ELECTROSTATIC FORCES BETWEEN CLAY AND CATIONS AS CALCULATED AND INFERRED FROM ELECTRICAL CONDUCTIVITY*

by

I. SHAINBERG and W. D. KEMPER

U.S. Department of Agriculture and Colorado State University
Fort Collins, Colorado

ABSTRACT

EQUIVALENT conductivities of adsorbed cations were determined in clays saturated with Na^+, Cs^+, Ca^{++} and with mixtures of these cations. Measurements were also made on Ca^{++} clays which had been forced by previous drying into bundles of platelets or tactoids. The average mobility of adsorbed Ca^{++} and Cs^+ is much lower than that of adsorbed Na^+.

It was concluded that the average mobility of adsorbed Ca^{++} is low because most of this Ca^{++} is on the internal surfaces of tactoids. Ca^{++} adsorbed between these internal surfaces appears to have a mobility much lower than Ca^{++} on the external surfaces which has a mobility of the same order of magnitude as Na^+. Polarization of adsorbed Cs^+ accounts at least partially for its low mobility in these clays.

Demixing of adsorbed cations (segregation with Na^+ dominant between some platelets and Ca^{++} between others) is suggested as an initial step leading to breakup of a Na^+–Ca^{++} clay mass into tactoids. The tactoid model, with Ca^{++} and Na^+ preferentially on the internal and external surfaces respectively, furnishes an explanation of the instability of clay and soil aggregates with 15% exchangeable sodium.

INTRODUCTION

VARIOUS workers in recent years have found that the Gouy–Chapman theory of the diffuse double layer provides useful predictions of the swelling behavior of monovalent-bentonite systems (e.g. Warkentin *et al.*, 1957). This theory involves the assumption of ideal behavior of the ions in the double layer and neglects specific interactions between the ion and the particles, or the ion and the water molecules around it.

The standard theory does not predict differences in the mobility of adsorbed monovalent cations. According to the classic double layer theory the charge on the surface is continuous and uniform and the ions are not localized

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but are free to move parallel to the clay surface in the equipotential plane. The experimental results (van Olphen, 1956, 1957; van Schaik *et al.*, 1965; Gast and East, 1964; Shainberg and Kemper, 1966) indicated that about half of the adsorbed monovalent cations do not participate in the mobility phenomena. To explain this observation "specific forces", of covalent nature, between the ions and the clay particle have been assumed. In the case of small alkali and alkali earth cations, with noble gas structures, no covalent forces are likely. Moreover, no short-range forces between a cation and the surface are possible if a water molecule (water of hydration) exists between the ions and the surface, and it has been generally assumed that adsorbed cations were hydrated.

Calculation of the electrical ion-dipole association energies of the different cations for water and inclusion of this term in the classic diffuse double layer theory (Shainberg and Kemper, 1966*a*) indicated that a fraction of the adsorbed cations reside directly on the clay surface and are not completely hydrated (will not have a water molecule between them and the surface). It was also calculated, (Shainberg and Kemper, 1966*b*) that the ions residing directly on the surface must attain a high activation energy to move from one exchange spot to the other and therefore their mobility is limited. Only the completely hydrated adsorbed cations should have mobilities near the mobilities of these ions in bulk solution.

The portion of adsorbed cations that reside directly on the surface and do not participate in the mobility phenomena, as calculated by Shainberg and Kemper (1966a) is summarized in Table 1. (The calculations for cesium and calcium were made in a similar way to those made for the other ions.)

TABLE 1.—DISTRIBUTION OF ADSORBED CATIONS BETWEEN THE UNHYDRATED AND DIFFUSE (HYDRATED) PORTIONS OF THE DOUBLE LAYER. (NOT ACCOUNTING FOR POLARIZATION ENERGY.)

Adsorbed cation	Pauling radius Å	Fraction of ions unhydrated (Stern layer)	Fraction of ions in the diffuse layer
Li^+	0.60	0.16	0.84
Na^+	0.95	0.36	0.64
K^+	1.33	0.49	0.51
Cs^+	1.68	0.53	0.47
Ca^{++}	0.99	0.37	0.63

In the authors' (1966a) development, several second order factors were omitted after calculating that their effects would be of minor consequence. The result was a simple treatment of ionic distribution due to the electrical energies involved in cation-dipole, cation-clay charge and clay charge-dipole associations as determined by the radius of the cation. Exact theoretical

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evaluation of the accuracy of the resulting equations is not possible. However, indications of their utility and precision may be obtained by comparing their predictions to measurable physical phenomena as is done in this and other papers.

