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Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXIII. The Surface Tensions of Aqueous Solutions of Polyoxyethylene Glycols[1]

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The synthesis[2] of a series of long-chain polymer homologs of uniform chain length[3] (polyoxyethylene glycols), fully characterized as pure chemical compounds,[4] has made it possible for the first time to examine the properties of macromolecules without the complicating effects which may arise from the presence of chains of many different lengths. As part of a series of such studies,[5] the properties of soluble surface films of these homologs have been investigated by measuring the surface tensions of their aqueous solutions at various concentrations. Only a few such measurements are available for other polymers,[6] and in none of these was the effect of chain length examined systematically.

Experimental Part

Measurements of the surface tensions of solutions, especially those of long-chain compounds or other strongly-adsorbed solutes, must be carried out in such a manner that the surface of the solution is not disturbed during the process, as otherwise the structure of the adsorbed film may be destroyed and the surface tension changed from its true static equilibrium value. The capillary-rise method seems to meet this requirement, and was used in one of its modified forms in these experiments.

Apparatus.—The apparatus was a slightly modified version of the instrument devised by Speakman,[7] in which the pressures required to depress the solution in two capillaries of different diameters, respectively, to the same level as observed through a fixed reading-telescope (with hair-line), are measured. The difference between these pressures is directly proportional to the surface tension, the proportionality constant being determined by calibration with a liquid of known surface tension.

The capillarimeter and all its connections without exception were constructed of Pyrex glass. The capillaries had the approximate diameters of 0.56 mm. and 1.4 mm., respectively, and were reasonably uniform and circular in bore (true uniformity of bore is not required for this apparatus). The capillarimeter was mounted rigidly in a thermostat controlled to ±0.02° by a mercury-toluene thermoregulator. Illumination was provided by the reflection from a section of white porcelain mounted behind the two capillaries at the fixed point of observation.

Cyclohexane ($d^{20}{}_4$ 0.7794) was used as the manometer liquid, corrections to the density being applied for small temperature variations between different experiments. Each side of the manometer was connected directly to the corresponding side of the capillarimeter, the whole system being closed from the atmosphere. The pressures were measured with a suitable cathetometer reading to 0.001 cm. It was found that 1 dyne of surface tension corresponded to approximately 0.6 mm. height on the manometer; the reproducibility of any single determination was about ±0.06 mm., corresponding to an error of ±0.1 dyne.

Procedure.—The capillarimeter was first cleaned with chromic acid cleaning solution, which was removed by thorough rinsing, finally with very pure water. Rapid drying was accomplished by using an evacuated vessel heated to 50°, and containing a little solid potassium hydroxide. The capillarimeter was then filled with solution and mounted in the thermostat. The solution was lowered into the capillaries to a point near the fixed mark by reducing the pressure over one limb of the instrument. After a period of eight hours, necessary to permit complete adsorption equilibrium, the final adjustments of each meniscus to the fixed mark were made, and the pressures noted. This was repeated twice at intervals up to one hour to test the reproducibility of each measurement. The adjustment of the meniscus to the mark was always made by *lowering* the meniscus.

Calculation of Results.—Surface tension values were calculated from the formula

$$\sigma = C\delta Pd\phi$$

where

$$\phi = 1 - (0.3r'r'')\rho g/2\sigma'$$

and where C is the capillarimeter constant, δP the recorded pressure difference (mm. cyclohexane), d the density of the manometer liquid, r' and r'' the approximate radii of the two capillaries, ρ the solution density and σ' the approximate surface tension as calculated without use of the factor ϕ.

All the experiments were carried out at 25°.

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[1] Taken from a thesis presented by Edwin L. Lovell to the Faculty of Graduate Studies and Research, McGill University, April, 1940, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Fordyce, Lovell and Hibbert, THIS JOURNAL, **61**, 1905 (1939); Fordyce and Hibbert, *ibid.*, **61**, 1910 (1939).

[3] It is suggested that the name "unipolymeric" (and hence "unipolymer") be applied to preparations with this property. The unipolymer may show outstanding differences in properties from a mixture of homologs with the same average molecular weight.

[4] Lovell and Hibbert, THIS JOURNAL, **62**, 230 (1940).

[5] Fordyce and Hibbert, *ibid.*, **61**, 1912 (1939); Lovell and Hibbert, *ibid.*, **61**, 1916 (1939); **62**, 2140 (1940); Lovell, Ph.D. Thesis, McGill University, 1940.

