

## ELECTROCHEMICAL BEHAVIOUR OF ION-EXCHANGING SUBSTANCES

### X. Further Potential Measurements in NaCl and KCl Solutions.

by

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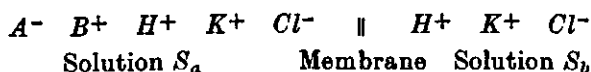
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Potentials of young plant roots in KCl solutions have been investigated in this laboratory for a number of years.<sup>1-9</sup>

Measurements have been reported for several plant species. Recently, a more extensive investigation was started of potentials of Lucerne clover, *medicago sativa*, Northern France variety.

The observed shifts of potential with KCl and HCl concentration show characteristic trends. Analogous trends might be expected for Donnan membrane potentials of various systems. A model, representing conditions at the root wall, was proposed by Vervelde and Tendeloo<sup>6,7</sup> and discussed further by MacGillavry and Tendeloo. This type of system containing a single membrane is represented in diagram I.

Diagram I



The non-permeating anions  $A^-$  and cations  $B^+$  are supposed to derive from a mixture of weakly ionizing substances.

As far as this analogy goes one should expect similar behaviour in NaCl and in KCl solutions. Biologically, however,  $Na^+$  and  $K^+$  are not similar. Hence, it was thought of interest to compare root potentials in NaCl and in KCl solutions.

It is implicit in this approach that electrolytes can diffuse into and out of certain sections of a root without much hindrance. This space is lined on the outside by the root wall, or a membrane just within the root wall, and on the inside by membranes showing

definite physiological activity and selectivity. Hope and Stevens<sup>10</sup> consider that the greater portion of this "apparent free space" contains protoplasm having a spatial arrangement of negative immobile ions. According to the extended theory of Donnan equilibria the concentration of immobile ions—anions and cations—will vary with the pH. (See ref. 6).

It is recognized by plant physiologists that on purely physico-chemical grounds sodium and potassium may show a somewhat different behaviour. Even the equilibrium distributions of potassium through the protoplasm, Butler<sup>11</sup> points out, might be different from the equilibrium distributions for sodium because of the smaller radius of the hydrated potassium ion. This difference in ionic volume already offers a possible explanation of the observed differences between the steady potentials for the two ions.

Another explanation, admittedly less probable, would be selective permeability of the root wall for potassium and sodium; sodium should not be able to penetrate in measurable amounts within the time of measurements. On account of the comparable lengths of time required for establishing NaCl and KCl potentials, this explanation appears less satisfactory.

The authors mentioned above and also Robertson, Wilkins and Weeks<sup>12</sup>, it may be added, showed that the initial uptake of KCl by various plant roots at first is rapid and then becomes slower until after about 20 minutes a steady metabolic rate is established. As a rule steady potentials are established within a few minutes, 4-10 minutes, sometimes a longer time is required. This time lapse is of the same order of magnitude, and it can hardly be doubted that a steady metabolic rate is accom-

panied by a stationary root potential as observed with usual techniques.

Since Donnan systems of the type indicated can account for the observed shifts of potential (see earlier publications), they are primarily due to the conditions at the outside membrane.

*Experimental results and variance analysis :*

The electric chain as now used is shown in Figure I. It was originally developed by Tendeloo, Vervelde and Zwart Voorspuy. AgCl/Ag and also HgCl/Hg electrodes have

been used. Other minor modifications were adopted from time to time. Further experimental details are given in (1) and (9).

A first series of measurements was reported on in publication (8). A root was measured first in a set of NaCl solutions and then in the corresponding set of KCl solutions. All solutions contained  $5 \times 10^{-6}$  N HCl. It was noted that apparently stationary potentials could be established also in the NaCl solutions, usually after a few minutes, as was the case in the KCl solutions. Such a behaviour is indicative of a quick adjustment of the roots to these changes

