

ELECTRICAL CONDUCTIVITY OF Na/Ca-MONTMORILLONITE GELS

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Abstract—The specific conductivity, κ_g , of Na/Ca montmorillonite gels (0.02 and 0.04 g clay/cm³) as a function of the specific conductivity of the interclay solution, κ_w , was measured. For low values of κ_w (<3 mmho/cm) the conductivity curves were convex with respect to κ_w ; at higher values they were linear. The κ_w at which deviation from linearity began increased with increasing sodium content from 0.7 mmho/cm for the Ca-montmorillonite gel to 2.6 mmho/cm for Na-montmorillonite gel. The intercept of the linear portion of the conductivity curve increased and its slope decreased with increasing exchangeable sodium.

The experimental results were described by a conductance model comprised of two elements connected in parallel: an element consisting of the solid and solution phases connected in series, and another consisting of the solution phase. At low electrolyte concentrations, the first element accounts for the curvature of the κ_g - κ_w curve, whereas at high electrolyte concentrations, the second element dominates, and the curve is linear with a slope determined by a formation factor and an intercept determined by exchangeable cation mobility.

An adjustable parameter in the conductivity term for the first element, which accounts for the thickness of the clay particles, increased with exchangeable Na, and its numerical value indicated that the solid phase also includes the diffuse double layer. The mobility of the exchangeable cation relative to that in water increased from 4% for Ca to 41% for Na with the largest increase occurring between 20 and 40% exchangeable Na. Similar effects of exchangeable Na were evident on the axial ratio of the clay particles calculated from the slopes of the linear lines. These observations are consistent with an exchangeable-ion demixing model where the initial exchangeable Na is adsorbed on the external surfaces of the Ca-montmorillonite tactoids without affecting exchangeable ion mobility or tactoid size. Further additions of exchangeable Na result in Na adsorption on the internal surfaces of the tactoid and tactoid breakdown with a subsequent increase in both exchangeable ion mobility and the axial ratio of the clay particles.

Key Words—Cation mobility, Electrical conductivity, Electrolyte, Montmorillonite.

INTRODUCTION

Measurements of bulk-soil electrical conductivity, κ_a , can be used to assess soil solution salinity (Rhoades and Ingvalson, 1971). However, the electrical conductivity of the soil is the result of both the surface and the solution electrical conductivities. Also, the bulk-soil electrical conductivity depends on the moisture content and the tortuosity of the current path in the soil (Rhoades *et al.*, 1976). Unless the contribution of the surface conductivity and the tortuosity parameters and their interaction with the liquid phase chemistry (concentration and electrolyte composition) can be estimated, estimates of the electrical conductivity of the soil solution from the bulk-soil electrical conductivity are subject to question. The objectives of the present study were to determine the effect of salt concentration and composition, (SAR²) and clay concentration on the electrical conductivity of Na/Ca-montmorillonite gels. The concept developed in this study may be used, sub-

sequently, in the study of the electrical conductivity of bulk soils.

THEORY

The electrical conductivity of a clay gel (κ_g) can be divided into that contributed by the liquid phase (κ_w) and that contributed by the clay particles and their counter ions (κ_s). The simplest and most widely used model considers the conductivity cell as consisting of the two conductors (the clay and the interclay solution) in parallel (Cremers *et al.*, 1966; Waxman and Smits, 1968; Rhoades *et al.*, 1976). According to this model,

$$\kappa_g = \kappa_s' + \kappa_w/f, \quad (1)$$

where κ_s' is the apparent specific conductivity of the clay particles and f is the formation factor. If the electric current transported by the counter ions associated with the clay is assumed to travel along the same tortuous path as the current attributed to the ions in the liquid water (Cremers *et al.*, 1966; Waxman and Smits, 1968), Eq. (1) becomes

$$\kappa_g = \kappa_s/f + \kappa_w/f, \quad (2)$$

where κ_s is the specific conductivity of the clay particles and the counterions.

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² SAR = $C_{Na}/(C_{Ca})^{0.5}$, where the ion concentrations, C_i , are expressed in mmole/liter.

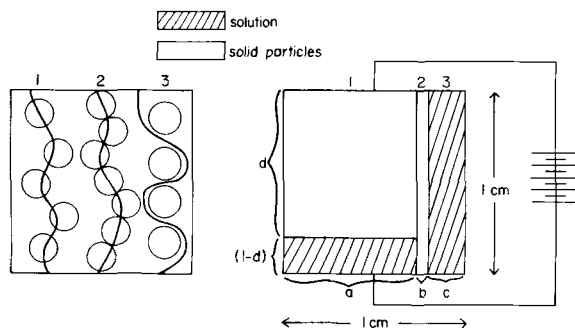


Figure 1. Resistance model representing a saturated clay-electrolyte system.

