6. Molecular Weight of Polyoxyethylene Glycols and Their Derivatives. (I)

Cryoscopic Measurements and Solvent Effects

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INTRODUCTION

It is well-known that polyoxyethylene glycol mono-alkyl ether is a non-ionic surfactant. In the course of our studies on physical and chemical properties of polyoxyethylene compounds, it was necessary to determine the molecular weight. For this purpose the cryoscopic method was used, because this method was suitable for the molecular weight determination of the compound whose molecular weight is less than several thousands.

First, molecular weights of polyoxyethylene glycol mono-alkyl ethers were measured in benzene solution, and anomalous depressions of freezing point were observed below a certain low concentration and so the molecular weights were obtained by ignoring these anomalous points. The values of molecular weight observed in benzene solution were in good agreement with the theoretical ones. However, in phenol solution the observed values were much smaller than those in benzene.

Hence, to know whether these anomalous phenomena are due to the polyoxyethylene group or not, the molecular weights of lower-membered polyoxyethylene glycols were measured with seven different solvents. In this case the anomalous depression was also noted and the observed values of molecular weight varied with the solvent used.

This article presents the experimental results on the cryoscopic measurments and gives some discussion on the solvent effects and the anomalous depression of freezing point.

EXPERIMENTAL

1. Materials

Polyoxyethylene glycol mono-alkyl ethers (abbreviated to PEGAE), $HO(CH_2CH_2O)_n \cdot (CH_2)_m \cdot H$——Various samples of mono-lauryl, cetyl and oleyl ethers of polyoxyethylene glycols were prepared for us by Mr T.Kariyone, Chief Research Engineer of Kaô Soap Co. These samples were further decolorized by active carbon in benzen

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solution and extracted with dry ether to eliminate a trace of inorganic catalyst and free polyoxyethylene glycol. They were white or slightly yelllowish waxy solids at room temperature. The materials are abbreviated to the following sample notation for simplicity: L, C and O represent lauryl, cetyl and oleyl groups respectively, and figures the average degree of polymerization of polyoxyethylene group.*

Pure polyoxyethylene glycols (abbreviated to PEG), HO $(CH_2CH_2O)_n$ H—— Pure samples of tetra-, penta-, and hexa-oxyethylene glycols were prepared in the laboratory by the following method. A mixture of polyoxyethylene glycol was obtained by the reaction of ethylene oxide with ethylene glycol in the presence of acid catalyst and it was separated into each polymer by the fractional distillation under a reduced pressure and finally each polymer was several times fractionated by the vacuum distillation. Tetramer : b.p. 165-175° (5 mm.), $n^{20°}D$ 1.4591, Pentamer : b.p. 185-205° (5 mm.), $n^{20°}D$ 1.4621, Hexamer : b.p. 210-230° (5 mm.), $n^{20°}D$ 1.4636. The boiling point and the refractive index for each polymer were referred to the values reported by Gallaugher and Hibbert[1].

ω,ω'-Dichloropentaoxyethylene Cl $(CH_2CH_2O)_4CH_2$ CH_2Cl —— This was obtained by the similar method to that for hexaoxyethylene glycol dichloride prepared by Fordyce, Lovell and Hibbert[2]. b.p. 140-150° (1mm.).

2. Method

The measurements of the freezing-point depression were made with the usual Beckman method[3]. The solvents used were benzene, dibromoethane, nitrobenzene, 1.4-dioxane, tert-butanol, water and phenol. These solvents were purified by the method described in "Organic Solvent"[4] and recrystallized several times at each freezing point.

In a dilute solution the molecular weight M is calculated from the lowering of freezing point ΔT and the concentration of solute C in g. solute per 1000 g. solvent. by the following formula

$$M = K_f \cdot C / \Delta T,$$

where K_f is the freezing-point constant. The value of K_f for each solvent are as follows : benzene 5.12 ; dibromoethane 12.5 ; nitrobenzene 8.1 ; 1.4-dioxane 4.80 ; tert-butanol 8.37 ; water 1.85 and phenol 7.27.

RESULTS

1. Molecular Weight of PEGAE

In determining the molecular weight by the cryoscopic method, it is necessary that the molecular weight M is obtained by extrapolating the values of apparent molecular weight Mc to infinite dilution which are calculated from the relation men-

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* For example, C-10 is mono-cetyl ether of about 10-membered polyoxyethylene glycol.

-tioned above at several low concentrations C, to eliminate the effect of the interac-tion between solute molecules.

