found to be 2.4,[3] and for polyisobutylene at 25°, 1.95.[2] Thus, the comparison with free rotation distances also contradicts the alleged rod-like character of the cellulose chains.

Even in good solvents the end-to-end distance has not been sufficiently increased as to warrant the assertion that the chains are highly extended; nor is there any evidence for the postulate that low molecular weight cellulose esters are stiff, the chains becoming more flexible as the molecular weight is increased.[25,26]

Cellulose tributyrate displays a rather strong dependence of K on temperature, which is not shared by cellulose tricaprylate. The behavior of the latter is similar to that of other polymers.[2,3]

The temperature dependence of K is related to the nature of the barriers hindering free rotation which must be quite different for these two cases—a subject requiring further investigation. The large decrease of K with increasing temperature accounts for the almost universal decrease in the intrinsic viscosity of cellulose and its derivatives with temperature, even in poor solvents.

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(20) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

(21) See equation (18) ref. 18, for further discussion.

(22) Recently A. Oth and P. M. Doty, *J. Phys. Chem.*, **56**, 43 (1952), have shown that this value of Φ when applied to intrinsic viscosities of fractions of polymethacrylic acid at various degrees of neutralization, give values of $(\overline{r^2})^{1/2}$ which are in approximate agreement with those directly measured over an intrinsic viscosity range exceeding one hundred-fold.

(23) H. Benoit, *J. Polymer Sci.*, **3**, 387 (1948).

(24) P. H. Hermans, *Kolloid Z.*, **102**, 169 (1943).

(25) A. Peterlin, *J. Polymer Sci.*, **5**, 473 (1950).

(26) R. M. Badger and R. H. Blaker, *J. Phys. Colloid Chem.*, **53**, 1051 (1949).