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# Cationic Activities and the Exchange Phenomena of Plant Roots. I. A Preliminary Report

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CATIONIC ACTIVITIES AND THE EXCHANGE PHENOMENA  
OF PLANT ROOTS. I. A PRELIMINARY REPORT\*

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This probably is the first attempt to measure the cationic activities of plant roots; however, initial results confirm the possibility of such determinations. Results of studies of this nature give promise of adding to the knowledge of plant nutrient uptake. This study is possible only as a result of the coming together of three different streams of research which, until recently, were not intentionally considered very closely related. The first of these branches of research, analogous to the upper tributary to a main stream, began slightly more than a century ago with the classical experiments of H. S. Thompson (27) which were extended and confirmed soon thereafter by J. T. Way (28). Liebig also made some contribution to this early work (10). These studies demonstrated beyond any doubt that soils have a capacity to hold and to exchange cations on an equivalent basis. Although these results were published, they were lost to the average agronomist until their significance became more appreciated some 3 or 4 decades ago. Without this capacity to adsorb nutrients the problem of maintaining the fertility of the soil would be infinitely greater. Prior to the general recognition of this ability of the soil to hold nutrients in a more or less available form, total chemical analysis was considered the best index of soil fertility. With the gradual rediscovery of the significance of the exchange mechanism, most soil chemists changed the emphasis of soil fertility from one based upon the soil's total analysis to one based upon "available" or exchangeable nutrients. Not long thereafter soil chemists began to recognize that not all of the exchangeable nutrients were equally available. Leaching experiments showed that there were differences in the ease of release of different cation species and also that the presence of a second cation affected the release of the first (6). Although this was not designated as such, these were the first attempts to measure the activities of cations in soil systems. Up to that time research involving the exchange phenomena of soils had dealt principally with determinations of the exchangeable cations present as well as the exchange capacities of different soils.

The second and third research "contributaries" started much later than the first. In fact, most of the investigations dealing with these phases have been made within the past two decades. The development of membrane electrodes for measuring cationic activities will be considered first.

By means of pure chemical and physical arguments and certain assumptions, both Planck and Henderson had arrived at similar equations for liquid junction potentials. Theorell (26) and Meyer and Sievers (22), working independently, took this liquid junction potential theory and developed it into a membrane electrode theory by substituting for the simple liquid junction a charged membrane with its accompanying Donnan equilibrium. At this point Marshall (11) attempted with some success to make charged membrane electrodes from zeolite mineral crystals. Later, it was found that clay films, when heated, worked more satisfactorily as cation electrodes (15). As the technique was perfected with

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true solutions (15), (17), (20), (12), (13), (19), it also was found feasible to measure cationic activities in clay and soil systems (16), (18), (20), (21), (14), (1). Using different materials and different heating techniques, it was possible to measure monovalent and divalent cations in mixed systems (25), (23), (24). This permitted cation interactions such as would be found when lime and fertilizers are applied to the soil. From the activities of the cations the mean free bonding energies could be computed (14). This gave quantitative figures to the ease of release of cations from the exchange phenomena of the soil. Although this meant much in understanding nutrient availability, there still was much to be learned about uptake by plants.

At the time that membrane electrodes were being perfected, a third research stream was developing around the exchange mechanism of the plant root. That plant roots have the ability to adsorb and release cations by exchange was perhaps first demonstrated by Jenny and co-workers (8), (9), (7), (3) in their studies with barley roots. Later experimenters have determined that roots have definite exchange capacities which are affected by plant species (4), (29), (2), (5), temperature (5), age (5), and other influences.

In summarizing the historical "contributaries" leading to the present status of this stream of knowledge, it may be said that the research which originally dealt only with the exchange mechanisms and adsorbed cations of soils and clays was supplemented with research making use of the clay membrane electrodes as tools to throw more light upon the ease of release of the adsorbed cations. Now it appears that the exchange mechanism of plant roots has been sufficiently demonstrated and characterized to warrant the use of the same tool in an attempt to understand better the motive for nutrient uptake.