The plots of Mc *versus* C for PEGAE in benzene solution are given in Figs. 1, 2 and 3. In Fig. 1 some Mc-C plots in phenol solution are also shown. As shown in these Figures, the plots showed linear relations between Mc and C in some
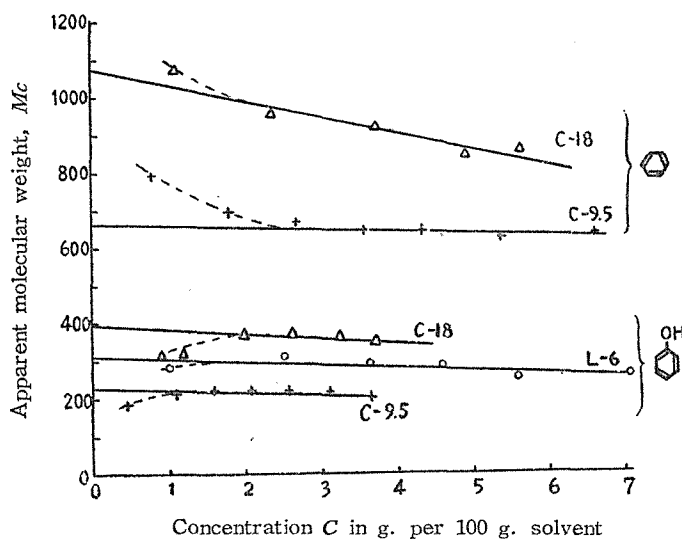

Fig. 1. Plots of Mc *versus* C for PEGAE in benzene and phenol.
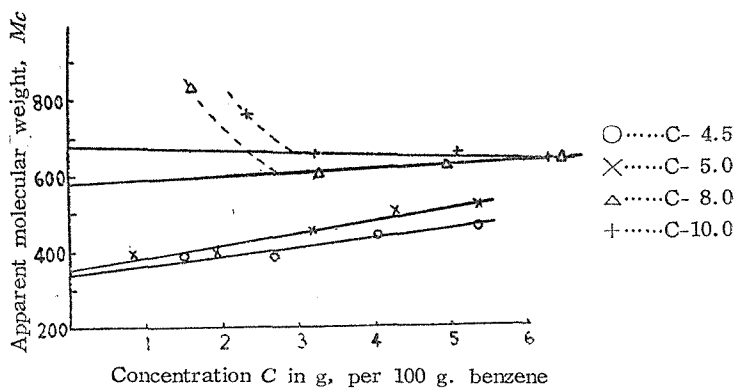

Fig. 2. Plots of Mc *versus* C for mono-cetyl ether of PEG.

concentration range, but the value of Mc deviated from this linear relation in the concentrations lower than about 0.3 % mole fraction.* The observed values of mole-cular weight given in Tables 1 and 2, are the values obtained by extrapolating the

* The concentration was evaluated from the extrapolated value of molecular weight.

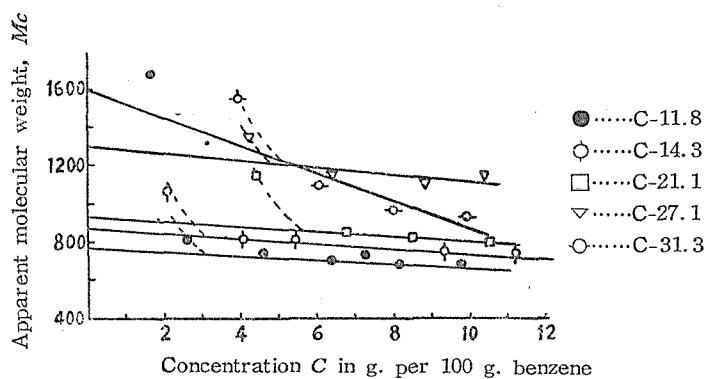straight line in Mc-C curve to zero concentration.

Fig. 3. Plots of Mc *versus* C for mono-cetyl ether of PEG.

Table 1. Molecular weight of polyoxyethyleneglycol mono-alkyl ethers.

Sample	Theoretical[a]	Observed in benzene	in phenol
L- 6	450	525	312
L-17	934	1130	306
L-20	1066	1060	329
C- 9.5	660	661	227
C-13	814	1094	473
C-18	1034	1074	392
O- 8	620	665	350
O-20	1148	1110	249

[a] See reference (5).

Table 2. Molecular weight of polyoxyethylene glycol mono-cetyl ethers.

Sample	Theoretical[a]	Observed in benzene
C- 4.5	440	340
C- 5.0	462	350
C- 8.0	594	580
C-10.0	682	680
C-11.8	762	770
C-14.3	872	870
C-21.1	1171	930
C-27.1	1432	1300
C-31.3	1620	1600

[a] See reference (5).

