sist of molecules of double chain length in the crystalline state, at least in the form obtained by solvent crystallization.

Although evidence for three melting phases was determined from warming and cooling curves and from capillary tube data, difficulty was experienced in obtaining X-ray diffraction patterns on the different forms because of relatively rapid phase transition. The transition temperatures of the different polymorphic forms are listed in Table I together with the long-spacing values of the solvent-crystallized form.

Summary

Long and short spacing X-ray data are reported for three homologous triacid triglycerides, two of which are new compounds, namely, 1-palmityl-2-myristyl-3-laurin and 1-myristyl-2-lauryl-3-caprin.

It appears from the X-ray evidence presented that the homologous triacid glycerides in the crystalline state are of a double chain length, and that the solvent-crystallized form (beta-prime type) for 1-myristyl-2-lauryl-3-caprin is its most stable form.

The Effect of Molecular Weight Distribution on the Reduced Viscosity–Concentration Coefficient

BY W. E. DAVIS

Introduction

During the past ten years, the determination of the solution viscosity of high polymers has assumed increasing importance as a means of estimating their molecular weights. The generally accepted procedure now is to relate molecular weight to intrinsic viscosity (limiting value of specific viscosity/concentration at infinite dilution), as suggested by Kraemer,[1] rather than to specific viscosity/concentration at a "sufficiently low" concentration, as originally proposed by Staudinger.[2] The determination of this quantity, intrinsic viscosity, therefore requires an extrapolation of viscosity data to infinite dilution. Such a procedure attains its maximum accuracy when the extrapolation is linear, and a number of equations expressing specific viscosity/concentration or some related quantity as a linear function of concentration have been proposed and used. Among the most frequently used of these equations are the following

$$\eta_{sp}/c = [\eta](1 + k'[\eta]c) \qquad (1)$$
$$\log \eta_{sp}/c = \log [\eta] + ac \qquad (2)$$

where

$$\eta_{sp} = \text{specific viscosity}$$
$$c = \text{concentration}$$
$$[\eta] = \text{intrinsic viscosity}$$
$$k' \text{ and } a = \text{constants}$$

Equation (1) has been used by Guth[3] and others, and is directly related to another equation (making the substitution $[\eta]c \leftrightarrow \eta_{sp}$)

$$\eta_{sp}/c = [\eta](1 + k'\eta_{sp}) \qquad (3)$$

derived on a hydrodynamical basis by Huggins[4] and used empirically by Schulz and Blaschke.[5]

Equation (2) has been used by Staudinger[6] and others, and is particularly useful because it appears to be valid over a rather wide range of concentration. This equation has been modified by Martin,[7] who presented data indicating that the constant, a, is a linear function of intrinsic viscosity for a given solute–solvent system, i. e., that

$$a = k[\eta] \qquad (4)$$

so that equation (2) should be written

$$\log \eta_{sp}/c = \log [\eta] + k[\eta]c \qquad (5)$$

where k is a constant independent of all factors except the chemical nature of solute and solvent. It is readily shown, by writing equation (5) in exponential form

$$\eta_{sp} = [\eta]c \cdot 10^{k[\eta]c}$$

expanding in powers of $[\eta]c$ and dropping the higher terms that equations (1) and (3) are approximations to equation (5), valid at low concentration, and that the following relation holds between the constants

$$k' = 2.303k \qquad (6)$$

In determining intrinsic viscosity, the usual procedure is to plot the viscosity data according to equation (5) (or, at sufficiently low concentration, according to equation (1) or (3)) and extend the straight line obtained to zero concentration (or to zero η_{sp} in equation (3)). It is obvious that this procedure could be greatly shortened if the contention of Martin,[7] that the constant k (and therefore also k') has a single characteristic value for a given solute–solvent system, were true. In that case it would not be necessary to make viscosity determinations at several concentrations in order to establish a good straight line; once the correct value of k or k' was known, one viscosity

(1) E. O. Kraemer, Ind. Eng. Chem., 30, 1200 (1938).

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

(3) E. Guth, Kolloid-Z., 74, 147 (1936); 75, 15 (1936).