If the contribution of κ_s and $1/f$ are not influenced by the solution concentration, a plot of κ_g vs. κ_w would be a straight line. The formation factor is evaluated from the slope of this line. The above assumptions do indeed apply to the electrical conductivity of clay gels (Cremers and Laudelout, 1965; Cremers *et al.*, 1966), shaley sands (Waxman and Smits, 1968), and soils (Rhoades *et al.*, 1976) at moderate to high electrolyte concentrations, and Eq. (1) was used by these authors to calculate the formation factors of their systems. At low electrolyte concentration, the plot deviates from a straight line, and the curve becomes convex with respect to the abscissa; the increase in κ_g is greater than that attributable to the conductivity of the added electrolyte alone. Application of the two conductors in a parallel model would require the assumption of an increase in surface conductance of exchangeable ion with an increase in concentration (Letey and Klute, 1960; Waxman and Smits, 1968). This assumption is not acceptable, as argued by van Olphen and Waxman (1958), who concluded that because the charge of the clay double layer is determined mainly by imperfections within the clay lattice, the addition of electrolyte does not change the total double-layer charge. However, because the counter-ion atmosphere is compressed by the electrolyte addition, a shift of counter ions into the space between the slipping plane and surface is expected, and thus the surface conductance should decrease.

To explain these contradictions, Sauer *et al.* (1955) suggested that geometrical parameters account for the shape of the curve and that the specific conductivity of an aggregate of conductive particles saturated with a conducting electrolyte can be described by an equivalent resistance model comprised of three elements in parallel (Figure 1): (1) an element, κ_1 , consisting of particles and solution in series with each other; (2) an element, κ_2 , consisting of particles in sufficiently close contact with one another to form continuously conducting paths; and (3) an element, κ_3 , consisting of fluid in-between the particles. The parameters a , b , and c in Fig-

ure 1 represent the fractional cross sections of the first, second, and third elements, respectively, and d is the fractional cross section of the solid particles. The conductivities of the three elements are given by the following equations:

$$1/\kappa_1 = (1 - d)/a\kappa_w + d/\kappa_s' = x/\kappa_w + y/\kappa_s', \quad (3)$$

$$\kappa_1 = (\kappa_s'\kappa_w)/(x\kappa_s'w + y\kappa_w), \quad (4)$$

$$\kappa_2 = b\kappa_s', \quad \text{and} \quad (5)$$

$$\kappa_3 = c\kappa_w = \kappa_w/f, \quad (6)$$

where

$$x = (1 - d)/a, \quad y = d/a, \quad (7)$$

and c is equal to $1/f$, which would characterize the tortuosity of the gel if the solids were nonconductive. The specific conductivity of the clay gel is the sum of the conductivities of the three elements:

$$\begin{aligned} \kappa_g &= \kappa_1 + \kappa_2 + \kappa_3 \\ &= \kappa_s'\kappa_w/(x\kappa_s' + y\kappa_w) + b\kappa_s' + \kappa_w/f \end{aligned} \quad (8)$$

Sauer *et al.* (1955) applied their model to describe the electrical conductivity of ion-exchange resin-solution systems. They suggested a method to calculate the cell parameters (a , b , c , and d in Figure 1). However, this method is not applicable to clay suspensions for two reasons: (1) The cell parameters in clay systems are also a function of the interstitial solution concentration. For example, the thickness of Na-montmorillonite platelets is ~ 10 Å, whereas the thickness of the diffuse double layer (which is part of the particle conductance) is 30, 100, and 300 Å for NaCl concentrations of 0.01, 0.001, and 0.0001 M, respectively. (2) The method of Sauer *et al.* (1955) involves measurements of electrical conductivity in very dilute, intercalated solutions and extrapolating the results to distilled water. In dilute solutions ($M < 0.001$) clays dissolve rapidly and significantly increase the conductivity of clay suspensions (Shainberg *et al.*, 1974; Frenkel and Suarez, 1977), causing the extrapolation for clay systems to be very inaccurate. Thus, another approach is considered.

The specific surface of montmorillonite is $750 \text{ m}^2/\text{g}$, and the average distance between the platelets, when single platelets are assumed, is 1330 and 665 Å for suspensions of 2.0 and 4.0% clay, respectively. The average "thickness" of the diffuse double layer at NaCl concentration greater than 0.001 N is less than 100 Å. Evidently under these experimental conditions, where the diffuse double layer does not overlap, the contribution of the second element (conductance through or along surfaces of particles in contact with each other) is negligible. For Na/Ca-montmorillonite systems, where tactoids are formed and the thickness of the diffuse double layer is reduced, the contribution of the

second element is further reduced. Under these conditions $b \sim 0$ and Eq. (8) reduces to

$$\kappa_g = \frac{\kappa_s' \kappa_w}{\kappa_s'(1-d)/a + \kappa_w(d/a)} + \kappa_w/f. \quad (9)$$

Considering Figure 1 and the requirement that the dimensions of the solid phase should be the same in all directions, $a = d$, Eq. (8) reduces to

$$\kappa_g = \frac{\kappa_s' \kappa_w}{\kappa_s'(1-d)d + \kappa_w} + \kappa_w/f, \quad (10)$$

and when $\kappa_w \gg \kappa_s'$, i.e., at high solution concentration, Eq. (10) further reduces to

$$\kappa_g = \kappa_s' + \kappa_w/f \quad (11)$$

which is identical with Eq. (1). Evidently at low electrolyte concentrations, the first element in Eq. (10) determines the shape of the curve. For relatively high salt concentrations, the second term is the dominant one, and the first element gives the intercept.