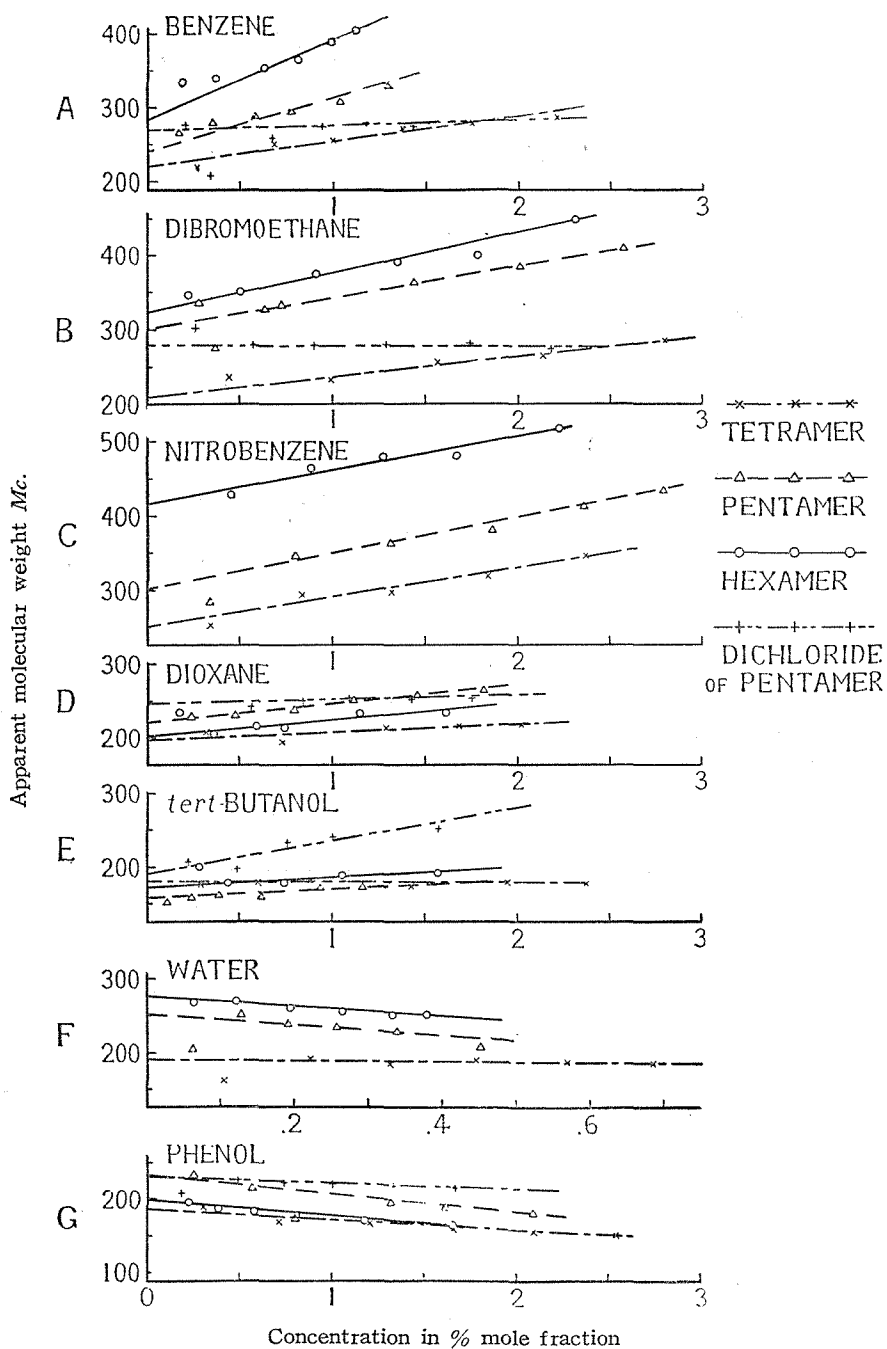In the case of benzene solution the observed values of molecular weight were

Fig. 4. The plots of *Mc versus C* for PEG and dichloride in various solvents

fairly consistent with those determined chemically[5]. These latter values were assumed to be the theoretical ones in this report.

On the other hand in the case of phenol solution the observed molecular weights were considerably lower than the theoretical and fell in a range of 200 to 400 for all the samples (Table 1).

