The Velocity of Ascending Air Bubbles in Aqueous Solutions of a Surface Active Substance and the Life of the Bubble on the Same Solution

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The surface tension and the adsorption from an aqueous solution of a surface active substance have been studied by many authors with refererence to the problem of surface activity. However, from the practical point of view, the properties of the system in the dynamic state[1-4] are more important than those in equilibrium, as in the cases of emulsification, dispersion, foaming, detergency and wetting. Unfortunately, the studies of such dynamic properties are very few, especially concerning the mechanism of surface activity. In this connection, it is important to study the phenomena of the ascending of air bubbles in an aqueous solution of a surface active substance.

Concerning these phenomena, an empirical formula for the velocity of bubbles ascending in a liquid and various effects upon the velocity, for instance, the effects of the size and the shape of the bubble, of the circulation of gas inside the bubble, of impurities in the solution, and of bubbles rising in succes-

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1) E. J. Burcik, *Colloid Sci.*, **5**, 421 (1950).
2) H. Lange, *Kolloid Z.*, **121**, 131 (1951).
3) D. G. Dervichian, *Z. f. Elektrochem.*, **59**, 290 (1955).
4) K. Schäfer, ibid., **59**, 273 (1955).

sion have been reported.[5-8] However, as to the actual conditions of the system under which the above formula can be applied or the effects appear, the results reported by vavious authors are not concorbant. Garner and Hammerton,[5] for instance, made an experiment with vaseline-contaminated bubbles and confirmed a retarding action of the hydrocarbon film on the bubble surface for the ascending velocity; Stuke[8] also reported an extreme sensitivity of the ascending velocity of bubbles to the presence of a surface active substance in the solution. However, the results and the explanations of these findings differ greatly. The present author has, therefore, made a similar experiment for the aqueous solutions of surface active substances and has also measured the density, the viscosity, the compressibility, the surface tension, and the stability of bubbles for the same solution in order to elucidate the phenomena.[9,10] The present report will discuss these results in detail.

Experimental, Results and Discussion

Materials.—For the study of the surface active substances, sodium dodecyl sulfate (SDS) and isoamyl alcohol were selected as two typical substances for producing stable and unstable aqueous foams respectively. SDS was prepared and purified by the usual method. In order to eliminate any possible error due to aging, the solution of SDS was prepared and kept overnight in a stoppered glass bottle before use. The sample of isoamyl alcohol was purified by the distillation of a commercial product over calcium oxide.

The Ascending Velocity of Bubbles in the Solution of a Surface Active Substance.—The velocity of an air bubble ascending in an aqueous solution of a surface active substance was measured in a glass cylinder (9 cm. in diameter and 50 cm. high) which had been filled with an aqueous solution of SDS or isoamyl alcohol to the depth of 40 cm.[9,10] By means of a capillary tube varying in size, air bubbles were produced at the center of the bottom of the cylinder and were made to ascend through the liquid. Special care was taken to keep the orifice of the capillary clean by drawing it anew in each run. Each bubble was made to ascend separately, allowing a time interval of at least three seconds between successive bubbles, this interval is needed to avoid the error due to the streaming bubble effect,[5] which will be discussed later. The uniform velocity portion of the bubbles was measured for the varying distances from 10 to 40 cm., to the accuracy of 1/10 sec.

Ascending air bubbles were also caught under a watch glass which was held near the surface of the solution, and their radii were measured by a microscope equipped with an ocular scale.

The measurements were mainly conducted at room temperatures ranging from 20 to 25°C. The temperature fluctuation of this range did not obscure the results obtained.

The ascending velocity, V, of the bubble in an aqueous solution of SDS is plotted against its radius, r, in Fig. 1. We can see in this diagram that in the region of $r<0.03$ cm. all of the plots for different concentrations of the SDS solution fall on one straight line, while in the region of $0.03<r<0.07$ cm. they break into separate and nearly straight lines of different inclinations for different concentrations of SDS.