EXPERIMENTAL PROCEDURE

A clay-size fraction of Wyoming montmorillonite was separated from larger size fractions by sedimentation. Na- or Ca-clays were prepared by repeatedly washing the clay with 1 N chloride solutions. Thereafter, the clay was washed with distilled water in a high speed centrifuge until tests with $AgNO_3$ indicated that the equilibrium solution was free of chlorides. The salt-free gel was quick frozen, freeze-dried, and stored in a desiccator.

The Na/Ca-montmorillonite gels were prepared by mixing appropriate amounts of the clay with the corresponding solutions. Bi-ionic clay mixtures were prepared by mixing appropriate amounts of the two homoionic clays to obtain Na/Ca clays with ESP³ values of 0.0, 10, 20, 40, and 100%. The corresponding solution SARs were 0, 10, 20, 40, and ∞ (or NaCl), respectively. The electrolyte concentration of the solutions were 0.0, 1, 4, 10, 30, 60, and 100 meq/liter; the corresponding electrical conductivities were about 0.003, 0.13, 0.37, 1.15, 3.40, 6.7, and 10.6 mmho/cm, respectively. Two clay concentrations (2.0 and 4.0 g clay/100 cm³ solution) were studied. After equilibration by shaking for 1 hr, κ_g was measured. The gels were then centrifuged in an ultracentrifuge, and κ_w was determined. All conductivity measurements were made with the same cell ($K = 2 \text{ cm}^{-1}$) and conductivity bridge (800 Hz).

RESULTS AND DISCUSSION

The specific conductivity of 4.0% Na/Ca-montmorillonite gels as a function of κ_w is presented in Figure 2.

³ ESP = 100[NaX/(NaX + CaX)], where NaX and CaX are the exchangeable cations, and concentration is expressed in meq/g of clay.

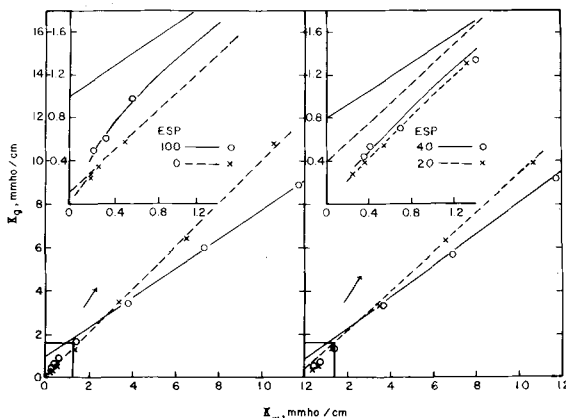


Figure 2. Specific conductivity of 4% Na/Ca-montmorillonite gels, κ_g , vs. specific conductivity of interlayer solutions, κ_w .

At all Na/Ca ratios, the initial increase in κ_g is greater than that attributable to conductance of the added electrolyte alone. However, at the higher electrolyte concentrations, the two axes are linearly related. In the following discussion, the linear portion of the conductivity curves with its derived parameters is discussed first.

Linear portion of the conductivity curves

The parameters of the straight lines relating κ_g to κ_w (Table 1) show that both the intercepts and the slopes depend on chemical composition of the system. The intercept increases and the slope decreases as exchangeable sodium increases.

For the straight line portion of the conductivity curve, a constant exchangeable-cation mobility is assumed, and the equivalent conductivity (or mobility) of the exchangeable ions may be calculated from the intercept. The specific conductivity of the solid phase is calculated from the intercept (κ_s') by the relation

$$\kappa_s = \kappa_s' f, \quad (12)$$

and is equal to

$$\kappa_s = F(Z_m C_m U_m + Z_a C_a U_a), \quad (13)$$

where F is the Faraday constant, Z is valence, C is con-

Table 1. The electrical conductivities of Na/Ca-montmorillonite gels.¹

Chemical composition (ESP)	4% Gels		2% Gels	
	Intercept (κ_s') (mmho/cm)	Slope (l/f)	Intercept (κ_s') (mmho/cm)	(l/f)
0 (Ca)	0.09	0.98	0.08	0.96
10	0.28	0.93	0.10	0.95
20	0.40	0.89	0.10	0.93
40	0.80	0.72	0.26	0.88
100 (Na)	1.00	0.67	0.50	0.84

¹ Clay concentrations of 4 and 2 g clay/100 cm³ solution are expressed as 4 and 2% gels.

