Studies on Foams. VIII. Effects of Alcohols on the Foaminess of Soap Solutions

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In the previous papers in this series[1], the foaminess of aqueous solution has been explained, considering the work required to remove a unit area of adsorption layer. In the present report, this idea is extended qualitatively to three component systems, to elucidate the defoaming and foam-promoting action of alcohols on soap solutions.

As for the foaminess of ternary mixtures, systematic studies have not yet been made, except some solution containing electrolyte, or chemically complex substances, e.g. tannine, saponine, and proteins. Foaminess of aqueous solutions of two simple organic substances was studied by O. Bartsch[2] on nonanoic acid—ethyl alcohol—water, isoamyl alcohol—ethyl alcohol—water, isoamyl alcohol—benzyl alcohol—water, and *m*-cresol—benzyl alcohol—water, and studied by M. Nakagaki[3] on

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[1] M. Nakagaki, This Bulletin, **23**, 127 (1950); **24**, 269 (1951).

[2] O. Bartsch, *Kolloid-Beih.*, **20**, 1 (1924).

[3] M. Nakagaki, This Bulletin, **21**, 30 (1948); **22**, 21 (1949).

methyl alcohol—ethyl alcohol—water, and ethyl alcohol—grycerol—water. Few studies, however, on the effects of homologous series of alcohols to soap solution have been reported.

Experimental

Alcohols used were purified by fractional distillation using a glass packed column. A column of 2-ft in height was used for propyl-(b.p. 97.5°C.), and butyl-(b.p. 117°C.) alcohol, 3-ft column for isoamyl-(b.p. 131°C.), hexyl-(b.p. 156°C.), octyl-(b.p. 96°C./16 mmHg.), and decyl-(b.p. 101°C./5mmHg.) alcohol, and 1-ft column for nonyl-(b.p. 96∼96.5°C./8 mmHg.), and undecyl-(b.p. 120.5°C./8 mmHg.) alcohol. Heptyl alcohol was Kahlbaum's pure grade material. All these showed definite boiling points.

In fatty acids, caproic-(b.p. 109.5°C./20 mmHg.) and caprylic-(b.p. 120.5°C./9 mmHg.) acids were purified by fractional distillation through a 3-ft column. Capric-(m.p. 31.5°C.), lauric-(m.p. 44.5°C.), and myristic-(m.p. 54.1°C.) acids were Nihon Yushi's purest grade materials. All these showed definite melting points the same as or somewhat higher than those cited in the literature.

Soap solutions were prepared by the neutralization of above acids with carbonate free potassium hydroxide. Stock solution was about four times as concentrated as the critical micelle concentration (C.M.C.), and 2% excess (to soap) of potassium hydroxide was added to supress hydrolysis of soap.

Foaminess was measured by shaking test in a test tube of 30 cc. in capacity, 15 cm. in height, using 5 cc. of solution. The test tube was immersed in thermostat water. After the temperature became constant, it was taken out and shaken 20 times in 10 sec. Foam height was read after 5 sec (or 30 sec for stable foams) and foam stability was measured as the time required for the foam height to become a half of its original height.

Foaminess of soap solution and alcohol solution

Foaminess of some soap solutions are shown in Figs. 1∼3. Fig. 1 shows A_{30}-log C_s relations at 15°C., where A_{30} is the foam height after 30 sec. and C_s is the concentration of soap in mol./l. Fig. 2 shows $t_{1/2}$-log C_s curves at 15°C., where $t_{1/2}$ is the foam stability. Fig. 3 is A_{30}-log C_s relation at 35°C. The foaminess increases with the increase of concentration near to C.M.C. (shown in figures as vertical lines) and then becomes nearly constant or somewhat decreases. At least in dilute solutions near C.M.C., the foam formation of soap solution may be ruled not by micelles but by single ions, since the single ion concentration increases up to C.M.C., and then remains nearly constant. This conclusion coincides with that previously obtained by the studies on the foaminess of dye solutions[4]. Comparing homologous series of soaps, foam height becomes maxi-

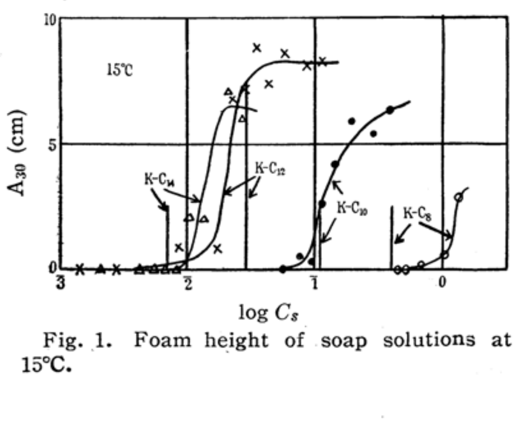

Fig. 1. Foam height of soap solutions at 15°C.

