Effects of Salts on Oxygen Diffusion Rate Measurements in Unsaturated Soils[1]

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ABSTRACT

Current-voltage curves determined with tips of platinum electrodes touching a solution surface were used to evaluate the effect of solution electrical conductivity and specific ions on measurements of oxygen diffusion rates in unsaturated soil. Current was found to be dependent upon electrical conductivity in pure monovalent cation solutions. In divalent cation solutions, or mixed monovalent-divalent cation solutions, current was only slightly affected by electrical conductivity of the solution. The presence of divalent cations caused a lower measured current with identical solution-electrode geometry and measured electrode potential than when only monovalent ions were in solution. Based upon the assumption that these determinations reflect at least the magnitude of such phenomena that occur in soils, conditions are described under which the platinum electrode should operate most satisfactorily or have a minimum interference from salt.

Additional Key Words for Indexing: salt interference, unsaturated media, platinum microelectrode.

BOTH VAN DOREN and Erickson (9) and Birkle et al. (1) found that electrical conductivity (EC) of solutions and clay suspensions had no effect on oxygen diffusion rate (ODR) measurements. Gradwell (2) found no difference between measured ODR's in unsaturated aggregates of silt loam wet with distilled water or with 0.1N KCl.

For field determinations, however, workers have found that electrical resistance through the soil, which is largely determined by EC of the soil solution, does influence ODR measurement. For example, Kristensen (3) has prepared a figure from which measured currents can be corrected to a standard electrode potential. McIntyre (8) has also emphasized the importance of knowing actual electrode potential rather than applied potential during an ODR measurement. The actual potential of an electrode can be calculated by correcting the applied potential for voltage drops across resistances in the ODR measuring system. It can also be measured directly for individual electrodes by using a vacuum tube volt meter (VTVM) and an independent reference electrode. An improved design of the oxygen diffusion meter would provide automatic applied potential adjustment based on such a direct measurement of electrode potential as obtained in quality laboratory polarographs.

The potential field around an electrode in a soil wet with a solution of low conductivity has a larger gradient than it would in the presence of a soil solution of higher conductivity. An electrode in a low conductivity soil solution will affect the potential of a larger volume around it than will an electrode in a soil solution of higher conductivity. The potential difference between the electrode and the solution immediately adjacent to it (which is the actual potential of the electrode as far as reduction of oxygen is concerned) will, therefore, be less than that measured with a VTVM and an independent reference cell unless the reference cell is located in the solution immediately adjacent to the electrode. Since the reference cell cannot practically be placed that close to an electrode for ODR measurement, it is necessary to determine the magnitude of the solution conductivity effects on ODR currents when using measured "actual" electrode potentials.

Any interference from specific ions that influence ODR measurement and their interpretation should also be determined. Van Doren and Erickson (9) have discussed the influence of such ions as Fe^{3+}, Mn^{2+} and Cu^{2+} under saturated conditions. Cation influences that are different in saturated and unsaturated media have not been reported.

A study of the operation of platinum electrodes in unsaturated media is complicated by the lack of a reproducible standard unsaturated media. The geometry of the electrode-soil-soil solution contact is not the same for any two measurements in different locations within a soil sample. Successive measurements at one location are suspect because of possible electrode "poisoning" (chemical change of the electrode surface or physical coating of parts of the electrode). A reproducible medium that would approximate the conditions to which an electrode is exposed in an unsaturated soil was sought to replace the unsaturated soil and so remove the uncontrollable variability associated with it.

There is reason to believe that the current flowing through an electrode that is only partly immersed in a salt solution will be controlled by the same factors that control the current flowing through an electrode in an unsaturated medium. McIntyre (8) maintains that the migration of ions in water films on the electrodes in unsaturated soils will change the actual potential of the electrode surface. This same phenomenon is proposed by Will (10) as the factor causing local surface potential of a partially immersed electrode to approach zero above a solution meniscus. Although Will (10) was speaking of the oxidation of hydrogen on platinum, the same physical processes—(i) diffusion of an uncharged gas molecule through solution to an electrode where it reacts, and (ii) movement of charged ions in solution away from the electrode—must occur in the reduction of oxygen. Maget and Roethlein (6) studied the reduction of oxygen on platinum in sulfuric acid. They also indicate that the unsubmerged portion of a partially immersed electrode has a near zero polarization potential because of the migration of ions parallel to its surface. As McIntyre (7) has pointed out, ions must move parallel to an electrode surface to points of contact with soil particles in unsaturated soils in order to conduct current from an electrode to the soil.

