New Amphoteric Surfactants Containing a 2-Hydroxyalkyl Group: II. The Dependence of Physicochemical Properties on the pH Value for N-(2-Hydroxyethyl)-N-(2-Hydroxyalkyl)-β-Alanines

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ABSTRACT

The dependence of physicochemical properties on the pH of micellar solutions for N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines (HAA) was studied by means of a differential titration method (DTM), Fourier transform infrared (FTIR) spectra, and measurements of critical micelle concentration, surface tension, and foaming power. The aspect of the dissociation of HAA was pursued by DTM. The mutual transformation among cationic, zwitterionic, and anionic forms with the change of pH range was confirmed by FTIR spectroscopy. The micelle formation energy was determined at each pH value. Further, the dependence of surface active properties on the pH value for the adducts of ethylene oxide to Na-HAA was also investigated.

INTRODUCTION

In a recent paper (1), we have reported the preparation and fundamental properties of N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanines (HAA) and the adducts of ethylene oxide to Na-HAA (Na-HAA-nEO). Only a few studies have hitherto been reported on the physicochemical properties of amphoteric surfactants containing hydroxy groups (2-4). In this paper, we wish to report our extended study of the effect of pH on the critical micelle concentration (cmc), micelle formation energy, surface tension and foaming power for HAA and Na-HAA-nEO. Further, the structural change of the HAA by pH variation was elucidated by means of Fourier transform infrared (FTIR) spectra.

EXPERIMENTAL PROCEDURES

Materials

The samples of HAA and Na-HAA-nEO homologs used in this paper are the same as described in the previous paper (1).

Cmc Measurements

The surface tension was measured by a Wilhelmy's vertical plate method with a Shimazu ST-1 tensiometer. The cmc value was determined from the surface tension vs. log concentration curves at different pH values and temperatures. Acidity and alkalinity were controlled by adding 2N HCl and 2N NaOH.

Potentiometric Titrations

The titrations were carried out with a Hitachi-Horiba F-5 pH meter at 40 C in an atmosphere of nitrogen. HAA was dissolved in a 0.1 N NaOH solution so as to prepare a 0.3 mmole/liter (or 10 mmole/liter) solution. An aliquot (20 ml) of the solution was titrated with a 0.1N HCl solution.

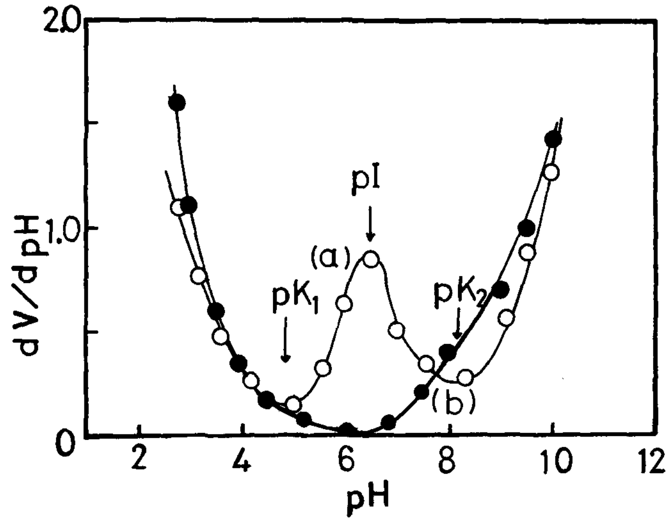
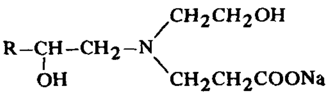


FIG. 1. Differential curves calculated from the titration curves for C_{12}-HAA in solution (3 mmole/liter) at 40 C: (a) Titration of Na-HAA with HCl; (b) Titration of HAA with NaOH.

