Foam Performance of Fatty Acid Soaps of Odd Carbon Numbers

K. OGINO and **F. TAKIGAMI**, Faculty of Science and Technology,
Science University of Tokyo, Noda, Chiba, Japan

ABSTRACT

The foam capacities, foam stabilities, expanding single bubble stabilities, surfact tensions, and surface viscosities of the straight chain C_9-C_{14} sodium soaps were measured at various concentrations. The C_{12}-C_{14} soaps, most notably the C_{13}, gave the best overall foam performance of the compounds studied. The critical micelle concentrations for these soaps were also determined.

INTRODUCTION

Although many reports have been presented on foam characteristics studies of sodium soaps, they have been concerned with the fatty acid salts of even carbon numbers originating from natural fatty oils (1-5). Recently, however, advances in organic synthesis have made the fatty acids of odd carbon numbers readily available for technical uses. We have investigated the foam performance of the odd carbon numbered soaps included in the range C_9-C_{14}, and herein report the results.

EXPERIMENTAL PROCEDURES

Materials

The sodium soaps of nonanoic (C_9), decanoic (C_{10}), undecanoic (C_{11}), dodecanoic (C_{12}), tridecanoic (C_{13}), and tetradecanoic (C_{14}) acids were prepared by neutralizing these acids with ethanolic sodium hydroxide. These soaps were purified by recrystallization and stored in a dessicator at room tempetature. The fatty acids were obtained from Ajinomoto Co., Ltd., and their properties have been described in a previous work (6).

Hydrolysis is the main source of error in studies of soap solutions. Therefore, in most of the work performed on the physio-chemical properties of soap, alkaline solutions have been used as the solvent in place of pure water to prevent hydrolysis. In this work, however, we used distilled water free from carbon dioxide as the solvent, because the foam performance of alkaline solutions is not as good as solutions in pure water.

Apparatus and Conditions

Foaming capacity and foam stability. The foaming capacity of the soaps was observed in 50 ml marked Pyrex test tubes in which 7 ml of soap solution was shaken 50 times at 45 C. Foaming capacity was determined as foam volume (ml) immediately after shaking, and the foam stability was determined as the half-life period, e.g., the time (min.) required for the foam volume to be reduced to one-half its initial volume.

Expanding single bubble stability. The apparatus shown in Figure 1 was used for the expanding single bubble stability measurements. A volume of 3.0×10^{-3} ml of soap solution was dropped on capillary A by means of a micro-syringe connected to a micrometer. The flow rate of air was kept constant at 0.33 ml/sec. and temperature kept at 45 C throughout all runs.

Surface viscosity. The surface viscosities were measured by a vibrating decay method described in the literature (7).

Surface tension. The surface tensions were measured by means of a Whilhelmy-type Surface Tensiometer ST-1 (Shimazu Seisakusho).

RESULTS AND DISCUSSION

The foaming capacities of the sodium soaps of nonanoic (C_9), decanoic (C_{10}), undecanoic (C_{11}), dodecanoic (C_{12}), tridecanoic (C_{13}), and tetradecanoic (C_{14}) acids are shown in Figure 2. It is clear from Figure 2 that the foaming capacities of all the soaps increased as a linear function of the concentration up to their respective critical threshold values. Beyond these critical thresholds, the foaming capacities approach saturated values for solutions. It is also clear that generally the foaming capacities of these soaps increased with increasing alkyl chain length. The foaming capacities of this series were in the following order: $C_{13}>C_{14}>C_{12}>C_{10}>C_9$. It is noteworthy that C_{13} exhibited a greater foaming capacity than C_{14}.

The critical threshold concentrations observed in Figure 2 agreed closely with critical micelle concentrations (CMC) obtained by the measurement of surface tension. The surface tension vs. concentration curves of these sodium soaps are shown in Figure 3. As soap concentration increases, the surface tension decreases to a minimum for a concentration which always lies in the neighborhood of the CMC of the soap solution, and for higher concentrations the surface tension increases. The respective CMCs (moles/L) for these soaps are as follows:

$C_{10}, 7.72 \times 10^{-2}; C_{11}, 3.84 \times 10^{-2}; C_{12}, 2.02 \times 10^{-2};$
$C_{13}, 1.18 \times 10^{-2}; C_{14}, 4.40 \times 10^{-3}.$

Figure 4 shows the foam stability of these soaps. The results are expressed as the time required for the foam value