If similar processes do control the relation between current and voltage of a platinum electrode in an unsaturated soil and when partially immersed in a solution, then the partially immersed electrode may be used to study factors that influence current in unsaturated soils.

The experiments reported in this paper attempted to demonstrate the similarity of conditions discussed immediately above and use partially immersed electrodes to establish the magnitude of the effect of solution electrical conductivity and specific cations on ODR measurements taken in unsaturated media, using measured electrode potential.

PROCEDURE

ODR measurements were taken with an applied potential of −0.65 volts vs. Ag-AgCl in saturated KCl in sand samples located on a tension table. The sand samples were wet with different salt solutions of various conductivities. Plastic sheeting covered the surface of each tension table to minimize evaporation.

The sand was held in acrylic plastic cylinders 15.2 cm (6 inches) in diameter and 6.4 cm (2½ inches) high. A lid for each cylinder had holes for 10 electrodes and two reference

cells. A small bolt was located near each electrode hole to allow electrode leads to be held securely once the electrodes were installed. Electrical contact was made to the bolts in the container lid so the electrodes were not moved when leads were connected and disconnected. The 6-mm-long, 25-gauge electrodes were left undisturbed in the sand for up to 4 weeks.

In one experiment, two tension tables were used. After the experiment, electrical conductivity of the solution was 3.1 mmho cm^{-1} in the one wet with tap water and 70 mmho cm^{-1} in the one wet with NaCl solution. Electrodes were installed in saturated samples. Daily ODR measurements were made as the water tables were lowered in various steps.

Current-voltage curves were determined on electrodes in the sand samples. Voltage was applied in 0.1-volt steps at 1-min intervals from an ODR meter (5). The voltage of each electrode was monitored with a Simpson[3] Model 312 VTVM vs an independent Ag-AgCl in saturated KCl fiber junction reference cell. Measured electrode voltage, not applied voltage, was plotted against measured current. Current was recorded on a Sargent Model SR recorder that was driven by a Keithley Model 610B electrometer. The electrometer was in series with the electrode of interest.

Setting up the tension tables for each salt solution was time-consuming, and numerous measurements were necessary to establish a representative curve for each salt. Therefore, a more rapid technique was sought for finding the information desired in a system simulating the conditions in an unsaturated soil. For this purpose, the same current and voltage measuring systems were used to determine current-voltage curves on electrodes with only their tips touching a salt solution surface.

The reference cell used for the measurements was in direct contact with the solution. An anode contacted the solution through an agar-filled salt bridge. Salt solutions of Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} Cl$^-$ and SO$_4{}^{2-}$, and NaHCO$_3$, with conductivities ranging from 0.1 to 100 mmho cm^{-1} were used for these measurements. Current at given measured electrode potential was plotted vs. solution conductivity for each salt. A capillary tip reference cell made from drawn glass tubing was used to measure electrode potential as a function of distance from an electrode. All measurements were made in a room with maximum temperature fluctuation of 3C.

RESULTS

ODR measurements in two sand samples wet with tap water or NaCl solution (made up with tap water) provided only an indication of possible differences between results in the two media. In Fig. 1 is shown the average ODR from 10 electrodes for each sample. Measured ODR values appear greater in the salt solution sample than in the tap water sample at 24 cm of H$_2$O tension.

In Fig. 2 is shown a series of current-voltage (i–v) curves taken with one electrode submerged in, partially submerged in, and with only its tip touching a K$_2$SO$_4$ solution. As less of an electrode was submerged, the i–v curve lost its diffusion plateau." The i–v curves of partially submerged electrodes and those with only their tip touching the solution are similar in shape to the i–v curves found in unsaturated soils.

The i–v curves from submerged electrodes could be reproduced within 5% at will. Those from a partially submerged electrode or one with its tip only touching the solution could be reproduced within 20% with a single
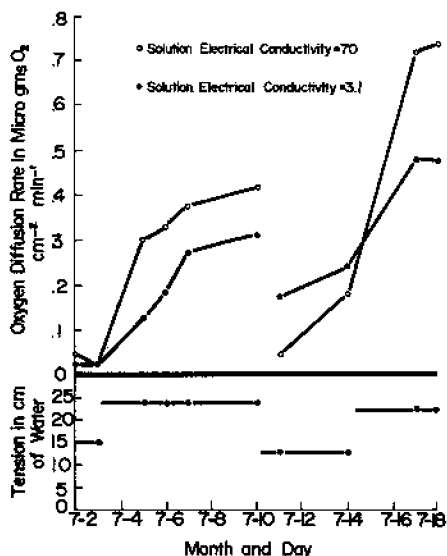
Fig. 1—Oxygen diffusion rate and tension in a medium sand wet with tap water and NaCl solution.

electrode. Different electrodes that were apparently equally immersed in the same solution would yield currents that were different by as much as a factor of 3 depending on the pretreatment history of the electrodes.

