

Effect of Exchangeable Sodium Percentage, Cation Exchange Capacity, and Soil Solution Concentration on Soil Electrical Conductivity¹

I. SHAINBERG, J. D. RHOADES, AND R. J. PRATHER²

ABSTRACT

The electrical conductivity of eight soils was measured as a function of the solution electrical conductivity over a wide range of salt concentration and salt composition. The soils electrical conductivity increased nonlinearly with respect to the equilibrium solution electrical conductivity in the low range of salt concentration (< 2-3 mmho/cm). In the higher salt concentration range, straight line relationships were obtained. The shape of the curves was explained by the inclusion of a solid-water in series element in the conductance model. The effect of the soil ESP on the electrical conductivity curve parameters is slight and is not significant when the electrical conductivity method is used to survey soil salinity.

Additional Index Words: surface conductivity, four-electrode conductivity, soil salinity.

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RHOADES AND INGVALSON (1971) demonstrated that measurement of soil electrical conductivity (κ_a) can be used when the soil is near "field capacity" to assess soil solution salinity (κ_w). They concluded that small deviations from field capacity water content did not interfere with salinity diagnosis because the salt concentration of the soil water would increase as the volume of soil water decreased by evapotranspiration; hence, the current carrying capacity would not appreciably decrease by such relatively small variations in water content. Rhoades et al. (1976) evaluated the effect of water content on κ_a to extend the use of the method. They derived the theoretical relationship described in Eq. [1], assuming that the electrical conductivity of the bulk soil is made up of the conductivities of the liquid phase (κ_w) and the solid phase (κ_s) which behave analogously to two conductors in parallel.

$$\kappa_a = \kappa'_s + \kappa_w \theta T. \quad [1]$$

In Eq. [1], κ_a and κ_w are as previously defined; θ is volumetric water content, κ'_s is apparent soil surface electrical conductivity, and T is a transmission coefficient. These researchers found experimentally that, over soil water contents of practical concern, the bulk electrical conductivity followed the theoretical relation over the range of κ_w studied, which was about 2 to 40 mmho/cm. This range covers that of concern for appraising soil salinity effects on crop growth in arid land soils. However, studies made using resin beds (Sauer et al., 1955), shaley sands (Waxman and

Smits, 1968), and clay suspensions (Cremers and Lau-delout, 1965; Cremers et al., 1966; Gast, 1966; Shainberg and Levy, 1975) show that Eq. [1] is invalid for such materials at low electrolyte concentration (electrical conductivities below about 4 mmho/cm) since the κ_a - κ_w plots become curvilinear in this region. In these solution-exchanger systems, an initial rapid increase in κ_a occurs with increase in salt concentration (κ_w) which is seemingly greater than that attributable to the conductivity of the added electrolyte alone. This observation would require the assumption of an increase in surface conductance with increase in concentration if the two conductors in parallel model is valid (Waxman and Smits, 1968). This assumption is not likely for clay-water systems, where an increase in salt concentration is expected to compress the diffuse double layer, to increase the electrical interaction between the cations and the clay surfaces and hence to reduce, not increase, surface conductivity.

With the above in mind, we undertook this study to evaluate the dependence of soil κ_a and κ_w over a wide range of salt concentration with emphasis on solution concentration below 40 meq/liter ($\kappa_w < 4$ mmho/cm) to see if they behaved like resins at low electrolyte levels. Since at low κ_w the electrical contribution of the solid phase, κ_s , becomes relatively more important, a second objective was to measure the dependence of the soil surface conductivity on clay concentration, cation exchange capacity (CEC), and the exchangeable sodium percentage (ESP) of the soil. A third objective was to develop a theory which accounts for and explains the relation between κ_a and κ_w over the entire κ_w range. Meeting these objectives will enable us to extend the use of the four-electrode devices and techniques developed for in situ salinity measurements of soils (Rhoades and Ingvalson, 1971) to other uses such as determining solute movement in nonsaline soils, etc.

