

(3) The change of the concentration of alkali with time at the discharging end was investigated by titrating the liquid flowing out from feeders successively at definite intervals with hydrochloric acid. The concentration - time curve thus obtained was confirmed to be similar in shape to those given by Bishop and others, who have analysed the content of the indicators, for instance cerium, in the glass, turned out from the operating tank.

From the curves, obtained by repeating the same kind of experiments by changing the pull rate, the concentration of alkali and the charging amount of glycerin, the authors have confirmed that the concentration-time curves may be expressed, approximately, by the equation including two parameters  $E$  and  $\bar{u}$  such as

$$\frac{\partial c}{\partial t} = E \frac{\partial^2 c}{\partial x^2} - \bar{u} \frac{\partial c}{\partial x},$$

in which  $c$  is the concentration of alkali,  $t$  the time,  $x$  the longitudinal distance from the charging end. The constants  $E$  and  $\bar{u}$  vary according to the degree of agitation and the pull rate.

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## 10. Physico-chemical Properties of Surface Active Agents. (VIII)

### Molecular Weight of Pure Polyoxyethylene Glycol

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Molecular weights of pure polyoxyethylene glycols were determined by the cryoscopic method in five different solvents (benzene, dibromoethane, dioxane, *tert*-butanol and phenol).

Samples used were tetra-, penta-, hexa-oxyethylene glycols and *sym*-penta-oxyethylene dichloride. These substances were synthesized in the laboratory by the following method: The mixture was prepared by the successive addition reaction of ethylene oxide to ethylene glycol and was separated to each polymer by fractional distillation under reduced pressure. Finally each polymer was several times carefully purified by fractional vacuum distillation. Penta-oxyethylene dichloride ( $\omega, \omega'$ -) was obtained by the reaction of thionyl chloride with penta-oxyethylene glycol in pyridine.

Some typical curves of molecular weight  $M_c$  calculated from the lowering of freezing point against the concentration  $C$  g/100g. solvent are shown in the figure.

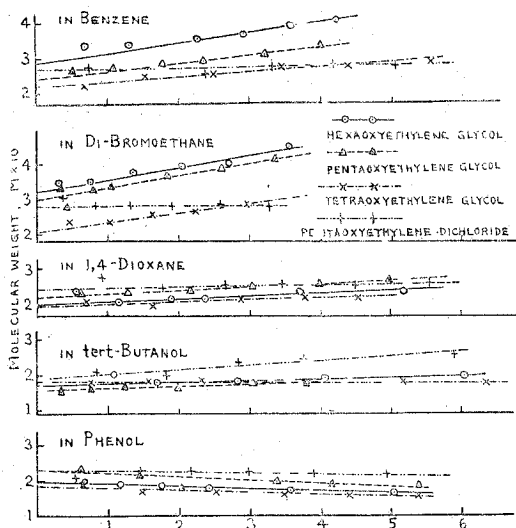


Fig. 1. Effect of concentration on cryoscopic molecular weight of polyoxyethylene glycols in various solvents.

As shown in the figure, molecular weight  $Mc$  increased with increasing concentration in all solvents used except in phenol. The inclination of curves of  $Mc$  vs.  $C$  in benzene and dibromoethane solutions of polyoxyethylene glycols was very similar to each other, but it was different from that in other solvents.

On the other hand the slope of  $Mc$ - $C$  curve for *sym*-pentaoxyethylene dichloride did not so varied with the solvent.

In some cases, below a certain lower concentration it was found that the values of freezing point depression over the concentration  $\Delta T/C$  were smaller than those expected theoretically, giving a higher values of molecular weight. Such anomalous behavior was previously reported on a number of polyoxyethylene glycol mono alkyl ethers (This Bulletin 28 64, 1952).

The molecular weights in the following table show the values obtained by ignoring anomalous values and extrapolating to infinite dilution.

Substance	Molecular weight					
	theoretical	observed				
		in benzene	in dibromoethane	in dioxane	in <i>tert</i> -butanol	in phenol
Hexa- <i>oxyethylene glycol</i>	282.3	287	320	200	172	190
Penta- <i>oxyethylene glycol</i>	238.3	240	300	220	158	230
Tetra- <i>oxyethylene glycol</i>	194.2	220	208	195	180	185
Penta- <i>oxyethylene dichloride</i> ( $\omega, \omega'$ -)	275.2	270	279	245	190	230

Of the solvents used, benzene gave the best results except that this solvent gave somewhat a large value for tetraoxyethylene glycol. This may be due to the fact that lower-membered polymer is less soluble in benzene.

On the contrary, in those solvents as dioxane, phenol and *tert*-butanol, the observed values for tetraoxyethylene glycol were nearly consistent with

the theoretical ones, but for penta- and hexa-oxyethylene glycol were smaller than the theoretical ones.

As is mentioned above, it is noticeable that in the cryoscopic determination of molecular weight of polyoxyethylene glycol and its derivatives the observed value varies with the solvent. Although the concentration dependence of the value of  $Mc$  has a close relation with the interactions between solute molecules, and solute and solvent molecules, no further detailed discussion on these interactions or solvent effects can be given from the present results alone.

## II. Studies on the Heat Stability of Polyvinylacetals

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Heat stability of polyvinylacetals was measured by the weight loss during heat-treatment at various temperatures. Polyvinylformal and -butyral were found to decompose measurably at 180–220°C. But the rate of decomposition was markedly retarded by boiling in aqueous solution of  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ .

For polyvinylalcohol, as the raw material of acetals, and for various acetals such as formal, acetoacetal, butyral, octylacetal and laurinacetal, the decomposition curves were obtained and shown in Figure 1.

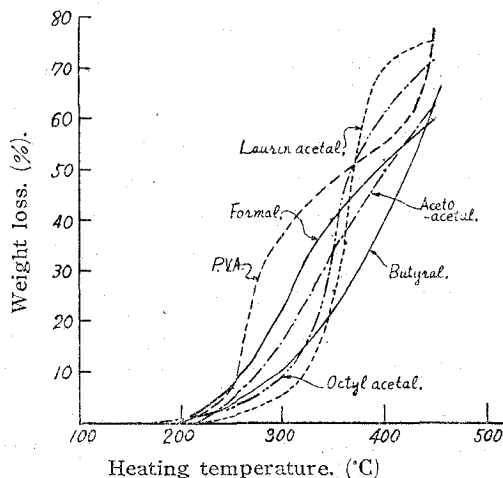


Fig. 1. Decomposition curves. (Acetalization degree 65~70%)

The maximum rate of decomposition falls in the series laurin acetal > octyl acetal > butyral > formal and acetoacetal. The decomposition of polyvinylalcohol occurs at relatively lower temperature and at slightly faster velocity. The viscometric measurements in 80% formic acid solution were