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Structural Effects on the Properties of Nonionic Surfactants. I. The Synthesis and Some Surface Activities of Acetal Type Homogeneous Nonionics[1]

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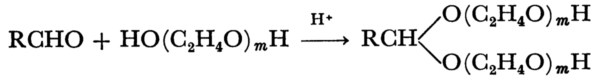
Higher aliphatic aldehydes (C_8—C_{16}) were treated in the presence of mineral acid with several pure polyoxyethylene glycols (m : 2—6), to give the corresponding acetals (AG types) with a general formula $RCH[O(C_2H_4O)_mH]_2$. These AG types are soluble in water, fairly stable in neutral and weakly basic aqueous solutions, and they exhibited the characteristic properties of nonionics. The hydration of the geminal polyoxyethylene (POE) chains are discussed on the basis of the data of unexpectedly low cloud points. Surface tension measurements on the aqueous solutions of AG types indicated that the critical micelle concentration (CMC) value decreases with an increment of oxyethylene units (m), and that the molecular area does not depend so greatly on m and is significantly smaller than that predicted from the data of conventional nonionics (S types) having one hydrophobic and hydrophilic chain each. For the gross effects of AG types, it has been found that the foam stability is considerably low and the dependence of the wetting power for canvas discs on m is larger than that of S types. The results are discussed on the basis of structural characteristics related to the unfavorable hydration and restricted configuration of the geminal POE chains. The acid-catalyzed hydrolysis of AG types in the micellar solution was significantly slower than that of acetaldehyde diethylacetal in water.

The preparation of pure polyoxyethylene alkanols and alkyl phenols has been described in many reports as thoroughly reviewed by Mulley.[2] In most cases two main methods have been used. (1) The mixture produced by ethylene oxide condensation is separated into individual compounds by distillation and (2) a pure POE glycol is joined to a hydrophobe by the Williamson ether synthesis. However, the yields are insufficient in both procedures. Introduction of two POE chains of definite length to a hydrophobe is, therefore, troublesome and has never been established hitherto.

In previous investigations,[3,4] several new type nonionic surfactants containing one to three hydrocarbon or POE chains have been synthesized from α,α′-glyceryl diethers and mono-, di-, and triethers of pentaerythritol by polyaddition of ethylene oxide, and the structural effects on their properties have been discussed. The role of the multi-chain type hydrophile in the behavior of these nonionics, however, could not be interpreted clearly because of the distribution of the POE chain length and the additional effects of the the joint parts in the surfactant molecules. In this investigation, a series of homogeneous nonionics in which two POE with the same chain length were attached to a hydrophobe by acetal linkage were synthesized and the effect of the multi-chain hydrophile on some surfactant properties was discussed. The reaction scheme and abbreviations are as follows.



$$RCHO + HO(C_2H_4O)_mH \xrightarrow{H^+} RCH\begin{matrix}O(C_2H_4O)_mH\\O(C_2H_4O)_mH\end{matrix}$$

R: C_nH_{2n+1} AG-$(n+1)(2m)$

It is of interest that AG types are easily hydrolyzable in the presence of acid, from the viewpoint of degradation after the utilization in an industrial process. Preliminary information on the hydrolysis of AG types is given in this paper.

Experimental

Materials. Commercially available aliphatic aldehydes were purified by distillation and then checked by gas-liquid chromatography (glc) for satisfactory purity (more than 99%). Pure POE glycols were obtained by fractional distillation of commercial products. The purity and the number of oxyethylene unit were checked and determined by glc, NMR, physical indices and analytical method.

Preparation of AG Acetals. To avoid the formation of diacetals by further condensation of acetal with unreacted aldehyde, a large excess of the glycol was used in each runs. In a 300 m*l* three-necked flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer were placed 0.1 mol of aldehyde, 1 mol of the glycol and a catalytic amount of concentrated hydrochloric acid. The reaction mixture was maintained at room temperature with stirring for 1 hr and then gradually heated up to 60—80°C for 4—6 hr. The contents in the reaction vessel were immiscible and formed a suspension at the initial stage of the reaction. It gradually became homogeneous and produced a foam with the progress of reaction. The mixture was cooled, diluted with benzene and neutralyzed with powdered potassium carbonate. The inorganic salts were filtered off and benzene was then distilled off. Unreacted aldehyde and glycol were removed under reduced pressure. The residue was then dissolved again in benzene, warmed, and washed with a small amount of water several times to remove the remaining glycol and salts. Complete removal of benzene under a high vacuum gave a paste-like product in a high yield. Purity and structure of the products were confirmed by elementary and functional group analyses, paper and thin layer chromatographs and IR and NMR spectra. In paper chromatography, 10 mg of the sample was dissolved in an appropriate amount of benzene, spotted on filter paper (Toyo No. 50), developed by mixed solvents (*e.g.*, upper layer of the mixture of *n*-butanol : pyridine : water=

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[1] Presented in part at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] B. A. Mulley, "Nonionic Surfactant", ed. by M. J. Schick, Marcel Dekker Inc., New York, (1967), p. 421.

