tion of oxygen at $-183°$ approaches, in order of magnitude, that of iron oxide formation; and the form of the time–temperature curves with oxygen at $-183°$ indicates that the adsorption process in-volved is complex. A similar complex process was previously observed with chromic oxide gel at $-183°$.

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXII. The Relation between Concentration and Viscosity of Polyoxyethylene Glycols

By Edwin L. Lovell[1] and Harold Hibbert

In a recent communication, Fordyce and Hibbert[2] have described the relation between the degree of polymerization of polyoxyethylene glycols $HO(CH_2CH_2O)_xH$ and their solution viscosities at basic-molar concentration (4.4%) in two solvents (dioxane and carbon tetrachloride). They found that their data could be accurately represented by the Staudinger equation written in the form $\eta_{sp}/c_{bm} = K'_m(M) + \beta$, where β is a small constant. However, the Staudinger equation, although invariably written in terms of the reduced viscosity η_{sp}/c_{bm}, is apparently not meant to imply that the specific viscosity is a linear function of the concentration over any appreciable range of concentrations, as Staudinger has used[3] the early empirical equation of Arrhenius[4]—ln $\eta_r = Kc$ —(where K is a constant) for both polyethylene oxides and polystyrenes. This is also the equation used by Kraemer[5] for the extrapolation of viscosity results to zero concentration in calculating the "intrinsic viscosity," an important quantity for characterizing high-polymer solutions. However, the question of the concentration effect of viscosity for such solutions has been the subject of controversy for many years, and a wide variety of empirical equations has been suggested.[6] In a recent investigation by Daneš,[7] carried out with carefully fractionated polystyrenes, it is shown that neither the Arrhenius nor the Staudinger equation is capable of describing the experimental results. No alternative is suggested. Inasmuch as Daneš' investi-gation was carried out under much more care-fully-controlled conditions than used by Staud-inger, especially with regard to the use of uniform products, considerable doubt is thrown on the validity of either of these equations. A similar investigation has therefore been carried out with a number of synthetic, chain-uniform polyoxy-ethylene glycols. Furthermore, some synthetic mixtures of these substances have been pre-pared, and their viscosities compared with theory.

Experimental

The synthesis and proof of chain-uniformity of the polyoxyethylene glycols and the dichloride used in the ex-periments have been reported elsewhere.[8] 1,4-Dioxane was purified according to the recent method of Hess.[9] Carbon tetrachloride was fractionated and redistilled from solid potassium hydroxide.

The solutions were prepared as follows. The pure, dry solute (about 0.5–2 g.) was weighed into a 10-ml. volu-metric flask (previously standardized with water) and dis-solved by adding solvent to a point just below the volume mark. When a uniform solution finally resulted, the total volume was adjusted accurately to the mark by adding a further small portion of solvent (less than one drop). These operations were carried out in a thermostat. Fin-ally, the total weight of the solution was measured.

During use, each solution was stored in a desiccator con-taining an open dish filled with the anhydrous solvent. This was found to be completely effective in preventing evaporation. Other precautions were taken to avoid evaporation during the subsequent operations.

Mixtures were prepared by weighing the solutions di-rectly into a weighing bottle (again with suitable pre-cautions) and measuring the resulting density.

The viscometer was the same instrument as used by Fordyce and Hibbert.[2] A thermostat maintained the temperature constant to within $\pm0.02°$. In calculating the viscosities, the solution densities were taken into ac-count. A summary of the experimental data appears in Table I.

(1) Holder of a Studentship of the National Research Council of Canada, 1939–1940.

(2) Fordyce and Hibbert, This Journal, 61, 1912 (1939).

(3) Staudinger, "Der Aufbau der hochmolekularen Verbin-dungen," Verlag von Julius Springer, Berlin, 1932.

(4) Arrhenius, Z. physik. Chem., 1, 287 (1887).

(5) Kraemer, Ind. Eng. Chem., 30, 1200 (1938).

(6) Many of these have been reviewed critically by Hess and Philippoff, Ber., 70B, 639 (1937); see also Meyer and Wolff, Kolloid-Z., 89, 194 (1939).

(7) Daneš, Kolloid-Z., 68, 110 (1934).

(8) Fordyce, Lovell and Hibbert, This Journal, 61, 1905 (1939); Fordyce and Hibbert, ibid., 61, 1910 (1939).