[6] (a) Chowdhury and Bardhan, *J. Indian Chem. Soc.*, **13**, 294 (1936); Lee, *J. Soc. Chem. Ind.* (Japan), **40**, 459B (1937); Dogadkin and Pantschenkov, *Rubber Chem. Tech.*, **5**, 249 (1932); (b) Traube, *Ann.*, **265**, 27 (1891); (c) du Noüy, *Colloid Symposium Monograph*, **3**, 25 (1925).

[7] Speakman, *J. Chem. Soc.*, 1449 (1933).

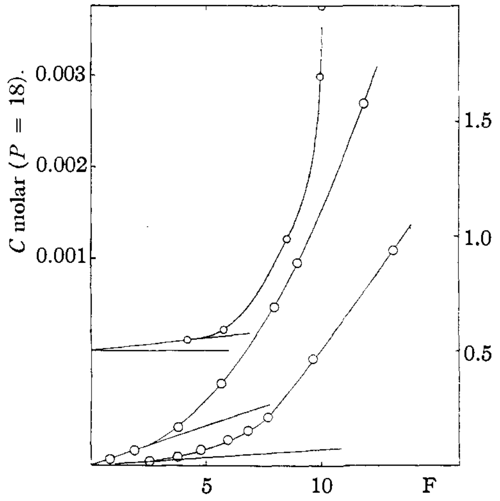

Fig. 1.—Surface tension–concentration curves for three oxyethylene glycols; $P = 3$, 6 (lower curve) and 18 (inset).

Treatment and Discussion of Results

The effect of concentration of the various polyglycols on the surface tensions of their aqueous solutions is shown in Figs. 1, 2 and 7, which express in graphical form the data for six individual members of the homologous series. It is seen that there is a steady change in the characteristics of these curves as the solute chain-length is increased. Thus, the two lowest members (tri- and hexaoxyethylene glycols) show an appreciable region of linearity before commencing a steady upward swing concave to the concentration axis. With the higher glycols ($P > 18$), this initial linear region tends to disappear, and furthermore the solutions seem to show a limiting surface tension lowering. It appears that the concentration, at which a given surface-tension lowering is observed, very rapidly becomes smaller as the series is ascended, until finally with the highest members all the concentrations used are extremely small. This is illustrated in Table I.

All these facts are in accordance with expectation, based on experience with short-chain compounds especially as described in the early work of Traube.[6b] In fact it is possible to calculate the value of Traube's constant $\left(\beta = \lim_{c \to 0} F/c\right)$ for at least the first two members of the series, and these may be compared with the apparent order of magnitude found for the higher members (Table II).

Other comparisons between the polyoxyethylene and polymethylene chains may be made, showing the differences produced when every third methylene group of the latter, in effect, is replaced by an oxygen atom. For instance, it is well known that the value of any property (x, say) in the polymethylene series increases from member to member by factors of 3, *i. e.*

$$x_1 : x_2 : x_3 : \cdots = 1 : a : a^2 : \cdots$$

where $a = 3$. For the polyoxyethylene chains the value of a is found to be considerably less, namely, 1.6 (up to the 18-membered glycol) when x is the solution surface tension, despite the fact that each repeating unit contains three atoms (CH_2OCH_2) in the straight chain instead of only one. This low value is reflected in the calculated results for the work done in transferring one mole of the solute from the interior of the solution to the surface region (the work of adsorption). According to Langmuir,[8] this is given by the expression

$$\lambda = RT \ln (1000q/ct)$$

where q is the surface excess at the concentration c, and t is the thickness of the surface layer. Assuming the latter to have the value 6 Å., the following results are obtained

$$P = 3 \qquad \lambda = 11{,}691 \text{ cal.}$$
$$P = 6 \qquad \lambda = 12{,}570 \text{ cal.}$$
$$d\lambda/dP = 290$$

The increase in λ per repeating unit is therefore only 290 calories. If the adsorbed films are of the

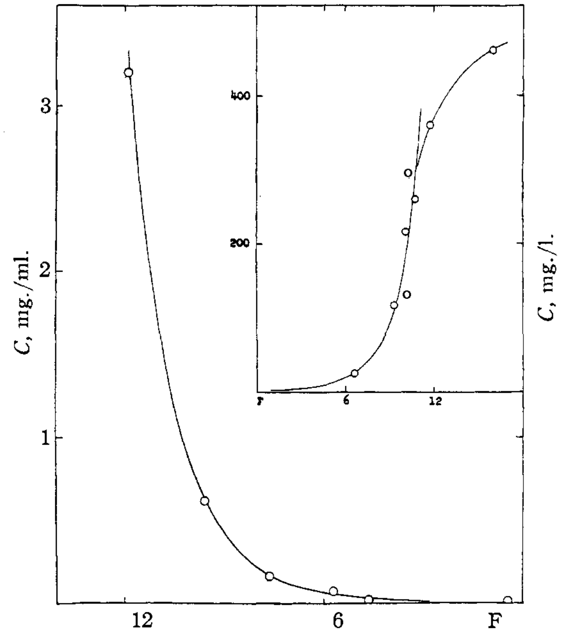

Fig. 2.—Surface tension–concentration curve for 42-membered and (inset) 90-membered glycol.