In Fig. 3 is shown the results of several solution measurements from similarly pretreated electrodes with only their tips touching the solutions. Current for NaCl is typical of currents that were obtained for all monovalent cation salt solutions, and current for $CaCl_2$ is typical of those taken from curves made for divalent cation salt solutions. There was an increase in current with increasing EC in the monovalent cation salts up to an EC of about 10. Above an EC of 10, current changed little with increasing conductivity. A monovalent cation associated with a divalent anion (such as Na_2SO_4 which was used for Fig. 3) caused a smaller change in current with increased conductivity than when a monovalent anion was present, and the conductivity above which no increase in current occurred was
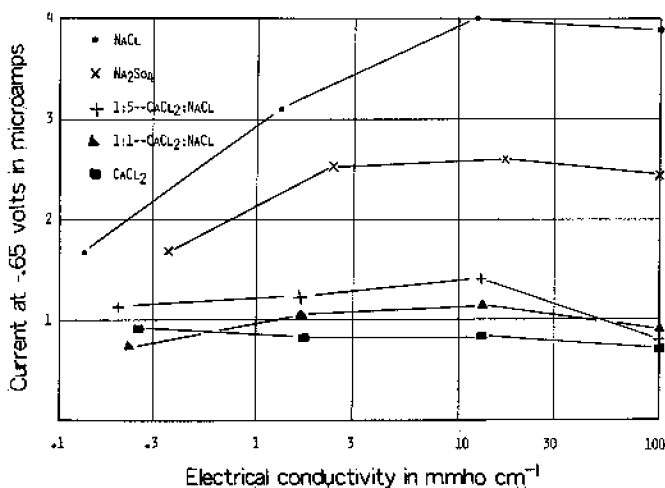

Fig. 3—Current from a platinum electrode just touching salt solutions of various electrical conductivities. The ratio of salts is in terms of equivalents.
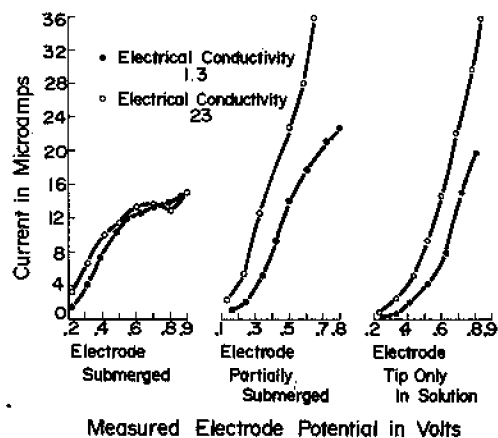

Fig. 2—Current-voltage curves from a platinum electrode just touching, half submerged in, and submerged in K_2SO_4 solution.

lower. For the divalent cation salts there was little change in current with increasing salt concentration. Current was lower at any EC with a divalent cation solution than with a monovalent cation solution with the same measured electrode potentials and solution geometry around the electrodes.

Mixtures of monovalent and divalent cations yielded currents between the values obtained in a pure solution of either salt. Only a small percentage of divalent ions caused a major depression of measured current.

The addition of clay to a solution had little or no effect on the influence of the monovalent or divalent ions. In Fig. 4, currents measured in $0.1N$ KCl or $CaCl_2$ clay suspensions are illustrated. When the electrodes were submerged, there were no specific salt effects on the measure-
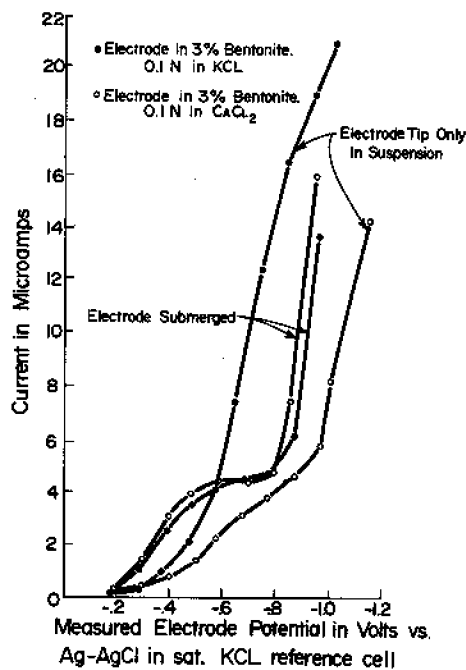

Fig. 4—Current-voltage curves from an electrode just touching and submerged in 2% clay suspensions which were $0.1N$ in KCl or $CaCl_2$.

