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ON THE ELECTRODE PROBES DESIGNED FOR THE SPECIFIC ELECTRICAL CONDUCTANCE OF UNSATURATED SOIL

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SYNOPSIS

This paper studies the specific electrical conductance (C) of NaCl salt solutions of varying concentrations and the C of NaCl solutions with glass beads under unsaturated conditions using electrode probes of different sizes. To provide accuracy in obtaining C values in solutions, a parameter called contact conductance (*ki*) was introduced. Under unsaturated conditions, the value of the total electrical conductance measured by the probe was affected not only by the concentration and moisture content, but also by the shape of the probe and temperature. The properties of the probe were studied theoretically and checked by experiments.

INTRODUCTION

Contamination of groundwater and soil water due to various pollutants and radioactive waste has become a serious environmental problem in recent years. The distribution of contaminants in the soil is the result of mass transport processes such as diffusion, dispersion and convection (1). However, these processes have been mainly studied in saturated porous media rather than unsaturated ones. When solute movements are studied in saturated-unsaturated porous medium, specific electrical conductance (C) is sometimes used, because it has the excellent characteristics of easy handling, least disturbance to the flow and continuous measurements. In such cases, commercial specific electrical conductance meters are not available, because they are usually designed only for use in solutions and not in saturated-unsaturated porous media, and researchers are obliged to make modified meters by themselves for their own purposes (3), (8). On the other hand, specific electrical conductance is influenced by many factors other than solution concentration, such as moisture content, temperature, soil type, kind of ion, mobility of ion and geometry of the electrode (6), (7). The probes produced by researchers,however, are designed rather empirically and the relationship between the resistance of the probe and the concentration of the solution can only be found through experiments.

Based on these problems, this paper aims to make clear the characteristics of a specific electrical conductance probe, designed for an unsaturated porous medium. In this research, relationships between the concentration of the solution, moisture content and electrical conductance of a soil-air-solution system were obtained. Using these relationships, the concentration of the solution in an unsaturated soil can be estimated by observing electrical conductance and moisture content which is measured separately by tensiometer. The probe we investigated is composed of parallel cylindrical electrodes which less disturb water flow in the soil. We used NaCl salt as a solute and glass beads for the porous medium, which do not react with each other.

THEORETICAL CONSIDERATIONS

Specific electrical conductance (C) of a medium is the conductance of a cube of substance one centimeter on a side. The material is assumed homogeneous and isotropic electrically. Though specific electrical conductance is inherently defined in solution systems, this study extends the definition into the unsaturated soil-water system which is composed of water with dissolved salts, the solid material and the air.

From potential theory (4),(5), the electrical current flux i (A/cm^2) is related to the potential gradient $\partial E/\partial r$ as in Eq. 1:

$$i = -C\frac{\partial E}{\partial r} \tag{1}$$

where r = the space coordinate in the direction of current, C = the specific electrical conductance (μS/cm) of the medium. The electrical potential distribution can be calculated by solving Eq. 1 with the conservation law of current with given boundary conditions, (e.g. electric potential on the surfaces of the electrodes). The schematic diagram of the probe studied here is shown in Fig. 1. Electrically the probe consists of sections of two finite parallel cylinders and four ends which contribute differently to the total potential at any point. To include these field contributions, we combine half-spheres at the two ends of each cylinder and assume that the addition of the four half-spheres will represent the three-dimensional electrical field of the total potential.

Fig.2 shows the electrical field for two infinitely long parallel cylinders with electric potential at each electrode surface and zero at a point a long distance from the electrode. The solution of Eq. 1 for this problem gives the total potential at any point in the medium as the algebraic sum of the contributions from the two electrodes and hence,

$$E_C = E_{C+} + E_{C-} = \frac{I_C}{2\pi C l}\, ln\left(\frac{r_2}{r_1}\right) \tag{2}$$

where I_C = a partial current of the cylindrical electrode for the length l and r_1, r_2 = distances between the point and electrodes. Using the probe dimensions, i.e., radius a and separation d, and taking the potential difference ΔE between the two parallel cylinders, we then have

$$\Delta E = E_{C1} - E_{C2} = \frac{I_C}{\pi C l}\, ln\left(\frac{d}{a}\right) \tag{3}$$

where E_{C1} and E_{C2} = the electric potential on two electrodes calculated by Eq. 2.

The electric potential field for two spheres can be derived in a similar manner as;

$$E_S = E_{S+} + E_{S-} = \frac{I_S}{4\pi C}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{4}$$

where I_S = the current between the spherical electrodes. Again using the dimensions of the probe, and taking the potential difference between the two spheres, we then have

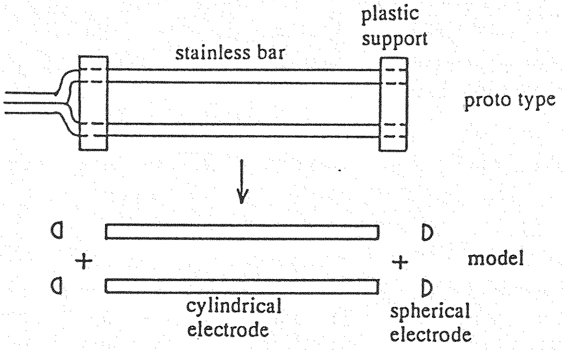

Fig. 1 A schematic diagram of the probe and its ideal representation.