THEORY

Sauer et al. (1955) suggested that the specific conductivity of columns of ion exchange resin spheres saturated with solutions of electrolytes can be represented by an equivalent resistance model consisting of three elements in parallel: (i) conductance through alternating layers of particles and interstitial solution, (ii) conductance through or along the surfaces of particles in direct contact with each other, and (iii) conductance through the interstitial solution. A schematic presentation of their model is presented in Fig. 1 where a , b , and c represent the fractional cross sectional areas of the first, second, and third elements, respectively, and d is the length parameter of the solid particles. If κ'_s and κ_w are the apparent specific conductivities of the solid phase and the specific conductivity of the interstitial solution, respectively, the conductivities of the three elements are given by the following equations:

$$\frac{1}{\kappa_1} = \frac{(1-d)/a}{\kappa_w} + \frac{d/a}{\kappa'_s} = \frac{x}{\kappa_w} + \frac{y}{\kappa'_s}, \quad [2]$$

$$\kappa_1 = \frac{\kappa'_s \kappa_w}{x \kappa'_s + y \kappa_w}, \quad [3]$$

$$\kappa_2 = b \kappa'_s, \text{ and} \quad [4]$$

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² Visiting Soil Scientist, Supervisory Soil Scientist, and Soil Scientist, respectively. I. Shainberg's permanent address is Institute of Soils and Water, The Volcani Center, Bet-Dagan, Israel.

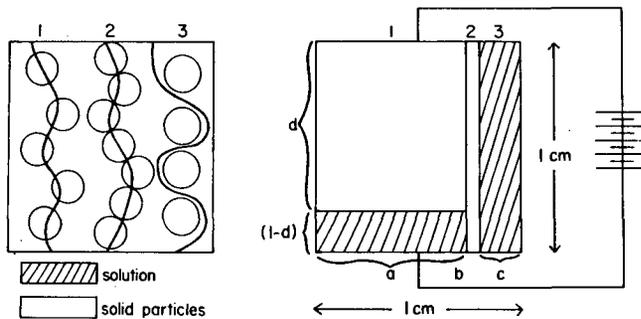


Fig. 1—Resistance models representing the solid particles and the intersolid-solution. d is the length of the solid phase, a , b , and c represent the fractional cross-section areas of the first, second, and third elements, respectively.

$$\kappa_s = c\kappa_w = \frac{\kappa_w}{F}, \quad [5]$$

where

$$x = (1-d)/a, \quad y = d/a, \quad [6]$$

and c is equal to $1/F$ with F being the "formation factor" which would be a measure of the tortuosity of the plug if the solids were nonconductive.

The specific conductivity, κ_a , of the simulated porous medium is the sum of the conductivities of the three elements:

$$\kappa_a = \kappa_1 + \kappa_2 + \kappa_3 = \frac{\kappa'_s \kappa_w}{x\kappa'_s + y\kappa_w} + b\kappa'_s + \frac{\kappa_w}{F}. \quad [7]$$

The method of Sauer et al. (1955) to evaluate the parameters x , y , b , and F cannot be applied to soil water systems for the following reasons: (i) it involves the experimental determination of the κ_a - κ_w slope at $\kappa_w = 0$. Due to chemical instability of soils (Rhoades et al., 1968) and clays (Shainberg et al., 1974) in dilute salt solutions, the conductivity of soil solution cannot be adjusted to zero even by leaching the soil with distilled water. Hence, determination of a κ_a - κ_w curve below about 1 meq/liter is not possible; (ii) it cannot be applied to clay water systems because it assumes that the cell parameters (a , b , c , and d) are constant and independent of the solution concentration, whereas in clays, the solid conductivity is mainly due to surface conductivity, and the thickness of the surfaces (including the exchangeable cations in the diffuse double layers) is very sensitive to salt concentration.

However, for soil water systems, where stable aggregates exist and direct solid to solid contact between aggregates is negligible, the contribution of the second element to the bulk soil conductivity can be neglected, and Eq. [7] reduces to

$$\kappa_a = \frac{\kappa'_s \kappa_w}{[(1-d)/a]\kappa'_s + (d/a)\kappa_w} + \frac{\kappa_w}{F}. \quad [8]$$

This assumption is further justified by considering Sauer et al. (1955). Sauer et al. (1955) obtained b values ranging between 0.01 and 0.03 for Na and Ca resin, respectively. The product of these small values times the apparent specific conductivity of the solid particles (which are also small) renders the second element contribution to be negligible.