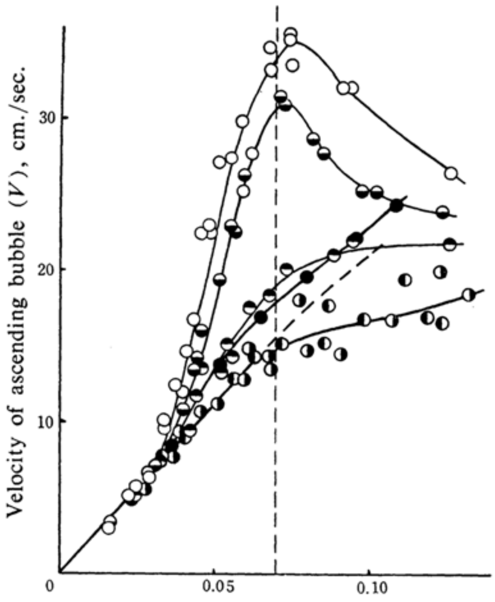

Fig. 1. Velocity of air bubbles ascending in the aqueous solutions of SDS.
○ Distilled water
◒ 1.0×10^{-6} molar aqueous SDS
◓ 1.2×10^{-5} molar aqueous SDS
◑ 1.0×10^{-4} molar aqueous SDS
◐ 1.0×10^{-3} molar aqueous SDS
● Rigid sphere in distilled water by empirical formula
Broken line; distilled water by Garner

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[5] F. H. Garner and D. Hammerton, *Chem. Eng. Sci.*, **3**, 1 (1954).

[6] K. L. Sutherland and M. Linton, *2nd International Congress of Surface Activity*, **1**, 494 (1957); S. G. Mason and F. D. Rumscheidt, *Colloid Sci.*, **61**, 238 (1961); W. L. Harberman and R. K. Molton, *NAVY Department, the David W. Taylor Model Basin Report 802 Sept.* (1953).

[7] J. M. Dallavalle, "Micromeritics," 2nd ed., Pitman Publishing Corp., New York (1952), p. 23.

[8] B. Stuke, *Z. f. Elektrochem.*, **59**, 281 (1955).

[9] T. Sasaki, Y. Miyazaki and S. Okazaki, *3rd International Congress of Surface Activity*, **2B**, 549 (1960).

[10] S. Okazaki, *Kolloid-Z. Z. Polymere*, **185**, 154 (1962).

The inclination is largest for pure water, decreases with the increase in the concentration of SDS, and is smallest for 10^{-3} molar and 10^{-4} molar SDS, which give a common straight line without a break point at $r=0.03$ cm. We can further confirm this by the visual observations that above a certain critical radius the bubble fluctuates and that all of the polts deviate from the lineality rather abruptly.* In our experiments this critical radius is about 0.07 cm. for all solutions, independent of their concentrations (as shown by a dotted vertical line in Fig. 1). In Fig. 2 a similar relation between V and r is shown for an isoamyl alcohol solution. All these findings are similar as a whole to what was briefly reported by Stuke,[8] while it differs in some respects from what was reported by Garner and Hammerton.[5]

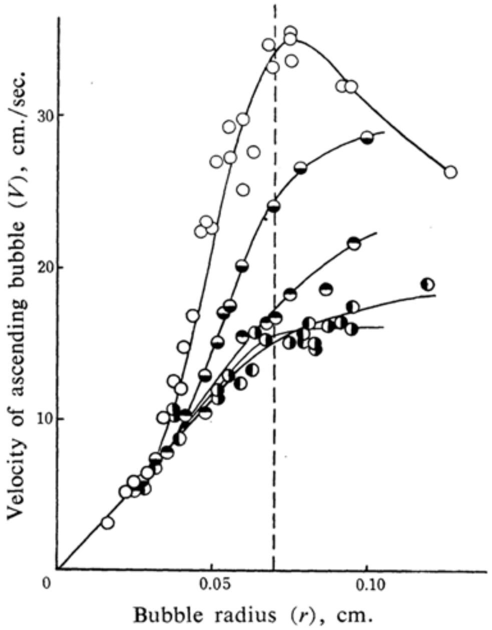

Fig. 2. Velocity of air bubbles ascending in the aqueous solutions of isoamyl alcohol.

