Technical

New Amphoteric Surfactant Containing a 2-Hydroxyalkyl Group: III. Performance of Binary Systems of Amphoteric/Anionic Surfactants

M. TAKAI, H. HIDAKA,[1] S. ISHIKAWA, M. TAKADA and M. MORIYA,
Miyoshi Oil and Fat Co., Ltd., 66-1, Horikiri 4-chome, Katsushika-ku, Tokyo 124 Japan

ABSTRACT

The performance of new amphoteric surfactants, N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines (HAA), and their oxyethylated derivatives (HAA-nEO) was studied in blends with conventional anionic surfactants. Viscosity, ultraviolet (UV) spectroscopy, surface tension, foaming power, dye solubilization and detergency were measured for the blends of various compositions. The interaction between HAA and sodium linear alkylbenzene sulfonate (LAS) was discussed with respect to the deviation of molar extinction coefficient in the UV spectra. A complex formation was assumed. A notable change in viscosity of 1.0% aqueous solutions was observed at pH 8.0 for the compositions of HAA/LAS (3:1) and HAA/sodium lauryl sulfate (4:1). The binary systems exhibited excellent detergency and other surface active properties, and indicated synergistic effects at a certain weight ratio. Human and rabbit skin irritation also was evaluated.

INTRODUCTION

Our previous papers (1,2) described the preparation and basic physicochemical properties of the amphoteric surfactants, N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines (HAA), and their oxyethylated derivatives (HAA-nEO).

These surfactants have been used commercially as silk and raw wool scouring agents and as surface modifiers for some polymers. They are also expected to be used in the field of shampoos, cosmetics and light duty detergents. Amphoteric surfactants have been used in combination with other commercially available surfactants because the blends of a certain composition give improved performances or synergistic effects (3-8). It is thus important to know the fundamental properties of the aqueous solutions of such blends.

In this study, HAA or HAA-nEO was mixed with anionic surfactants such as sodium linear alkylbenzene sulfonate (LAS), sodium lauryl ether sulfate (LES), and sodium lauryl sulfate (SLS), and the performance of these mixtures was evaluated.

EXPERIMENTAL PROCEDURES

Materials

The preparation and purification of HAA and HAA-nEO were carried out by the same procedures as described in our previous paper (1). The 1,2-epoxyalkanes employed were from commercial sources of AOE X24 and AOE X68 (Daisel Co., Ltd.). The component ratio of 1,2-epoxydodecane and 1,2-epoxytetradecane for AOE X24 was 56/44 by gas chromatographic analysis; oxirane oxygen content, 7.71%; acid value, 0.06; iodine value, 1.42. The component ratio of 1,2-epoxyhexadecane and 1,2-epoxyoctadecane for AOE X68 was 57/43; oxirane oxygen content, 5.95%; acid value, 0.39; iodine value, 1.72. The neutral equivalents of HAA homologs were as follows: C_{12-14}-HAA, 171.2 (calcd 170.4); C_{16-18}-HAA, 145.2 (calcd 145.7). The notations, C_{12}-, C_{14}-, C_{16}- and C_{18}- denote the number of carbon atoms in the 2-hydroxyalkyl group. The elemental analyses for C, H and N were within ±2% of the theoretical values. However, C_{12}-HAA used in Figures 1 and 2 was the same sample as described in the previous paper (1). Other surfactants, LAS and SLS (Tokyo Kasei Co., Ltd., Tokyo) and LES (Miyoshi Oil & Fat Co., Ltd., Tokyo) were of commercial grade.

Physicochemical and Surface Active Properties Measurements

Viscosity was measured at 30 C with an Ostwald viscosimeter after adjusting pH of the sample solution and permitting it to stand for 1 hr. The UV spectra were recorded in the range of 240-300 nm on a Shimadzu UV-200 spectrophotometer. Surface tension (Wilhelmy method) and foaming power (Ross-Miles method) were measured as previously described (1). Hard water of desired hardness was prepared by adding $CaCl_2$ to distilled water, and hardness was expressed as $CaCO_3$ ppm. Dye solubilization using Orange OT was determined by a colorimetric analysis at 497 nm and 45 C according to the Lambert method (9).

