Studies on Foams. IX[1]. *Foaminess and Foam Stability of Polyvinyl Alcohol Solutions*

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(Received September 18, 1961)

Recently polyvinyl alcohol has been used widely as a synthetic protective colloid soluble in water, e. g., as an emulsifier, a dispersing agent and so forth. In this paper, the protective action for gas particles, that is, the foaminess and foam stability of polyvinyl alcohol solutions, will be studied.

Among the various methods for producing foams(2), such as the pneumatic method, agitation and boiling, the shaking method has thus far been used exclusively in the present series, but this method is not suitable for stable foams like that of polyvinyl alcohol solutions, because sometimes a vessel is filled with the foam after shaking. Therefore, instead of the shaking method, the pour method, which has also been used extensively to test the foaming properties of detergents, will be used in this paper.

Experimental

Materials. — As samples of polyvinyl alcohol, six specimens, Gohsenol GH-20, GM-14, GL-05, NH-20, NM-14 and NL-05, were used. These are the same as those used in previous experiments(3). The symbol G means partially saponified, (the saponification degree is 87.0～87.6%), and N means almost perfectly saponified (98.8～99.3%) specimens, while 20, 14 and 05 indicate polymerization degrees of about 2000, 1400 and 500 respectively.

A specimen of known weight was put into 800 ml. of distilled water in a flask and left alone at room temperature overnight. Then, after placing the flask in a water bath at room temperature, the bath was warmed up to boiling within 15 min. and kept boiling for 30 min. The flask was then taken out of the bath and cooled by dipping it in cold water, and the solution was transferred to a volumetric flask and made up to 1000 ml. From this original solution, solutions of the desired concentration were prepared by dilution.

Pour Test. — The apparatus used for the pour test is that prescribed by JIS (Japanese Industrial Standards)(4) and similar to that used by Ross and Miles(5). The apparatus consists of a pipet and a long, cylindrical, jacketted glass receiver. Both the pipet and the receiver are held vertically, and the receiver is kept at 30°C by circulating water from a thermostat. The orifice at the lower end of the pipet is made of a glass capillary tube 2.9 mm. in inner diameter, 7 mm. in outer diameter and 10 mm. in length. The content of the pipet is 200 ml. The upper end of the pipet is connected through a valve with a capillary tube to regulate the flow rate so that the 200 ml. solution in the pipet will fall through the orifice within 30 ± 1 sec. To make the pour test, 50 ml. of the solution is placed in the receiver and 200 ml. is run in from the pipet, the orifice of the latter being held exactly 90 cm. above the surface of the solution in the receiver. The height of the foam thus formed is read, as is its change with time, the time being recorded from just the moment when the pouring of the solution finishes.

Results and Discussion

Change of Foam Height with Time. — The height of the foam zone, A (mm.), was measured at various times, t (min.), for various concentrations of six polyvinyl alcohol solutions. For example, the relation between the foam height and concentration at various times is shown in Fig. 1 for GH-20. At first the curve has a very flat maximum at about 0.4 g./100 ml., but, during the destruction of the foam, another maximum appeared at about 0.1 g./100 ml. and the maximum point was shifted to 0.05 g./100 ml. in time. The similar pattern of GM-14 showed that a slight maximum, which had not been observed at first, appeared at about 0.05 g./100 ml. at $t \simeq 4$ min. and disappeared at $t \simeq 12$ min. Although no maximum was observed in this case at about 0.4 g./100 ml., the foam height at 0.6～1.0 g./100 ml. remained high until $t \simeq 9$ min. The behavior of GL-05 was similar to that of GM-14, except that a maximum of foam height appeared at about 0.01 g./100 ml. during the destruction of the foam. The foam formation of NL-05 was poor, but a maximum of foam height appeared at 0.1 g./100 ml. during the destruction of the foam. On the other hand, the foams of NM-14 and NH-20 were very stable, and the foam height scarcely changed within 35 min.

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1) The preceding paper is M. Nakagaki and K. Shinoda, This Bulletin, **27**, 367 (1954).

2) J. J. Bikerman, "Foams", Reinhold Publ. Corp., New York (1953), p. 33.

