

Effect of pH on Saturated Hydraulic Conductivity and Soil Dispersion¹

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ABSTRACT

The adverse effects of exchangeable sodium on soil hydraulic conductivity (K) are well known, but at present only sodicity and total electrolyte concentration are used in evaluating irrigation water suitability. In arid areas, high sodicity is often associated with high dissolved carbonate and thus high pH, but in humid areas high sodicity may be associated with low pH. To evaluate the effect of pH (as an independent variable) on K , solutions with the same SAR and electrolyte level were prepared at pH 6, 7, 8, and 9. Saturated K values were determined at constant flux in columns packed at a bulk density of 1.5 Mg m^{-3} . At pH 9, saturated K values were lower than at pH 6 for a montmorillonitic and a kaolinitic soil. For a vermiculitic soil with lower organic carbon and higher silt content, pH changes did not cause large K differences. Decreases in K were

not reversible on application of waters with higher electrolyte levels. The results from the K experiments were generally consistent with optical transmission measurements of dispersion. Although anion adsorption was at or below detection limits and cation exchange capacity (CEC) was only slightly dependent on pH, differences in pH effects on K among soils are likely due to differences in quantities of variable-charge minerals and organic matter.

Additional Index Words: sodium adsorption rate, electrolyte concentration, optical transmission.

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THE ADVERSE EFFECTS of high levels of exchangeable sodium on the hydraulic conductivity (K) of soils are well established. The onset of reduced K at a given soil exchangeable sodium percentage (ESP)

varies with total electrolyte concentration and soil properties (Quirk and Schofield, 1955; McNeal and Coleman, 1966; Frenkel et al., 1978; Shainberg et al., 1981a). Despite these and numerous other studies, the exact levels of ESP and electrolyte concentration at which reductions in K will occur for a given soil still cannot be predicted accurately. In published laboratory column studies, neutral or slightly acidic chloride salt solutions (pH \approx 6.0) were normally used with a carbon dioxide partial pressure (P_{CO_2}) near atmospheric ($10^{-1.5}$ kPa). The pH values of water in the columns were likely \approx 6.0 in the upper portion and 7.5 to 8.0 in the lower portions when CaCO_3 was present. Arid and semiarid soils are usually calcareous in the subsurface. Sodic soils in this environment are generally associated with high pH and high dissolved carbonate and bicarbonate concentrations. With such soils, pH values can exceed 10 but are more likely in the range of 8 to 9.5 near the surface. Sodic soils may occur also under acid conditions (pH < 6) in humid environments, where CaCO_3 is absent. El-Swaify (1973) found an anion effect on K for several tropical soils and interpreted this as due primarily to the different pHs measured. If pH has an effect on dispersion and hence on soil K , the published threshold relations between soil ESP and electrolyte levels are applicable only to slightly acidic conditions and not to the more prevalent arid-land sodic-soil conditions of higher pH.

In the present study, we examine the effect of pH (at fixed electrolyte concentration and ESP level) on the saturated hydraulic conductivity of three mineralogically different arid land soil types using laboratory soil columns. We also examine the relationship between optically measured dispersion and pH.

MATERIALS AND METHODS

Hydraulic Conductivity Studies

Three soils of different properties were chosen for study (Table 1). The Fallbrook and Bonsall soils have similar textures, whereas the Arlington soil is higher in silt content. All three soils are low in organic carbon content (determined using the method of Allison, 1960), with Arlington having the lowest value. The soil clays are predominantly kaolinite, vermiculite, and montmorillonite for Fallbrook, montmorillonite-vermiculite intermediate (according to x-ray analysis), mica and kaolinite for Bonsall, and vermiculite, mica and kaolinite for Arlington. The soils are noncalcareous and exhibit relatively low salt release by mineral weathering (e.g., see Fig. 1, Shainberg et al., 1981b). Low salt release is a necessary criterion in this study, because mineral weathering (largely release of Ca and Mg) alters solution composition and total solute concentration during flow measurements. Surface areas were measured using the method of Cihacek and Bremner (1979).