Considering Fig. 1 and the randomness and approximate equal dimensions of the solid phase in all directions, one sees that the thickness of the solid phase, d , is about equal to its fractional cross section, a . Thus, for $a = d$, Eq. [8] reduces to

$$\kappa_a = \frac{\kappa'_s \kappa_w}{[(1-d)/d]\kappa'_s + \kappa_w} + \frac{\kappa_w}{F}. \quad [9]$$

When $\kappa_w > \kappa'_s$; i.e., at high solution concentration, Eq. [9] reduces to

$$\kappa_a = \kappa'_s + \kappa_w/F. \quad [10]$$

Equation [10] is equivalent to Eq. [1] with the convention that $1/F = \theta T$.

It is evident that at low electrolyte concentration, the first element in Eq. [9] determines the shape of the κ_a - κ_w curve. At relatively high salt concentrations, the second term becomes

Table 1—Physical and chemical characteristics of the soils.

Soil type	Mechanical composition, %			CEC, meq/100 g	Dominant clay type
	Sand	Silt	Clay (<2 μ m)		
Typic Haploxeralfs					
Fallbrook A	71.5	20.5	8.0	12.0	Montmorillonite and kaolinite
Fallbrook B	62.5	21.3	16.2	16.9	
Natric Paloxeralfs					
Bonsall A	70.0	22.0	8.0	8.2	Montmorillonite
Bonsall B	45.5	19.0	36.5	25.0	
Mollic Haploxeralfs					
Pachappa	49.0	37.8	11.2	9.2	Montmorillonite and mica
Haplic Durixeralfs					
Arlington	42.0	45.0	13.0	18.0	Vermiculite
Vertic Torrifluents					
Imperial	35.7	46.3	18.0	15.5	Montmorillonite and mica
Typic Natrixeralfs					
Waukena	41.3	39.0	19.7	18.0	Montmorillonite and mica
Typic Torriorthents					
Panoche (3636)	64.4	19.0	16.8	18.0	Montmorillonite and mica
Delta† (organic soil)					

† No data available.

dominant, with the first element determining the intercept, and Eq. [10] is a good approximation of Eq. [9].

The real specific conductivity of the solid phase, κ'_s , which is related to the concentrations and mobilities of adsorbed cations, can be calculated from the apparent specific conductivity, κ'_a , if one knows the "formation factor" for the exchangeable ion. Cremers et al. (1966) found for clay gels and soils that the same formation factor applies to both the solution and the solid phases. This conclusion was also applied successfully by Waxman and Smits (1968) to shaly sands. The physical explanation to this conclusion is as follows. In clay-water systems, the solid crystals are not conductive and the solid conductivity is due to the cations which reside in the diffuse double layer. Any separation of the ions in the soil pores into the solution and adsorbed cations envelope is arbitrary. Thus if the same geometry factor applies to both conductors, Eq. [10] becomes

$$\kappa_a = \frac{\kappa'_s}{F} + \frac{\kappa_w}{F}. \quad [11]$$

MATERIALS AND METHODS

The electrical conductivity of the A and B horizons of two California soils, Fallbrook (fine-loamy, mixed thermic Typic Haploxeralfs) and Bonsall (fine, montmorillonitic, thermic Natric Paloxeralfs) soils, were studied in detail. The conclusions derived from the detailed study on these two soils were subsequently tested on six additional soils more representative of California irrigated soils. The properties of the soils are given in Table 1.

Columns of these soils were prepared by packing about 350 g of sieved soils (< 2 mm) into plastic cylinders (5 cm in diam by 14 cm in length) at bulk densities of 1.5 g/cm³. The Waukena (fine-loamy, mixed, thermic Typic Natrixeralfs) and the organic soil were packed to a density of 1.3 and 1.0 g/cm³, respectively. Eight electrodes were inserted through the cylinder walls at 45° intervals around the middle of the soil column. Any four neighboring electrodes were regarded as a Wenner array—the outer two were used as current electrodes and the inner two as potential electrodes. By rotating the connections, we obtained eight independent measurements of soil electrical conductivity for any treatment. The appropriate cell constants were obtained by calibration with 0.01M KCl solution.

