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Structural Effects on the Properties of Nonionic Surfactants. II. Acetal Type Homogeneous Nonionics Having Polyoxyethylene Chains Terminated with Methoxyl Group[1]

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A series of homogeneous acetal nonionics (AGM types) with the general formula $RCH[O(C_2H_4O)_mCH_3]_2$ were prepared from higher alkanals (C_8–C_{14}) and several pure polyoxyethylene (POE) glycol monomethylethers (m: 3—6), and purified by repeated distillation *in vacuo*. Cloud point, critical micelle concentration (CMC) and molecular area on adsorbed film were determined for AGM types. The results were compared with data on homogeneous acetals (AG types) having terminal hydroxyl in POE chains. The result confirms the suggestion that two POE chains in AG strongly interact with each other owing to intramolecular hydrogen-bonding and intertwisting. AGM are extremely low foaming nonionics although their ability to lower surface tension is comparable to that of the usual nonionics.

The object of this study is to clarify the effect of multi-chain hydrophile in polyether type nonionics on surfactant properties. It is well-known that molecular area (A) of polyether type nonionics is determined by the chain length of POE. Van Voorst Vader[2] theoretically interpreted the fact that $A/m^{1/2}$, where m is a unit number of POE chain, is constant, on the basis of a random coil configuration of POE chain. However, A of AG types with the general formula $RCH[O(C_2H_4O)_mH]_2$ is only slightly greater than that of simple type nonionics $RCH_2O(C_2H_4O)_mH$ (S types).[3] Thus, we have assumed that two POE chains are closely situated by acetal linkage and by mutual interaction owing to hydrogen-bonding of terminal hydroxyl groups, holding an intertwisted configuration rather than random coil. We have also suggested that the configurational characteristics of AG types should be related to the fact that their cloud point is unexpectedly low and CMC decreases with increasing m.

We measured cloud point, surface tension and foaming power for a series of AGM having terminal methoxyl in place of hydroxyl in POE chains in order to confirm the interaction between two geminal POE chains. Discussion is given on surface film state and the configuration of acetal type nonionics in aqueous solution.

Experimental

Materials. Straight alkanals purified as described previously were used.[3] POE monomethylethers were obtained by the fractional distillation of polyaddition products of ethylene oxide to methyl cellosolve. They were determined to be 99% pure by glc on Carbowax 20 W. Unit number m was evaluated from integrated NMR spectra, where signals of terminal methyl and methylene protons of POE chains appeared at 3.30 and 3.55 ppm, respectively.

Preparation of AGM Acetals. In a reaction flask, were placed 0.75 mol of POE monomethylether, a catalytic amount of concentrated hydrochloric acid and 0.15 mol of alkanal which were heated at 60°C for 4 hr. The reaction mixture was then treated in the same way as described in the preparation of AG[3] and finally distilled under reduced pressure in a stream of nitrogen to give a colorless AGM acetal. Purity and structure of the products were confirmed by elementary analysis, thin layer chromatography, IR and NMR spectra.

Measurements. Cloud point was measured on a 1.0% aqueous solution. Equilibrium surface tension γ at 20 ± 1°C and foaming power at 25 ± 1°C were measured by the methods described previously.[3] In addition to the surface tension method, iodine solubilization method[4] was used for the determination of CMC. In the latter the minimum transmittance at 390 mμ (T_{390}) referring to iodine-surfactant micelle complex was measured with a Hitachi spectrophotometer ES-20 and plotted against concentration.

Results and Discussion

Preparation of pure acetal nonionics was insured by use of pure starting materials and careful final purification. Physical constants, properties and analytical data to assess the purity of POE monomethylethers and AGM products are shown in Tables 1 and 2.

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[1] Presented in part at the 9th Annual Meeting of the Oil Chemists' Society of Japan, Sendai, 8th. October 1970.

[2] F. van Voorst Vader, *Trans. Faraday Soc.*, **56**, 1078 (1960).

[3] T. Kuwamura and H. Takahashi, This Bulletin, **45**, 617 (1972).

[4] S. Ross and J. P. Olivier, *J. Phys. Chem.*, **63**, 1671 (1959).