Mixtures of Na and Mg salts rather than Na and Ca salts were used to prepare the solutions at each pH to prevent CaCO_3 precipitation at high pH and low SAR.³ The effects of Mg on K are similar to those of Ca over the range of SAR used (McNeal et al., 1968). Two sets of solutions were prepared, SAR 20 and SAR 40, by mixing salts of Mg-Na-Cl- HCO_3 . The solutions were prepared to have total electrolyte levels of 8, 15, 25, 50, 100, 250, and 500 $\text{mmol}_c \text{L}^{-1}$ (mmoles of charge per liter) and pH levels of 6, 7, 8, and 9 by adjusting the Cl/ HCO_3 ratio and P_{CO_2} . The pH 6 and 9 solutions were the same except that the pH 6 solutions were equilibrated at $P_{\text{CO}_2} = 97$ kPa and the pH 9 solution at 35 Pa P_{CO_2} (atmospheric CO_2). The composition and P_{CO_2} necessary to achieve the desired pH for each solution were calculated from the equilibrium constants listed by Suarez (1977); prepared solutions were within 0.03 units of the desired pH. In a parallel experiment, the K values of one treatment (SAR 20, pH 8) and soil (Fallbrook) were determined using Na-Ca salts for comparison.

For the K measurements, plastic cylinders (5.5 cm i.d.) were packed with 300 g of sieved (< 2 mm), air-dried soil to a bulk density of 1.5 Mg m^{-3} . All columns were slowly wet from below by capillary rise, and then the same solution was applied from above using a peristaltic pump with constant flow of $17 \mu\text{L s}^{-1}$. The K values were determined by measuring the head developed in each column under constant flow with mercury or water manometers. The effluent from the columns flowed through a U tube and into a fraction collector. Each column was initially leached with the most concentrated solution of the desired pH and SAR treatment. When the K of the column and the composition and pH of the effluent had stabilized, the next more dilute solution of the same SAR and pH was applied. Usually > 1.3 L of each solution was passed through the column. The pH 6 solutions were maintained at pH 6 by bubbling CO_2 gas into the 5-L Pyrex solution reservoir. An exit tube at the bottom of the reservoir was placed at the same height as the peristaltic pump to eliminate CO_2 degassing during the pumping operation. The pH of the leachate was measured in the U tubes before degassing could occur. Influent and effluent solutions were analyzed for Ca, Mg, Na, and K by atomic absorption, alkalinity by acid titration, and Cl by AgCl titration (Rhoades and Clark, 1978). At the conclusion of the experiment, the columns were separated into 1-cm sections and analyzed for exchangeable cations.

For purposes of comparison, the K data were scaled to the initial K (K_i) values determined with the 100 $\text{mmol}_c \text{L}^{-1}$, SAR 20 solution, or 500 $\text{mmol}_c \text{L}^{-1}$, SAR 40 solution. Based on six replications on the Bonsall soil, SAR 40, pH 9 treatment, $\log K/K_i$ standard deviations of 0.08, 0.18, 0.19, and 0.11 were determined for solutions of 250, 100, 50, and 25 $\text{mmol}_c \text{L}^{-1}$, respectively.

Dispersion Studies

Each of the three soils were air-dried and lightly ground. Twenty 0.50-g samples of each soil were placed into poly-

³ SAR = $\text{Na}/(\text{Mg} + \text{Ca})^{1/2}$, where solute concentrations are in mmol L^{-1} .

Table 1—Selected physical and chemical properties of soils used.