In a previous paper (1966b) the authors found that agreement between the observed equivalent conductivity of adsorbed alkali ions and the equivalent conductivity predicted from the amended diffuse double layer was generally good (except for adsorbed K^+ whose experimental mobile fraction was lower than predicted). In this paper the equivalent conductivities of adsorbed cesium and calcium is studied and discussed as it relates to forces between bentonite particles and mono and divalent ions.

THEORY

The mobilities of exchangeable cations can be determined from electrical conductivities or diffusion experiments. Mobilities obtained in both ways will be compared. The diffusion coefficient D is related to the ionic mobility u by the Nernst Einstein equation

$$D = \frac{uRT}{zF} \tag{1}$$

where R is the molar gas constant, T the absolute temperature, z the ionic valence, and F is the Faraday.

The equivalent conductivity of an ion, Λ, is related to its mobility by the equation

$$\Lambda = Fu \tag{2}$$

The equivalent conductivity is defined by

$$\Lambda = \frac{K}{C} \tag{3}$$

where C is the concentration of the solution (equivalents/c.c.), and K is the specific conductivity measured in bulk solution.

Van Olphen (1957) found that the equivalent conductivities of clay suspensions increased with increasing concentration of clay in the range of concentration between 0.5 to 5.0 gm clay per 100 ml suspension. At higher clay concentrations the equivalent conductivity became constant and was typical of the adsorbed cation. It is assumed that the low equivalent conductivities measured at low clay concentrations resulted from incomplete overlapping of the diffuse double layers of adjacent clay particles. At higher clay concentrations there is enough overlapping so cations can move freely from one particle to another. In clay pastes with more than 10 gm clay per 100 ml of suspension the clay is immobile (van Olphen, 1957, and Low, 1958) and all the electrical charge is transferred by the adsorbed cation. The

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apparent equivalent conductivity Λ_p, in a porous media may be calculated from the equation

$$\Lambda_p = \frac{K_p}{\theta C} \tag{4}$$

where K_p is the measured specific conductivity of the porous media, θ is the volumetric moisture content, and C is the concentration of ions in the pore solution as calculated from equation (5)

$$C = \frac{C^* \times E.C.}{\theta} \tag{5}$$

where C^* is the clay concentration in gm/c.c. of gel, and $E.C.$ is the exchange capacity in equivalent/gm of clay.

The apparent equivalent conductivity in porous media is reduced further by the following factors. The paths in the porous media are tortuous and hence are longer, by the factor L_e/L than the paths through bulk solution. The effective fluidity of water near the clay particle is lower by the factor a_e than the fluidity of water in bulk. The mobility of the ions may be reduced by a factor γ due to electrical interaction with the clay particles.

The effect of these factors on the apparent equivalent conductivity of adsorbed ions was discussed by the authors (1966b) and summarized in the following equation

$$\Lambda_p = (L/L_e)^2 \, a_e \, \gamma \Lambda \tag{6}$$

where Λ is the equivalent conductivity of the ion in bulk solution. Values of a_e were taken from those obtained by Kemper *et al.* (1964) for this clay at similar moisture contents, and similarly a value of 0.67 was assumed for the tortuosity factor.

Values of the electrostatic interaction term were calculated by combining equations (4) and (6).

$$\gamma = \frac{K_p}{\theta C (L/L_e)^2 \, a_e \Lambda} \tag{7}$$

EXPERIMENTAL METHODS

The procedure described by the authors previously (1966b) was followed. The clay fraction of Wyoming bentonite was leached with sodium bicarbonate until the system was saturated with sodium and free of anions other than $(HCO_3)^-$. Then hydrogen resin free of electrolytes was added and the suspension was placed under vacuum to remove the H_2CO_3 formed. Clay suspensions were converted to the calcium and cesium forms by passing dilute suspensions (1%) through columns packed with exchange resins saturated with calcium or cesium respectively. The concentrated gels were prepared by centrifuging the suspensions and decanting the supernatant

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liquid. The conductivities of the gels were measured in cylindrical cells as described by van Olphen (1956). A sample of the centrifuged gel was taken from the centrifuge tube with a glass tube of slightly larger bore than that of the cell. Then the gel was pushed from the glass tube into the cell, avoiding inclusion of air. The gel was restrained between ceramic plates on both sides.

