

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

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LIX. The Precipitability of Pure Hemicolloidal Polyoxyethylene Glycols

BY EDWIN L. LOVELL¹ AND HAROLD HIBBERT

Introduction

In a recent communication describing the quantitative precipitation behavior of a polymer homologous series of polystyrenes, G. V. Schulz² has investigated a new property of these high molecular products which it is suggested may lead to a new method for the determination of molecular weights of moderately high polymeric substances. This property is the "precipitability (γ)," or relative proportion of a non-solvent which must be added to the solution of a polymer in order to initiate precipitation. Schulz has endeavored to correlate the precipitability of such high polymers with their solubility and degree of polymerization, respectively, and, proceeding on the basis of certain assumptions, has arrived at two equations expressing these relationships

$$\ln c = a - b\gamma \quad (1)$$

$$\gamma^* = \alpha + (\beta/P) \quad (2)$$

where c is the solubility of the polymer in grams per liter, in a mixture of solvents having the composition represented by γ , γ^* is the precipitability expressed as percentage of non-solvent added to bring about precipitation at any particular solubility value, and P the degree of polymerization. The other symbols refer to constants. In the first equation P is regarded as constant, while in the second the solubility c is constant.

Such a mathematical derivation is of great interest to all workers in the field of macro-molecular chemistry, not only from the purely practical point of view, since it would seem to offer a simple and accurate means of molecular weight determination, but also from the theoretical standpoint in that it concerns the solution states of long molecules. However, the only experimental data so far available have been those obtained by Staudinger and Heuer³ on a single type of polymer, namely, the polystyrenes. Nevertheless Schulz's conclusions, as he has shown, appear to find support in the molecular weight data of these authors, as obtained from viscosity meas-

urements on these same products. In the present case, the solubility and precipitability of four pure, long chain polyoxyethylene glycols, with molecular weights ranging from 1000 to 9000, have been studied in methanol-ether and dioxane-ether mixtures at 0° with a view to determining the general validity of the relations between the variables, postulated by Schulz.

It appears from this work that the relationship between the precipitability and degree of polymerization is not in conformity with the Schulz generalization, but instead follows a simple empirical law which also seems to fit the polystyrene data of Staudinger and Heuer. The relation between precipitability and solubility for these crystalline polyoxyethylene glycol polymers follows the law to be expected in the case of *pure crystalline* substances.

Experimental

The measurements were carried out in a very simple apparatus (Fig. 5), consisting of a removable glass cylinder open at one end and attached, by means of a large ground-glass joint, to a second glass cylinder provided with a pair of side arms into which the delivery ends of two micro-burets were closely fitted. The first cylinder had a capacity of about 20 ml. of solution. Precautions were taken to avoid entrance of moisture into either the solution undergoing precipitation or the anhydrous solvents contained in the burets. The latter were used without lubricating grease. The apparatus was provided with a suitable stirring arrangement.

The preparation, purification and identification of the pure polyoxyethylene glycols used in this work have been described in previous papers.⁴ The solvents used were carefully purified, anhydrous products.

In determining the precipitation point at various concentrations, usually about 0.1–0.4 g. of glycol was weighed into the precipitation cylinder, together with 1–8 g. of solvent. The resulting solution was cooled to 0°, by surrounding it with a large beaker of ice, and then titrated slowly with the non-solvent—observing the solution meanwhile under strong illumination, and with the use of a black background, until minute crystals first became visible. The amount of precipitate at the end-point was always negligible as compared with the amount remaining in solution. This precipitation point could be reproduced to within $\pm 1\%$ or better, the quantity of ether added being obtained by direct weighing, rather than by volume measurement.

(1) Holder of a Bursary under the National Research Council of Canada, 1938–1939.

(2) Schulz, *Z. physik. Chem.*, **A179**, 321 (1937).

(3) Staudinger and Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

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

The method of determining solubility in mixed solvents by measuring the precipitation concentration has been used both by Brönsted⁵ and by Staudinger and Heuer,³ for high molecular polystyrenes.

The measurements in dioxane solution were carried out in a slightly different manner. Ground-molar solutions (44 mg./cc.) of the glycols in dioxane were made up and in each case a volume of just 2 cc. was placed in a 15-cc. precipitation tube by means of a pipet. Titration with ether was then carried out as described above, but the volume of non-solvent required was read directly from the microburet. Suitable precautions were taken to avoid evaporation of the ether during an experiment.