TABLE I

Isoelectric Point of Values β-Alanine Compounds

Compound	Formula	Alkyl group	pK_1	pK_2	pI
Sodium N-(2-hydroxyethyl)-N-(2-hydroxyalkyl)-β-alanine	 $R{-}CH(OH){-}CH_2{-}N(CH_2CH_2OH)(CH_2CH_2COONa)$	$R{=}C_{10}H_{21}{-}$	5.15	8.45	6.80
		$R{=}C_{12}H_{25}{-}$	5.10	8.50	6.75
		$R{=}C_{14}H_{29}{-}$	5.06	8.14	6.60
		$R{=}C_{16}H_{33}{-}$	5.03	7.97	6.50
N-Dodecyl-β-alanine[a]	$R{-}NH{-}CH_2CH_2COOH$	$R{=}C_{12}H_{25}{-}$	5.55	8.40	6.97
N-Dodecyl-β-amino-dipropionic acid[b]	$R{-}N{-}(CH_2CH_2COOH)_2$	$R{=}C_{12}H_{25}{-}$	---	---	3.4 ~ 4.6
3-Aminopropionic acid[c]	$NH_2{-}CH_2CH_2COOH$		3.55	10.24	6.97

[a] Measured using a sample of commercial grade.

[b] Ref. (5).

[c] Ref. (6).

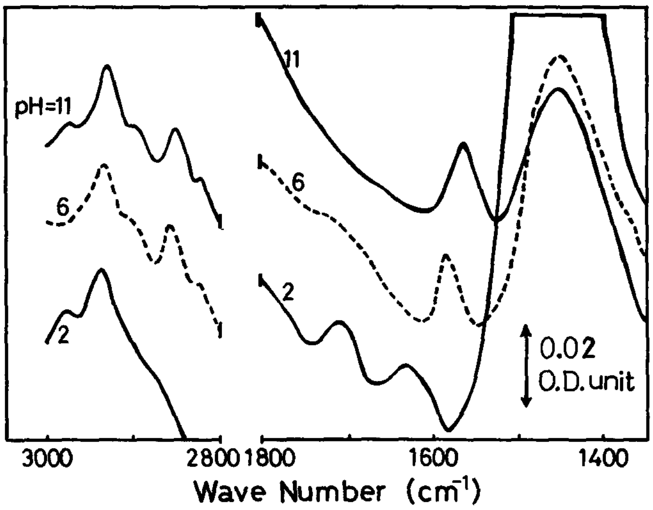


FIG. 2. FTIR spectra for C_{12}-HAA in D_2O solution (5 mmole/liter).

On the other hand, HAA was dissolved in a 0.1N HCl solution, and the titration was similarly performed with a 0.1N NaOH solution. The change of the pH value was followed potentiometrically. The differential curves of dV_{HCl}/dpH (ml of HCl solution per unit pH) vs. pH value are shown as titration curves in Figure 1. The acid dissociation constant pK_1 and the base on pK_2 were determined from two minimum values on the differential curves and the isoelectric point pI was calculated from the relationship of $pI = (pK_1 + pK_2)/2$.

Foaming Power

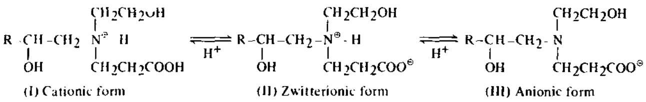
The foaming power was measured at a fixed temperature according to the Ross-Miles method. The foaming height (mm) was recorded immediately after dropping the test sample and after standing for 5 min.

FTIR Spectra

FTIR spectra were measured by means of a Digilab-FTS-14 spectrometer in an atmosphere of dry air. The cell used was made of CaF_2 with a Pb-spacer in 50 mμ width, and the number of scannings was 220 times. Its resolving power was 4 cm^{-1}. The D_2O solution of HAA (5 mmole/liter) was adjusted to pH 11.0 with NaOD (supplied by E. Merck Chemicals) and to pH 2.0 with DCl (by E. Merck Chemicals), respectively.