[3] T. Kuwamura and E. Kameyama, *Kogyo Kagaku Zasshi*, **65**, 1266 (1962).

[4] T. Kuwamura and H. Fukutomi, Proc. Intern. Congr. Surface Active Substances, 5th, Barcelona, Vol. I, p. 71 (1968).

5 : 2 : 3) and detected by Dragendorff reagents. In the same way, thin layer chromatography was carried out on silica gel (Wakogel B-5).

Cloud point of the products was measured on a 0.5% aqueous solution.

Surface Activities Measurements. Aqueous surface tension of AG types were continuously measured by the vertical plate method, at 20±1°C using a Shimadzu ST-1 type tensiometer. Wetting power was evaluated by measurement of the sinking time of a canvas disc (diameter : 1 in.) at 40°C, according to the method described by Yano and Kimura.[5] To evaluate foaming properties, volume of the initial foam and foam remaining after 5 min were measured at 25±1°C according to the method by Yano *et al.*[6]

Hydrolysis. No reliable techniques by chemical or chromatographic analysis have yet been establisehd for the kinetic measurement of hydrolysis of AG type acetals in dilute aqueous solution. We have tried to follow the acid-catalyzed reaction through the measurement of cloud point, which might depend upon a concentration of the higher aldehyde produced and solubilized in aqueous solution during the hydrolysis of AG. The following facts are of use for this method. AG acetals are so stable in neutral and weakly basic aqueous solution that the cloud point of the solution was kept practically constant for periods more than 12 hr at 25—35°C as illustrated in Fig. 11. No appreciable depression of the cloud point was observed when a small amount of inorganic salt (less than 0.02 mol/*l*) was added to the solution.

The required calibration curve was obtained in the following way. Aqueous solutions containing three components (AG, the related aldehyde and POE glycol) were prepared at a definite total concentration, in the proportion corresponding to various extents of hydrolysis. Their cloud points were measured and plotted against the calculated % of conversion of AG as in Fig. 12.

Thus, the rate of hydrolysis at 30±0.2°C was measured on the acidic aqueous solutions of 0.5—1.0% initial concentration which are much higher than the CMC. Immediately after sampling, the catalyst in the sample solution was neutralized with a slight excess of alkali.

Results and Discussion

By the procedure mentioned above, a series of AG type homogeneous nonionics containing 8 to 16 carbon atoms in hydrophobe and 4 to 12 oxyethylene units in hydrophile were successfully prepared in one step from the corresponding aldehydes and glycols. Physical properties of the latter are listed in Table 1.

Table 1. Properties of the used polyoxyethylene glycols

Glycol	Bp, °C/mmHg (lit[8])	n_D^{20} (lit[8])
Diethylene	140—142/20 (139/18)	1.4475 (1.4477)
Triethylene	120—121/0.5 (121—122/0.3)	1.4567 (1.4567)
Tetraethylene	149—150/0.5 (150—152/0.35)	1.4600 (1.4602)
Pentaethylene	173—175/0.4 (175/0.35)	1.4620 (1.4623)
Hexaethylene	218—221/0.6 (219—222/0.6)	1.4645 (1.4648)

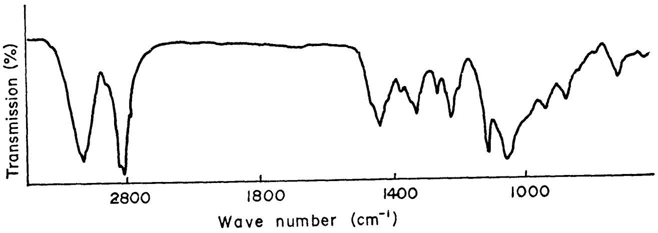

Fig. 1. IR spectrum of AG-12(6).

