Dehydroquassin prepared from quassin was reported previously[1] as having a melting point of 254°. As there was little doubt that the two materials under consideration here were the same, a new preparation was made from quassin and purified exhaustively by the method used for the preparation from isoquassin. In the process melting points between 256 and 263° were obtained, but it was found that in these preparations the proportions of the spindles and rods varied from one crystallization to another, and this accounted for the variation in melting points. The mixed melting points of the two preparations, *i. e.*, from quassin and isoquassin, were usually depressed slightly. The optical crystallographic properties of the two preparations were identical, however, so there is no doubt as to their identity.

Summary

Certain reactions of neoquassin have been studied and compared with analogous reactions of quassin. The results indicate that the two substances are very closely related. A chart indicating these relationships is presented.

The experiments show that quassin contains two methoxyl groups and probably a tertiary hydroxyl group. The formation of anhydro and dehydro compounds is interpreted as involving reactions of the tertiary hydroxyl group.

WASHINGTON, D. C. RECEIVED OCTOBER 4, 1937

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

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LIV. The Surface Tension Constants of the Polyethylene Glycols and their Derivatives[1]

BY A. F. GALLAUGHER AND HAROLD HIBBERT

In the liquid state, molecules are probably oriented under certain conditions. A number of liquids have been found which give abnormal values for the Ramsay and Shields constant K. Ramsay and Aston[2] noticed that in long normal aliphatic chains K increases with the number of CH_2 groups in the molecule. Hunten and Maass[3] have shown experimentally that the value of K rises with increase in the length of chain in a homologous series such as the fatty acids. From the point of view of orientation at the surface, it is not necessary to assume dissociation in order to explain the experimental facts. The calculation of the molecular surface to obtain the Ramsay and Shields constant is given by $(M/d)^{2/3}$, that is, it is assumed that the molecules are spherical or cubical in shape. Orientation would imply that a far larger number of molecules can occupy unit area in the case of the long chain derivatives. The longer the carbon chain, the greater the Ramsay and Shields constant, and this is in agreement with the experimental data given by Hunten and Maass.[3] Thus, there exists the possibility of a connection between orientation and abnormal values of the Ramsay and Shields constant. Accordingly, with a homologous series of polar compounds such as the polyethylene glycols, a determination of the surface tension constants such as the total surface energy and the parachor should yield data capable of interpretation in terms of the orientation theory.

Measurement of the Surface Tension.—The surface tension was measured by the capillary rise method. The temperature bath consisted of a four-liter Pyrex beaker, lagged with asbestos and filled with glycerol stirred with a motor-driven propeller. The temperature was regulated to 0.1° by a de Khotinsky thermo-regulator, fitted with a tapping device to prevent lag of the contacts. All temperatures were measured by means of a thermometer calibrated at the German "Reichsanstalt."

The tube in which the surface tension was measured is of the type used by Richards and Coombs[4] with the modification that millimeter scales were etched on the two arms of the tube. By calibrating these scales, the height of a column of liquid in the capillarimeter could be measured with great accuracy. The capillarimeter was made and kept vertical by the use of two plumb lines.

The capillary rise was measured by means of a cathetometer provided with a vernier scale reading to 0.002 cm. and kept vertical by means of a plumb bob. The lighting and observation of the meniscus was similar to that described by Richards and Coombs.

On account of the highly hygroscopic nature of the polyethylene glycols and some of their derivatives, special precautions were necessary to obviate the presence of moisture during the filling of the capillarimeter. An apparatus similar to that shown in Fig. 1 was attached to the top of the capillarimeter and was closed at the top. Through this, air, dried with concentrated sulfuric acid and phos-

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[1] Constructed from a thesis presented by A. F. Gallaugher to the Faculty of Graduate Studies, McGill University, in May, 1932, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. For the first communication on this subject see THIS JOURNAL, **58**, 813 (1936). Original manuscript received March 9, 1936.

[2] Ramsay and Aston, *Z. physik. Chem.*, **15**, 101 (1894).

[3] Hunten and Maass, THIS JOURNAL, **51**, 159 (1929).

[4] Richards and Coombs, *ibid.*, **37**, 1656 (1915).