- ○ Distilled water
- ◒ 0.5×10^{-3} molar aqueous isoamyl alcohol
- ◓ 1.0×10^{-3} molar aqueous isoamyl alcohol
- ◑ 1.9×10^{-3} molar aqueous isoamyl alcohol
- ◐ 5.0×10^{-3} molar aqueous isoamyl alcohol

It can be noticed at once that the ascending velocity of air bubbles in water is retarded by the presence of SDS, even in such a small concentration as 10^{-6} molar. This is rather surprising, considering the physico-chemical properties of the solution of a surface active substance in such a dilution where the properties are not practically different from those of pure water, as will be mentioned later. We can further see in Fig. 1 that a straight line expressing $V-r$ relations up to $r=0.03$ cm. for all concentrations of SDS solution, and up to $r=0.07$ cm. for 10^{-3} and 10^{-4} molar SDS solutions, together with the deviation from this linearity above $r=0.07$ cm. for the latter solutions, show an apparent coincidence with the results obtained by Garner[5] for the ascending bubble contaminated with vaseline, where he insists that the linearity indicates the spherical shape of the rising bubble and that the deviation from the linearity above $r=0.07$ cm. is explained by the deformation of the bubble due, in his case, to the hydrocarbon film on the bubble surface. However, before the results of his experiment are accepted, a marked difference should be pointed out between his results and ours for the rising velocity of air bubbles in distilled water, as is shown in Fig. 1. To check this point, the $V-r$ relation for a rigid spherical bubble will be established independent of these measurements.

The Ascending Velocity of a Rigid Spherical Bubble.—The $V-r$ relation for a rigid spherical bubble is calculated by using an entirely empirical formula[7] and is plotted as solid circles in Fig. 1. This curve coincides with the $V-r$ relation of a 10^{-5} molar SDS solution and is somewhat greater than those of 10^{-3} and 10^{-4} molar SDS. This may predict a possible deformation from a sphere of rising bubble of $r<0.07$ cm. in 10^{-3} and 10^{-4} molar SDS solutions. However, is also probable that the uncertainty is due to the empirical nature of the equation,[7] which has no adjustable constnats relating to the dimensions of the apparatus used. Thus, it was further necessary to make an experiment in our own apparatus to obtain an actual $V-r$ relation of the rising velocity of a rigid spherical bubble which exactly fits our experimental conditions.

For this purpose the present author has measured the falling velocity of rigid glass spheres, the density being 2.37, in water and in the solution under experimental conditions similar to those which held in the measurement of the rising bubble velocity, from which the rising velocity, V, and the radius, r, of an air bubble considered to be a rigid sphere, with the same drag coefficient and Reynolds number, were calculated.[11] The $V-r$ relation thus obtained is plotted with

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* The present discussion is mainly concerned with the phenomena occuring in the region of $r<0.07$ cm. in order to avoid the complications coming from the bubble fluctuation. The discussion is also restricted to the bubble radius far greater than about 0.008 cm., a point which corresponds to the upper limit of the Stockes velocity region of this system. Ref. 7, p. 24.

[11] Ref. 7, p. 19.

TABLE I. PHYSICAL CONSTANTS OF SDS SOLUTION

	Distilled water	SDS solution 10^{-5} mol./l.	Temp. °C
Density, g./cm^3	0.9983	0.9986	20
Compressibility, cm^2/dyn.	45.48×10^{-12}	$45.46\times{}^{-12}$	20
Viscosity, centipoise	0.855	0.855	20
Surface tension, dyn./cm.	73.3	73.3	16

circles and curve 1 in Fig. 3, where the V—r curves for the actual air bubble in the aqueous solution of SDS shown in Fig. 1 are reproduced.

Now in the range of $r<0.07$ cm., the V—r curve for the rigid spherical bubbles obtained from a glass sphere experiment and the curves for the actual air bubbles in concentrated aqueous solutions of 10^{-3} and 10^{-4} molar SDS coincide with each other, while the curve for 10^{-5} molar SDS is somewhat higher.