The soils were first leached with 0.5N solutions of NaCl/

Table 2—Bulk electrical conductivity straight line parameters for SAR†0 treatment.

Soil	Intercept	Slope	$\kappa_s \ddagger$
Bonsall A	0.12	0.225	0.53
Bonsall B	0.88	0.235	3.74
Bonsall A-B	0.48	0.233	2.06
Fallbrook A	0.22	0.230	0.96
Fallbrook B	0.32	0.230	1.39
Arlington	0.46	0.256	1.80
Pachappa	0.29	0.233	1.24
Imperial	0.39	0.270	1.44
Waukena	0.45	0.250	1.80
Panoche	0.63	0.266	2.47
Delta	0.30	0.322	0.9

† SAR = (Na)/(Ca)^{1/2} where the ion concentrations are expressed in mmol/liter.

‡ κ_s = intercept/slope.

CaCl₂ of the desired SAR (sodium adsorption ratio)³ (SAR 0, 20, 30, and 40). Subsequently the Fallbrook and Bonsall soil columns were successively leached with solutions of the same SAR but of decreasing salt concentration (0.13, 0.10, 0.08, 0.06, 0.04, 0.02, 0.01, 0.005, 0.003, 0.001, and 0.00N) until new steady states were achieved. The other six soils were leached only with CaCl₂ and SAR 30 solutions and salt concentrations of 0.5, 0.10, 0.08, 0.06, 0.04, 0.02, 0.01, and 0.005. Since the distilled water leaching treatment was avoided, no physical deterioration of the soil structure resulted and the Ca solutions were subsequently leached with the SAR 30 solutions (i.e., using the same columns). The electrical conductivity of the soil, κ_s , (using the four-probe array), and that of the effluent, κ_w , were measured when the columns were at steady state. The conductance measurements of the effluent solutions were made using an RC bridge (Industrial Instruments, Inc., Model RC 16B2)⁴ whereas that of the soil were made using an SCT meter (Marek Instruments, Inc.).

RESULTS AND DISCUSSION

The electrical conductivity of the saturated soils (κ_s) as a function of the electrical conductivity of the soil solution (κ_w) for the Bonsall soils from the A and B horizon is presented in Fig. 2 for SAR 0 treatments. The following observations should be noted.

1) At relatively saline solutions ($\kappa_w > 4.0$ mmho/cm), κ_s is a linear function of κ_w as predicted from Eq. [1] and [10]. The slopes of these lines are the same regardless of the different clay percentage of the two soils. The slope of the A horizon soil with 8% clay is 0.225, whereas that of the B horizon soil with 35% clay is 0.235. The slopes obtained for the other soils are similar (Table 2). Conversely, the apparent specific conductivity of the soil phase (κ_s , the intercept) increases with increase in clay percentage. The linearity of the relation between κ_s and κ_w indicates that at these concentrations, (i) the surface conductance, i.e., mobility of the exchangeable ions, is constant and has its maximum value; and (ii) the geometry factor is not influenced by the solution concentration. It should be recognized that this noted independence of slope on soil type is an artifact of the experimental conditions used (i.e., fragmented samples of soils were packed to the same bulk density giving them all about the same saturated porosity, i.e., θT in Eq. [1]. Under real field situations, as has been shown by Rhoades and van Schilfhaarde (1976),

³ SAR = Na/(Ca²⁺ + Mg²⁺)^{1/2}, where the solute concentrations are expressed in mmol/liter.

⁴ Mention of company trade names is for the benefit of the reader and does not imply endorsement of the equipment by the USDA.