Table 1—Minus 0.65-volt current in microamps from current-voltage curves taken with undisturbed electrodes in medium sand on a tension table

Tension in cm of water	Solution in sand				Date of measurement
	CaCl₂ EC ≈ 1.2		KCl EC ≈ 1.2		
	Electrodes		Electrodes		
	34	92	26	82	
0	0.5	0.5	0.2	0.4	9/18
24	2.0	1.7	13.0	16.0	9/19
34	1.3	1.2	4.7	12.0	9/21
5	2.1	0.3	1.7	0.3	9/25
0	0.2	0.2	0.2	0.6	9/26

ments. When the electrode tips only touched the suspensions, a difference between measured currents for K and Ca chlorides with the same electrode potential was evident.

Minus 0.65-volt currents from i–v curves taken in sand wet with KCl and CaCl₂ solutions at a conductivity of about 1.2 mmho cm⁻¹ are given in Table 1. Current was lower by a factor of about four from electrodes in CaCl₂-wetted sand than from KCl-wetted sand with a tension of 24 cm of H₂O, or greater. At zero tension there was no difference between treatments. The date of each measurement is given in Table 1 to provide the sequence of the measurements and times allowed for equilibrium of water movement within the samples.

DISCUSSION

From only ODR measurements in sand, one has difficulty establishing the influence of solution salt concentration on the ODR measurement. In Fig. 1 it is shown that in a saturated sand little difference existed between measurements in the two different media. At a suction of 24 cm of water (air entry into the sand occurred at 20 cm of water) there appeared to be a difference in the average currents. Even though each plotted point is the average from 10 measurements there is no statistical difference between the curves. One can only state that average current from the sand wet with salt solution appeared to be higher than average current from the sand wet with tap water when both were at a tension of 24 cm of water.

McIntyre (7), Gradwell (2) and Birkle et al. (1) have shown that i–v curve from an unsaturated soil lacks a diffusion plateau. A similarly shaped curve was obtained with an electrode that was not completely submerged in a solution (see Fig. 2). Measurements shown in Table 1 indicate that the same trends in measured current do occur in unsaturated sands as well as in solutions with the same salts present. Most of the conclusions of this paper are therefore based on the assumption that a partially immersed electrode provides at least an order of magnitude approximation of an electrode in an unsaturated granular medium.

In Fig. 3 it can be seen that currents increase with increasing NaCl concentration up to a conductivity of approximately 10. At conductivities higher than this, currents change little. At the lower conductivities, the current may be lower than expected because of a potential drop within the potential measuring circuit itself. Even the measured electrode potential may not be the correct one.

In order to check this factor, resistance measurements

were made. The measured resistance between a reference cell and an electrode with its tip only in solution was from 20,000 to 70,000 ohms, depending on solution conductivity and contact between the electrode and solution. Conductivity of solutions used for measurements ranged from 50 to 0.5 mmho cm⁻¹. Assuming a resistance from the electrode through the reference cell of 10⁵ ohms, with the VTVM used, any difference between actual electrode potential and measured potential was of the order of 5 mv or less. A potential difference of this order would make little difference in current.

If the potential field near the electrode extends significantly into solution, the potential difference between the electrode and the solution immediately adjacent to it will be less than that measured with the VTVM and reference cell in the bulk solution. Using a reference cell with a capillary tip of drawn glass tubing, the potential of an electrode was determined with the reference cell at different distances from the electrode. In a KCl solution with an electrical conductivity of 1.3, the electrode potential differed as much as 0.03 volt between placing the reference cell tip within 1 mm of the electrode and placing it 1 cm or farther away from the electrode. In an unsaturated medium wet with a solution of low conductivity, therefore, the actual electrode potential can be different from the measured potential. If the currents from an environment containing only monovalent cations are corrected for measureable potential differences, they still are not high enough at low salt concentrations to show current independent of salt concentrations.

Lowered currents at low salt concentrations could be explained by Will's (10) contention that migration of ions parallel to the electrode surface above the meniscus causes local depolarization of the electrode. The measured electrode potential was, therefore, not equal to that which existed between the electrode and the film of water on it. The conductivity of the film would be expected to exert a major controlling influence on the current flowing through the electrode.