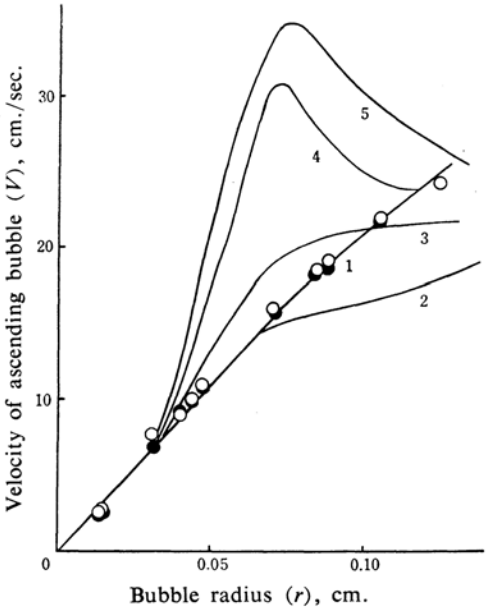

Fig. 3. Velocity of air bubbles ascending in the aqueous solutions of SDS.
(1) Rigid spherical bubble in distilled water (○) and in 1.0×10^{-3} molar SDS solution (●), actual air bubble in aqueous SDS of (2) 1.0×10^{-3} and 1.0×10^{-4} molar, (3) 1.2×10^{-5} molar, (4) 1.0×10^{-6} molar solution and (5) in distilled water.

This shows the rigid spherical nature of the rising bubble in 10^{-3} and 10^{-4} molar SDS. It may also be inferred that, though our V—r curves for 10^{-3} and 10^{-4} molar SDS actually coincide with Garner's curve (shown in Fig. 1), they do not represent the rising velocity in distilled water, as Garner insisted; rather, they correspond to the spherical bubble rigidly covered with the adsorbed film, and the effect of vaseline-contamination is considered to appear already in the region of $r<0.07$ cm. His explanation of the rising velocity of the bubble of $r>0.07$ cm. mentioned above may also be invalid. Since, as has been mentioned above, this critical radius of 0.07 cm. is largely independent of the SDS concentration and is equal to the value in distilled water, such a critical radius and the retardation of the rising velocity of bubbles beyond this radius is likely to be explained mainly by the hydrodynamic effect prevailing even in distilled water. The fairly good coincidence of our critical value with those of Garner⁵⁾ and Coppock¹²⁾, who used different substances or worked under widely differing conditions, also confirms this.

The Ascending Velocity of Bubbles in a Dilute Solution.—As for the extremely sensitive effect of 10^{-5} and 10^{-6} molar SDS solutions in retarding the ascending velocity of bubbles in the region of $0.03<r<0.07$ cm., the following factors may be pointed out in explanation;

(1) A change in the physical properties of the solution, a change which affects the hydrodynamic properties of the solution.

(2) The streaming bubble effect.

(3) The contamination or adsorbed film on the bubble surface.

As for 1, the density, velocity, compressibility, and surface tension were measured for these solutions and distilled water as shown in Table I. None of the data of this table can, however, in any way explain the retardation of the ascending velocity since there is no difference in the magnitude of these properties between pure water and a SDS solution.

Next we may take account of the streaming bubble effect, that is, the acceleration of an ascending bubble by another one rising just above it.⁵⁾ It has been reported that, at the speed of one bubble per second, the rising velocity of bubbles in a series is about three times as large as that of a solitary bubble,¹³⁾ and that the apparent increase in the rising velocity due to such an effect is less than 1%

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12) P. D. Coppock and G. T. Meikeljohn, *Trans. Inst. Chem. Engrs., London*, **29**, 75 (1951).

13) R. I. Datta and D. G. Napier, ibid., **28**, 14 (1950).