(4) M. L. Huggins, THIS JOURNAL, 64, 2716 (1942).

(5) G. V. Schulz and F. Blaschke, J. prakt. Chem., 158, 130 (1941).

(6) H. Staudinger and W. Heuer, Z. physik. Chem., A171, 129 (1934).

(7) A. F. Martin, Am. Chem. Soc. Meeting, Memphis, April 23, 1942.

determination would suffice for calculation of intrinsic viscosity. However, a number of investigators[8,9,10] have recently presented data which they interpret as showing that the value of k (or k') is dependent on the molecular weight distribution in the sample under investigation. It is the purpose of this paper to present some new data on this point, and to offer another interpretation of the data in the literature.

Experimental

Materials.—Cellulose nitrates with a degree of substitution of about 2.85 were prepared from samples of chemical cotton, wood pulp and high-tenacity viscose rayon, using a nitrating mixture containing 48% nitric acid, 50% orthophosphoric acid and 2% phosphorus pentoxide.[11] The nitrates were fractionated by precipitation from acetone solution with hexane. In the case of the nitrates from chemical cotton and wood pulp, each sample was separated into two large fractions containing the high-molecular weight material and a number of small fractions containing material of lower molecular weight. The latter fractions may be presumed to have a narrower molecular weight distribution than the former. Nitrates from rayons were carefully fractionated in three stages, the number of fractions increasing and the concentration of the solution from which precipitation took place decreasing in successive stages. These fractions should all have fairly narrow molecular weight distributions.

Viscosity.—Viscosity determinations were carried out using an Ostwald viscometer of the Cannon–Fenske type[12] on solutions of cellulose nitrate in a solvent made up of 77.5% n-butyl lactate and 22.5% diacetone alcohol by weight, with 1.5 ml. of water per 100 g. of mixture added. Determinations were made at four or five concentrations for each sample, the highest concentration being such that η_{sp} was less than 2, the lowest concentration usually about one-tenth of the highest. From these data, values of log $[\eta]$ and k in equation (5) were determined by the method of least squares. For each sample in Table II, one additional viscosity determination was made at such concentration that η_{sp} was approximately 10. From these data, a value of log η_{sp}/c was calculated for each sample, and k in equation (5) was then determined from this value of log η_{sp}/c and the value of log $[\eta]$ previously determined.

Results and Discussion

The results of viscosity determinations on 141 samples are summarized in Table I. The samples have been divided into groups as described below, and for each group the table gives the number of samples in it, the extremes of intrinsic viscosity represented by these samples, the average value of k in equation (5) and the standard deviation of k.

The nitrates from chemical cotton and wood pulp have been classified in three groups: Group I includes low-molecular weight fractions precipitated from dilute solution with a high ratio of solution volume to volume of precipitated gel, and therefore presumably of fairly narrow molecular weight distribution; Group II includes fractions of higher molecular weight precipitated from more concentrated solution with a lower ratio of

(8) F. Howlett, E. Minshall and A. R. Urquhart, *J. Textile Inst.*, **35**, 133T (1944).

(9) S. Coppick, *Paper Trade J.*, **119**, No. 26, 36 (Dec. 28, 1944).

(10) R. S. Spencer and R. F. Boyer, *Polymer Bull.*, **1**, 129 (1945).

(11) G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).

(12) M. R. Cannon and M. R. Fenske. *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

TABLE I

VALUES OF SLOPE CONSTANT k IN EQUATION (5) FOR VARIOUS CELLULOSE NITRATES

Group	Description[a]	Samples	Range of $[\eta]$	Av. k	Standard deviation of k
I	Low-mol. wt. fractions from chemical cotton and wood pulp	37	7.13–1.53	0.157	0.012
II	High-mol. wt. fractions from chemical cotton and wood pulp	12	18.45–5.99	.188	.010
III	Unfractionated chemical cotton and wood pulp	6	11.73–9.91	.183	.008
IV	Head fractions from rayons	15	7.13–4.46	.171	.024
V	Main fractions from rayons	71	7.18–1.12	.154	.013

[a] These descriptions are expanded in the text.