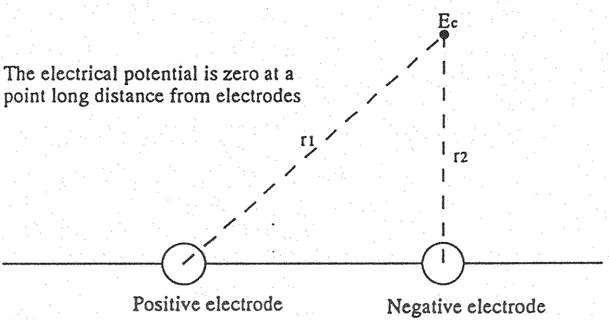

Fig. 2 The electric field of two infinitely long parallel cylinders .

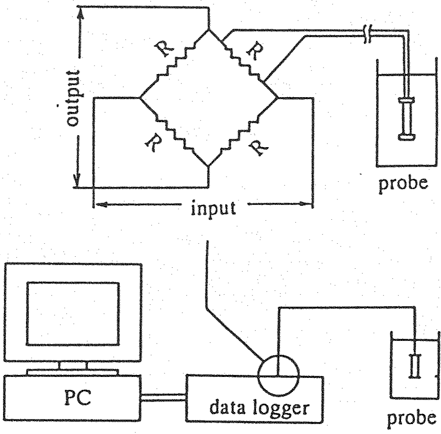

Fig. 3 Schematic diagram of measurement system.

$$\Delta E = E_{s1} - E_{s2} = \frac{I_s}{2\pi C}\left(\frac{1}{a} - \frac{1}{d}\right) \tag{5}$$

The total current of the electrode of finite length are the contributions from the two superimposed shapes expressed as;

$$I = I_C + I_S \tag{6}$$

Rearranging and substituting Eqs. 3 and 5 to Eq. 6, a consequent relationship is obtained as

$$\frac{I}{\Delta E} = \frac{1}{R} = \frac{\pi Cl}{\ln(d/a)} + \frac{2\pi C}{1/a - 1/d} \tag{7}$$

Equation 7 is used in converting a measured resistance R into specific electrical conductance values C of the medium. This equation is initially used in the preliminary experiments. As discussed later, Eq. 7 is modified to a more refined form.

ROLE OF CONTACT CONDUCTANCE

Preliminary Experiment

To check the adequacy of Eq. 7, a preliminary experiment was conducted using NaCl solution as the conductive medium. The setup of the experiment is schematically shown in Fig. 3. The electric resistance of the solution is usually very large. Therefore, the probe was installed in a bridge circuit shown in Fig. 3, and resistance R in Eq. 7 was measured through the offset of output voltage by a strain gage data logger. Strain values measured were converted into resistance values using conversion relations of the bridge circuit. Finally, the resistance R was converted into specific electrical conductance C by Eq. 7. The control of measurements and data acquisition was provided by a personal computer.

The parameters controlled in the experiment were the dimensions of the probe and specific electrical conductance of the solution, i.e., the concentration of NaCl solution. Temperature and other conditions were kept constant.

Results of the experiment are summarized in Fig. 4a as a comparison between C values estimated by Eq. 7 and true C values measured by an ordinary conductance meter. From the figure, it can be found that the computed C values are lower than those measured by the conductance meter especially at higher C values. This result indicates that the factors considered in Eq. 7 are not sufficient and some important factors are missing in the derivation. Other possible factors affecting the conductance of electricity are the differences in chemical nature between the electrode material and medium, and electrochemical reactions that occur between the metal (electrode surface) and the solution.

Contact Conductance

Based on the electrochemistry, it is manifested that there exists a region between the metal and the solution, where water molecules are adsorbed. This is shown in Fig. 5a and 5b. Under a non-homogeneous electric field, the water molecules or dipoles tend to align themselves along the direction of electric field. They are pulled towards an increasing electric field, i.e., towards the metal. Because of these field-dipole forces, the metal is covered around by a sheath of immobile water dipoles.

This immobile water layer prevents the passage of electrical charges. Therefore, a resistance appears in the interface of these two substances. This phenomenon is called polarization (2) and this resistance ri is called contact resistance. Since we are particularly discussing the conductance, we will treat this factor as a form of contact conductance ki ($=1/ri$;Siemens/cm^2).