Because of this movement of ions in thin films on the electrode surface, lowered currents in the presence of divalent ions might be explained by considering the mobility of the ions involved. Values for the mobilities of Na⁺, K⁺, Ca²⁺, Cl⁻, and SO₄²⁻ were taken to be the ratio of the equivalent conductance of the separate ions at 25C (taken from standard tables) to the Faraday. The values for mobilities ranged from 5.3×10^{-4} (cm₂/sec volt) for Na⁺ to 8.4×10^{-4} for SO₄²⁻. K⁺, Ca²⁺, and Cl⁻ mobilities all are within the range of values given. No consistant relation between ionic mobilities and measured currents was apparent.

It is clear that there is a major difference between currents measured in the presence of monovalent and divalent cations. For electrodes with tips only contacting the divalent cation solution, the current is only 25 to 50% that measured from monovalent cation solutions of equal conductivity.

Kozawa (4) pointed out that the oxide surfaces of platinum are expected to exhibit ion exchange properties. In

basic solution the platinum oxide acts as a cation exchanger. Since the oxide takes an integral part in the oxygen reduction process, one might expect, as appears to be the case, that the nature of the cations around an electrode influences oxygen reduction.

What effect will this have on the interpretation of ODR measurements? Rarely will a soil solution contain only monovalent or only divalent cations. In Fig. 3 is also shown current from mixed salt solutions. There is a gradation of the currents in mixed salts between that in a monovalent and divalent salt solutions. Current is not directly related to the ratio of divalent to monovalent cations, however. With only 1 part of $CaCl_2$ solution to 5 parts NaCl solution of equal conductivity, measured current is still only one-third that in NaCl solution at an EC of 10.

It should be pointed out that the currents reported are typical of measurements made in various solutions used. The absolute values obtained will, of course, depend upon electrode size and the total area of meniscus as indicated by the difference in magnitude of currents in Fig. 2 and 3. The differences between currents from the various solutions are indicative only of the magnitude of differences caused by the salts involved.

The differences shown in Fig. 3 among measurements taken in solutions with Ca^{2+} present can be considered insignificant for most field purposes. If differences no larger than those indicated occur in field measurements, the ratio of monovalent to divalent cations should have little influence on the measurements. If significant effects do occur, they might be expected when a saline soil is limed and leached. Preleaching measurements will be from a soil solution of high EC and high ratio of Na^+ to Ca^{2+}. Postleaching measurements will be from a soil solution of lower EC and lower Na^+ to Ca^{2+} ratio.

Greenhouse or laboratory plant cultures may provide conditions in which the type or concentration of a particular salt can significantly influence ODR measurements. Note that different ODR measurements are to be expected from unsaturated media with only monovalent ions present than if divalent ions are present too.

CONCLUSIONS

Two factors have been discussed that may influence ODR measurements—conductivity of soil solution, and the ratio of monovalent to divalent ions in the soil solution. Both of these factors vary from soil to soil and on occasion within any one soil. In what soils, then, can the electrodes be expected to operate most satisfactorily as far as these two factors are concerned?

The reason for the influence of solution conductivity on the measurement is evidently the migration of ions parallel to the electrode surface. If this is the case, the more directly the ions can be removed from an electrode, the less will be the effect of conductivity on the measurement. Fine-textured soils will provide more opportunity for direct

particle contact (and, therefore, solution contact) with an electrode than will coarse-textured soils. The electrodes should operate more satisfactorily in fine-textured soils than in coarse-textured or well-aggregated ones. Fortunately it is in fine-textured soils that one is most often concerned about poor aeration.

For maximum consistency in comparison of measurements between soils, one ideally should compare readings from soils that provide comparable solution geometry and similar monovalent to divalent cation ratios. It is again fortunate that in mixed salt solutions there is little effect of solution conductivity on measurements. Rarely will only monovalent cations be present in soils. With a maximum difference of a factor of not quite two between currents from 100% $CaCl_2$ solution and that from 80% NaCl, 20% $CaCl_2$ solution at EC 10 as shown in Fig. 3, the actual influence of various ratios of monovalent to divalent cations upon measurements appears to be relatively unimportant. Even if major changes in cation populations occur in fields because of such practices as gypsum application, leaching, or long-term use of poor quality irrigation water, the changes would not be expected to be sufficient to cause changes in ODR because of the salts.

In laboratory work where only monovalent ions may be used in unsaturated media, quite different ODR measurements are to be expected from media with, and those without, divalent ions.

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