Clays and Clay Minerals, Vol. 25, pp. 39–48. Pergamon Press 1977. Printed in Great Britain

LOW FREQUENCY CONDUCTIVITY DISPERSION IN CLAY–WATER–ELECTROLYTE SYSTEMS

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(*Received* 30 *March* 1976; *and in final form* 25 *August* 1976)

Abstract—The electrical conductivity of a colloid–water–electrolyte system increases with the frequency of the applied alternating electric current. The phenomenon is referred to as conductivity dispersion. This paper reports on the effects of electrolyte type, electrolyte concentration, and water content on the dispersion characteristics of kaolinite, illite, and silty clay soils, with emphasis on the mechanisms governing the dispersion phenomenon. It was observed that magnitude of conductivity dispersion increases with a reduction in water content, electrolyte concentration, and cation-exchange capacity of the clay. The type of ions influence the electrical dispersion through their size and mobility. Frequency effect increases as the hydrated radius of the counterions associated with the clay surface increases. Conductivity dispersion is explained primarily in terms of counterion/co-ion ratio in the diffuse double layer. Increase in the ratio of counterions to co-ions is an indication of a larger contribution to conduction by counterions than by co-ions, which in turn results in a larger frequency effect. Although diffusion coupling has an important role in the electrical dispersion characteristics of clay–water–electrolyte systems, other coupling phenomena, particularly electro-osmotic coupling, plays a significant part.

INTRODUCTION

The electrical parameters of porous materials are useful for characterizing the structure of clay–water–electrolyte systems (Arulanandan 1966; Arulanandan and Mitchell, 1968; Mitchell and Arulanandan, 1968), ionic transport across membranes (Spiegler, 1958), estimation of permeability (Arulanandan, 1969), electrical log interpretation, determination of soil moisture content (Selig and Mansukhani, 1975) and prospecting in geophysical work (Marshall and Madden, 1959). The electrical conductivity of a variety of materials, such as polymers (Juda and McRae, 1953), mineralized rocks (Marshall and Madden, 1959), synthetic membranes (Spiegler and Arulanandan, 1967) and clays (Vacquier *et al.*, 1957; Henkel and Van Nostrand, 1957; Olsen, 1961; Arulanandan, 1966) has been shown to increase with an increase in frequency of the applied electric current. The change in electrical conductivity with frequency is called conductivity dispersion.

Marshall and Madden (1959) claimed that the diffusion coupling and transference properties of the conducting fluid in geophysical materials have a significant effect on the maximum frequency effect. They suggested that there must be different zones of selectivity since otherwise there would be no frequency effect. Schwarz (1962) reported that the counterion density on the surface of the particles is an important parameter in their dispersion characteristics. It was proposed that the low-frequency dispersion of colloidal particles is due to the application of an electric current. It was suggested that the counterions on the surface of the highly charged colloidal particle are strongly bound by electrostatic attraction. They cannot escape from the surface into the free solution except by overcoming a high potential barrier. Since they can be moved along the surface easily, an external field will move them tangentially, polarizing the ion atmosphere and inducing an electric dipole moment of the particle.

Vacquier *et al.* (1957) made measurements on sand particles coated with clay particles. Their data showed that cations had the greatest influence on dispersion whereas anions appeared to have no effect. Schwan *et al.* (1962) made conductance and capacitance measurements on a suspension of polystyrene spheres of colloidal size. They claimed that the magnitude of conductivity dispersion is almost independent of the suspending medium. This finding suggests that the external electrolyte concentration has no effect on the surface conductance of the colloidal systems. There is some evidence suggesting that the magnitude of conductivity dispersion depends on the electrolyte concentration in clay–water–electrolyte systems (Arulanandan, 1966). A systematic study has been carried out to investigate dispersion characteristics of clay–water electrolyte systems with regard to the properties of the medium such as water content, electrolyte concentration, and cation-exchange capacity. This investigation was made to obtain a better understanding of low-frequency conductivity dispersion as affected by the above properties, with emphasis on the mechanisms involved.

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https://doi.org/10.1346/CCMN.1977.0250107 Published online by Cambridge University Press

EXPERIMENTAL INVESTIGATION

Three materials were used: illite (grundite), kaolinite (hydrite R), and a mixture of 50% hydrite R and 50% silica flour (silty clay). Their properties are given in Table 1. The clays were first treated with concentrated solution of NaCl (approximately 1 N) to replace all the ions on the exchange sites. The suspension was then leached with distilled water to remove excess salt before treatments with desired concentrations of NaCl. To prevent hydrolysis and alteration of clay lattices, the suspensions were neither dried nor kept in low external electrolyte concentrations (less than 10^{-3}N). Before the samples were consolidated, vacuum was applied to the slurries to remove air bubbles dissolved in the medium.