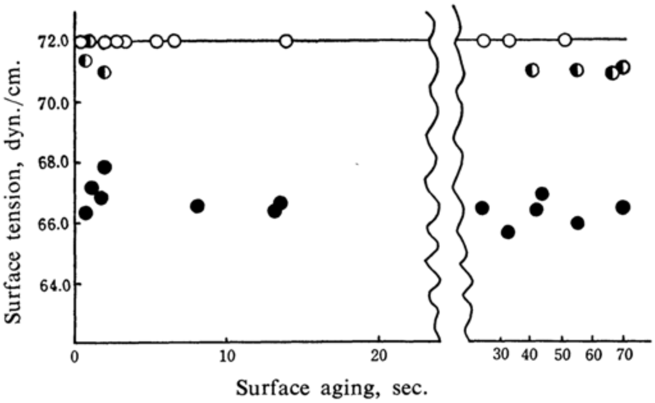

Fig. 4. Dynamic surface tension of the aqueous solutions of SDS.
○ 1.0×10^{-5} molar aqueous SDS
◐ 1.0×10^{-4} molar aqueous SDS
● 1.0×10^{-3} molar aqueous SDS

only when the time interval between two neighboring bubbles exceeds three seconds.(5) In our experiment, however, the time interval of the successive bubbles is longer than three seconds, as has been mentioned above, so the possibility of the streaming bubble effect can be eliminated.

We may, therefore, concentrate on the effect of the third factor. The effect of surface contamination is considered to appear in two ways, namely, by deforming bubbles and by inhibiting both the circulation of gas taking place inside and the liquid flow at the surface of ascending bubbles in pure water.(6) Of these two possibilities, the former seems not to occur in all solutions of the concentration studied, since in 10^{-3} and 10^{-4} molar SDS, the ascending bubble can be treated as a rigid sphere, as has already been mentioned, and deformation from the sphere, if any, should result in a $V—r$ line of the inclination less than this, as in the case of the retardation at $r>0.07$ cm. This is, however, just opposite to what was observed.

Therefore, the inhibition of gas circulation or liquid flow remains as the only possible explanation for the remarkable retardation of the ascending velocity of the bubble. Here, it is interesting to note that our $V—r$ curves between $0.03<r<0.07$ cm. are very similar in shape to what was obtained by Nawab(14) for the effect of the emulsifier film surrounding emulsion droplets upon the emulsion viscosity, where not only the viscosity of the liquid of the external phase but also that of the internal phase, namely, the emulsion droplets, have an influence upon the emulsion viscosity. Both of these phenomena may be similarly explained by the adsorbed film on emulsion droplets or bubbles, which acts to retard or inhibit the circulation or flow inside and at the surface of the droplets or bubbles. In the studies of circulation in sedimenting fluid spheres, the inhibition of the internal circulation by the addition of surface active impurities to the external phase has been confirmed, from which the rigid nature of the adsorbed film surrounding the liquid droplets has been inferred.(15) The movement inside the ascending bubble was reported to start in pure water at a bubble radius as small as 0.02 cm. and to reach a maximum speed at the radius of 0.125 cm.(5) Bond(16) calculated the effect of circulation inside the bubble in increasing the ascending velocity of a spherical bubble from a Stokes law velocity without internal gas circulation. The adsorbed film of a surface active substance is also inferred to dissipate the kinetic energy at the bubble surface through the relaxation effect.(5) A similar explanation for the retardation is possible by introducing the concept of surface transport proposed by Sutherland.(17) Thus, we are of the opinion that the increase in the ascending velocity beyond the velocity of a rigid spherical bubble in pure water at $0.03<r<0.07$ cm. is chiefly aided by the gas circulation inside the bubble, and that the sensitive action of retarding the rising velocity of bubbles in an aqueous SDS solution is to be ascribed to the adsorbed film of the surface active substance, which acts to reduce or inhibit both the movement of liquid at the surface and the circulation of gas inside the bubbles.

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14) M. A. Nawab and S. G. Mason, *Trans. Faraday Soc.*, **54**, 1712 (1958).

15) F. H. Garner and A. H. P. Skelland, *Chem. Eng. Sci.*, **4**, 149 (1955).

16) W. N. Bond, *Phil. Mag.*, (7) **4**, 889 (1927).

17) W. E. Ewers and K. L. Sutherland, *Austr. J. Sci. Res.*, **A5**, 697 (1952).

