LXIV. THE PENETRATION OF ELECTROLYTES INTO GELS.

V. THE DIFFUSION OF MIXTURES OF CHLORIDES IN GELS.

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INTRODUCTION.

CONSIDERABLE emphasis has been laid during recent years on the analogies between colloidal systems and living cells in regard to their behaviour towards water and dissolved substances and it has become evident that the study of colloidal systems must throw light on the constitution and behaviour of living tissues. It is therefore of interest to enquire whether anything analogous to the phenomenon of antagonism between ions in their entrance into living tissues is exhibited in the penetration of electrolytes into gels.

Among the many antagonistic actions recorded for various plant tissues, those between different chlorides were among the earliest, and are perhaps now the best, known. Thus a very definite antagonism between sodium and calcium chlorides, between potassium and calcium chlorides, and between potassium and magnesium chlorides, and even between chlorides of the univalent metals, has been recorded by different writers [see Stiles, 1923, 1]. Experiments were therefore made on the diffusion of mixtures of chlorides through gels of agar-agar and gelatin with a view to determining whether any mutual hindrance to the penetration of salts through the gel resulted from the presence of one salt along with the other, such as might be compared with the antagonistic effects observed in living systems.

METHOD.

The measurements were made by means of the indicator method already described [Stiles, 1920; Adair, 1920]. In the earlier experiments, carried out four years ago, the original crude "half test-tube" method was employed. Subsequently, the refined technique recently described in detail [Stiles, 1923, 2] was employed, and coefficients of diffusion calculated from the measurements made.

Two gels were used: a 1 % agar-agar gel made from shred agar-agar, and a 10 % gelatin gel. In both cases the material was washed with distilled water before use until the washing water was free from chloride. The gels contained silver nitrate as indicator, which was present in a concentration of 0.005*N*.

The earlier experiments were conducted in a dark cupboard in the laboratory without temperature control, but the results obtained in any one series are strictly comparable as all the experiments in a series were carried out together. The latter was also the case with the later more exact experiments, but these were carried out in water-baths maintained at constant temperature by means of gas-mercury-toluene thermo-regulators.

Experiments were conducted with a number of pairs of chlorides, the two chlorides of the pair being present in a variety of proportions, but in all cases the solutions were normal as regards chloride. In the calculation of the coefficient of diffusion the solutions are assumed to be normal solutions, as they are such in regard to chloride, and Adair's second and more exact formula is used. For the purposes of the calculation the coefficient of diffusion of silver nitrate in the gel is taken as 10^{-5} sq. cm. per second [cf. Adair, 1920]. An error of 50 % in this does not alter appreciably the final values obtained for the coefficients of diffusion of the chlorides.

EXPERIMENTAL RESULTS.

1. *Agar-agar.*

The diffusion of the following mixtures was examined by the half test-tube method: sodium chloride and calcium chloride, potassium chloride and calcium chloride, potassium chloride and magnesium chloride, and potassium chloride and sodium chloride. The experiments were carried out in duplicate. Each tube contained a length of 7 cm. of gel surmounted by the same length of solution of diffusing salt. Solutions of the pure salts and solutions containing varying relative proportions of the two chlorides were used, but in no case could any indication of a hindrance to diffusion of the salt in a mixed solution be discovered. The penetration was measured after a number of different times; the results obtained for measurements made after diffusion had proceeded for about 27 hours are recorded in Table I. Similar results were obtained after both shorter and longer periods.

Table I. *Penetration of chlorides into gels of 1 % agar-agar from pure and mixed solutions.*

Relative proportions of chlorides First named : second named	Penetration in centimetres			
	NaCl + CaCl ₂	KCl + CaCl ₂	KCl + MgCl ₂	KCl + NaCl
	27.3 hrs.	27.8 hrs.	27.25 hrs.	27.63 hrs.
10 : 0	4.19	4.60	4.59	4.59
9 : 1	4.15	4.525	4.50	4.56
8 : 2	4.15	4.525	4.49	4.52
7 : 3	4.165	4.505	4.43	4.51
6 : 4	4.09	4.43	4.40	4.49
5 : 5	4.08	4.41	4.32	4.42
4 : 6	3.965	4.32	4.29	4.42
3 : 7	3.95	4.23	4.15	—
2 : 8	3.94	4.13	4.09	4.345
1 : 9	3.81	4.01	3.915	—
0 : 10	3.76	3.79	3.655	4.21