Degreasing power was measured as follows: wool-muslin cloth (JIS L-0803) was soiled with olive oil (4%), and a 10-g piece of the test cloth was washed in 1ℓ of the test solution using a Terg-O-Tometer. After washing, the test cloth was extracted with benzene/ethanol (1:1,v/v%) for 3 hr to determine the olive oil remaining in the test cloth. The fabric detergency was carried out using a Terg-O-Tometer and artificially soiled test cloths containing 8.0 ± 0.5% of soil. Cotton test cloth (A-2, Senshokukizai Co., Ltd., Tokyo) and polyester/cotton (65:35) test cloth (C-8, Senshokukizai Co., Ltd.) were used. The artificial soil used was that recommended by Kashiwa et al. (10). Soil removal was calculated from the reflectance measurement (11). The dishwashing test was carried out using refined soybean oil/corn starch (2:1 v/v%) according to the Mayhew method (12). The soiled dishes were washed in the foamed test solution under standardized conditions. When the foam disappeared, the number of the dishes washed up to that point were counted.

Irritation Test

Closed patch test and photosensitization test on human skin. The patch test was carried out on the back skin of 10 males and 10 females in good health. An aliquot (ca. 0.05 ml) of a 1% solution of the test surfactant was incorporated

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[1] Meisei University, Faculty of Science and Engineering, 337, Hodokubo, Hino-shi, Tokyo 191 Japan.

into an adhesive plaster (Torii Pharmaceutical Co., Ltd., Tokyo). The patches were attached to the subjects' backs for 48 hr. About 1 hr after the patches had been removed, the skin reaction was examined and evaluated. The photosensitization test was performed using ultraviolet irradiation (the amount of sub-MED) on the same area of the skin where the patches had been removed. The photoallergic reaction was then evaluated.

Cumulative open patch test on rabbit skin. The hair on the back of 2 male rabbits weighing 3.0 and 2.5 kg was shaved off to make 4 and 5 selected spots of 2.0 cm diameter, respectively. The test surfactant (4% solution) was applied there 3 times a day for 7 days. The spots were examined and evaluated.

RESULTS AND DISCUSSION

Viscosity of Solutions of Binary Surfactant Systems

Saul et al. presented the viscosity measurement for the solutions of amphoteric hexadecyl dimethyl ammoniopropane sulfonate/SLS system resulting in their maximum of ca. 7/3 weight ratio (4). Moreover, Evans and Hudson reported the dependence of viscosity on pH value for the 1:1 mixture of C_{12}-β-alanine and cetyl trimethyl ammonium bromide, showing that the apparent viscosity increased with increasing pH to reach a maximum at pH 9.5 and become lower above pH 9.5 (5).

Figure 1 shows viscosity as a function of composition of C_{12}-HAA/LAS, C_{12}-HAA/SLS and C_{12}-HAA/LES binary systems for 1% solutions (ca. 30 mmol/ℓ) of the surfactants at pH 8.0, indicating that the aqueous solutions of HAA/LAS and HAA/SLS are viscoelastic. Maximal viscosities were attained in the HAA-rich point of 7/3 and 8/2 weight ratios, respectively. By contrast, the HAA/LES binary system did not exhibit any increase in viscosity. However, the change in viscosity was not observed for these binary systems at 0.5% total surfactant concentration. We thus obtained results similar to those reported by Saul (4). The mixed system consisted of an isotropic liquid (L) and lyotropic liquid crystalline phase (LC). A maximal peak in viscosity corresponded to the LC region which was assumed to form a hexagonal or lamellar structure. Each side of the LC region roughly corresponded to the L + LC solution. The subsidiary peak at 4/6 (HAA/LAS) seems to relate to the difference of LC/L component ratio, but further examination to determine the precise reason for this would be required. Although viscosity on the acid side (below pH 5.1) was measured for the HAA/LAS binary system, these measurements were invalid because of turbidity or formation of an insoluble complex. The solution of 7/3 (HAA/LAS) displayed a maximum in viscosity at pH 8. From these results it was concluded that such interaction occurred to a great extent. A lowering of viscosity was observed at pH 10.