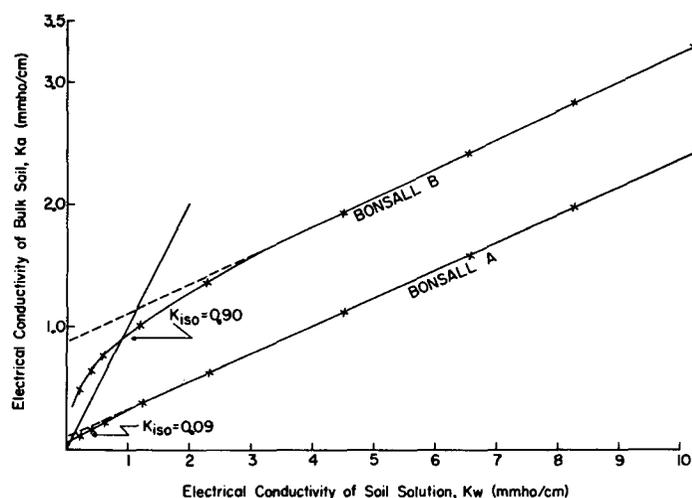


Fig. 2—The electrical conductivity of the saturated Bonsall soils from the A and B horizon as a function of the electrical conductivity of the soil solution. κ_{iso} is the isoconductivity point where the conductivity of the bulk soil is equal to the conductivity of the soil solution.

the slopes of κ_s - κ_w relations vary from soil to soil, depending upon their field capacity water contents. For this reason κ_s - κ_w calibrations are routinely established in field conditions by soil type to interpret salinity from κ_s determinations (Rhoades and Halvorson, 1977).

2) In the dilute concentration range ($\kappa_w < 4.0$ mmho/cm), κ_s is not linearly related to κ_w . With dilution of the soil solution, κ_s is reduced sharply as predicted from Eq. [9]. The results shown in Fig. 2 for Bonsall-B soil represent the extreme case among the soils studied. For this soil, the departure from linearity occurred at κ_w values of < 3 mmho/cm (or approximately 1.5 mmho/cm on a saturation extract equivalent basis). As will be shown later, the deviation from the straight line is a function of both the clay percentage in the soil (and CEC) and the degree of Na saturation of the adsorbed phase. With an increase in clay content and ESP of the soil, the deviation from linearity begins at higher soil solution concentration and the departure is greater.

The slopes and intercept values of the linear portions of the κ_s - κ_w curves of the SAR 0 treatment are listed in Table 2. The specific electrical conductivities of the solid phase, κ_s , can be calculated from the intercepts and Eq. [11] ($\kappa_s = F\kappa_s$). These data and analyses for other SAR treatments (not shown) are presented in Fig. 3, as a function of both the CEC of the soil, and the SAR (and ESP) of the system. It is evident that the specific conductivity of the adsorbed phase increases with the CEC. Possibly κ_s increases with the ESP of the soils though this generalization is not conclusive because of the scatter in the data.

The specific conductivity of the adsorbed phase in the soil may be used to calculate the equivalent conductivity and the mobility of adsorbed cations. The equivalent conductivity of an electrolyte in solution, Λ , is defined as

$$\Lambda = (\kappa \cdot 1,000)/C \quad [12]$$

where C is the concentration of the electrolyte in eq/

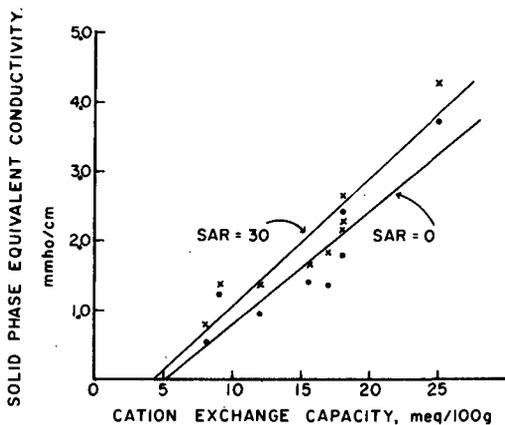


Fig. 3—The solid conductivity of the soils as a function of both the cation exchange capacity of the soils and the SAR (and ESP) of the soil systems. Treatment symbols are ● for SAR=0 and × for SAR=30.

