UNEQUAL DISTRIBUTION OF IONS IN A COLLODION CELL

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Collander (1) found that the permeability of "dry" collodion membranes was essentially the same as that of living cells in that they allowed the passage of weak acids, bases, etc., but not of salts nor strong acids. Living cells possess another striking characteristic in that they are able to maintain a constant difference in concentration of solutes between the interior of the cell and the surrounding solution. This behavior can be accounted for if it be assumed that the substance becomes changed after entering the cell to one which cannot pass through the membrane. The non-diffusible form will then concentrate inside the cell. The results obtained in the previous study (2) of dry collodion membranes predict the conditions necessary for this result.

Concentration of Iodide Ion

Dry collodion membranes are readily permeable to iodine but are impermeable to iodide ion or to thiosulphate. If, therefore, a saturated solution of iodine is separated from a solution of thiosulphate by such a membrane the iodine will diffuse through the membrane and become reduced to iodide which cannot diffuse out. The iodide will therefore continue to collect in the cell. This will continue until all the thiosulphate has been used up and the activity (vapor pressure) of the iodine becomes equal on the two sides of the membrane.

The result of an experiment set up in this way is shown in Fig. 1. The membranes were made as previously described and were suspended in 500 cc. of a saturated solution of iodine in water with excess solid iodine present. The concentration of iodine outside remained constant. The concentration of iodide inside increases slowly, and until about the 50th day no iodide was found outside showing that the mem-
brane is impermeable to both thiosulphate and iodide. At this time the membranes became yellow and crinkled and the concentration of iodide inside suddenly increased, while at the same time iodide began to appear in the outside solution. The membranes had evidently lost their semipermeability and become like dead cells.

**Concentration of Chloride Ions**

It was found previously that mercury chloride passed through dry collodion membranes while all other chlorides tested could not pass through. A system, therefore, in which the mercury chloride was changed to another chloride after entering the cell would concentrate chloride ions.

The results of such an experiment are shown in Fig. 2. The cell contained originally 0.011 M HgCl₂ and 0.05 M Na₂CrO₄ inside and 0.011 HgCl₂ and 0.05 Na₂SO₄ outside. On mixing the mercury was precipitated as HgCrO₄. The activity of the mercury chloride was therefore less inside than out and so more mercury chloride diffuses in and the chloride ion concentration increases as shown in the figure. This would continue until the product of the Hg and Cl ion activities inside and out were equal. Since the membrane is permeable for water it would also be necessary that the vapor pressure of the water
FIG. 2. Concentration of Cl⁻ ions in cell: 0.011 HgCl₂, 0.05 Na₂CrO₄/0.011 HgCl₂, 0.05 Na₂SO₄.

FIG. 3. Concentration of acetate ion in cell: 0.01 acetic acid/CaCO₃ — water.
be the same on both sides at equilibrium. In this case the condition is nearly fulfilled because of the sodium sulfate outside. The condition could be equally well fulfilled by exerting pressure on the inside solution.

**Concentration of Acetate Ions**

Acetic acid penetrates the membrane while acetate ion does not. If the acid is changed to an acetate after entering evidently acetate ion will become concentrated in the cell. This may be accomplished in a number of ways but the most convenient is to place solid calcium carbonate in the cell. The result of such an experiment in which a cell containing a suspension of calcium carbonate in water was placed in a solution of 0.01 M acetic acid is shown in Fig. 3. The concentration of acetate ion in the cell was determined by titrating a sample from pH 7 to pH 3.0 with 0.01 M HCl. The acetate ion concentration in the cell increases slowly and becomes greater than the total acetic acid concentration outside, and therefore many times greater than the acetate ion concentration outside. The process would continue presumably until the activity of the acetic acid (which is proportional to the product of the activities of the H times the acetate ion) was equal on the two sides. The vapor pressure of the water must also be equal at equilibrium due either to hydrostatic pressure on the inside or to the addition of some non-diffusible solute outside, or to proper adjustment of the acetic acid-calcium acetate concentrations.

This experiment is very similar to Osterhout's (3) results with H₂S and *Valonia* cells.

The preceding experiments show that a model may be made which will concentrate ions just as do living cells. It is, of course, unlikely that the same ions take part in the transfer in the case of the living cells but it seems possible that the general mechanism is the same. Since the permeability appears to be a property of the molecular species rather than the ion it is possible that the potassium or calcium salt of some organic acid is able to penetrate the cell membrane. Most organic acids are oxidized in the cell and if this occurred, the ion which entered with the organic ion could not escape and would be concentrated in the cell. There are evidently a number of other possibilities which would lead to the same result.
SUMMARY

The properties of dry collodion membranes previously described allow the prediction that cells of these membranes will concentrate solutes under certain conditions. Three such cases have been studied experimentally.

1. A membrane containing thiosulphate and immersed in a solution of iodine concentrates iodide ion.
2. A membrane containing sodium chromate and immersed in mercury chloride concentrates chloride ion.
3. A membrane containing calcium carbonate and immersed in acetic acid concentrates acetate ions.

BIBLIOGRAPHY