TABLE 1. PROPERTIES AND HYDROXYL CONTENT OF POLYOXYETHYLENE GLYCOL MONOMETHYLETHERS $CH_3O(C_2H_4O)_mH$

m	Bp, °C/mmHg	n_D^{25}	OH% Found	OH% Calcd
3	86— 89/1	1.4355	10.7	10.4
4	123—125/1	1.4439	8.3	8.2
5	145—147/1	1.4489	6.5	6.7
6	160—167/1	1.4513	5.6	5.7

The IR spectra of AGM showed no carbonyl and hydroxyl absorption but a strong absorption at 1000—1100 cm^{-1}. In the NMR spectra (in CCl_4), five signals at δ=0.88, 1.27, 3.30, 3.55, and 4.50 ppm due to the protons of methyl, methylene in the alkyl chain, methoxyl, methylene in POE chains and methine in acetal linkage respectively, were observed with reasonable intensity (Fig. 1). Plotting of refractive index of AGM against m gave a smooth curve suggesting no contamination with impurity (Fig. 2). In all cases of preparation, purity rather than yield was emphasized. The yields given in Table 2, however, represent practical values as compared with those in the conventional method which consists of several steps to build up a homogeneous nonionics containing such a large number of m.

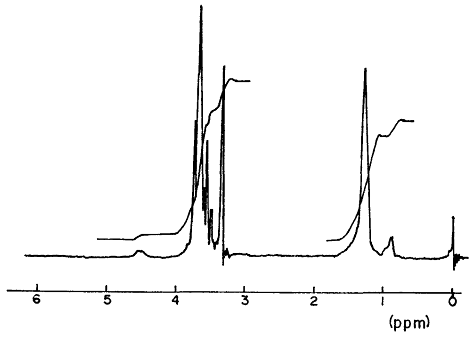

Fig. 1. NMR spectrum of AGM-12(6).

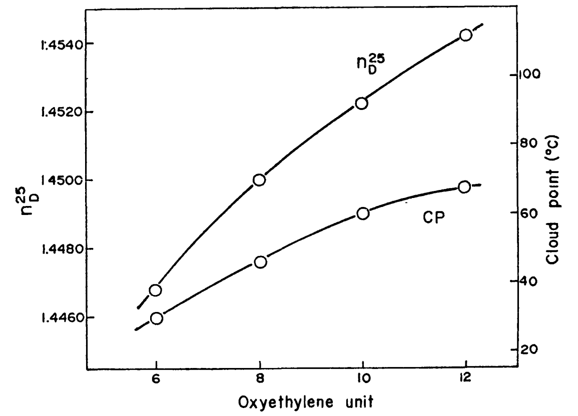

Fig. 2. Plots of refractive index and cloud point *vs*. oxyethylene unit number (m).

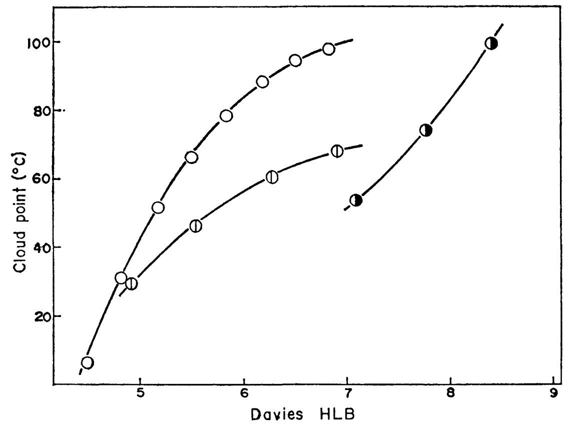

Fig. 3. Plots of cloud point *vs*. Davies HLB. ⦶; AGM-12, ◑; AG-12, ○; S-12 (Data in Ref. 6 for the homogeneous polyoxyethylene *n*-dodecanol).