TABLE I

SUMMARY OF SURFACE TENSION DATA[a]

Compound	Surface tension at the b. p., dynes	Av. total surface energy, ergs	Av. Ramsay and Shields constant	Parachor Obsd.	Parachor Calcd.	Parachor $\left(\frac{\text{Calcd.} - \text{Obsd.}}{\text{Obsd.}}\right) \cdot 100$	Parachor Obsd. − Calcd.
Ethylene glycol	32.33	74.52	1.06	148.9	152.2	2.2	−3.3
Diethylene glycol	26.28	68.96	1.37	248.4	250.2	0.7	−1.8
Triethylene glycol	22.45	72.09	1.84	350.9	348.2	−0.8	2.7
Tetraethylene glycol	18.81	72.81	2.31	453.7	446.2	−1.6	7.5
Pentaethylene glycol		72.39	2.59	555.6	544.2	−2.0	11.4
Hexaethylene glycol		72.93	3.01	657.4	642.2	−2.3	15.2
Heptaethylene glycol		71.09	3.29	759.1	740.2	−2.5	18.9
Trimethylene glycol	28.30	71.25	1.24	189.3	191.2	1.0	−1.9
Tetraethylene glycol monochlorohydrin	19.38	70.50	2.47	485.4	463.4	−4.5	22.0
Ethylene glycol monomethyl ether	20.42	61.78	1.59	186.9	191.2	2.3	−4.3
Diethylene glycol dimethyl ether	14.44	62.20	2.63	327.4	328.2	0.2	−0.8
Ethylene dichloride	24.02	71.59	2.12	188.5	186.6	−1.0	1.9
β,β'-Dichloroethyl ether	17.78	74.74	2.51	291.6	284.6	−2.4	7.0
1,4-Dioxane	22.11	74.23	2.24	202.0	202.1	0.0	0.0
Ethylene oxide[b]	25.8	73.2	1.79	112.4	114.7	2.0	−2.3

[a] The surface tensions (and molecular volumes) of the penta-, hexa- and heptaethylene glycols at their boiling points are not given, since, as will be shown later, the boiling points of these compounds were not determined owing to experimental difficulties. The values given for the surface tension (and molecular volume) at the boiling point, in the case of the polyethylene glycols and their derivatives, were obtained by extrapolation of the surface tension–temperature (and molecular volume–temperature) curves to the boiling points calculated from the vapor pressure data.

[b] The values given for ethylene oxide were taken or calculated from the data of Maass and Boomer,[9] and have been inserted in this table for purposes of comparison.

TABLE II

SUMMARY OF DENSITY DATA[a]

Compound	Mol. vol. obsd. at b. p.	Mol. vol. calcd.[b]	Mol. vol. Calcd. − Obsd.	Δ Mol. vol.
Ethylene glycol	65.2	70.6	5.4	
Diethylene glycol	112.0	122.4	10.4	46.8
Triethylene glycol	161.7	174.2	12.5	49.7
Tetraethylene glycol	213.6	226.0	12.4	51.9
Trimethylene glycol	83.0	92.6	9.6	
Tetraethylene glycol monochlorohydrin	230.3	243.3	13.0	
Ethylene glycol monomethyl ether	87.8	92.6	4.8	
Diethylene glycol dimethyl ether	162.9	166.4	3.5	
Ethylene dichloride	85.1	89.6	4.5	
β,β'-Dichloroethyl ether	136.6	141.4	4.8	
1,4-Dioxane	91.9	103.6	11.7	
Ethylene oxide[c]	49.9	51.8	1.9	

[a] See note *a* Table I. [b] Using the values given by Kopp for the atomic volumes at the boiling point. [c] See note *b* Table I.

phorus pentoxide, was circulated, and the capillarimeter was filled with the aid of the small funnel. The liquid was then boiled under reduced pressure to remove all the dissolved air, and thereupon the apparatus sealed off.

The validity of the results with the capillary rise method of determining surface tension depends on the meniscus of the liquid surface being exactly tangential to the inner wall of the capillary tube at its highest point. As evidenced by the results of Richards and Carver,[5] and Hunten and Maass,[3] on a number of different liquids, it would seem that in most cases the angle of contact is zero.

Before each reading was taken, the apparatus was inclined so that the glass walls were well wetted above the meniscus. Then the apparatus was clamped exactly vertical and a reading was not taken until the top of the column of the liquid had been stationary for several minutes.

The capillarimeter was immersed bodily in the constant temperature bath to maintain uniform temperature throughout its interior. The values of the capillary rise given are the result of from four to six different observations for each temperature, and the value selected is that taken from those which lay on a smooth curve. It is believed that the surface tension measurements are accurate to one part in 300.