Treatment and Discussion of Results

In Table I are given the solubility (mg. of glycol per gram of mixed solvent added) and precipitability values for each of the five polyoxyethylene glycols $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_P\text{H}$ investigated, using methanol as the solvent and ether as the precipitant. The data are expressed graphically in Figs. 1 and 2. It is seen that in all cases the solubility varies in logarithmic fashion with the precipitability, in agreement with the behavior of the polystyrene polymers.

TABLE I
SOLUBILITY IN METHANOL-ETHER AT 0°

Glycol (P)	γ^* %	c (mg./g.)	$\text{Log}_{10} c$
6	90.2	360.0	
	90.9	322.2	
18	86.4	68.0	1.8325
	87.0	52.3	1.7185
	87.8	31.9	1.5038
42	68.4	38.9	1.5894
	68.7	35.6	1.5519
	70.2	24.4	1.3878
	70.8	28.8	1.4597
	71.5	20.4	1.3096
90	42.9	37.3	1.5715
	43.4	34.0	1.5311
	45.1	29.8	1.4744
	45.1	25.3	1.4031
	47.2	19.9	1.2995
186	29.6	32.25	1.5085
	28.3	29.49	1.4697
	26.0	44.19	1.3836
	25.4	17.39	1.2403
	28.4	24.25	1.3847
	22.3	11.27	1.0519
	20.8	8.77	0.9430
	23.8	14.63	1.1652
23.1	11.20	1.0492	

It may be remarked that Brönsted⁵ found that the solubility of a very high-molecular polystyrene

(5) Brönsted, *Compt. rend. trav. lab. Carlsberg, sér. chim.*, **22**, 99 (1938).

(mol. wt. 600,000) had no effect on the precipitability at very high dilutions.

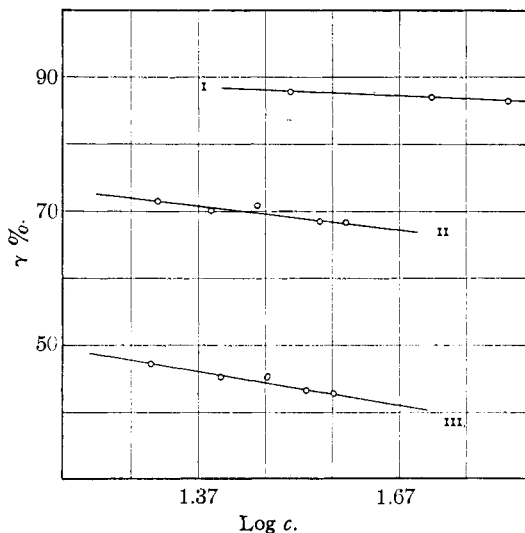


Fig. 1.—The relation between solubility c (mg./gr.) and precipitability in methanol-ether: I, 18-membered; II, 42-membered; III, 90-membered.

Methanol Solutions.—Before considering the effect of degree of polymerization on the precipitability of these glycols at constant solubility, it is necessary to examine the underlying basis of the Schulz equations, (1) and (2). The assumptions made by him in deriving these equations are really adapted to a specific case, namely, that of the high-polymeric polystyrenes or related polymers; they are based on the theory that these products are not precipitable in a purely crystalline form, and on the fact that their melting points are in general high or indeterminable. Neither of these conditions apply to the polyoxyethylene glycols used in the present experiments. There is no doubt as to the crystallinity of the latter when precipitated in the manner described, as has been shown in a previous communication.⁴ Furthermore the relatively low setting points (25–45°) of each of these pure glycols have been determined very accurately. It is found that they are in very close agreement with the values derived from the equation

$$t_s = P/(a + bP) \quad (3)$$

(Fig. 4) where t_s is the setting point in degrees centigrade, P the degree of polymerization and a and b constants having the values of 0.391 and 0.02036, respectively. The equation of Austin⁶ connecting the melting points and molecular

(6) Austin, *THIS JOURNAL*, **52**, 1049 (1930).