The bi-ionic clay mixtures were prepared by mixing the appropriate amounts of the two homo-ionic suspensions. The mixtures were stirred for about 2 hr to assure equilibrium, then they were centrifuged to obtain concentrations in the range 10–20 gm clay per 100 c.c. gel. During centrifugation of the large volume of dilute suspension, separation of the bi-ionic clay, with tactoids containing higher portions of Ca^{++} settling first, and largely Na^{+} saturated platelets last, was possible. To achieve homogeneity after the supernatant solution had been poured off, the concentrated gel was thoroughly mixed and then centrifuged at low speed for 1 min to remove air bubbles from the gel. The sample was then placed in the cell and conductivity readings were taken as with the homo-ionic gels.

In order to evaluate the effect of drying and rewetting, part of the Ca-bentonite was dried in the oven, then distilled water was added, the suspension was stirred for 1 hr, and the procedure outlined above was used to determine conductivity of the resulting gel.

EXPERIMENTAL RESULTS

Calcium-and Cesium-Clay

The concentration of the clay in the gels (C^*), the specific conductivity of the clay gels (K_p), the electrical interaction factor (γ) for the cesium- and the two types of calcium-clay, and γ values for Li^{+}, Na^{+}, and K^{+} clays obtained by Shainberg and Kemper (1966b) are reported in Table 2. The concentration of adsorbed ions in the pore solution, which is an intermediate step in calculating the apparent equivalent conductivity, was calculated from equation (5) using the value 0.84 meq/gm for the cation exchange capacity. The equivalent conductivities of cesium and calcium ions in bulk solution at 25°C are 77.2 and 59.5 mho cm^2/eq, respectively.

The γ values were calculated from equation (7), using values obtained by Kemper *et al.* (1964) for the tortuosity factor and the effective viscosity. In Kemper's paper the effective viscosity of the water adsorbed on clay when sodium was the dominant cation is reported. To be precise, a correction factor should be included to account for the specific effect of the other ions on the viscosity of water in this study. This correction factor, which would have changed the value of γ by a few per cent, was not included in calculation of the γ values given in Table 2.

Data in Table 2 show no consistent effect of clay concentration on the γ factor in the concentration range studied. This indicates that lack of particle to particle contact was not a factor affecting the ability of adsorbed ions to

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TABLE 2.—ELECTRICAL CONDUCTIVITIES AND ELECTRICAL INTERACTION FACTOR OF Cs^+ AND Ca^{++} IN BENTONITE WATER SYSTEM (THE AVERAGE VALUES FOR THE γ FACTOR FOR THE ALKALI IONS ARE ALSO INCLUDED FOR COMPARISON)

Cation	Clay in gel C^* (gm clay/c.c. gel)	Specific conductivity K_p (mmho cm)	Equivalent conductivity of gel Λ_p mho cm^2 eq^{-1}	Electrical interaction factor γ	Average γ
Cs^+	0.148	0.387	3.08	0.069	0.064
	0.151	0.321	2.53	0.067	
	0.179	0.345	2.32	0.064	
	0.195	0.361	2.19	0.055	
Ca^{++}	0.146	0.321	2.60	0.08	0.95
	0.169	0.485	3.41	0.11	
	0.212	0.640	3.58	0.10	
	0.221	0.524	2.81	0.092	
Ca^{++} (Previously dried)	0.190	0.167	1.04	0.035	0.038
	0.31	0.418	2.03	0.041	
Li^+					0.64
Na^+					0.57
K^+					0.39

transmit electrical current except, perhaps, in the previously dried Ca^{++}-clay).