Soil	Particle size			CaCO_3	Surface area	Organic carbon	Dominant clay
	Sand	Silt	Clay				
	%				$\text{m}^2 \text{g}^{-1}$	%	
Bonsall (fine, montmorillonitic, thermic, Natric Palexeralfs)	58	23	19	0	69	0.45	montmorillonite-vermiculite, mica, kaolinite
Fallbrook (fine-loamy, mixed, thermic Typic Haploxeralfs)	51	22	27	0	130	0.28	kaolinite, vermiculite, mica, montmorillonite
Arlington (coarse-loamy, mixed, thermic Haplic Durixeralfs)	25	52	23	tr	111	0.21	vermiculite, mica, kaolinite

ethylene centrifuge tubes and treated twice with 30 mL of either SAR 20 or SAR 40 solution of $200 \text{ mmol}_c \text{ L}^{-1}$ and then treated twice with 30 mL of the same solutions as used in the K study. Each suspension was placed on a reciprocating shaker for 30 min at three cycles s^{-1} and then centrifuged at 9000 g for 30 min at 25°C . The electrical conductivity and pH of each supernatant were subsequently measured. A few samples had to be reacted a third time to produce the desired pH. The soils were next treated with an additional 30 mL of solution, shaken for 30 min, and left to stand for 1, 3, 4, and 22 h. Optical transmissions were measured at 410 nm . Solutions were covered to maintain pH during the settling period. The pH and ion composition of the supernatants were determined after 22 h of settling. Reproducibility of one dispersion treatment (Bonsall soil, SAR 40, pH 9) was evaluated. The percent optical transmission standard deviations of six replications were 0.50, 0.36, 0.75, 0.86, and 2.2, at 250, 100, 50, 25, and $15 \text{ mmol}_c \text{ L}^{-1}$, respectively.

Adsorption Studies

Anion exchange capacities (AEC) were determined using a modification of the procedure described by van Raij and Peech (1972). For each soil either 3- or 9-g samples were

reacted three times with $0.5M \text{ CaCl}_2$ (40 mL) and then four times each with either 0.001, 0.01, 0.1 or $1M \text{ CaCl}_2$. For each electrolyte level, a series of samples at pH 3, 4, 5, 6, 7, 8, and 9 were obtained by adjusting the pH with either HCl or CO_2 -free NaOH. The pH was determined in the supernatant of the fourth reaction of samples and solutions. After the final centrifugation, the tubes were weighed to determine residual solution. The samples were then extracted five times with $0.5M \text{ NaNO}_3$. Extract solutions were analyzed for Cl and Ca using standards prepared in $0.5M \text{ NaNO}_3$. An additional cation and anion exchange capacity determination was performed by reacting 0.5-g samples twice with 30 mL of either SAR 20 or SAR 40 solution of $500 \text{ mmol}_c \text{ L}^{-1}$ and then reacting three times with pH 6, 7, 8, and 9 solutions at various solute concentrations. After the final centrifugation, the tubes were weighed and samples extracted three times with $0.5M$ ammonium acetate. Extract and reacting solutions were analyzed for Cl and alkalinity and Ca, Mg, and Na using standards prepared in $0.5M$ ammonium acetate. Anion exclusion was corrected by calculating the expected "carryover" of anions based on the residual mass of solution and subtracting the amounts of Cl and alkalinity in the extracting solution. An equivalent amount of cations were subtracted from the analysis to give the resultant cation exchange capacity (CEC).