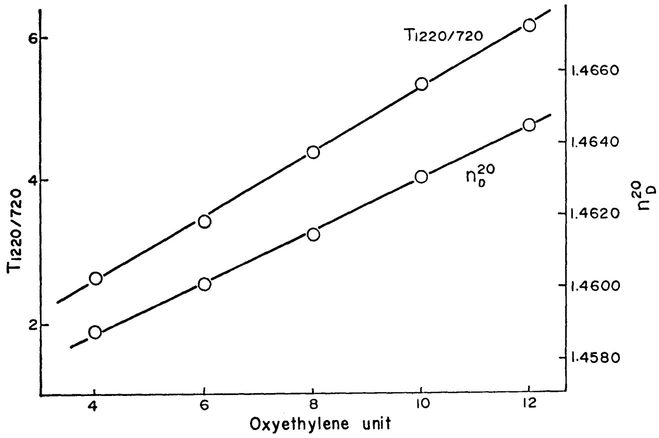

Fig. 2. Plots of the strength ratio ($T_{1220/720}$) of IR absorption *vs.* 2*m* and refractive index *vs.* 2*m* for AG-12 series.

The adsorption band of IR spectra at 1600—1700 cm^{-1} of aldehyde carbonyl was not observed for all products. As an example IR spectrum of AG-12(6) is shown in Fig. 1. In Fig. 2, the strength ratios ($T_{1220/720}$) of IR adsorption bands at 1220 and 720 cm^{-1} and the refractive indices are given as a function of *m*. Deviation from these curves, indicating almost certainly the presence of impurity, was not observed as well as in some cases pointed out by Glassman,[7] Schüring,[8] and Wrigley[9] for S type nonionics. From chromatographic analyses, it was confirmed that the use of a large excess of glycol successfully prevented the formation of diacetal and that the unreacted glycol was almost completely removed by distillation and subsequent washing with water.

NMR spectra provided the proof on the structure of the products. The spectrum (in CCl_4) of AG-12(6) is shown in Fig. 3, where five bands are found at 0.88, 1.27, 3.10, 3.58, and 4.50 ppm in the proton ratio of 3 : 20 : 2 : 24 : 1. They can be ascribed to the protons on methyl, methylene in hydrophobe, hydroxyl, methylene in POE chains and methine groups, respectively. Physical properties, analytical data, and the yields of AG types are listed in Table 2. We see that

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[5] W. Yano and W. Kimura, *Yukagaku*, **11**, 138 (1962).

[6] W. Yano, T. Isaji, and W. Kimura, *ibid.*, **11**, 183 (1962).

[7] V. C. Glassmann and K. Malnnchen, *Fette, Seifen, Anstrichm.* **65**, 741 (1963).

[8] S. Schüring and W. Zeigenbein, *Tenside*, **4**, 161 (1967).

[9] A. N. Wrigley, A. J. Stirton and E. Howard, *J. Org. Chem.*, **25**, 439 (1960).

Table 2. Properties, analytical data, and yields of AG types

Nonionics	$2m$	Cloud point °C	n_D^{20}	Anal (Calcd) C%	H%	OH%	Yield %
AG-8(6)	6	72.5	1.4591	59.10 (58.51)	10.45 (10.31)	8.0 (8.3)	70
AG-10(6)	6	76.5	1.4618[a]	59.90 (60.24)	10.24 (10.57)	7.8 (7.9)	85
AG-12(4)	4	<0	1.4588	63.51 (63.45)	11.47 (11.18)	9.3 (9.0)	80
AG-12(6)	6	53.5	1.4601	61.83 (61.77)	11.10 (10.80)	8.0 (7.3)	85
AG-12(8)	8	74.0	1.4615	60.86 (60.67)	10.61 (10.55)	6.9 (6.2)	95
AG-12(10)	10	99.0	1.4631	60.04 (59.79)	10.48 (10.35)	5.3 (5.8)	90
AG-12(12)	12	>100	1.4645	59.74 (59.15)	10.35 (10.20)	4.9 (4.7)	90
AG-14(6)	6	51.0	1.4632	63.88 (63.13)	11.30 (11.00)	6.7 (6.9)	85
AG-14(10)	10	96.5	1.4649	61.76 (60.87)	10.23 (10.52)	5.3 (5.1)	80
AG-16(10)	10	82.0	—	61.92 (61.86)	10.60 (10.67)	4.6 (4.9)	75

a) At 18°C.