In the development of the standard double-layer theory, it is assumed that an ion in the diffuse part of the double layer does not interact with discrete surface charge sites. The charge sites are regarded as being so close together that an ion in any plane parallel to the clay surface should not have to surmount any electric barrier in moving from one equilibrium position to another. This was calculated (Shainberg and Kemper, 1966b) to be essentially true for ions moving in planes 4 Å or more above the surface of the clay platelets. But when the cations are in a plane 1 Å from the surface (they do not have a water molecule between the ion and the surface) electrical forces greatly restrict movement of ions within that plane and practically prevent these ions from participating in electrical transport. Consequently, the fraction of the adsorbed ions which is in the diffuse layer (Table 1) should be approximately equal to the measured electrical restriction factors, γ, in Table 2.

Comparing the experimental values (Table 2) with the predicted values (Table 1) for Li^+, Na^+, and K^+ reveals that the agreement is not bad. The authors (1966b) have refined the experimental values in Table 2 by considering the specific effect of the ions on viscosity of salt solution, and by realizing that part of the adsorbed ions have hydrolyzed and were replaced by hydro-

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nium ions with low degree of dissociation, to get the values of 0.76, 0.62, and 0.40 for the γ factor of Li^+, Na^+, and K^+, respectively, which are in reasonably good agreement with the predicted values.

Refinement of the Cs^+ and Ca^{++} data and subsequent calculations might increase the γ factor by as much as 20% of the values in Table 2. This would not be enough increase to reconcile the measured γ factors for Ca^{++} and Cs^+ systems with the fraction of the adsorbed ions which were calculated to be in the diffuse layer.

Similar reductions in the mobility phenomena on Ca-clay have been observed. Kemper *et al.* (1964) found that the mobility of water in Ca-saturated bentonite at low moisture content was much less than the mobility of water in Na-saturated bentonite. Van Schaik *et al.* (1965) found that the mobility of adsorbed Ca ions was even lower than the mobility or fluidity of water in these systems would predict. Van Schaik *et al.* (1965) found that the fraction of adsorbed sodium participating in the mobility phenomena was about 0.70, whereas, for Ca^{++} it was about 0.25. Van Olphen (1957) found values of 0.55 and 0.19 for the γ factor of Na and Ca, respectively. Calculations from data of Gast and East (1963) indicates γ values 0.34, 0.082, and 0.05 for Na^+, Cs^+, and Ca^{++} adsorbed on bentonite, respectively.

Dried Ca^{++} Clay

Some of the electrolyte free calcium bentonite gel was dried in the oven, rewetted by mixing thoroughly with distilled water, centrifuged, and the conductivity of the resulting gel measured. In the centrifugation step, lower speed and shorter time of centrifugation were needed to bring down the calcium clay which had been dried compared to Ca-clay which had not been dried. The specific conductivities of clay gels, saturated with calcium and previously dried, along with the equivalent conductivities of Ca^{++} in the gels and the γ factors are reported in Table 2. The average mobility of adsorbed calcium in gels which were previously dried was less than half the mobility of adsorbed calcium in gels which had not been dried. Related observations were made by Blackmore and Miller (1961) who found that Ca-bentonite swelled appreciably in dilute $CaCl_2$ solutions, but much less than predicted by theory, and to an extent depending on previous compression history. They concluded that drying of a calcium–montmorillonite should minimize subsequent reswelling.

Bi-ionic Systems

The bi-ionic clays were prepared by mixing the appropriate amount of the two clays. The ionic mole fractions Na/(Na + Ca) in the mixtures of sodium and calcium clay were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and in Na–Cs systems Na/(Na + Cs) = 0.1, 0.25, 0.50, 0.75, and 0.90. The conductivity for each of the mole fractions was measured in four concentrations of clays and the average is plotted in Fig. 1. The equivalent conductivities in bulk

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solution of the mixture was taken as the weighted average, e.g. when a mixture of 0.3 part Na with equivalent conductivity of 50.1 ohm^{-1} cm^2 eq^{-1} was mixed with 0.7 part of Cs with equivalent conductivity of 77.2 ohm^{-1} cm^2 eq^{-1} the weighted average of these equivalent conductivities is $50.1 \times 0.3 + 77.2 \times 0.7 = 15.05 + 54.1 = 69.1$ ohm^{-1} cm^2 eq^{-1}. The two straight lines for Cs–Na and Ca–Na system represent the conductivities that would have resulted if there had been no interactions between the ions and clays when the clays were mixed.