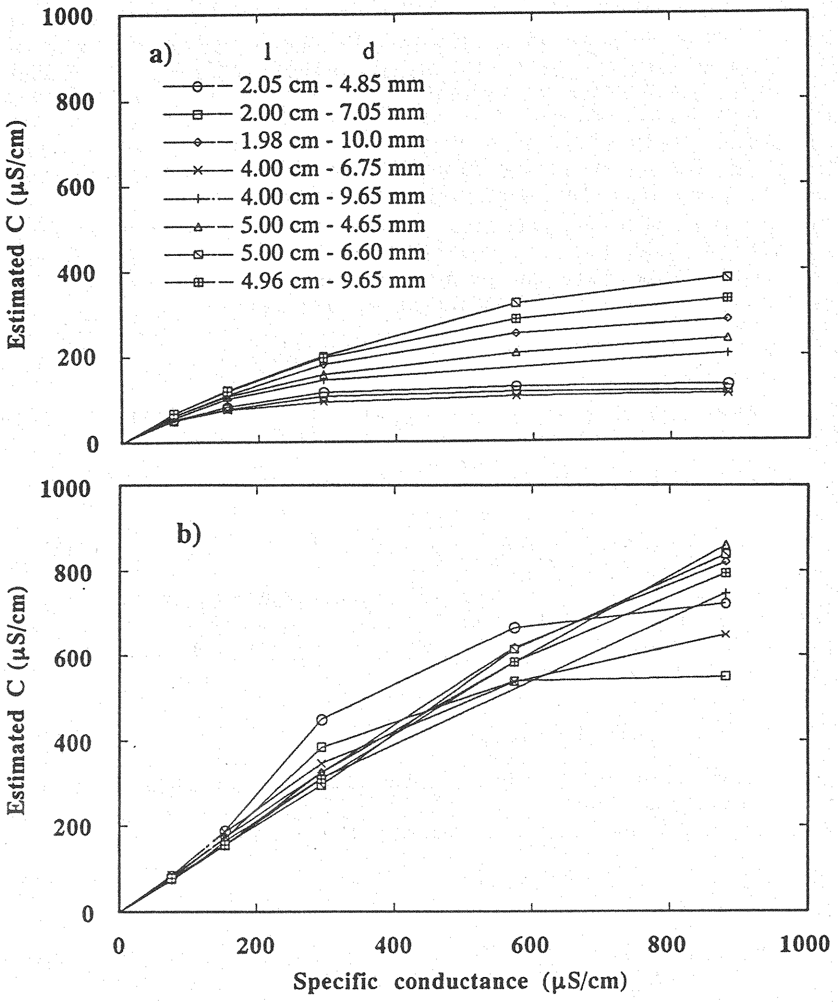

Fig. 4 The comparison of estimated and real C value of the preliminary experiment.
a)without considering the contact conductance,
b)considering contact conductance.

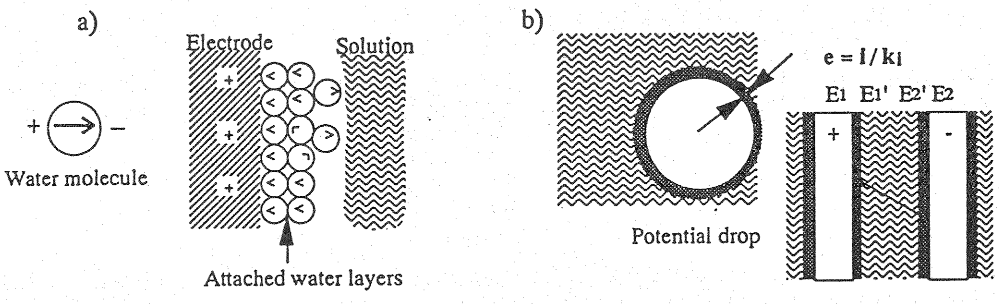

Fig. 5 The electrochemistry of the interface between metal and solution.
a) Attached water molecules or dipoles,
b) The true potential is reduced by a contact resistance r_i.

Contact conductance ki is a property of the interface between the electrode and medium used, which yields an additional potential drop at any point on the electrode. Consequently, the potential at the metal surface E is reduced to the potential at the medium surface E' because of contact conductance ki. We introduce this contact conductance in Eq. 7, and derive a more reasonable conversion equation. Although the contact conductance may involve many mechanisms, and may not be a single constant, we assume ki to be a constant value for probes of the same size, geometry and material used in the same medium.

For the portion of two cylinders, the electric potential E at the metal surface is uniformly reduced as a result of contact conductance ki wherein the additional potential gap ec between the metal surface and liquid surface is related to the current flux i (A/cm^2) and the current Ic (A) as;

$$e_c = \frac{i}{k_i} = \frac{I_c}{2\pi a l k_i} \qquad (8)$$

The higher and lower potentials of the liquid surfaces on the electrodes are expressed as;

$$E_{c1}' = E_{c1} - e_c = E_{c1} - \frac{I_c}{2\pi a l k_i} \qquad (9a)$$

$$E_{c2}' = E_{c2} + e_c = E_{c2} + \frac{I_c}{2\pi a l k_i} \qquad (9b)$$

Therefore, for the cylindrical case, the total potential drop ΔE is composed of the potential difference as obtained in Eq. 5 and the potential gap ec between the electrode surface and the solution. However, the potential difference ΔE in Eq. 5 corresponds to $Ec1'$-$Ec2'$ in this section.

$$\Delta E = E_{c1} - E_{c2} = \frac{I_c}{\pi C l} \ln\left(\frac{d}{a}\right) + \frac{I_c}{\pi a l k_i} \qquad (10)$$

For the spherical portion of the electrodes, the potential gap at the interface of the electrode and the solution es is given in Eq. 11. The resulting potentials at these electrodes are given as Eqs.12a and 12b.

$$e_s = \frac{I_s}{4\pi a^2 k_i} \qquad (11)$$

$$E_{s1}' = E_{s1} - \frac{I_s}{4\pi a^2 k_i} \qquad (12a)$$

$$E_{s2}' = E_{s2} + \frac{I_s}{4\pi a^2 k_i} \qquad (12b)$$

The total potential difference of the spherical electrodes will be shown as follows.

$$\Delta E = E_{s1} - E_{s2} = \frac{I_s}{2\pi C}\left(\frac{1}{a} - \frac{1}{d}\right) + \frac{I_s}{2\pi a^2 k_i} \qquad (13)$$