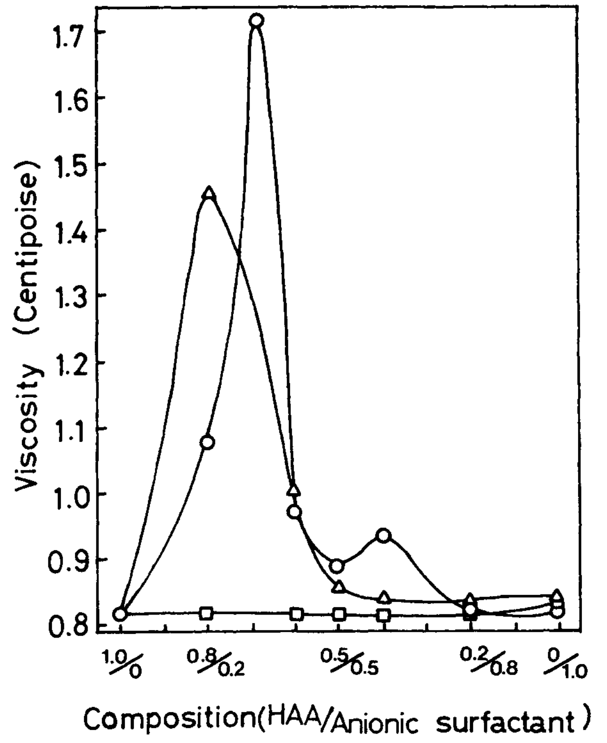

FIG. 1. Relationship between the viscosity of the solutions (1.0% total concentration) and the composition of C_{12}-HAA/anionic surfactants at 30 C and pH 8.0. C_{12}-HAA/LAS = ○; C_{12}-HAA/SLS = △; C_{12}-HAA/LES = □.

UV Spectra of Binary Surfactant Systems

The UV spectra for the solutions of HAA/LAS (total concentration, 2 mmol/ℓ) were measured at pH 6.7 and 11.0. Since 2 absorption bands of 261 and 253 nm relate closely to the vibration of the benzene ring in LAS molecule, the deviation ($\Delta\epsilon$) of the molar extinction coefficient of HAA/LAS solutions (ϵ_{mix}) from that of LAS alone (ϵ_0) was calculated by the equation, $\Delta\epsilon=\epsilon_{mix}-\epsilon_0$. No shift of the 2 absorption bands was observed. The deviation curves against the HAA/LAS ratio are shown in Figure 2.

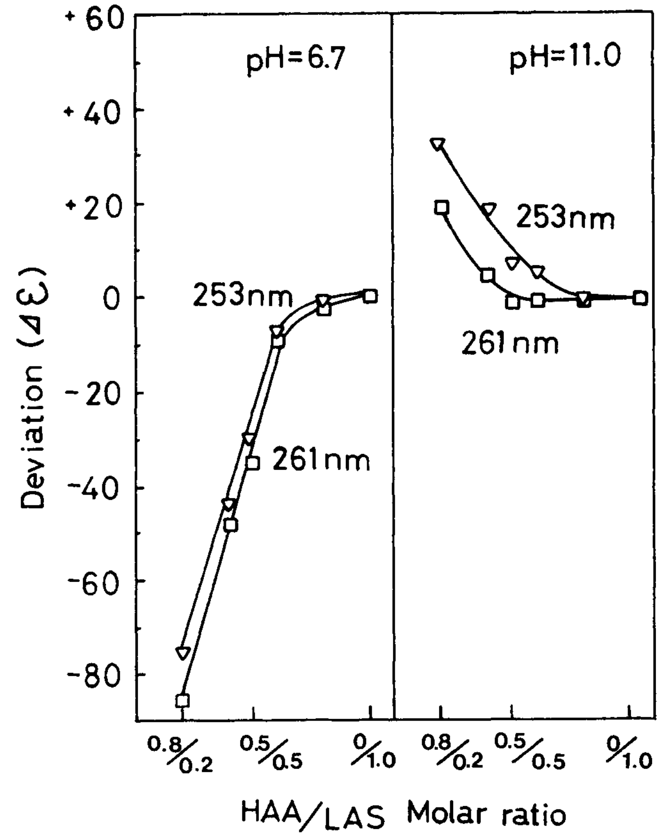

FIG. 2. Difference of molar extinction coefficient ($\Delta\epsilon$) between HAA/LAS mixed system and LAS alone at pH 6.7 and 11.0. 253 nm = ▽; 261 nm = □; C_{12}-HAA + LAS = 2 mmol/liter.

In the neighborhood of the isoelectric point of HAA (pH 6.7), the deviation gave a negative value and increased with increasing HAA/LAS ratio. The negative deviation is presumably caused by complex formation between $-\overset{|}{\underset{|}{N}}{}^{\oplus}-$cationic group of HAA and $-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-O^{\ominus}$ anionic group of LAS by Coulomb forces. On the other hand, the deviations were positive for the alkaline solution (pH 11.0). From protonation, a complex between $-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ and $-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-O^{\ominus}$ group was formed, and thus the absorption band due to the vibration of benzene ring was intensified. The UV spectra of the acidic solution (pH 4.0) could not be measured because of turbid appearance.

Cmc of Solutions of Binary Surfactant Systems

Figure 3 shows the relationship between surface tension and concentration for HAA and LAS alone and for the mixture of HAA/LAS (molar ratio, 4/1) at pH 6.8 and 11.0.