RESULTS AND DISCUSSION

The amphoteric surfactants can exist in three ionic forms depending upon pH value of the solution. These forms are shown in the following equilibrium.



$$\underset{\text{OH}}{\underset{|}{\text{R-CH}}}\text{-CH}_2\text{-}\overset{\text{CH}_2\text{CH}_2\text{OH}}{\overset{|}{\underset{\text{CH}_2\text{CH}_2\text{COOH}}{\underset{|}{\text{N}^{\oplus}}}}}\text{-H} \underset{\text{H}^+}{\rightleftharpoons} \underset{\text{OH}}{\underset{|}{\text{R-CH}}}\text{-CH}_2\text{-}\overset{\text{CH}_2\text{CH}_2\text{OH}}{\overset{|}{\underset{\text{CH}_2\text{CH}_2\text{COO}^{\ominus}}{\underset{|}{\text{N}^{\oplus}}}}}\text{-H} \underset{\text{H}^+}{\rightleftharpoons} \underset{\text{OH}}{\underset{|}{\text{R-CH}}}\text{-CH}_2\text{-}\overset{\text{CH}_2\text{CH}_2\text{OH}}{\overset{|}{\underset{\text{CH}_2\text{CH}_2\text{COO}^{\ominus}}{\underset{|}{\text{N}}}}}$$

(I) Cationic form (II) Zwitterionic form (III) Anionic form

To determine the possible buffering effect and isoelectric point of the amphoteric surfactant, the consumption of HCl or NaOH per unit pH was followed on the basis of the titration curves for C_{12}-Na-HAA with HCl and C_{12}-HAA with NaOH, respectively. C_{12}-, C_{14}-, C_{16}- and C_{18}- prefixed to the abbreviations used in this paper denote, respectively, the carbon number, 12, 14, 16, and 18, in the 2-hydroxyalkyl group.

The differential curves are shown in Figure 1.

The curve (a) indicates a complex diagram showed two minima and a maximum presumably attributable to the neutralization of Na carboxylate and to the formation of quaternary ammonium salt from the tertiary amine, respectively. On the other hand, the curve (b) indicates a simple diagram having a dull minimum around pH 5 ~ 7. Two minima of the curve (a) correspond to pK_1 5.15 and pK_2 8.45, respectively. The cationic structure (I) is predominantly formed in acidic solutions of pH below 5.15, the zwitterionic one (II) in the range of pH 5.15 ~ 8.45, whereas the anionic one (III) mainly in alkaline solutions of pH above 8.45. Although the influence of alkyl chain length upon the titration curve was investigated for the homologs of Na-HAA with HCl, similar patterns were observed regardless of the alkyl chain length. The isoelectric point of C_{12}-HAA occurs at pH 6.80 as an average of pK_1 and pK_2. Although pK_1 and pK_2 for C_{14}, C_{16}, and C_{18} homologs were measured in the same way, no great difference attributable to the alkyl chain length was observed. The isoelectric points and dissociation constants of various β-alanine compounds are listed in Table I.

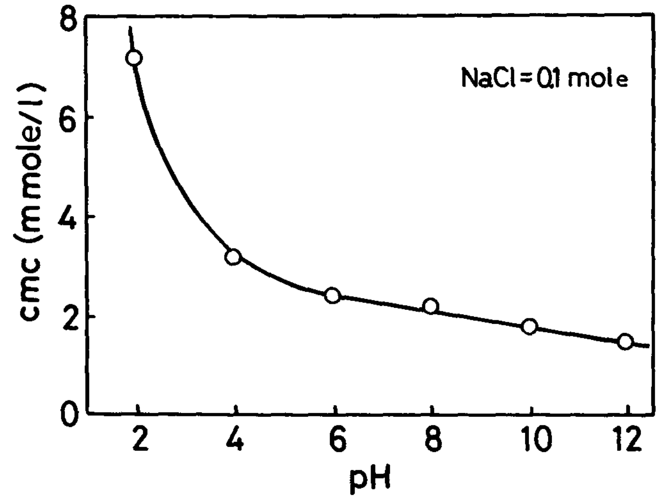


FIG. 3. Dependence of the cmc value on pH value for C_{12}-HAA at 30 C.