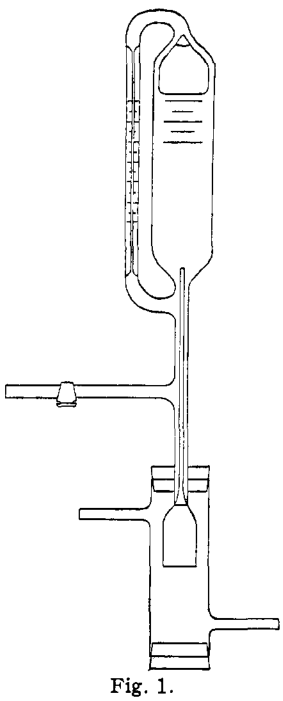
Fig. 1.

Measurement of the Density.—Densities were measured by the use of a dilatometer having a bulb of about 3.0-cc.

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(5) Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

capacity. A Beckmann thermometer scale, calibrated by means of a traveling microscope, was fixed to the stem of the dilatometer. Known weights of pure mercury were weighed with the bulb and the volume was plotted against the scale reading (above scratch) on a large scale. The volume occupied by any substance under examination could then be read from the curve. Weighings were corrected for air displaced, and allowance was made for the expansion of the bulb at temperatures differing from those at which the calibration was carried out.

The dilatometer was filled and sealed off in a similar manner to that described in the case of the capillarimeter. The correction necessary for the amount of polyethylene glycol or derivative present as vapor in the dilatometer was obtained using the gas equation

$$pv = (m/M) \times RT$$

The accuracy claimed for these measurements is one part in 2000.

Experimental Results

Tables I and II, respectively, contain the summary of the surface tension data and density data for the polyethylene glycols and their derivatives. The empirical equation connecting surface tension or density with temperature (derived from substituting the calculated constants in the equation of the form $y = ax + b$) is given in Tables III and IV.

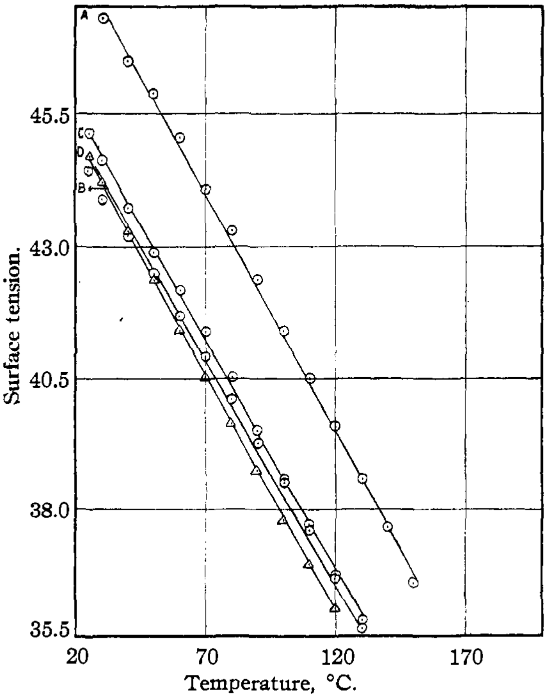

Fig. 2.—A, Ethylene glycol; B, diethylene glycol; C, triethylene glycol; D, heptaethylene glycol.

Figs. 2 and 4 show the densities and surface tensions of the polyethylene glycols plotted against the temperature, the corresponding data in the derivatives of the polyethylene glycols being given in Figs. 3 and 5.

TABLE III

Compound	Empirical equation connecting surface tension and temperature
Ethylene glycol	$y = -0.089x + 50.21$
Diethylene glycol	$y = -.088x + 46.97$
Triethylene glycol	$y = -.088x + 47.33$
Heptaethylene glycol	$y = -.089x + 50.17$
Trimethylene glycol	$y = -.0903x + 47.43$
Tetraethylene glycol monochlorohydrin	$y = -.0925x + 45.47$
β,β'-Dichloroethyl ether	$y = -.1306x + 40.57$
1,4-Dioxane	$y = -.1391x + 36.23$
Ethylene glycol monomethyl ether	$y = -.139x + 35.36$
Ethylene dichloride	$y = -.1023x + 33.21$
Diethylene glycol dimethyl ether	$y = -.1164x + 32.47$

y = Surface tension in dynes. x = Temperature in °C.

TABLE IV

Compound	Empirical equation connecting density and temperature
Ethylene glycol	$y = -0.00076x + 1.1293$
Diethylene glycol	$y = -.00075x + 1.1317$
Triethylene glycol	$y = -.00080x + 1.1403$
Heptaethylene glycol	$y = -.00080x + 1.1411$
Trimethylene glycol	$y = -.00138x + 1.2800$
Tetraethylene glycolmonochlorohydrin	$y = -.00112x + 1.2420$
β,β'-Dichloroethyl ether	$y = -.00083x + 1.1520$
1,4-Dioxane	$y = -.0007x + 1.0672$
Ethylene glycol monomethyl ether	$y = -.00109x + 1.0705$
Ethylene dichloride	$y = -.00098x + 0.9865$
Diethylene glycol dimethyl ether	$y = -.00106x + 0.9829$

y = Density. x = Temperature in °C.