The consolidation cells were made of clear Lucite cylinders, 22.86 cm long and inside dia. of 3.56 cm. The base was made of a separate piece with provision for drainage. Figure 1 is a schematic diagram of the consolidation cell. Before the slurry was placed in the cylinder, a porous stone covered with a filter paper was placed on the base. NaCl solution of the same concentration as the pore fluid was first poured into the cell to cover the porous stone and the filter paper. Then the slurry was gradually poured into the cylinder through a funnel to avoid trapping of the air. All the samples, solutions, and the porous stones were under vacuum prior to use in the experiment. The slurry was allowed to consolidate under a small hydraulic head (10 cm water) before any load was applied. Then a filter paper and a porous stone were placed on top of the sample and allowed to consolidate to different water contents.

At the end of each consolidation period the sample was pushed into a smaller cell equipped with platinum electrodes. The sample was held between two flat circular electrodes coated with platinum black. The length of the sample was determined by measuring the distance between the outer ends of the two electrodes. The schematic diagram of the cell and its dimensions are shown in Figure 2. The cell was connected to a "Comparator" Type 1605 AM for impedance and capacitance measurements. At each frequency, the measurements were carried out on two different lengths of the sample. This procedure can eliminate the electrode polarization effects in the low-frequency range (Schwan, 1963). From the measurements of resistance and capacitance of the sample at two different lengths it was possible to calculate the conductivity at each frequency knowing the dimensions of the cell (Mitchell and Arulanandan, 1968). The applied current density in conductivity measurements was less than 1×10^{-3} A/cm^2, which is in the linear range (Cole and Curtis, 1937).

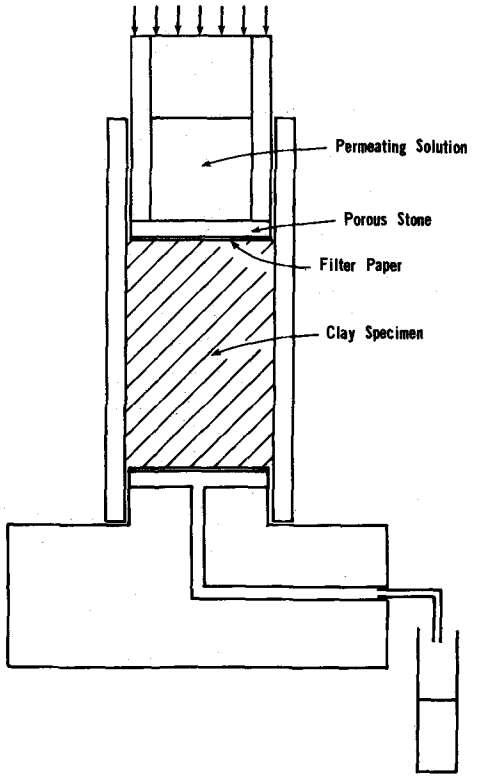


Fig. 1. Schematic diagram of consolidation cell.

RESULTS

Figure 3 is a typical representation of the low-frequency conductivity dispersion in clay–water–electrolyte systems. It shows the data obtained in silty clay soil with pore fluid concentration of 1.35×10^{-3} N NaCl. As the frequency of the alternating electric current increases, so does the electrical conductivity of medium. At both extremes of the low-frequency range

Table 1. Name and properties of the materials

Descriptive name	Mineralogy	Particle size	Cation exchange capacity (meq/100 g)	Specific gravity
Silty clay	50% hydrite R 50% silica flour	< No. 200 Mesh	1.8	2.60
Kaolinite (hydrite R)	100% kaolinite	< 10 μm	3.5	2.60
Illitic clay (grundite)	55% illite* 10% kaolinite 20% quartz 15% mixed layer	< 10 μm separated by fractionation	20.0	2.70

* Based on X-ray diffraction analysis by Esrig (1964).

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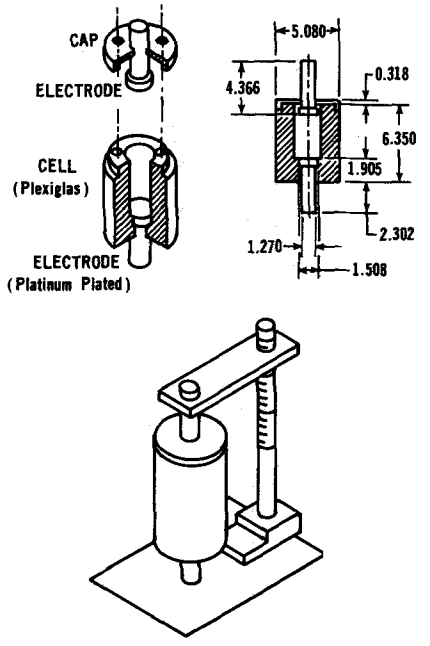


Fig. 2. Schematic representation of cell for low-frequency measurements, cell dimensions are in centimeters.

