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Studies on Reactions Relating to Carbohydrates and Polysaccharides. LVIII. The Relation between Chain Length and Viscosity of the Polyoxyethylene Glycols¹BY REID FORDYCE² AND HAROLD HIBBERT**Introduction**

In applying the Staudinger equation, $\eta_{sp}/c = K_m M$, to the determination of the chain length of polymeric substances or, conversely, as a method of determining its validity, Staudinger³ has found it necessary to restrict the experimental conditions surrounding its application within certain definite limits based both on theoretical and practical considerations, a fact which many investigators have unfortunately ignored.

In the first instance, the products under investigation must be the members of a polymer homologous series having a straight chain structure and a relatively high molecular weight. That both these requirements are satisfied in the case of the synthetic polyoxyethylene glycol polymers has been shown in previous communications.⁴

In addition, Staudinger considers it advisable, if not actually necessary, to carry out the viscosity measurements in homopolar solvents since only under these conditions are the long chain molecules surrounded by a monomolecular layer of solvent molecules.⁵ The applicability of the equation has been further extended recently by Staudinger and Daumiller⁶ to include certain heteropolar solvents, as, for example, cellulose in phosphoric acid. In the present investigation only solvents of homopolar character, namely, 1,4-dioxane and carbon tetrachloride, have been employed.

A further and very important factor emphasized by Staudinger is that all viscosity measurements must be made in very dilute solutions. This restriction is based upon his concept of the "sol" and "gel" states of macromolecules in solution and is a point of view emphasized by him repeatedly in numerous publications.⁷ The viscosities re-

ported in the present communication are those for "ground molar" solutions (4.4% by weight) of the polyoxyethylene glycols. The viscosities have been determined at three different temperatures, 20, 40 and 60°, in order to show the effect of temperature variation on the validity of the Staudinger relationship connecting specific viscosity and chain length.

Materials and Methods

The synthesis and purification of the polyoxyethylene glycols already have been reported.⁴ The triethylene glycol was a commercial product purified by careful fractionation. 1,4-Dioxane was purified according to the method of Eigenberger⁸ (f. p. 11.7°). The carbon tetrachloride was allowed to stand over solid potassium hydroxide for three days and then distilled from it, a middle fraction being employed (b. p. 76.5° at 750 mm.).

The viscometer was an Ostwald type instrument constructed according to the specifications given in British Engineering Standards⁹ with dimensions corresponding to those for a uniform capillary of diameter 0.493 mm. and having a range of 0.9 to 7.2 cp.

Kinetic energy corrections were not necessary with this instrument since, using water as standard, a value was found for the absolute viscosity of aniline at 20°, agreeing within 0.35% with that obtained by Appleby.¹⁰ Density corrections were not applied to the viscosity measurements of the polyoxyethylene glycol solutions since Staudinger³ has shown, and confirmation is provided by the authors, that the change in density of such dilute solutions can be neglected. Since the volume of fluid is adjusted within the viscometer itself, no error is introduced by thermal expansion of the fluid or the viscometer.

The temperature of the bath used was kept constant within $\pm 0.02^\circ$. Loss of solvent due to volatilization at high temperatures, as well as contamination of the solutions in the viscometer with moisture, was prevented by means of the customary connection joining the upper parts of the two limbs of the instrument.

Discussion of Results

The tabulated specific viscosities of the polyoxyethylene glycols in carbon tetrachloride and dioxane at 20, 40 and 60° are shown in Tables I and II. It can be seen that the curves (Fig. 1) obtained by plotting specific viscosity against molecular weight (or chain length), both in dioxane and carbon tetrachloride and at different tempera-

(1) Paper presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Holder of a Bursary and Studentship under the National Research Council of Canada, 1937-1939.

(3) Staudinger, "Der Aufbau der hochmolekulären organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932.

(4) (a) Fordyce, Lovell and Hibbert, *THIS JOURNAL*, **61**, 1905 (1939); (b) Fordyce and Hibbert, *ibid.*, **61**, 1910 (1939).

(5) Staudinger, *Trans. Faraday Soc.*, **29**, 30 (1933).

(6) Staudinger and Daumiller, *Ber.*, **70B**, 2508 (1937).