Discussion of Results

Surface Tension Data.—The total surface energy of the polyethylene glycols is high in comparison with the constant value of 54 ± 1 erg reached in the fatty acid series, as recorded by Hunten and Maass.[3] This large value undoubtedly is due to the presence of the two strongly polar hydroxyl groups in the glycol molecule, added to the effect of the polar ethylene oxide groups.

Examination of the experimental values found for the total surface energy of the polyethylene glycols shows that this value becomes constant at 72 ± 1 erg at the third member of the series, triethylene glycol. This result is analogous to the findings of Hunten and Maass.[3] According to the theories of Langmuir,[6] Harkins[7] and Adams,[8] the surface molecules are oriented so that the most strongly polar groups are directed toward the bulk of the liquid, the value of the total surface energy being governed by the outer groups. Partial orientation of the surface molecules is assumed by the writers in explanation of the total surface energy values found in this series. This assumption finds support in the anomalous values of the Ramsay and Shields constant and of Sugden's parachor derived from these measurements.

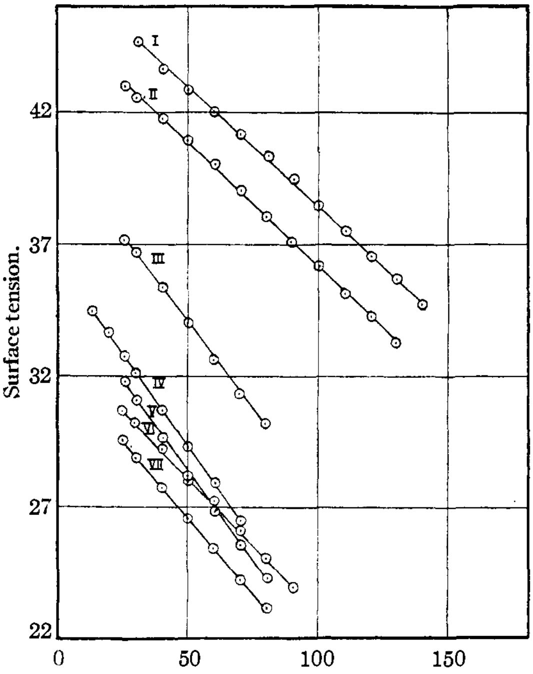

Fig. 3.—I, trimethylene glycol; II, tetraethylene glycol monochlorohydrin; III, β,β'-dichloroethyl ether; IV, 1,4-dioxane; V, ethylene glycol monomethyl ether; VI, ethylene dichloride; VII, diethylene glycol dimethyl ether.

The constant value for the total surface energy reached at triethylene glycol indicates that in this and subsequent members of the series the surface tension is governed almost entirely by the ethylene oxide groups at the surface. The attractive forces of the hydroxyl groups are presumably exerted largely on the molecules in the bulk of the liquid, and hence their influence at the surface is diminished rapidly as the length of the chain increases and they are removed further from the surface. This view is supported by the observation that the constant value found for the total surface energy is almost identical with that of ethylene oxide itself and of 1,4-dioxane. The conclusion that may be drawn is that at the liquid surface the higher polyethylene glycol molecules are oriented in the form of an inverted "U" with at least one ethylene oxide group in the surface, the rest of the chain forming the sides of the "U" in the interior of the liquid.

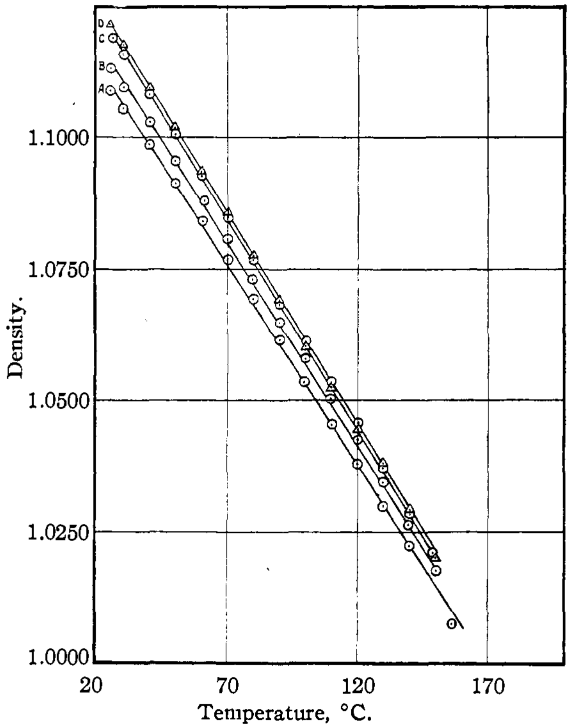

Fig. 4.—A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; D, heptaethylene glycol.