0 Hz to 10^5–10^6 Hz) the conductivity does not vary ith change in frequency. Electrical conductivity at these respective extremes is called low-frequency conductivity, σ_{dc}, and high frequency conductivity, σ_{ac}. Other regions of dispersion on both sides of the frequency range under investigation are not being considered in the present analysis. The magnitudes of σ_{dc} and σ_{ac} depend on the properties of the particles and the pore fluid. The results of conductivity dispersion in this paper are expressed in terms of either $(\sigma_{ac} - \sigma_{dc})/\sigma_{ac}$ or σ_f/σ_{ac}. The first expression is referred to as the magnitude of conductivity dispersion and the second as the frequency effect. σ_f is the conductivity at frequency f. The summary of the treatments and the results are given in Table 2.

Figure 4 plots conductivity dispersion data for Silty Clay soil in terms of frequency effect. Each curve represents the variation of frequency effect with water content at pore fluid electrolyte concentration of 1.67×10^{-4} N NaCl. It is shown that frequency effect increases as water content decreases.

All of the experiments illustrate a consistent relation between conductivity dispersion and electrolyte concentration of the pore fluid. Figures 5, 6, and 7

Table 2. Magnitude of conductivity dispersion and counterion/co-ion ratio

Ext. elect. conc. (N)	Water content (%)	$1\text{-}\sigma_{dc}/\sigma_{ac}$ (%)	$C^{II}_{Na}/C^{II}_{Cl} = \psi$
	Silty clay 50% hydrite R 50% silica flour		
	56.08	46.0	37,038
1.67×10^{-4}	60.34	38.0	31,894
	61.11	34.5	30,784
	52.00	18.7	659
	53.25	15.8	630
1.35×10^{-3}	56.40	15.0	561
	64.39	5.0	432
	Kaolinite (hydrite R)		
	43.14	47.0	26,019
	48.79	40.0	20,705
5×10^{-4}	53.39	33.0	17,316
	54.81	26.5	13,682
	43.80	35.0	1,602
2×10^{-3}	49.24	27.0	1,269
	51.60	26.5	1,151
	40.82	25.5	76
	43.96	23.5	65
1×10^{-2}	48.78	20.7	53
	55.06	15.2	43
	Illite (grundite)		
	33.00	45.0	1,204,820
	43.00	34.5	701,755
5×10^{-4}	48.72	29.0	460,830
	59.00	23.5	372,440
	41.50	28.8	24.302
	44.50	24.3	21,630
2.75×10^{-3}	51.30	20.1	16,231
	56.60	17.5	13,367
	37.59	25.0	369
	41.12	18.6	310
2.5×10^{-2}	48.81	18.2	218
	55.81	12.8	167
	64.90	11.8	125

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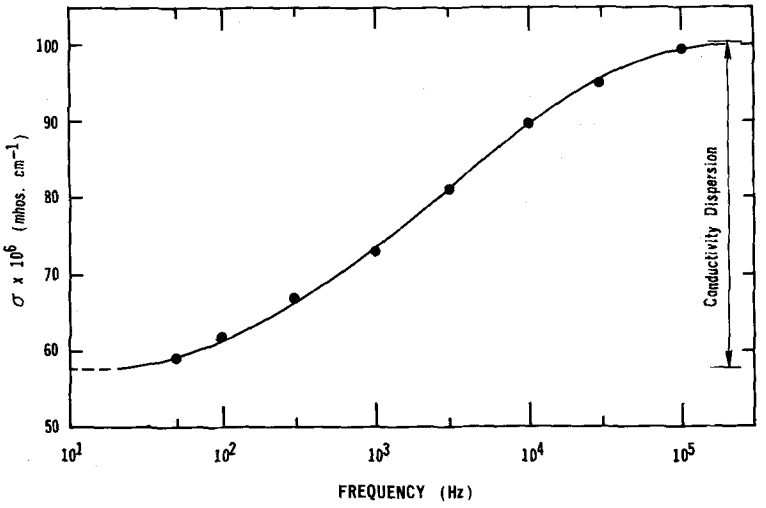


Fig. 3. Low-frequency conductivity dispersion of saturated silty clay soil; pore fluid concentration = 1.35×10^{-3}, water content = 56.4 %.

show that magnitude of conductivity dispersion is higher at lower electrolyte concentrations for all three clay types. This behavior is more pronounced in clays of low cation-exchange capacity (Figure 8).