Cloud point was plotted against m giving characteristic smooth curve (Fig. 2). In order to clarify the structural effect of hydrophile on hydration, cloud point is represented as a function of Davies's HLB value in Fig. 3. If the "group numbers" proposed by Davies[5] have a universality for various types of nonionics, the curve of AGM would be superimposable on those of S and AG types.[3] However, they are situated separately in the following order: S, AGM, and AG from left to right in Fig. 3. The result suggests a discount of Davies "group number" for acetal type nonionics. Such a hindrance to hydration for AG could be discussed on the basis of the following three structural factors. (1) The interaction between two POE chains

TABLE 2. PROPERTIES, ANALYTICAL DATA AND YIELDS OF AGM TYPES

Nonionics	R	2m	Bp, °C/mmHg	n_D^{25}	Cloud point, °C	Anal (Calcd) C%	Anal (Calcd) H%	Yield %
AGM-8(6)	C_7	6	189/1.5	1.4440	34.0	60.01(60.25)	10.49(10.57)	35
AGM-10(6)	C_9	6	190—192/1.0	1.4453	33.0	61.52(61.77)	10.66(10.80)	30
AGM-12(6)	C_{11}	6	213—216/1.0	1.4468	30.0	63.03(63.13)	10.97(11.00)	45
AGM-12(8)	C_{11}	8	238—240/1.0	1.4500	46.0	61.77(61.83)	10.70(10.72)	45
AGM-12(10)	C_{11}	10	266—270/1.0	1.4522	60.5	60.82(60.87)	10.53(10.52)	40
AGM-12(12)	C_{11}	12	300—304/0.5	1.4542	67.0	60.09(60.13)	10.31(10.36)	20
AGM-14(6)	C_{13}	6	220—222/0.2	1.4484	28.5	64.26(64.33)	11.10(11.18)	40
AGM-14(8)	C_{13}	8	266—271/0.9	1.4509	45.0	62.84(62.92)	10.85(10.89)	40
AGM-14(10)	C_{13}	10	300—306/0.9	1.4532	59.0	61.79(61.86)	10.63(10.67)	20

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

6) S. Schüring and W. Ziegenbein, *Tenside*, **6**, 161 (1967).

in a molecule due to hydrogen-bonding of terminal hydroxyl groups. (2) Very close situation of two POE chains by acetal linkage. (3) The presence of two oxyethylene units adjacent to the hydrophobe. The hindrance related to (2) and (3) can be observed in some multi-chain type nonionics derived from α,α'-glyceryl diethers7) and alkyl ethers of pentaerythritol.8) On the basis of (1), the fact that the replacement of two terminal hydroxyl with methoxyl causes the shift of the cloud point-HLB curve to the left side can be explained (Fig. 3), but the curve for AGM cannot be superimposed on that for S type. We see that, in the region of cloud point 50—60°C, 40—60% of the hindrance for AG is due to (1) and the rest to (2) and (3). In the region of high cloud point, however, the interaction in (1) may be significantly released and the cloud point markedly rises up by regaining of hydration capacity, so that the curve for AG is somewhat concave in contrast to the typical convex curves for AGM and S types.

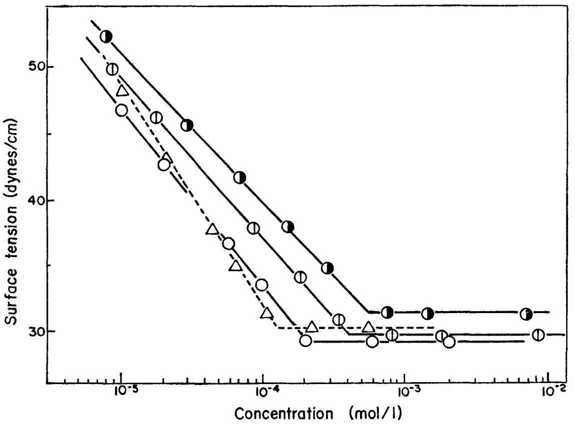

Fig. 4. Plots of γ *vs.* concentration. ○; AGM-12(6), ⦶; AGM-12(8), ◑; AGM-12(10), △; AG-12(6).

