[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. XLIX. Molecular Weight, Molar Refraction, Freezing Point and Other Properties of the Polyethylene Glycols and their Derivatives[1]

BY A. F. GALLAUGHER AND HAROLD HIBBERT

In a previous communication in this series[2] several new methods were described for the synthesis of the higher polyethylene glycols.

Experimental evidence already obtained definitely establishes the structure of the polymerization products formed by the action of alkaline catalysts on ethylene oxide as normal long-chain polyethylene glycols, and the latter are known to possess a definite chemical relationship with polysaccharides such as cellulose, starch, etc.

For this reason an extensive study was undertaken of the physical properties of the polyethylene glycols and of some of their derivatives.

Preparation and Purification of Materials

The Polyethylene Glycols.—The synthesis and purification of the tetra-, penta-, hexa- and heptaethylene glycols were carried out by the methods described previously.[2] Ethylene, diethylene and trimethylene glycols, obtained from the Carbide and Carbon Chemicals Corporation, New York, were purified by preliminary vacuum distillation, shaken mechanically with activated anhydrous alumina, and allowed to stand for two days. Each product was then distilled twice, under reduced pressure.

Pure fractions of tri-, tetra-, penta-, hexa- and heptaethylene glycols were obtained from the crude products furnished by S. Z. Perry,[2] by distilling the individual polyethylene glycols five times using a Hyvac oil and a Langmuir mercury pump in series. In all these distillations, especially in the final purification of the polyethylene glycol, the operation was carried out so that the distillate passed over at a rate of one drop in five to twelve seconds. Unless this procedure was adopted considerable superheating occurred. On account of the highly hygroscopic nature of the polyethylene glycols, they were preserved in glass-stoppered bottles and these, in turn, were placed in a desiccator over phosphorus pentoxide.

Table I contains the observed boiling points of the polyethylene glycols and their analyses.

Derivatives of the Polyethylene Glycols.—Tetraethylene glycol monochlorohydrin was obtained as a by-product in the synthesis of hexaethylene glycol by the condensation of the sodium derivative of diethylene glycol with β,β'-dichloroethyl ether,[2] b. p. 134.6–136.0° (0.94 mm.).

Anal. Calcd. for $C_8H_{17}O_4Cl$: C, 45.20; H, 8.00; Cl, 16.67. Found: C, 45.16; H, 7.99; Cl, 16.37.

TABLE I

Glycol	Obsd. boiling point °C.	Mm.	Analyses, % Calcd. H	C	Found H	C
Monoethylene	80–81	3.0				
Diethylene	119–120	6.5–7.0				
Triethylene	115.5–117.0	0.10	9.33	48.0	9.53	48.3
Tetraethylene	144.0–145.5	.10	9.27	49.4	9.28	49.0
Pentaethylene	174.0–176.0	.14	9.23	50.0	9.14	49.0
Hexaethylene	203.0–205.0	.30	9.21	51.0	9.28	51.2
Heptaethylene	241.0–244.0	.60	9.19	51.5	9.22	51.8

Ethylene dichloride (A) and β,β'-dichloroethyl ether (B), obtained from the Carbide and Carbon Chemicals Corporation, were purified by three vacuum distillations: b. p. (A) 83.4–83.6° (753.5 mm.); (B) 175.0–175.4° (753.1 mm.).

The β,β'-dichloroethyl ether, when tested for acidity and unsaturation, gave negative results.

1,4-Dioxane and ethylene glycol monomethyl ether were also obtained from the Carbide and Carbon Chemicals Corporation. The former was purified by allowing to stand over sodium for twenty-four hours, and then redistilling three times; b. p. 101.0–101.2° (754.8 mm.). The latter was purified by three careful refractionations, b. p. 124.0–125.1° (765 mm.).