3) M. Nakagaki and A. Shimazaki, This Bulletin, **29**, 60 (1956).

4) JIS K 3361-1953 and JIS K 3362-1955.

5) J. Ross and G. D. Miles, *Oil and Soap*, **18**, 99 (1941); G. D. Miles and J. Ross, *J. Phys. Chem.*, **48**, 280 (1944).

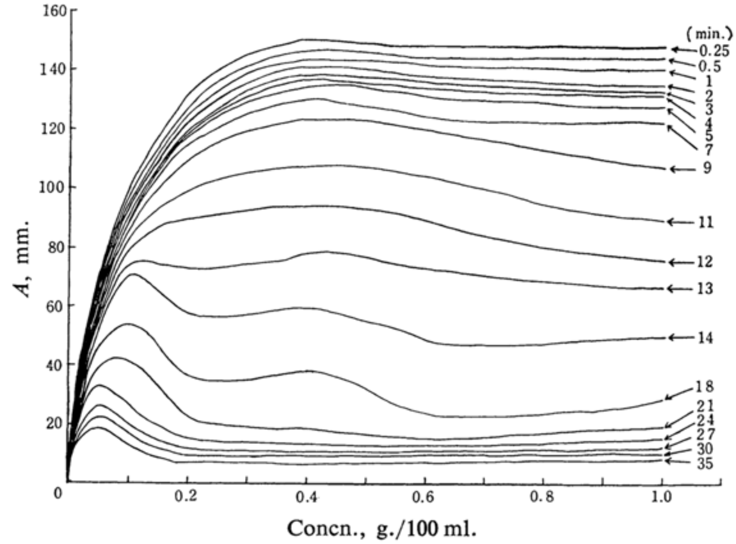

Fig. 1. The relations between foam height and concentration for GH-20 at various times.

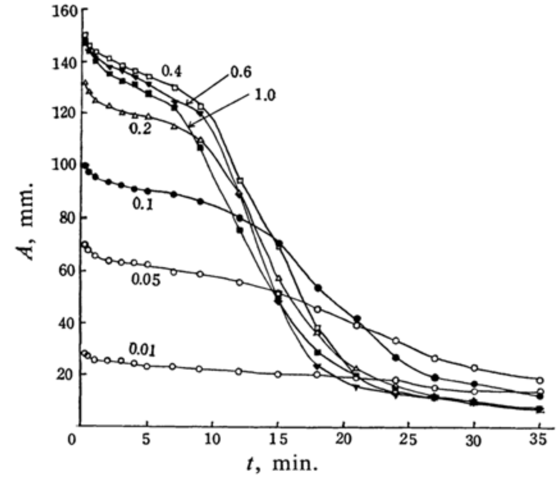

Fig. 2. Time dependence of foam height at various concentrations of GH-20.

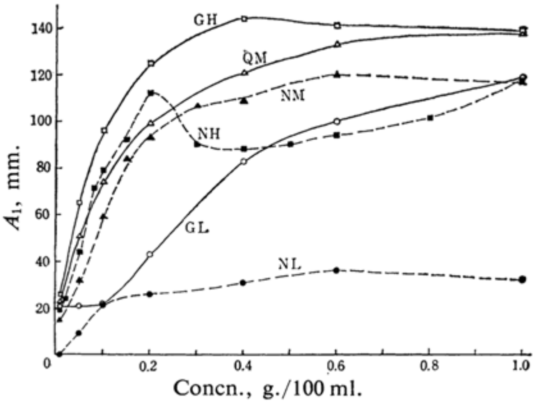

Fig. 3. Relation between foaminess and concentration.

The relationship between the foam height and the time at various concentrations is shown in Fig. 2 for GH-20 as an example. It can be seen that the foam height tends to show a stationary state after about 1 min., and then again rapidly decreases after a certain time. The first rapid decrease of foam height within 1 min. is due to the establishment of a better packing of bubbles in the foam zone, while the second rapid decrease corresponds to the collapse of the foam.

On the basis of these data, the foaminess, lingering fraction and half life of the foam of various polyvinyl alcohol solutions will be discussed.