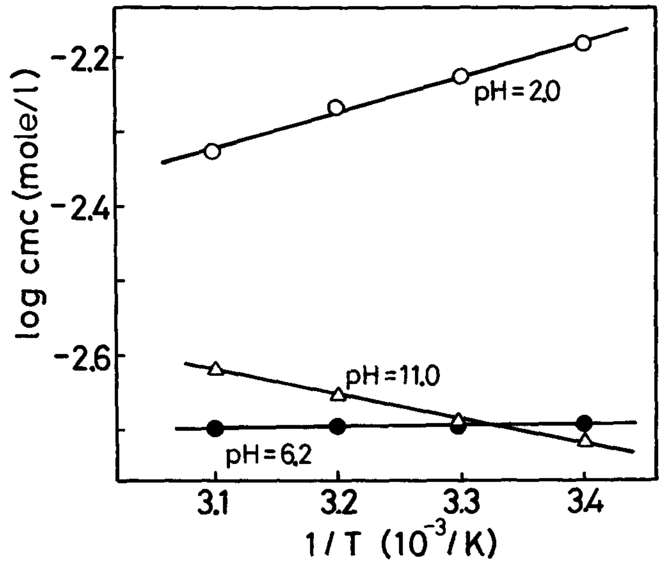


FIG. 4. Effect of temperature on the cmc value of C_{12}-HAA.

The dissociation constants and isoelectric point for C_{12}-HAA approximate those of N-dodecyl-β-alanine. An influence of two hydroxy groups on the isoelectric point is not observed. 3-Aminopropionic acid which does not have a long alkyl chain, shows nearly the same isoelectric point,

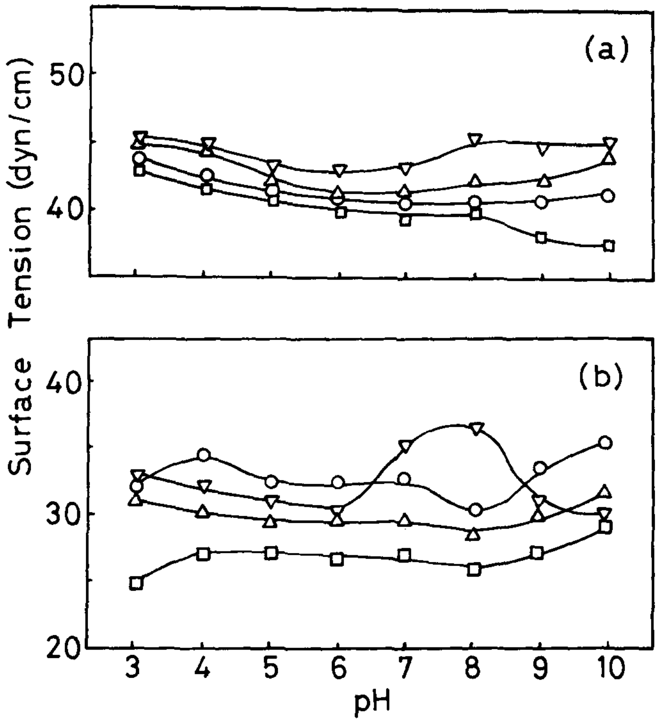


FIG. 5. Dependence of surface tension on pH value for HAA homologs in solution above and below each cmc at 50 C: (a) ○ C_{12}-1.00, △ C_{14}-0.10, □ C_{16}-0.05, ▽ C_{18}-0.20 mmole/liter; (b) ○ C_{12}-7.0, △ C_{14}-0.5, □ C_{16}-0.3, ▽ C_{18}-0.6 mmole/liter.

but pK_1 and pK_2 for C_{12}-Na-HAA are considerably shifted to the neutral range as compared with those for 3-aminopropionic acid. β-Alanine surfactants containing monocarboxyl group have pI 6.5 ~ 7.0, whereas pI for the compound containing two carboxyl groups is located at the acidic side.