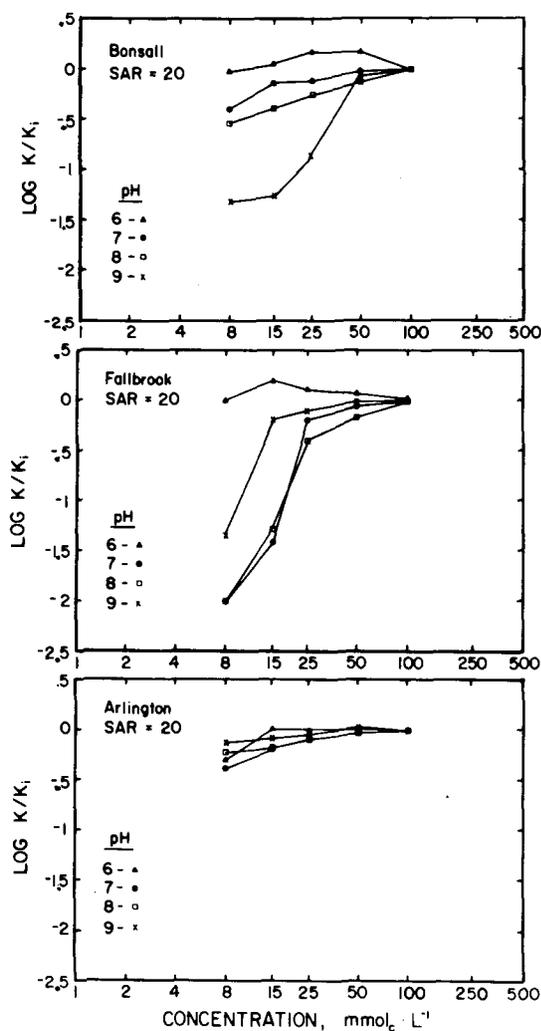


Fig. 1—Relative hydraulic conductivity vs. electrolyte concentration for Bonsall, Fallbrook, and Arlington soil at SAR = 20 and pH 6, 7, 8, or 9.

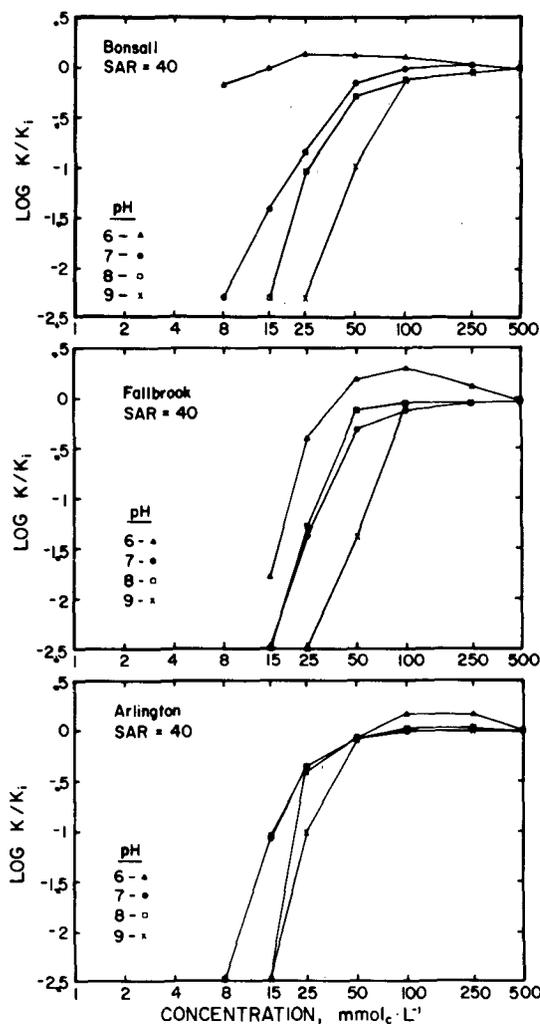


Fig. 2—Relative hydraulic conductivity vs. electrolyte concentration for Bonsall, Fallbrook, and Arlington soil at SAR = 40 and pH 6, 7, 8, or 9.

RESULTS

Hydraulic Conductivity

Measured compositions and pHs of prepared leaching solutions were within $\pm 3\%$ and ± 0.03 units, respectively, of desired values. Effluent solutions were mostly within ± 2 SAR units and within ± 0.1 pH units of the leaching solution values. As we expected, there was a trend toward increased Mg preference on the exchange sites with dilution ($ESP < SAR$). However, the assumption $ESP = SAR$ produced a relatively minor error (a few percentage points in exchangeable Na) and more importantly was not pH dependent (data not shown).