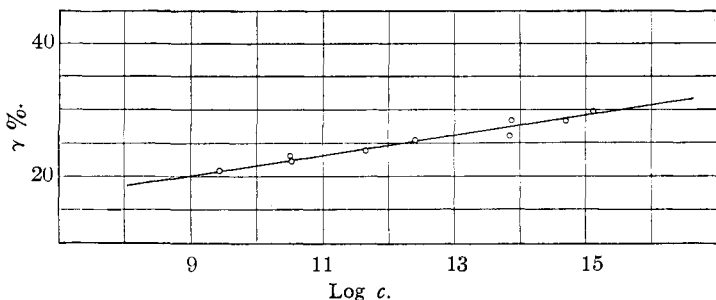


Fig. 2.—Effect of increasing concentration of ether upon the solubility of 186-membered glycol in methanol.

weights of the series of paraffin hydrocarbons, alcohols, etc., is quite inapplicable in the case of these polymer homologous glycols.

It follows that with the pure crystalline products used by the authors it is not necessary to resort to the assumptions and approximations applied by Schulz; instead it is possible to find very simply a theoretical equation connecting the variables—degree of polymerization, precipitability and solubility, of this type of polymer—by applying the thermodynamic solubility equation⁷

$$\ln N_2 = \frac{Q}{RT} \frac{T_s - T}{T_s} \quad (4)$$

where N_2 is the mole fraction of solute, T_s the absolute melting point and Q the molecular heat of solution. According to Schulz, on the basis of experiments with the polystyrenes

$$Q = P(A' + B'\gamma) \quad (5)$$

where A' and B' are constants. This may be expected to be a general relation for the heats of solution of polymer homologous substances. For high-molecular substances dissolved in common solvents, it may further be written approximately that

$$N_2 \doteq c/M \quad (6)$$

where M is the molecular weight of the polymer, nearly a simple multiple of P . Combining equations (3), (4), (5) and (6) gives

$$RT \ln c = RT \ln P + \frac{A'P^2}{a' + b'P} + \frac{B'P^2}{a' + b'P} \gamma \quad (7)$$

where $a' = 273a$, $b' = 1 + 273b$ and the other symbols and constants have the same values as previously mentioned. For a given polymer (P constant) this last equation becomes identical in form with (1) which is in good agreement with the present experimental data. If c is regarded as constant, the result obviously is not in accord

(7) Hildebrand, "Solubility of Non-electrolytes," Reinhold Puh. Co., New York, N. Y., 1936.

with Schulz's generalization (equation 2), and indeed Table II shows that γ is not a linear function of $1/P$.

The validity of this treatment may be confirmed semiquantitatively by measuring the ratio of the log c - γ slopes for two glycols. The calculated ratio from the coefficient of γ in equation (7) for the 18- and 42-membered glycols is 2.26 (using the empirical constants of equation (3)); the observed ratio is 2.3, in excellent agreement.

The slope of this curve for the 90-membered glycol, however, is somewhat less (ratio 1.4) than

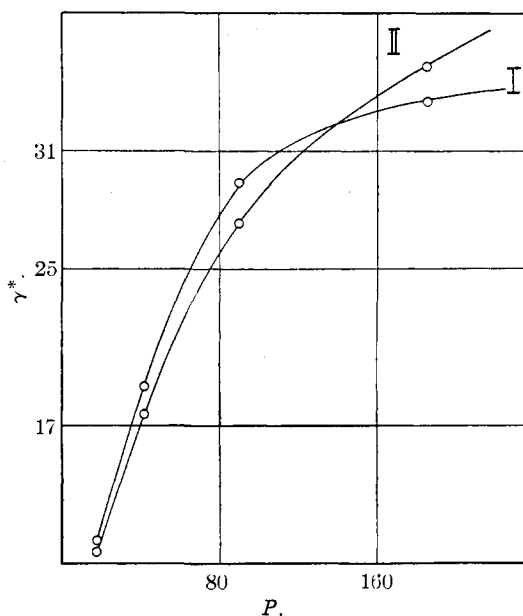


Fig. 3.—Precipitation of the polyoxyethylene glycols at two concentrations: curve II ground-molar (4.4%); I 0.5 ground-molar (2.2%).

that calculated in this manner (ratio 1.55), while that of the 186-member is actually negative, over the concentration range 0.9–3.2% (Fig. 2).