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[8] Langmuir, THIS JOURNAL, **39**, 1848 (1917).

TABLE I

CHARACTERISTICS OF SURFACE TENSION–CONCENTRATION CURVES

P	$F_{\text{max.}}$	Molar concn. (at $F_{\text{max.}}$)	(at $F = 9$)
3	>12	>1.6	0.885
6	>13	>1.4	.359
18	10	0.0035	.00165
42	c. 12	.0019	.00023
90	11	.00015	.000026
186	11	.000037	.0000035

TABLE II

VALUES OF THE INITIAL SLOPES, F/c

P	β
3	29.33
6	135.1
18	4×10^4
42	4×10^5
90	6×10^6
186	3×10^7

TABLE III

TOTAL SURFACE CONCENTRATION, TRIOXYETHYLENE GLYCOL

F	$dF/(d \log c)$	c (molar)	$10^{11}q_s$[a]	$10^{11}\Gamma$[b]	$10^{11}q$[c]
1.0	2.34	0.0359	1.286	4.10	5.39
2.0	4.23	.0716	2.038	7.40	9.44
3.5	5.08	.1738	3.656	8.88	12.54
6.0	6.82	.4018	6.436	11.92	18.36
9.0	10.0	.881	10.86	17.5	28.36
11.0	12.0	1.349	14.43	21.0	35.43
13.0	16.97	1.828	17.67	29.7	47.32
13.5	18.81	1.996	18.75	32.9	51.67

[a] q_s, (moles/cm.^{2}), normal surface concentration. [b] Γ, adsorbed surface excess (Gibbs). [c] q, total surface concentration.

gaseous type with each molecule oriented horizontally to the surface, it would be expected that the total work of adsorption would be equal to the sum of the contributions of the end-groups and the main-valence chain. In the case of the six-membered glycol, therefore, the former must have the value 12,570 − 1450 = 11,120 calories. This is considerably higher than the value (550 cal.) which is obtained for two CH_2OH groups using Langmuir's data.[8] Furthermore, the difference seems to become steadily greater in order of magnitude as the series is ascended. These facts might be explained by an increasing degree of vertical orientation in the films as the chains are made longer.

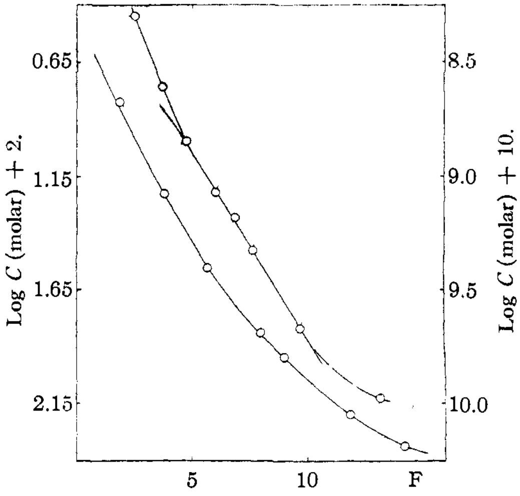

Fig. 3.—Trioxyethylene glycol (lower curve); hexaoxyethylene glycol (upper curve).

This conclusion is supported by calculations of the area per molecule in the films, using Gibbs' adsorption isotherm.[9]

Molecular Areas of the Lower Glycols.—The experimental values for the surface tensions of aqueous tri- and hexaoxyethylene glycol solutions at various concentrations have been used to plot the relation between F (the surface tension lowering or "surface pressure") and log c, from which the values of the slope $dF/d \log c$ are obtained at a series of convenient concentrations (Table III). No correction was made for activity coefficients.