TABLE II

VISCOSITY-CONCENTRATION DATA FOR FRACTIONS AND A BLEND OF CELLULOSE NITRATE

Sample	Concentration, g./100 g.	Log η_{sp}/c	k in equation (5) From low concn. data[a]	k in equation (5) From high concn. data[a]	Intrinsic viscosity Obs.	Intrinsic viscosity Calcd.[b]
Fraction A	0.1618	0.8183				
	.1203	.7872				
	.0893	.7640	0.161	0.157	4.910	...
	.0663	.7430				
	.0492	.7274				
	.6321	1.1793				
Fraction B	.5053	0.2945				
	.3774	.2700				
	.2818	.2482	.141	.138	1.536	...
	.2098	.2297				
	.1557	.2196				
	2.047	.6202				
50.3% A	0.1867	.6058				
49.7% B	.1393	.5823				
	.1040	.5630	.161	.154	3.230	3.233
	.0774	.5489				
	1.015	1.0124				

[a] See experimental part for method of obtaining these k values. [b] From $[\eta]_{calc.} = \sum_i w_i [\eta]_i$ where w_i and $[\eta]_i$ are weight fraction and intrinsic viscosity, respectively, of ith component of mixture.

solution volume to volume of gel, and, therefore, of wider molecular weight distribution; Group III includes unfractionated nitrates, which have the widest molecular weight distribution of all. If it is true, as suggested by Spencer and Boyer,[10] that k' in equation (1) increases with increasing width of molecular weight distribution, then the same should be true of k in equation (5), because of the relationship between the two constants shown in equation (6). The first three values of k in Table I offer some support for this hypothesis, in that the values for Groups II and III are higher than that for Group I; this difference is readily shown

to be statistically significant by "Student's" t-test,[13] the chance that it is due to random variation being much less than 1%. Against the hypothesis is the fact that the values of k for groups II and III do not differ significantly, whereas, if k is affected by distribution, it should be higher for Group III than for Group II. However, the weight to be assigned to this fact depends on the actual degree of difference in distribution between these two groups, and this is not known with any certainty. There are two other possible explanations for the variation in k which has been observed: (1) if the unfractionated nitrates contained a small amount of material whose solubility in acetone–hexane was lower than normal for its molecular weight (perhaps due to presence of polar groups or bound ash), then such material would tend to concentrate in the high-molecular weight fractions and might be expected to have a higher value of k than normal nitrate; (2) k might increase with increasing intrinsic viscosity.

Support for the first of these two hypotheses is offered by the data on fractions from rayon nitrates in Table I. These fractions have been divided into two groups: Group IV contains those fractions in which material of abnormally low solubility might be expected to concentrate, and Group V, the remaining fractions. Once again there is a difference in k values, and again it is statistically significant; also it is in the expected direction, the fractions suspected of containing material of abnormal solubility having the higher value of k.

The second hypothesis mentioned above, that k increases with increasing intrinsic viscosity is easily disposed of by arranging all the fractions of Groups I and V (which contain little or no material of abnormal solubility) in order of increasing intrinsic viscosity. The variations in k are then found to be completely random, thus disposing of the possibility that k is appreciably affected by intrinsic viscosity.

Since the fractions of Group IV probably do not differ much from those of Group V in width of molecular weight distribution, it seems likely that the high k values observed are due primarily, if not entirely, to the presence, in the sample exhibiting them, of material with abnormal solubility and viscosity–concentration characteristics. In order to settle this point definitely, viscosity determinations were carried out on two fractions of cellulose nitrate and on a mixture of the two, with the results shown in Table II. Values of k were determined by two methods, as described under "Experimental." The method involving a viscosity determination at a higher concentration was adopted for two reasons: (1) to demonstrate the validity of equation (5) over a range of concentration much wider than that used in determining

(13) R. A. Fisher, "Statistical Methods for Research Workers," 9th ed., Oliver and Boyd, Ltd., Edinburgh, 1944, pp 122 et seq.

intrinsic viscosity, and (2) to obtain a check on the value of k, since, as the standard deviations in Table I show, viscosity determinations at low concentration do not give values of k of a high order of accuracy. It is apparent from the data in Table II that the two methods of determining k give concordant results, and that the value of k for the mixture is not significantly different from the values for its components. This result should be considered in the light of the fact that on the basis of the hypothesis of Spencer and Boyer,[10] to be discussed below, this mixture should have had a k value of 0.18 or higher. In addition to the agreement between corresponding pairs of k values, the accuracy of the determinations is attested to by the agreement between observed and calculated values of intrinsic viscosity for the mixture, as shown in Table II.