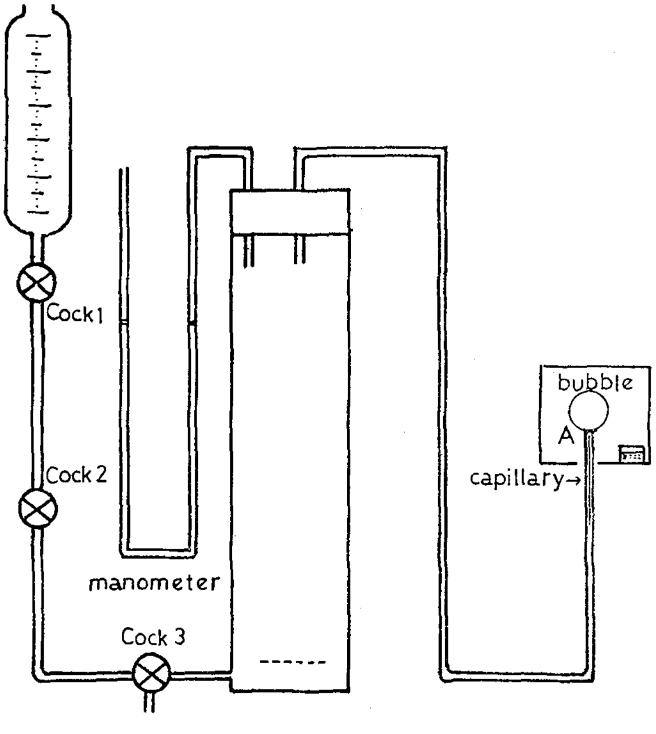

FIG. 1. Apparatus.

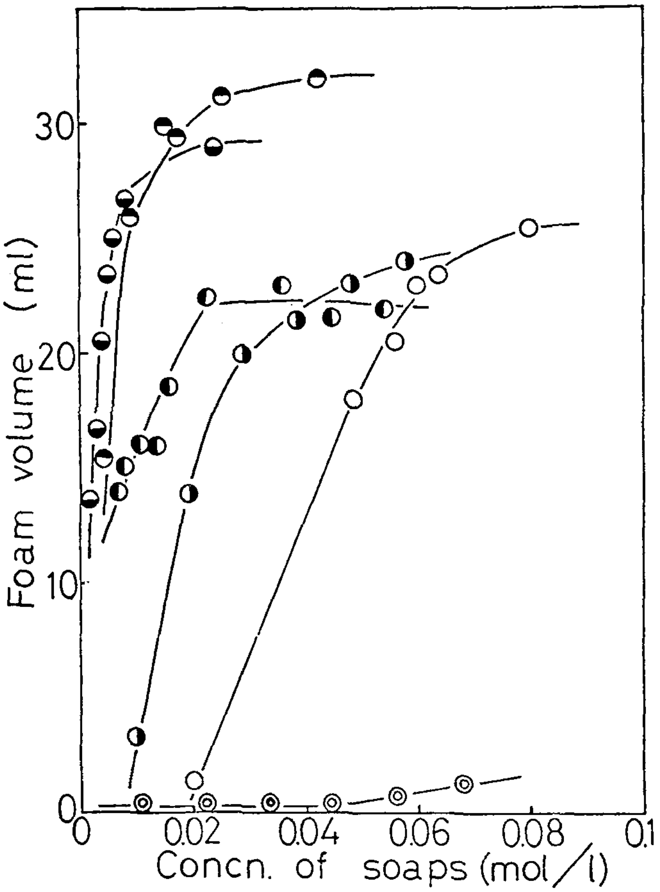

FIG. 2. Foaming of sodium soap solutions at 45 C. ◎: sodium nonanoate; ◑: sodium decanoate; ○: sodium undecanoate; ◐: sodium dodecanoate; ◓: sodium tridecanoate; ◒: sodium tetradecanoate.