Although, according to the above assumptions, the two hydroxyl groups situated at the ends of the polyethylene glycol molecules may not affect the surface tension of the liquid to any extent, yet these strongly polar groups are an important factor in the production of the partial orientation of the molecules at the liquid surface. For, due to the attractive forces exerted by these groups, they anchor, as it were, the molecule in the bulk of the liquid in the vertical, or almost vertical, position. The other forces which contribute toward this production of partial orientation are those resulting from the assumed intermolecular lateral attractions of the ethylene oxide portions of the polyethylene glycol chains which are immersed in the liquid.

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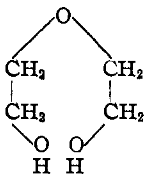
(6) Langmuir, *Met. Chem. Eng.*, **15**, 468 (1916); THIS JOURNAL, **39**, 1848 (1917).

(7) Harkins, *ibid.*, **39**, 354, 541 (1917).

(8) Adams, *Proc. Roy. Soc.* (London), **A99**, 336 (1921); **A101**, 452, 516 (1922); **A103**, 656, 687 (1923).

The anomalous value of 68.96 ergs for the total surface energy of diethylene glycol may be accounted for by the assumption that the spatial configuration of the diethylene glycol molecule is of the form



If this is the case, then, since the two polar hydroxyl groups are close together, some of their attractive forces will be used up in what might be termed intramolecular neutralization or coördination, and, consequently, the total surface energy will be diminished.

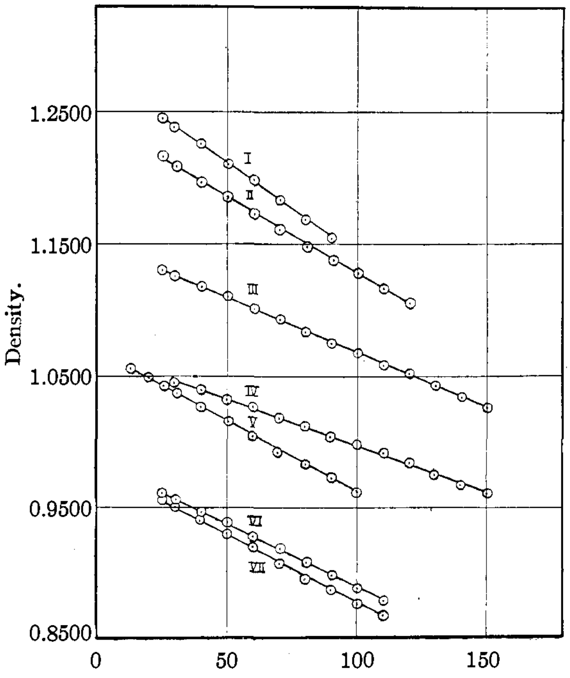


Fig. 5.—I, ethylene dichloride; II, β,β'-dichloroethyl ether; III, tetraethylene glycol monochlorohydrin; IV, trimethylene glycol; V, 1,4-dioxane; VI, ethylene glycol monomethyl ether; VII, diethylene glycol dimethyl ether.

As regards the configuration of the higher polyethylene glycol molecules, the position in space of the hydroxyl groups in these molecules does not appear to affect the value of the total surface energy, and this latter constant is, presumably, to a great extent contributed to by the ethylene oxide group or groups in the liquid surface.

The total surface energy value of 70.50 ergs for tetraethylene glycol monochlorohydrin is less than that for the corresponding glycol (72.81 ergs). showing that the nature of the polar terminal groups exerts a definite effect at the liquid surface, weaker though this be than that of the ethylene oxide groups.

The effect of the substitution of a slightly polar methoxyl group for a strongly polar hydroxyl group is shown on passing from ethylene glycol (74.52 ergs) to ethylene glycol monomethyl ether (61.78 ergs).

