RHYTHMIC PRECIPITATES. III. ON THE EFFECTS OF THE PRESENCE OF ACIDS, ALCOHOLS, OR AMINO-ACIDS IN GELATINE JELLIES.

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In the previous communication,[1] the author reported the effects on the rhythmic precipitates of light and the aging of gel before the superposition of the diffusing electrolyte on it. In the present paper the experimental results are described on the effects of the presence of some fatty acids, alcohols, and amino-acids in the gelatine jellies. It is a known fact that the addition of a small quantity of a capillarily active material such as fatty acids or alcohols decreases the surface tension of water, while the addition of some amino-acids increases it. It may be interesting, therefore, to study the effects of these substances on the bands of rhythmic precipitates.

Ordinary rhythmic precipitates of silver chromate in gelatine jelly have been tested, It is desirable, in the present experiment, that impurities contained in the gelatine should be as little as possible. Powdered "Gelatine white" from Merck has been dialyzed for about five days in distilled water. In this dialyzed gelatine the secondary rhythmic precipitates in gelatine-silver chromate system has no more been observed which were pointed out as the chloride and phosphate of silver.[2]

The gel was prepared by mixing equal volumes of the sol containing 0.2 per cent. potassium dichromate and the aqueous solution of the acid or alcohol. After 24 hours the 20 per cent. silver nitrate solution was superposed on the gel. Caution was taken so that in one series of experiments the sol used in preparing the jelly should be the same and the test-tubes should be of possibly equal diameters. Moreover, the heights of the jelly and the upper electrolyte in each test-tube were made as equal as possible.

The Effect of Fatty Acids. According to Traube's rule, the larger the molecular weight of the fatty acid in water is, the greater the decrease of surface tension of water is, provided the concentrations of the acid being the same. Propionic, butyric, capronic, and caprylic acids have been tested, and the gelatine jelly containing 0.05 mol. of the fatty acid per litre has been used. The results of the experiments are as follows:

(1) Isemura, this Bulletin, **8** (1933), 108.

(2) Hedge, "Liesegang Rings," (1932), 23. Riegel and Reihard, *J. Phys. Chem.*, **31** (1927), 713. Schleussner, *Kolloid-Z.*, **31** (1922), 347; **34** (1924), 338.

No acid: well-known rhythmic precipitates were observed.
Propionic acid: no band or a few faint bands were observed.
Butyric acid: no band or a few faint bands were observed.
Capronic acid: a few bands consisting of large crystals were observed.
Caprylic acid: two kinds of bands were recognized.

In the cases of propionic and butyric acids, bands did not appear in general. Under certain circumstances, however, a few bands have been observed near the contact surface with the upper electrolyte. In the case of capronic acid, several bands were observed, each of which was composed of considerably large crystals. This was caused, probably, by the deposition of silver chromate crystals on the initially formed bands of the silver soap. At first, white silver capronate in small granules deposits into bands, which then are coated gradually with brick-red silver chromate. The same process has been recognized much more distinctly in the case of caprylic acid. The solubility of caprylic acid in water is small, and the solution containing 0.05 mol. per litre is not homogeneous, but forms an emulsion. In this case, first the long orange layer of silver chromate deposited and in this layer the banding of comparatively large crystals were observed, which is considered silver caprylate. In the lower part of the test tube banding of white granules appeared, which then changed into brick-red in colour in the course of time. It is conceived that the granules of silver caprylate were coated with silver chromate.

In general, the addition of the fatty acid to the gel makes the particles of silver chromate larger. The greater the number of carbon atoms in fatty acid is, the more remarkable this effect is. From Traube's rule, it is known that the higher the fatty acid is in the homologous series, the greater depression is caused in the surface tension of the solution. It may be supposed that from the jelly of lower surface tension the deposition of crystals is easier than from the jelly of higher surface tension. By the addition of a fatty acid, therefore, the supersaturation limit of crystallization of silver chromate falls steeply, and this makes the banding impossible. But, on the contrary, the solubility of the silver salt of the fatty acid decreases with the increase in the number of carbon atoms in the acid. So the banding of silver soap occurs and that of silver chromate appears as a secondary phenomenon.

The Effect of Alcohols. The experiments on the effects of the addition of alcohols to the gel have been undertaken with methyl, ethyl, propyl, and butyl alcohols. The number of bands was examined in about 4 per cent. gelatine jellies containing 0.25 mol. of alcohol per litre. The concentrations of upper and lower electrolytes were the same as in the experiments with

acids. It was observed that the number of bands did not change on addition of the alcohol to the gelatine jelly. However, when the concentration of the alcohol in jellies was 0.5 mol. per litre the effect of the alcohol became distinct. The results are shown in Table 1.

Table 1.

Dispersion medium	Number of bands formed	
	alcohol 0.25 mol./l.	alcohol 0.5 mol./l.
no alcohol	19	19
with methyl alcohol	19	25
with ethyl alcohol	18	25
with propyl alcohol	19	26
with butyl alcohol	19	—

Table 2.

Conc. of methyl alcohol mol./l.	Number of bands formed
0	28
0.25	28
0.50	30
1.00	31
2.00	33

The effect of the concentration of methyl alcohol in the jelly on the number of bands is shown in Table 2.

Thus, the higher the concentration of the alcohol is, the greater the number of bands formed. It was observed that the distance between the upper surface of the jelly and the last-formed band was shorter in the jelly with higher concentration of the alcohol.

In short, the addition of the alcohol to the jellies makes the crystallization of silver chromate easier than without the alcohol. This may be caused, on one hand, by the depression of the surface tension of the jelly, and, on the other hand, by the depression of upper limit of supersaturation of silver chromate crystals, owing to the less solubility of gelatine in the aqueous solution of the alcohol, that means the less protective action of gelatine than in water. The number of bands, therefore, must increase on addition of the alcohol.

The Effect of Amino-Acids. The surface tension of the aqueous solutions of some amino-acids were measured by Ito.[1] He showed that glycine and alanine, unlike other amino-acids, increased the surface tension of water. So the effect on banding of silver chromate may be in the opposite direction to the case of the alcohol, that is to say the distance between bands will be wider and the number of the formed bands will be smaller.

(1) Ito, *Nippon Nogei-kwagaku-kaishi*, **6** (1930), 178, 930.

This was verified by the experiments. One of the results obtained is tabulated in Table 3.

Table 3.

Dispersion medium	Number of bands formed
without amino-acid	28
with 0.05 mol. glycine per litre	24
with 0.05 mol. alanine per litre	26

Glycine increases the surface tension more than alanine does, so the effect of the former is more remarkable than that of the latter.

The Formation of Rhythmic Precipitates of Silver Soap. It has been described in the preceding paragraph that the bands of silver capronate or silver caprylate accompanies the silver chromate bands. Moreover, the author succeeded in obtaining the rythmic precipitates of silver soap only. Well dialyzed gelatine, freed from chlorides and phosphates, was dispersed into 4 per cent. sol, the acid was added, and then the whole was allowed to set. The concentration of the acid was between 0.05 and 0.1 mol. per litre. In the case of caprylic acid, an emulsion was formed. After setting the gel, 20 per cent. silver nitrate solution was poured on it. White thin bands appeared. The photograph shows an example of the bands of silver capronate. Thus two new examples of rhythmic precipitates were found, namely silver capronate and silver caprylate in gelatine jellies.

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