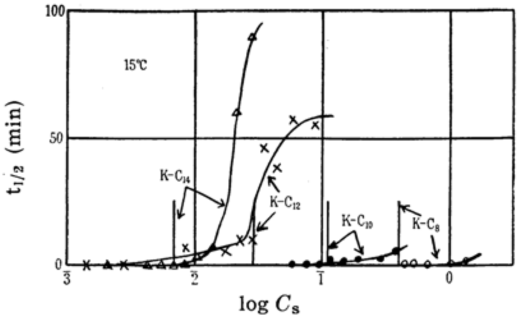

Fig. 2. Foam stability of soap solutions at 15°C.

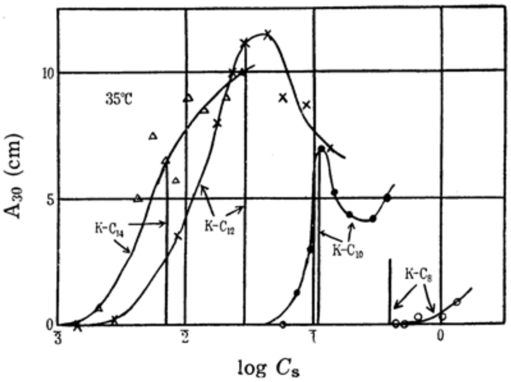

Fig. 3. Foam height of soap solutions at 35°C.

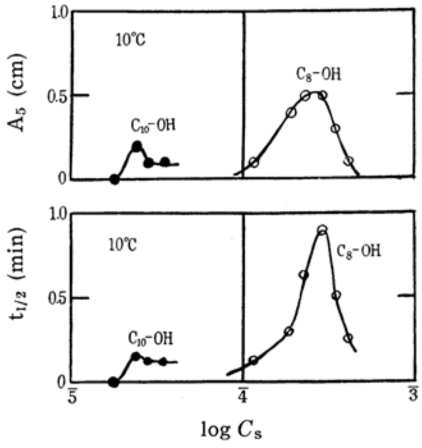

Fig. 4. Foaminess of alcohol solutions at 10°C.

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[4] M. Nakagaki, This Bulletin, **22**, 200 (1949); **23**, 47, 102 (1950).

mum at about K—C_{12}∼K—C_{13} at ordinary temperature.

Foaminess of aqueous solutions of *n*-octyl- and *n*-decyl alcohol are shown in Fig. 4. It is ascertained that the foaminess of alcohol solution is far poorer than that of soap solution. Foam height measured after 5 sec. is smaller than 0.5 cm. for alcohol solutions, while, for soap solutions, it is several cm. even after 30 sec. Foam duration is smaller than 1 min. for alcohols and far more unstable than soap solutions. O. Bartsch⁵⁾ reported that the foam formation of homologous series of alcohols showed a maximum at about C_5-OH, and then decreased as alcohols were higher. The results shown here are coincident with Bartsch's, since the higher C_{10}-OH shows smaller foaminess than the lower C_8-OH.

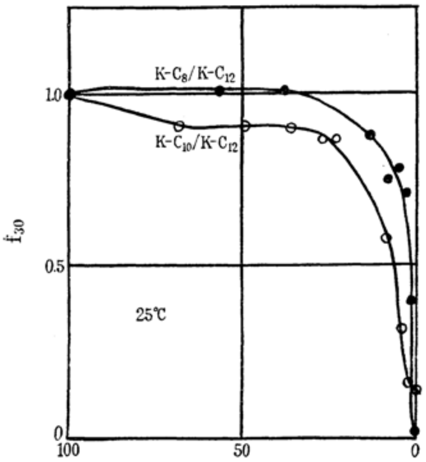

Fig. 5. Foam height of mixed soap solutions at C.M.C. (25°C.).