The FTIR spectra of C_{12}-HAA at each pH value are shown in Figure 2. The spectrum in an acidic solution at pH 2.0 is characterized by the presence of the absorption at 1750 and 1580 cm^{-1} corresponding to C=O str. in the carboxyl group and -N$^+$H- deg. def., respectively (7), whereas the spectrum in an alkaline solution at pH 11.0 is characterized by the disappearance of the band at 1750 cm^{-1} corresponding to C=O str. and by the appearance of the band at 1595 cm^{-1} corresponding to CO_2^- anti. str. in the carboxylate group. The spectrum at pH 6.0 is characterized by the concurrent appearance of the bands at 1620 and 1545 cm^{-1} corresponding to CO_2 anti. str. and -N$^+$H- sym. def., respectively. The characteristic feature of the spectrum at pH 6.0 suggests the presence of the zwitterion. These spectral differences at different pH values are thought to be caused by the equilibria among structures such as (I), (II), and (III). The absorption bands appearing in the spectral range from 2800 to 3000 cm^{-1} do not show any distinct changes with pH and are assigned to CH absorption bands.

The effect of pH on cmc value for C_{12}-HAA in the presence of 0.1 mole/liter NaCl at 30 C is shown in Figure 3. The cmc rises on the acidic side and remains almost unchanged on the alkaline side. The change of cmc with pH can be classified into two types of depending on the chemical structure of the surfactants. The first type is a surfactant whose cmc increases as the pH increases. For example, surfactants such as sodium N-dodecyl-N,N-bisethoxy acetate (8), 2-[N,N-bis(2-hydroxyethyl)amino] lauric acid (3), and 2-{[2-(2-hydroxyethoxy)ethyl] amino} lauric acid (4) show a higher cmc value in alkaline solution than in acidic solution, because the function of carboxylate is inferred to be more intense than that of the amine. On the other hand, the second type is a surfactant whose cmc is higher in acidic solution than in alkaline solution. N-Dodecyl-β-alanine (9), N,N,N-trimethyl aminododecane imide (10), and diethyldodecylamine oxide (11) belong to this group. It can therefore be presumed that the effect of an amino group is stronger in the acidic range. C_{12}-HAA containing two hydroxy groups shows the same tendency as the second type surfactants, and the function of amino group is relatively more intense than that of carboxyl group. These phenomena are also presumably due to the effect of micelle charge upon the micelle size and shape which are closely associated with the relative location of amino and carboxyl groups in a molecule. As predicted from the configuration of the micelle, the cationic ionization of amino group will take place inside the micelle, whereas the anionic ionization of carboxyl group will occur on the surface of the micelle. A detailed discussion of this electrostatic potential for ionization will be presented in a subsequent paper.