The data thus far presented are all consistent with the view that, for cellulose nitrate at least, the constant k in equation (5) is not appreciably affected by either intrinsic viscosity or width of molecular weight distribution, but probably varies due to the presence in some samples of material of abnormal solubility and viscosity–concentration characteristics. This is at variance with the conclusions drawn by Coppick[9] from viscosity–concentration data for cellulose nitrates prepared from wood meal, from pulps cooked to varying degrees, and from blends of such pulps. Coppick stated that nitrates from well-cooked pulps or from blends of pulps so prepared as to have a smooth molecular weight distribution had lower values of k than nitrates from wood or raw pulps, which were said to have an irregular or "two-colony" distribution. This conclusion was based on values of k obtained graphically. In Table III are given values of intrinsic viscosity and k calculated from Coppick's data by the method of least squares. The only value of k which is outstandingly high is that for Nitrate Number One, which was prepared from wood meal. It can also be shown that this k value is the only one whose difference from the others is statistically significant. It seems probable that a nitrate prepared from raw wood would contain appreciable

TABLE III

VISCOSITY DATA FOR CELLULOSE NITRATES FROM WOOD AND WOOD PULPS—COPPICK[9]

| Coppick's nitrate number | Least-squares value of: | |
	Intrinsic viscosity	k in equation (5)[a]
1	17.0	0.256
2	13.6	.229
3	10.7	.225
4	8.41	.233
5	8.15	.230
6B	13.7	.208
7B	12.1	.206
8B	9.71	.224

[a] These k values differ from those in Tables I and II because of the use of a different solvent and a different nitrogen content for the nitrates.

amounts of nitrates of carbohydrates other than cellulose (possibly also non-carbohydrate material, despite some purification); such materials would in all probability exhibit viscosity–concentration properties differing from those of pure cellulose nitrate. We are therefore once more led to the conclusion that for cellulose nitrate departure of a given sample from the normal value of k is usually to be attributed to departure of the sample from the ideal conception of cellulose as polyanhydroglucose.

The idea that the value of k in equation (5) is not sensibly affected by molecular weight distribution is also roughly substantiated by the data reported by Martin,[7] who found k to be a characteristic constant for a given solute–solvent system. The apparent exceptions noted for cellulose acetate by Howlett, Minshall and Urquhart[8] are in every case unfractionated acetate or head fractions, which come under the same classifications as Groups III and IV in Table I, or else fractions of very low molecular weight. If abnormal solubility behavior of polymers is sometimes to be explained by the presence of polar end groups, as suggested by Morey,[14] these would be expected to exert their maximum effect on the short-chain material; this is one possible explanation of the above observations on cellulose acetate fractions.

It should be noted that if k is independent of molecular weight distribution, as indicated by the data cited above, it must follow that k' in equations (1) and (3) will show the same independence, because of the relationship between k and k' indicated in equation (6). A direct test of the effect of molecular weight distribution on k' is afforded by the data of Spencer and Boyer,[10] who interpreted their results (Table IV) to mean that distribution did have an effect on k'. This conclusion was based on the fact that the observed values are higher than the calculated values of η_{sp}/c in Table IV, and on a certain derivation, presented in equations (3) to (9) of reference (10), according to which the observed values of η_{sp}/c for a mixture of fractions should obey the relations

$$\eta_{sp}/c = <[\eta]> + k'Q<[\eta]>^2 c \quad (7)$$
$$Q = <[\eta]^2>/<[\eta]>^2 \quad (8)$$

where

$$<[\eta]> = \sum_i [\eta]_i c_i / \sum_i c_i \quad (9)$$

$$<[\eta]^2> = \sum_i [\eta]_i^2 c_i / \sum_i c_i \quad (10)$$

However, Spencer and Boyer obtained their calculated values of η_{sp}/c for the mixtures at a given concentration by averaging the values of η_{sp}/c for the components at the same concentration. Symbolically

$$(\eta_{sp}/c)_{calcd.} = \sum w_i (\eta_{sp})_i/c$$

where

w_i = weight fraction of ith component in mixture
$(\eta_{sp})_i$ = specific viscosity of a solution of ith component at the concentration c.