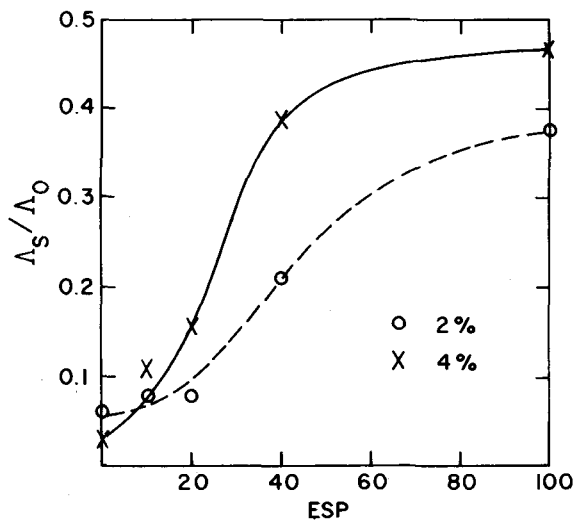


Figure 3. Relative equivalent conductivity of adsorbed cations as a function of the exchanger composition.

centration, U is mobility, and the subscripts m and a represent the exchangeable ions and clay particles, respectively. Because of electroneutrality

$$|Z_m C_m| = |Z_a C_a| \quad (14)$$

Eq. (13) becomes

$$\kappa_s = F |Z_m C_m| (U_m + U_a). \quad (15)$$

It follows from Eq. (15) that the specific conductivity of the exchangeable ions, κ_m , is related to the specific conductivity of the clay-exchangeable ion complex by the relation

$$\kappa_m/\kappa_s = U_m/(U_m + U_a). \quad (16)$$

For Na-montmorillonite $U_{Na} = 5.0 \times 10^{-4}$ cm²/sec volt and $U_a = 3.0 \times 10^{-4}$ cm²/sec/volt (van Olphen and Waxman, 1958), and Eq. (16) reduces to

$$\kappa_{Na}/\kappa_s = 5.0/8.0 = 0.625. \quad (16a)$$

For Ca-montmorillonite $U_{Ca} = 5.9 \times 10^{-4}$ cm²/sec volt

and $U_a = 1.0 \times 10^{-4}$ cm²/sec volt (Bar-On *et al.*, 1970), and Eq. (16) gives

$$\kappa_{Ca}/\kappa_s = 5.9/6.9 = 0.85. \quad (16b)$$

To calculate the equivalent conductivity of the exchangeable ions, Λ_m ($\Lambda_m = \kappa_m/C_m$), the concentration of the exchangeable cation in the pore solution must be known. This concentration is given by

$$C_m = C_a X/\theta, \quad (17)$$

where C_a is the clay concentration in g/cm³ of gel, X is the cation-exchange capacity of the clay ($X = 1$ meq/g), and θ is the volumetric water content of the gel (which was calculated by assuming a density for the clay particles of 2.75 g/cm³). The calculated equivalent conductivities of the exchangeable ions are presented in Table 2.

It is obvious from Table 2 and Figure 3 that the relative electrical conductivity of the exchangeable cation relative to that at infinite dilution, Λ_0 , increases with an increase in ESP. Whereas the relative electrical conductivity of exchangeable Ca in Ca-montmorillonite is about 4% of that at infinite dilution, the relative electrical conductivity of exchangeable Na in Na-montmorillonite is about 41%. In the bi-ionic systems, the addition of 10 and 20% exchangeable Na into Ca-montmorillonite did not greatly change the relative electrical conductivity. However, a further increase in the ESP caused a sharp increase. A similar increase occurred in concentrated Na/Ca-sols prepared with distilled water (Shainberg and Kemper, 1966). Their explanation is also applicable to our systems: Ca-montmorillonite platelets form packets or tactoids. The mobility of the Ca ions inside the packets is low due to the electrical interaction with the discrete charge at the clay surface and increased water viscosity. The mobility of Ca ions on external surfaces is similar to that of exchangeable Na. The relative equivalent conductivity of adsorbed Na is 40% of that in bulk solution. When Na replaces Ca on the external surfaces of Ca-montmorillonite (ESP < 20), little change in the relative equivalent conductivity is observed. The addition of more Na causes packet breakdown, exposing more

Table 2. The equivalent conductivity of exchangeable cations.¹

ESP (%)	4% Gels						2% Gels				
	κ_s (mmho/cm)	κ_m (meq/cm ²)	C_m (meq/cm ³)	Λ_m (cm ² /ohm eq)	Λ_0 (cm ² /ohm eq)	$(\Lambda_m/\Lambda_0)100$ (%)	κ_s (mmho/cm)	κ_m (meq/cm ²)	C_m (meq/cm ³)	Λ_m (cm ² /ohm eq)	$(\Lambda_m/\Lambda_0)100$ (%)
0	0.09	0.08	0.04	2.0	59.5	3.3	0.08	0.068	0.02	3.4	5.7
10 ²	0.30	0.24	0.04	6.2	58.6	10.6	0.11	0.091	0.02	4.6	7.8
20 ²	0.45	0.36	0.04	9.1	57.6	15.8	0.11	0.089	0.02	4.4	7.7
40 ²	1.12	0.85	0.04	21.3	55.7	38.2	0.30	0.228	0.02	11.4	20.5
100	1.49	0.93	0.04	23.3	50.1	46.5	0.60	0.375	0.02	18.8	37.4

¹ Calculated from Eq. (16).

² The weighted average of individual ion parameters was used.

Table 3. Formation factor, *f*, and axial ratio, *k*, in Na/Ca-montmorillonite gels.

