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New Amphoteric Surfactants Containing a 2-Hydroxyalkyl Group: I Preparation and Properties of N-(2-Hydroxyethyl) -N-(2-Hydroxyalkyl)-β-Alanines

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ABSTRACT

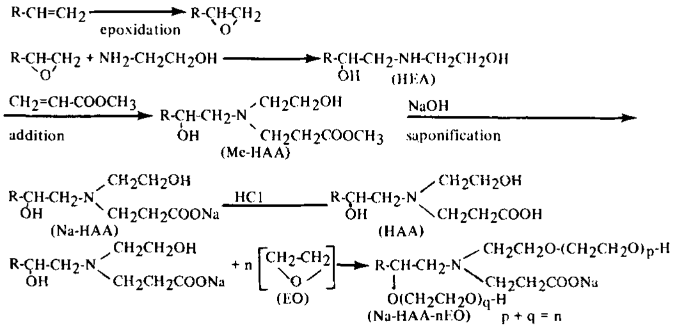
A series of new amphoteric surfactants, sodium salts of N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines (Na-HAA) was prepared by adding methyl acrylate to N-(2-hydroxyalkyl)-ethanolamine and subsequent saponification. Neutralization with HCl gave N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines, and the addition of ethylene oxide to Na-HAA gave oxyethylated drivatives. The structures of these compounds prepared were confirmed by infrared spectra, proton magnetic resonance spectra, elementary analyses, etc. Solubility in water, surface tension, foaming power, and critical micelle concentration were determined.

INTRODUCTION

Sodium salts of long chain N-alkyl-β-alanines are well known as amphoteric surfactants containing a nitrogen and a carbonyl group in one molecule (1-5). The surfactants of β-alanine type have been used in such fields as shampoos, cosmetics, emulsion paints, textile industry, corrosion inhibition, industrial cleaning, and many others (6). One of the most important features of these surfactants is that they are effective over a wide pH range, in their cationic form in acidic solution, and in their anionic form in alkaline solution, except at the isoelectric points (7). Furthermore, these compounds are less toxic to higher animals and less irritating to human skin because they have structures similar to amino acids (8).

No literatures have been found so far on the preparation and properties of β-alanine type surfactants containing both a long chain 2-hydroxyalkyl and a 2-hydroxyethyl group in one molecule.

The present paper deals with the preparation and the functional properties of a series of N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines, their salts, and their ethylene oxide adducts. A series of these compounds was synthesized according to the following scheme:



The following abbreviations are used: HAA for N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanine; Na-HAA for sodium salt of HAA; Na-HAA-nEO for ethylene oxide adduct of Na-HAA, where n stands for the number of moles of EO added; the notations, C_{12}-, C_{14}-, C_{16}-, and C_{18}- placed in front of these abbreviations denote, respectively, the carbon numbers, 12, 14, 16, and 18, in the 2-hydroxyalkyl group. For example, C_{12}-HAA = N-(2-hydroxyethyl)-N-(2-hydroxydoecyl)-β-alanine. And HEA for N-(2-hydroxyalkyl)-ethanolamine.

EXPERIMENTAL PROCEDURES

Materials

The α-olefins employed as starting materials, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene, were of commercial sources and purified by redistillation. The purity of each α-olefin was over 98% by gas chromatographic analysis.

Preparation of 1,2-Epoxyalkane

The α-olefin was epoxidized with peracetic acid in benzene in the presence of sulfuric acid as a catalyst accord-

TABLE I

Physical Properties of 1,2-Epoxyalkane, HEA, and HAA

Number of C atoms	1,2-Epoxyalkane boiling point (C/mmHg)	HEA Boiling point (C/mmHg)	HEA Melting poing (C)	HAA Melting point (C)
12	81 ~ 85/1	175 ~ 177/2	66.3 ~ 67.5	114.2 ~ 114.8
14	92 ~ 95/0.6	183 ~ 186/2	72.5 ~ 74.0	115.3 ~ 115.8
16	125 ~ 128/1.5	204 ~ 206/2	77.5 ~ 78.5	113.5 ~ 114.0
18	175 ~ 180/5.0	223 ~ 226/2	81.8 ~ 83.3	104.5 ~ 105.5