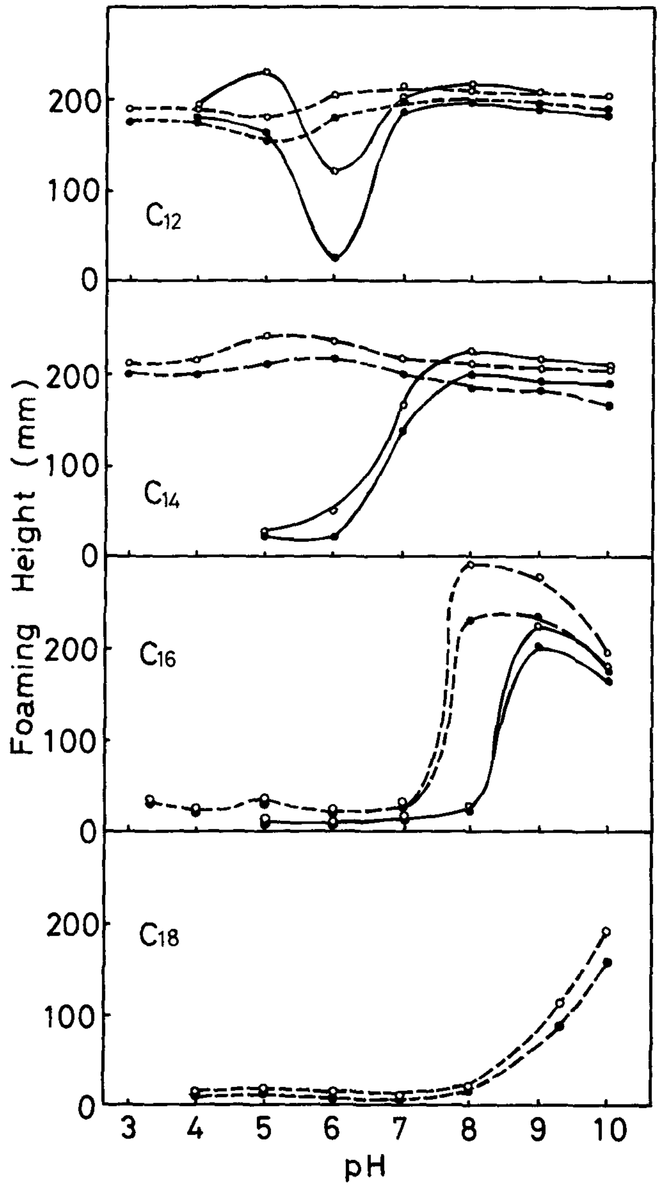


FIG. 6. Dependence of foaming power on pH value for HAA homologs in solution (0.25 wt%). At 25 C (solid line) and at 40 C (dotted line); ○ (height immediately after dropping the test sample), ● (height after standing for 5 min).

The dependence of cmc on temperature for C_{12}-HAA at each pH value is shown in Figure 4. From each slope of log cmc vs. 1/T plot, the micelle formation energy (ΔHm) was

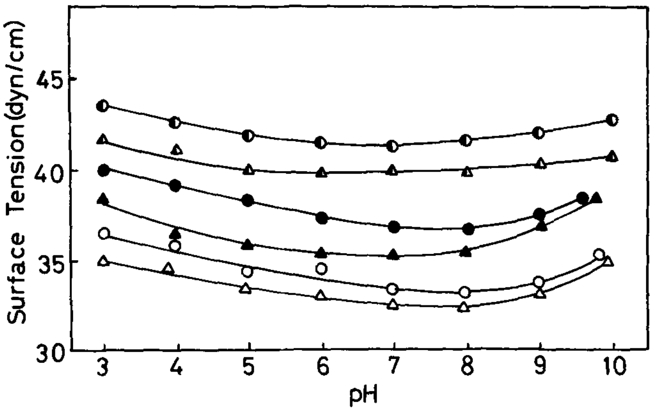


FIG. 7. Dependence of surface tension on pH value for Na-HAA-nEO in solution (0.05 wt%) at 40 C. ○ C_{12}-2.4 EO; ● C_{12}-6.0 EO; ◐ C_{12}-12.0 EO; △ C_{14}-2.5 EO; ▲ C_{14}-5.4 EO; ▲ C_{14}-12.0 EO.

calculated from the following equation; log cmc = ΔHm/2.303 RT. In an alkaline solution (pH 11.0), the cmc increased slightly with increasing temperature like other ionic surfactants and the micelle formation energy ΔHm was found to be +1.5 Kcal/mole. On the other hand, in an acidic solution (pH 2.0), the cmc decreased with increasing temperature. The micelle formation energy ΔHm was -2.15 Kcal/mole. In a neutral solution (pH 6.2), however, the cmc was unaffected by a change in temperature.