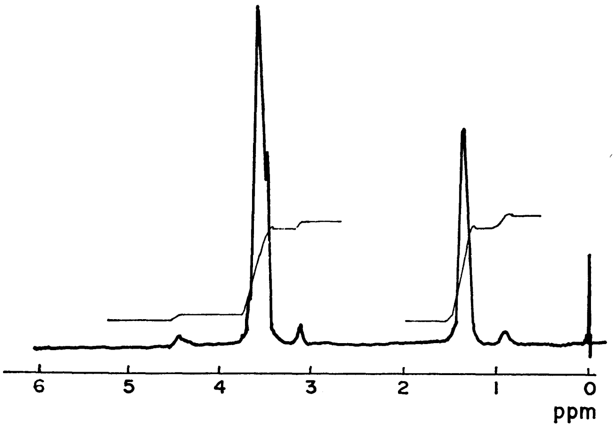

Fig. 3. NMR spectrum of AG-12(6).

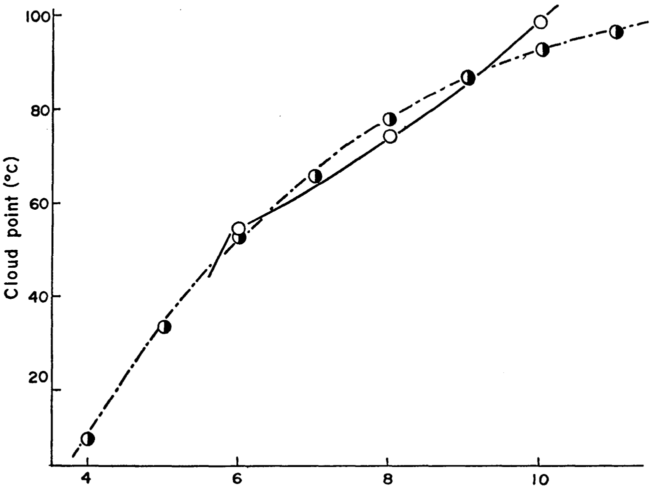

Fig. 4. Plots of cloud point *vs.* number of oxyethylene unit. ○; AG-12 series, ◐; homogeneous polyoxyethylene *n*-dodecanol (S-12 series).[8]

the method established in this investigation has the advantage of high yield in the preparation of homogeneous nonionics.

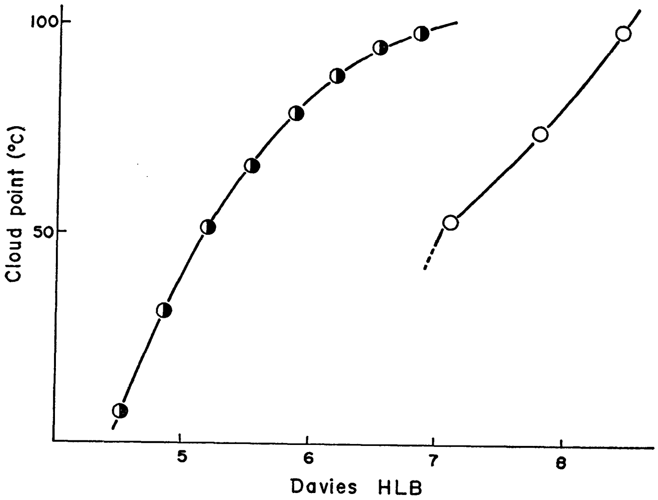

Fig. 5. Plots of cloud point *vs.* Davies HLB value. ○; AG-12 series, ◑; S-12 series.

The cloud point of nonionics is a measure of the solubility in water and closely related with the hydrophile-lipophile balance (HLB). Smooth and characteristic curves were obtained by the plots of the cloud point *vs.* *m*. A representative example is shown in Fig. 4 for AG-12 series. It can be expected from the structural feature of AG having two terminal hydroxyl groups in a molecule, that the cloud point is higher than that of S types having one hydrophilic chain. On the contrary, the curve for AG lies close to that for S types provided by Schüring[8] as can be seen in Fig. 4. When the cloud point was plotted against HLB value based on the "group numbers" proposed by Davies,[10] the curve for AG was apparently shifted to the right side of that for S types as shown in Fig. 5. If the same group numbers are applicable to both type nonionics regardless of the variation in hydrophile structure, the curves for both types would be superimposable. The results suggest that hydration of the geminal POE chains, especially of the oxyethylene unit adjacent to hydrophobe, is significantly hindered and the hydration of two terminal hydroxyl groups in a molecule of AG is incomplete owing to the stronger intramolecular hydrogen-bonding. Such a characteristic hindrance to hydration for AG can be esti-

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[10] J. T. Davies, Proc. Intern. Congr. Surface Active Substances, 2nd, London, Vol. I, p. 426 (1957).

mated from Fig. 5 to be 1.5—2.0 in Davies's HLB value.