The total current is a summation of the currents at two portions of the probe as shown in Eq. 6. Solving for Ic and Is from Eq. 10 and Eq. 13, and substituting them into Eq. 6, we have an expression for the total conductance as;

$$\frac{I}{\Delta E} = \frac{1}{R} = \frac{1}{\dfrac{\ln (d/a)}{\pi C l} + \dfrac{1}{\pi a l k_i}} + \frac{1}{\left(\dfrac{1}{2\pi C}\right)(1/a - 1/d) + \dfrac{1}{2\pi a^2 k_i}} \qquad (14)$$

The value ki is obtained by solving Eq. 14 using the observed total resistance R and C value of the solution. Regarding the effect of temperature, it should be noted that we are discussing not the specific conductance C of the solution but the contact conductance ki. Therefore, in identifying ki in Eq. 14, we use the C value of the solution without the conversion to a standard temperature of 25 degrees Celsius.

The averaged values of the contact conductance obtained for each probe is substituted back to Eq. 13. Figure 4b gives a comparison of the C values in Eq. 14 to those obtained by the specific electrical conductance meter. The results show a marked improvement in the estimation of C values as compared to the previous results illustrated in Fig. 4a. Estimating C by using a contact conductance term was found to give sufficiently good results.

FACTORS AFFECTING CONTACT CONDUCTANCE

Calibration of the probe requires the determination of the contact conductance ki values at different concentrations and temperatures. For this purpose, another set of experiments were conducted by changing both temperature and concentration. In these experiments, new sets of probes were used. The nominal and actual size of the probes are listed in Table 1. Figure 6 shows an example of the behavior of the contact conductance at different C values and temperatures for a probe with the length of 2cm and separation of 5mm.

From the observations, it is found that the contact conductance is influenced by the temperature, the concentration of the solution and the geometry of the probe. As for the effect of the concentration of the solution, the contact conductance is almost zero at low concentration of distilled water. However, it was found that there is a steep rise in contact conductance values at 50 μS/cm of the solution which is the lowest value of the specific electrical conductance used. Unfortunately, we do not have precise data in this low range. The dashed lines indicate the possible peaks of the ki values. Having the highest values at 50 μS/cm for each temperature level, the ki values decrease linearly with an increase of C of the solution. Although the contact conductance value differs from probe to probe even at the same temperature and C of solution. These trends were observed for all probes.

It is also found in the observations that the parameter ki is strongly affected by temperature, i.e., ki value increases when temperature increases. This may be because the mobility of ions increase when temperature increases. The effect of the geometry of the electrode on the value of ki was also observed in the results.

Relationship between Temperature, Specific Conductance and Contact Conductance

Based on the results, the relationship between the contact conductance ki, specific conductance of the solution C and temperature T is formulated. From Fig. 6, it is assumed that ki changes linearly with C of the solution with a gradient $m(= - dki/dC)$ and ki has a common point of intersection with the horizontal axis at $C=C_o$ for all temperatures. Therefore, the relationship between ki and C is expected as Eq. 15.

$$k_i = m(C_o - C) \qquad (15)$$

As for parameter m in Eq. 15, Fig. 7 shows the change of m with temperature for all probes. The figure shows that m increases linearly with temperature as;

$$m = m_o + \alpha T \qquad (16)$$

where m_o is the intersection value to the vertical axis and α is the slope of each line. Substituting Eq. 16 to Eq. 15 we obtain a ki-T-C relationship in a very simple form described in Eq. 17.

$$k_i = (m_o + \alpha\ T)(C_o - C) \qquad (17)$$

Because the values of C_o are large (ranging from 4,000 to 5,000 μS/cm) as compared to the C value, the effect of C is not so dominant. The effect of the temperature T

Tab. 1 Dimensions of the probes used in the calibration

Nominal		Actual	
Length l (cm)	Separation d(mm)	Length l (cm)	Separation d(mm)
2	5	2.05	4.85
2	10	1.98	10.0
4	5	4.0	6.75
4	10	4.0	9.65
6	5	5.85	5.3
6	7	5.89	7.2
6	10	5.86	9.7

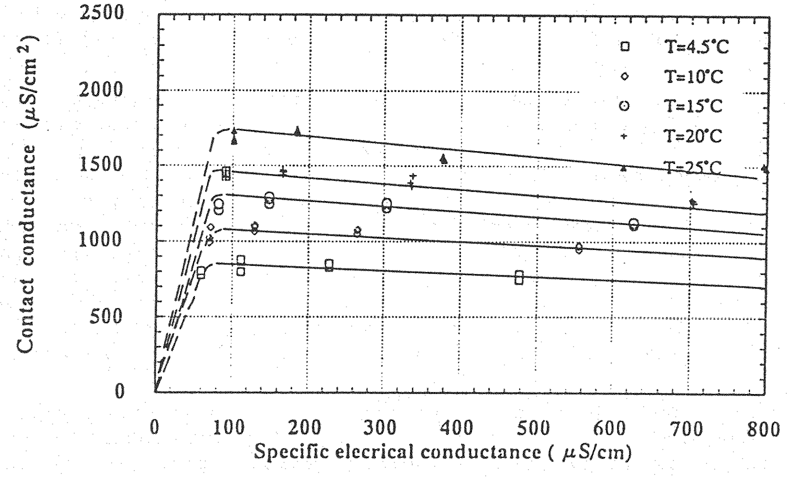

Fig. 6 The relationship between contact conductance, C of solution and temperature.