To study the effect of ion type, consolidated Hydrite R samples were leached with LiCl, NaCl, and KCl solutions to produce a 0.01 N concentration of electrolyte in pore fluid in all three systems (Arulanandan, 1966; Mitchell and Arulanandan, 1968). The effect of counterions on conductivity dispersion is shown in Figure 9. It is clear that frequency effect is largest for Li^+, intermediate for Na^+ and smallest for K^+. The dispersion characteristics of clay–water–electrolyte systems are affected by the mobility and transference properties of the ions associated with the electrolyte.

The data indicate that conductivity dispersion is generally higher in clays of low cation-exchange than in clays of high cation exchange capacity. This behavior was observed consistently at low electrolyte concentrations of the pore fluid. Figure 10 shows the effect of clay type on the magnitude of conductivity dispersion at various water contents for low electrolyte concentrations. The changes in the magnitude of conductivity dispersion becomes less pronounced as cation exchange capacity increases.

DISCUSSION

Interpretation of the results requires the introduction of two parameters: charge density; and counterion/co-ion ratio. Charge density is defined as the

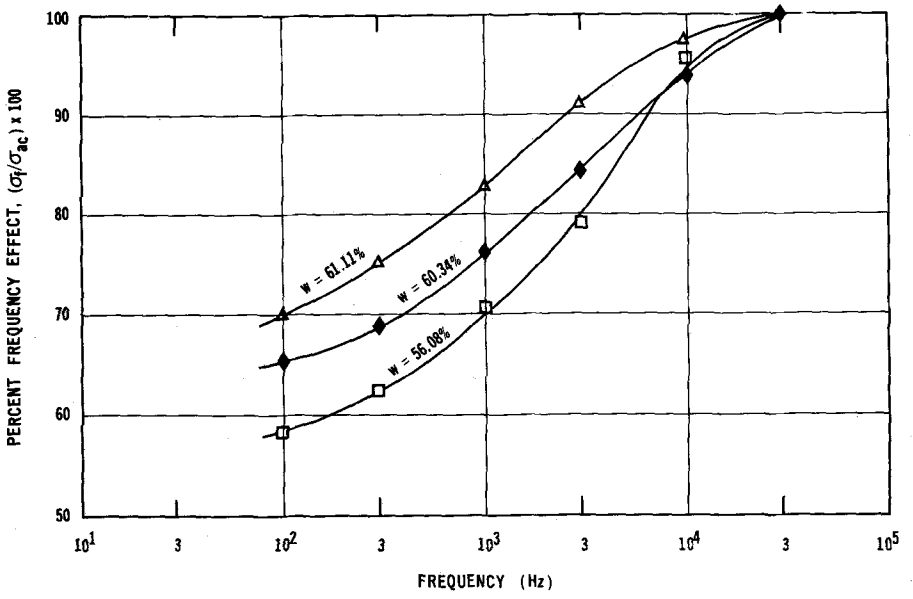


Fig. 4. Frequency effect at different water contents—silty clay, homoionized with Na^+, pore fluid concentration = 1.67×10^{-4} N.

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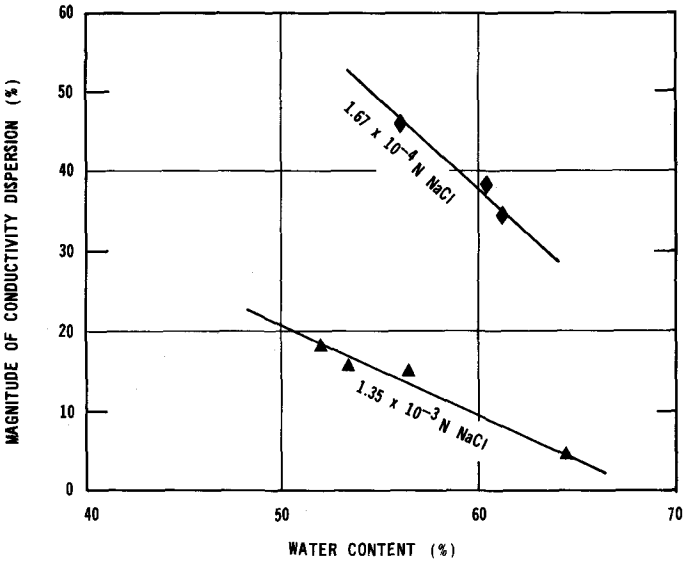


Fig. 5. Magnitude of conductivity dispersion as a function of water content in silty clay soil at different electrolyte concentrations.

