

# ELECTROCHEMICAL BEHAVIOUR OF ION-EXCHANGING SUBSTANCES.

## I. Potential Measurements on Plant Roots

BY

H. J. C. TENDELOO, G. J. VERVELDE and  
A. J. ZWART VOORSPUIJ.

1. According to the literature and to our own measurements the potential of plant roots is found to react sharply to the ion concentration of the medium around the roots. The roots of different plants behave as relatively good cation electrodes.

2. A scheme is proposed for describing the relation between root potential and ion concentration of the medium by the assumption of a Donnan equilibrium between the root and the medium. The root appears to act as a mixed electrode.

Following investigations of the behaviour of various substances as electrode<sup>1)</sup>, a more detailed investigation of different kinds of glass bij Zwart Voorspuij<sup>2)</sup> led to conceptions in which the glass is represented as a weak acid which is capable of exhibiting exchange reaction with cations. The assumption of dissociation constants in the cation adsorption led to the use of other substances besides glass as electrode material, if possible substances with more or less well known dissociation properties, in order to test in that way the theory proposed.

Usually the technique of transforming the substance in question into a usable electrode led to great difficulties. Nevertheless a few modest results were obtained which will be discussed in due time.

Conversely, it seemed possible, by potential measurements on insufficiently well known substances to obtain information about the chemical behaviour of the substance. It would appear to us that one of the most important applications in this line lies in the field of agriculture. Lundegårdh<sup>3)</sup>, in detailed investigations, had already called attention to the fact that plant roots behave as fairly good cation electrodes. An interpretation of the electrode behaviour as a function of the chemical properties of the root would perhaps be able to furnish support for a quantitative treatment of the ion intake by roots, a problem which is still far from being solved. There was all the more reason for working on this problem, since other investigators<sup>4)</sup> had proposed an hypothesis for the ion intake by plant roots, in which the electrode potential of the root plays an important rôle.

<sup>1)</sup> H. J. C. Tendeloo, Researches on adsorption electrodes, I. The Glass Electrode, Proc. Akad. Wetenschappen Amsterdam **37**, 212 (1934). II. Mineral Electrodes, Ibid. **38**, 484 (1935). III. Mineral Electrodes, Rec. trav. chim. **55**, 227 (1936). H. J. C. Tendeloo and A. J. Zwart Voorspuij, IV. Glass Electrodes, Rec. trav. chim. **61**, 531 (1942).

<sup>2)</sup> A. J. Zwart Voorspuij, Onderzoekingen over Glaselectroden, Diss. Utrecht 1943. H. J. C. Tendeloo and A. J. Zwart Voorspuij, Rec. trav. chim. **62**, 784 and 793 (1943).

<sup>3)</sup> a. Lundegårdh, Über biologische Grenzflächenpotentiale, Biochem. Z. **300**, 167 (1939). b. Investigations as to the adsorption and accumulation of inorganic ions, Ann. Agr. Coll. Sweden **8**, 233 (1940). c. Untersuchungen über das chemisch-physikalische Verhalten der Oberfläche lebender Zellen, Protoplasma **35**, 548 (1941).

<sup>4)</sup> a. A. C. Schuffelen and R. Loosjes, The importance of the growth medium for the absorption of cations by plants, Proc. Akad. Wetenschappen Amsterdam **45**, 726 (1942). b. The Influence of the Ion Activity and the Ion Concentration, in the Medium on the Absorption of Cations by Plants, Ibid. **45**, 944 (1942).

Lundegårdh describes a method for the measurement of the root potential in which the roots are cut off and the upper part fixed into a bent tube and brought there into contact with  $10^{-2}$  N KCl, while the tip of the root is immersed in a flowing solution of the electrolyte whose influence on the root potential is being studied.

Our measurements were carried out with a very simple arrangement, which, however, was very satisfactory in many respects, especially with respect to the rapidity of working.