Foaminess.—In order to show how well the solution foams, the concentration dependence of foaminess is compared in Fig. 3 for six polyvinyl alcohol specimens. As has already been shown above, the foam zone tends to show a steady state at about $t=1$ min., the collapse of foam being not yet serious at that moment. Therefore, the foam height at 1 min., A_1 (mm.), will be of an appropriate quantity to represent the foaminess. The relation between the foaminess, A_1, and the concentration is shown in Fig. 3.

Comparing the partially saponified (G series) and the perfectly saponified (N series) polyvinyl alcohols of the same polymerization degree, the foamer forms better than the latter; that is, GH > NH, GM > NM and GL > NL. Comparing, then, polyvinyl alcohols of the same degree of saponification, the foaminess is the greater, the greater the degree of polymerization; that is, GH > GM > GL and NH > NM > NL, except that NM foams better than NH at the concentration range between 0.26 to

1.0 g./100 ml. It is especially to be noted that the foaminess of NH has a maximum point at about 0.2 g./100 ml.

Lingering Fraction. — In order to compare the stability of foams, the quantity defined by the following equation and called, here, the "lingering fraction" after 35 min., L_{35} (%), is used.

$$L_{35}=(A_{35}/A_1)\times 100 \quad (\%) \qquad (1)$$

where A_{35} is the height of the foam zone remaining after 35 min. The concentration dependencies of the lingering fractions of six polyvinyl alcohol specimens are shown in Fig. 4. At concentrations greater than 0.2 g./100 ml., the foams of partially saponified polyvinyl alcohol solutions are very unstable and mostly collapse within 35 min., while the foams of the perfectly saponified polyvinyl alcohols NM and NH are very stable and practically do not collapse at all within 35 min. The foam of HL is not so stable, but it is still more stable than the partially saponified G specimens. Therefore, the lingering fractions are in the sequence of NH, NM > NL > GH, GM, GL. At concentrations smaller than 0.2%, the lingering fraction of the partially saponified G-series increases with the decrease in the concentration, while the lingering fraction of the perfectly saponified NH and NM decreases with the decrease in the concentration. Therefore, the foams of GH, GM and GL are the less stable, the higher the concentration, while the foams of NH and NM are the more stable, the higher the concentration. On the other hand, the foam of NL has its maximum stability at 0.1 g./100 ml.

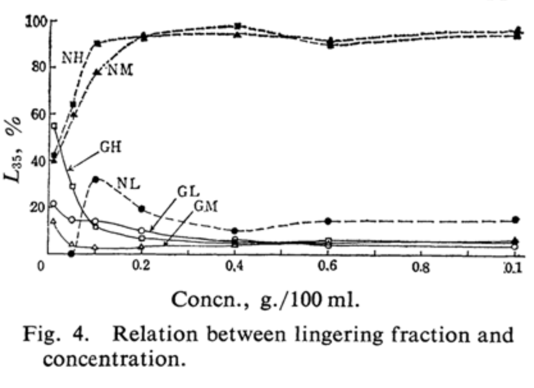

Fig. 4. Relation between lingering fraction and concentration.

Half Life.—Since the decrease in the foam height with time is generally in the manner as shown in Fig. 2, the half life $t_{1/2}$ (min.), defined as the time when the foam height becomes just one half of A_1, is another measure of foam stability. The half lives are shown in Fig. 5, except for NH and NM, the half lives of which can not be determined because the values are greater than 35 min. The curves of unstable GL, GM and GH foams, overlapped with each other in Fig. 4, have been separated clearly in Fig. 5. The features observed in both Fig. 4 and Fig. 5 are that the foam stability of GH, GM and GL increases with the decreasing concentration, and that the stability of NL reaches its maximum at about 0.1 g./100 ml. In Fig. 5, however, the points different from Fig. 4 are that half life of GH is greater than that of NL, GM and GL, and that the half life of GM is greater than GL. Consequently, the sequence of half lives is NH, NM > GH > (NL) > GM > GL, although the half life of NL varies greatly with the concentration.