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TABLE II

Analytical Values for Ethylene Oxide Adducts of Na-HAA

Na-HAA compound	EO/Na-HAA[a] mole ratio	Calculated molecular weight: The value based on the increase in weight	Calculated molecular weight: The value based[b] on the nitrogen content
	2.4	452.1	460.5
C_{12}-Na-HAA	6.0	610.5	636.4
	12.0	874.0	853.7
	2.5	486.3	494.7
C_{14}-Na-HAA	5.4	613.9	636.4
	12.0	904.3	880.5
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C_{16}-Na-HAA	5.9	665.0	642.2
	13.2	995.0	965.5
	2.0	526.9	532.3
C_{18}-Na-HAA	5.2	667.7	707.1
	12.9	1006.5	1052.6

[a] The value based on weight increase.
[b] The Kjeldahl method.

ing to the procedure reported by Suhara (9). A pure 1,2-epoxyalkane was obtained by repeated vacuum distillation. Oxirane oxygen content (%) of 1,2-epoxyalkane was measured according to the method reported by Suhara (10). The analytical data agreed with calculated values as follows: 1,2-epoxydodecane, 8.43 (calc. 8.68); 1,2-epoxytetradecane, 7.40 (calc. 7.53); 1,2-epoxyhexadecane, 6.31 (calc. 6.66); 1,2-expoxyoctadecane, 5.96 (calc. 5.16).

Synthetic Procedures

Monoethanolamine (9 moles) was placed in a four-neck, round bottom flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel. 1,2-Epoxyalkane (1 mole) was added dropwise at 80~90 C, and heating of the mixture was continued for 1.5 hr. After excess monoethanolamine had been removed under reduced pressure, the residue of reaction product was subjected to vacuum distillation in an atmosphere of nitrogen to give HEA in 70~80% yields based upon 1,2-epoxyalkane. Analytical procedures for total amine value (TAV) and the partial amine value (PAV) were based upon AOCS method Tf la 64 and ASTM method D 2073-56, with necessary modifications. TAV agreed with calculated value as follows: C_{12}-HEA, 225.1 (calc. 228.6); C_{14}-HEA, 201.2 (calc. 205.2); C_{16}-HEA, 177.2 (calc. 186.1); C_{18}-HEA, 164.4 (calc. 170.3). PAV was given as follows: C_{12}-HEA, 224.7;C_{14}-HEA, 202.6; C_{16}-HEA, 174.7. The elemental analyses of HEA homologs for C, H, and N were within 2.5% of the calculated values.

Preparation of N-(2-Hydroxyethyl)-N-(2-Hydroxyalkyl)-β-Alanine (HAA) and Its Sodium Salt (Na-HAA)

HEA (1 mole), as obtained above, and methyl acrylate (1.2 mole) purified by the usual method, were subjected to the Michael addition at 70~80 C for 4 hr. After completion of the reaction and removal of excess methyl acrylate, the product was saponified with 220 g of a 20% aqueous sodium hydroxide for 2 hr at 85~95 C, and then water and methanol were removed by heating at reduced pressure. The crude Na-HAA thus obtained was dissolved in methanol containing a little water at 50~60 C, and to this solution was added gradually HCl-methanol (conc. HCl/methanol = 1:1 v/v) until the pH of the solution was brought to 6.0~6.5. The salt precipitate was filtered off, the filtrate concentrated and dried under reduced pressure, the dried material dissolved in anhydrous ethanol at 30~40 C. The insoluble salt was again filtered off, and the filtrate was allowed to cool to room temperature for some time to precipitate white crystals of crude HAA. Three more recrystallizations from anhydrous ethanol gave HAA of high purity. The neutral equivalents of HAA homologs were as follows: C_{12}-HAA, 177.0 (calc. 176.7); C_{14}-HAA, 163.5 (calc. 162.4); C_{16}-HAA, 149.5 (calc. 150.2); C_{18}-HAA, 139.4 (calc. 139.7). The elemental analyses for C, H, and N were within 2% of the theoretical values. Each sample of Na-HAA was obtained by neutralizing HAA with NaOH as follows. An alcoholic solution of HAA was neutralized with a calculated amount of concentrated aqueous sodium hydroxide, and the crystals precipitated by adding a large amount of acetone were separated and then dried in a vacuum oven at ca. 60C. The physical properties of 1,2-epoxyalkane, HEA and HAA are summarized in Table I.