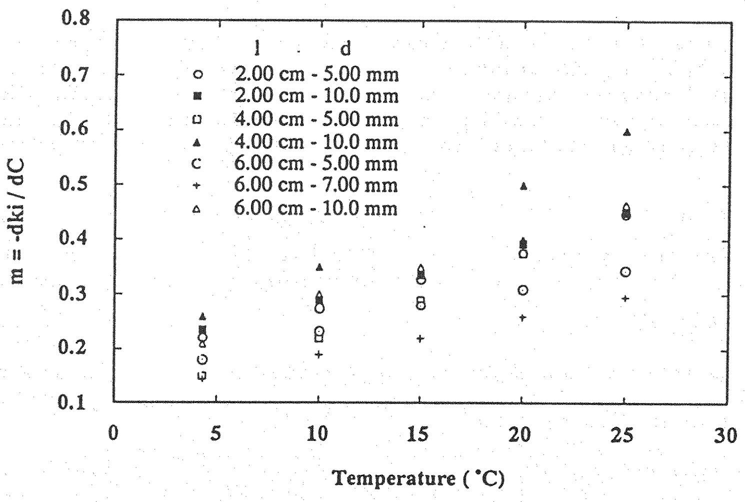

Fig. 7 The relationship between m(=-d*ki*/dC) and temperature.

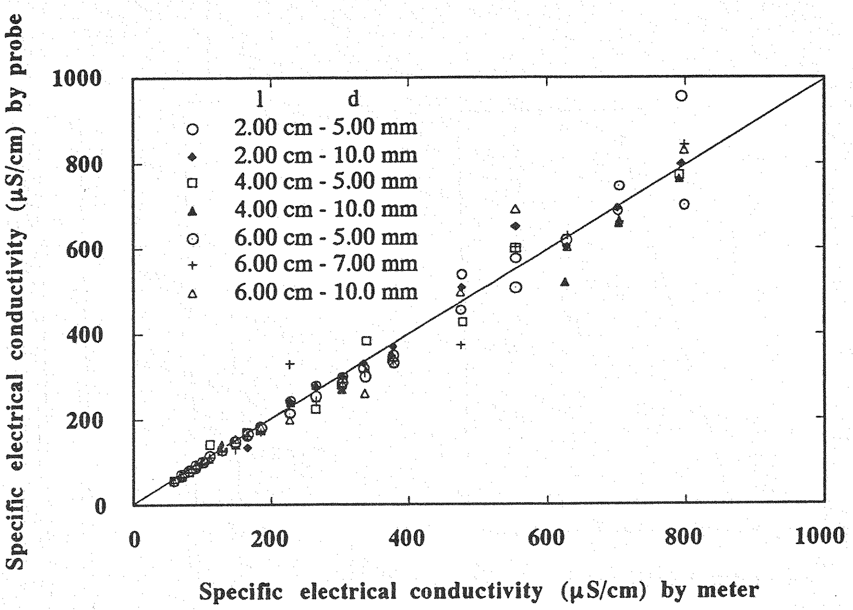

Fig. 8 The estimated C with the identified *ki* value and real C of solution.

on the contact conductance *ki* can be explained as follows. The increase of T will mobilize water molecules or dipoles attached to the surface of electrodes and will decrease the resistance to the passage of electrical charges. Consequently, the contact conductance *ki* increases.

Although Eq. 17 is applicable for all probes within a certain range of temperature and concentration, the coefficients m_o and α differ from probe to probe. This means that contact conductance *ki* is size-dependent and the characteristics of the probe should be determined individually.

Figure 8 shows a comparison of C values estimated by Eq. 17 using the identified *ki* value to specific conductance of the solution measured by a specific electrical conductance meter. All the data are adjusted at a temperature of 14 degrees Celsius. In Fig. 8, the data scatter at higher range of C values which are due to error in estimated *ki* values. Therefore, it is recommended to use this conversion equation(Eq. 14), for this lower range of concentration of the solution. Comparing Fig. 4a and Fig.8, however, it may be agreed that the conversion equation provides good estimates of C by introducing a contact conductance.

Physical and electrochemical explanations of these relationships are difficult at this moment and this formulation may be a guideline for future investigations.

SPECIFIC ELECTRICAL CONDUCTANCE OF SOLUTION IN UNSATURATED POROUS MEDIUM

Based on the properties of the probe obtained above, applicability of the probe in measuring C of the solution in an unsaturated porous medium is discussed here. To test the effectiveness of the probe, a column experiment was devised using glass beads as a porous medium. Figure 9 shows the grain size distribution of the glass beads. It can be seen that the beads are quite homogeneous in size. Figure 10 shows a set up of the experiment. The probe and a tensiometer were placed at the same level in the column. Suction head was measured by a pressure bulb connected to a porous cup. The measurements of both specific conductance and suction head were controlled by a computer through a data logger. In this experiment, we investigated the effects of moisture content, concentration of the

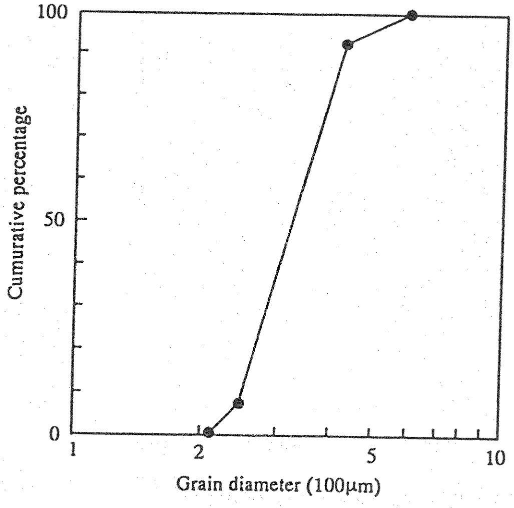

Fig. 9 The grain size distribution of the glass beads.