Measurement of surface activities for AG types gave some interesting results. Aqueous surface tension of AG considerably depends upon time as can be seen in Fig. 6. The equilibrium surface tension (γ), was thus taken at the time when the lowering of surface tension is no longer observed. The obtained γ was plotted against logarithm of the concentration and no minima in the γ-log C curves were found for all the AG types studied as shown in Figs. 7 and 8. Surface excess (Γ) and molecular area (A) at CMC were calculated from these γ-log C curves by applying the simple form of Gibbs' adsorption equation, and listed in Table 3. From the fact[12] that A of nonionics of polyglycol ether type is determined by the POE chain, it can be predicted that A of AG types (A_{AG}) is about twice as large as that of S types (A_S) containing the POE chain of the same length as in AG. As can be seen in Table 3, however, A_{AG} are considerably smaller than $2A_S$ and close to A_S.

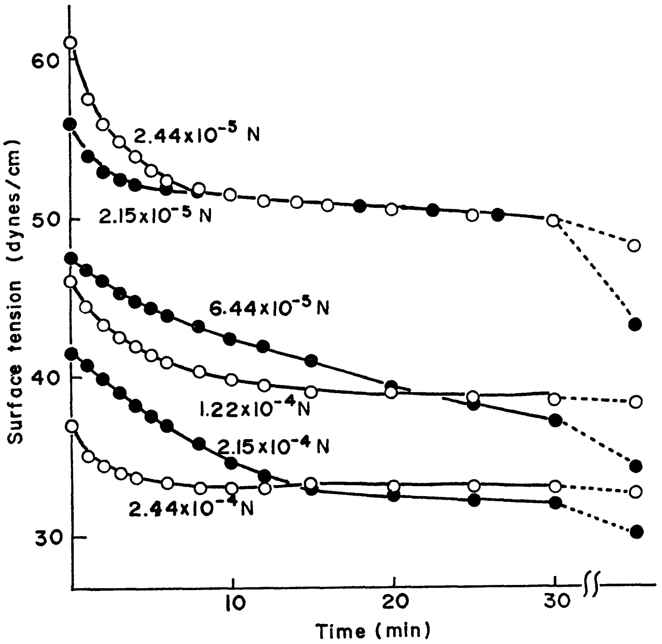

Fig. 6. Time dependence of γ of aqueous solution of AG type at different concentrations (mol/l). ○; AG-8(6), ●; AG-12(6).

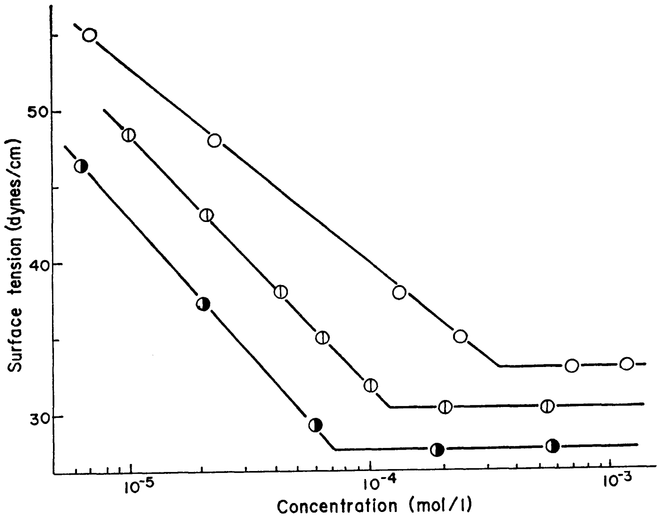

Fig. 7. Plots of γ vs. concentration. ○; AG-8(6), ⦶; AG-12(6). ◑; AG-14(6).