The cut off roots are inserted into the container A (fig. 1) which is drawn out narrow at the lower end, and fastened in it by allowing a drop of still

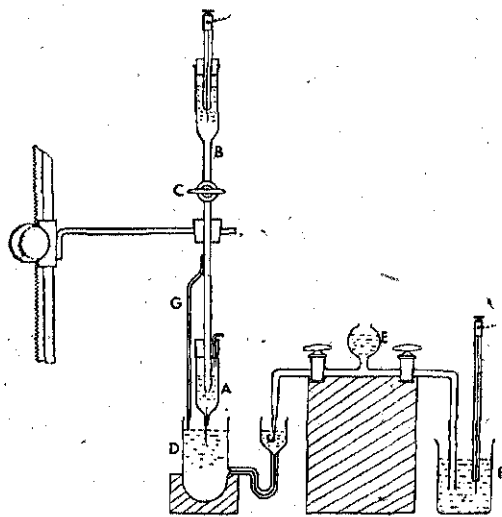


Fig. 1.

just liquid gelatine to flow around the root and to solidify there. This gives the advantage that the KCl solution with which the container A is afterwards filled cannot come into contact with the surface of the root with the liquid to be measured in container D. Container A is filled with KCl by connecting it by means of a double-holed cork stopper to a second container B filled with the KCl solution in question, and then by opening stopcock C allowing the liquid to flow into A until the level of the liquid in A makes contact with the solution in B. In container B is an Ag—AgCl electrode. The solution to be measured is in container D which is provided with a capillary

with an enlargement and bent as shown in the figure. This prevents saturated KCl in the siphon E from reaching the liquid to be measured. The left-hand end of the siphon is further provided with a tip bent in a U-form, since otherwise the saturated KCl having a greater specific gravity, would run out of the siphon, and disturb the measurements. This siphon was more satisfactory than the often used KCl-agar siphons. The right-hand end of the siphon is placed into a container F with saturated KCl, in which another Ag—AgCl electrode is placed. The container with the liquid to be measured and the KCl siphon are set up on loose paraffin blocks so that they can be quickly moved and changed. The container B is movable in the vertical directions by means of a rack and pinion. As measuring instrument we used a Cambridge electrometer with valve amplification (British Patent No. 396817).

To make the measurements the container B is screwed down until the root is immersed to the desired depth in the liquid. There is no objection to having the root immersed up to fairly close to the end of A. At the same time this makes it unnecessary to protect the root against drying out. In order to be able to immerse the root to the same depth in the liquid in all the subsequent

measurements, a glass rod G with pointed tip is fastened to container B; the tip of this rod must be just in contact with the surface of the liquid during the measurements. As contact liquid in container B,  $10^{-2}$  N KCl is used, following the example of Lundegårdh.

For reasons which will be made clear later, it is desirable to discuss as the simplest case the potential measurements in neutral KCl media of different concentrations.

In table I a few series of measurements on individual roots of various plants are included. The E.M.F. at room temperature is given of the circuit: Ag—AgCl—0.01 KCl—root—liquid to be measured—KCl, sat.—AgCl—Ag. The roots were cut off a few hours (3 to 5) before the measurements and placed in distilled water. This water treatment is found to have a favourable effect on the establishment of the potential. The series were run beginning with low and passing to the high concentrations. The value for  $10^{-5}$  N is usually only sufficiently constant after standing for some time in the liquid to be measured. Immediately before each final reading of the value of the potential the liquid around the root was renewed by lifting the root out of the liquid for a moment (in the case of  $10^{-5}$  N KCl this had to be repeated several times). For the sake of comparison a series of measurements by Lundegårdh is included.

Table I.

Normality KCl Plant	E. M. F.						Curve
	$10^{-5}$	$10^{-4}$	$10^{-3}$	$10^{-2}$	$10^{-1}$	$10^0$	Fig. 2
Solanum tuberosum	161	169	202	240	263	265	1
Phaseolus vulgaris	161	180	210	242	259	271	2
Beta vulgaris	172	190	222	254	269	274	3
Triticum vulgare	115	125	149	174	198	215	4
Triticum vulgare (Lundegårdh)	115	132	180	222	267	—	5

The potentials given here are not corrected for the difference in potential between the two Ag—AgCl electrodes, which moreover was not the same on the different days when measurements were made.

In fig. 2 the values are represented graphically. Lundegårdh's measurements deviate considerably from ours, which is however not surprising. In addition to the relatively large differences which, according to our experience, are found between the individual roots of a given plant, differences in variety and method of cultivation also probably play a part. While Lundegårdh grows his specimens under fairly accurately fixed and moreover sterile conditions, our water cultures were made without any special precautions.

It is in any case clear that except for the larger changes in potential in Lundegårdh's case the form of the curves is approximately the same.