ESP	Slope		<i>f</i>		<i>k</i>		Average <i>k</i>	Relative "thickness" of Na/Ca-packets
	2%	4%	2%	4%	2%	4%		
0 (Ca)	0.96	0.98	1.04	1.02	5.3	1.3	3.3	8.7
10	0.95	0.93	1.05	1.08	6.6	5.0	5.8	4.9
20	0.93	0.89	1.08	1.12	10.5	7.9	9.2	3.1
40	0.88	0.72	1.14	1.40	18.4	26.5	22.4	1.3
100 (Na)	0.84	0.67	1.19	1.49	25.0	32.4	28.7	1.0

surfaces to the solution and increasing the relative equivalent conductivity. These conclusions are further supported by those derived from slopes of the straight lines.

Formation factors calculated from the slopes of the straight lines are presented in Table 3. Following Cremers *et al.* (1966), *f* is related to the porosity, θ , as follows:

$$f = 1 + k(1 - \theta)/\theta, \quad (18)$$

where *k* is a parameter which depends on the axial ratio of the oblate ellipsoids used to simulate the shape of the clay particles. The values of *k*, as calculated from Eq. (18) for the 2.0 and 4.0% clay gels, are presented in Table 3. The values of *k* obtained for Na-montmorillonite (25.0 and 32.4 for the 2.0 and 4.0% gels, respectively) and for Ca-montmorillonite (5.3 and 1.3 for these two suspensions, respectively) agree with corresponding values available in the literature (Cremers *et al.*, 1966; Gast, 1966; Shainberg and Levy, 1975). For example, using the experimental values of Gast (1966), the *k* values for Na- and Sr-montmorillonite are 41.3 and 13.5, respectively. If the "thickness" of Na-montmorillonite platelets is 1.0, the relative "thickness" of the Ca-packet is 8.7, and the corresponding number of platelets in Ca-montmorillonite, as estimated from the electrical conductivity measurements, is 5.0. Further, it is evident from Table 3 that the tortuosity of the ion movement path and the shape of the clay particles depend on the ESP. Generally, exchangeable Na breaks up the Ca-packets. Most of the breakdown of the packets takes place between ESP 20 and 40. These observations resemble those reported in the literature (Shainberg and Kemper, 1966), and the same mechanism is applicable—addition of a small amount of Na to Ca-montmorillonite packets does not affect the size of the packet. The adsorbed ions are demixed, and the exchangeable Na is concentrated on the external surfaces of the packets whereas the exchangeable Ca resides on internal surfaces of the packets. Further addition of exchangeable Na results in the Na ions penetrating into the packets and the packets dispersing. The packets break down, according to this study, in the range between ESP 20 and 40.

Convex portion of the conductivity curve

At low electrolyte concentration, there is a more rapid increase in κ_g than is attributable to the conductivity of the solution phase alone. This phenomenon results in the conductivity curves (Figure 2) convexing with respect to the abscissa. The parameters of the straight lines (κ_s' and *f*) and the experimental values for κ_w and κ_g were inserted in Eq. (10) to obtain individual values for *d*. The average *d* values and the associated average deviations between calculated and experimental κ_g values are given in Table 4. They were also used to calculate the ratio of κ_g from Eq. (10) to that from Eq. (1). This ratio expresses the relative deviation of gel conductivity from a linear dependence on the conductivity of the solution phase. The calculated ratios as a function of κ_w are presented in Figure 4. The agreement between experimental and calculated ratio is good. Evidently the interclay solution concentration at which the deviation begins and its extent depends on the percentage of exchangeable Na in the system. For Ca-montmorillonite systems the deviation starts at $\kappa_w \sim 0.7$ mmho/cm, whereas for Na-clay the deviation starts at ~ 2.6 mmho/cm.

The *d*-values in Table 4 suggest that the thickness of the clay phase in the 4% gels ranged from about 0.2 to

Table 4. Average *d*-value and deviations between predicted and measured electrical conductivities of Na/Ca-montmorillonite gels.

Chemical composition (ESP)	4%		2%	
	<i>d</i> ¹	Deviation ² (mmho/cm)	<i>d</i>	Deviation (mmho/cm)
0 (Ca)	0.26	0.01	0.10	0.06
10	0.14	0.03	0.09	0.01
20	0.15	0.01	0.13	0.01
40	0.40	0.07	0.28	0.02
100 (Na)	0.67	0.03	0.35	0.05

¹ Average *d* values are calculated using Eq. (10) and experimental κ_g and κ_w values ($0.1 < \kappa_w < 7$ mmho/cm).

² Deviation was calculated from the difference between calculated, κ_g^c (Eq. 10), and measured electrical conductivity, κ_g^m , of the clay suspension ($0.1 < \kappa_w < 1.5$ mmho/cm), and the number of observations, *n*, according to $[\sum(\kappa_g^c - \kappa_g^m)^2]^{0.5}/n$.