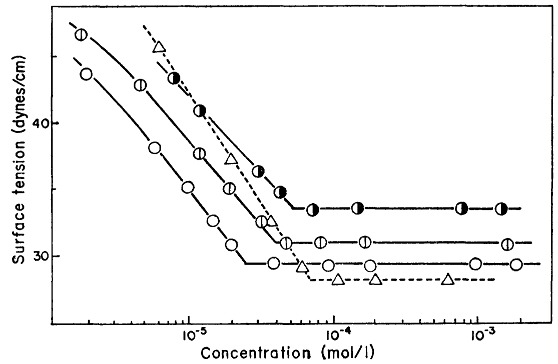

Fig. 5. Plots of γ *vs.* concentration. ○; AGM-14(6), ⦶; AGM-14(8), ◑; AGM-14(10), △; AG-14(6).

On the measurement of aqueous surface tension, considerably long periods of ageing (2—4 hr) were observed for AGM as well as AG. Plots of the obtained γ *vs.* logarithm of the concentration for AGM are shown in Figs. 4 and 5. From the slope of the curves, surface excess Γ and molecular area A at CMC were determined by applying the simple form of Gibbs' adsorption equation. They are listed together with the related data for AG and S in Table 3.

The magnitude of A apparently increases in the order S<AG<AGM. However, A of AGM does not yet attain twice as large as that of the corresponding S9,10) (*e.g.*, it is appropriate to compare among AGM-12(10), AG-12(10), and S-12(5)). Plots of $A/m^{1/2}$ for S and of $A/(2m^{1/2})$ for AG and AGM against m gave three straight lines which increase the negative slope in the order S<AGM<AG (Fig. 6). This indicates that A of S expectedly increases in proportion to $m^{1/2}$ and that the increment of A per one POE chain for AGM with increasing m is smaller than that for S and greater than that for AG.

Table 3. Surface active properties of AGM, AG, and S types at 20°C

Nonionics	γ_{CMC} (dynes/cm)	CMC×10^4 (mol/l) I c)	II d)	$\Gamma\times10^{10}$ (mol/cm²)	A (Å²)	$A/m^{1/2}$
AG-12(6)	30.2	1.23	—	3.05	54.5	31.5
AG-12(10)	33.8	0.206	—	2.83	58.6	26.2
AGM-12(6)	29.2	2.11	1.72	2.42	68.5	39.5
AGM-12(8)	29.7	4.05	3.40	2.17	76.3	38.2
AGM-12(10)	31.3	5.78	5.00	1.99	83.2	37.2
AG-14(6)	28.2	0.650	—	3.19	52.0	30.0
AG-14(10)	36.2	0.170	—	3.05	54.5	24.4
AGM-14(6)	29.5	0.250	0.320	2.51	66.1	38.2
AGM-14(8)	31.0	0.403	0.430	2.28	72.8	36.4
AGM-14(10)	33.6	0.552	0.605	2.05	81.0	36.2
S-12(5)a)	29.7	6.8	—	3.88	43	19.2
S-12(5)b)	—	—	—	—	56.0	25.0

a) Data in Ref. 10 for the homogeneous polyoxyethylene *n*-dodecanol, the number of oxyethylene unit is shown in parentheses.
b) Data in Ref. 9.
c) Determined by surface tension method.
d) Determined by iodine solubilization method.

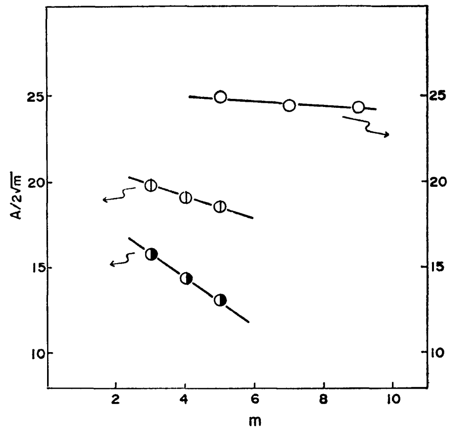

Fig. 6. Plots of $A/m^{1/2}$ and $A/(2\ m^{1/2})$ *vs.* m. ⦶; AGM-12, ◑; AG-12, ○; S-12 (Data in Ref. 9 for the homogeneous polyoxyethylene *n*-dodecanol).

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

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

9) H. Lange, *Kolloid-Z.*, **201**, 131 (1965).