TABLE II

PRECIPITATION FROM METHANOL SOLUTIONS

P	γ^* %	γ^* %	γ^* %	$\frac{1000}{P}$
	$c = 2.2\%$ (0.5 grd.-molar)	$c = 2.8\%$ (0.6 grd.-molar)	$c = 4.4\%$ (1.0 grd.-molar)	
18	88.6	88.2	87.3	55.56
42	71.0	70.2	67.5	23.81
90	46.5	45.2	41.5	11.11
186	26.7	27.9	31.3	5.38

A very careful study of the system methanol-ether which has been made by Saggir⁸ shows that

(8) Saggir, *Bull. soc. chim. Belg.*, **38**, 392 (1929).

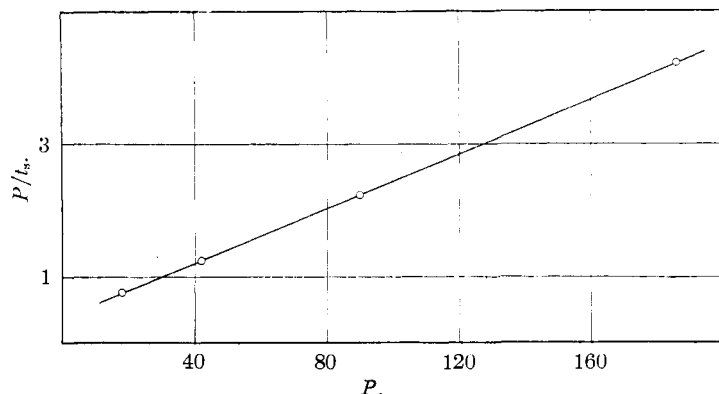


Fig. 4.—Setting points of the polyoxyethylene glycols.

these two solvents do not form mutual complexes, such as might have a complicating effect on the solubility relations of any substance in the mixture. The effect, however, appears to be peculiar to the methanol solutions, for in dioxane solution the 186-membered glycol shows the normal decrease in solubility with increasing proportion of precipitant (Table III). It is not entirely clear, however, why the 186-membered glycol, alone of all the glycols studied, should show this abnormal behavior in methanol.

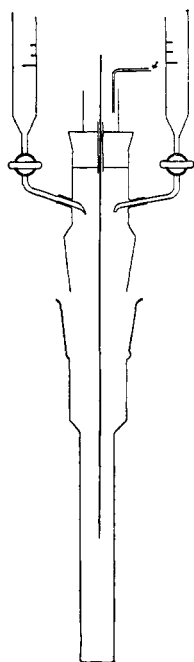


Fig. 5.—Apparatus.

in Curve I of Fig. 6 to be a direct linear function of the degree of polymerization.

Dioxane Experiments.—

These results are given in Table III; here γ_0 is the volume percentage of non-solvent at the end-point when a 4.4% solution of the glycol is titrated. This quantity is shown

TABLE III

PRECIPITATION OF 4.4% DIOXANE SOLUTIONS			
P	$10 \times \text{vol. Et}_2\text{O}$ per cc. initial volume	γ_0 , vol. %	c (end-point), mg./cc.
18	2.5	71.4	12.58
42	16	61.5	16.92
90	10.4	51.0	21.58
90	17.1	(63.1)	16.23 ^a
186	2.95	22.7	33.99
186	...	(39.2)	20.12 ^b

^a Experiment at 8.6°.

^b c init. = 33.02 mg./cc.

The characteristic precipitability γ_0 for any polymer differs from the γ^* used above in that the latter quantity is expressed always at the same solubility for the polymeric series, while the solubility value corresponding to γ_0 is necessarily different for each polymer, as of course the volume of the solution being titrated changes with the amount of precipitant which it is necessary to add. To bring the results of the methanol experiments into line with those in dioxane, the data of Table II are recalculated in Table IV in terms of

volume percentages; these in turn are readily converted into γ_0 values, also given in the Table. Figure 6 demonstrates that these values also show

TABLE IV

PRECIPITATION OF 4.4% METHANOL SOLUTIONS			
P	γ , vol. %	c mg./cc.	γ_0 calcd.
18	88.4	31.80	92.2
	89.7	15.89	
42	69.8	32.46	76.3
	73.3	16.21	
90	44.2	33.44	46.9
	49.2	16.61	
186	33.68	33.80	33.0
	28.86	17.00	