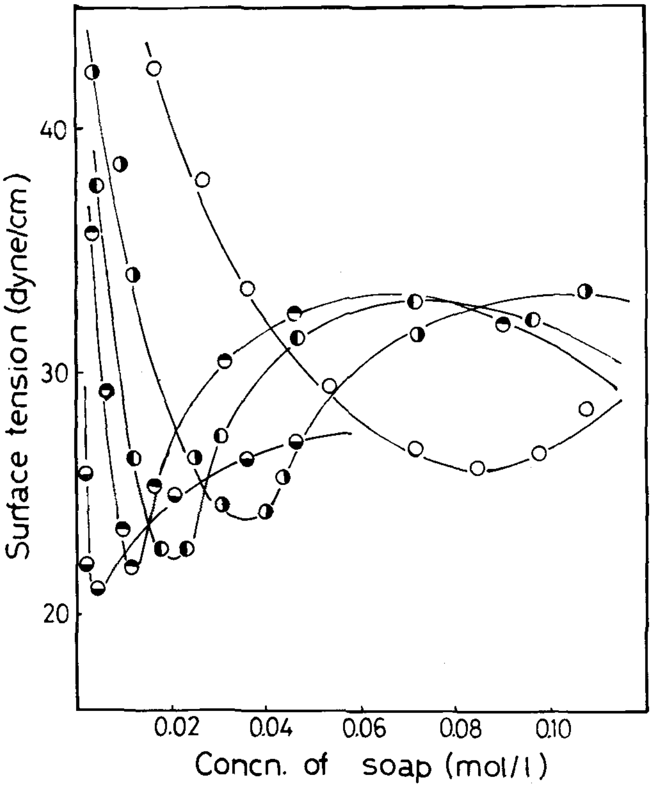

FIG 3. Surface tension of sodium soap solutions at 45 C.

○: Na decanoate
◑: Na undecanoate
◐: Na dodecanoate
◓: Na tridecanoate
◒: Na tetradecanoate.

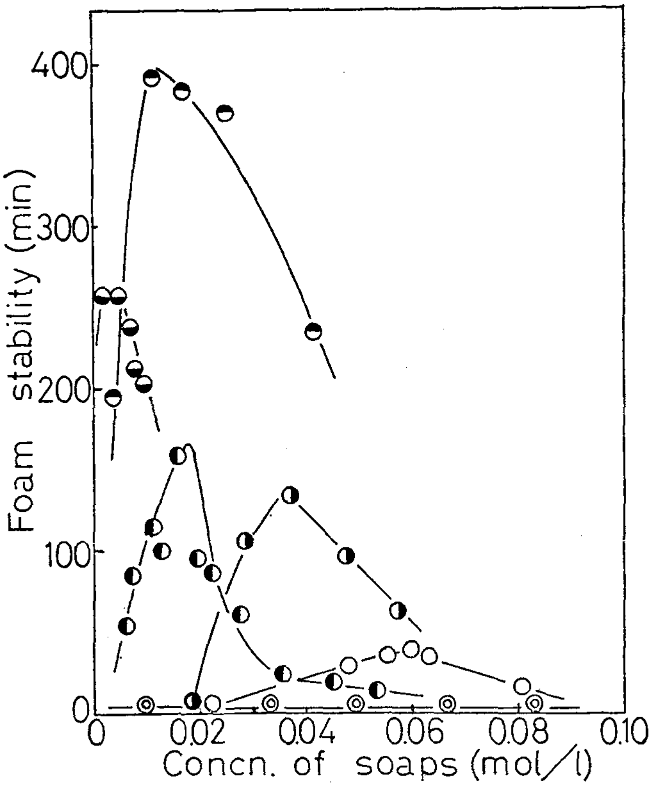

FIG. 4. Foam stability of sodium soap solutions at 45 C. ◎: sodium nonanoate; ○: sodium decanoate; ◑: sodium undecanoate; ◐: sodium dodecanoate; ◓: sodium tridecanoate; ◒: sodium tetradecanoate.

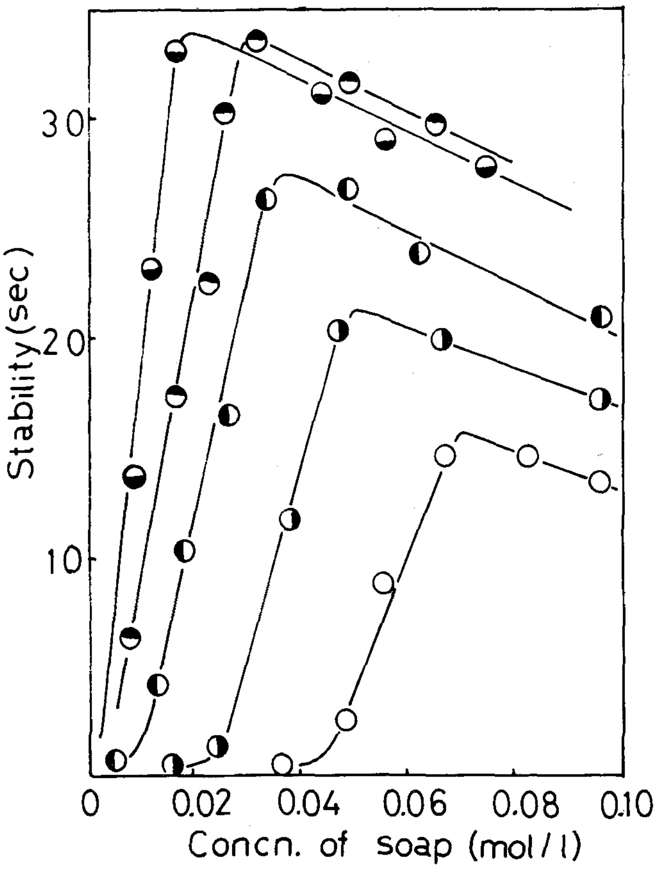

FIG. 5. Stability of expanding single bubble at 45 C (expanding rate: 033 ml/sec).