Diethylene glycol dimethyl ether was synthesized by the action of sodium methylate, dissolved in methyl alcohol, on the theoretical quantity of β,β'-dichloroethyl ether. A small quantity of an unidentified, unsaturated, low-boiling product was formed simultaneously; this was probably vinyl methoxyethyl ether. A number of condensations were carried out under varying conditions. At 80° the reaction proceeded violently and gave a 50–60% yield of diethylene glycol dimethyl ether; while at approximately 25°, using vigorous agitation, the reaction proceeded quietly. Reaction period two to three days; yield 70%. The tendency toward vinyl compound formation is thus decreased, but in no case was the formation of divinyl ether observed. Presumably the reaction proceeds as indicated

$$(1)\quad Cl{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}Cl + 2NaOCH_3 \longrightarrow (OCH_3){-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2(OCH_3) + 2NaCl$$

$$(2)\quad Cl{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2Cl + 2NaOCH_3 \longrightarrow CH_2{=}CH{-}O{-}CH_2{-}CH_2(OCH_3) + 2NaCl + CH_3OH$$

According to Cretcher and Pittenger[3] sodium alcoholates do not react with β,β'-dichloroethyl ether at room temperature, and it is necessary to heat for eight to fifteen hours to bring about a complete condensation. These results are quite at variance with those found by the above-mentioned authors.

Pure diethylene glycol dimethyl ether, b. p. 160.5–161.0° (756.6 mm.), was obtained by careful refractionation.

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(1) Abstracted from a thesis presented by A. F. Gallaugher in 1932 to the Faculty of Graduate Studies, McGill University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

(2) Perry and Hibbert, *Can. J. Research*, **A14**, 77 (1936).

(3) Cretcher and Pittenger, THIS JOURNAL, **47**, 163 (1925).

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.73; H, 10.44. Found: C, 53.15; H, 10.58.

Molecular Weight Determinations

The molecular weights of the polyethylene glycols, tetraethylene glycol monochlorohydrin and diethylene glycol dimethyl ether were determined cryoscopically (Beckmann) using ethylene dibromide as solvent. The polyethylene glycols and the chlorohydrin were found to be associated in this solvent, and the true molecular weight was therefore determined by plotting the observed molecular value against percentage molar concentration of the solute.

The curves (Fig. 1) for the tri- and tetraethylene glycols and tetraethylene glycol monochlorohydrin are normal, that is, association increases with the concentration throughout, while those for the penta-, hexa- and heptaethylene glycols are abnormal, the true molecular weight being found by extrapolation. In the latter cases the association appears to be very great at the lower concentrations, but soon decreases to a minimum value, followed by a normal increase with concentration.

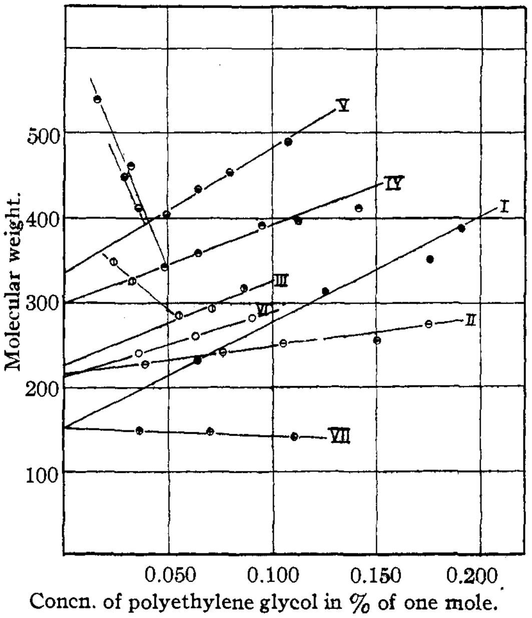


Fig. 1.—Apparent molecular weight of polyethylene glycols: ●, triethylene; ⊖, tetraethylene; ⦶, pentaethylene; ◓, hexaethylene; ◒, heptaethylene; ○, tetraethylene glycol monochlorohydrin; ⊕, diethylene glycol dimethyl ether.