For the three-membered glycol (Fig. 3) the log curve is at no point linear, *i. e.*, no "limiting slope" is found; instead, the surface adsorption increases continuously with the bulk concentration (Table III). It would therefore seem that the surface does not become saturated in the concentration range studied, *i. e.*, the smallest area observed in the film (Table IV) is not the minimum or true area for this glycol. At the lowest surface pressures, the large areas indicate a gaseous type of adsorbed film, as would be expected for a molecule with a strong lyophilic group at each end. The smallest area recorded (32 Å.^{2}) is only slightly greater than the minimum area which the horizontally-oriented molecule is capable of assuming (on the basis of the atomic dimensions involved). Hence in order for the adsorption to reach its constant value, the area in the film would have to be decreased still further, which is in accordance with the observed facts (Fig. 3).

When the result of plotting FA *vs.* F is viewed over the whole concentration range (Fig. 4), an unusual situation appears to exist. Above 5 dynes pressure, the slope FA/F suddenly changes its direction at about 100 Å.^{2}, so that FA there-

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(9) The basis of such calculations has been discussed by a number of authors, such as the following: (a) Bartell and Mack, *Colloid Symposium Monograph*, **9**, 65 (1931); (b) Harkins and Wampler, THIS JOURNAL, **53**, 850 (1931).

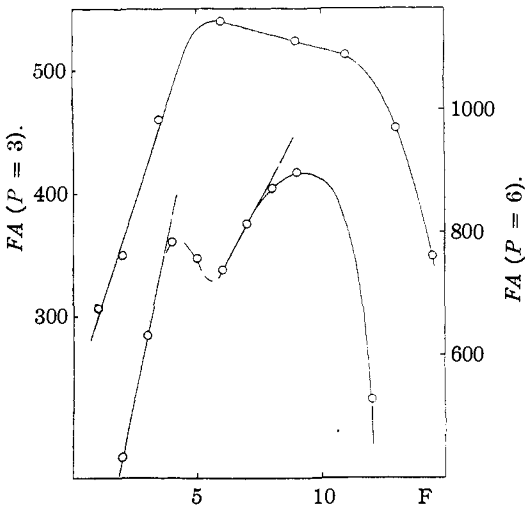

Fig. 4.—Trioxyethylene glycol (upper curve); hexaoxyethylene glycol (lower curve).

after decreases rapidly as the surface pressure rises. This behavior is probably due to a change in state of the adsorbed film as it is compressed, causing the area per molecule to suddenly decrease much more rapidly than it would in a gaseous film far removed from the condensation point. Support for this view is to be found in the observation of Kozakevich and Ushakova[10] that such a behavior is found with adsorbed films of small molecules at *very high* surface pressures (25 dynes).

TABLE IV

FORCE-AREA DATA FOR TRIOXYETHYLENE GLYCOL

F, dynes	A, per molec.	FA
1.0	306.4	306
2.0	174.8	350
3.5	131.6	460
6.0	89.9	540
9.0	58.2	524
11.0	46.6	513
13.0	34.9	454
13.5	31.9	430

TABLE V

TOTAL SURFACE CONCENTRATION, HEXAOXYETHYLENE GLYCOL

F	c (molar)	$dF/(d \log c)$	$10^{11}\Gamma$	$10^{11}q$ moles
2	0.0145	3.94	6.90	7.60
3	.0259	3.94	6.90	7.93
4	.0465	3.94	6.90	8.43
5	.078	5.00	8.75	10.90
6	.116	6.06	10.61	13.42
7	.169	6.06	10.61	14.22
8	.240	6.06	10.61	15.18
9	.359	6.06	10.61	16.58
12	.827	15.56	27.23	37.58

TABLE VI

FORCE-AREA DATA FOR HEXAOXYETHYLENE GLYCOL

F, dynes	A, per molecule	FA
2	216.8	434
3	210.0	630
4	195.5	782
5	151.1	756
6	122.9	737
7	116.0	812
8	108.7	870
9	99.5	896
12	43.9	528

TABLE VII

MOLECULAR AREAS OF HIGHER GLYCOLS

P	$dF/(d \log c)$	A, found	A, zigzag form
18	4.38	216 ± 30	223
42	3.29	287 ± 10	512
90	4.01	235 ± 10	1088
186	1.59	79	2235

For hexaoxyethylene glycol (Fig. 3 and Tables V, VI) the FA, F curve (Fig. 4) shows a similar behavior to that of the three-membered glycol, except that a rather curious minimum appears in the region of five dynes pressure. This does not seem to be due to any experimental error; indeed the point of "collapse" of each of the films represented by the two slopes is just that indicated by the limiting area per molecule calculated from the Schofield–Rideal equation.[11]

The Higher Glycols.—All the four higher glycols show a constant adsorption over the entire concentration range, the slope $dF/(d \log c)$ being