(14) D. R. Morey, paper presented at A. A. A. S., Organic High Polymers Conference, Gibson Island, Maryland, July 2, 1946.

TABLE IV

VISCOSITY–CONCENTRATION DATA FOR BLENDS OF POLYSTYRENE FRACTIONS: SPENCER AND BOYER[10]

Sample	Concn., g./cc.	Spencer and Boyer's values of		η_{sp}/c calcd. from equation (5)[a]
		η_{sp}/c Calcd.	η_{sp}/c Obsd.	
Fractions	0.000	0.15888	0.15895	0.15888
1 and 3	.002	.16050	.16250	.16083
	.004	.16219	.16350	.16281
	.008	.16666	.16725	.16686
	.016	.17438	.17511	.17524
		(k' = 0.385)	(k' = .0409)	(k' = .0385)
Fractions	.000	.14004	.14030	.14004
1 and 4	.002	.14100	.14150	.14135
	.004	.14325	.14175	.14268
	.008	.14563	.14623	.14536
	.016	.15129	.15222	.15089
		(k' = 0.333)	(k' = 0.361)	(k' = 0.333)
Fractions	.000	.16638	.16652	.16638
2 and 3	.002	.16838	.16975	.16847
	.004	.17017	.17175	.17059
	.008	.17475	.17500	.17490
	.016	.18310	.18360	.18386
		(k' = 0.376)	(k' = 0.390)	(k' = 0.376)

[a] See text for description of calculation.

Since each component is assumed to obey equation (1), we have

$$(\eta_{sp})_i/c = [\eta]_i + k'[\eta]_i^2 c$$

Therefore

$$(\eta_{sp}/c)_{calcd.} = \sum_i \{w_i[\eta]_i + k'w_i[\eta]_i^2 c\}$$
$$= \sum_i w_i[\eta]_i + k'c \sum_i w_i[\eta]_i^2 \quad (11)$$

Now since $\sum_i c_i = c$ we can rewrite equation (10)

$$<[\eta]^2> = \sum_i [\eta]_i^2 c_i/c$$
$$= \sum_i w_i[\eta]_i^2$$

since

$$c_i/c = w_i$$

Therefore, from equation (11), since $\sum_i w_i[\eta]_i = [\eta] = <[\eta]>$

$$(\eta_{sp}/c)_{calcd.} = <[\eta]> + k'<[\eta]^2> c \quad (12)$$

Substituting in equation (12) from equation (8), we have

$$(\eta_{sp}/c)_{calcd.} = <[\eta]> + k'Q <[\eta]>^2 c$$

the right side of which is identical with equation (7). This shows that on the basis of the assumptions made by Spencer and Boyer, the observed and calculated values of η_{sp}/c in Table IV, should be the same. That this is not the case is attributed by the writer to an unjustified assumption in Spencer and Boyer's derivation, namely, that in their equation (4)

$$\sum_i \{\eta_{sp}/c - [\eta]\}_i = \eta_{sp}/c - [\eta]$$

This assumption is without theoretical basis, and could only be justified by appeal to experiment. As we have seen, the experimental results do not support it.