(9) Hess, Ber., 71B, 262 (1939).

Discussion of Results

In any consideration of the concentration function of high-polymer solutions, there are three distinct regions of concentration to be defined. The first is the region of "dilute" solutions, where it is commonly expected that a nearly ideal behavior of the solute will be found. The second is the region of "moderately concentrated" solutions, where deviations from ideality first become apparent. Finally, there is the region of "concentrated" solutions. The region of validity of any equation connecting viscosity and concentration must therefore be defined. Furthermore, it is a common observation when dealing with high-molecular substances that the dilute region becomes continually smaller as the molecular weight is increased; the extent of the region in each case is therefore of some practical interest.

For the polyoxyethylene glycols, it appears that the range of dilute solutions extends to at least basic-molar concentration for even the longest chain investigated ($P = 186$). In this region a simple relationship exists between the concentration and specific viscosity

$$\eta_{sp} = A(c - b) \qquad (1)$$

where A is a constant and b another small constant, both depending on the molecular weight of the solute. The equation is arrived at from consideration of Fig. 1, which shows that η_{sp} is strictly a linear function of c (in grams per liter of solution), and that the straight lines so obtained do not precisely meet the origin. This causes a noticeable drift in the values of K calculated from the Staudinger equation $\eta_{sp} = K_m$ $(M)c = Kc$, as is seen in Table I; the drift is negligible only for the shortest-chain glycol ($P = 42$). It is to be borne in mind that the experiments were carried out with greater accuracy than would be justified in dealing with any but pure, fully characterized substances.

The values of b are estimated approximately by extrapolation of the curves of Fig. 1; for the 42- and 90-membered glycols the results are 0.5 and 1.0, respectively, and for the 186-membered glycol, $b = 3.5$.

Table I also contains data for one oxyethylene dichloride ($P = 42$) to permit comparison with the corresponding glycol. According to the often-expressed theories of Staudinger,[3,10] there should

(10) Staudinger, *Trans. Faraday Soc.*, **32**, 112 (1936).

be no difference in the specific viscosities of two solutes with the same chain-length but differing only in the end-groups. It is seen that in the present case this is not true; on the contrary, the dichloride shows a definitely higher viscosity. The reason is perhaps not difficult to find. Many experiments—some of them carried out by Staudinger[11] himself—have served to show that a large part, perhaps even one-half or more, of the total solution viscosity of macromolecular substances is due to the presence of a solvate layer. The precise nature of this interaction with the solvent is not yet fully understood, but its existence[12] and great viscosity-producing effect may be regarded as proven. The present experiment with dotetracontaoxyethylene dichloride seems to demonstrate the magnitude of the effect in another way; a chain of 136 atoms, dissolved in a solvent of very similar chemical nature, displays a different specific viscosity when the attached end-groups are OH, than when they are Cl. The application of corrections for the difference in molecular weights or partial specific volumes, only increases this discrepancy. It therefore seems logical to account for this behavior on the ground of a difference in the degree of solvation in the two cases, with each solvate layer
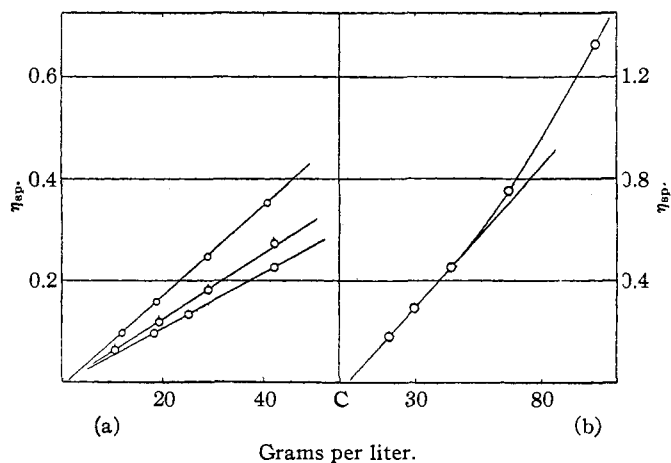

Fig. 1.—Solution viscosities (dioxane); (a) upper curve $P = 90$; lower curve, $P = 42$; center curve, 42-dichloride; (b) 186-membered glycol in CCl_4.

contributing largely to the specific viscosity of the solution. This conception is also in accordance with the large temperature coefficient of specific viscosity observed by Fordyce and Hibbert.[2]

(11) Staudinger and Heuer, *Z. physik. Chem.*, **A171**, 148 (1934).