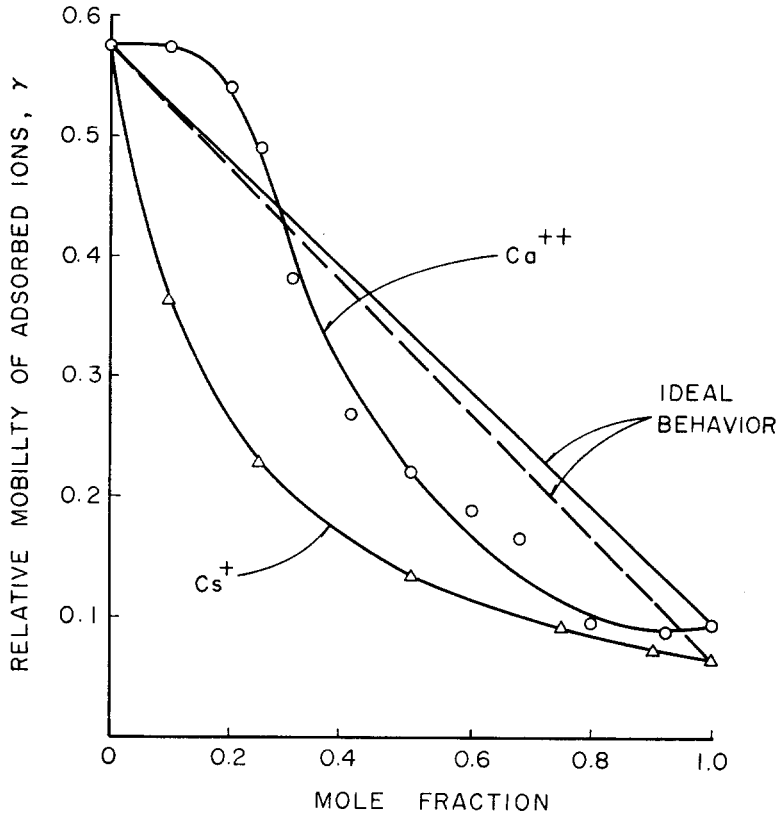


FIG. 1. The electrical interaction factor in bi-ionic systems (Na the complementary ion).

It is obvious from Fig. 1 that (a) there was a strong interaction between the adsorbed ions, and (b) the mechanisms responsible for the reduction in mobility in the Cs and Ca bentonite are different. Up to about 20% calcium on a dominantly sodium bentonite results in no appreciable change in the conductivity and the γ factor, indicating that the fraction of adsorbed

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calcium participating in the electrical transport is essentially the same as of sodium. Cesium showed the opposite trend. Addition of small amounts of Cs-bentonite to Na-bentonite results in a sharp drop in the fraction of adsorbed sodium participating in the mobility phenomena. On the other hand, when small amounts of sodium bentonite were added to calcium or cesium bentonite, the mobility of the sodium ions was apparently reduced.

DISCUSSION

Calcium Systems

X-ray diffraction data obtained by Norrish and Quirk (1954) and Blackmore and Miller (1961) indicate that Ca-bentonite, prepared by exchange resin from the sodium form exists in packets, or "tactoids" averaging about 4.5 platelets each. The indicated number of particles increased irreversibly to about eight as the maximum pressure experienced by a specimen increased to 100 atmospheres. Blackmore and Miller (1961) found that observed swelling pressures of Ca-clays were predicted by diffuse layer theory if they took account of this "condensed" phase and assumed that only the external surface of packets was active in swelling. Van Olphen (1957) came to the same conclusion. He observed that more clay is required to obtain a gel or a certain sediment volume with calcium bentonite than with sodium bentonite. This result was quantitatively interpreted on the basis of a larger average particle thickness in the calcium bentonite suspension. From rheological and sedimentation studies he concluded that there are 3.8–4.0 particles in a packet. It was furthermore concluded that the interparticle forces are of the same order in both calcium- and sodium-bentonite suspensions.