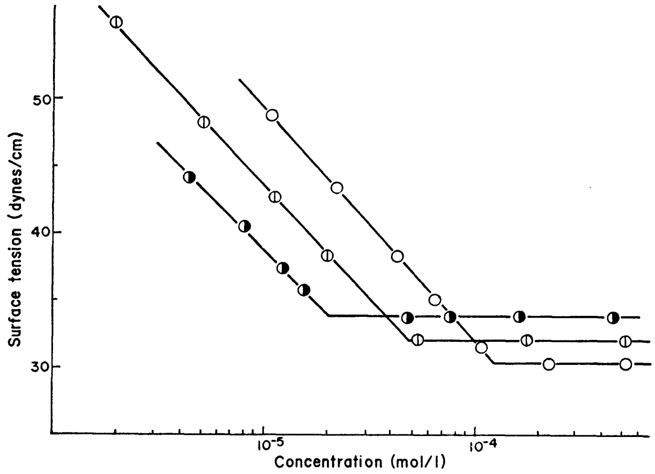

Fig. 8. Plots of γ vs. concentration. ○; AG-12(6), ⦶; AG-12(8), ◑; AG-12(10).

TABLE 3. SURFACE ACTIVE PROPERTIES OF AG TYPES AT 20°C

Nonionics	γ_{CMC} (dyne/cm)	CMC×10^5 (mol/l)	$\Gamma\times10^{10}$ (mol/cm²)	A (Å²)	$A\times m^{-1/2}$
AG-8(6)	32.9	33.5	2.14	70.0	40.4
AG-12(6)	30.2	12.3	3.05	54.5	31.5
AG-12(8)	31.8	5.00	2.89	57.5	28.8
AG-12(10)	33.8	2.06	2.83	58.6	26.2
AG-14(6)	28.3	6.50	3.19	52.0	30.0
AG-14(10)	36.2	1.70	3.05	54.5	24.4
AG-16(10)	36.0	0.63	3.23	51.5	23.0
S-12(5)[a]	29.7	6.8	3.88	43	19.2
S-12(6)[a]	31.5	7.10	3.52	47	19.2
S-12(5)[b]	—	—	—	56.0	25.0
S-12(7)[b]	—	—	—	64.8	24.5

a) Data in Ref. 11 for the homogeneous polyoxyethylene n-dodecanol, the number of oxyethylene unit is shown in parentheses.
b) Data in Ref. 12.

Concerning the surface film of nonionics, van Voorst Vader[13] has given a theoretical explanation for the fact that $A/m^{1/2}$ of S types is constant on the basis of a random coil configuration of POE chain. Fairly good agreement for $A/m^{1/2}$ has been obtained by many investigators as referred to by Lange in his review.[12] For AG-12 and AG-14 series, $A_{AG}/m^{1/2}$ were not constant but decreased with the increment of m, as can be seen in Table 3. Thus, it is suggested for the film state of AG types that two POE chains linked to the same carbon atom in hydrophobic chain never individually hold a random coil configuration but intertwisted with each other and penetrate into the solution.

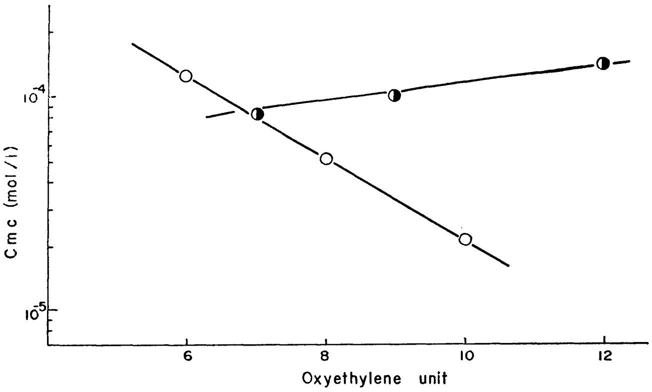

Fig. 9. Plots of log CMC *vs.* number of oxyethylene unit. ○; AG-12 series. ◑; S-12 series, based on the data in the following reference; H. Lange, Proc. Intern. Congr. Surface Active Substances, 3rd, Cologne, Vol. I, p. 279 (1960).