No explanation can be given, as yet, for this apparent anomaly, and it would seem to be an impossible condition from physico-chemical considerations. A similar anomaly has been observed in this Laboratory with the monoallyl ethers of these polyethylene glycols, and the ease of duplication of the results would seem to rule out any possibility of error due to experimental technique.

A summary of the data is given in Table II.

TABLE II

Concn. in % of one mole of compound	Mol. wt. obsd.	Mol. wt. by extrapolation	Mol. wt. theoretical
I. Triethylene glycol			
0.064	228.9	150	150.1
.125	312.4		
.175	351.7		
.191	387.8		
II. Tetraethylene glycol			
0.039	224.7	215	194.1
.076	238.0		
.125	250.7		
.149	252.0		
.174	273.5		
III. Pentaethylene glycol			
0.024	346.0	226	238.2
.033	323.8		
.055	283.4		
.071	290.7		
.086	313.8		
IV. Hexaethylene glycol			
0.016	538.5	298	282.2
.032	460.0		
.048	339.0		
.064	357.4		
.095	389.2		
.112	396.3		
.141	412.0		
V. Heptaethylene glycol			
0.029	447.0	334	326.2
.036	410.0		
.049	403.0		
.064	437.0		
.079	452.0		
.107	489.0		
VI. Tetraethylene glycol monochlorohydrin			
0.036	238.3	211	212.6
.063	260.2		
.090	279.4		
VII. Diethylene glycol dimethyl ether			
0.036	147.6	153	134.0
.070	146.7		
.109	139.3		

Freezing Points

The freezing points of trimethylene glycol and tetraethylene glycol monochlorohydrin were difficult to measure owing to their highly viscous nature and tendency toward supercooling.

The liquid of unknown freezing point was placed in a test-tube which was air-jacketed by means of another larger test-tube. The inner tube was fitted with a stirrer and an alcohol thermometer which had been checked previously against a standard pentane thermometer. Precautions were taken to obviate the presence of moisture in the substance by suitably closing the mouth of the tube.

The determination of the freezing point was carried out in the following manner using the same degree of supercooling throughout. A sample of the polyethylene glycol was frozen by supercooling the compound to between −40 and −60° (acetone–solid carbon dioxide mixture). Even at these low temperatures, crystallization took place only on vigorous stirring. Another sample of the same polyethylene glycol was then placed in the inner test-tube described above, and the compound supercooled slightly, stirred slowly, and then inoculated with a few crystals of the previously frozen polyethylene glycol. At this point the supercooled compound was vigorously stirred and the rise in the temperature observed. The maximum temperature attained was taken to be the approximate freezing point. The polyethylene glycol was then melted and the above procedure repeated, the compound being supercooled only to about 3° below the freezing point determined above. A lesser degree of supercooling yielded only a viscous mass on inoculation with the crystals of the compound in question. The results shown represent an average of six to eight freezing point determinations, error ±0.5°.

Tetraethylene glycol monochlorohydrin was supercooled to −70° before incomplete crystallization occurred, so that the freezing point determination is inaccurate.

TABLE III

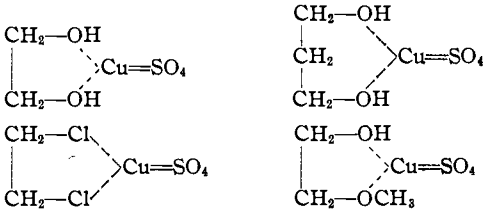
Compound	Freezing point, °C.
Ethylene glycol	−13.2
Diethylene glycol	−10.1
Triethylene glycol	− 9.4
Tetraethylene glycol	− 9.4
Pentaethylene glycol	− 8.7
Hexaethylene glycol	1.3
Heptaethylene glycol	7.7
Trimethylene glycol	−32.0
Tetraethylene glycol monochlorohydrin	−54.0
1,4-Dioxane	11.0

There is a definite trend toward the solid state on passing from pentaethylene to hexaethylene and heptaethylene glycols due to the increasingly larger molecular forces of attraction assumed to be operative with increased chain length, so that pure decaethylene and possibly nonaethylene glycols should be solids at ordinary temperatures.