A similar explanation is possible for the system of an isoamyl alcohol solution, as may be understood from the similar V—r curves in Fig. 2.

Dynamic Surface Tension, Surface Viscosity, and Bubble Life.—As for the remarkable effect of SDS on the ascending velocity of the bubble, it has already been stated that all the static properties of the solution fail to explain the phenomena. Now let us take into account such surface properties as the surface viscosity or the dynamic surface tension, as Bryn and Garner suggested.5)

The dynamic surface tension was measured by using a stalagmometer.18) This enabled us to regulate the dropping speed and thus facilitated the detection of the aging of the solution which might occur during the bubble ascension. In order to estimate the surface tension of a relatively fresh surface of a solution, the age of the drop surface was decreased by increasing the dropping speed. Precautions were taken to eliminate the error due to the dropping speed by conducting a similar experiment with pure water. The results obtained are shown in Fig. 4. This figure again shows no difference in surface tension between pure water and 10^{-5} or 10^{-6} molar SDS, at least for the aqueous surface aged more than two seconds, though an apparent slight time effect can be seen for the 10^{-4} molar SDS solution. Concerning the effect of surface viscosity, we did not actually make any measurements, but its order of magnitude may also be very small for the 10^{-6} and 10^{-5} molar SDS solutions; at least this can be expected from the data of McBain.19) This quantity too, therefore, may not be sensibly different from that of water. Thus, we can find no difference in either the static or the dynamic properties of the system between pure water and 10^{-5} molar SDS to elucidate the phenomena as far as the above measurements are concerned.

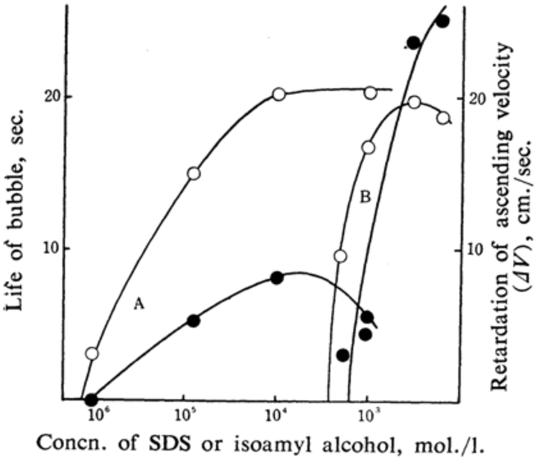

Fig. 5. Bubble life and retardation of the ascending velocity of bubbles.

○ $\Delta V = V_{\text{water}} - V_{\text{solution}}$ at $r = 0.07$ cm.

● Life of single bubble ($r = 0.07$ cm.) on surface of solution

A SDS solution

B Isoamyl alcohol solution

However, the ascending bubble has been estimated to have a surface zone of considerable thickness in which the viscosity of the liquid is not normal,20) and there is ample reason to believe that the surface viscosity or flow resistance near the bubble surface, though directly undetectable in magnitude, sensitively affects the ascending velocity of bubbles in water. In this connection it is important to measure the stability or the life of bubbles on the aqueous surface, which has also been known to be sensitively affected by the adsorbed layer of the surface.21) The life time of bubbles was measured in a glass vessel 10 cm. in diameter. As is shown in Fig. 5, the stability of bubbles at the surface of the SDS solution becomes perceptible and gradually increases when the concentration exceeds 10^{-6} molar, the whole appearance of the stability concentration curve being very similar to the concentration dependence of the retardation of the ascending velocity of the bubble, which is also shown in Fig. 5. It is known that the drainage of liquid in the bubble film is one of the factors determining the life time of bubbles.22) Particularly in our very dilute solution of SDS, where the surface tension is not sensibly different from that of pure water and where the strength of the bubble film due to the solute adsorption is almost imperceptible, the bubble life is affected chiefly by the rate of drainage, which is in turn influenced by the surface viscosity or the resistance to surface flow.17) Thus, the surface viscosity affects the rate of drainage and, therefore, the life of sessile bubbles at a liquid surface, just as it affects the velocity of the ascending bubbles. The common cause of resistance to flow and a similar high sensitivity to surface active substances makes the two phenomena very similar, as may be seen in Fig. 5.