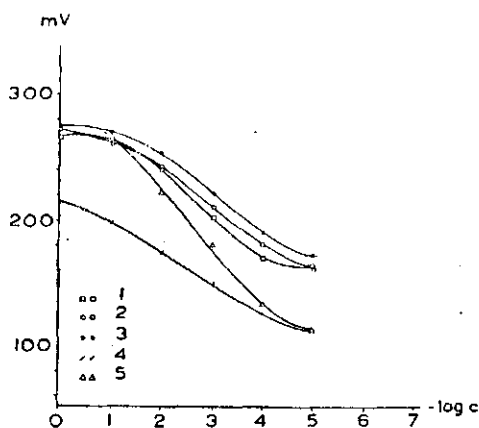


Fig. 2.

The curves are characterized by a middle section which is rectilinear, while at high as well as at low concentrations the curves bend towards the abscissa.

#### Theoretical considerations.

Lundegårdh found similar curves upon using varying concentrations of HCl as liquid to be measured. In that case the maximum slope of the curve was very close to 58 mV per tenfold dilution of the liquid to be measured, so that Lundegårdh came to the conclusion that the root should be considered as an ideal hydrogen electrode. The explanation of this behaviour

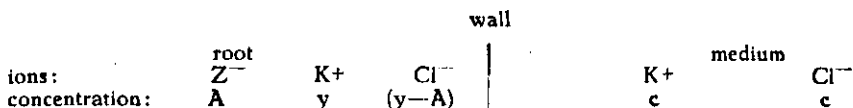
would be that in addition to a small number of spots with positive charges the plasma wall contains chiefly spots with negative charges which adsorb H-ions. The number of these H-ions, assuming complete dissociation, is equal to the number of the negative spots, and thus constant. According to Nernst the result must then actually be a behaviour as an ideal hydrogen electrode. The deviations from the rectilinear form were at first considered by Lundegårdh to be due to the fact that at the extremely high and low potentials the plasma surface modified its properties. Later on Lundegårdh<sup>3c)</sup> found a better explanation in the assumption of a Donnan equilibrium between plasma wall and liquid to be measured, which makes the bending at high concentrations understandable. The bending at low concentrations was thought to be a result of the spots of positive charges intervening in this region, a point of view which seems to be poorly founded, and which would also be rather strange since the more the  $p_H$  increases the less the positive spots will take part in the determination of the potential, on account of their decreasing dissociation. In addition to this explanation of the HCl curve Lundegårdh gives an explanation of the salt curves which is based on the fact that the ion is exchanged for a metal ion up to a definite equilibrium state, which is determined according to the law of mass action. The H-ion here keeps on being the potential-determining ion, its action is only modified by the presence of the metal ion.

We are unable to follow Lundegårdh as to his preference for hydrogen as the potential-determining ion, nor do we agree with the assumption of the validity of the Donnan equilibrium exclusively for the hydrogen ions, whereas the metal ions would behave according to the law of mass action, quite apart from the question whether metal ions behave according to the law of mass action at all. In the following therefore we shall attempt to give a perhaps more correct and better founded explanation of the facts.

Recognizing the correctness of Lundegård's theory that in the root potentials the Donnan equilibrium plays a predominant part, we shall in the following attempt to give a picture of the origin of root potentials on the basis of this principle, which has also been applied with considerable profit to similar problems by other investigators (Loeb, Hitchcock, Mattson and many others).

We assume that roughly speaking a root consists of a space filled with water in which molecules and molecular aggregates of different sizes occur, which in turn contain groups of acidoid and basoid character and which thus may split off H and OH-ions, respectively. If for the present we leave the basoid groups out of consideration, we may say that we have a solution of a certain total concentration A of anions Z, which for the sake of electrical neutrality have an equal concentration of cations as partners. Because of the fact that the whole root is surrounded by a wall of cellulose the large anions are unable to pass through the wall of the root. Thus in principle the conditions for the occurrence of a Donnan equilibrium are essentially present as soon as we bring the root into contact with an aqueous solution of an electrolyte whose ions are capable of diffusing through the root wall.