Preparation of the Ethylene Oxide Adduct of Na-HAA (Na-HAA-nEO)

The calculated amount of ethylene oxide (EO) was directly added to each Na-HAA in the absence of a catalyst at a temperature higher than the melting point of the substrate, 130~140 C and at atmospheric pressure. The number of moles of EO added was estimated from the increase in weight after oxyethylation and from the nitrogen content of the oxyethylated product. The mean mole number of EO adducts of Na-HAA was given in Table II. Subsequently we designate them by integers as 2,6, and 12.

Physical and Surface Active Properties Measurement

Infrared (IR) spectra were obtained with a Hitachi EPI-500 infrared spectrometer by the KBr pellet method. The proton magnetic resonance (PMR) spectra in D_2O were obtained with a Hitachi-Perkin-Elmer 90 MHz spectrometer R-22 using sodium 3-(trimethylsilyl)-propane sulfonate (DSS) as an external reference. Differential thermal analysis (DTA) was run on a Shinkuriko DTA apparatus with a thermal balance; the test sample weighing 40 mg was placed in a quartz cell and the analysis carried out over a temperature range from room temperature to 200 C.

A given weight of each surfactant was dissolved in 25 g of distilled water at 20 C and at 40 C. Undissolved material was separated by filtration through a Toyo-Roshi filter paper 5C, dried at 70 C in vacuo and weighed. Solubility was calculated as g/H_2O 100 g. The surface tension was measured by the Wilhelmy vertical plate method in a constant temperature bath with a Shimazu ST-1 tensiometer using a strain gauge as a transducer. The cmc value was determined from the inflection point of a plot of surface tension against the logarithm of concentration

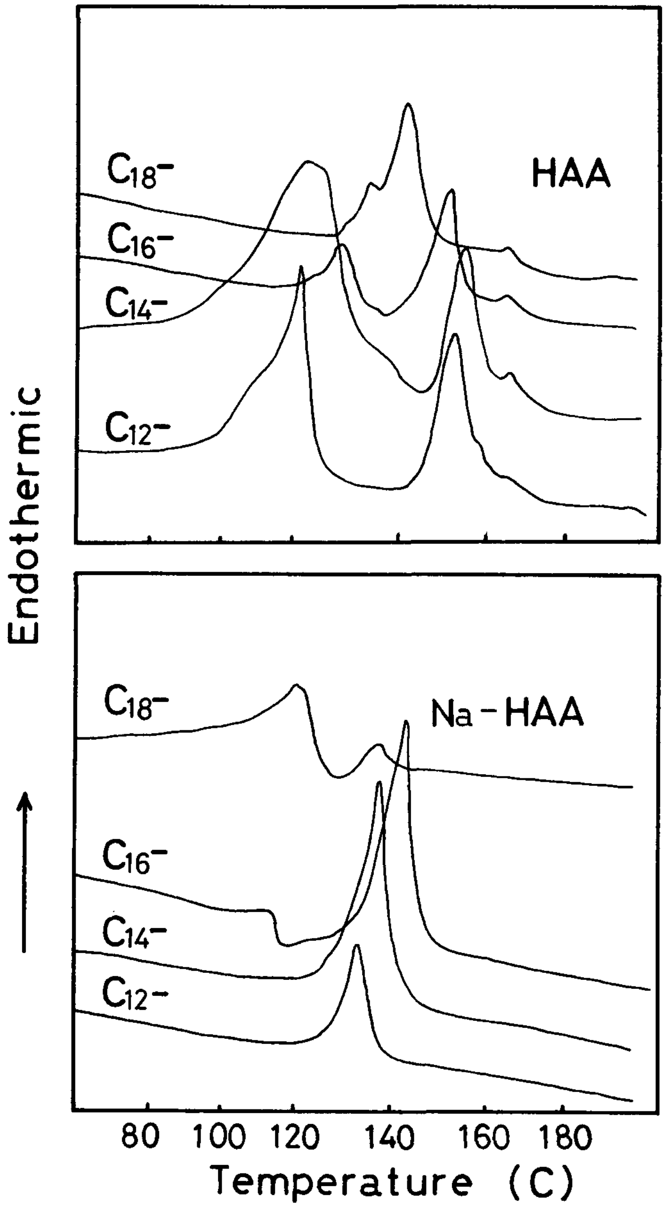

FIG. 1. DTA curves for HAA and Na-HAA homologs.