Further consideration of Spencer and Boyer's data will even lend support to the conclusion which we reached above, namely, that k' is *not* affected by molecular weight distribution. For each mixture in Table IV take $[\eta]$ equal to the calculated value of η_{sp}/c for $c = 0$, and take $k = k'/2.303$, where k' is the value given in parentheses in the calculated column of Table IV. (These values of k' are average values for the *components* of the mixtures.) Using these values for $[\eta]$ and k, calculate values of η_{sp}/c for each concentration, using equation (5). The results of this procedure are shown in the last column of Table IV, and it is apparent that the values of η_{sp}/c so calculated are in good agreement with those observed by Spencer and Boyer. Statistical analysis shows that the chance that the difference between Spencer and Boyer's values of η_{sp}/c calculated and η_{sp}/c observed is due to random variation is less than 1%, while the same chance for the differ-

ence between η_{sp}/c observed and η_{sp}/c calculated from equation (5) as described above is greater than 14%. This means that both the fractions and mixtures thereof most probably obey equation (5) with the same value of k, and must therefore have the same value of k'.

Summary

Original data for cellulose nitrate and data from the literature for cellulose nitrate and polystyrene have been analyzed to show that the slope constant (k or k') in various equations connecting solution viscosity and concentration is a characteristic constant for a given solute–solvent system, and, in particular, is not appreciably affected by the molecular weight distribution of the solute. Cases in which high values of the slope constant are obtained for cellulose nitrate and cellulose acetate can reasonably be attributed to variation in the chemical nature of samples, which are in all cases examined either unfractionated materials, head fractions, or fractions of very low molecular weight.

The Esterification Rate of Dibasic Acid Anhydrides with Primary Alcohols at Room Temperature

BY ERNEST F. SIEGEL AND MARGUERITE K. MORAN

In the course of some work carried out with dibasic acid anhydrides it was found that they titrate only half of the expected titer of the dibasic acids when the anhydrides were dissolved in ethanol in the cold. The only plausible explanation for this was that the anhydride formed a half ester leaving only one carboxyl group for titration.

The esterification of dibasic acid anhydrides with polyhydric alcohols has been investigated thoroughly in the past, particularly in reference to the formation of alkyd resins. In this study dibasic acid anhydrides were esterified with polyhydric alcohols at temperatures far above 100°.[1] It was stated that the acidity dropped to half its original value within a matter of minutes and assumed that the acid ester was formed. The literature references[2] concerning the reaction of dibasic acid anhydrides and monohydric alcohols show that the esterification was carried out also at higher temperatures and claim that it could be speeded up by the addition of potassium cyanide

as a catalyst. No mention is made anywhere in literature that the esterification of dibasic acid anhydrides proceeds at room temperature.

Incited by our preliminary finding mentioned above, the reaction of phthalic anhydride and maleic anhydride with several primary mono- and polyhydric alcohols at room temperature (20–25°) was studied. It was found that the monoester formation was instantaneous and quantitative and its rate almost comparable with that of an ionic reaction, e. g., between an inorganic base and an inorganic acid. The esterification rate is rapid for all primary alcohols under investigation, so rapid as to make a comparison of rates or of the effect of chain length or the functionality of the alcohols impossible. Maleic anhydride reacts as readily with primary n-amyl alcohol or ethylene glycol as with methanol. The rapidity of the esterification is not decreased when carried out in presence of an inert diluent. The amount of excess alcohol is of no importance since a 1:1 molecular ratio of alcohol to anhydride gives the same result as that of 2:1 or 4:1. Secondary alcohols, e. g., i-propyl alcohol do not esterify at all under our chosen reaction conditions. Therefore no attempt was made to esterify tertiary alcohols.

This investigation found an interesting application in testing the rearrangement of fumaric acid to maleic anhydride in the presence of rosin which

(1) Kienle and Hovey, THIS JOURNAL, 51, 509 (1929); 52, 3636 (1930); Kienle, Vander Meulen and Petke, *ibid.*, 61, 2258 (1939); 61, 2268 (1939); Kienle and Petke, *ibid.*, 62, 1053 (1940); Savard and Diner, *Bull. Soc. Chim.*, 51, 597 (1932); Hirano and Ohashi, *J. Soc. Chem. Ind., Japan*, 41, Suppl. binding 90 (1938).

(2) Shields, *J. Chem. Soc.*, 59, 740 (1891); Walker, *ibid.*, 61, 710, 711 (1892); *Beilstein*, 9, 797; Sudborough, Roberts, *J. Chem. Soc.*, 87, 1844 (1905); Goggins and Copenhaver, THIS JOURNAL, 61, 2909 (1939).