OSMOTIC EXPERIMENTS WITH COLLODION MEMBRANES

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Because of the results obtained by Kahlenberg¹ and others with membranes and solvents other than those which have been so extensively studied since the time of the classical experiments of Pfeffer—results which are quite opposed to the generally accepted views of the nature of the process of osmosis—it seemed desirable to extend the study to still other membranes, solvents and solutes. From the results obtained by Kahlenberg it would seem that osmotic pressures are merely equilibrium pressures, and that in the process of osmosis there is always a current in both directions, though in some cases the major current is so great in comparison that the minor current becomes almost insignificant. In other words, there is in reality no such thing as a truly semi-permeable membrane. The experiments made seem to indicate that whether passage of the solvent through the membrane takes place or not is, in the first place, dependent upon the specific nature of the membrane and solvent employed and, secondly, upon the relative attraction between membrane and solvent and solute and solvent. The solvent must be of such nature that it is taken up by the membrane: it must be capable of wetting and permeating it. The solution bathing the other side of the membrane must have an attraction for the solvent greater than that between membrane and solvent, the result being that the solvent is extracted from the membrane by the solution and more solvent is thereupon taken up by the membrane, to be again extracted in turn. We then have a continual process of transfer of solvent through the membrane and into the solution. At the same time some of the solution permeates the membrane and passes out into the pure solvent, so that we have a current in both directions. In every case so far studied a small

¹ Jour. Phys. Chem., 10, 141 (1906).

quantity, at least, of the solute has always been found to pass through the membrane. This passage of solute through the membrane is not in any way due to imperfections in the membrane, but is a part of the osmotic process itself.

Collodion is a substance quite different chemically from the membranes ordinarily used, and it lends itself nicely to such qualitative experiments as were here desired. It is essentially a nitro-cellulose (of uncertain structure) in solution in a mixture of ether (about 75 percent) and alcohol (about 25 percent). The membranes were prepared by pouring out a layer of collodion on the surface of mercury. When sufficiently dry to be handled, but still quite moist on the lower side, the membrane was picked off the surface of the mercury, stretched over the end of a thistle tube and securely tied with strong thread. The edges were then trimmed down smooth and painted with fresh collodion. When dry the membrane so formed was very tight and exceedingly thin: and, if carefully made, gave no evidence of mechanical leaks. The membranes so made varied from 0.002 inch to 0.004 inch in thickness. Their tensile strength is remarkably great. They are so strong that they can scarcely be broken with the hands. After preparation, the membranes were placed over a large steam coil and left to dry for several days at least, in order to dry out all the ether and alcohol.

If the membrane exerts a selective action in such a way that only those liquids can go through which themselves have an affinity for the material composing the membrane, we should expect that such liquids as carbon bisulphide, carbon tetrachloride, benzene, the paraffine hydrocarbons, etc., which have no solvent action on the collodion, would not pass through the membrane; while, on the other hand, such liquids as are somewhat similar in chemical character to the membrane would be able to pass through it. Since collodion is a hydroxyl bearing body we should naturally expect that liquids containing hydroxyl groups, such as alcohols, would be imbibed by it;¹ and, on the other hand,

¹ Compare, Kahlenberg, Vice-presidential address, *Science*, Jan. 14, 1910.

that the hydrocarbons would not. How far this conclusion is verified will be seen from the following experiments.

Ethyl Alcohol and Camphor.—Ethyl alcohol (96 percent) does not dissolve the membrane at once but it does wet it and exerts a slow solvent action upon it. A block of pure camphor, cut in the shape of a cube with sharp edges, was placed upon a collodion membrane. The lower side of the latter was bathed with 96 percent alcohol. Within a few minutes it was observed that the surface of the camphor appeared wet and within a half hour the sharp edges of the block had become dull and rounded. At the end of two or three hours there was a strong alcoholic solution of camphor within the osmometer and this kept on increasing in quantity for a couple of days at the end of which time the solid block had entirely disappeared, only the solution remaining. A considerable amount of camphor was thus taken through the membrane into the outside compartment, as was to be expected.¹

Mercuric Chloride in Alcohol.—Mercuric chloride is quite soluble in alcohol. A solution of mercuric chloride in 96 percent alcohol was placed within an osmometer and 96 percent alcohol placed outside. Within a few minutes the level of the solution in the osmometer began to rise and continued to do so for several hours, until a total rise of about 20 cm had been attained, whereupon the level sank again. The outer liquid was tested and found to contain a considerable quantity of mercuric chloride. After standing a week, the level within was 2.5 cm below the initial point, and the membrane was greatly distended.