A mixture of 2 surfactants usually forms mixed micelles in aqueous solution and the aqueous solution of such mixtures has greater surface activity than that of each component. The cmc for 2-component mixture of amphoteric surfactant/soap (13), soap/soap (14), or nonionic/anionic surfactant (15) was reported to lie between those of the individual components. Furthermore, the cmc for a cationic/anionic surfactant system has also been reported (16). The cmc of HAA/LAS system lies between those of HAA and LAS alone at pH 6.8 and 11.0. Although the surface tension curves for the individual surfactants had single sharp break points at each cmc, those of the mixtures exhibited broad minima at each cmc. A comparison between the surface tension curves at pH 6.8 and at pH 11.0 shows that the cmc of the individual surfactants and of the mixtures at pH 11.0 was larger than those at pH 6.8, the isoelectric point of HAA. The cmc of the mixture at pH 11.0 was shifted to that of HAA by itself.

Surface Activity of Solutions of Binary Surfactant Systems

Figure 4 shows the foaming power for the mixed system of

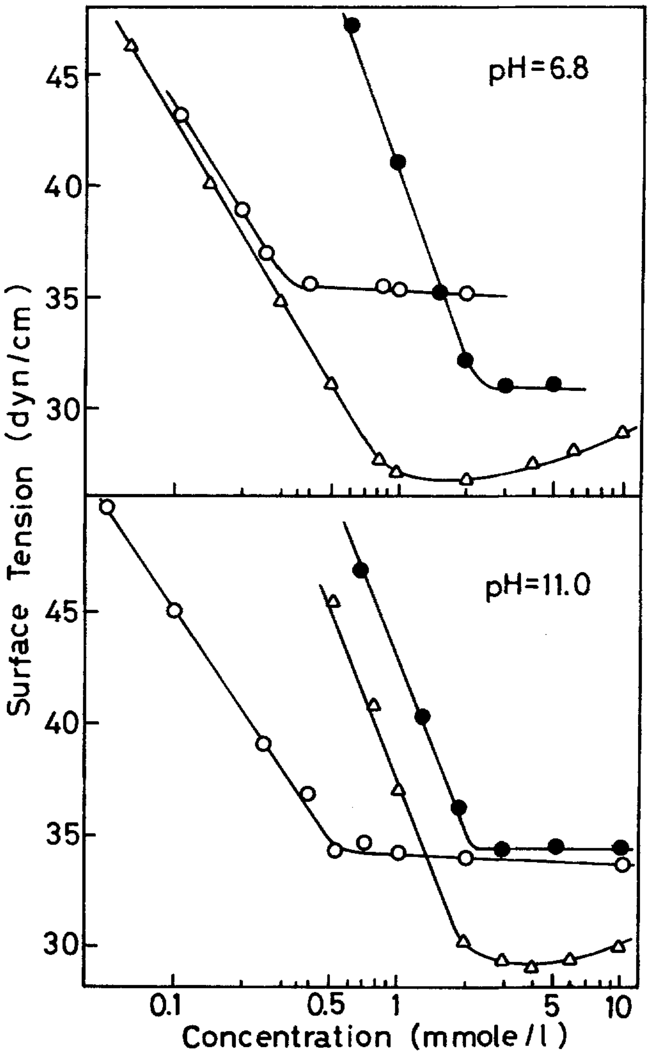

FIG. 3. Relationship between surface tension and concentration for C_{12}-HAA = ●; LAS = ○; and C_{12}-HAA/LAS (molar ratio:4/1) = △; at pH 6.8 and 11.0 and 30 C.