In the case of β,β'-dichloroethyl ether, the value of 74.74 ergs for the total surface energy is greater than that for the first member of the series, ethylene dichloride (71.59 ergs). It would seem that, in addition to the contribution of the two polar chlorine atoms to the total surface energy, the ethylene oxide group adds its effect. Further, since the total surface energy of the corresponding diethylene glycol is 68.96 ergs, it may be that the two chlorine atoms in the β,β'-dichloroethyl ether molecule are not so close together in space as was postulated for the two hydroxyl groups in the diethylene glycol molecule.

The value of 74.23 ergs for the total surface energy of 1,4-dioxane is slightly higher than that observed by Maass and Boomer[9] for ethylene oxide (73.2 ergs), which might be accounted for by assuming the molecule suggested by Hibbert.[10]

The Ramsay and Shields constant, K, increases in a continuous manner with the length of the ethylene oxide chain, and this may be accounted for by orientation if $K = 2.12$ for all equimolecular surfaces. If all of the polyethylene glycol molecules are assumed to be completely oriented, the area occupied by any glycol molecule will be almost the same as that occupied by an ethylene glycol molecule. Hence, the volume which should be considered in the case of the higher polyethylene glycol molecules to obtain equimolecular surfaces is not that given by their molecular volume but by the portion of it which is proportional to the volume of the ethylene glycol molecule. This reasoning gives

$$K = 1.06\,(M/62.048)^{2/3}$$

where the value 1.06 is arbitrarily taken as the constant for ethylene glycol (mol. wt. 62.048) and K is the constant for a higher polyethylene glycol of molecular weight M.[11] This calculation obviously is not rigorous, and may be criticized

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[9] Maass and Boomer, This Journal, **44**, 1709 (1922).

[10] Hibbert, *Science*, **73**, 500 (1931).

[11] Hunten and Maass, This Journal, **51**, 163 (1929).

on the grounds that it assumes that all of the polyethylene glycols are associated to the same extent and have the same density. The values for K calculated in this manner are given in Table V and are in fair agreement with the experimental values.

TABLE V

Glycol	Ramsay and Shields constant K Obsd.	Ramsay and Shields constant K Calcd.
Ethylene	1.06	1.06
Diethylene	1.37	1.52
Triethylene	1.84	1.91
Tetraethylene	2.31	2.27
Pentaethylene	2.59	2.60
Hexaethylene	3.01	2.91
Heptaethylene	3.29	3.21

While these values are put forward only to indicate that the explanation of the marked increase in value of the Ramsay and Shields constant on the basis of orientation is justifiable, nevertheless, it seems unlikely that the high values for this constant can be interpreted accurately in terms only of orientation.

The parallelism between the values for the Ramsay and Shields constant and the percentage difference of the calculated and observed values of Sugden's parachor is of considerable interest (see Table I). It has been established that the parachor is too high in the case of compounds of high molecular weight, and it has been suggested that when the observed value of the parachor is too low this is due to association, the low value of the Ramsay and Shields constant being ascribed to the same cause.[8] If this is so, it appears reasonable to suppose that the source of the large values of the parachor and the Ramsay and Shields constant is the same, and partial orientation of the molecules is advanced as a possible explanation.[3] Extension of this comparison to the polyethylene glycols and their derivatives appears to provide further support for this view.

A further parallelism between the Ramsay and Shields constant and the parachor is shown in the effect of temperature. Examination of the experimental data[12] shows that both these values increase with temperature in the case of all the compounds measured except ethylene oxide, 1,4-dioxane and ethylene dichloride. Of these exceptions, the first two are certainly non-associated liquids, while this may be the case with ethylene dichloride. Sugden[13] states that, in the case of associated liquids, it is usually found that the parachor is not independent of the temperature of measurement but increases with rise in temperature.

It is necessary to point out that the comparisons made in this discussion should be regarded purely from a qualitative point of view.

Comparison of the calculated and observed values of the parachor (Table I) shows that the initial negative anomaly decreases, to become increasingly positive with triethylene glycol and the higher members. This behavior is also exhibited by the fatty acid series.[3] The appearance of a positive anomaly in these two homologous series of associated compounds is at variance with Sugden's[13] (pp. 167–168) statement that positive anomalies have not been found for the non-conducting class of associated liquids and both the observed anomalies and the assumed association cannot be explained on the basis of his conceptions. From the electronic theory of valency, it would seem that the probable mechanism giving rise to association in the molecules of the polyethylene glycols is that of an intermolecular attractive force of a coördinating nature. It is assumed that these coördinating forces are operative principally between the ethylene oxide groups, although the terminal hydroxyl groups (and chlorine groups in the case of some of the derivatives) may also assist in producing this association.