The results of the Ca^{++} mobility experiments can probably be interpreted in terms of tactoid formation. On external surfaces of bentonite particles a good description of the distribution of calcium ions is provided by the diffuse double layer (taking into account hydration energies). The mobility of adsorbed calcium ions on these external surfaces is apparently about the same as of sodium ions (except for specific effects of calcium ions on the viscosity of water). On the other hand, inside the "tactoids"—where there are on the average 1.5 molecular layers of water on each surface, the concentration of the cations is very high, most of the water molecules there are under strong influence of the adsorbed cations (water of hydration of the cation) and this water has a much higher viscosity than bulk water. The greater viscosity between platelets and the probability that interplatelet Ca^{++} is held in more stable position by two exchange spots directly opposite each other on adjacent platelets may greatly reduce the mobility of Ca^{++} within the tactoids as compared to Ca^{++} on external surfaces.

If it is assumed that Ca^{++} on the internal surfaces of the tactoids makes relatively insignificant contributions to the electrical conductivity of the clay, the electrical conductivity should be approximately inversely proportional to the number of clay platelets per tactoid. The Ca^{++} curve in Fig. 1 indicates

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that external surface Ca^{++} ions are essentially as mobile as Na^{++} ions, while the average mobility of Ca^{++} in Ca^{++}-saturated clay is only about one-sixth the mobility of Na^{+} in Na^{+}-clay. These mobility data indicate that the average thickness of the tactoids is about 6 platelets of bentonite, which is in line with the Blackmore and Miller (1961) observations.

It was pointed out by Blackmore and Miller (1961) that the average size of the tactoids depended on the drying history of the sample. In the present study it was found that the γ factor was reduced from 0.10 to about 0.04 by drying the Ca-bentonite in an oven and then redispersing the clay. This indicates that the average number of platelets per tactoids was increased from 6 to 15 by this drying treatment.

Cesium System

Jacobs (1965) conducted time studies of cesium sorption on bentonite and collapsed lattice clay mineral (e.g. illite and biotite). He concluded that on bentonite all the exchange sites are readily accessible since equilibrium with salt solutions was attained within a few minutes of contact. He has also concluded that interlayer fixation of cesium occurred when the cesium was sorbed at basal exchange sites prior to, or coincident with, lattice collapse. On expanding minerals, such as montmorillonite, no fixation of Cs^{+} was observed.

On the other hand, although most adsorbed Cs^{+} on bentonite is available for exchange, the strength of the bonding forces, which can be inferred from exchange equilibrium constants, is very high. For example, the data of Schachtschabel (in Grim, 1953, p. 151) or Jacobs (1965) may be used to calculate the exchange equilibrium constants between Cs^{+} and other alkali ions. It is found that the affinity of bentonite for Cs^{+} is 10 to 20 times the affinity for Na^{+}.

The usual "explanation" for the high affinity of clay for Cs^{+} is that a large cation like cesium is not hydrated and can come very close to the negative charge on the particles. It has been calculated (Shainberg and Kemper 1966b) that if the adsorbed cation resides directly on the surface, it will not participate appreciably in mobility phenomena. Consequently, the high affinity of clay for Cs^{+}, and low fraction of adsorbed Cs^{+}, which is mobile, are related and probably originate from the same mechanism.

Consideration of only electrostatic forces between net charges, upon which the classic diffuse double-layer theory is based, predicts that the various monovalent cations would each be adsorbed with the same strength. In a previous paper the authors have included the energy of interaction between the net charges and the permanent dipole moments of the water molecules in calculating the distribution of adsorbed ions and in determining what fraction of the adsorbed ions is not hydrated. This energy term was sufficient to explain most of the observed differences between Li^{+}, Na^{+}, and K^{+} but fails to explain the high specificity of clay for Cs^{+}, and the low mobility of adsorbed Cs^{+} which was observed in this study. We shall now consider and

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calculate the energies of interaction between ions (the oxygen ions on the surface of the clay) and a dipole induced by them in the adsorbed cations. Theory and equations for polarizability are well developed (e.g. Glasstone, 1959, pp. 534–41) and are outlined briefly for application to the ion-clay system as follows.

The electrons and nuclei in any molecule, atom or ion are to some extent mobile. Consequently, when the molecule is placed in an electric field there will be a small displacement of the electrical centers with the result that a dipole will be induced in the atom. If m is the electrical moment of the induced dipole produced by a field of intensity, F acting on the ion then

$$m = \alpha F \tag{8}$$

where α is the polarizability of the atom. It is proportional to the volume of the molecule, and has the dimensions of volume.