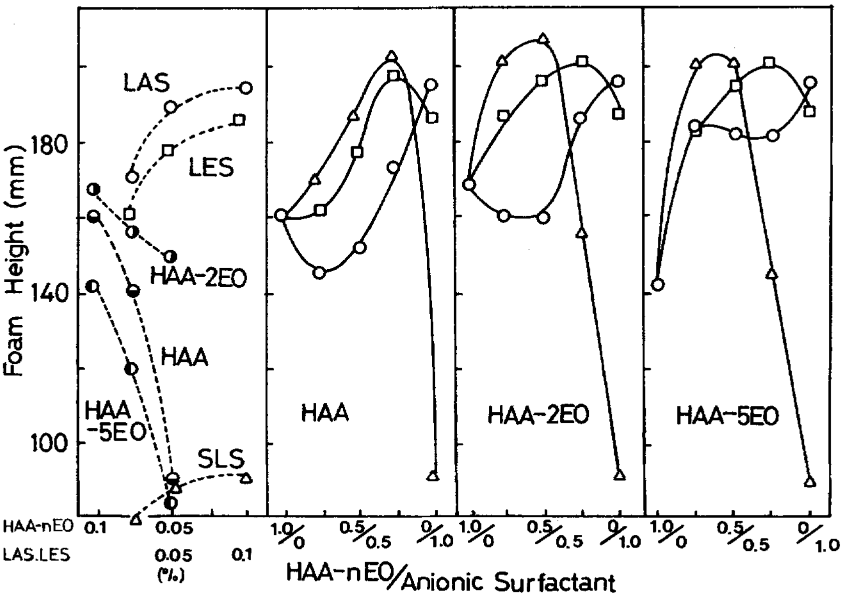

FIG. 4. Foaming power of 0.1% solutions of C_{12-14}-HAA or C_{12-14}-HAA-nEO/anionic surfactants in 50 ppm $CaCO_3$ hard water at 25 C and pH 6.5. LAS = ○; SLS = △; LES = □. The dotted line indicates data for the individual surfactant alone.

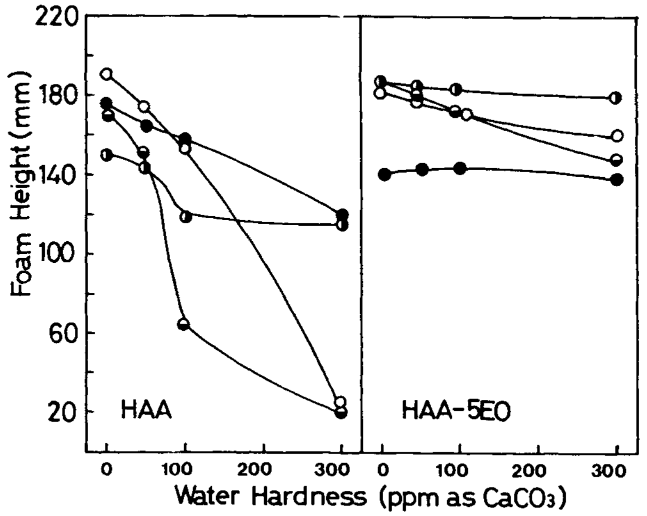

FIG. 5. Effect of water hardness on foaming power of 0.1% solutions of C_{12-14}-HAA/LAS and C_{12-14}-HAA-5EO/LAS at 25 C and pH 6.5. HAA/LAS, 1.0/0 = ●; 0.75/0.25 = ◑; 0.5/0.5 = ◓; 0.25/0.75 = ○.

C_{12-14}-HAA or C_{12-14}-HAA-nEO and anionic surfactant. The foam height data were obtained according to the Ross-Miles method after a 0.1% total concentration solution stood for 1 min. In addition to this, the foaming power for each individual surfactant in the range of 0.05-0.1% concentration was measured for comparison purposes. The foam height for HAA/LAS and HAA-2EO/LAS gave a concave curve with a minimum at the component ratio of 0.75/0.25 to 0.5/0.5. On the other hand, the foam height for HAA/SLS, HAA/LES, HAA-nEO/SLS and HAA-nEO/LES gave convex curves. These systems showed excellent foaming power.

The effect of water hardness on the foaming power of C_{12-14}-HAA/LAS and C_{12-14} -HAA-5EO/LAS is shown in Figure 5. The foam height for HAA alone and HAA/LAS decreased with increasing water hardness. On the other hand, the foam height for HAA-5EO alone and HAA-5EO/LAS was little influenced in the range of hardness examined.

Figure 6 shows surface tension for various combinations at a 0.04% total concentration and at pH 6.5. A marked synergistic effect on the surface tension was observed for all binary systems except HAA/LAS. All minimums of the concave occurred around the component ratio 0.5/0.5 and the surface tension at the above component ratio was in the order of LAS > SLS > LES for HAA-containing system and LES > SLS > LAS for HAA-nEO-containing system.

Figure 7 shows the dye (Orange OT) solubilization by a 0.4% solution of HAA-2EO/LAS at 45 C and pH 8.0. The binary system of C_{12-14}-HAA-2EO/LAS had good solubilization capacity at all ratios, whereas that of C_{16-18}-HAA-2EO/LAS exhibited an anomalously high solubilization capacity just at the 0.5/0.5 component ratio.