molarity of fixed negative charges, expressed as follows:

$$A_0 = \frac{CEC \cdot \rho_w}{w} 100,$$

where CEC = cation-exchange capacity, meq/g soil, ρ_w = density of water, g/cm^3, w = water content, % by weight. The calculation of A_0 is based on the assumption that the effective counterion concentration is determined by considering all the water in the pores rather than adsorbed water (Waxman and Smits, 1968). Counterion/co-ion ratio can be calculated by either diffuse double layer or by application of Donnan theory to clay–water–electrolyte systems. Assuming that clay particles are flat parallel plates, the half spacing between particles can be calculated by the following equation

$$d = \frac{w'}{\gamma_w A_s}$$

where w = % water content, γ_w = unit weight of water (g/cm^3), and A_s = specific surface (cm^2/g). For A_s = 7 m^2/g and w = 56% in silty clay soil, d = 800 Å. According to the double layer theory,

$$\text{double layer thickness} = d_L = \left(\frac{Dk'T}{8\pi n_0 e^2 v^2}\right)^{1/2},$$

where D = dielectric constant, k' = Boltzmann constant (1.38×10^{-16} erg/K), T = temperature (K), n_0 = concentration of external solution (ions/cm^3),

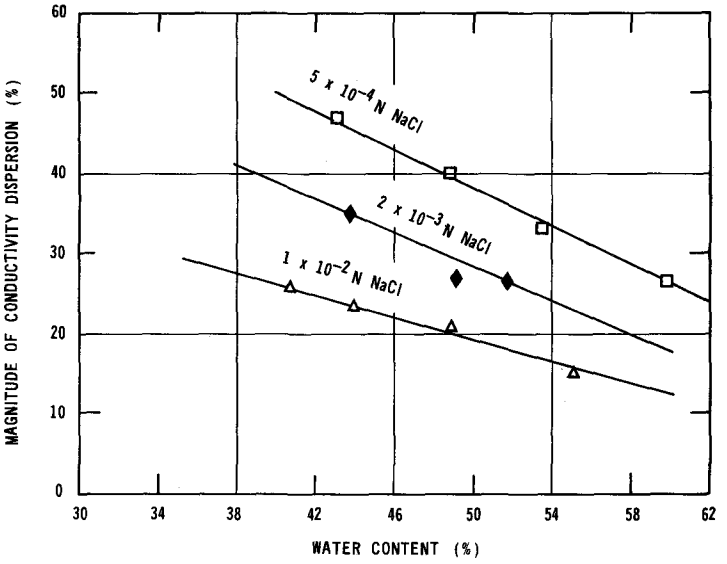


Fig. 6. Magnitude of conductivity dispersion as a function of water content in kaolinite at different electrolyte concentrations.

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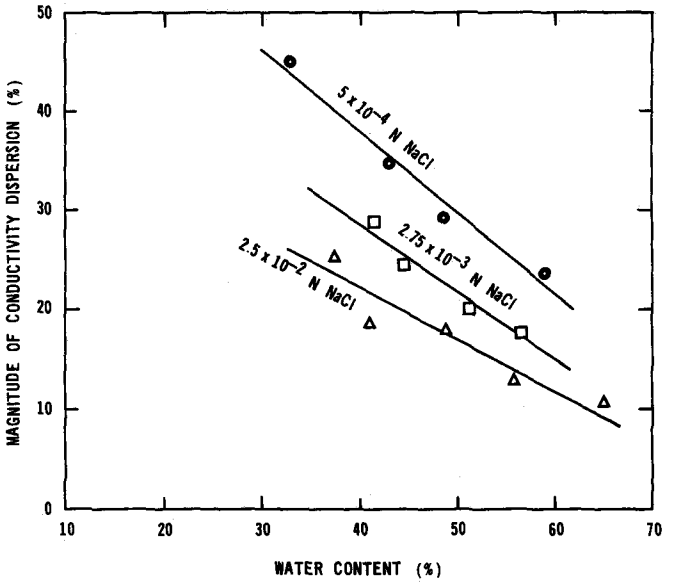


Fig. 7. Magnitude of conductivity dispersion as function of water content in illite at different electrolyte concentrations.

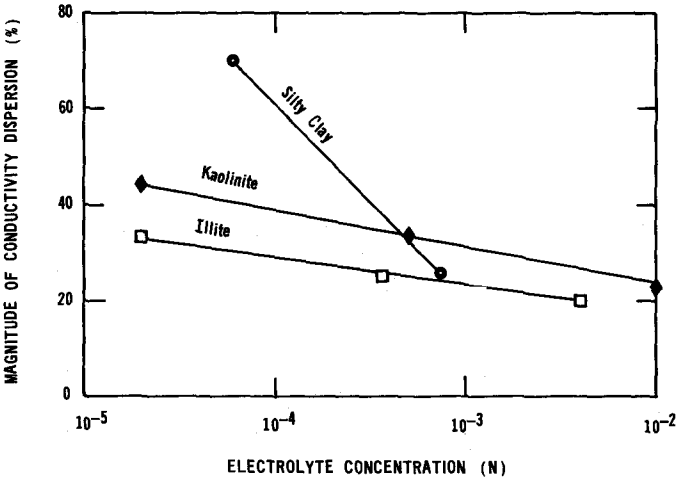


Fig. 8. Magnitude of conductivity dispersion as a function of electrolyte concentration for three clay types, water content = 45 %.