Foam height of mixed soap solution is measured at C.M.C., since the C.M.C. is considered as a corresponding state of soap solution. As in pure soap solution, C.M.C. can be determined also in mixed soap solution by the change in color of pinacyanol chloride⁶⁾. Fig. 5 shows the relation between f_{30} and the mol. percents of K-C_{12} in two soaps, where f_{30} is defined as the ratio:

$$f_{30}=A_{30}/A^0_{30} \qquad \cdots\cdots(1)$$

A_{30} and A^0_{30} are foam height after 30 sec. for mixed solution and pure K-C_{12} solution at C.M.C., respectively. Foaminess decreases with the increase of the added amount of K-C_{10} or K-C_8. This coincides with the fact that the foaminess of pure soap solution at C.M.C. decreases, as shown in Fig. 1∼3, in the sequence of K-C_{12}>K-C_{10}>K-C_8. Higher K-C_{12}, however, dominates the foaminess more influentially than lower K-C_{10} or K-C_8. This is explained by the theory that the nature of foam is dominated by molecules adsorbed at the surface, and the higher soap is adsorbed more strongly than the lower. This also explains the fact that higher K-C_{10} shows its effect at smaller addition than lower K-C_8.

Effects of Alcohols on Soap Solution

Effects of the homologous series of alcohols on the foam height of K-C_{10} and K-C_6 are measured, and f_{30} for K-C_{10} or f_5 (*f*-values after 5 sec.) for K-C_6 are shown in Fig. 6 as a function of $\log(C_{OH}/C_S)$. C.M.C. of mixed solution⁷⁾ is adopted as the concentration to be tested, since the C.M.C. is considered to be a corresponding state for mixed solution of soap and alcohol. C_{OH} and C_S are the concentrations of alcohol and soap in mol./1,

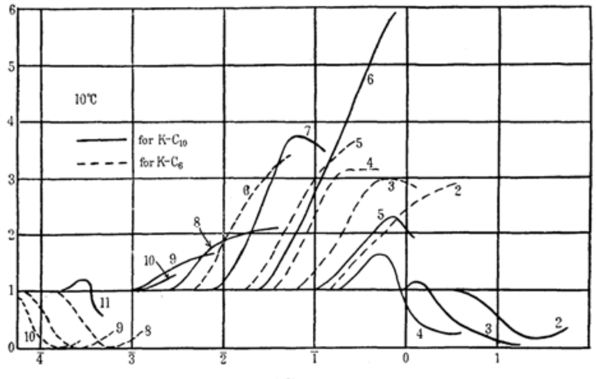

Fig. 6. Foam height ratio of soap-alcohol mixed solution at C.M.C. (10°C.). Numerals show numbers of carbon atoms of alcohol.

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5) O. Bartsch, *Kolloid-Z.*, **38**, 177 (1926).
6) K. Shinoda, *J. Phys. Chem.*, **58**, No. 7, (1954).
7) K. Shinoda, *J. Phys. Chem.*, In Press.

respectively. Added amounts of alcohols were smaller than the solubilities of each kind of alcohol in distilled water[8]. In soap solutions, the solubilities of alcohols increase by solubilization, so that the deposition of alcohol drops on the surface cannot be expected.

The effects of alcohols on K-C_{10} are, first, discussed. As for C_2-and C_3-OH, little effects is observed in small addition, but foam height decreases distinctly when the amount of alcohol is increased to $1\sim10^2$ times that of soap. Also for C_4-OH, foam height decreases when the mol. ratio is greater than 1:1, though, at a smaller amount of alcohol, foaminess somewhat increases. The decreases of foaminess of the solution by large addition of lower alcohol (but within the limit of their solubilities) is explained as follows. As stated before[1], the foaminess of a solution is large when the work required to remove a unit area of adsorption layer is large. As the large amount of alcohol is added, the hydrocarbon chain of soap molecule is dissolved easily in bulk solution owing to the oil-dissolving ability of alcohol. The work then, to pull the soap molecule into the solution becomes small, to decrease the foaminess. This effect may be, therefore, named as the defoaming by solvent effect.