Plots of relative K ($\log K/K_i$) vs. electrolyte concentration at SAR 20 and pH 6, 7, 8, and 9 are presented in Fig. 1. The slight increase in relative K that sometimes occurred initially with decreasing concentration seems likely to result from the evolution of small amounts of air trapped in the columns during initial wetting. This phenomenon would be obscured when dispersion or swelling effects caused reductions in K . The relative K values for the 100 $\text{mmol}_c \text{L}^{-1}$ solutions were essentially independent of pH, but pH effects were evident at lower concentrations. At pH 6, no significant reduction in relative K occurred even at 8 $\text{mmol}_c \text{L}^{-1}$ for any soil. At pH 7 and 8, a gradual drop in relative K values of the Bonsall soil occurred with de-

creasing concentration. The final relative K was about 0.5 lower at 8 than at 100 $\text{mmol}_c \text{L}^{-1}$. At pH 9 a sharp drop in relative K started at 25 $\text{mmol}_c \text{L}^{-1}$. The relative K of the Fallbrook soil was reduced sharply below 25 $\text{mmol}_c \text{L}^{-1}$ for pH 7 and 8 and below 15 $\text{mmol}_c \text{L}^{-1}$ for pH 9. The relative K of the Arlington soil at SAR 20 was not appreciably affected by pH or electrolyte concentration.

Greater reductions in relative K occurred at SAR 40 than at SAR 20 (Fig. 2). There was a significant adverse effect of increasing pH on relative K of the Bonsall and Fallbrook soils. Reductions in the relative K of Arlington soil occurred with decreases in concentration at SAR 40 but showed little sensitivity to pH.

Reversibility of decreases in relative K was evaluated for the Bonsall soil. The decreases were not reversible on application of 250 $\text{mmol}_c \text{L}^{-1}$ solutions (data not given).

Dispersion Study

The optical transmission data of soil/water suspensions equilibrated with SAR 20 solutions of varying pH and allowed to settle for 22 h are presented in Fig. 3. At all pH values there appeared to be two distinct layers in the suspensions of Bonsall soil at 25 and 15 $\text{mmol}_c \text{L}^{-1}$ (the readings given apply to the upper layer). The onset of decrease in optical transmission

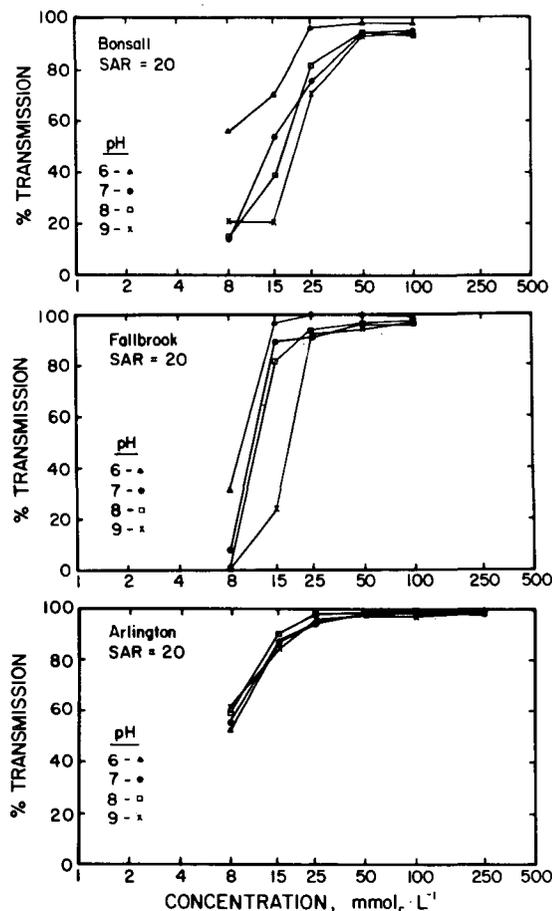


Fig. 3—Optical transmission (percent) vs. electrolyte concentration for Bonsall, Fallbrook, and Arlington soil at SAR = 20 and pH 6, 7, 8, or 9.