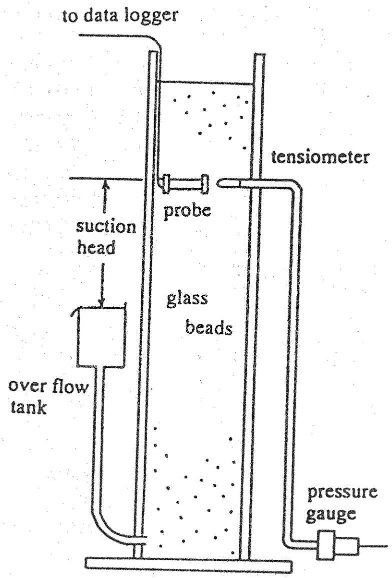

Fig. 10 The schematic diagram of the column set-up for the beads-solution-air system.

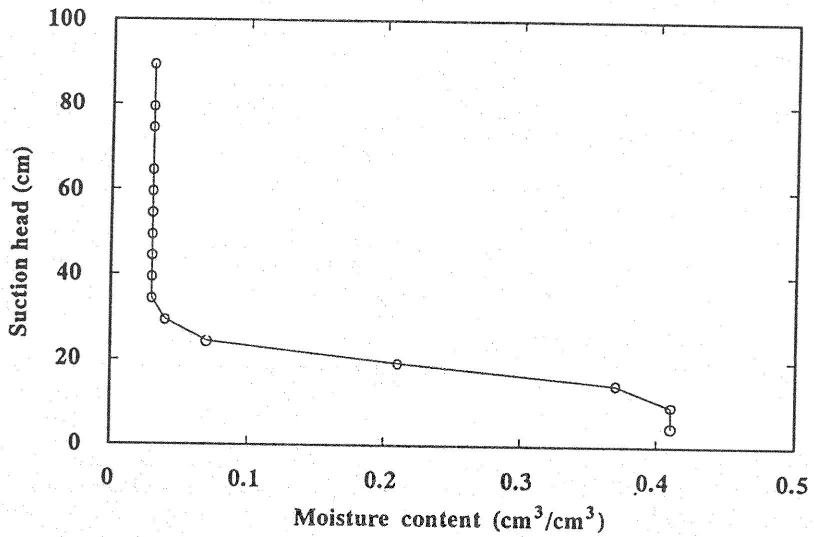

Fig. 11 The relationship between suction and moisture content of glass beads.

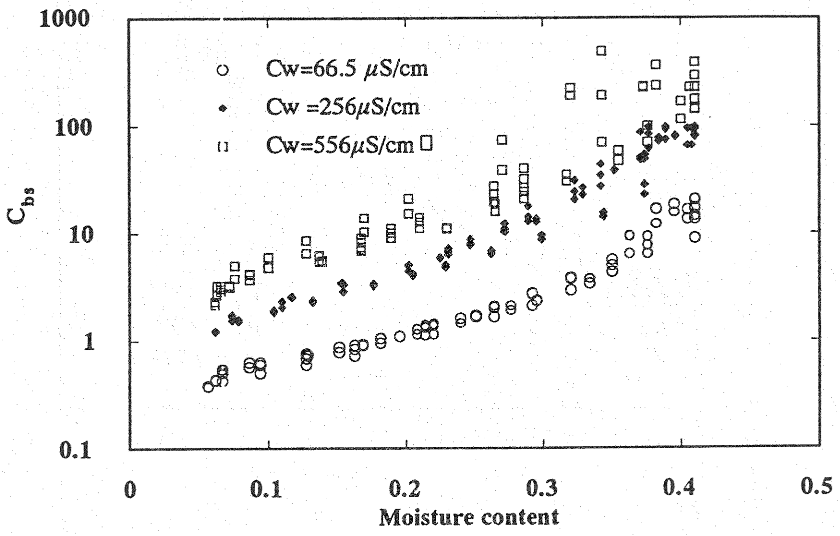

Fig. 12 C_{bs}-θ relations at different C_s values.

solution and temperature on C values. The moisture content at the location of the probe was controlled by adjusting the water level in the column as shown in Fig. 10. The moisture content was controlled within the range 5% to 40% and the concentration of NaCl was varied between 0.05g/*l* to 0.8g/*l* .

In order to estimate k_i for the beads-solution system, it was assumed that thin water layers cover the electrode surface uniformly under the unsaturated condition and that the contact conductance is unchanged by the presence of beads and the air between the metal and the solution. Therefore, Eq. 15 is used for estimating contact conductance k_i. The conductance of beads-solution-air system was also obtained by Eq. 14 by using the estimated k_i. In this case, however, the conductance obtained is not only a function of C of the solution but also the moisture content θ. To make the discussion clear, we will define C_{bs} as the C of beads-solution-air system and C_s as the C of the solution itself. If we have a relationship between C_{bs}, C_s and θ, it is possible to calculate C_s from C_{bs} and θ which is determined by suction head Ψ, through a suction - moisture content (Ψ-θ) relationship of the glass beads-solution-air system shown in Fig. 11.