The energy of interaction between an induced dipole m and an electric field F is approximately

$$E_p = \alpha F^2/2 \tag{9}$$

and the intensity of the electrical field formed near the bivalent anion O^{2-} is

$$F = 2e/Dr^2 \tag{10}$$

where e is the electronic charge, D is the dielectric constant, and r is the distance from the center of the oxygen.

NUMERICAL CALCULATIONS

The polarizability of molecules and ions can be calculated from the measured molar refraction R_m, which is related to the polarizability by the equation

$$R_m = 4\pi N\alpha/3 \tag{11}$$

where N is the Avogadro number.

The molar refraction indexes of the alkali metal ions were taken from Glasstone (2nd ed. p 540) and are reported in Table 3 along with the polarizability values calculated from equation (11).

The polarization energy of the adsorbed cations which do not have a water molecule between them and the surface of the clay was calculated from equations (9) and (10) by substituting the sum of the radii of the oxygen and the adsorbed cation for r, and assuming the value of the dielectric constant to be 3.5. This value was arrived at as an average of the dielectric constants for the cation and the oxygen of 2 and 5 respectively, as estimated by Haggis *et al.* (1952) and Howell and Licastro (1961). The polarization energy of cations that have a water molecule between them and the surface is small and was neglected.

The polarization energy reduces the potential energy of adsorbed cations which are not hydrated, relative to those which have a water molecule

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TABLE 3.—MOLAR REFRACTION (R_m), POLARIZABILITY (a) AND POLARIZATION ENERGY (E_p) OF ADSORBED CATIONS

Cation	R_m "gaseous ion"	$a \times 10^{24}$ (cm^3)	$E_p \times 10^{14}$ (ergs/ion)
Li	0.2	0.08	0.9
Na	0.5	0.2	1.2
K	2.1	0.83	2.7
Cs	6.1	2.42	4.9

between the cation and the surface. The results of including the polarization energy in the theory described (Shainberg and Kemper, 1966a) are summarized in Table 4.

TABLE 4.—DISTRIBUTION OF ADSORBED IONS BETWEEN THE "FIXED" AND DIFFUSE LAYER (ACCOUNTING FOR POLARIZATION ENERGY)

	Differences in potential energy between the fixed and hydrated states		Fraction of adsorbed ions which are fixed		
			Calculated		
Ions	Not accounting for polarization (ergs/ion)	Accounting for polarization (ergs/ion)	Not accounting for polarization	Accounting for polarization	Experimental estimates
Li^+	$+ 5.5 \times 10^{-14}$	$+ 4.6 \times 10^{-14}$	0.16	0.18	0.24
Na^+	$- 0.4$	$- 1.6$	0.36	0.40	0.38
K^+	$- 3.4$	$- 6.1$	0.49	0.59	0.60
Cs^+	$- 4.4$	$- 9.3$	0.53	0.73	0.93

The polarization energy term is small for Li^+ and Na^+. This term is appreciable for K^+ and apparently accounts for the discrepancy between previous predictions and experimental data.

The polarization energy causes even greater stability of Cs^+ adsorbed directly on the clay surface. However, it appears that the stabilization caused by polarization does not completely account for the high affinity of the clay for Cs^+.

Bi-ionic Systems

In most of the past considerations of exchange phenomena, and other ion movement, the two ions have been pictured as being randomly mixed

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throughout the exchange complex. This picture is probably correct for Na and Cs systems. But in mixed Na- and Ca-montmorillonite, Mering and Glaeser (in Brown, 1961, p. 180) have shown that "demixing" of the cations occurs so that some interlayer spaces have only Na^+ and others only Ca^{++}. They also showed that in the first stages of substituting Ca^{++} for Na^+ complete mixing occurred. The demixing starts at approximately 30 per cent substitution and is complete at 40 per cent. McAtee (1956 and 1958) and N. T. Coleman (personal communication) have also obtained X-ray diffraction patterns of clay saturated with mixtures of mono- and divalent ions They have inferred from their results that "demixing" occurred. Their systems were equilibrated at 30 to 52 per cent relative humidity. If water were added to such systems, it would seem likely that water would be adsorbed by stronger osmotic forces between the sodium saturated interfaces and that these interfaces would then become external surfaces of tactoids. Calcium ions will reside on the internal surface of the tactoids.