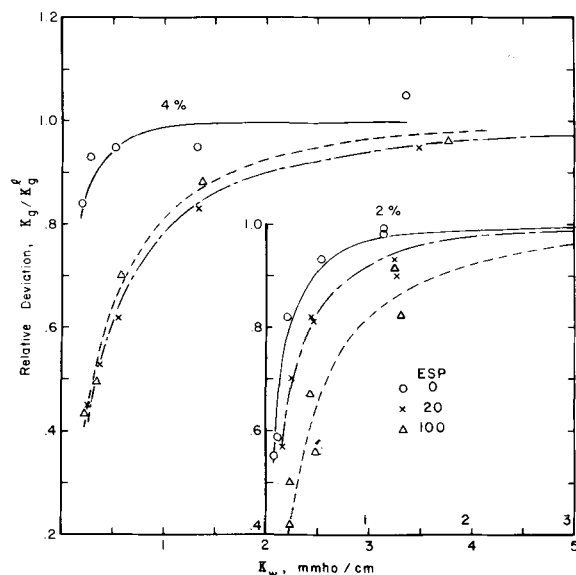


Figure 4. The relative deviation of the gel conductivity, κ_g , to that of the extrapolated straight line conductivity, κ_g^e , as a function of the interclay solution conductivity. Points represent experimental data; solid lines are theoretical curves based on Eq. (10) and d-values given in Table 4.

0.7 as ESP increased from 0 to 100. Similarly, the thickness of the clay phase in the 2% gels ranged from 0.1 to 0.4 as ESP increased from 0 to 100. The following observations should be noted: (1) The volumetric fraction of the crystal clay in the 4.0 and 2.0% gels are only 0.016 and 0.008, respectively. Thus, the "thickness" of the solid phase in the conductivity cell is more than 10 times that of the crystals. Evidently, the thickness of the solid phase in the conductivity model also includes the diffuse double layer. (2) The thickness of the solid phase is a function of both the clay percentage and the exchangeable ions. The d-parameter is more than doubled in going from Ca- to Na-montmorillonite. This observation supports the previous conclusion that the d-parameter includes also the diffuse double layer in addition to the volume of the crystals.

Isoconductivity point

The specific conductivity of the solid phase, κ_s , and the equivalent conductivity of the exchangeable ions may also be calculated from the isoconductivity point. At this point, κ_g and κ_w are equal. (At low electrolyte concentration, κ_g is higher than κ_w due to the contribution of the exchangeable ions. At high electrolyte concentrations, κ_g is lower than κ_w due mainly to the tortuosity of the path. The point at which both effects balance each other is the isoconductivity point.) At the isoconductivity point, the presence of the clay particles leaves the conductivity of the solution unaffected. Thus, the isoconductivity point is independent of the

Table 5. Isoconductivity points and the relative equivalent conductivity of the adsorbed ions derived from them.

Chemical composition (ESP)	Isoconductivity ¹ point (mmho/cm)	Axial ratio k	Λ_g/Λ_o
0 (Ca)	2.8	3.3	5.9
10	1.6	5.8	6.0
20	1.1	9.2	6.6
40	1.6	22.4	24.3
100 (Na)	2.4	28.0	50.6

¹ The average of 2% and 4% gels.

clay concentration in the gel (Dakshinamurti, 1960) and is related to the surface equivalent conductivity of the adsorbed ions. Following Cremers and Laudelout (1965), the isoconductivity value is given by

$$\kappa_{iso} = 2.65 \Lambda_m \sigma S / k, \quad (19)$$

where Λ_m is the equivalent conductivity of the adsorbed ions, σ is the charge density at the clay surface (meq/cm²), S is the specific surface area of the clay (cm²/g), and k is the axial ratio defined by Eq. (18). Substituting the value for k obtained previously and realizing that σS is equal to the cation-exchange capacity of the clay, Λ_m can be calculated from the isoconductivity values by Eq. (10). These values are presented in Table 5 and are compatible with those calculated from the intercept (Table 2). The effect of ESP on the relative equivalent conductivities are similar in both methods.

CONCLUSION

For Na/Ca-montmorillonite gels at low electrolyte concentrations, the increase of κ_g with increasing κ_w was greater than that attributable to the increase in κ_w alone. Using a conductance model consisting of the liquid and solid phases connected in parallel would lead one to conclude that the mobility of the exchangeable cations increased with increasing solution concentration. However, the introduction of another parallel conductance element, consisting of the solid and liquid phases connected in series, explains the κ_g - κ_w relationship by geometrical considerations. Based on this model we concluded that (1) the thickness of the solid phase includes the diffuse double layer, and (2) the increase in exchangeable-ion mobility and in the axial ratio of the clay particles with increasing exchangeable sodium percentage is consistent with the effects of exchangeable calcium and sodium on tactoid formation. When Na replaces Ca on the external surfaces of Ca-montmorillonite (ESP < 20) little change in tactoid size occurs. More Na causes tactoid breakdown and increased mobility of the exchangeable cations.

REFERENCES

- Bar-On, P., Shainberg, I., and Michalli, I. (1970) The electrophoretic mobility of Na/Ca montmorillonite particles: *J. Colloid Interface Sci.* **33**, 471-472.