(7) (a) Staudinger, *Trans. Faraday Soc.*, **30**, 110 (1935); (b) *Ber.*, **68B**, 1682 (1935).

(8) Eigenberger, *J. prakt. Chem.*, **130**, 75 (1935).

(9) British Standard Specification No. 188-1929, British Engineering Standards Association, London, May, 1929.

(10) Appleby, *J. Chem. Soc.*, **127**, 1836 (1925).

TABLE I
 VISCOSITIES IN CARBON TETRACHLORIDE

Members in oxyethylene glycol	20°			40°			60°		
	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.187$)	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.159$)	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.121$)
6	0.156	5.52		0.127	4.50		0.097	3.43	
18	.240	2.96	0.64	.199	2.46	0.49	.148	1.83	0.33
42	.275	1.47	.47	.242	1.30	.45	.184	0.98	.34
90	.414	1.04	.57	.343	0.86	.47	.261	.66	.34
186	.678	0.83	.60	.560	.68	.49	.393	.48	.33
	Average		0.57			0.48			0.34

 TABLE II
 VISCOSITIES IN DIOXANE

Members in oxyethylene glycol	20°			40°			60°		
	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.128$)	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.119$)	$\eta_{sp.}/c$	$K_m \times 10^4$ Staudinger	$K'_m \times 10^4$ Eq. 1 ($\beta = 0.095$)
2	0.076	7.16		0.064	6.04		0.047	4.46	
3	.082	5.48		.073	4.86		.056	3.71	
6	.135	4.73		.102	3.63		.083	2.95	
18	.195	2.40	0.67	.179	2.21	0.59	.159	1.96	0.59
42	.239	1.28	.54	.214	1.15	.50	.189	1.01	.43
90	.383	0.96	.61	.351	0.88	.55	.320	0.81	.53
186	.686	0.83	.67	.623	0.76	.60	.597	0.73	.59
	Average		0.62			0.56			0.53

tures, all have the same general shape, namely, a linear form within the molecular weight range 810-8200, and characterized in the lower members of the series by a sharp departure from the linear form.

A curve of the same general type is obtained by plotting the values found by Staudinger for the viscosities of his fractionated polyethylene oxide polymers in dioxane at 20°. The deviations found in the case of the lower members, namely, diethylene-, triethylene- and hexaoxyethylene glycols, from the linear relationship is to be expected, since Staudinger³ has emphasized repeatedly that the lower members of any polymer homologous series do not obey his viscosity law, which is strictly applicable only to the longer chain molecules of a series. In other words, it is confined to the class of long, linear, thread-like molecules and does not include polymers of low molecular weight whose configuration is not far removed from a spherical shape.

The effect of increase in temperature upon the shape of the $\eta_{sp.}/c$ -mol. wt. curve was found to vary in the two solvents. From Table II it can

be seen that in dioxane there is only a slight lowering of the specific viscosity value, in other words, K_m changes only slightly with increasing temperature in this solvent. Similar results were also

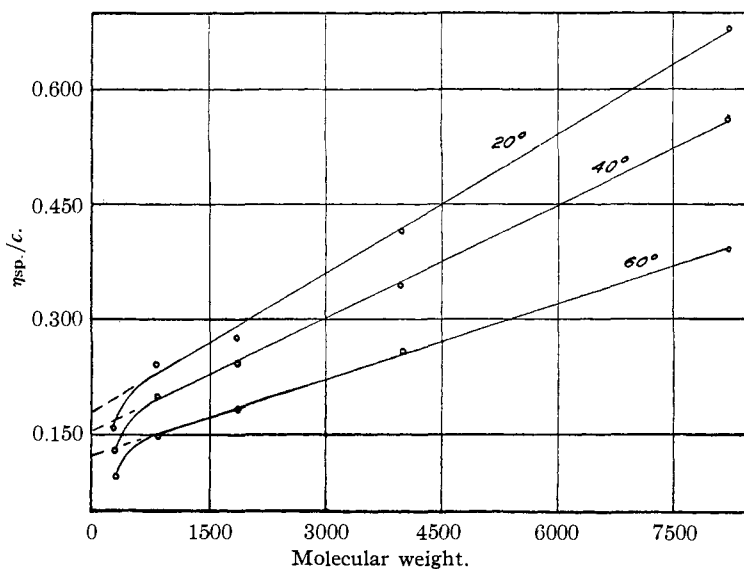


Fig. 1.—The mol. wt.- $\eta_{sp.}/c$ curves for carbon tetrachloride solutions of polyoxyethylene glycols at 20, 40 and 60°.