Ethylene, trimethylene and diethylene glycols exhibit negative surface tension anomalies possibly arising from an intramolecular coördination of the hydroxyl groups in some of the observed anomalies. The fact that the various physical constants of these three glycols give indications of a large degree of association existing in these compounds may be used as an argument against intramolecular coördination, and, in turn, favor Sidgwick's[14] views on the source of association in the alcohols, namely, an intermolecular coördination through hydroxyl groups. Intramolecular coördination would appear to be ruled out in the case of the higher polyethylene glycols since such would make itself felt in the values for the surface tension data.

The almost constant increase in the value of the positive parachor anomaly from triethylene to heptaethylene glycol would indicate that this

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(12) The complete experimental data are given in the Ph.D. Thesis of Arthur F. Gallaugher, McGill University, May, 1932.

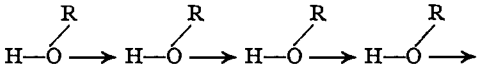
(13) Sugden, "The Parachor and Valency," Alfred H. Knopf, New York, 1930, p. 116.

(14) Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1927 p. 134.

associating influence, whatever it may be, increases in a regular manner with each ethylene oxide addition.

According to Sugden,[13] the sharing of two electrons by one atom with another, resulting in a coördinate link, should give rise to a negative anomaly of 1.6 units per linkage. If this is so, then the explanation advanced above to account for the observed positive anomaly is subject to criticism. However, the evidence in favor of the influence of an intermolecular attractive force in the polyethylene glycol molecules, and in those of their derivatives, through the medium of the ethylene oxide groups in these molecules, is too great to be disregarded. The association may arise through attractive forces of a coördinating nature, the source of which cannot be stated at the present time.

Although the association of primary alcohols may arise through coördination in the following manner as suggested by Sidgwick[13] (pp. 167–168)



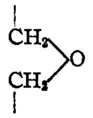
it has been pointed out by Smyth[15] that this association or orientation of molecules cannot apply in the case of the more complex molecules such as the secondary and tertiary alcohols. Furthermore, while this type of association may exist in the case of the simple ethylene and trimethylene glycol molecules, this would not seem to be true for the higher polyethylene glycols and some of their derivatives.

The explanations which Sidgwick and Sugden have advanced to account for the association of polar organic compounds are based on a limited amount of experimental evidence. It would therefore seem necessary, before arriving at any definite conclusions as to the operation and type of forces giving rise to association in this series, to investigate a number of different homologous series and to compare their surface tension and dielectric constant relationships over a range of temperatures. The following are suggested as likely to yield information on this problem: primary, secondary and tertiary alcohols, polyglycerols, acid chlorides, amines, polyisoprenes, polyindenes, polystyrenes and methylated derivatives of pentoses, hexoses and polysaccharides. From results obtained with the three latter, light might be thrown on the nature of the valence forces operative between the anhydroglucose units forming the long cellulose chains.

Density

An examination of the results in Table II indicates that the polyethylene glycols and their derivatives all exhibit large negative anomalies between the calculated and observed values. This observation may be deduced as a result of the conclusions drawn from the surface tension relationships in that in the case of the polyethylene glycol molecules and those of their derivatives (especially those containing ethylene oxide groups), large intermolecular forces of attraction are presumably operative. These, in turn, may effect an orientation in the molecules in an associated complex so as to account for the observed molecular volume contractions.

The molecular volume of an ethylene oxide group as deduced from the difference in the observed values for diethylene and ethylene glycols, triethylene and diethylene glycols and for tetraethylene and triethylene glycols are 46.8, 49.7 and 51.9, respectively. The observed molecular volume of ethylene oxide as recorded by Maass and Boomer[9] is 49.9, so that it is possible to conclude that the valence angle of the oxygen in an ethylene oxide chain is approximately identical with that of the oxygen in the ethylene oxide ring. This may afford evidence in favor of a zig-zag structure in the ethylene oxide chain occurring in the polyethylene glycols. As the latter series is ascended, the value for the molecular volume of the



group increases and this may be accounted for by the distortion in the oxygen valence angle induced by stereochemical factors and the intermolecular forces of attraction.[16]

Acknowledgment.—The writers wish to acknowledge the kindness of Dr. O. Maass who assisted in the designing of the apparatus used in this research.

Summary

The surface tension and density of the poly-

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[15] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, Chapter 9.