Therefore, the purpose of this chapter is to establish the relationships between these variables.

Results of C_{bs} values for three different concentrations are given in Fig. 12, where C_{bs} is plotted in a semi-logarithmic scale against moisture content θ. The plots generally show that the specific electrical conductance decreases as the porous media become dry. It is because that as the moisture content decreases both the number of ions as the carrier of electron, and the continuity of the solution as the path of ions decrease. Consequently ion flux decreases drastically.

Figure 12 shows the effects of C_s on C_{bs}. For increasing C_s values, the plots of C_{bs} vs θ becomes vertical in relation to each other. This means that ratios of C_{bs} between different C_s cases are constant over the whole range of moisture content. Moreover it is also found that the ratio is almost equal to the ratio of C_s . To make this point clear, vertical axis in Fig. 12 is nondimensionalized by C_{bs}/C_s as shown in Fig. 13a. From this figure, it is shown that all the plots can be expressed by a single curve.

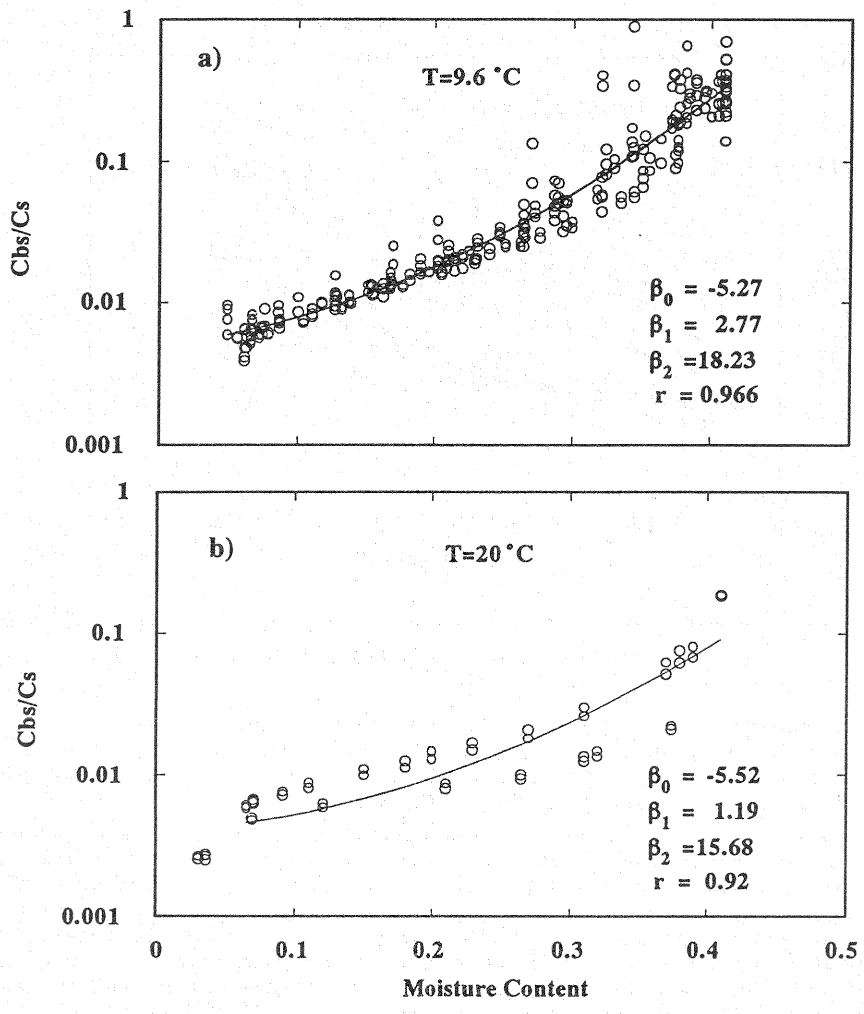

Fig. 13 (C_{bs}/C_s)-θ relations.
a) at T=9.6 °C b) at T=20 °C

This may indicate that the main role of the concentration of the solution is to magnify C_{bs} values linearly. The C_{bs}/C_s-moisture content relationship of the beads-solution-air system can be formulated as Eq. 18.

$$\frac{C_{bs}}{C_s} = \exp\{\beta(\theta, T)\} \qquad (18)$$

where $\beta(\theta,T)$ is a function representing the effects of the geometrical characteristics of the probe and porous medium, moisture content and temperature. In discussing the form of the function β, the effect of temperature is not discussed because of insufficient data about T. Instead, we will show another set of C_{bs}/C_s - θ plots in Fig. 13b which was obtained at a T=20 °C. The equation used in fitting curve to the data is

$$\frac{C_{bs}}{C_s} = \exp\{\beta_o+\beta_1\theta+\beta_2\theta^2\} \qquad (19)$$

where β_0, β_1 and β_2 are the coefficients which indicate the conduction characteristics of the probes in the unsaturated medium at a particular temperature.

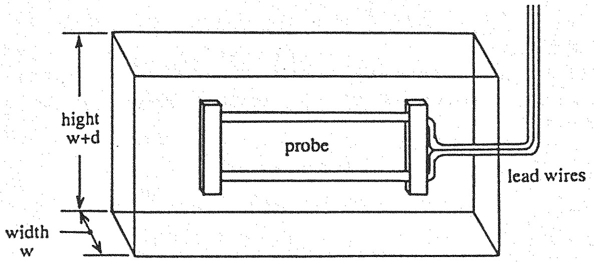

Fig. 14 The schematic diagram of the experiment for representative size.

