THE COMPOSITION OF THE SURFACE LAYERS OF AQUEOUS AMYL ALCOHOL

BY CLARA C. BENSON

In October, 1900, J. von Zawidski[1] published the results of some experiments on the composition of the foam of aqueous solutions of hydrochloric acid and of acetic acid which indicated that the concentration of the acid in the surface layers of these solutions was slightly greater than in the rest of the liquid. In order to obtain a durable foam a small quantity of saponin was mixed with the solutions.

It was suggested to me by Dr. F. B. Kenrick that I should examine a dilute solution of amyl alcohol which itself produces a sufficiently durable foam, the concentration of which can be estimated by measurements of surface tension.

Since these experiments were begun, von Zawidski has published the results of measurements[2] with dilute saponin solutions, the amount of the latter substance being determined by the refractive index. His measurements show that in this case also the surface layers are more concentrated than the rest of the liquid. These experiments with amyl alcohol were nevertheless continued in order to ascertain whether the amyl alcohol behaves in the same way.

The solution of amyl alcohol in water was prepared by making up 4 cc of the alcohol (a preparation from Kahlbaum, which had been re-distilled) to a volume of 1 liter. About 40 cc of this solution were shaken vigorously in a separating funnel holding about 200 cc of the liquid, and as much as possible of the drainings from the walls of the vessel were run out through the tap. The froth left in the bulb settled to a clear liquid after a few minutes and was run into a small stoppered bottle.

[1] Zeit. phys. Chem. 35, 1 (1900).
[2] Zeit. phys. Chem. 42, 1 (1903).

The compositions of the various solutions were determined from the number of drops which fell from a pipette provided with a capillary tube, ground to a flat surface at the tip. While this method requires certain corrections in order to determine actual surface tensions, it is quite satisfactory for comparative measurements when the differences in value are slight.[1] The method, moreover, gives very accurate determinations of concentration since a slight alteration in the amount of amyl alcohol, in the neighborhood of the concentration used, corresponds to a considerable change in surface tension.

The pipette used in most of the measurements held about 30 cc. It was kept at constant temperature by immersion in the vessel A (Fig. 1), which was connected by a large siphon and

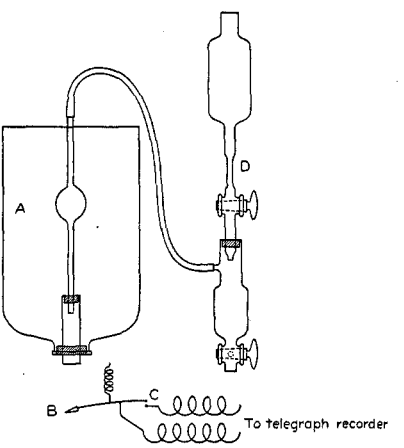

Fig. 1.

pump to a water-bath whose temperature was maintained at 31 degrees. By the arrangement shown, the drops were formed in a space whose temperature was the same as that of the rest of the liquid. After closing the lower end of the pipette by a rubber cap attached to a glass rod, the solution to be analyzed was run in quickly from the stock, which had been kept in the water-bath, and the whole allowed to stand for a few minutes in order to bring the solution to the temperature of A, which was

[1] Duclaux. Ann. Chim. Phys. (5) 13, 82 (1878).

0.3 degree below that of the bath. This temperature did not vary more than 0.2 degree during the entire measurements.

In order to obtain accurate results the rate of dropping must be slow and constant. The flow of liquid was regulated at first by using a pipette with a constriction in the capillary tube, but it was found that this was easily stopped with particles of dust. The pipette used in these measurements, therefore, had no constriction, but the rate was regulated by connecting the top of the pipette by fine rubber tubing to a small air reservoir into which glycerine was dropping (see Fig. 1). Owing to the viscosity of the glycerine, a slow enough rate was obtained even with fairly large tubing at D, and the difficulty of stoppage by dust was avoided. With this arrangement the rate of flow could be kept constant to within a few percent.

A record of the number of drops was kept by a mechanical counter, which is a modification of that used by Duclaux. The impact of the drop on the inclined plate, B, broke an electrical current at C, which actuated a telegraph recorder, thus leaving a mark on a moving tape.

That both temperature and rate of flow affect the number of drops will be seen from the following tables :

TABLE I.

INFLUENCE OF TEMPERATURE

Amyl alcohol solution : 4 cc in 1 liter ; rate : 36 drops per minute. Volume of liquid : 30 cc.

Temperature	Number of drops
30.7°	693
36.7°	700
36.7°	699.5

A rise of 1 degree causes an increase of 0.16 percent in the number of drops.

An increase of 50 percent in rate decreases the number of drops by about 1 percent.

In the experiments (Table IV) for the comparison of the

foam with the liquid the alterations of temperature and rate of dropping were therefore negligible in their effect on the number of drops.

Another possible source of error lay in the fact that the foam might become more concentrated by evaporation. In order to investigate this point, a solution was set aside to evaporate at the room temperature for about three days, after which time its composition was compared with that of the original solution. (See Table III.)

TABLE II.

INFLUENCE OF RATE OF DROPPING

Amyl alcohol solution : 4 cc in 1 liter ; temperature : 30.7°.
Volume of liquid : 8.8 cc.

Drops per minute	Number of drops
44	212
35	212
52	210
8 to 17	217
Volume of liquid : 30 cc.	
32	693
36	693
75	678

TABLE III.

EFFECT OF EVAPORATION ON CONCENTRATION

Amyl alcohol solution : 4 cc in 1 liter ; temperature : 30.7° ; rate : 30 drops per minute

Pct. loss in weight by evaporation	Volume of liquid	Number of drops original solution	Number of drops evaporated solution
11	11 cc	270	213
12	30 cc	694	548

It is clear, therefore, that any change in composition due to evaporation would be in the opposite direction to that actually observed. (See Table IV.)

In the above table, Expt. No. 10 was made with the origi-

nal (unfrothed) liquid; Nos. 6, 11, 13, and 15 were made with the liquefied foam; the rest with the liquid from which the foam had been separated. In Expt. No. 15 greater care was taken to thoroughly remove the drainings from the foam and for this reason, no doubt, its composition shows a greater deviation from that of the liquid than is seen in the other cases.

TABLE IV.

COMPARISON OF LIQUID AND FOAM

Amyl alcohol solution: 4 cc in 1 liter; temperature: 30.7°

Number of experiment	Volume of liquid	Drops per minute	No. of drops Liquid	No. of drops Foam	Comp. of foam cc per liter
1	8.8 cc	34	212	—	—
2	"	34	213	—	—
3	"	35	212	—	—
4	"	44	213	—	—
5	"	44	213	—	—
6	"	44	—	214.5	4.12
7	"	44	212	—	—
8	30 cc	32	693	—	—
9	"	32	693.5	—	—
10	"	33	694	—	—
11	"	33	—	697	4.086
12	"	34	694	—	—
13	"	33	—	699.5	4.135
14	"	36	693	—	—
15	"	36	—	703	4.235

It is therefore evident that the foam from amyl alcohol contains a larger proportion of the alcohol than the rest of the liquid. The composition of the foam, calculated by the use of Duclaux's measurements on the surface tensions of different solutions of amyl alcohol, is given in the last column, Table IV. No difference could be observed in the composition of the original solution and the liquid from which the froth had been separated.

In conclusion I wish to express my indebtedness to Dr. F. B. Kenrick for his assistance and interest in these experiments.

University of Toronto,
Chemical Laboratory,
May, 1903.