(12) Eirich and Mark, *Ergeb. exakt. Naturw.*, **15**, 1 (1936).

TABLE I

SUMMARY OF SOLUTION VISCOSITIES

	Conditions	c, g./l.	$1000\eta_{sp}$	$10^5\eta_{sp}/c$
42	Dioxane, 20°	42.06	226	536
		25.07	134	535
		18.38	97	527
42, Cl	Dioxane, 20°	42.12	272	646
		29.04	182	628
		19.40	119	613
		10.65	63	594
90	Dioxane, 20°	40.68	353	867
		28.91	247	855
		18.82	159	845
		11.92	97	808
186	CCl₄, 50°	101.8	1328	1303
		66.90	753	1125
		43.45	451	1025
		29.70	291	980
		19.69	182	926

TABLE II

VISCOSITY OF SYNTHETIC MIXTURES

Components		η_{sp} Calcd.	η_{sp} Obsd.	Difference, %
90	186	0.382	0.377	1.3
186	42, Cl	.314	.312	0.6
90	186	.239	.235	1.7
42	186	.198	.201	−1.5

Approximate error in η_{sp}, ±2%.

Mixed Solutes.—Consideration of the experiments with mixed solutions of unipolymeric oxyethylene glycols reveals the fact (Table II) that in such synthetic mixtures each separate polymer molecule exerts its own influence on the total specific viscosity of the mixture, independently of the presence of other molecules of different chain-lengths, even when the end-groups are not the same for each member. This simple additivity of specific viscosities also is said to hold for mixtures of lyophilic sols,[13] although several authors[14] have used more complicated expressions in the case of mixtures of actual high-polymer solutions.

More recently, Schulz[15] has derived an expression for the total viscosity of a continuously-distributed mixture of polymer-homologs, in terms of the distribution function; it is assumed in this derivation that the specific viscosities of all members from the longest to the shortest are strictly additive, so that $d\eta_{sp} = KPdc$. The results of the present experiments seem to justify this procedure.

Moderately Concentrated Solutions.—A wider range of concentrations (2–10%) than those described above was investigated with the 186-membered glycol in carbon tetrachloride solution, at 50°. The choice of solvent and temperature was based on consideration of the experiments of Fordyce and Hibbert,[2,16] which seem to indicate that these conditions are the most nearly "ideal" from the point of view of the absence of large associative or solvation effects, particularly the latter. The results (Fig. 1(b)) show that the linear relationship which exists between the specific viscosity and concentration up to a concentration of about 5% gives way at higher concentrations to a curve which is strongly convex to the concentration axis. This behavior is quite commonly observed with solutions of high polymers, and according to present ideas is due[17] largely to the superposition of the single disturbed regions about each particle, as the concentration is increased beyond a critical value.

On this basis it is to be expected that a general equation of the type

$$\eta_{sp} = Ac + Bc^2 + Cc^3 + \cdots \quad (2)$$

will describe the viscosity–concentration function over all ranges of concentration. Naturally, it has no theoretical significance, since a great many theoretical equations may be developed into the form of a power series in c.[18] Such a series has recently[19] been used by Sakurada to examine a large number of solutions of synthetic and natural high polymers; as a result it is stated that for "moderately dilute" solutions at least two constants (A, B) are required, and that the ratio $A^2/B = m$ has the average value of 1.8 for the natural polymers and about 5 for the synthetic polymers.

It is now found that the experimental results for the 186-membered glycol are accurately represented by the Arrhenius equation (Fig. 2)

$$\eta_r = a^{kc} \quad (3)$$

(where a is a constant). This equation may be written[20] in the form

$$\eta_{sp} = Ac + A^2c^2/2 + A^3c^3/6 + \cdots \quad (4)$$

(where $A = k \ln a$), i. e., in terms of the general

(13) De Jong and Gwan, Biochem. Z., **221**, 166 (1930).

(14) Fikentscher and Mark, Kolloid-Z., **49**, 135 (1929); Atsuki and Ishiwara, J. Soc. Chem. Ind. (Japan), **33**, 508B (1930); Fikentscher. Cellulosechem., **13**, 58 (1932); Philippoff, Ber., **70B**, 827 (1937).