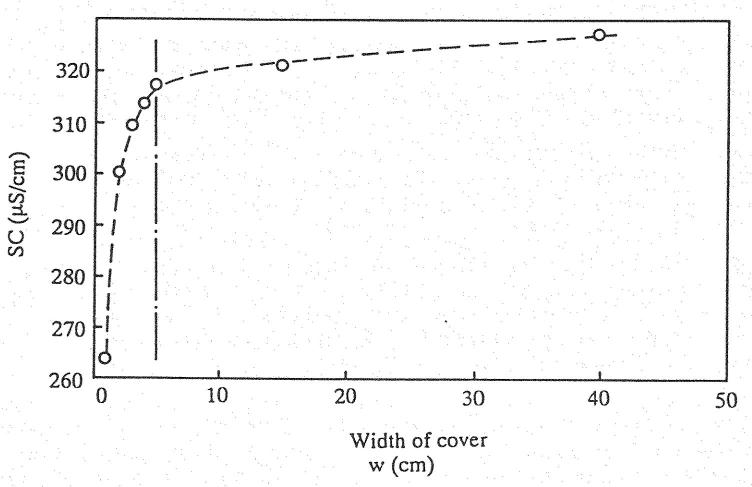

Fig. 15 The relationship between C values and the size of covers.

These parameters represent the function of the current lines in the medium, the mobility of the conducting ions due to the presence of the beads and the changing moisture content. From these figures, it is found that $\beta(\theta,T)$ changes with temperature, but β_0 is nearly the same at both temperatures. Examining these figures in detail, we found individual characteristics of $C_{bs}/C_s - \theta$ relationship for each probe. Therefore, we need precise calibration for each probe in practical use. However, the discussion of the nondimensional form of Eqs.18 and 19 will provide guidelines for formulating $C_{bs}/C_s - \theta$ relationships.

REPRESENTATIVE SIZE OF THE MEDIUM MEASURED BY THE PROBE

Equation 14 is derived based on the assumption that the conductive medium extends infinitely. Therefore, the C values obtained by the probe are the contributions from all over the medium. From the point of a performance of the probe, the measured C value is desired to express C value at a point or a small zone of the medium. Here, we will examine the representative size of the medium in measuring C value by the probe, i.e., the change of C value according to the volume of the medium.

To do this, we prepared several sizes of plastic covers partitioning the probe from the surrounding medium. Figure 14 shows a schematic diagram of the experimental set up. The internal dimension of the cover we used are 1.0cm x 1.7cm, 2.0x2.7, 3.0x3.7, 4.0x4.7 and 5.0x5.7 and length is 8cm. We measured C values in a certain concentration of the solution with these covers. Figure 15 shows a result of the experiment plotting C values on vertical axis and width of the cover on horizontal axis.

Figure 15 shows that C value rises sharply as the width increases and gradually converges into a constant value. From the figure, it can be concluded that the representative thickness of the medium measured by this probe is about 5cm.

CONCLUSIONS

In this paper, the characteristics of the probe designed to measure the specific electrical conductance (C) of NaCl solution in an unsaturated porous medium were discussed. The conclusions obtained through this research may be summarized as follows:

1) The electric potential field of a conductive medium including the probe was analytically solved to obtain a conversion equation for C value from total resistance observed by the probe. In the equation, the effect of probe geometry on electrical conductance was explicitly included.
2) A new parameter *ki* expressing a contact conductance was introduced to modify the conversion equation mentioned above. The effects of temperature and specific electrical conductance of the solution on *ki* were also evaluated.
3) The probe was used on an unsaturated porous medium of glass beads. The relationship between C of the solution, C of a beads-solution-air system, moisture content and temperature was discussed. Although the parameters of the relationship should be determined for each probe, the general non-dimensional formulation is suggested.
4) The size of the medium, within which the observed C value represents the true value, was examined by changing the size of the partition surrounding the probe. As the result, it is concluded that the measured C value represents the conductance of the solution within 5 cm in thickness of medium.

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APPENDIX - NOTATION

The following symbols are used in this paper:

a = radius of the cylinder;

C = specific electrical conductance;

C_0 = C-intercept of *ki*-C relationship ;

C_{bs} = C of beads and solution;

C_s = C of solution;

d = center to center separation distance between the electrodes;

e_c, e_s = otential gap at the interface of electrode and solution for cylindrical and spherical electrodes, respectively

E = electrical potential;

E_c, E_s = electrical potential on the surface of cylindrical and spherical electrodes, respectively;

E_c', E_s' = electrical potential of solution on the surface of cylindrical and spherical electrodes,respectively;

i = current density;

I = total current passing;

I_c, I_s = current per unit length of the cylinders and total current of sphere respectively;

k_i = contact conductance;

l = length of electrode;

m = slope of *ki*-C relationship;

m_0 = m-intercept of m-T relationship;

r_i = contact resistance;

r_1, r_2 = radial distance from the two cylinders;

R = total observed resistance;

T = temperature;

w = width of the partitioning cover;

α = coefficient to express the effect of temperature on contact conductance ki;

β = shape parameter of the C-moisture content-concentration curves;

ΔE = electric potential difference between electrode surfaces; and

0 = moisture content.

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