- Cremers, A. and Laudelout, H. (1965) On the "isoconductivity value" of clay gels: *Soil Sci.* **100**, 298–299.
- Cremers, A., van Loon, J., and Laudelout, H. (1966) Geometry effects for specific electrical conductance in clays and soils: in *Clays and Clay Minerals, Proc. 14th Natl. Conf., Berkeley, California, 1965*, S. W. Bailey, ed., Pergamon Press, New York, 149–192.
- Dakshinamurti, C. (1960) Studies on the conductivity of clay systems: *Soil Sci.* **90**, 302–305.
- Frenkel, H. and Suarez, D. L. (1977) Hydrolysis and decomposition of Ca-montmorillonite by leaching: *Soil Sci. Soc. Amer. J.* **41**, 887–891.
- Gast, R. G. (1966) Applicability of models to predict rates of cation movement in clays: *Soil Sci. Soc. Amer. J.* **30**, 48–52.
- Letey, J. and Klute, A. (1960) Apparent mobility of potassium and chloride ions in soils and clay pastes: *Soil Sci.* **90**, 259–265.
- Rhoades, J. D. and Ingvalson, R. D. (1971) Determining salinity in field soils with soil resistance measurements: *Soil Sci. Soc. Amer. Proc.* **35**, 54–60.
- Rhoades, J. D., Raats, P. A. C., and Prather, R. J. (1976) Effects of liquid phase electrical conductivity, water content, and surface conductivity on bulk soil electrical conductivity: *Soil Sci. Soc. Amer. J.* **40**, 651–655.
- Sauer, M. C., Jr., Southwick, P. E., Spiegler, K. S., and Wylie, M. R. J. (1955) Electrical conductance of porous plugs: ion exchange resin-solution systems: *Ind. Eng. Chem.* **47**, 2187–2193.
- Shainberg, I. and Kemper, W. D. (1966) Electrostatic forces between clay and cations as calculated and inferred from electrical conductivity: in *Clays and Clay Minerals, Proc. 14th Natl. Conf., Berkeley, California, 1965*, S. W. Bailey, ed., Pergamon Press, New York, 117–132.
- Shainberg, I. and Levy, Rachel (1975) Electrical conductivity of Na-montmorillonite suspensions: *Clays & Clay Minerals* **23**, 205–210.
- Shainberg, I., Low, P. F., and Kafkafi, U. (1974) Electrochemistry of sodium-montmorillonite suspension. I. Chemical stability of montmorillonite: *Soil Sci. Soc. Amer. Proc.* **38**, 751–756.
- van Olphen, H. and Waxman, M. H. (1958) Surface conductance of sodium bentonite in water: in *Clays and Clay Minerals, Proc. 5th Natl. Conf., Urbana, Illinois, 1956*, Ada Swineford, ed., Natl. Acad. Sci. Natl. Res. Council. Publ. **566**, Washington, D.C., 61–80.
- Waxman, M. H. and Smits, L. J. M. (1968) Electrical conductivities in oil-bearing shaley sands: *Soc. Petrol. Eng. J.* **243**, 107–122.

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Резюме—Измерялась удельная проводимость, κ_g , Na/Ca-монтмориллонитовых гелей (0,02 и 0,04 г гдины/см³) как функция удельной проводимости межглинных растворов, κ_w . Для низких значений κ_w (меньше 3 мом/см) кривые проводимости были выпуклые относительно κ_w ; при больших значениях они были линейные. Значения κ_w , при которых отклонение от линейности начинало увеличиваться с увеличением содержания натрия, изменялось от 0,7 мом/см для Ca-монтмориллонитового геля до 2,5 мом/см для Na-монтмориллонитового геля. Размер линейной части кривой проводимости увеличивался, а ее наклон уменьшался с увеличивающимся количеством обменного Na.

Экспериментальные результаты были описаны моделью проводимости, состоящей из двух параллельно соединенных элементов: один элемент состоит из двух—твердой и растворимой—фаз, соединенных поочередно, и другой состоит из растворимой фазы. При низких концентрациях электролита первый элемент отвечает за кривизну кривой $\kappa_g - \kappa_w$, в то время как при больших концентрациях электролита второй элемент доминирует и кривая становится линией с наклоном, определенным мобильностью обменного катиона.

Регулируемый параметр в выражении для проводимости для первого элемента, который отвечает за толщину частиц глины, увеличивается с количеством обменного Na и его численное значение указывает на то, что твердая фаза тоже включает диффузионный двойной слой. Мобильность обменного катиона относительно мобильности в воде увеличивается от 4% для Ca до 41% для Na с самым большим увеличением, получающимся в диапазоне 20 и 40% обменного Na. Похожие эффекты для обменного Na были видны на аксиальном соотношении частиц глины, вычисленным по наклонам линейных линий. Эти наблюдения согласуются с ионообменной моделью, в которой начальный обменный Na адсорбируется на внешней поверхности тактоидов Ca-монтмориллонита без изменения мобильности обменного иона или размера тактоида. Следующее добавление обменного Na приводит к адсорбции Na на внутренних поверхностях тактоида и к разрушению тактоида с последующим увеличением мобильности обменного иона вместе с аксиальным соотношением частиц глины. [E.C.]