[16] In connection with the earlier communication on this subject [THIS JOURNAL, 58, 813 (1936)], the authors wish to thank Prof. A. Grün (Basel) for calling their attention to the fact that, in previous work by Grün and co-workers [*Ber.*, **41**, 3465 (1905); **43**, 1051 (1910); *Monatsh.*, **37**, 205, 409 (1916)], the existence of definite coördination compounds formed from copper sulfate and glycols as well as other hydroxy derivatives had already been shown.

ethylene glycols from monoethylene to heptaethylene glycol and of seven of their derivatives have been measured over a range of approximately 100°. The series constant of 72 ± 1 erg for the total surface energy is attained at triethylene glycol. This series constant closely approaches the value for the total surface energy of ethylene oxide, namely, 73.2 ergs.

A continuous increase in the value of the Ramsay and Shields constant is exhibited as the polyethylene glycol series is ascended. A similar increase in the positive direction for the percentage difference of the calculated and observed values of the parachor is noted. Some phenomenon presumably is taking place in the liquid surface of the polyethylene glycols which affects the surface in an abnormal manner, possibly the result of partial orientation of the surface molecules.

The algebraic difference between the calculated and observed values of the parachor is negative in ethylene and diethylene glycols, becoming continuously positive in triethylene and the higher polyethylene glycols. This suggests that a definite relation exists between the valence forces in operation, and each addition of an ethylene oxide group to the polyethylene glycol molecules. The positive anomalies are unusual and cannot be accounted for on the basis of Sugden's interpretation of the parachor and its relation to valence forces. A possible explanation of the association of the polyethylene glycol molecules arising through coördination, or other intermolecular attractive forces of the ethylene oxide groups, is advanced to account for the positive anomalies.

Attention is drawn to the fact that the parachor anomalies for the fatty acids show a behavior identical with that for the polyethylene glycols.

The molecular volumes of the polyethylene glycols exhibit large negative anomalies between the calculated and observed values. Evidence is obtained which possibly supports a zig-zag structure for the ethylene oxide chain in the polyethylene glycol molecules, the ether oxygen angle in the chain being similar to that present in the ethylene oxide molecule.

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

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LV. Vapor Pressures of the Polyethylene Glycols and their Derivatives[1]

BY A. F. GALLAUGHER AND HAROLD HIBBERT

In the preceding papers of this series[2,3] surface tension and other measurements on polyethylene glycols and their derivatives were considered in relation to the question of molecular association. The present study continues the investigation to cover the vapor pressures of these substances.[4]

Measurement of the Vapor Pressure.[5]—The apparatus used in the measurement of the vapor pressure is shown in Fig. 1 and is a modified form of that devised by Sutherland and Maass.[5]

A and B are safety bulbs, introduced to minimize possible errors in the manometer readings due to leaks in the stopcocks. C represents a manometer of 20-mm. diameter tubing, the scale used being found correct to 0.1 mm. It was read by means of a hand-lens to 0.2 mm.

The constant temperature bath J is identical with that previously described.[3] I is a differential manometer and E the bulb containing the liquid of which the vapor pressure is to be determined. This is fitted with a magnetic stirrer operated by the coil G, housed in the glass container as shown and actuated by a metronome. The system may be evacuated at N and air admitted through the stopcocks M and K and the reservoir L.

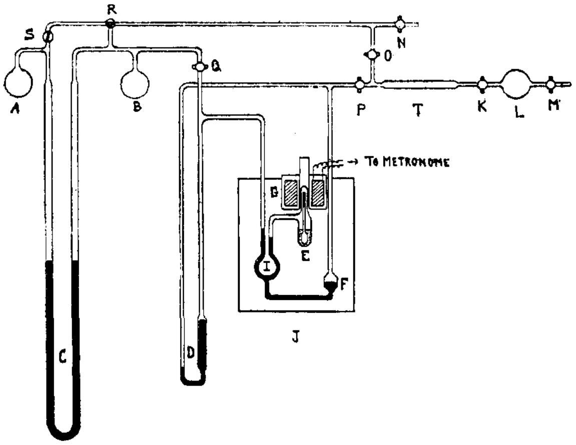

Fig. 1.—Apparatus.

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[1] Contribution from a thesis presented by A. F. Gallaugher to the Faculty of Graduate Studies, McGill University, in May, 1932, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. Original manuscript received March 9, 1936.

[2] Gallaugher and Hibbert, THIS JOURNAL, **58**, 813 (1936).

[3] Gallaugher and Hibbert, *ibid.*, **59**, 2514 (1937).

[4] The preparation and purification of the materials used have been described previously.[3]

[5] Sutherland and Maass, *Trans. Roy. Soc. Can.*, **20**, 499 (1926).