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

The results could be discussed on the basis of structural factors as regards the hindrance of hydration for acetal nonionics. For AG containing factors (1) and (2), the interaction between two POE chains in a molecule is so pronounced that POE chains in surface film might take a significantly stretched and intertwisted configuration. Although the interaction is considerably released for AGM lacking factor (1), the POE chains still do not take such free random coils as those of S but undergo a sort of configurational restriction. All acetal nonionics we studied contain the shorter POE chains ($m<6$), for which van Voorst Vader's theory might virtually not be applicable. Thus, the characteristic film state of acetal nonionics might be due to shortness of POE chains attached. As for homogeneous S types ranging in m 1—10, however, the data obtained by Lange[11] with the use of film balance method gave no evidence for configurational transformation in surface film with variation in m.

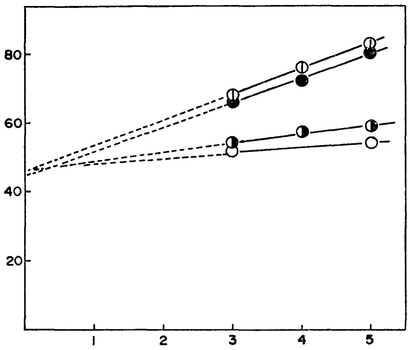

Fig. 7. Plots of A *vs.* *m*. ⦶; AGM-12, ●; AGM-14, ◑; AG-12, ○; AG-14.

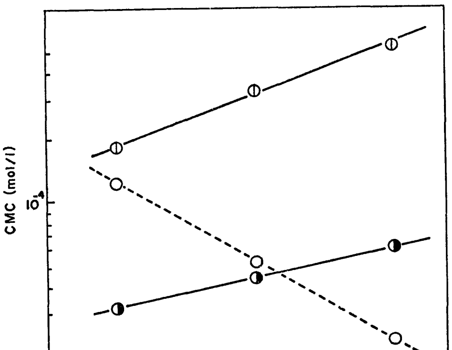

Fig. 8. Plots of CMC *vs.* *m*. ⦶; AGM-12, ◑; AGM-14, ○; AG-12.

Table 4. Foam volume (ml) of AGM, 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
AGM-12(6)	60	0	—	70	0	—
AGM-12(8)	50	0	—	50	0	—
AGM-12(10)	60	0	—	70	0	—
AGM-12(12)	70	0	—	80	0	—
AGM-14(8)	70	0	—	90	0	—
AG-12(6)	130	10	0	170	20	0
S-12$\overline{(6.1)}$[a]	250	200	100	260	260	160

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

Interesting information was obtained from plots of *A vs. m* for acetal nonionics. In Fig. 7, is shown the extrapolation of the linear *A vs. m* plots for AG and AGM varying in hydrophobe chain length. All the extrapolations converge at $m=0$ and give a limiting area, 45—47 Å^2, which seems to be equivalent to molecular area of hydrated higher alkanal, $RCH(OH)_2$, in a closely packed film.

The CMC values determined by two methods are listed in Table 3. We found that[3] CMC of AG decreases with an increase in m contrary to m dependence of CMC for the conventional nonionics[12] and suggested that this phenomenon is closely related to a configurational feature of hydrophile in AG. Plots of logarithm of CMC *vs.* *m* gave a straight line with positive slope for AGM in contrast to negative one for AG (Fig. 8). We also see that CMC of acetal nonionics increases by the replacement of terminal hydroxyl groups with more hydrophobic methoxyl groups.

It is concluded that the relatively low CMC and the abnormal trend on micellization of AG is caused by factor (1), which significantly affects hydration and configuration of POE chains.

The foaming property of AGM is markedly low as compared with those of S and AG (Table 4). It is likely that the greater cross section of the hydrophile and the hydrophobic terminal groups in AGM are unfavorable to closely packed alignment as regards the strength of foam film.

The authors wish to thank Miss Y. Umezu and the late Mr. M. Gotoh for their assistance in the experiment, and Givaudan Co. Ltd. for the supply of alkanal. Acknowledgement is made to the Ministry of Education for financial aid.

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11) H. Lange, *Kolloid-Z.*, **182**, 123 (1962).

12) P. Becher, "Nonionic Surfactant," ed. by M. J. Schick, Marcel Dekker Inc., New York, (1967), p. 478.