Resümee—Es wurde die spezifische Leitfähigkeit, κ_g , von Na/Ca-Montmorillonitgelen (0,02 und 0,04 g Ton/cm³) als eine Funktion der spezifischen Leitfähigkeit der Zwischentonlösungen, κ_w , gemessen. Für kleine κ_w -Werte (<3 mmho/cm) waren die Leitfähigkeitskurven in Bezug auf κ_w konvex, behöheren Werten waren sie linear. Der κ_w -Wert, bei dem die Abweichung von der Linearität begann, wuchs mit zunehmendem Na-Gehalt von 0,7 mmho/cm für das Ca-Montmorillonitgel bis 2,5 mmho/cm für das Na-Montmorillonitgel. Mit zunehmendem austauschbarem Na nahm der Achsenabschnitt des linearen Anteils der Leitfähigkeitskurve zu, während ihre Neigung abnahm.

Die experimentellen Ergebnisse wurden durch ein Leitfähigkeitsmodell beschrieben, das zwei parallel verknüpfte Elemente umfaßte: ein Element besteht aus den festen und den flüssigen Phasen, die in Serie geschaltet sind, und das andere Element besteht aus der Lösungsphase. Bei niedrigen Elektrolytkonzentrationen bewirkt das erste Element die Krümmung der κ_g - κ_w -Kurve, während bei höheren Elektrolytkonzentrationen der Einfluß des zweiten Elementes überwiegt und die Kurve linear ist mit einer Neigung, die durch einen Formfaktor bestimmt wird, und der Achsenabschnitt von der Mobilität der austauschbaren Kationen abhängt.

Ein veränderlicher Parameter im Leitfähigkeitsterm für das erste Element, der für die Dicke der Tonteilchen zuständig ist, nahm mit austauschbarem Na zu. Sein numerischer Wert deutet darauf hin, daß die Festphase ebenfalls die diffuse Doppelschicht enthält. Die Mobilität der austauschbaren Kationen relativ zu der im Wasser nahm von 4% für Ca bis 41% für Na zu, wobei die größte Zunahme zwischen 20 und 40% austauschbarem Na auftrat. Ähnliche Effekte von austauschbarem Na zeigten sich bei dem axialen Verhältnis der Tonteilchen, das aus den Neigungen der linearen Kurventeile berechnet wurde. Diese Beobachtungen stimmen mit einem Entmischungsmodell für austauschbare Ionen überein, wobei das ursprünglich austauschbare Natrium an den äußeren Oberflächen von Ca-Montmorillonittaktoiden adsorbiert wird, ohne daß die Mobilität des austauschbaren Ions oder die Taktoidgröße beeinflußt wird. Eine weitere Zugabe von austauschbarem Na führt zu einer Na-adsorption an den inneren Oberflächen des Taktoids und zu einem Zusammenbruch des Taktoids, wodurch die Mobilität des austauschbaren Ions zunimmt und ebenso das axiale Verhältnis der Tonteilchen. [U.W.]

Résumé—La conductivité spécifique κ_g de gels de montmorillonite Na/Ca (0,02 et 0,04 g d'argile/cm³) en fonction de la conductivité spécifique de la solution interargile κ_w a été mesurée. A de basses valeurs de κ_w (<3 mmho/cm), les courbes de conductivité étaient convexes respectivement à κ_w , à de plus hautes valeurs, elles étaient linéaires. La valeur de κ_w à laquelle commençait la déviation de la linéarité augmentait en proportion à l'augmentation de sodium, de 0,7 mmho/cm pour le gel de montmorillonite-Ca à 2,5 mmho/cm pour le gel de montmorillonite-Na. L'intercept de la portion linéaire de la courbe de conductivité a augmenté et son inclinaison a diminué proportionnellement à l'augmentation de Na échangeable.

Les résultats expérimentaux ont été décrits par un modèle de conductance comprenant deux éléments associés en parallèle: un élément consistant des phases solide et solution associés en série, et un autre consistant de la phase solution. A de basses concentrations d'électrolyte, le premier élément rend compte de la forme de la courbe κ_g - κ_w , tandis qu'à de hautes concentrations d'électrolyte, le second élément domine, et la courbe est linéaire avec une inclinaison déterminée par un facteur de formation et un intercept déterminé par la mobilité du cation échangeable.

Un paramètre ajustable dans le terme de conductivité pour le premier élément, qui rend compte de l'épaisseur des particules d'argile, a augmenté proportionnellement au Na échangeable, et sa valeur numérique a indiqué que la phase solide comprend aussi la couche double diffuse. La mobilité du cation échangeable comparé à sa mobilité dans l'eau a augmenté de 4% pour Ca à 41% pour Na, la plus grande augmentation se passant entre 20 et 40% de Na échangeable. Des effets semblables de Na échangeable étaient évidents sur la proportion axiale des particules d'argile calculée à partir des inclinaisons des droites linéaires. Ces observations sont consistantes avec le modèle de démélange d'ion échangeable où le Na échangeable initial est adsorbé sur les surfaces externes des tactoïdes de montmorillonite-Ca sans affecter la mobilité de l'ion échangeable ou la taille tactoïde. Une addition supplémentaire de Na échangeable résulte en l'adsorption de Na sur les surfaces internes du tactoïde et la désintégration du tactoïde accompagné d'une augmentation ultérieure de la mobilité de l'ion échangeable et de la proportion axiale des particules d'argile. [D.J.]