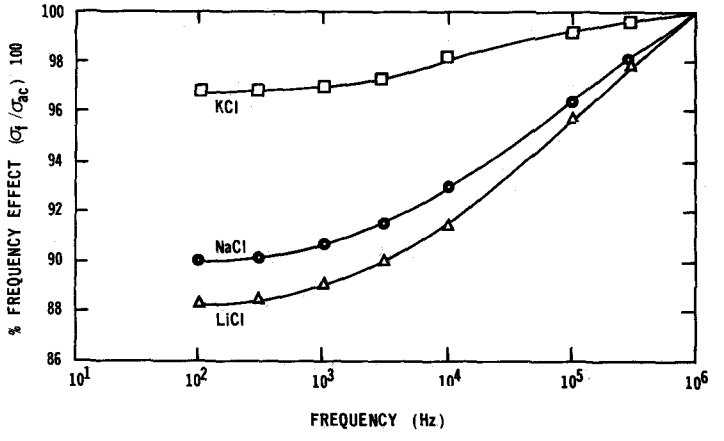


Fig. 9. Effect of electrolyte type on conductivity dispersion of kaolinite pore fluid concentration = 0.01 N.

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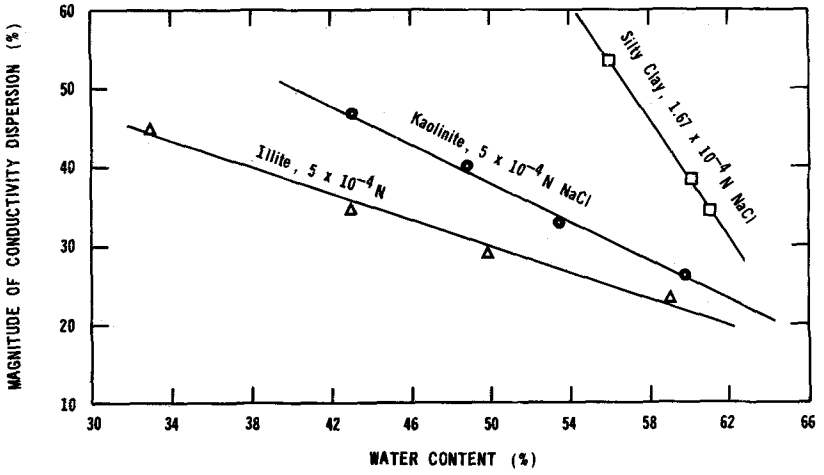


Fig. 10. Effect of clay type on the magnitude of conductivity dispersion at low electrolyte concentrations.

e = unit electronic charge (4.8×10^{-10} e.s.u.), and v = ionic valence. For silty clay soil with $n_0 = 1.67 \times 10^{-4}$ N NaCl at 23°C, the double layer thickness is 238 Å which is much smaller than the half spacing. Therefore, we can compute the counterion/co-ion ratio on the basis of the assumption that there is very little interaction between particles and the case of single diffuse double layer is applicable. According to the double layer theory, the counterion/co-ion ratio for silty clay soil at 238 Å from the particle surface is 16.5 and as we approach the surface the ratio increases, i.e. at 12 Å from the surface the ratio is 32.9×10^5. Since we are only interested in the average counterion/co-ion ratio in the diffuse double layer and not its distribution, application of a macroscopic theory such as Donnan theory appears more useful. According to Donnan theory of clay–water–electrolyte systems (Donnan, 1924; Babcock, 1963; Gray, 1966), the counterion/co-ion ratio can be calculated as follows:

$$\psi = \left[\frac{Na^+}{Cl^-}\right]^n = \frac{1 + \sqrt{1 + z^2}}{1 - \sqrt{1 + z^2}},$$

where

$$z = \frac{2\,C_{NaCl}}{A_0} \cdot \frac{a^{I}_{\pm}}{a^{II}_{\pm}}$$

and ψ = counterion/co-ion ratio, C_{NaCl} = external electrolyte concentration, $a_{\pm}$ = mean activity coefficient, I = external phase (non-selective), II = colloidal phase (selective).

Table 2 illustrates the variation of the magnitude of conductivity dispersion with corresponding values of ψ at different water contents, electrolyte concentrations, and clay types. In the calculation of ψ it has been assumed that the mean activity coefficients are unity (Helfferich, 1962). Comparing the ψ values obtained by the two theories indicate that at $d_{L/6}$ to $d_{L/7}$ from the surface of the clay particle, the counterion/co-ion ratios correspond well.