For higher alcohols, C_5-$\sim C_{10}$-OH, foam height becomes large with the addition of alcohol, at the ratio of $10^{-3}\sim1$ alcohol to soap. This is compared with the antifoaming action shown as these alcohols are sprinkled upon froth. Such an antifoaming action is explained by S. Ross[9] with a mechanism that a portion of foam membrane is substituted by an oil drop, and this portion becomes thinner to break the foam by the spreading of oil on the surface. In this case, it is necessary for alcohol to exist as an oil drop. When the oil dissolves homogeneously into the bulk after the long lapse of time, the solution becomes again foamable. As shown in Fig. 6, homogeneous dissolution of these alcohols increase foam height. As the number of carbon atoms of these alcohols is somewhat smaller than that of soap, the surface activities of alcohol and soap are about equal, since the hydrophilic property of -OH is weaker than -COO^-. Then, a simultaneous adsorption takes place and mixed monolayer is formed, and the surface viscosity may become large, as Matalon and Shulman[10] have shown on the penetration of Na-cetyl sulfate to cetyl alcohol monolayer. The foam promoting action may be attributed to the increase of surface viscosity.

The foam promoting action becomes maximum, as shown in Fig. 6, at C_6-OH and then decreases for higher alcohols. Higher alcohols, C_8-$\sim C_{10}$-OH, having greater surface activity than soap, may expel some of the soap molecules from the surface to decrease the foam height. At last, C_{11}-OH shows a defoaming action in extremely small addition. This alcohol is thought to be much higher in its surface activity than soap, to be adsorbed preferentially to the surface. Then, the greater part of the adsorption layer may be occupied by alcohol molecules, at the addition of $10^{-4}\sim10^{-3}$ to soap. Since the foam height of alcohol is much smaller than soap, the foam height of the mixed solution becomes very small. This effect may be named as defoaming by preferential adsorption.

The defoaming or foam promoting action of alcohol to soap solution is determined by the balance of surface activities between alcohol and soap. The same effects as shown by higher alcohol to higher soap will be shown by lower alcohol to lower soap. Taking the difference of the number of carbon atoms in alcohol and soap as a measure of relative surface activity, alcohols, having $8\sim6$ carbon atoms less than soap, showed defoaming by solvent effect to K-C_{10}, $5\sim0$ less showed foam promoting action, and 1 or more larger showed defoaming by preferential adsorption. Then, as for K-C_6 soap, C_2-$\sim$ C_6-OH should show foam promoting action, and alcohols higher than C_7-OH should show defoaming by preferential adsorption. Fig. 6 shows that this estimation is in good agreement with the experiments. C_2-OH and C_3-OH which always showed defoaming effect to K-C_{10} now show foam promoting action to K-C_6, and C_8-, C_9- and C_{10}-OH which always showed foam promoting action now show defoaming action. These three kinds of effects, defoaming by solvent effect, foam promoting action, and defoaming by preferential adsorptions, are entirely different in their phenomenological features, but are closely related in their essential nature.

The defoaming action by preferential adsorption at extremely small addition seems important in its application. The mechanism of defoaming by higher esters, amines, amides, ethers and so on, may be explained by it.

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[8] K. Kinoshita and K. Shinoda, presented before the 7th Annual Meeting of the Chemical Society of Japan (1954) at Tokyo.

[9] S. Ross, *Rensselaer Polytech. Inst. Bull., Eng. Sci. Ser.,* No. 63 (1950).

[10] R. Matalon and J. H. Shulman, *Trans. Faraday Soc.,* **43**, 479 (1947).

Summary

Foaminess of soap solution increases with the increasing concentration up to the C.M.C., and then becomes nearly constant. In homologous series, K-C_{12} or K-C_{13} show the greatest foaminess at ordinary temperature. Foaminess of alcohol solution is much smaller than the soap solution. In homologous series of alcohols higher than C_5-OH, the higher foams poorer. For the mixed solution of two soaps, the foaminess becomes smaller when the ratio of lower soap is larger.

The effects of homologous series of alcohols on soap solution are measured and three types are observed: defoaming by solvent effect (by C_2-$\sim C_4$-OH for K-C_{10}) is observed at $\log C_{OH}/C_S = 0 \sim 2$; foam promoting action (C_5-$\sim C_{10}$-OH for K-C_{10} and C_2-$\sim C_6$-OH for K-C_6) at $\log C_{OH}/C_S = 3 \sim 0$: and defoaming by preferential adsorption (C_{11}-OH for K-C_{10} and C_8-$\sim C_{10}$-OH for K-C_6) at $\log C_{OH}/C_S = \bar{5} \sim \bar{3}$. These three effects are correlated with each other.

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