Detergency of Solutions of Binary Surfactant Systems

Fabric detergency for various soils was evaluated as shown in Figures 8, 9 and 10. The degreasing power of the 0.04% solutions of C_{12-14}-HAA-2EO/LAS or SLS for wool-muslin cloth soiled with olive oil is illustrated in Figure 8. A slight synergistic effect was observed for both the LAS and SLS systems. Fabric detergency of the solutions of various compositions for cotton and polyester/cotton cloth was evaluated at pH 7.0 and 9.5 as shown in Figure 9. Cotton detergency exhibited a synergistic effect only in the case of HAA-5EO/LAS at pH 7.0 and 9.5. There is slight synergism

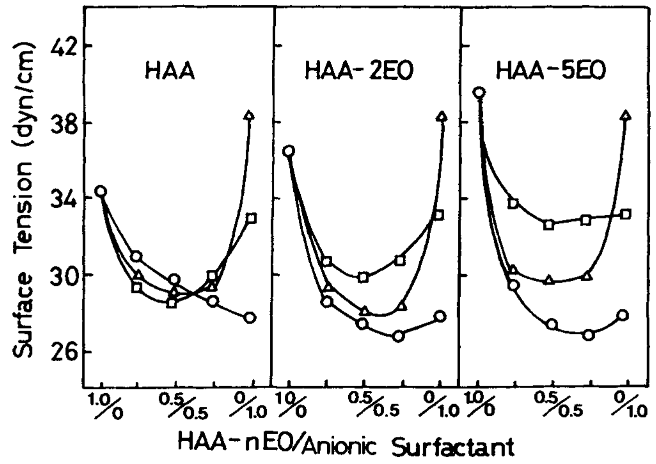

FIG. 6. Surface tension of 0.04% solutions of C_{12-14}-HAA or C_{12-14}-HAA-nEO/anionic surfactants in 50 ppm $CaCO_3$ hard water at 25 C and pH 6.5. LAS = ○; SLS = △; LES = □.

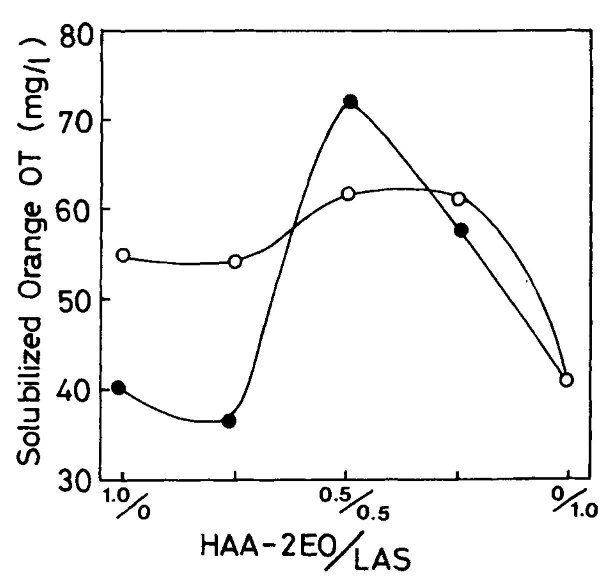

FIG. 7. Dye solubilization of Orange OT by 0.4% solutions C_{12-14}- or C_{16-18}-HAA-2EO/LAS in 50 ppm $CaCO_3$ hard water at 45 C and pH 8.5. C_{12-14}- = ○; C_{16-18}- = ●.

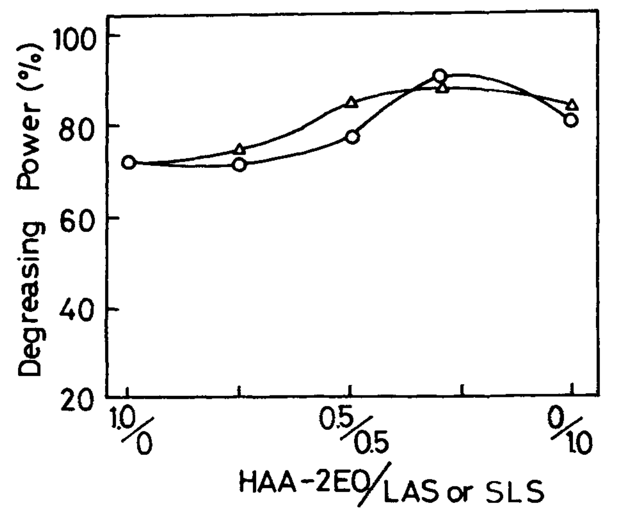

FIG. 8. Degreasing power of 0.04% solutions of C_{12-14}-HAA-2EO/LAS or SLS in 50 ppm $CaCO_3$ hard water at 25 C and pH 9.5 for wool-muslin cloth soiled with olive oil. LAS = ○; SLS = △.

with HAA-2EO also. On the other hand, the detergency for polyester/cotton cloth gave synergistic effects in all combinations except one. The detergency was improved in the order of HAA < HAA-2EO < HAA-5EO. In particular, HAA-5EO/LAS had the best detergency at pH 9.5. The detergency of HAA-2EO/LAS (3/1) did not change even in solutions of high hardness as shown in Figure 10.