2. Molecular Weight of Pure PEG and its Dichloride

To examine the anomalous depression of freezing point and the solvent effect, the molecular weights of some pure polyoxyethylene glycols and dichloride of penta-mer were measured with seven different solvents. The Mc-C curves for each solvent are shown in Fig. 4 (A,B,C,D,E,F and G) and the observed values are compared with

Table 3. Molecular weight of pure polyoxyethylene glycol and dichloride of pentamer.

Substance	Theoretical	Observed						
		in benzene	in dibro-methane	in nitro-benzene	in 1,4-dioxane	in *tert*-butanol	in water	in phenol
Tetra-oxyethylene glycol	194.2	220	208	250	195	180	190	185
Penta-oxyethylene glycol	238.2	240	300	300	220	158	250	230
Hexa-oxyethylene glycol	282.3	287	320	416	220	172	276	198
ω,ω'-Dichloro-penta-oxyethylene	275.2	270	279	— [a]	245	190	— [b]	230

[a] Not measured. [b] Insoluble.

the theoretical in Table 3. The anomalous behavior of Mc in lower concentrations was also noted on those pure samples of lower-membered polymer, though the concentration at which Mc began to deviate from the straight line was different with solvent, and the inclination of Mc-C curve varied with the nature of solvent. The observed and theoretical values were in good agreement in the cases of benzene and aqueous solutions.

DISCUSSION

1. The Relation between Freezing-Point Depression and Concentration. (Solvent Effect)

In the cryoscopic determination of molecular weight the following departure from ideality should be taken into consideration.

(1) If the solute molecule interacts with each other or associates, the number of

effective molecules in the system will be reduced accordingly and the observed lowering of the freezing point will be less than that predicted for the ideal case, giving the larger value of molecular weight.

(2) Another form of deviation occurs when the solvent and solute molecules combine partially in the solution to form a third substance. In such case, the deviation from ideality is often to be due to solvation or molecular compound formation and is a negative case in Raoult's law.

In the case of those solvents as benzene, dibromoethane and nitrobenzene (Figs.4 A, B and C), the slope of Mc-C curve for all PEG was positive, and so it was considered that the interaction between solute molecules increased with increase of concentration. In other words there appears to be a positive deviation from Raoult's law or the association of solute molecule with concentration.

Such effect may be ascribed to end hydroxyl groups of solute molecule by taking into consideration the following fact : In the case of ω,ω'-dichloropentaoxyethylene which was substituted for the end hydroxyl groups of pentamer of PEG by chlorine atoms, the Mc-C plot showed no appreciable inclination, or the effect of concentration on the value of Mc was not observed. The observed values of this dichloride were in good agreement with the theoretical one in both benzene and dibromoethane solutions. Pentamer and hexamer of PEG in benzene gave reasonable values of molecular weight, but the observed value of tetramer was somewhat larger than the theoretical and further, for lower-membered polymer than tetramer, the tendency of association was considerably noted.

Also in the case of mono-cetyl ethers (Figs. 2 and 3), the value of Mc for those samples as C-4.5 and C-5.0 having lower-membered polyoxyethylene group increased with concentration and the effect of association was observed. However with increase of the number of oxyethylene group the slope of Mc-C curve became smaller and smaller, and for the sample above C-10 it was negative. This rather corresponds to a negative deviation from Raoult's law. Therefore, for these long polyoxyethylene chain compounds there appears to be the interaction between solute and solvent molecules.

The molecular weight of Carbowax 300 measured in nitrobenzene by Couper and Eley [1] was larger than the theoretical in accordance with our results.

In dioxane solution (Fig. 4, D), the observed molecular weight for tetramer and pentamer agreed with the theoretical value, but for hexamer was smaller than the theoretical. Such tendency was remarkable in the case of the solvent with hydroxyl group. The Mc-C curve for *tert*-butanol solution (Fig. 4, E) was similar to that for dioxane solution, but the observed molecular weight in the former was smaller than that for the latter.

Furthermore, in both aqueous and phenol solutions (Fig. 4 F and G) the inclination of Mc-C plots was negative and so there appears to be the appreciable solute–solvent

interaction. In the case of the solvents having hydroxyl group it may be possible that the hydrogen bond is formed between the end hydroxyl group or oxygen atom of oxyethylene group and hydroxyl group of solvent molecule. In particular the formation of strong hydrogen bonding is possible in the case of phenol which has a strong proton-donative power.

Nagakura and Baba[7] pointed out the hydrogen-bond formation in petroleum ether solution of diethyl ether and phenol from the results on the ultra-violet absorption spectrum.