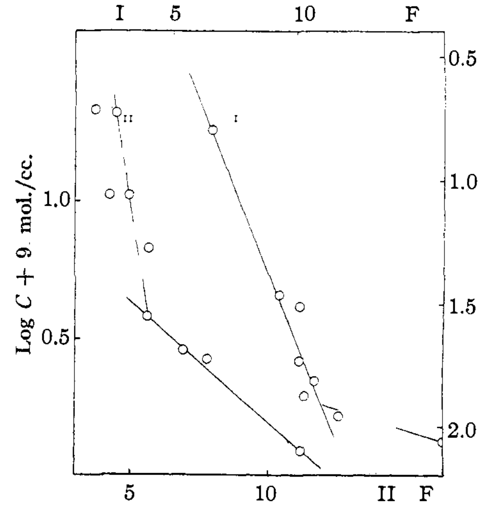

Fig. 5.—90-Membered glycol (I) and 186-membered glycol (II).

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[10] Kozakevich and Ushakova, *Z. physik. Chem.*, **A157**, 188 (1931).

[11] Rideal, "Surface Chemistry," Cambridge University Press, 1930, p. 66.

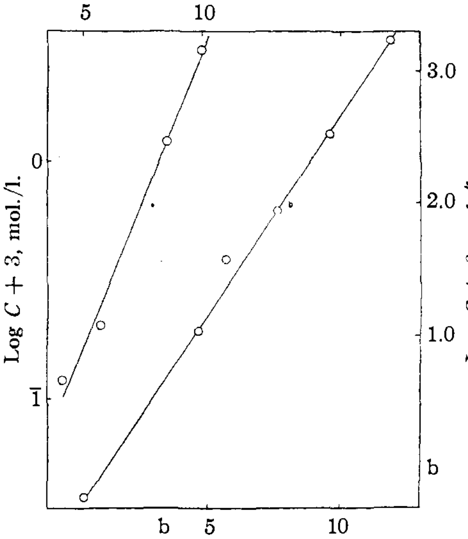

Fig. 6.—(a) 18-Membered glycol (upper curve); (b) 42-membered glycol (lower curve).

constant (Figs. 5 and 6). This indicates a saturated surface layer in each case and the ability to reach surface saturation at very low bulk concentrations. As all the concentrations are very small, the area per molecule is calculated directly from the slopes of the log curves (Table VII). As a basis for comparison, the table also contains the areas calculated on the basis of horizontally-oriented zigzag chains.

It is seen that only the 18-membered glycol shows agreement between the two values, all the other areas being consistently too small. It therefore seems probable that the long chains tend more and more to assume a vertical orientation as the chain length is increased above 18 units. This is not an unexpected behavior for such very long chains.[12] It is not found in any of the available data for insoluble films of high-polymeric substances,[13] because all the long chains previously investigated are characterized by the presence of strong polar groups (carbonyl) at short intervals, thus serving to anchor their entire lengths firmly to the substratum. The ether group in the polyoxyethylene chain apparently does not restrict the orientation in this way.

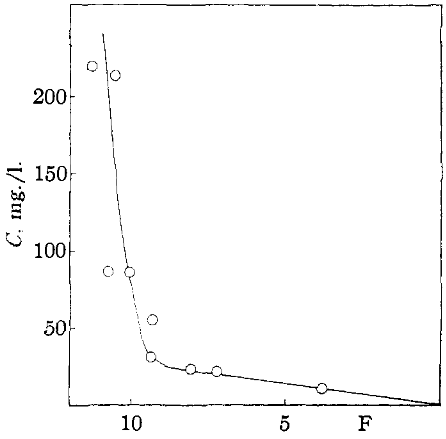

Fig. 7.—186-Membered glycol.

Summary

1. The surface tensions of aqueous solutions of a number of unipolymeric oxyethylene glycols (with 3, 6, 18, 42, 90 and 186 repeating units, respectively) have been measured at various concentrations.

2. For the higher members, the surface tension lowering is a linear function of the logarithm concentration.

3. The results have been compared with the known behavior of short-chain polymethylene compounds, and some molecular areas calculated from Gibbs' adsorption isotherm.

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[12] Adam, "The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, 2d ed., 1938, pp. 58 and 94.

[13] Adam, *Trans. Faraday Soc.*, **29**, 90, 837 (1933); Moss, THIS JOURNAL, **56**, 41 (1934); Harkins, Carman and Ries, *J. Chem. Phys.*, **3**, 692 (1935).