In all experiments where diffusion through the membrane takes place rapidly, the minor current, *i. e.*, the passage of the solute through the membrane, is very much in evidence, and *vice versa*. In all cases where it takes place rapidly, the membrane becomes weakened and distended. It is also found, invariably as far as we know, that after the maximum

¹ Compare a similar experiment by Kahlenberg (Jour. Phys. Chem., 10, 170 (1906)), who used a rubber membrane.

pressure has been attained the level begins to sink again. No adequate explanation of this phenomenon has yet been advanced. It is likely, however, that it is due to some change in the membrane caused by the passage of the solvent through it. Possibly it has a greater bearing on the process than we realize.

Ethyl Alcohol plus Iodine, and Carbon Bisulphide.—Iodine is considerably more soluble in carbon bisulphide than in ethyl alcohol. Carbon bisulphide has no action upon collodion membranes. A solution of iodine in 96 percent ethyl alcohol was placed outside of the osmometer and pure redistilled carbon bisulphide placed within, the level being marked immediately. Three minutes thereafter, the carbon bisulphide, about 50 cc in volume, had become pink throughout, due to iodine. The intensity of color increased rapidly and the level of the carbon bisulphide began to rise, slowly. At the end of two days it had risen to a height of about 5 cm., and had then commenced to fall again. At the end of a week, the level within and without was the same, and the membrane was badly disintegrated by the alcohol.

The explanation of this experiment is not difficult. The carbon bisulphide was not imbibed by the membrane, while the alcohol was imbibed and carried iodine along with it. The carbon bisulphide, inside, being a better solvent for iodine than is alcohol, extracted it from the latter, whereupon the alcohol took up more iodine from the solution outside and this in turn was given up to the carbon bisulphide. We have here merely a partition experiment. The membrane impedes the process, the carbon bisulphide being insoluble in it. The alcohol, being capable of permeating the membrane, serves as a carrier of iodine through the membrane to the carbon bisulphide. Since the two solvents are miscible, and since carbon bisulphide has no action on the membrane, it was to be expected that alcohol would also pass out from the membrane into the carbon bisulphide, thus causing the level to rise.

At the close of the experiment, the membrane was removed

and examined. It was found to be opalescent, due to iodine. Its thickness was the same as before the experiment (0.004 inch), and its strength seemed unimpaired.

Carbon bisulphide was shown to have no action on the membrane in the following way. Three disks cut from a dried membrane were carefully weighed. Their combined weight was 0.1173 grams, their combined area approximately 6 sq. in., and their individual thickness 0.002 of an inch. The circles were placed in a strong solution of iodine in carbon bisulphide, where they remained twelve hours. They were then removed, rinsed with ligroin, and quickly dried and weighed. They had gained in weight but 2 mg. In appearance they were quite unchanged, except for the opalescence caused by the iodine. The thickness remained the same, the edges were sharp, no soginess was evident and their strength seemed unimpaired.

Since these membranes have been bathed with carbon bisulphide for months without any determinable change. Iodine does not cause any deep-seated change in the nature of the membrane, as it does in the case of rubber, which it greatly weakens.

Carbon tetrachloride, chloroform, and the hydrocarbons are similar to carbon bisulphide in their inactivity toward collodion. Pyridine, nitrobenzene and the esters dissolve the membranes very quickly, and cannot be used. Ethyl benzoate has a peculiar action on collodion films. Instead of swelling up and softening, the film remains firm, but presents a ground glass appearance after the solvent has acted for a short time.

Carbon Tetrachloride plus Iodine, and Carbon Bisulphide.—Iodine is very soluble in both of these solvents. A solution of iodine in carbon tetrachloride was placed outside of an osmometer and pure carbon bisulphide placed within. In a short time the carbon bisulphide had become colored, but by no means as quickly as in the preceding experiment where alcohol was used. The level of the liquid rose for a short time, after which it began to fall again, slowly. After standing a week,

the membrane was examined and found to be unaffected, to all appearances at least. Its strength was unimpaired and its thickness was 0.004 of an inch.