It may be reasonable that phenol solutions give small observed values of molecular weight particularly for compounds having long polyoxyethylene chain. Because, by the formation of hydrogen bond between the solute and solvent molecules, the number of molecules of free solvent remaining decreases and the mole fraction of solute becomes greater than expected so that the depression of the freezing point is more than that predicted by the freezing-point equation.

Although in aqueous solution the effect of hydrogen bonding on the mole fraction of solute is also expected from the negative inclination of $Mc\text{-}C$ curve, the observed molecular weight was fairly consistent with the theoretical and the anomalous depression in lower concentration was not always appreciable for these lower-membered PEG. This results were thought to be due to the reason that the relative change in the mole fraction of solute mentioned above was not so large, because the molecular weight of water is much smaller than those of other solvents.

However, in aqueous solution of high molecular-weight PEG or Carbowax, Couper and Eley[6] pointed out that the anomalous behavior in lower concentration was appreciable and the extrapolated molecular weight was different from the theoretical value.

2. Anomalous Depression of Freezing Point in Lower Concentration

As was already pointed out by Gallaugher and Hibbert,[1] the similar anomalous cryoscopic behavior was observed in benzene and dibromoethane solutions. In these solvents the apparent molecular weight Mc increased with decreasing concentration below a certain concentration (about 0.3 % mole fraction for PEGAE). Such anomalous behavior of Mc was more appreciable with increase of chain length of polyoxyethylene. (Figs. 1, 2 and 3). However, in phenol solution, the value of Mc decreased rather with dilution in contrast with the case of benzene and dibromethane solutions (Fig. 1). Unfortunately, the reason for these anomalous cryoscopic behaviours has not been clarified for lack of accurate measuments in further lower concentrations.

Another example of the anomalous cryoscopic phenomenon was reported on benzene and cyclohexane solutions of polystyrene and polyisobutylene by Kemp and Peters[5]. In this case the anomaly in low concentrations was noted on isobutylene polymers whose molecular weight was more than about 2,000. Kemp and Peters pointed out the occurrence of a polymer-solvent complex in benzene solution and suggested

the possibility of the segment action in high polymer solution.

In connection with the cryoscopic anomaly mentioned above, we have measured the solution viscosity[9] of PEGAE in carbon tetrachloride and observed the similar anomaly that the reduced viscosity η_{sp}/c increased with decreasing the concentration C below a certain low concentration as in cryoscopic measurements.

Considering that such anomalous phenomena appeared in both cryoscopic and viscosity measurements, we would rather suppose the change in the molecular config-uration of polyoxyethylene compound than the association of it in lower concentration. Staudinger[10] suggested that the polyoxyethylene chain is very flexible and takes the 'meander' form in solution. And it is noticeable that in the case of polyoxyethylene compounds the anomalous cryoscopic depression was observed for much lower polymers than those of polyisobutyrene whose molecular chain is composed of carbon atoms alone. From the results metioned above it may be inferred that there is a close rela-tion between the dissolved state of polyoxyethylene compound or its molecular confi-guration in solution and the anomalous depression of freezing point.

SUMMARY AND CONCLUSION

(1) The molecular weights of various mono-alkyl (lauryl, cetyl, oleyl) ethers of 5-30 membered polyoxyethylene glycols were measured by the cryoscopic method. Below a certain lower concentration the anomalous depression of freezing point was observed. Ingoring these anomalous points, the value of Mc extrapolated to infinite dilution was taken as the observed value of molecular weight. In benzene solution the observed values were fairly consistent with the theoretical ones. On the other hand the values observed in phenol solution were very small.

(2) The molecular weights of tetra-, penta-, hexa-oxyethylene glycols and ω,ω'-di-chloro-penta-oxyethylene were measured with seven different solvents. The molecular weights observed in benzene were similarly in good agreement with the theoretial values as in the case of mono-alkyl ether and for these low-membered polyoxyethylene glycols good results were also obtained in aqueous solution, but other solvents having hydroxyl group gave smaller values of molecular welght. The observed molecular weight of ω,ω'-dichloropentaoxyethylene did not so vary with the solvent as in the case of polyoxyethylene glycols.

(3) The solvent effects mentioned in (1) and (2) were interpreted in terms of the interactions which correspond to the tendency of association in non-hydrogen bonding solvents and to the formation of solute-solvent complex in hydrogen-bonding solvents.

From the present results it was concluded that among the solvents used benzene is most suitable for the cryoscopic measurement of molecular weight of polyoxyethylene compound. However when the member of polyoxyethylene chain exceeds about 30, the anomalous depression in benzene is so remarkable that the measurements are inacur-rate. On the other hand for lower-membered polyoxyethylene glycols water may be

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a suitable solvent as well.

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