found by Staudinger³ for dioxane solutions of his polyethylene oxide polymers. In carbon tetrachloride (Table I), on the other hand, there is a considerable decrease in specific viscosity as the temperature is increased. The general shape of

the specific viscosity-molecular weight curve for polyoxyethylene glycols in carbon tetrachloride is indicated in Fig. 1, as well as the influence of an increase in temperature. This latter effect can be regarded as a desolvation of the solute molecules brought about by an increase in temperature.

Of far greater significance than temperature variation of specific viscosity is the fact that a linear relationship between specific viscosity and chain length is clearly shown to exist, both in different solvents and at different temperatures. The validity of the Staudinger viscosity equation has been disputed by Hess and Rabinovitch,¹¹ Sakurada,¹² Karrer and Ferri,¹³ Meyer and Van der Wijk,¹⁴ and many others, but there are presented here, for the first time, viscosity data based on pure, long chain, chemical individuals, and which definitely point to a straight line relationship between specific viscosity and molecular weight in the case of solutions having the same "ground molar" concentration.

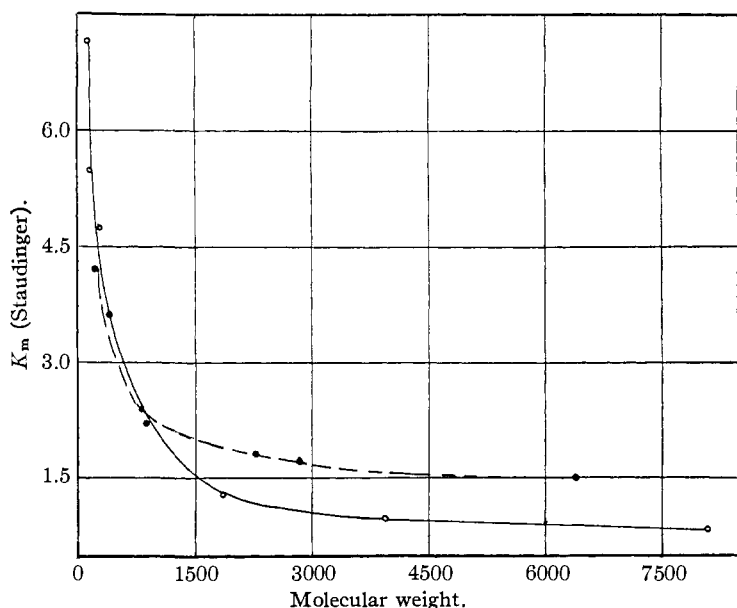


Fig. 2.—Variation of K_m with mol. wt.: (a) pure polyoxyethylene glycols, solid curve \circ ; (b) Staudinger's polyethylene oxides, broken curve \bullet .

The Staudinger equation, $\eta_{sp}/c = K_m M$, which expresses a linear relationship between η_{sp}/c and M , implies a straight line passing through the origin. However, extrapolation of the linear section of the specific viscosity-molecular weight curves obtained from the data presented here,

as well as those based on Staudinger's own data for other polymer homologous series, in general, shows an intercept on the specific viscosity axis. In other words, neglecting the lower members of a given series, the new data submitted indicate that the Staudinger equation should be modified as follows

$$\eta_{sp}/c = K'_m M + \beta \quad (1)$$

where β is the η_{sp}/c intercept.

The values of K'_m and β , as well as the values of K_m calculated according to the Staudinger equation, are tabulated in Tables I and II. It can be seen that K'_m has a constant value, especially for carbon tetrachloride solutions at 40 and at 60° whereas the Staudinger constant K_m is still only approaching a constant value. For higher molecular weights the effect of the η_{sp}/c intercept upon the value of K_m in Staudinger's equation becomes negligible and K_m then has a constant value.