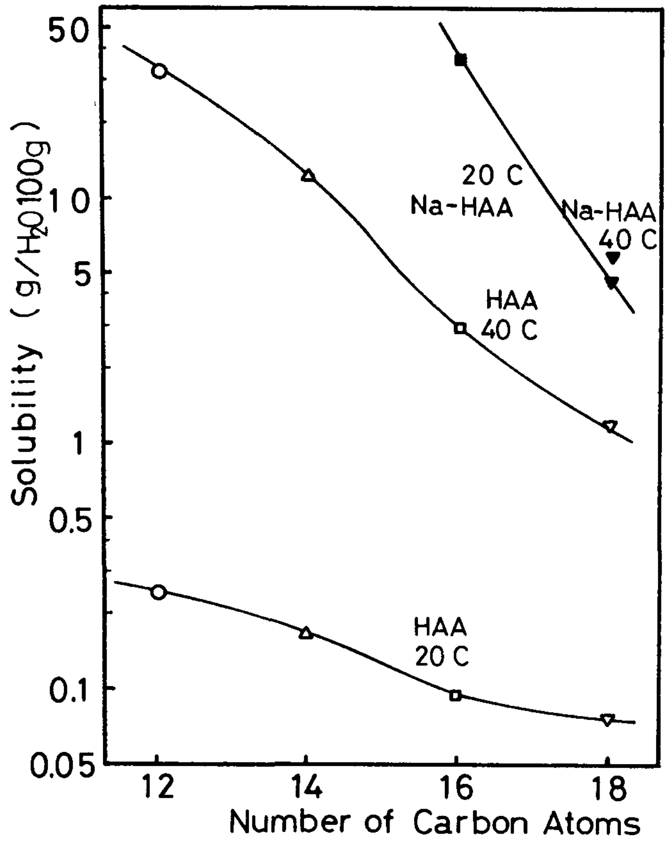

FIG. 2. Relationship between solubility and number of carbon atoms in the 2-hydroxyalkyl group of HAA and Na-HAA.

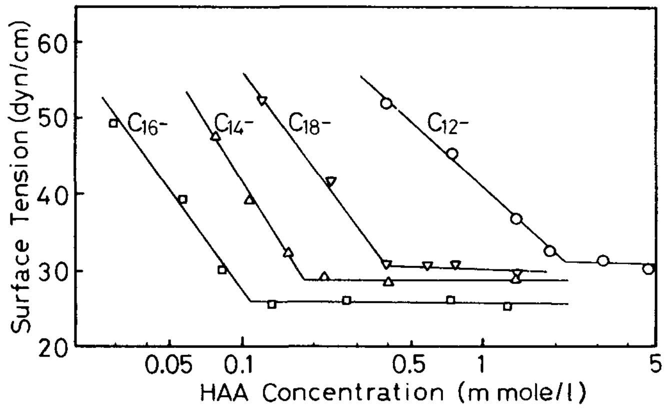

FIG. 3. Relationship between surface tension and log concentration at pH 7.0. C_{12}- and C_{14}-HAA at 30 C; C_{16}- and C_{18}-HAA at 50 C.

(mmole/liter). The foaming power was measured at a fixed temperature according to the Ross-Miles method. The foam height (mm) was recorded immediately after dropping the test sample and after standing for 5 min. The calcium ion stability of Na-HAA was measured by a modified Hart method. A 40 ml portion of 0.5 wt % surfactant solution adjusted to pH 10.5 before measuring was titrated with a 1.00 wt % solution of calcium acetate at 40 C. The end point was determined by visual observation of the cloudiness of the surfactant solution. The Krafft point of Na-HAA was determined by a conventional conductivity method using a Toa-Dempa conductmeter CM-1DB. The rapid increase of the solubility at the Krafft point was accompanied by a rapid increase in electrical conductivity. Thus, the measurement of the change in the conductivity of the surfactant solution at increasing temperatures in the presence of the solid surfactant made it possible to estimate the Krafft point (11).