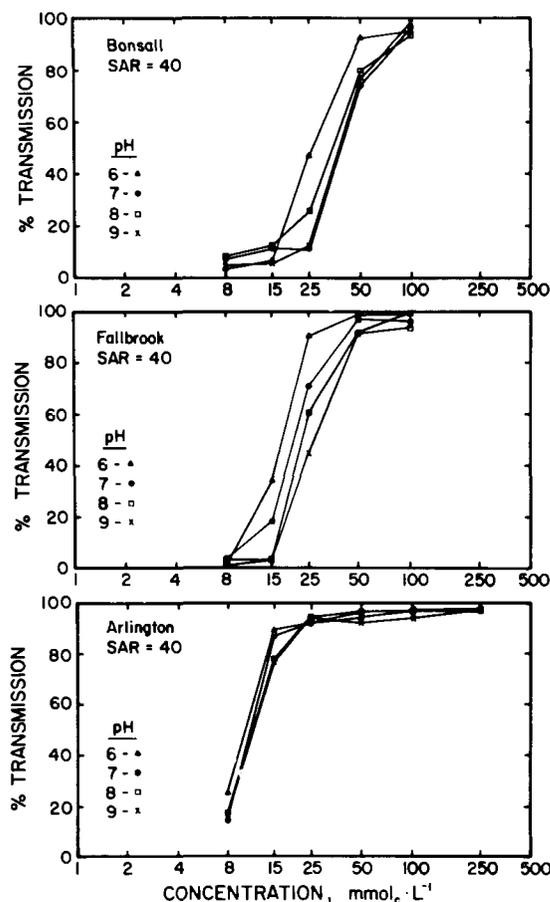


Fig. 4—Optical transmission (percent) vs. electrolyte concentration for Bonsall, Fallbrook, and Arlington soil at SAR = 40 and pH 6, 7, 8, or 9.

values occurred at 15 to 25 mmol_c L⁻¹, just as did most reductions in *K* (Fig. 1). The optical transmission data for Fallbrook suspensions at SAR 20 showed a sharp decrease starting at 15 mmol_c L⁻¹. Bonsall and Fallbrook both had decreasing optical transmission with increasing pH, consistent with the relative *K* data (Fig. 1). Dispersion occurred at 8 mmol_c L⁻¹ for Arlington soil and was almost independent of pH. The transmission and *K* measurements both indicate that Arlington soil is more resistant to dispersion than the other soils.

The optical transmissions of the corresponding suspensions at SAR 40 are displayed in Fig. 4. For Bonsall suspensions, optical transmission began to decrease at a solute concentration of 50 mmol_c L⁻¹, which coincided with the analogous onset in relative *K* reduction. As was true for SAR 20, Bonsall suspensions at SAR 40 contained two distinct phases, except at pH 6. The effect of pH on optical transmission was in reasonable agreement with the effect of pH on relative *K* (Fig. 2). The optical transmission data for Fallbrook suspensions showed a decrease beginning generally at 25 mmol_c L⁻¹. Optical transmission decreased with increasing pH consistent with the corresponding relative *K* data (Fig. 2). The optical transmission data for Arlington suspensions at SAR 40 showed dispersion at 8 mmol_c L⁻¹, with decreasing optical transmission as pH increased (although the differences were very small). As we expected, dispersion occurred at a higher electrolyte concentration at SAR 40 than SAR 20.