The probable mechanism of the resistance to flow may be such that, on the surface of

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18) C. G. McGee, in the textbook of J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, London (1961), p. 172.

19) A. G. Brown, W. C. Thuman and J. W. McBain, *J. Colloid Sci.*, **8**, 491 (1958).

20) J. C. Henniker, *Rev. Modern Phys.*, **21**, 322 (1949).

21) J. T. Davies, *2nd International Congress of Surface Activity*, **1**, 241 (1957).

22) S. Ross and G. J. Young, *Ind. Eng. Chem.*, **43**, 2520 (1951).

the ascending bubble, there may occur some uneven distribution of the adsorbed solute molecules of the surface active substance arising from the sweeping action of liquid flow around the ascending bubble. Accordingly, during ascension, a surface pressure difference, though slight, is produced on the bubble surface, which sets up the force to oppose the liquid flow near the bubble, as Sutherland pointed out in terms of the surface transport.[17] This may cause a decrease in its ascending velocity.

Here one should further refer to the electrophoretic velocity of a highly purified paraffin oil (Nujol) droplet in water.[23] In has been reported that the mobility of Nujol in water alone is $-4.35\,\mu$/sec./V./cm., but that the addition of as little as $7.5\times10^{-5}\%$ of pyridinium salt reduces the mobility to zero. In spite of this marked change in mobility, the lowering of the interfacial tension is appreciable at a concentration below 0.01% of this salt. This suggests the important rôle of the change in a diffuse electrical double layer surrounding the oil droplet. In our case of an ascending bubble, similar conditions may also be considered to exist which act to retard its motion. However, the effect of inorganic ions on the ascending velocity of the bubble is rather opposite in its action in this respect, at least so far as our experiment is concerned.[10] Further detailed studies should be made of this point.

Summary

1) The velocity of an air bubble ascending in water is remarkably retarded by the addition of a minute amount of sodium dodecyl sulfate (SDS) or isoamyl alcohol. With an air bubble with a radius ranging from 0.03 to 0.07 cm., the decrease in velocity is perceptible even in a 10^{-6} molar SDS solution, while it tends to a limiting value in 10^{-3} and 10^{-4} molar SDS solutions, where the rising velocity is about half as large as that in pure water.

2) To elucidate this retardation, the static properties of the solution, such as surface tension, density and compressibility, and the dynamic properties, such as viscosity and the change in surface tension with time, have been measured. However, no difference could be found in these properties between pure water and a 10^{-5} molar SDS solution to account for the retardation phenomena.

3) The rising velocity of a bubble considered to be a rigid sphere calculated by using an empirical formula fails to explain the results, since the formula does not fit our experimental conditions. The rising velocity of a rigid spherical bubble calculated from the observed data of a falling velocity of glass spheres in water in our apparatus is found to be in good agreement with that in 10^{-3} and 10^{-4} molar SDS solutions.

4) It has been concluded that, in all concentrations of the solution studied and for the bubble with a radius less than 0.07 cm., the bubble rises as a sphere and that the air circulation inside the bubble is closely related to the rising velocity of the bubble. The air circulation, which is strongest in the rising bubble in pure water, is hindered in 10^{-5} and 10^{-6} molar SDS solutions by the formation of an adsorbed film of SDS on this bubble, and the rising velocity is also thereby retarded. The circulation is actually suppressed, and the bubble rises as a rigid sphere in 10^{-3} and 10^{-4} molar SDS solutions. The retardation of the rising velocity of bubbles with radii larger than 0.07 cm. is due to the deformation of the bubbles from a sphere.

5) The life time of bubbles on an aqueous solution is affected by the surface active substance as sensitively as in the case of the effect of the same substance on the velocity of the rising bubble. Both phenomena are explained by the common factor of the retardatoin of the flow around the bubble surface.

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[23] J. Powney and L. J. Wood, *Trans. Faraday Soc.*, 37, 152 (1941).