Chelate Ring Formation.—A chelate coördinate link is always the source of instability since the products of its rupture are, in general, more stable than those formed by breaking a normal covalency as shown by the fact that, while normal rings with any number of carbon atoms from 3 to 18 are known, chelate rings never contain less than 4, and very rarely more than 6.

Experimental Observations.—Treatment of well-dried samples of the polyethylene glycols and their derivatives at room temperature with anhydrous copper sulfate for several hours showed the following: (1) ethylene and trimethylene glycols—rapid development of a blue coloration resembling that of a copper salt; (2) ethylene dichloride and ethylene glycol monomethyl ether—a slight blue coloration; (3) diethylene and higher polyethylene glycols and dioxane—no coloration.

It is possible that this blue coloration is due to formation of chelate rings representing a coördination compound in which two groups of the glycol molecule, or its derivatives, are attached to the copper atom of copper sulfate, for example



Molecular Refraction.—Molecular refraction is generally accepted as a measure of the space actually occupied by the molecules and hence this property appears to be closely related to molecular volume. Herz[4] attempted to trace a relationship between molecular refraction and the parachor, but a simple relation between the two is not to be expected except within a narrow range of compounds.

Measurement of the Refractive Index.—The refractive indices were measured by means of an Abbé refractometer with temperature control within 0.1°. Table IV gives the refractive indices, the molecular refraction calculated by means of the Lorentz and Lorenz formula, the theoretical refractive index obtained using the atomic refractivity values of Eisenlohr[5] and finally the difference between the "observed" and "calculated" values of the molecular refraction. The value δ represents the increase in the "observed" molecular refraction in the homologous series. In Fig. 2 refractive indices of the polyethylene glycols are plotted against molecular weight.

TABLE IV

Compound	Refrac. index n^{20}_D	Mol. refrac. obsd.	Mol. refrac. calcd.	Diff. in obsd. mol. refrac. δ	Obsd. minus calcd. mol. refrac.
Ethylene glycol	1.4314	14.45	14.49	10.94	−0.04
Diethylene glycol	1.4472	25.39	25.36	10.92	0.03
Triethylene glycol	1.4557	36.31	36.24	10.94	0.07
Tetraethylene glycol	1.4593	47.25	47.12	10.97	0.13
Pentaethylene glycol	1.4617	58.22	58.00	10.97	0.22
Hexaethylene glycol	1.4637	69.19	68.88	11.03	0.31
Heptaethylene glycol	1.4653	80.22	79.76		0.46
Trimethylene glycol	1.4389	19.02	19.10		−0.08
Tetraethylene glycol monochlorohydrin	1.4574	51.09	50.46		0.63
Ethylene glycol monomethyl ether	1.4023	19.18	19.22		−0.04
Diethylene glycol dimethyl ether	1.4097	34.58	34.84		−0.26
Ethylene dichloride	1.4446	21.05	21.17		−0.12
β,β'-Dichloroethyl ether	1.4570	31.90	32.05		−0.15
1,4-Dioxane	1.4233	21.41	21.76		−0.35

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[4] Herz, *Z. anorg. allgem. Chem.*, **159**, 316 (1927).

[5] Roth, "Refraktometrisches Hilfsbuch," Veit and Co., Leipzig, 1911.

According to Smiles,[6] in a homologous series the specific refractive power increases with the molecular weight but the increment decreases as the series is ascended. On the other hand, the increase in molecular refractivity appears to be constant. The data on the polyethylene glycols (Table IV) appear to show that both these statements are true for this series, though the increment in molecular refraction exhibits a slight increase with increase in molecular weight.

