16. Physico-Chemical Properties of Surface Active Agents. (I)

Molecular Weight and Viscosity of Polyoxyethylene Glycol Alkyl Ethers

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Molecular weight: The molecular weights of alkyl (lauryl, cetyl, and oleyl) ethers of 6~20 membered polyoxyethylene glycols were determined by the cryoscopic method in benzene and in phenol.

The values of molecular weight calculated from the lowering of freezing point in benzene solution were in good agreement with the ones expected from the amount of ethylene oxide required in the synthesis of samples. The depression of freezing point in phenol, however, was much too large, giving much smaller molecular weight than that in benzene. Moreover, in phenol the higher the molecular weight, the smaller the observed values. Such anomalies were very similar to those in the cases of polyanethole and others reported by Staudinger.

Viscosity: In determining the chain length of linear polymer, applying the modified Staudinger equation $\lim_{c\to 0} \eta_{sp}/c_{g/100cc} = [\eta] = aP + c$, it is necessary that the polymer under investigation consists of one sort of "ground molecule." However, in such types of polymer as polyoxyethylene glycol alkyl ethers which have two different sorts of chain in an individual molecule, the validity of the Staudinger equation has not yet been examined. In the present work the solution viscosities of polyoxyethylene alkyl ethers were measured in carbon tetrachloride at 25° and in various concentrations with the Ostwald type instrument. The intrinsic viscosities observed and the molecular weights determined in benzene are as follows.

samples	PO-8	PO-20	PC-10	PC-13	PC-18	PL-6	PL-20
$[\eta]\cdot 10^2$	5.2	6.5	5.2	6.3	6.2	4.9	6.2
molecular weights	665	1110	661	1094	1074	520	1060

PO, PC and PL denote oleyl, cetyl and lauryl ether, respectively.

From the values of $[\eta]$ and molecular weights of polymers, it was found that the following relation existed among $[\eta]$ and the degree of polymerization in both ethlene oxide and alkyl chain,

$$[\eta] = aM + bN + c$$

where $a \simeq 8.9\times 10^{-4}$, $b \simeq 7.0\times 10^{-4}$, $c \simeq 3.27\times 10^{-2}$; M and N are the numbers of "ground molecules," $-OCH_2CH_2-$ and $-CH_2-$, in both chains, respectively.

It may be inferred that the constants, a and b, in the above equation have a close relation with the lengths of ethylene oxide and alkyl chains in solution.

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17. On the Electrical Conductivity of the Aqueous Solution of Sodium Oleate

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It is well known that the aqueous soap solution shows the complicated behaviours, which are caused by the aggregation of soap molecules into micelles in their solution.

In the present work, the aging phenomena of the aqueous solution of sodium oleate were examined by the electrical conductivity method.

Sodium Oleate was dissolved in water by heating and cooled to room temperature, and then the electrical conductivity of the solution was measured. The measurment were carried out at room temperature, 15~27°C, and in the concentration range from 0.01 to 0.1N, masking carbon dioxide in the air. And in a certain case, benzene was solubilized into the solution from 0 to 0.5% in volume percentage.

The electrical conductivity of the solution varied with the lapse of time. And it decreased from an initial value to a minimum during one day, and then increased again to a definite value during the following 2~6 days. And it was ascertained that the rates of these particular changes in the electrical conductivity were accelerated by the presence of carbon dioxide and benzene, and also by raising the temperature and the concentration of the solution.

The former process, i.e. the decrease of the electrical conductivity, is thought to be the micelle formation, and the rate of this process seems to depend on the degree of the hydrolysis of sodium oleate, and on the amount of benzene added.

The latter process, the increase of the electrical conductivity, may be ascribed to NaOH that is produced by the acid soap formation. And the rate of this process is increased by the micelle concentration. Hence it is easily understood that this process means the adsorption of oleic acid to the surface or the interior of the micelle.