Dishwashing performance is illustrated in Figure 11. The mixed solutions of HAA-nEO/anionic surfactants showed a markedly synergistic effect as was also observed for the detergency of polyester/cotton. The 2EO and 5EO derivatives exhibited equal dishwashing performance.

Irritation Test

The irritancy of HAA and HAA-2EO on human skin is shown in Tables I and II, which show that C_{16-18}-HAA

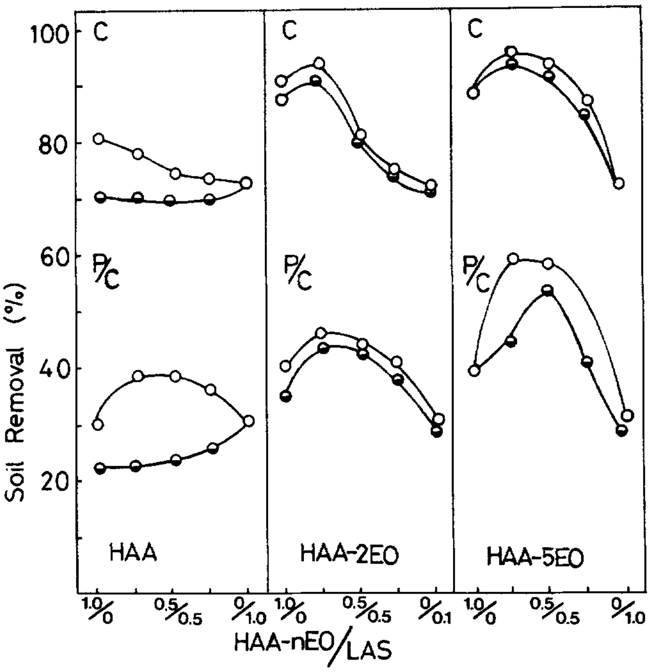

FIG. 9. Detergency for artificially soiled fabrics in 0.04% solutions of C_{12-14}-HAA or C_{12-14}-HAA-nEO/LAS in 50 ppm $CaCO_3$ hard water at 25 C; pH 7.0 = ◐; pH 9.5 = ○; cotton = C; polyester/cotton = P/C.

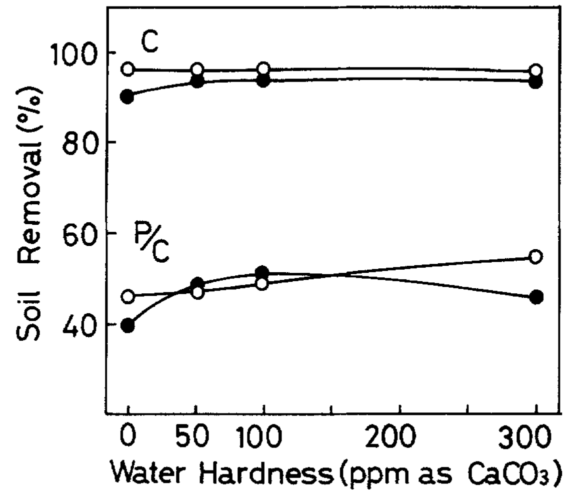

FIG. 10. Effect of water hardness on detergency for artificially soiled fabrics in 0.1% solutions of HAA/LAS (3/1) at 25 C and pH 9.5. C_{12-14}- = ○; C_{16-18}- = ●; cotton = C; polyester/cotton = P/C.

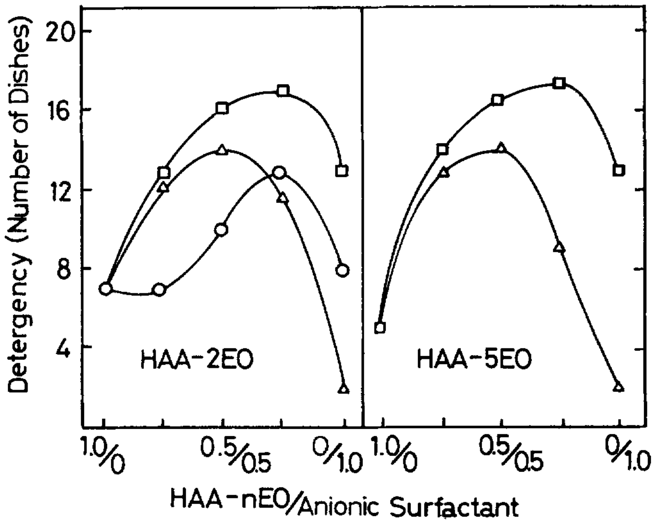

FIG. 11. Dishwashing in 0.04% solutions of C_{12-14}-HAA-nEO/anionic surfactants in 50 ppm $CaCO_3$ hard water at 25 C and pH 6.5. HAA-nEO/LAS = ○; HAA-nEO/SLS = △; HAA-nEO/LES = □.