(15) Schulz, Z. physik. Chem., **B41**, 466 (1938).

(16) Fordyce, Ph.D. Thesis, McGill University, 1939.

(17) For example, see Guth and Simha, Kolloid-Z., **74**, 266 (1936), and later papers of Eirich and co-workers; also Kratky and Saito, Cellulosechem., **16**, 85 (1935).

(18) Sakurada, Kolloid-Z., **63**, 311 (1933); Bredee and de Booys, ibid., **79**, 31 (1937).

(19) Sakurada, ibid., **82**, 345 (1938).

(20) Sakurada and Hess, Ber., **64**, 1184 (1931), in a footnote.

equation (2), $B = A^2/2$ and $m = 2$. Thus only a single constant appears to be necessary. Some values of A are given in Table III. The observed

TABLE III

VISCOSITY-CONCENTRATION CONSTANTS, A

dp	$2.3(\delta \log \eta_r)/\delta c$	Conditions
42	0.00202	Dioxane, 20°
42, Cl	.00250	Dioxane, 20°
90	.00301	Dioxane, 20°
186	.0082	CCl₄, 50°

value of $m = 2$ is seen to be quite close to the value assigned by Sakurada to natural polymers.

The Coefficient "A."—Perhaps the most well-founded of the theoretical equations for the viscosity of chain-molecules in solution is that of Huggins.[21] If this equation is expressed in terms of a power series in c, it appears that $A = 5.93 \times 10^{20} n(l_0^2 r)$, where n is the number of chain atoms, l_0 the average distance between the centers of adjacent atoms and r the average effective radius. The latter quantity is thus readily calculated if A is known. For the 186-membered glycol (using the data of the above table[22]) the result so obtained is $\bar{r} = 0.18 \times 10^{-8}$ cm. This is about six times smaller than would be expected, despite the fact that the equation gives very good agreement when applied to paraffin solutions.[21] Furthermore, under the experimental conditions used, the oxyethylene chains are presumably very largely desolvated. It therefore must be concluded that the polyoxyethylene chain has a different configuration in solution than the polymethylene chain, such that the effective length is considerably reduced from

(21) Huggins, *J. Applied Phys.*, **10**, 700 (1939).

(22) Here $A = 0.0121$ in terms of base-molar concentration, taking an average base-molecular weight of 14.7. It is assumed that all the valency angles are tetrahedral.

the normally expected statistical value.

Summary

1. The viscosities of 42- and 90-membered oxyethylene glycols, and the 42-membered dichloride, have been measured at 20° over the concentration range 1 to 4.5%. Solutions of the 186-membered glycol in carbon tetrachloride have been similarly investigated over the concentration range 2 to 10%.

2. In the region of dilute solutions (below 5%) a linear relationship is found between the
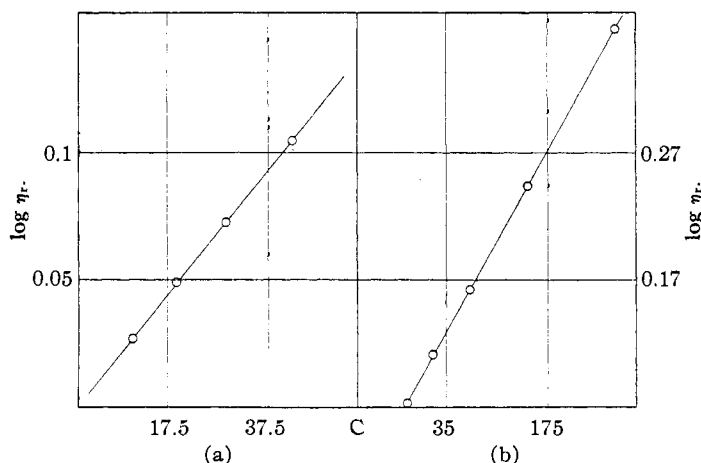

Fig. 2.—Plot of Arrhenius equation for (a) 42-dichloride; (b) 186-glycol.

specific viscosity and concentration (g./l.).

3. The data at all concentrations are in accordance with the Arrhenius equation, $\log \eta_r = Kc$.

4. When any two members of the series are mixed with one another, the resultant specific viscosity is the sum of the specific viscosities of the individual components.

5. The polyoxyethylene chain appears to be highly convoluted in solution, being unlike the polymethylene chain in this respect.