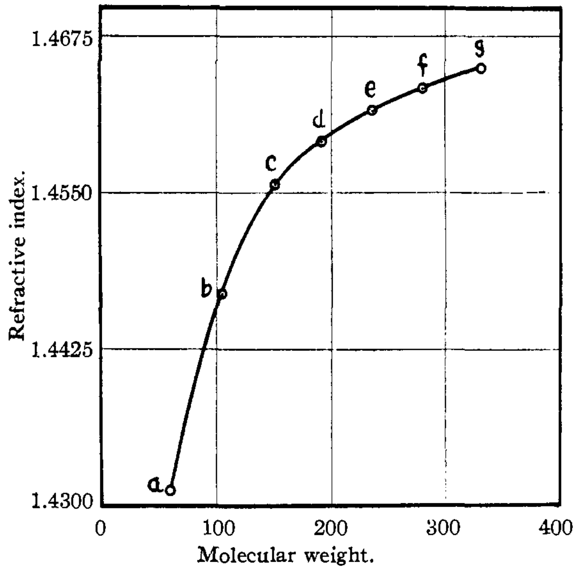

Fig. 2.—Refractive indices of polyethylene glycols: a, ethylene glycol; b, diethylene glycol; c, triethylene glycol; d, tetraethylene glycol; e, pentaethylene glycol; f, hexaethylene glycol; g, heptaethylene glycol.

Summary

The molecular weights (cryoscopic) in ethylene dibromide of tri-, tetra-, penta-, hexa- and heptaethylene glycols and of certain of their derivatives have been measured. Abnormalities in the variation of the degree of association with the concentration have been observed in the case of the glycols.

From the freezing point data on the polyethylene glycols it may be predicted that pure decaethylene glycol and possibly pure nonaethylene glycol will be solids at room temperature.

An indication of the formation of chelate rings was observed with ethylene and trimethylene glycols, and to a lesser degree with ethylene dichloride and ethylene glycol monomethyl ether, when these compounds were treated with anhydrous copper sulfate.

An approximately constant increase in molecular refraction with increasing molecular weight has been observed in the polyethylene glycol series.

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[6] Smiles, "Relations between Physical Properties and Chemical Constitution," Longmans, Green and Co., London, 1910, p. 257.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Catalyzed Reaction of Ethylmagnesium Bromide with Ethyl Bromide

BY C. B. LINN AND C. R. NOLLER

One of the side reactions encountered during the preparation of Grignard reagents from alkyl halides leads to the formation of saturated and unsaturated hydrocarbons in equivalent amounts.[1] Jolibois[2] was the first to discover the cause of this type of side reaction when he showed that the formation of ethylene and ethane was due to the reaction of ethyl iodide with ethylmagnesium iodide according to equation I.

$$C_2H_5MgX + C_2H_5X \longrightarrow C_2H_4 + C_2H_6 + MgX_2 \quad (I)$$

In the following year Späth[3] reported on a number of reactions between alkylmagnesium halides and alkyl halides in which coupling and disproportionation were observed.

More recently Job, Reich and Dubien[4] found that the evolution of gases during the preparation of ethylmagnesium iodide does not occur if the magnesium is pure, but that the side reaction is vigorously catalyzed by copper and iron. In a second note Job and Dubien[5] reported that the rate of reaction between ethylmagnesium bromide and ethyl bromide can be studied by adding a trace of cuprous or ferric chloride to catalyze the reaction. No velocity data or details of the procedure are given but they state that when the Grignard reagent is in excess, the reaction is

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[1] Bouveault, *Compt. rend.*, **138**, 1108 (1904); Tschelinzeff, *J. Russ. Phys.-Chem. Soc.*, **36**, 549 (1904); *J. Chem. Soc.*, **86**, 641 (1904).

[2] Jolibois, *Compt. rend.*, **155**, 213 (1912).

[3] Späth, *Monatsh.*, **34**, 1965 (1913).

[4] Job, Reich and Dubien, *Bull. soc. chim.*, [4] **37**, 976 (1925).

[5] Job and Dubien, *ibid.*, [4] **39**, 583 (1926).