liter. Similarly, the equivalent conductivity of adsorbed cations, $\bar{\lambda}^+$, may be calculated as follows

$$\bar{\lambda}^+ = (\kappa_s \cdot 1,000)/C^* \quad [13]$$

where C^* is the concentration of the adsorbed cations in the soil solution, and is equal to $C^* = (CEC \cdot \rho)/\theta$, where ρ is true density of soil particles. Assuming a value of 2.65 g/cm³ for the true density of the solid particles in the soil and the known bulk densities and moisture contents of the soil columns, the concentration of exchangeable cations may be calculated. Equation [13] can now be used to calculate the equivalent conductivity of the adsorbed ions (Table 3). It is evident that the average equivalent conductivity of adsorbed Ca in the Californian soils is about 3.5 mho cm²/eq. Since the equivalent conductivity of Ca ions in solution at 25°C is 59.5 mho cm²/eq, our results suggest that in these soils the relative equivalent conductivity of adsorbed Ca is 5.8% of that in solution. Shainberg and Kemper (1966) found for Ca montmorillonite gel that the corresponding percentages are 9.5 and 3.8% for freshly-prepared and previously-dried Ca montmorillonite gel, respectively. The agreement between these results and those of Shainberg and Kemper (1966), who obtained their values in a completely different experimental setup (Ca montmorillonite gel in distilled water), indicate that the model and assumptions used in this study are valid to soil-solution systems.

Table 3—The equivalent conductivity of adsorbed calcium and the isoconductivity point.

Soil	C^*	Equivalent conductivity	κ_{iso}
	eq/liter	mho cm ² /eq	
Bonsall A	0.28	2.28	0.09
Bonsall B	0.86	4.70	0.90
Bonsall A-B	0.64	3.63	—
Fallbrook A	0.41	2.98	0.32
Fallbrook B	0.58	3.16	0.38
Arlington	0.62	2.90	0.42
Pachappa	0.32	3.88	0.25
Imperial	0.54	2.93	0.36
Waukena	0.46	4.28	0.42
Panoche	0.62	3.98	0.72
Delta	—	—	0.22

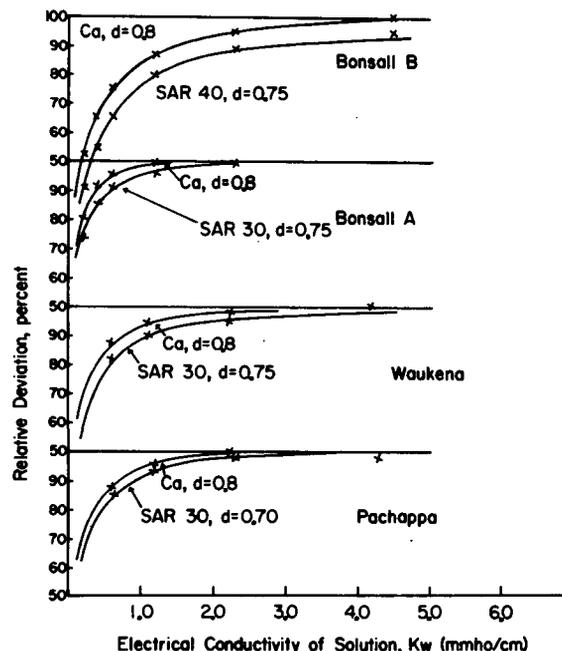


Fig. 4—The relative deviation from the electrical conductivity straight lines as a function of the electrical conductivity of the soil solution for four of the soils and for two SAR compositions, experimental points and theoretical curves. The d parameter which gives the best apparent fit with the experimental data is indicated in the figure.

The equivalent conductivities of adsorbed ions in the four soils tended to increase with increase in the percentage of Na in spite of the fact that the equivalent conductivity of Na in bulk solution is lower than that of Ca ($\lambda_{Na}^0 = 50.1$ mho cm²/eq). Shainberg and Kemper (1966) obtained only a slight increase in $\bar{\lambda}^+$ with increase in exchangeable Na in the low exchangeable Na percentage rate. It seems that the electrical conductivity of soils is more sensitive to exchangeable Na than is that of montmorillonite gels. It is possible that the slaking of the soil aggregates, which starts at low ESP values, and the rearrangement of the particles brings about this increase in electrical conductivity with increase in exchangeable Na.