RESULTS AND DISCUSSION

In the infrared spectrum of C_{12}-HEA, two bands at 3330 cm^{-1} and 1075 cm^{-1} are due to the O-H and C-O (in primary hydroxy group) stretching vibrations, respectively, and are attributable to the hydroxyethyl group. The C-N stretching and N-H bending vibrations are observed at 1125 cm^{-1} and 830 cm^{-1}, respectively. The spectra for C_{12}-HAA, its sodium salt, and its ethoxylate show an intense band near 1560 cm^{-1} indicating the presence of C=O group. The spectrum for C_{12}-HAA shows absorptions at 1720 cm^{-1} (C=O stretching in carboxyl group), 1210 cm^{-1} (C-O stretching) and 1588 cm^{-1} (C-N bending). The spectrum of C_{12}-Na-HAA-nEO having a broad band at 3250 cm^{-1} due to the hydroxy group and the C-O-C stretching band due to the ether linkage near 1100 cm^{-1} indicate that EO was obviously reacted with Na-HAA. The chain length of the alkyl group of Na-HAA and Na-HAA-nEO did not greatly affect the spectra. In the reaction of EO with Na-HAA,

TABLE III

Critical Micelle Concentrations of Various Amphoteric Surfactants

Surfactant	Formula	Decyl mmole/liter(C)	Dodecyl mmole/liter(C)pH	Method[a]	Ref.
N-(2-Hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanine	$R\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}N\langle{}^{CH_2CH_2OH}_{CH_2CH_2COOH}$		2.2 (30 C) 7.0	S.T.	Present work
N-Alkyl-β-alanine	$R\text{-}NH\text{-}CH_2CH_2COOH$	13 (30 C)	0.9 (30 C) 6.3	S.T.	(5)
N-Alkyl-β-amino-dipropionic acid	$R\text{-}N\langle{}^{CH_2CH_2COOH}_{CH_2CH_2COOH}$		0.7 ~ 1.8 (25 C) 4.8 ~ 11.0		(3)
C-Alkyl betaine	$R\text{-}\underset{N^+(CH_3)_3}{CH}\text{-}COOH$	13.1 (27 C)	1.32 (27 C)	S.T.	(14)
N-Alkyl betaine	$R\text{-}\overset{CH_3}{\underset{CH_3}{N}}\text{-}CH_2\text{-}COOH$	18 (23 C)	1.8 (23 C)	S.T.	(15)
Dimethylaklyl ammonio 2-hydroxypropane sulfonate	$R\text{-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}SO^-$		2.0 (30 C)	L.S.	(16)
N-Alkyl-N,N-bis-ethoxyacetic acid	$R\text{-}N\langle{}^{CH_2CH_2OCH_2COONa}_{CH_2CH_2OCH_2COONa}$		0.8 (25 C) 7.0	D.T.	(17)

[a] S.T.=surface tension; L.S.=light scattering; D.T.=dye titration.

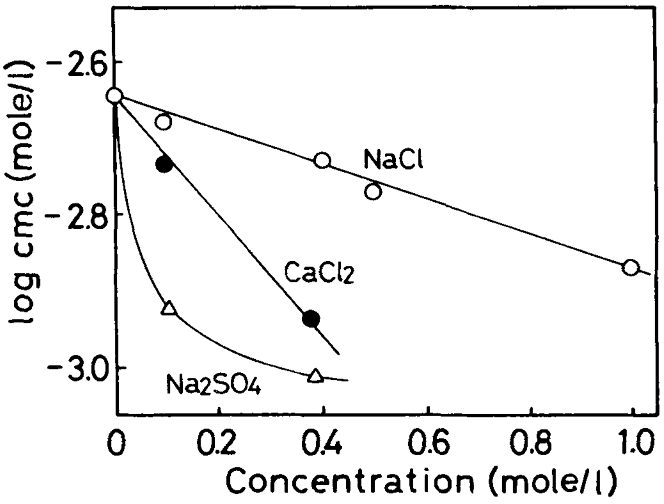

FIG. 4 Effect of electrolytes on cmc value of C_{12}-HAA.