If we first consider the simple case where this Donnan system contains only one cation, for instance K<sup>+</sup> and one diffusing anion, for instance Cl<sup>-</sup>, and if we further assume complete dissociation of the compound KZ, then upon the establishment of equilibrium a distribution of ions inside and outside the wall occurs according to the following scheme:



In this case  $(y-A)y = c^2$ , . . . . . (1)

from which it may be calculated that in the root the K-ions occur in a higher concentration and the Cl-ions in a lower concentration than in the medium. Due to this unequal ion distribution there must be a potential jump E at the

boundary surface, which has according to Nernst the value  $E = \frac{RT}{F} \ln v^2$ ,

when v is the ratio of concentrations of each of the ions to the left and right of the wall. If we express the potential in mV, the following is valid at 18° C:

$$E = 57.7 \log v \quad \dots \dots \dots (2a)$$

For the case above mentioned we obtain  $v = \frac{c}{y} = \frac{y-A}{c}$ , and when we substitute this in (1) we find that v can be found as the root of the equation

$$v^2 + \frac{A}{c} v - 1 = 0 \quad \dots \dots \dots (3)$$

On varying c, changes in the potential evidently occur. These changes in the potential can be measured by introducing an unpolarizable electrode to the left and right of the wall and measuring the changes in the E.M.F. of the element thus formed. The above described arrangement for measuring the root potential meets these requirements.

When we calculate the potentials at different values of  $c$  with the aid of equation (3), assuming that  $A = 10^{-1}$  (an assumption which for the present is quite arbitrary), we obtain the values given in table II, which for an actual case must of course be increased or decreased by the other potential jumps which occur in the circuit.

Table II.

Conc. $c$	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$
$E$	-1	-12	-58	-116	-174	-232	-290	-348

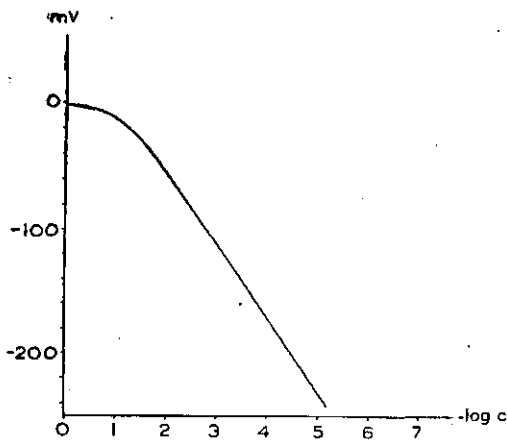
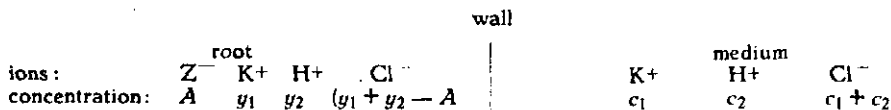


Fig. 3.

Fig. 3 gives the corresponding curve in which  $E$  is plotted against  $-\log c$ . From this curve we note that in this (imaginary) case in the region of low concentrations the root behaves as an ideal potassium electrode, i. e. the change in potential is 58 mV with a tenfold dilution. At higher concentrations the curve bends off towards the abscissa and is finally asymptotic. The same phenomenon was observed in the case of the actual root potentials. The bending off there occurring at low concentrations is still missing in our theoretical case.

It is however not difficult to make this also clear on the basis of a simple case. For that purpose we assume the Donnan system with two diffusing cations, for example  $K^+$  and  $H^+$  and one diffusing anion, for example  $Cl^-$ , while  $KZ$  and  $HZ$  are both completely dissociated.

The distribution of ions to the right and left of the wall now becomes as follows upon establishment of equilibrium:



In this case

$$y_1(y_1 + y_2 - A) = c_1(c_1 + c_2), \dots \dots \dots (4)$$

and also

$$y_2(y_1 + y_2 - A) = c_2(c_1 + c_2), \dots \dots \dots (4a)$$

so that between  $y_1$  and  $y_2$  there is the relation

$$\frac{y_1}{y_2} = \frac{c_1}{c_2} \dots \dots \dots (4b)$$

Again  $E = 57.7 \log v$  at  $18^\circ \text{C}$ , with  $v$  as ratio of concentration of each ion on either side of the wall, thus

$$v = \frac{c_1}{y_2} = \frac{c_2}{y_1} = \frac{y_1 + y_2 - A}{c_1 + c_2} \quad \dots \quad (5)$$

From (4) and (5) it now follows that  $v$  may be found as the root of the equation

$$v^2 + \frac{A}{c_1 + c_2} v - 1 = 0 \quad \dots \quad (6)$$

an equation which passes over into equation (3) for  $c_1 = 0$  or  $c_2 = 0$ .