More recently Staudinger and Daumiller¹⁵ have published data concerning the variation of K_m of cellulose triacetates with degrees of polymerization varying from those of the oligosaccharide acetates to the very high molecular weight cellulose acetates. The general trend of the K_m variation in that series is quite similar to that observed in the present investigation of the polyoxyethylene glycols (Fig. 2). It would seem from this that more accurate values for the molecular weight of the lower members of a series, and still within the range of validity of the Staudinger viscosity law, can be obtained by the application of the authors' modified viscosity equation, (1). While it is true that Staudinger³ also has postulated a similar equation $\eta_{sp}/c = ny + x$, this is derived from an entirely different concept than the one on which that of the

authors is based. Moreover, the application of the above modified Staudinger equation has been confined almost entirely to polymeric homologous forms of hydrocarbon series.

In any interpretation and comparison of the viscosity results obtained with pure polyoxyethylene glycols, it must be remembered that the present results are based on an examination, for

(11) Hess and Rabinovitch, *Ber.*, **65B**, 1407 (1932).

(12) Sakurada, *ibid.*, **67B**, 1045 (1934).

(13) Karrer and Ferri, *Helv. Chim. Acta*, **17**, 358 (1934).

(14) Meyer and Van der Wijk, *ibid.*, **18**, 1067 (1935).

(15) Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

the first time, of the behavior of pure, homogeneous, individual, long chain polymers, whereas all similar investigations in this field have been carried out on polymers obtained by fractionation of synthetic and natural polymers, and therefore necessarily mixtures. From the form of the Staudinger viscosity equation as well as from consideration of the assumptions involved in its evolution, it readily can be shown that the viscosity-producing influence of extremely long molecules is very great as compared with that exerted by those of shorter chain length. In brief, the solution viscosity of a polymeric mixture is influenced profoundly by the distribution of molecular weights about the mean value. Schulz¹⁶ has derived an equation connecting the value of K_m for a polymer of uniform chain length with that of a polymeric mixture of the same substance, in terms of a defined distribution function. He shows, experimentally, as well as theoretically, that in the case of the polyisobutylene polymers it is possible for the value of K_m of such a polymeric mixture to be double that of a pure polymer of the same series.

In Fig. 2 the variation of K_m with increasing degree of polymerization in the case of the pure polyoxyethylene glycols is compared with that found by Staudinger and Lohmann³ (p. 287) for polymeric ethylene oxide mixtures. It is readily seen from this that the K_m value for the pure glycol is lower than that of the polymeric mixture of the same average molecular weight. The observed lower K_m values for the uniform polymers are in agreement with the views of Schulz.

Work is in progress in these Laboratories with

(16) Schulz, *Z. physik. Chem.*, **B32**, 27 (1936).

the object of obtaining a quantitative relationship between these two constants in terms of the distribution function.

Regarding the question of Staudinger's much-discussed "Fadenmolekül" very little can be said concerning the configuration of the polyoxyethylene glycols. Sakurada,¹⁷ Mark¹⁸ and Huggins¹⁹ have demonstrated quite conclusively that there is no *a priori* reason for assuming a rigid stretched-out form of the molecule in order to explain a linear relationship between molecular weight and specific viscosity. The presence of numerous ether linkages in the polyoxyethylene glycols, considering the well-known difference in, and variability of, the oxygen valence angle as compared with carbon,²⁰ indicates that these compounds probably exist in solution in a convoluted form rather than as rigid rod-like structures.

Summary

1. The solution viscosities of long chain polyoxyethylene glycols have been measured in carbon tetrachloride and dioxane at 20, 40 and 60° and agreement with the Staudinger linear relationship between chain length and η_{sp}/c has been obtained in each case.

2. A slightly modified form of the Staudinger equation, *viz.*, $\eta_{sp}/c = K'_m M + \beta$, is suggested as a more accurate mathematical expression, especially in the case of the lower members of a given homologous series.

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(17) Sakurada, *Naturwissenschaften*, **25**, 523 (1937).

(18) Mark, "Der feste Körper. Vorträge an der Tagung der Physikalischen Gesellschaft Zürich anlässlich der Feier ihres 50 jährigen Bestehens," S. Hirzel, Leipzig, 1938, p. 65.

(19) Huggins, *J. Phys. Chem.*, **43**, 439 (1939).

(20) Allen and Hibbert, *Ber.*, **65**, 1362 (1932).