Figure 5 (a) shows the dependence of surface tension on pH at various concentrations below the cmc of each HAA homolog. Surface tension of all HAA homologs were within the narrow range from 37 to 45 dyn/cm over a wide pH range. Figure 5 (b) shows the curves of the surface tension of HAA homologs vs. pH at a concentration above the cmc value. The surface tension of HAA homologs except C_{18}-HAA indicated no characteristic change in either acidic or alkaline media. C_{18}-HAA displayed an anomalous maximum surface tension at pH 7 ~ 8, where the viscosity of solution was observed to increase markedly. The viscosity was measured with an Ubbelohde's viscosimeter at 50 C. The relative viscosity for 2.5 mmole/liter (ca. 0.1 wt%) solution was obtained at each pH value as follows; η-0.57 centipoise at pH 3, η=0.89 centipoise at pH 8, and η=0.56 centipoise at pH 10. From these data, it may be concluded that the change in surface tension is due to the corresponding increase of the solution viscosity.

The dependence of the foaming on pH for HAA homologs at 25 and 40 C is shown in Figure 6. The foaming of C_{12}-HAA at 25 C showed a minimum value in the neighborhood of the isoelectric point, but such a phenomenon disappeared at 40 C. The foaming of C_{14}- and C_{16}-HAA at 25 C gave a distinct rise of foam height in alkaline solution, whereas the foaming in acidic solution was extremely low. It should be mentioned that the measurements for C_{18}-HAA were performed at 40 C because of its poor solubility at 25 C.

The relationship between the surface tension and pH value for the EO adducts of C_{12}- and C_{14}-Na-HAA is illustrated in Figure 7. Changes of surface tension with pH variation were scarcely observed for either C_{12}- or C_{14}-Na-HAA-nEO. The result of the addition of EO to Na-HAA homologs was to improve the aforementioned dependence of foaming power, surface tensiôn, and solubility in both the acidic region and the neighborhood of the isoelectric point.

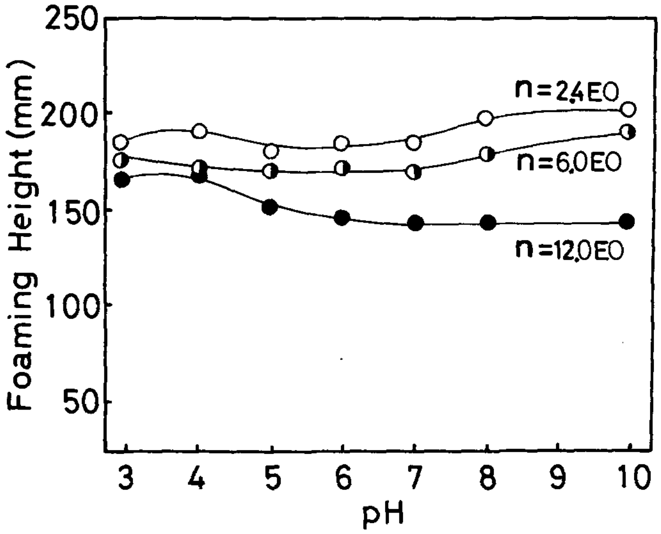


FIG. 8. Dependence of foaming power on pH value for C_{12}-Na-HAA-nEO in solution (0.1 wt%) at 25 C.

Figure 8 shows the foaming power for the EO adducts of C_{12}-Na-HAA. The dependence of the foaming on pH was observed for C_{12}-Na-HAA-nEO at 25 C. As the number of moles of EO added was increased, the foaming decreased. The 2.4 mole EO adduct exhibited the best foaming regardless of the pH value, and the poor foaming was improved in the neighborhood of the isoelectric point as well as in the acidic range. However, further addition of EO induced not only a decrease of foaming but also caused the elevation of surface tension for the system. A similar pattern of foaming for C_{14}-, C_{16}-, and C_{18}-Na-HAA-nEO homologs was also observed.

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