Changes in  $c_1$  as well as changes in  $c_2$  now result in changes in potential. One may also say that both kinds of ions now act as potential-determining ion, or, the root reacts like a mixed electrode. In the case of our measurements in KCl solutions we now actually have two potential-determining ions: in addition to K-ions there are always H-ions present in the solution, which, it is true, have no effect at higher KCl concentrations, but at lower concentrations of KCl take on for the greater part the function of potential-determining ion. Table III, which gives the potential values calculated with  $v$  (from (6)), accordingly shows the same potentials as table II at high KCl concentrations; at lower concentrations the deviations appear. We again assumed that  $A = 10^{-1}$ , while  $c_2$  is taken equal to  $10^{-5}$ , an H-ion concentration which may easily be attained in water which is not free of  $\text{CO}_2$ , while moreover the roots give off  $\text{CO}_2$  actively so that the concentration of the H-ion around the root is probably higher. In this connection *Lundegårdh* remarks that in this way, partially at least, the root creates its own medium.

Table III.

Conc. $c_1$	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$
$E$	-1	-12	-58	-116	-172	-215	-230	-232

Fig. 4 shows the corresponding curve (curve A);  $E$  is plotted against  $-\log c_1$ . It may be seen that the curve is asymptotic at high as well as at low concentrations, while over a certain traject (between  $c_1 = 10^{-3}$  and  $c_1 = 10^{-2}$ ) the maximum slope of 58 mV is still reached, so that the point of inflexion also lies in this region.

Also shown in fig. 4 (curve B) is the behaviour of the curve when we assume for  $c_2$ , not the value  $10^{-5} \text{N}$ , but  $10^{-4} \text{N}$ . The values of  $E$  are given in table IV.

Table IV.

Conc. $c_1$	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$
$E$	-1	-12	-58	-114	-157	-172	-174	-174

In nature this curve is similar to the previous one, but here the phenomenon appears that the maximum slope is no longer 58 mV, but 56 mV (between

$c_1 = 10^{-2}$  and  $c_1 = 10^{-3}$ ). If we took  $c_2$  still larger, the distance between the two asymptotes would become smaller and smaller, likewise the maximum slope.

The measurements show that this is actually the case; fig. 5 shows several curves as found by *Lundegårdh*<sup>3c)</sup> upon the use of KCl solutions of

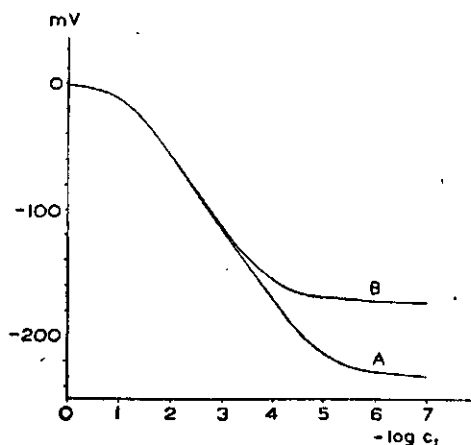


Fig. 4.

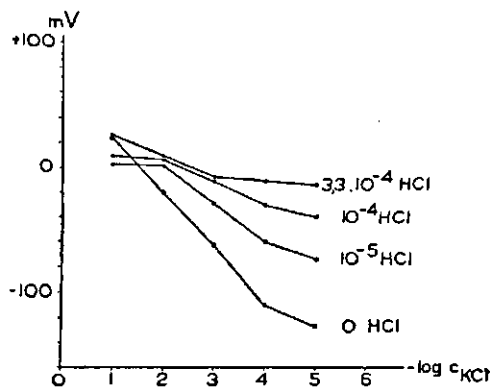


Fig. 5.

different concentrations acidified with different amounts of HCl. Between  $10^{-2}$  N and  $10^{-5}$  N KCl the expected behaviour is observed in the curves; the measurements of  $10^{-1}$  exhibit irregularities. Curves in many respects comparable to these were found by *Zwart Voorspuij*<sup>2)</sup> with glass electrodes when two cations were present in the medium.

It is thus clear that with the simplest possible assumption curves can be obtained which, as far as their appearance is concerned, agree very well with the curves found experimentally. Because of the assumptions which have been made and which do not correspond to reality in every respect, the above simple conception must still be elaborated in various directions.

The theory as a whole, however, does not meet with the objection to *Lundegårdh's* theory, which assumes a different mechanism for H-ions and metal ions as far as their influence on the potential is concerned.

It is our intention to work out this problem in more detail in subsequent publications.

Wageningen, *Agricultural College, Laboratory of Physical and colloid-chemistry,*

*Laboratory for the cultivation of agricultural plants,*  
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