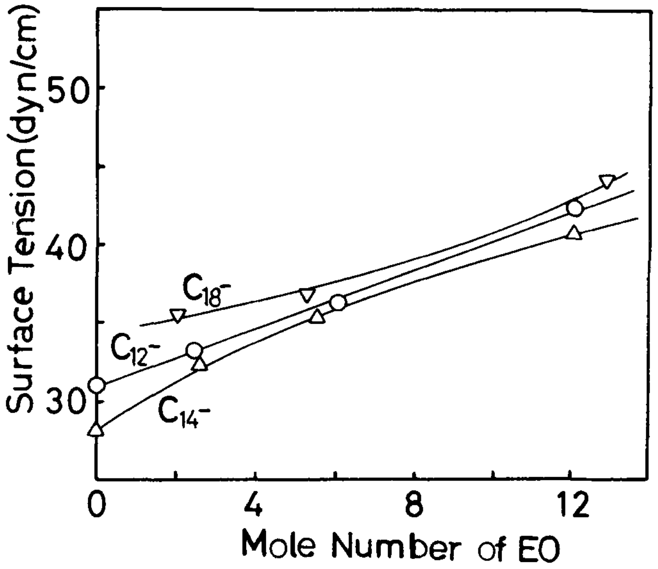

FIG. 5. Relationship between surface tension and number of moles of EO added of Na-HAA-nEO in aqueous solution (0.1 wt%) at 25 C and pH 6.5.

which has both a primary and a secondary hydroxy group, it has been assumed that the primary one is more reactive than the secondary (17,18). In the formation of the EO adducts of this study, probably both the primary and secondary hydroxy groups entered into reaction, though the addition of EO to the secondary hydroxy group is likely to occure to a less extent, (if indeed it occures at all). The PMR spectra were also consistent with the structures of Na-HAA homologs. The following peaks were observed: $\delta 0.88$ ppm (3H, $-CH_3$); $\delta 1.30$ ($-(CH_2)_n-$; n=9, 11, 13, 15); $\delta 2.43$ (2H, $-CH_2-COONa$); $\delta 3.00 \sim 2.70$ (6H, $-CH_2\text{-}N\langle{}^{CH_2-}_{CH_2-}$); $\delta 3.66$ (2H, $-CH_2-OD$). The proton at the second position in the 2-hydroxyalkyl group could not be confirmed because of too weak a signal.

Figure 1 shows the DTA curves of HAA and Na-HAA homologs. For HAA homologs, three endothermic peaks were observed in the range of ca. 110 C to 170 C. From these peaks, it was surmised that HAA homologs had thermotropic liquid crystalline properties. The C_{16}- and C_{18}-Na-HAA exhibited a liquid crystalline phase like the HAA homologs, while the single peak for C_{12}- and C_{14}-Na-HAA was observed at the melting point.

The solubility behavior of HAA and Na-HAA homologs is shown graphically in Figure 2. The solubility decreases as the alkyl chain length is increased, and Na-HAA homologs had higher solubility than the corresponding HAA homologs. C_{12}- and C_{14}-Na-HAA were found to be highly soluble in water. Solutions of C_{16}-Na-HAA at 20 C and C_{18}-Na-HAA at 40 C were clear, whereas C_{18}-Na-HAA at 20 C gave a cloudy dispersion. With respect to HAA, the phenomenon of gelling for concentrated aqueous solutions

TABLE IV

Calcium Ion Stability and Krafft Point of Na-HAA

Compound	Ca stability (ppm)[a]	Krafft point (C)
C_{12}-Na-HAA	35	40.6
C_{14}-Na-HAA	60	41.1
C_{16}-Na-HAA	78	42.6
C_{18}-Na-HAA	15	44.8
C_{12}-β-alanine[b]	20	—

[a] Expressed as ppm $CaCO_3$.

[b] Commercial grade of N-dodecyl-β-alanine.