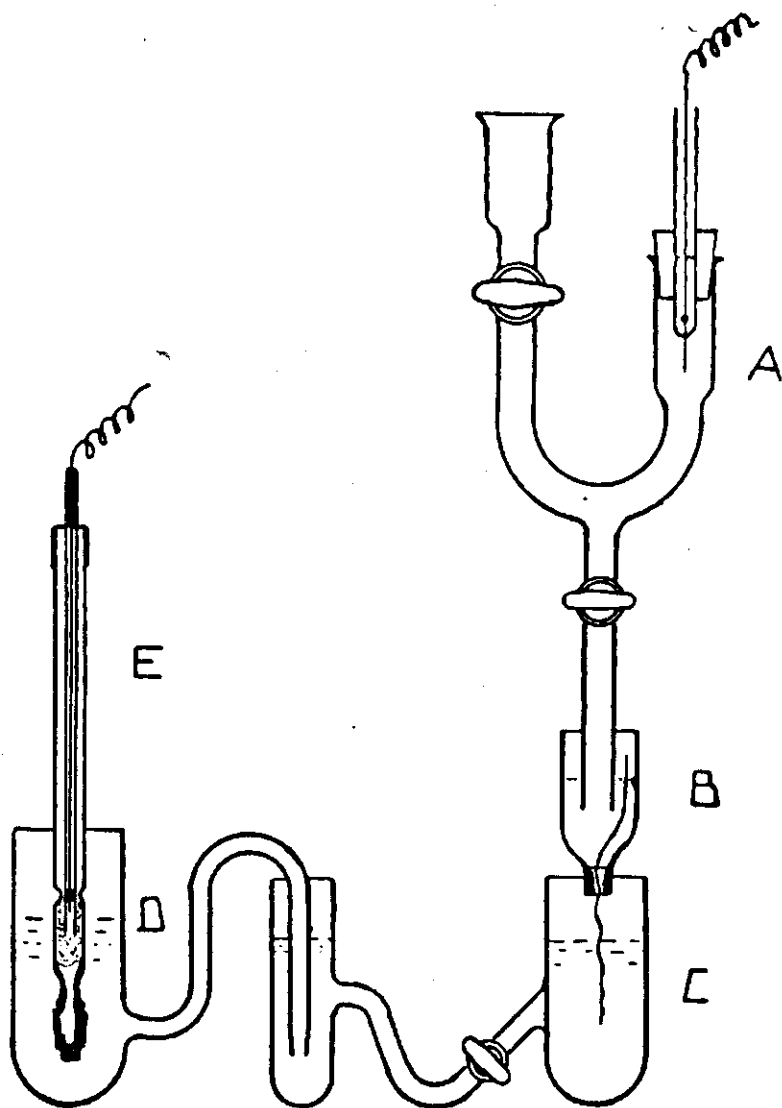


Fig. 1.

of medium and concentration. A quick adjustment would be expected also for a Donnan system with small inner volume (solution  $S_4$  in Diagram I).

The new series of measurements was done under slightly modified conditions, as it was noticed that especially the potentials in the most dilute KCl solutions of the first series might show a peculiar ambiguity. A potential fitting the normal pattern might be found and at times also an abnormal less negative potential. To forego, if possible, this ambiguity of steady potential, the range of concentrations was narrowed down. Also, as in the series of KCl solutions described in (9) and as well in all previous work (excepting 6), no HCl was added to the  $10^{-2}$  M KCl solution in the electrode holder A. In the first series of measurements in NaCl and KCl, the solution in A contained  $10^{-4}$  N HCl +  $10^{-2}$  M KCl. Finally, in the present series potentials were measured first in KCl and then in NaCl.

Of the different AgCl/Ag electrodes used some showed a somewhat different potential in  $10^{-2}$  M KCl against the saturated HgCl/Hg electrodes. Thus, the mean of the potentials in all solutions for each root would be the combined result of the true root level and the electrode level. Since an effect due to root level is not studied at this time, the measured mean potential was deducted from all potentials measured for the root. The values so obtained are listed in Table I.

The potential averages are listed in Table II.

TABLE II

Potential averages.

Molarity	$10^{-4}$	$5 \times 10^{-4}$	$2 \times 10^{-3}$	$10^{-2}$
KCl	-29	-10.5	+9.5	+35.5
NaCl	-21	-12.5	+2	+26.5

By this method, it will be seen from the variance analysis (Table III), the apparent root effect has been eliminated. The other variance estimates are not affected by this procedure. This is true also for the interaction of concentration and medium, which is of special interest as will become clear from the following.

TABLE III

Variance Analysis

Source of variation	Sum of squares	Dimension	Variance estimate	F	Critical F values
Concentration	21,201.2	3	7,067.1		
Medium	72.5	1	72.5	2.84	4.13
Roots	0.3	5	0.1		
Interaction cxm	540.2	3	180.1	7.62	2.88
Residual	889.2	35	25.4		
	22,703.4	47			

TABLE I

Potentials of Lucerne clover.

Molarity KCl\*

Molarity NaCl\*

Root	Molarity KCl*				Molarity NaCl*			
	$10^{-4}$	$5 \times 10^{-4}$	$2 \times 10^{-3}$	$10^{-2}$	$10^{-4}$	$5 \times 10^{-4}$	$2 \times 10^{-3}$	$10^{-2}$
1	-19	-10	+12	+39	-21	-13	-6	+19
2	-36	-16	+8	+37	-26	-6	+10	+29
4	-36.5	-10.5	+9.5	+37.5	-18.5	-11.5	+4.5	+26.5
12	-23	-5	+13	+26	-18	-12	-1	+22
5	-30	-14	+9	+38	-24	-16	+5	+33
17	-30.5	-8.5	+5.5	+36.5	-18.5	-15.5	+0.5	+30.5

\*All solutions contained  $5 \times 10^{-5}$  N HCl.

The variance analysis did not indicate an effect due to the medium, NaCl or KCl, but did show an interaction of medium and concentration. The averaged potentials in Table II already show that the potentials in KCl-HCl vary more than in NaCl-HCl. This was found also for series I (Ref. No. 8.)

Since there is interaction of medium and concentration, independent empirical equations may be derived for the two media. For the chosen concentrations the successive logarithms do not differ by a constant amount. This makes the question as to significance of linear and higher components harder to settle. As the range of concentrations is rather short it is improbable that the coefficients of the quadratic and the cubic terms, apart from significance, can be known with any certainty. Thus, we will merely indicate for the two media the slopes between the lowest and the highest concentrations, resp.  $10^{-4}$  and  $10^{-2}$  M. These slopes are

$$\text{for KCl } \frac{29+35.5}{2} \quad 32\text{mV}/\log \text{ M unit.}$$

$$\text{and for NaCl } \frac{21+26.5}{2} \quad 24\text{mV}/\log \text{ M unit.}$$

In comparison, figures reported by Hope<sup>13</sup> are for KCl 32mV/log M unit and for NaCl 28mV/log M unit. The slopes are of the same order of magnitude, but the difference is less marked.

The interpretation in terms of Donnan equilibria will be treated further in forthcoming publications.

In conclusion it may be said that the patterns of root potentials of Lucerne clover in NaCl-HCl and KCl-HCl solutions appear to be different and may not be considered identical. It is noteworthy that a difference became evident even in the fairly narrow range of concentrations selected this time.

#### SUMMARY

Comparison of root potentials of Lucerne clover in NaCl-HCl and KCl-HCl solutions was extended. A difference in behaviour was indicated also in the narrower range of concentrations of a new series of measurements. The shifts of potential are primarily due to the variations of the Donnan equilibria across the root wall membranes.

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