Reduction in water content, which results in an increase in frequency effect, is associated with an increase in charge density and counterion/co-ion ratio (see Table 2). Since the conductivity of the samples at very low frequencies did not vary to a great extent with changing water content, for the illite and kaolinite soils, the effect of pore geometry is considered to be negligible. However, for the silty clay the pore geometry effect with change in water content may be significant. The preponderance of counterions in the diffuse layer contributes to a higher fraction of conduction in comparison with that of co-ions, and hence a larger frequency effect is observed. It is evident that charge per unit pore volume is an important parameter in electrical dispersion studies. Waxman and Smits (1968) have shown that the same parameter controls the electrical conductivity of oil-bearing shaly sands. Another way of expressing the same phenomenon is the idea of surface conductance. An increase in surface conductance as a result of a decrease in water content will increase the magnitude of conductivity dispersion. Schwarz (1962) has shown that if a nonconductive spherical particle surrounded by an electric double layer is suspended in a conducting medium, application of an electric field will cause counter ion migration in the double layer. The extent of the counterion polarization within the double layer will depend upon the counterion mobility and surface concentration. It was theoretically shown that the higher the double layer charge density, the greater will be the dielectric increment, $\epsilon_0 - \epsilon_\infty$, i.e., the difference between the dielectric constants at very low (ϵ_0) and very high (ϵ_∞) frequencies. Experimental values of the dielectric increment (Arulanandan and Mitchell, 1968) on kaolinite were in the same order of magnitude as Schwarz (1962) model predicts. Therefore, data on dielectric dispersion leads to the same kind of interpretation with regard to the influences of charge density on dispersion characteristics of clay–water–electrolyte systems as in the case of conductivity dispersion.

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Reduction of water content as a result of consolidation not only affects the charge density but also has some effect on mobility of ions and viscosity of pore fluid in the double layer. Shainberg and Kemper (1966) have shown that pushing the clay particles closer together increases the adsorbed ions in the Stern Layer. However, as particles become closer, the interaction effects between the pore fluid and the particle surfaces become more complicated. The viscosity in the vicinity of the particles may vary greatly as a result of reduction in water content which, in turn, may cause mobility of ions to be affected. The above effects may be more significant at much lower water contents than the water contents under consideration. Although the variation of conductivity dispersion with water content is observed in a rather wide range of water content, extrapolation beyond the present experimental investigation would require further study.

The magnitude of conductivity dispersion increases as external electrolyte concentration decreases. This reduction in concentration is associated, again, with an increase in ψ, so the previous reason holds true for the observed phenomenon. Another way of explaining this behavior is to use the concept of co-ion invasion. As concentration increases, a greater number of co-ions and counterions enter into the diffuse double layer, which in turn lowers the counterion/co-ion ratio. Concentration changes not only affect the ratio, ψ, but also influence the mobility of the ions. There is evidence to show that counterion transference number in Na^+ and Li^+ montmorillonite systems decreases as electrolyte concentration increases (Mokady and Low, 1966). This indicates that as a result of increase in electrolyte concentration the cationic and anionic mobilities approach each other (Mokady and Low, 1966; Waxman and Smits, 1968). Thus, at high electrolyte concentrations the transport numbers in the diffuse layer approach those in the external solution, thereby reducing the difference in contribution to conduction from counterions and co-ions. Studies on conductivity spectra in rocks by Fraser *et al.* (1964) have revealed the same effect of concentration on conductivity dispersion. They observed that mineralized cores containing conductivities of less than 7.5×10^{-4} mhos/m yield less dispersion effect as pore electrolyte concentration increases.

Parallel effects of electrolyte concentrations have been observed in measurements of electro-osmotic water transport. Figure 11 shows that electro-osmotic water transport of hydrite R samples decreases as electrolyte concentration of the pore fluid increases. The same results for silty clay and Illite samples are given in Table 3. This behavior also can be explained in terms of the counterion/co-ion ratio. Reduction in ψ as a result of an increase in electrolyte concentration reduces the net flow of cations in the diffuse layer which, in turn, reduces the electro-osmotic water transport. The effect of concentration on the magnitude of conductivity dispersion for silty clay, kaolinite, and illite at 45% water content is shown in Figure 8. The change in dispersion is largest for low cation exchange eapacity material and decreases as cation exchange capacity increases. The same trend is observed in electro-osmotic transport measurements with respect to the variable under consideration (Table 3). At each water content, the difference in electro-osmotic flow as a result of change in concentration is largest for silty clay and smallest for illite.