Adsorption Studies

The procedure described by van Raij and Peech (1972) gave AEC results that were variable with pH and concentration. At high concentrations, negative AEC values resulted due to failure to account for anion exclusion from the substantial quantities of permanent charge in these soils. At low concentrations, the variable quantities of Cl added as HCl to lower the pH were substantial relative to the apparent adsorption. Some results from the alternative procedure using Na-Mg-Cl-HCO₃ solutions are given in Table 2. Cation exchange capacity was independent of electrolyte concentration when corrected for anion exclusion. The CEC values listed are averages from the 8 to 100 mmol_c L⁻¹ reactions. All three soils exhibited some pH dependence in CEC (about 10% increase from pH 6 to 9), but the AEC values showed no trend and were sufficiently low to be regarded as at the limits of detection. The 10 to 20 mmol_c kg⁻¹ increase in CEC

without a corresponding drop in AEC indicates that the zero point of charge (ZPC) for the variable charge substances is below pH 6.

DISCUSSION

In general, there is good agreement between the effects of SAR, pH, and electrolyte concentration on relative *K* and clay dispersion for the Fallbrook and Bonsall soils but less so for Arlington soil. The Arlington soil at SAR 20 dispersed under conditions for which its *K* was not markedly affected. However, settling rates depend on clay concentration (Oster et al., 1980) in a way that cannot be easily predicted. Also, different clays in the soil may disperse at different concentration levels. In addition, the optical measurements are time dependent. We chose to measure optical transmission after 22 h of settling since at earlier measurement times aggregated clays and larger particles would improperly be counted as dispersed clay.

It seems reasonable that the onset of dispersion should precede clay movement in a packed soil column. In addition to clay dispersion, swelling is expected to contribute to *K* reductions at SAR 40 and electrolyte levels of ≤ 25 mmol_c L⁻¹ (McNeal, 1968). However, existing models used to explain interlayer swelling (based on diffuse double-layer theory) do not show sufficient pH dependence to explain the results presented herein. Since the smallest *K* values occurred at SAR 40 and low concentration, we substituted the experimentally determined values, $K = 4.9 \times 10^{-4}$ cm s⁻¹ for Bonsall soil at pH 6 and $K = 8.3 \times 10^{-6}$ cm s⁻¹ for Fallbrook soil at pH 6, SAR 40 and concentration of 15 mmol_c L⁻¹ into Eq. [55] of Bresler et al. (1982), as adapted from Kemper (1961). We used the calculated volumetric water of 0.434 and appropriate constants for sandy loam soil (Bresler et al., 1982). The calculated midplane distances were 1.9×10^{-4} cm and 2.4×10^{-5} cm, respectively, indicating essentially infinite distance between platelets. The surface charge density, Γ_s is equal to the CEC divided by the surface area. Using the data from Table 1 and expressing Γ_s in esu cm⁻², Γ_s equals 3.58×10^4 for Fallbrook soil at pH 6 and 4.35×10^4 for Bonsall soil at pH 6. Corresponding Y_d (surface potential at the midplane) values were obtained from Fig. 23 in Bresler et al. (1982); since $C^+/C^{2+} = 110$, the monovalent graph was deemed appropriate. For the Fallbrook soil at pH 6, $Y_d \ll .01$, and an increase in Γ_s (due to increase in CEC) to a value of 3.91×10^4 at pH 9 produces a negligible change (< 1%) in midplane distance, if Y_d is assumed to be constant. This small change results in a negligible diffuse double-layer predicted change in *K*. This is in contrast to the measured change of slightly more than an order of magnitude. Similarly for Bonsall soil at pH 6, $Y_d \ll 0.01$. The increase in Γ_s to a value of 4.89×10^4 at pH 9 changes the midplane distance by < 1% (at constant Y_d); thus, a negligible change in *K* is predicted once again. This contrasts with the change in *K* of more than two orders of magnitude that was measured experimentally. For this reason we consider differences in relative *K* between pH 6 and 9 as due primarily to changes in dispersive forces. Also, the effects of swelling should be

Table 2—Cation and anion exchange capacities as a function of pH.