Although the method does not permit of the calculation of the coefficients of diffusion, and although the measurements on which each value for the penetration is based are few in number, it is clear from these results that there is no antagonism between the chlorides employed in regard to their diffusion through agar-agar. Nevertheless one series of experiments, that in which mixtures of calcium and sodium chlorides were employed, was repeated by the more exact method and the coefficients of diffusion calculated in each case, assuming that each solution was a normal chloride solution. The values for the coefficient of diffusion are recorded in Table II. They confirm the conclusion drawn from the experiments with the cruder "half test-tube" method as to the absence of any hindrance offered by the presence of one chloride to the diffusion of another, for as the proportion of calcium chloride in the mixture is increased there is a progressive lessening in the value of the coefficient of diffusion.

In order to indicate more clearly the relation between the composition of the solution and the diffusivity the results obtained are shown graphically in

Fig. 1. Curves to illustrate the diffusion through gels of chlorides in pure and mixed solutions

- I. Sodium and calcium chlorides in 1 % agar-agar.
- II. Sodium and calcium chlorides in 10 % gelatin.
- III. Potassium and calcium chlorides in 10 % gelatin.

Fig. 1. These results thus expressed show that so far from there being anything in the nature of a hindrance to diffusion in a mixed solution, the diffusivity in a mixed solution is actually slightly greater than would be expected from the values of the diffusivity of the pure chlorides, as the curve connecting the value of the coefficient of diffusion with the composition of the diffusing solution is concave to the axis of the composition of the diffusing salt and not a straight line.

2. Gelatin.

Determinations of the coefficient of diffusion of sodium and calcium chlorides and of mixtures of the two in 10 % gelatin were made by the more exact method, the temperature of experiment being $21.5^\circ \pm 0.5^\circ$. A similar series of experiments was carried out with potassium chloride and calcium chloride as diffusing salts at a temperature of 21.5° . As before, all the solutions employed were normal in regard to chloride. The results are shown in Table II, and also graphically in Fig. 1. The same phenomenon is obvious here as in the diffusion of mixtures of chlorides through agar-agar, namely, that the rate of diffusion of the mixed chlorides is always a little higher than would be expected from the values of the coefficients of diffusion of the respective salts in pure solutions.

Table II. *Penetration of chlorides into gels of agar-agar and gelatin from pure and mixed solutions. (Concentrations of chloride always normal.)*

Relative proportions of chlorides First named : second named	Coefficient of diffusion in sq. cm. per sec. $\times 10^{-5}$		
	NaCl + CaCl ₂ in agar-agar 20.5°	NaCl + CaCl ₂ in gelatin $21.5^\circ \pm 0.5^\circ$	KCl + CaCl ₂ in gelatin 21.5°
10 : 0	1.347	1.151	1.488
10 : 1	—	—	1.476
9 : 1	1.334	1.141	—
10 : 2	—	—	1.481
8 : 2	1.317	1.131	—
10 : 4	—	—	1.457
7 : 3	1.297	1.106	—
5 : 5	1.269	1.073	1.393
3 : 7	1.210	1.012	—
4 : 10	—	—	1.305
2 : 10	—	—	1.239
1 : 9	1.166	0.969	—
0 : 10	1.130	0.940	1.024

It does not appear easy to find a simple explanation of these results. Although the coefficient of diffusion no doubt increases with increase in the relative number of electrolytically dissociated molecules and hence with dilution, as has been shown to be the case for gels [Stiles, 1923, 2] as well as for free diffusion in water, and although both of the two constituent salts in any one of the mixtures employed are in less than normal concentration, yet the presence of the other salt will depress the degree of dissociation so that an appreciable rise in the value of the coefficient of diffusion is scarcely to be expected on this ground.

A decrease in viscosity of the gel would result in an increase in the rate of diffusion, but the results obtained by Fenn [1916], if rightly interpreted, suggest that in mixtures of salts such as those employed in the present investigation, the viscosity is greater than in pure salt solutions of the same concentration.

In the present state of our knowledge it would not be profitable to discuss this matter further. It is, however, clear from the investigation here recorded that the antagonistic effects observed with living tissues cannot be attributed to mutual interference between the antagonising salts in their diffusion through any gel layer in the cells of the tissues.

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