The converse of this experiment, *i. e.*, with the iodine dissolved in the carbon bisulphide with pure carbon tetrachloride on the other side, gave similar results, the iodine passing through the membrane in small amounts, though the membrane seems unaffected by either solvent. An exceedingly minute trace of alcohol remaining in the membrane would undoubtedly account for the passage of iodine through it. The membranes employed in this experiment were used a few days after making, and may not have been as dry as they should have been. Greater care in drying was thereafter used.

That iodine in itself is not capable of passing into the collodion without a suitable carrier is shown by the following experiment.

Crystals of iodine were placed upon the upper surface of a membrane whose lower surface was bathed with carbon bisulphide for several months. No iodine appeared in the carbon bisulphide, though the upper surface of the membrane showed a slight opalescence due to iodine deposited upon it.

The alcohols are capable of wetting collodion. The solvent action of methyl alcohol is so great that a membrane 0.004 inch thick lasts but a few seconds. The solvent effect decreases as we go higher in the series, *i. e.*, as the proportion of hydroxyl becomes less and less, and we more nearly approach the hydrocarbons, the latter class of substances being incapable of wetting collodion.

In 96 percent alcohol collodion is fairly permanent. A dried film was subjected to the action of 96 percent alcohol for a week, at the end of which time the membrane was quite firm but had bagged somewhat; however, it was still very strong. This membrane was thereupon put into absolute alcohol and it dissolved in a few minutes. It went into solution like gelatin into water. Fresh membranes, after

careful drying, were put into absolute alcohol, and they went into solution in a short time. Anhydrous propyl alcohol has a slower action than ethyl alcohol, and isoamyl alcohol has so slow an action that the membrane seems almost unaffected after being submerged in it for at least six months, though the membrane is wetted. The following experiments were made with alcohols as solvents.

Copper Oleate plus Ethyl Alcohol, and Ethyl Alcohol.—A solution of copper oleate, which had been carefully dried, in 96 percent alcohol was placed inside an osmometer and 96 percent alcohol was placed on the outside. The level remained practically unchanged, and copper oleate went through the membrane freely. The membrane was found to be greatly weakened, and badly disintegrated.

Propyl Alcohol plus Copper Oleate, and Propyl Alcohol.—A solution of dry copper oleate in propyl alcohol was placed inside of an osmometer and anhydrous propyl alcohol placed on the outside. Three days later the level of the solution had risen 1 cm and on the following day the membrane broke, due to the solvent action of the anhydrous alcohol.

Isoamyl Alcohol plus Copper Oleate, and Isoamyl Alcohol.—A 5 percent solution of dry copper oleate in isoamyl alcohol was placed inside of an osmometer and pure anhydrous isoamyl alcohol placed on the outside. No change was apparent for the first three months. At the end of three and a half months the level had risen slightly. This has continued steadily, though slowly, until now at the end of thirteen months the level has risen 57 mm. There seems to be no copper oleate in the outer liquid, but there is a fine grayish sediment deposited along the inner surface of the membrane. The membrane has commenced to sag very slightly and is evidently becoming somewhat weakened by the continued action of the alcohol.

Isoamyl Alcohol plus Copper Oleate, and Carbon Bisulphide.—Carbon bisulphide and isoamyl alcohol are miscible in all proportions and the former is a good solvent for copper oleate, much better than is the alcohol.

A 5 percent solution of copper oleate in isoamyl alcohol was placed within an osmometer and carbon bisulphide placed without. At the end of a week the level had risen twelve inches. This continued until finally a height of over eighty inches was attained, after which the experiment was discontinued.

The explanation of the action is evidently as follows: Isoamyl alcohol was imbibed by the membrane and the imbibed alcohol coming in contact with the carbon bisulphide on the other side takes it up and enables it to pass through into the alcoholic solution of copper oleate, for which it has a great affinity, whereas alone it would not be capable of going through, because it does not wet the membrane.

Some isoamyl alcohol naturally passed out into the carbon bisulphide. The membrane became somewhat weakened in consequence of the imbibition of the alcohol.

That the above explanation is the correct one is shown by the fact that when a solution of copper oleate in carbon bisulphide is separated from pure carbon bisulphide by a collodion membrane no action takes place. The solvent is incapable of penetrating the membrane without a carrier, such as alcohol.

Another experiment which also leads to the same conclusion regarding the necessity of a carrier is as follows: A solution of sulphur in carbon bisulphide, in which it is quite soluble, was separated from pure carbon bisulphide by a collodion film. Although the liquids bathed the membrane for several months, no carbon bisulphide passed through. No carrier of carbon bisulphide was present.