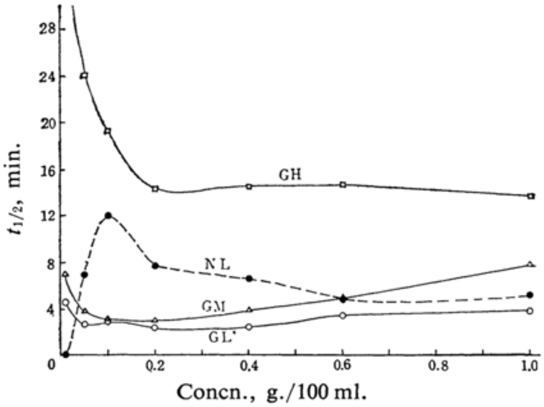

Fig. 5. Relation between half life and concentration. The half lives of NH and NM are not shown here.

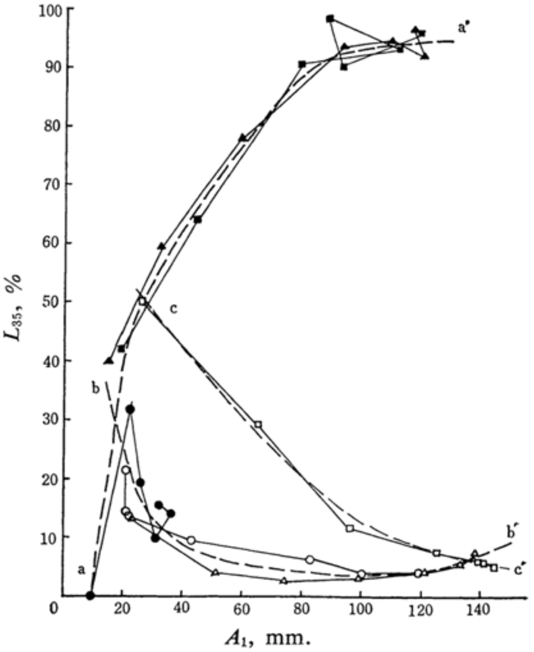

Fig. 6. The relation between A_1 and L_{35} for NH (■), NM (▲), NL (●), GH (□), GM (△) and GL (○).

Relation between Foaminess and Foam Stability.—In preceding papers of the present series[6], it has been observed that the foaminess and foam stability are parallel for at least unstable foams formed by shaking. In the case of stable foams of polyvinyl alcohol solutions formed by the pour method, however, the foaminess and foam stability are not always parallel. The relation between the foaminess A_1 and the lingering fraction L_{35} is illustrated in Fig. 6. In this figure, experimental plots are connected with straight lines in the order of concentration. Experimental plots for NH, NM and low concentration solutions of NL are located along a dotted curve, aa′, which indicates that the foam stability is the greater, the greater the foaminess. However, experimental plots for GH, GM, GL and high concentration solutions of NL are located along two dotted curves, bb′ and cc′, which indicates that the foam stability is the greater, the smaller the foaminess, although curve bb′ has a flat minimum and goes up again at high concentrations, at this range the foam stability being the greater, the greater the foaminess. The increase in foam stability at high concentrations of GM and GL has already been shown in Fig. 5.

Summary

The foaminess and foam stability of six polyvinyl alcohol solutions, GH-20, GM-14, GL-05, NH-20, NM-14 and NL-05, were measured by the pour test; the foaminess was represented by the height of the foam zone after 1 min., and the foam stability was represented either by the lingering fraction after 35 min. or by the half life of the foam.

The foaminess of the partially saponified polyvinyl alcohols was greater than that of the perfectly saponified ones of the corresponding molecular weights. Comparing specimens of the same degree of saponification, the foaminess was the greater, the greater the molecular weight. The foaminess was also the greater, the greater the concentration, except for NH, the fomianess of the latter showing a maximum at about 0.2 g./100 ml.

The foam stability of NH and NM was very large, but that of NL was small and showed a maximum at 0.1 g./100 ml. The foam stabilities of GH, GM and GL were small. Comparing the foaminess and the foam stability, these two quantities varied in a parallel manner in the cases of NH, NM, low concentrations of NL, and high concentrations of GM and GL, but in other cases they varied conversely.

The authors wish to thank Nippon Gosei Kagaku Kogyo Co., Ltd., which provided Gohsenols.

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