CXLIV. THE ACTION OF MONOHYDRIC ALCOHOLS ON GELATIN GELS

By JOHN ADAMSON SAUNDERS

*From the Department of Physiology and Biochemistry, University of Durham
College of Medicine, Newcastle-upon-Tyne*

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It is well known that ethyl alcohol dehydrates gels. In the experiments reported here, the action of methyl, ethyl, *n*-propyl, *n*-butyl and *isobutyl* alcohols on gelatin gels has been studied.

EXPERIMENTAL

Preparation. Coignet's Gold Label gelatin was dissolved in boiling water with stirring and then cooled in a refrigerator. Pieces were cut to a definite shape and weighed in a weighing bottle.

Dry weight was determined by heating samples of the gel to constant weight at 110°. Following Duke-Elder & Davson [1935] the dry weight of some of the gels was determined after treatment with ethyl alcohol. The dry weight of these alcohol-treated gels was greater by 2-5 % than that of untreated gels, and this increase in weight was due to the incomplete removal of alcohol by heating to 110°. The alcohol-treated gels do not melt on heating, but swell, their previously concave sides becoming convex. On section the outer walls are hard and tough, containing almost all the solid. When these gels are immersed in water, alcohol diffuses out and can be detected (after distillation) by its reducing action and by the formation of iodoform.

Degree of swelling. The pieces of gel were immersed in a measured quantity (usually 50 ml.) of the alcohol at room temperature, removed at intervals, dried superficially with filter-paper and weighed in a weighing bottle [Jordan-Lloyd, 1931]† In order to attain a true equilibrium between the pure alcohol and the gel, the alcohol which had been diluted by diffusion of water from the gel was replaced by fresh alcohol after each weighing. The figure used as a measure of swelling was obtained by dividing the weight of a gel by its calculated dry weight and multiplying by a hundred.

RESULTS

The gels rapidly decreased in weight in each of the five alcohols used, reaching a constant weight in 2 or 3 days. Those treated with methyl or ethyl alcohol became hard and cloudy in appearance, while those treated with propyl or butyl alcohol became extremely hard and quite opaque.

On reswelling in water, the gels increased in weight rapidly for 3 days and thereafter more slowly and at a rate similar to that of untreated gels in water (Fig. 1). The reswollen gels were softer and more friable than untreated ones and those treated with propyl or butyl alcohol did not regain their original weight in 17-18 days.

During dehydration bubbles of gas formed under the pieces of gel, especially in ethyl or propyl alcohol. This gas was found to be a mixture of oxygen, carbon dioxide and nitrogen and was probably air liberated from the alcohol by dilution with water which had diffused out from the gels.

On reswelling in water the alcohol diffused out from the gel and could be detected in the surrounding water, showing that dehydration is accompanied by the passage of alcohol into the gel.

Fig. 1.

Shape and size of the gel

Table I shows that swelling in ethyl alcohol varies slightly with the shape of the gel, inversely as the thickness and directly with the area of cross-section. The equilibrium swelling appears to bear no relation to either the volume, total surface or to the ratio volume/surface.

Table I

Initial swelling 1090. Treated with 93 % ethyl alcohol

Cross-section	Thickness mm.	Swelling at equilibrium
Circle, diameter 47 mm.	36	258
47 mm.	27	263
47 mm.	18	280
47 mm.	10	308
Square, side 10 mm.	10	196
20 mm.	10	237
40 mm.	10	298

Mixtures of ethyl alcohol and water

The swelling of the gels at equilibrium increased regularly as the amount of alcohol decreased to 20 % by volume. With concentrations of alcohol between 10 and 20 %, the weight of the gel decreased for 24-48 hr. and thereafter increased, while with 5 % alcohol there was no appreciable decrease in weight (Fig. 2).

Fig. 2.

Preliminary treatment

The effect of swelling in water or treatment with dilute alcohol solutions before dehydration by ethyl alcohol is shown in Table II. It is evident that swelling in water results in a proportionate increase in the equilibrium weight in

Table II

Initial swelling 1260. Dimensions 30.30.10 mm. Treated with 93% alcohol

Previous treatment	Swelling		Before/after
	Before	After	
None	1260	308	4.1
Water	1290	312	4.1
"	1345	325	4.1
"	1355	340	4.0
"	1392	346	4.0
"	1430	342	4.2
5% alcohol	1848	539	3.4
10% "	1521	494	3.1
15% "	1220	460	2.7
20% "	962	366	2.6
25% "	790	296	2.7
50% "	512	284	1.8

alcohol, but that this is not the case when the preliminary treatment is with alcohol-water mixtures. In this case the equilibrium weight is progressively greater than would be expected with an untreated gel or with one swollen in water.

DISCUSSION

Weber & Lederer [1936] published experiments similar to those reported here. They used a constant volume (50 ml.) of gelatin gel and the same volume of liquid superimposed on the gel set in a dish, measuring the volume of liquid at intervals. It is difficult to make deductions from their results as to the effects of pure alcohols on the gels because of the fact that they did not renew the alcohol at all.

This is especially marked in the case of the less soluble butyl alcohols which, according to Weber & Lederer's results have practically no dehydrating action, while Fig. 1 shows that they are as powerful as propyl alcohol. Also the increase in volume of the supernatant fluid cannot be taken as a quantitative measure of the decrease in volume of the gel because of the change in volume which occurs when water from the gel mixes with the alcohol. This effect, while small in relation to the total volume of liquid, is appreciable compared with the change in volume; e.g. if 18.7 ml. of water mix with 50 ml. of ethyl alcohol, the contraction is 2.1 ml., so that the apparent shrinkage of the gel is 16.6 ml. against a true decrease of 18.7 ml., a difference of 11 %.

Jordan-Lloyd [1931] showed that the thickness of a gel has an effect on its swelling in water and salt solutions similar to that shown here in connexion with dehydration by alcohol. Her experiments also showed the effect of the concentration of the gel at setting on the amount of water imbibed, either with or without previous drying. The amount of swelling varied inversely as the concentration of the gel. She deduced that the mechanical structure of the gel governed the amount of swelling, the implication being that the structure of the gel on setting remained during swelling, the extra water imbibed merely straining the gel structure without causing any fundamental rearrangement of the attractive forces between the gel particles.

My own experiments show that dehydration by methyl alcohol is similar to drying by heat, in that the dehydrated gels reswell rapidly in water up to their original weight and thereafter increase in weight similarly to untreated gels. Other alcohols, however, produce a permanent change in the gel structure.

It would seem to be clear, however, from Table II, that swelling in water results in a readjustment of the gel structure with imbibition and not merely in the straining of a structure which is essentially unchanged. If the latter were the case, one would expect all the gels in the first part of Table II to give the same swelling value in alcohol. The presence of small amounts of alcohol in the swelling fluid apparently prevents this readjustment, or renders it imperfect.

SUMMARY

On immersion in monohydric alcohols, gelatin gels are dehydrated and absorb some of the alcohol. The efficiency of the monohydric alcohols as dehydrating agents is methyl < ethyl < *n*-propyl, *n*-butyl and *isobutyl*.

The equilibrium weight of a gel in ethyl alcohol varies slightly with its shape. In very dilute solutions of ethyl alcohol, the gel first decreases and then increases in weight. In solutions containing more than 20 % alcohol the weight steadily decreases.

Swelling in water involves a readjustment of the gel structure, this not taking place in dilute alcohol solutions.

REFERENCES

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