Further studies on the effect of ion type on electrical dispersion (Arulanandan, 1966) have shown that hydrite R samples treated with KCl, NaCl, and LiCl exhibit different electrical response characteristics (see Figure 9). For monovalent ions, the magnitude of conductivity dispersion increases as hydrated radius increases. Due to electrical interaction between the ions and the clay particles the observed relative mobilities (relative to the external solution) of the counterions is the highest for Li^+, intermediate for Na^+, and lowest for K^+ (Shainberg and Kemper, 1966). It is then

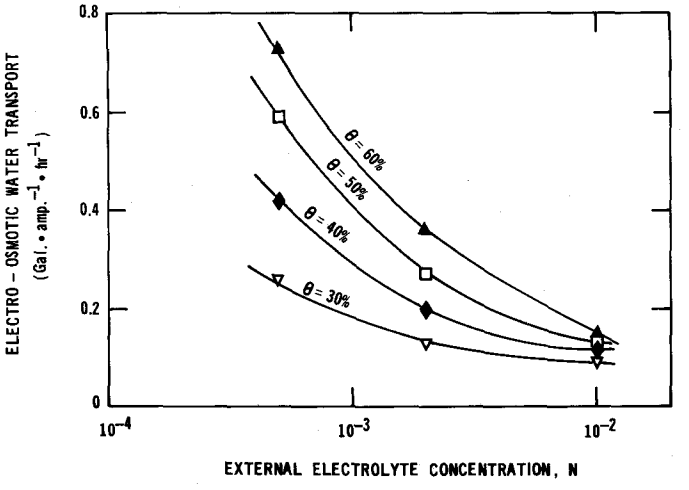


Fig. 11. The relationship between electro-osmotic flow and external electrolyte concentration in hydrite R at different water contents.

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Table 3. Electro-osmotic flow in gal. A^{-1} hr^{-1} at different water contents and electrolyte concentrations in silty clay, hydrite R, and illite

Clay type	Electrolyte concentration (N)	Water content (%) 30	40	50	60
Silty clay	1.67×10^{-4}	0.096	0.147	0.239	0.420
	1.35×10^{-3}	0.084	0.125	0.157	0.307
	1×10^{-2}	0.013	0.018	0.023	0.028
Hydrite R	5×10^{-4}	0.264	0.423	0.590	0.724
	2×10^{-3}	0.134	0.195	0.275	0.365
	1×10^{-2}	0.098	0.118	0.132	0.142
Illite (grundite)	5×10^{-4}	0.030	0.055	0.093	0.128
	2.75×10^{-3}	0.026	0.046	0.066	0.088
	2.5×10^{-2}	0.016	0.025	0.031	0.034

concluded that Li^+ ions are less rigidly bonded to the surface and therefore can move freely along the surface of the particles, producing a larger difference between the transference number of cations and anions and hence a larger frequency effect. Studies on low frequency conductivity dispersion of clay–water–electrolyte systems show that binding tendency of counterions to the negatively charged surfaces affects the dielectric increment. It has been shown that dielectric increment is smaller for K^+ clay and larger for Li^+ clay (Arulanandan and Mitchell, 1968). In light of this investigation and previous data on conductivity and dielectric dispersion, it appears that mobility of counterions in the double layer is one of the controlling factors affecting dispersion characteristics of clay–water–electrolyte systems.

Experimental results showed an increase in cation-exchange capacity causes a reduction in the magnitude of conductivity dispersion (see Figure 10). Due to electrical interaction of pore fluid with the clay particles, the mobility of the ions may be reduced and therefore result in a lower frequency effect. If the cations reside on the surfaces, their will be an energy barrier to overcome in order for the ions to move from one position to another (Shainberg and Kemper, 1966; Schwarz, 1962). Consequently, in high cation exchange capacity clays, the ions are bonded more rigidly to the negatively charged surfaces and hence less frequency effect is observed. Figure 10 shows that variation of conductivity dispersion with water content becomes increasingly less sensitive as cation exchange capacity increases. Electro-osmotic water transport is also affected by a change in cation exchange capacity in the same manner (Table 3). It appears then, that not only counterion/co-ion ratio and mobility of the ions but also the ratio of counterions to water molecules control the dispersion characteristics of clay–water–electrolyte systems. Further data on the effect of ionic mobility on dispersion characteristics is needed to substantiate the results more quantitatively.

In problems of transport phenomena in porous media, defining the mobile and immobile fractions of water and solutes, as they are affected by the soil properties is of interest to scientists. Kirda *et al.* (1973) have shown that in low water content and low electrolyte concentration, the exclusion volume is higher. It is then conceivable that conductivity dispersion data can be useful in interpretation of electrolyte composition of soil extracts and relative flow of solutes and water in soils.

From the present data on low-frequency conductivity dispersion and parallel effects of factors such as electrolyte concentration and cation-exchange capacity on electro-osmotic water transport, it is clear that although diffusion coupling may be the major mechanism for low-frequency conductivity dispersion of clay–water–electrolyte systems, the effect of electro-osmotic coupling can be significant. It is also evident that for a more quantitative treatment, comprehensive research should be conducted in measuring the ionic mobilities and diffusion coefficients along with electrical response characteristics of porous media.

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