○: Na decanoate
◑: Na undecanoate;
◐: Na dodecanoate
◓: Na tridecanoate
◒: Na tetradecanoate.

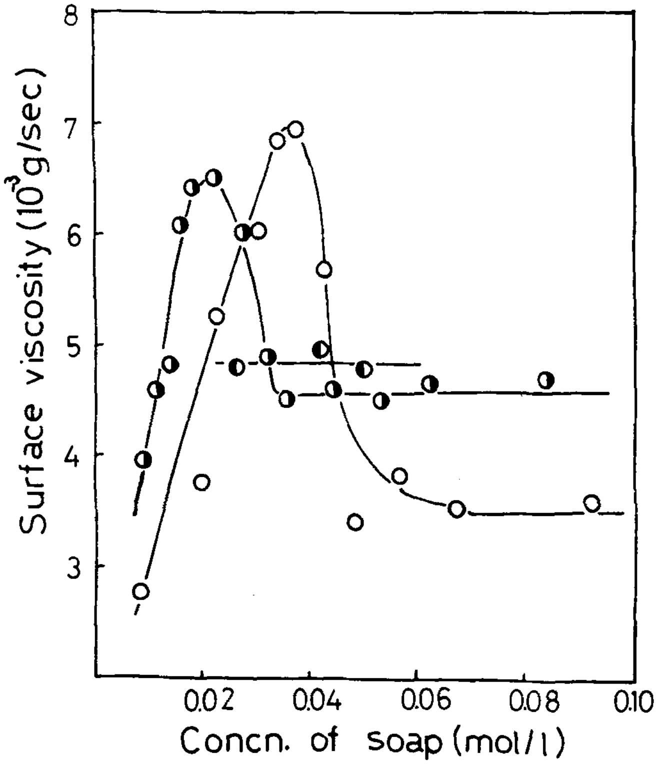

FIG. 6. Surface viscosity of soap solutions at 45 C.
○: Na undecanoate ◑: Na dodecanoate
◐: Na tridecanoate.

to be reduced to one-half its initial value. As shown in Figure 4 it was found that the foam stability of these soaps increased with concentration to a maximum value, then decreased rapidly. The maximum values of these curves show the degree of foam stability, and these values are as follows: C_{14}, 260 min.; C_{13}, 400 min; C_{12}, 160 min; C_{11}, 130 min.; C_{10}, 40 min. It is evident from these results that the C_{13} soap gave the most stable foam. It is also interesting to note that the concentration at which the foam is most stable is also quite close to the CMC.

Figure 5 expresses expanding single bubble stabilities in terms of time required for the bubble to burst.

As shown in Figure 5, the stability of the single bubbles increased with increasing concentration up to a point and then declined beyond that value. The maximum values are as follows: C_{14}~C_{13}, 33 sec.> C_{12}, 27 sec. >C_{11}, 21 sec. > C_{10}, 15 sec. As can be seen from these data, C_{14} and C_{13} give the most stable bubbles. It is also apparent that the soap concentrations which give the most stable bubbles are in general higher than the CMCs. Expanding single bubbles require a certain concentration of soap in the solution because of the Maragoni effect (8). However, at higher concentrations, the single bubble stability is decreased gradually because of the high density and rigidity of foam film.

Figure 6 shows surface viscosities of soap solutions. The maximum values obtained for C_{11} and C_{12} soaps were similar to the CMCs and concentration of maximum foam stability for these soaps. At higher concentrations the surface viscosities were approximately constant – a result which resembles the behavior of the surface tensions of these soaps as shown in Figure 3. It is possible that fatty acid, produced by hydrolysis, solubilized in the soap micelles and contributed to the surface viscosity and foam stability.

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REFERENCES

1. C. Stiepel, Seifensieder Ztg. 41:347 (1914).
2. T. Sasaki, Bull. Chem. Soc. Jpn. 13:517 (1938).
3. G.D. Miles and J. Ross, J. Phys. Chem. 48:280 (1944).
4. E.J. Burcil, J. Colloid Sci. 5:42 (1950).
5. M. Nakagaki and K. Shinoda, Bull. Chem. Soc. Jpn. 27:367 (1954).
6. K. Ogino and M. Okamoto, Yukagaku, 24:474 (1975).
7. W.D. Harkins, et al., J. Chem. Phys. 42:897 (1938).
8. J.A. Kitchener, "Recent Advances in Surface Science," Vol. 1, Academic Press, 1964, p. 51.

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