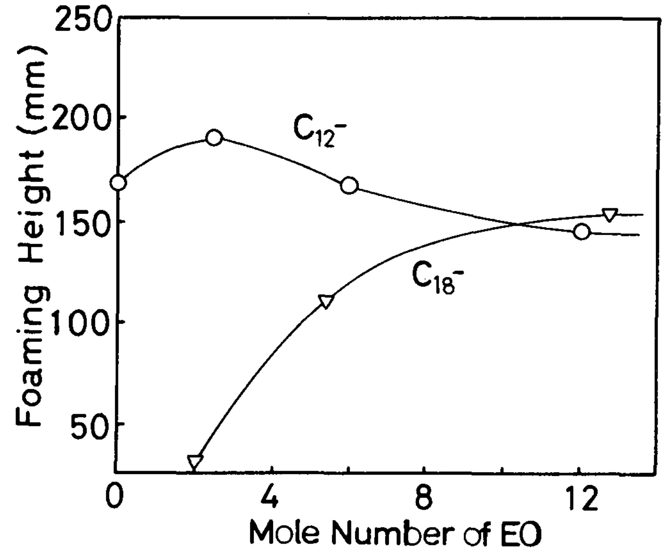

FIG. 6. Relationship between foaming power and number of moles of EO added of Na-HAA-nEO in aqueous solution (0.1 wt%) at 25 C and pH 6.5.

(ca. 6.25%) occured in the order of $C_{16} > C_{14} > C_{18}$ in the temperature range of 70 C to ambient.

Figure 3 shows the surface tension-concentration relationship for the homologous series of HAA at pH 7.0. The cmc values determined by breakpoints of the surface tension curves were 2.20 (mmole/liter) for C_{12}-HAA and 0.18 for C_{14}-HAA at 30 C. Since C_{16}- and C_{18}-homologs were poorly soluble, the cmcs were measured at 50 C to give the values of 0.12 (mmole/liter) for C_{16}-HAA and 0.40 for C_{18}-HAA. Although the cmc values of most surfactants decreased with increasing alkyl chain length, this relationship did not hold in the case of HAA.

The cmc values for other amphoteric surfactants are listed in Table III. We see that the cmc values of C_{12}-HAA and other amphoteric surfactants having the same dodecyl chain length are all alike regardless of the structure of the hydrophilic group.

The effect of electrolyte on the cmc value of C_{12}-HAA in a nearly neutral aqueous solution is shown in Figure 4. The logarithm of the cmc decreases linearly with increasing concentration of NaCl and $CaCl_2$ as is the case with nonionic surfactants (18), whereas for ionic surfactants the plot of log-log instead of semilogarithmic plot gives a straight line (19). This behavior is due to the zwitterionic nature of HAA in the isoelectric region where the ionic charges in the molecule are neutralized and the surfactant is considered to be nonionic like N-alkyl-β-alanine (5). And moreover, it appears to be due to two hydroxy groups in the HAA. The curve for the change of cmc in the presence of Na_2SO_4 shows a rapid drop. The routing of the decrease in cmc for various electrolytes was $NaCl < CaCl_2 < Na_2SO_4$.

The surface tension curves for C_{12}-, C_{14}, and C_{18}-Na-HAA and their EO adducts are shown in Figure 5. The homologous series of Na-HAA had the lowest surface tension. The surface tension of Na-HAA-EO increased for an increasing number of moles of EO added.

Figure 6 shows the foaming power of C_{12}- and C_{18}-Na-HAA and their EO adducts. For C_{12}-Na-HAA-nEO, the foaming power increased with increasing the number of moles of EO added and attained the maximum at ca. 2 moles of EO. Further increase of the number of moles of EO caused a decrease in foaming. C_{18}-Na-HAA-nEO showed good foaming only after more than 6 moles of EO had been added, probably because of insufficient solubility below 6 moles.

The calcium ion stability data for Na-HAA are shown in Table IV. The order of stability was $C_{16} > C_{14} > C_{12} > C_{18}$. C_{12}-Na-HAA had better calcium ion stability than N-dodecyl-β-alanine. The Krafft points of Na-HAA homologs are also summarized in Table IV. Although the Krafft points increased in the order of $C_{12} > C_{14} > C_{16} > C_{18}$, no remarkable difference among four homologs was observed.

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