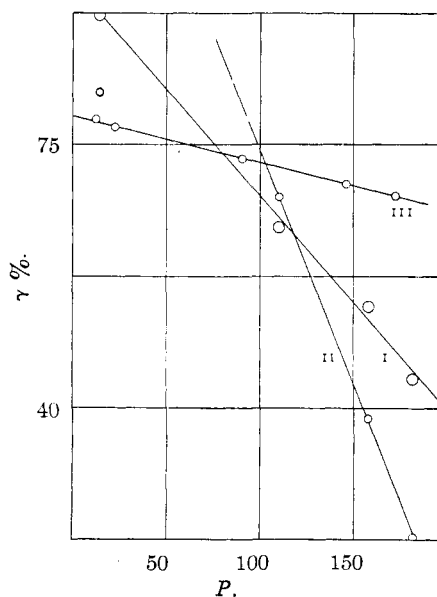


Fig. 6.—Relation between degree of polymerization (P) and precipitability of ground-molar solutions (γ_0): polyoxyethylene glycols, (I) in dioxane-ether; (II) in methanol-ether; polystyrenes³ (III) in benzene-ethanol (scale m. wt./50).

a linear variation of γ_0 with P although, as might be expected from the result discussed previously, the 186-membered glycol does not fit the curve.

To further establish the validity of this wider generalization, the precipitability results of Staudinger and Heuer³ for the hemicolloidal polystyrenes are included in Fig. 6. It is obvious from these curves that both types of polymers conform to this simple relationship.

Conclusion.—A point of interest in connection with the above experiments is the significance of the $\log c-\gamma$ slope changes as the higher degrees of polymerization are reached. It is customary to fractionate mixtures of polymer homologous compounds by successive additions of some precipitant to a solution of the mixture, the higher members being first precipitated and followed in order by the lower members as the precipitant concentration is increased.⁹

However, if the concentrations and nature of solvents used are such that the situation expressed in Fig. 3 exists, the results of such a fractionation would be unlikely to lead to the simple separation of high and low members expected. Indeed, the literature contains not a few examples of fractional precipitations which have apparently resulted in the low molecular weight members being precipitated first,¹⁰ but little attention seems to have been

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

(10) See, for example, Okamura, *Cellulosechemie*, **14**, 135 (1933); Glückmann, *Kolloid-Z.*, **76**, 84 (1936).

paid to this fact. The importance of obtaining as nearly uniform polymers (in chain length) as possible in studies of the macromolecular state points to the advantage and desirability of *quantitative* studies of precipitation and fractionation phenomena.

Summary

1. The relationships between the precipitability, solubility and degree of polymerization of a number of pure long-chain polyoxyethylene glycols have been determined in methanol-ether and dioxane-ether mixtures.

2. For each glycol, the logarithm of the solubility (in per cent.) was found to be a linear function of the percentage of precipitant (ether) in the mixed solvent methanol-ether.

3. An anomalous behavior of the 186-membered glycol, in this respect, is recorded, and its possible significance for the customary methods of fractionation of higher polymers, especially those of a micro-crystalline character, is pointed out.

4. The experimental results have been compared with those of other authors on polystyrene polymers, and certain theoretical and actual differences indicated. A new generalization relating the precipitability factor to the degree of polymerization is suggested, which brings both these sets of results into general agreement.

MONTREAL, CANADA

RECEIVED MAY 3, 1939

NOTES

The Crystal Structure of Synthetic Antimony Trisulfide

BY HAROLD P. KLUG AND G. B. HEISIG

Red (orange) and black varieties of antimony trisulfide have been prepared in various ways from very early times, and likewise occur in nature.¹ The red variety has been regarded as amorphous, while the black variety is crystalline and reported to be identical with the mineral stibnite, Sb_2S_3 , except in sp. gr.¹ Stibnite has been investigated

(1) Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. IX, Longmans, Green and Co., New York, 1929, p. 512.

by several workers,² but no one seems to have reported X-ray observations on the artificial sulfides. Recently we have been interested in the two varieties of antimony trisulfide as prepared in the laboratory, and have examined them with X-rays. The results are in accord with earlier observations by other methods, and we report them primarily as a matter of record.

Red antimony trisulfide was prepared by passing a current of hydrogen sulfide through a hydrochloric acid solution of antimony trichloride

(2) See for example: Gottfried, *Z. Krist.*, **65**, 428 (1927); Gottfried and Lubberger, *ibid.*, **71**, 257 (1929); Hoffmann, *ibid.*, **86**, 225 (1933).