From the sharp inflection point of γ-log C curves in Figs. 7 and 8, CMC was determined and is listed in Table 3. Apparently, in the series of same m, the inflection point shifts to lower concentration region with an increase in the hydrocarbon chain length as shown in Fig. 7, while the CMC of the homologues with same hydrophobe shifts to higher with a decrease in m (Fig. 8) in contrast to S types. It is known that as a surfactant molecule becomes more hydrophilic, *i.e.*, as the POE chain length increases, the CMC increases, although a certain class of nonionics having a shorter hydrocarbon chain exhibits a reverse trend.[14,15] These relations have been quantitatively treated by applying the equation proposed by Hsiao,[16] $\ln C_0 = a + bR$, where C_0 is a CMC, a and b are constants for a given hydrophobe and R is length of the POE chain. As shown in Fig. 9, a linear relation between log CMC and m was obtained for AG types. The slope is negative. It is still difficult to explain this anomalous trend from the present data. The phenomenon has been observed for AG series having shorter hydrophilic chains (m : 3—5), which are geminal POE chains unfavorable to hydration and hold a restricted configuration as regards the surface film state of AG. It seems that this configurational feature is closely related to the lowering of CMC with increasing m in a certain region of the smaller m.

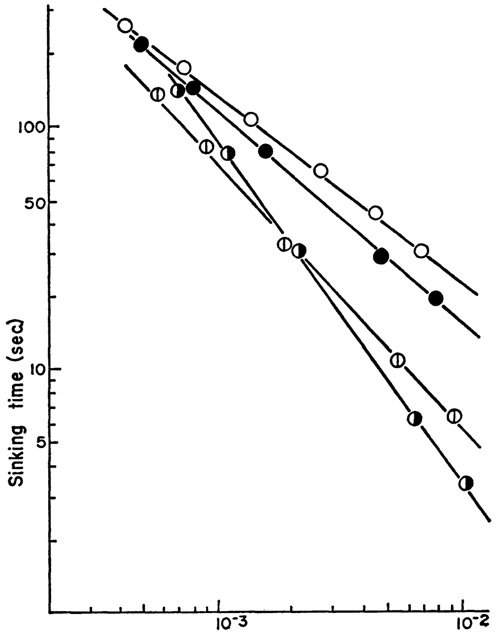

Fig. 10. Plots of log sinking time *vs.* concentration. ○; AG-12(12), ●; AG-12(10), ⦶; AG-12(8), ◑; AG-12(6).

Table 4. Foam volume (ml) of AG and S types at 25°C

Nonionics	Concentration of solution (wt%) 0.1			0.5		
	Standing time (min)					
	0	1	5	0	1	5
AG-12(6)	130	10	0	170	20	0
AG-12(8)	145	15	0	175	20	0
AG-12(10)	185	15	0	200	20	5
AG-12(12)	200	30	15	240	60	15
AG-10(6)	60	0	—	150	0	—
S-12($\overline{6.6}$)[a]	250	240	80	260	260	100

a) Ethylene oxide condensate of *n*-dodecanol prepared by the base-catalyzed method. The average number of ethylene oxide added is shown in parentheses.

On the basis of Draves wetting data obtained for various commercial nonionics of POE monoether type, Komor and Beiswanger[17] reported that textile wetting is primarily dependent upon CMC, and indicated that the concentration dependence of sinking time becomes greater with an increase in CMC of surfactant. Wetting data for a series of AG types are shown in Fig. 10, where sinking time is plotted against concent-

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11) N. Ohba and A. Takahashi, Proc. Intern. Congr. Surface Active Substances, 5th, Barcelona, Vol. II, p. 481 (1968).

12) H. Lange, "Nonionic Surfactant", ed. by M. J. Schick, Marcel Dekker Inc., New York, (1967), p. 443.

13) F. van Voorst Vader, *Trans. Faraday Soc.*, **56**, 1078 (1960).

14) D. Becher, *J. Phys. Chem.*, **63**, 1675 (1959).

15) J. E. Carless, R. A. Challis, and B. A. Mulley, *J. Colloid Sci.*, **19**, 201 (1964).

16) L. Hsiao, H. N. Kunning, and P. B. Kolenz, *J. Phys. Chem.*, **60**, 657 (1956).

17) J. Komor and J. Beiswanger, *J. Amer. Oil Chem. Soc.*, **43**, 435 (1966).

ration. The slope, *i.e.*, the concentration dependence of sinking time, increases with decreasing *m*. This agrees with the result in which CMC becomes greater with decreasing *m* for a series of AG types studied.