TABLE I

Patch Test on Human Skin[a]

		C_{12-14}-HAA	C_{12-14}-HAA-2EO	C_{16-18}-HAA	C_{16-18}-HAA-2EO	C_{12}-β-Alanine[b]
Male (10 cases)	(−)[c]	9	8	10	6	5
	(±)	0	1	0	4	2
	(+)	1	1	0	0	3
Female (10 cases)	(−)	9	5	10	9	5
	(±)	1	3	0	1	3
	(+)	0	2	0	0	2
Total (20 cases)	(−)	18(90%)	13(65%)	20(100%)	15(75%)	10(50%)
	(±)	1(5%)	4(20%)	0(0%)	5(25%)	5(25%)
	(+)	1(5%)	3(15%)	0(0%)	0(0%)	5(25%)

[a] Concentration 1.0 wt%, pH 6.5.
[b] Commercial grade of N-dodecyl-β-alanine.
[c] (−), no erythema; (±), slightly partial erythema; (+), erythema with definite margin.

TABLE II

Photosensitization Test on Human Skin[a]

		C_{12-14}-HAA	C_{12-14}-HAA-2EO	C_{16-18}-HAA	C_{16-18}-HAA-2EO	C_{12}-β-Alanine[b]
Male (7 cases)	(−)[c]	7	5	7	6	3
	(±)	0	1	0	1	2
	(+)	0	1	0	0	2
Female (8 cases)	(−)	5	6	8	7	2
	(±)	3	1	0	1	5
	(+)	0	1	0	0	1
Total (15 cases)	(−)	12(80%)	11(73%)	15(100%)	13(87%)	5(33%)
	(±)	3(20%)	2(13.5%)	0(0%)	2(13%)	7(47%)
	(+)	0(0%)	2(13.5%)	0(0%)	0(0%)	3(20%)

[a] Concentration 1.0 wt%, pH 6.5

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

[c] (−), no erythema; (±), slightly partial erythema; (+), erythema with definite margin.

TABLE III

Irritation Test on Rabbit Skin

		Evaluation after 7 days[b]		
Composition[a] (wt ratio)	Rabbit no.	Redness-tumor	Crusta	Recovery
C_{12-14}-HAA-2EO	1	++	++	
C_{12-14}-HAA-2EO/LAS (24/76)	1	+++	+++	
C_{12-14}-HAA-2EO/LAS (56/44)	1	+	+	
Physiological saline solution	1	−	−	
C_{12-14}-HAA-2EO/LES (20/80)	2	++	++	6 days after the last application.
C_{12-14}-HAA-2EO/LES (50/50)	2	+	+	
LAS	2	+++	+++	
LEA	2	+++	+++	
Physiological saline solution	2	−	−	

[a] Total concentration 4.0 wt%, pH 7.0.

[b] (−), no erythema; (+), only erythema; (++), small papule or dropsy; (+++), eczema or vesicle.

gave no irritation. The irritation decreased in the order of C_{12-14}-HAA-2EO > C_{16-18}-HAA-2EO > C_{12-14}-HAA. The irritancy of these amphoteric surfactants was less than that of C_{12}-β-alanine which is commonly used in the field of cosmetics and toiletries. The result of the photo patch test, as shown in Table II, indicates that incidence of photosensitization of the skin was marginal at most for all surfactants; none was observed for C_{16-18}-HAA. An irritation test on rabbit skin was carried out for the binary systems of C_{12-14}-HAA-2EO/LAS or LES as summarized in Table III. Redness-tumors began to occur one day after application and severe irritation dermatitis was observed after 6 days. The derma was regenerated in 2 weeks after application followed by recovery after 3 weeks as in the case of the test using physiological saline solution. C_{12-14}-HAA-2EO caused considerably less irritation dermatitis than LAS and LES. The binary systems of C_{12-14}-HAA-2EO/LAS (56/44) and C_{12-14}-HAA-2EO/LES (50/50) showed the least irritancy on rabbit skin.

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