Iodine plus Potassium Iodide plus Water, and Water.—This experiment was quite similar to the one last described, the difference being that the solution of iodine was stronger and that water was used in place of carbon bisulphide. The solution was placed within the osmometer, and the solvent outside.

At the end of three weeks, a very slight rise in the level of the solution had taken place. At the end of five and a

half months the level had risen twenty-five and one-half centimeters, whereupon it began to sink back again. Copious amounts of iodine passed out into the water outside.

This experiment makes it evident that water is responsible for the transfer of iodine through the membrane, in this and the preceding experiment; and that the reason that no rise was experienced in the former experiment, where carbon bisulphide and water were used, is that the two liquids are immiscible.

Glycerine plus Water, and Water.—A 50 percent solution (by volume) of glycerine in water was placed inside of an osmometer, and distilled water placed on the outside. The level rose about one centimeter the first twenty-four hours, and continued to rise regularly. The experiment was continued until a height of thirty centimeters was attained. Glycerine also passed out into the water outside. Here we have two hydroxyl compounds, both of which are capable of wetting the membrane. Evidently the mixture permeates the membrane more readily than pure water.

O-Kresol plus Isoamyl Alcohol, and Isoamyl Alcohol.—An osmometer was filled with a solution of *o*-kresol (approximately 25 percent) in isoamyl alcohol, and isoamyl alcohol was placed outside. The two liquids mix readily with each other. It should be remembered that isoamyl alcohol is but very slowly taken up by collodion, ordinarily. In this case the level of the solution rose 1 cm the first week and continued to rise for about five weeks, whereupon the level sank again, finally reaching its initial point at the end of an additional four weeks.

The relatively rapid rise was evidently due to the imbibition of kresol into the membrane, whereupon the alcohol is enabled to pass through the membrane more readily. Considerable quantities of kresol passed through into the solvent, until finally the concentration became about equal on both sides.

Sugar plus Water, and Water.—Water penetrates dry collodion but very slowly. The statement is often made

that dried collodion is insoluble in water, which is practically true. Yet that water has some action is shown by the following experiment.

A rather strong solution of sugar in water was separated from pure water by a collodion membrane. No change was apparent for the first two weeks. At the end of three weeks the level had risen 1.5 cm, and this has continued until now at the end of six months the level has risen 14 cm. The membrane appears perfect, being taut and smooth and entirely unchanged in appearance.¹ Some sugar has passed through into the water outside.

This experiment is very similar to the ordinary experiment where parchment is used, save that collodion is much more impermeable to water and therefore the process goes on more slowly. As usual we have the major and minor current, in opposite directions.

Other experiments have been made with aqueous and alcoholic-aqueous solutions of boric and oxalic acids with the same general results, the main current being from solvent to solution but always accompanied by a minor current in the opposite direction. When the maximum height has been attained the level always sinks back again.

Effect of Dissolved Halides on Collodion.—Mercuric chloride when dissolved in water has no destructive effect upon collodion films, nor does it when dissolved in 96 percent alcohol. When dissolved in absolute alcohol, however, the membrane is disrupted almost immediately when the solution is poured upon it. The effect is the same as if the membrane had been seized by some powerful mechanical device and torn mechanically. Other halides, soluble in alcohol, produce the same effect, though their aqueous solutions do not. Antimony trichloride in alcohol acts just as does mercuric chloride.

¹ Since the above was written the membrane has been allowed to remain in contact with the solvent and solution an additional eight months, with no apparent effect on the membrane.

Summary

1. Whether osmotic action through a membrane takes place or not seems to be dependent upon the solubility of at least one of the components in the membrane.

2. Whether an increase in volume of the solution takes place or not depends upon the miscibility of the solvents used.

3. The direction and extent of the osmotic action is evidently largely a question of relative solubility. The process is akin to a distribution process.

4. When osmotic action takes place it consists of a major and a minor current, in opposite directions, as has been previously pointed out.

5. It was noted repeatedly during these experiments that stirring of the liquids bathing the membranes served to hasten the osmotic process.

These conclusions afford an interesting confirmation of the results obtained by Kahlenberg from a study of other membranes and serve to emphasize the correctness of the views advanced by him concerning the nature of the osmotic process.

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February, 1910*