In Table 4, the foaming properties of AG is presented in initial foam volume and after 1 and 5 min. The low foam stability of AG is more characteristic than the foaming ability, like that observed for other multichain type nonionics.[3,4,18]

The data of hydrolysis of AG-12(10) were obtained by the cloud point depression method. As can be seen in Fig. 13, they gave good first-order rate plots in the region of conversion below 40%. The plots of the pseudo-first-order rate constant against the concentration of acid also gave a straight line passing the origin with a slope k 5.5×10^{-3} $l$mol^{-1}sec^{-1}. The k value is significantly small in comparison with the specific rate constant 0.39 $l$mol^{-1}sec^{-1}, for acid-catalyzed hydrolysis of acetaldehyde diethylacetal in water.[19] On the acid-catalyzed hydrolysis of monoalkyl sulfates, it was reported that the reaction is strongly accelerated by the aggregation of the reactant anions into micelle.[20-22] However, the result for AG acetal is apparently the reverse. It seems significant that the acetal linkages in the micellar AG are covered by the dome of closely packed POE chains. Probably, the reaction centers compete with many ether linkages in the POE chains for protonation, and the hydrolysis is also subjected to steric hindrance.

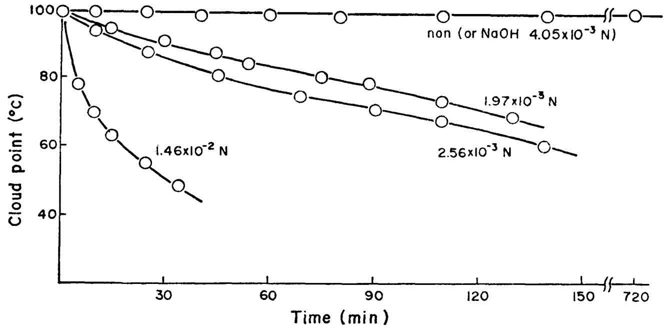

Fig. 11. Depression of cloud point of AG-12(10) in dil. HCl solution at 30°C.

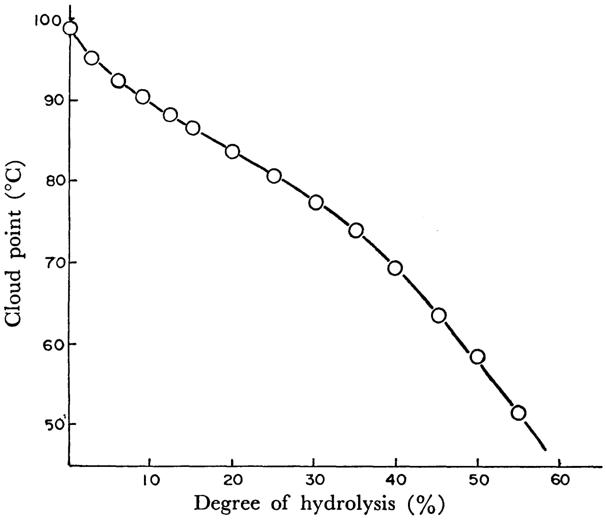

Fig. 12. Calibration curve for the hydrolysis of AG-12(10) at the total concentration of 0.5wt%.

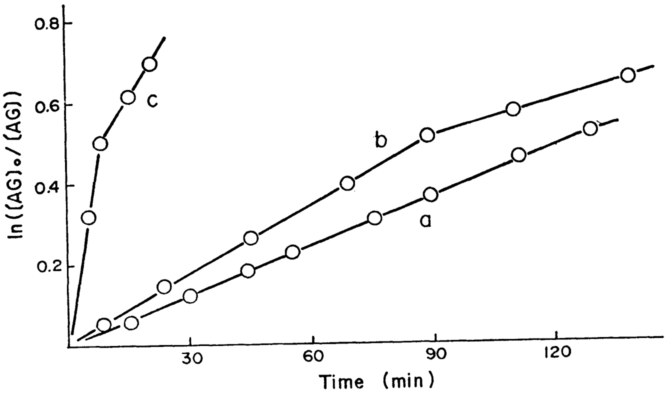

Fig. 13. First-order plots for the hydrolysis of AG-12(10) at 30°C in dil. HCl solutions: a; 1.97×10^{-3}N, b; 2.56×10^{-3}N, c; 1.46×10^{-2}N.

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[18] T. Kuwamura and H. Takahashi, Preprints for the 23rd Annual Meeting of the Chem. Soc. Japan, Tokyo, 1970, No. 07333.

[19] R. K. Wolford, *J. Phys. Chem.*, **67**, 632 (1963).

[20] J. L. Kurz, *ibid.*, **66**, 2239 (1962).

[21] V. A. Motsavage and H. B. Kostenbauder, *J. Colloid Sci.*, **18**, 603 (1963).

[22] K. Meguro and T. Hikota, *Yukagaku*, **17**, 164 (1968).