Soil	pH				pH			
	6	7	8	9	6	7	8	9
	— CEC, † mmol _c kg ⁻¹ —				— AEC, ‡ mmol _c kg ⁻¹ —			
Bonsall	83.5	86.8	87.8	90.1	0.01	0.50	-0.87	0.03
Fallbrook	161	165	169	176	0.06	-0.40	-0.20	-0.03
Arlington	167	174	172	188	0.05	0.03	-0.01	-0.05

† Based on averages of determinations made with 8, 15, 25, 50, and 100 mmol_c L⁻¹ and SAR = 20 solutions.

‡ Based on averages of determinations made with 8 and 15 mmol_c L⁻¹ and SAR = 20 solutions.

reversible, whereas the decline in K of our columns could not be reversed.

The effect of pH on clay dispersion has been observed by others, at least for Na-saturated clay. Schofield and Samson (1954) showed that kaolinite edge faces are positively charged at low pH and negatively charged at high pH. It seems likely that at least part of the dispersion on addition of NaOH was due to a change in the saturating cation. Suarez and Frenkel (1981) found substantial hydrolysis of Na-saturated kaolinite during the conventional preparation procedure of successive washings to remove excess salt. Presumably Al becomes the chief exchangeable cation on hydrolysis of the exchangeable cation. Addition of NaOH would thus not only raise the pH as Schofield and Sampson (1954) intended but also lead to Na replacement of the exchangeable Al, thus enhancing dispersion. Arora and Coleman (1979) observed that increasing pH resulted in increasing dispersion for their soil clays, but for specimen clays, maximum dispersion occurred at pH 8.3. The flocculation value for Wyoming montmorillonite at SAR of 20 is reported as $7 \text{ mmol}_c \text{ L}^{-1}$ (Oster et al., 1980); that of kaolinite in the presence of montmorillonite, $16 \text{ mmol}_c \text{ L}^{-1}$ at SAR 15 and $30 \text{ mmol}_c \text{ L}^{-1}$ at SAR 30 (Arora and Coleman, 1979). All of these values were obtained without specifying soil pH. For Bonsall soil (SAR 20), we observed dispersion at 15 to $25 \text{ mmol}_c \text{ L}^{-1}$ depending on the pH in a Mg-Na system. This range is consistent with the published data for kaolinite-montmorillonite (at unknown pH). For Fallbrook at SAR 20, dispersion was pH dependent and occurred at 8 to $15 \text{ mmol}_c \text{ L}^{-1}$ concentrations.

Changes in pH affect the edge charge on clays and the surface charge of variable charge minerals such as iron and aluminum oxides. There is considerable variability depending on structural composition and degree of crystallinity, but iron and aluminum oxides generally undergo a surface charge reversal around pH 7 to 9 (positively charged below that pH and negatively charged above). This is also the region in which kaolinite exhibits its edge charge reversal as evidenced by Cl adsorption studies (Schofield and Samson, 1954). In arid land soils, a mixture of minerals exist, each with a different ZPC. At low pHs we can expect edge to face bonding to occur, as well as bonding of positive iron and aluminum oxides to negative clay surfaces (van Olphen, 1977). This type of bonding should hinder dispersion and thus should result in optimum hydraulic conductivities. With increasing pH as the ZPC is approached, however, edge to face clay bonding decreases and iron and aluminum bonding to clays should also decrease. We expect that the sensitivity of soil hydraulic conductivity to pH changes will depend on the quantity of variable charge minerals and organic matter present in the soil. Soils with large amounts of variable charge should be most susceptible to pH effects.

The importance of the pH effect is demonstrated by the observation that differences in relative K between pH 6 and 9 were equivalent to differences between SAR of 20 and SAR of 40. The adverse effect of high exchangeable Na on soil K is thus magnified by high

soil and water pH in semiarid and arid regions. The assignment of threshold values for soil permeability must consider pH along with previous concepts of SAR and electrolyte concentration. Due to differences among soils, simple prediction of this pH effect is not possible at present; however, K decreases can be predicted from optical transmission measurements.

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