The deviation from the extrapolated straight lines for four of the soils and for two SAR compositions (SAR 0 and 30) as a function of the electrical conductivity of the soil solution are presented in Fig. 4. To simplify the discussion (and the presentation), the deviation is presented as the ratio (in percentage) between the measured bulk electrical conductivity, κ_w , and that obtained from the extrapolation of the κ_w - κ_w straight lines (Table 1). The following trends are observed:

1) The deviation from linearity increases with increase in clay content of the soil. In Bonsall A soil, with 8% clay, the deviation starts at soil solution κ_w of 1.5 mmho/cm, whereas in Bonsall B soil, with 35% clay, the deviation starts at soil solution κ_w of 3.0 mmho/cm.

2) The deviation for the Waukena (Typic Natriferals) and Pachappa (coarse-loamy, mixed thermic Mollic Haploxeralfs) soils is more pronounced than that for the Bonsall and Fallbrook soils with similar clay content.

3) The deviation from the $\kappa_a - \kappa_w$ straight line appears to increase with increase in exchangeable Na in the soil.

Theoretical deviations were calculated using Eq. [9] and [10], and are plotted as curves in Fig. 4. In constructing these curves, we have one degree of freedom—the d parameter. The d parameter, which gives the best apparent fit with the experimental data, is indicated in the figure. The d values varied between 0.7 and 0.8 for the four soils. Physical explanation for this value is as follows. The fraction of the conductivity cell occupied by the crystal phase is at least 0.57 ($d = 1.5/2.65$). However, the solid phase of the soil should include also a portion of the diffuse double layer. The thickness of the diffuse double layer in 0.01M NaCl and CaCl₂ solutions is 30 and 15 Å, respectively (van Olphen, 1977). The specific surface of the soils is as much as 75 m²/g (Rhoades et al., 1976). Thus the fraction of the conductivity cell occupied by the diffuse double layer in equilibrium with soil solution concentration of 0.1M is about 0.15 [(75 × 10⁴) × (20 × 10⁻⁸)]. Thus the total thickness of the solid phase (crystal plus adsorbed phases), corresponding to the above assumptions, should be between 0.7 and 0.8 depending on the texture, mineralogy, and exchangeable ions of the soils, values which are in reasonable agreement with the values derived from the fit of Eq. [9] with the data points of Fig. 4.

The specific conductivity of the adsorbed phase may also be calculated from the isoconductivity point. At low electrolyte concentration, the electrical conductivity of the bulk soil is higher than that of the soil solution (due to the contribution of the adsorbed ions). At high salt concentration, the opposite is true and the conductivity of the soil solution is higher than that of the bulk soil (due to the geometry factor). At the isoconductivity point, the bulk conductivities of the soil and of the interstitial solution are equal, namely, $\kappa_{iso} = \kappa_a = \kappa_w$. Substituting this value in Eq. [9], one obtains for κ'_s

$$\kappa'_s = \kappa_w \left\{ \frac{1 - (1/F)}{1 - (1-d/d)[1 - (1/F)]} \right\} \quad [14]$$

For a typical soil the value of $1/F$ is 0.250 and that of d is 0.75; thus the value of the term in the brackets is about 1.0 and $\kappa_s \approx \kappa_{iso}$. The values of κ_{iso} for Bonsall A and B soils are shown in Fig. 2. The experimental values for the other soils are presented in Table 3. There is a good agreement between the prediction based on Eq. [14] and the experimental intercept obtained from Eq. [1].

CONCLUSION

Plots of bulk soil electrical conductivity vs. the electrical conductivity of the equilibrium soil water solution gave concave curves with respect to the abscissa at low salt concentrations (nonsaline levels). In order to

explain the curvature of the plots, according to the two conductors in parallel model (Rhoades et al., 1976), it is necessary to assume that the double layer conductivity decreases with decreasing solution concentration in this range (Waxman and Smits, 1968). However, the inclusion of a solid-water in series model explains the shape of the curves by the geometry parameters, F and d . The thickness of the solid phase parameter, d , depends on both the texture of the soil and the exchangeable Na percentage. The differences between the soils are mainly due to differences in their particle's electrical conductivities and the thickness of their solid phase which are related to the cation exchange capacity of the soils. With increase in the soil ESP, both κ_s and d parameters change slightly. These departures from linearity are not significant when the electrical conductivity methods of Rhoades are used to measure soil salinity. However for measurements of solute concentrations in nonsaline soils, deviations from linearity are significant and the full relationship developed herein should be used.

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