*Experimental.* Using the technique of Drake *et al.* (2), two grasses and two legumes were grown in 1/5 Hoagland's solution. The grasses were grown 50 days and the legumes 30. The solution was allowed to drip intermittently, with occasional flushes with distilled water. Crushed limestone was used to support the plants. Although some preliminary work has been done on the two grasses (Reed Canary and red top) and the two legumes (Kansas common alfalfa and Ogden soybean), due to difficulties in perfecting the technique and the time necessary to grow the grasses, only the legume studies will be considered here. The tops and larger tap roots were cut from the root masses and discarded. The roots then were placed in collodion bags and placed in a Bradfield electro dialysis cell for 90 minutes with a current not less than 0.3 ampere at 110 volts. A few drops of HCl were placed in the cell at the start of the dialysis to speed up the process. After the dialysis the roots were washed with carbonated water and centrifuged for 5 minutes at 2,000 rpm. A 1.2-g sample of the centrifuged roots was placed in a 100-ml beaker. Enough NaOH, KOH, or Ca(OH)<sub>2</sub> was added to bring the pH up to 7 and maintain it for 10 minutes. Because it was necessary to keep constant the total volume of liquid added for the different bases and plant roots, .02 N solutions of each of the bases were prepared and enough water was added to make 7.5 ml total volume of liquid added to the 1.2 g of centrifuged roots. In order to facilitate rapid equilibrium, for 5 minutes after the base was added the roots were stirred with a rubber policeman. Then, for the second 5 minutes the roots, were stirred only occasionally in making the pH measurements. This procedure was duplicated as nearly as possible in making the activity measurements on a similar sample of roots. After three trials it usually was possible to determine accurately the amount of base required to maintain the pH at 7 for 10 minutes. This was taken as the exchange capacity of the roots and the basis on which the active fractions were determined and the bonding energies were calculated.

When the exchange capacity of the roots had been determined, the necessary amount of base was added to another 1.2-g sample of the roots and after stirring for 5 minutes to attain equilibrium, the clay membrane electrodes were placed in contact with the roots for 5 minutes. The root mass was stirred and turned occasionally before measurement was made.

To make certain that the cations added to the roots remained exchangeable and that significant amounts of contaminating cations from within the roots were not complicating the activity picture, a leaching experiment was performed on the roots after the 10-minute treatment. Approximately 40 ml of 0.1 normal HCl was leached by suction through the 1.2 g of roots. Essentially all of the cations added were recovered, and no appreciable amounts of sodium or potassium

came out of the roots to contaminate the systems. A small amount of calcium came out into the sodium and potassium systems. This, however, was not considered sufficient to affect the readings obtained. Whether this is a natural phenomenon or whether it was peculiar to this experiment is not known. Because these plants were grown on limestone gravel bathed in 1/5 Hoagland's solution, the high lime in the resulting solution may have been the cause of the calcium coming out by leaching with HCl. This will be investigated.

*Results.* The results obtained are summarized in Table 1. Little difference can be seen in the results from the two legumes except that their relative bonding energies for potassium and sodium are reversed in their order of magnitude. This may suggest some differences in their competitive ability to take up potassium. The grasses show promise of more noteworthy differences in these comparative values.

TABLE 1. Activities, Fractions Active, and Free Energies of Cations on Plant Roots.

Plant	Cation	Activity $\times 10^3$	Fraction active (per cent)	$\Delta F$ Cal.
Alfalfa	K	4.26	32.0	672
Alfalfa	Na	4.85	36.4	599
Alfalfa	Ca	0.49	7.3	1549
Soybean	K	3.81	30.1	711
Soybean	Na	3.05	24.1	843
Soybean	Ca	0.38	6.1	1654

*Summary.* It has been found possible to measure the activities of Na, K, and Ca in homoionic plant root systems, using clay membrane electrodes. It is not known what significance these values may have as indices in cation nutrient uptake.

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