Eriksson (1952) developed an exchange equation for mono and divalent ions from the diffuse double-layer theory. Bolt (1955) had surprisingly good success using Eriksson's equation to describe the adsorption of sodium and calcium ions in clays and soils. Eriksson's equation may be written:

$$\frac{\Gamma_1}{\Gamma} = \frac{r}{\Gamma\sqrt{B}} \sinh^{-1}\left[\frac{\Gamma\sqrt{B}}{r + 4V_d\sqrt{m_2^\circ}}\right] \tag{12}$$

in which

$$r = \frac{m_1^\circ}{\sqrt{m_2^\circ}} \tag{13}$$

is called the "reduced ratio", Γ is the surface charge density in meq/cm^2, Γ_1 is the portion of the surface charge density satisfied by monovalent ions, m_1° and m_2° are the molar concentrations in bulk solution of the mono- and divalent ions respectively,

$$B = \frac{8000\,\pi F^2}{DRT}, \tag{14}$$

where $F = 2.89 \times 10^{11}$ e.s.u./meq, D is the dielectric constant, R the molar gas constant, and T the absolute temperature. For water systems at 25°C, $B = 1.080 \times 10^{15}$ and V_d is defined by

$$V_d = \cosh Y_d \tag{15}$$

where Y_d is the dimensionless potential in the plane midway between the platelets. In most applications of equation (12) the value of V_d is taken as unity. This means $\cosh Y_d = 1$ or $Y_d = 0$, that is the platelets are at infinite distance from each other.

It was pointed out above that in systems containing about 30% Ca, demixing occurs, and the X-ray diffraction pattern shows peaks at 18.8 Å (001), meaning that the dominant spacing between the platelets is about 9 Å.

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In Table 5 the effect of particle collapse on the exchange equilibrium between mono and divalent cations on bentonite, according to the diffuse double-layer theory [equation (12)], is calculated (for two concentrations with reduced ratio, r is equal to 1.0 in both cases).

The calculated affinity for Ca^{++} of the internal surfaces of montmorillonite in a tactoid was 1.5 to 3 times that of the external surface depending on the concentration of the equilibrium solution. Babcock (1963) in arguing the virtues of another model, pointed out that according to Eriksson's equation the exchange ratio should be affected by the concentration of the divalent ion when r is held constant, as may be seen by comparing Γ_1/Γ at the different divalent ion concentrations ($m_2°$) in Table 5. He proceeded to show data in which the exchange ratio did not vary with the divalent ion concentration. It appears that this invariability is a result of the effect of equilibrium concentration on the potential (Y_d) between the "collapsed" clay platelets. Thus, as $m_2°$ increases, Y_d and consequently V_d decrease in the interior of the tactoid. Moreover, V_d increases more than $\sqrt{m_2°}$ decreases, and therefore, Γ_1/Γ increases. This effect in the interior of the tactoid apparently compensates for the opposite effect of concentration on the external surfaces.

TABLE 5.—THE EFFECT OF PARTICLE COLLAPSE ON THE EXCHANGE EQUILIBRIUM BETWEEN MONO AND DIVALENT IONS ON MONTMORILLONITE

Equilibrium solution concentration (molar)		Scaled midpoint potential Y_d*		Fraction of exchange capacity filled by monovalent ions Γ_1/Γ	
Monovalent cations ($m_1°$)	Divalent cations ($m_2°$)	Collapsed (i.e. internal surfaces)	Not collapsed (i.e. external surfaces)	Internal surfaces	External surfaces
10^{-3}	10^{-6}	7.6	0	0.19	0.58
10^{-2}	10^{-4}	4.8	0	0.26	0.55
10^{-1}	10^{-2}	2.0	0	0.33	0.49

* These values were calculated from standard diffuse layer theory using the Tables and equations given by Overbeek in Kruyt (1952) pp. 129 and 251.

The results presented in Fig. 1 may be explained on the basis of the tactoid model. The mobility of Ca^{++} on external surfaces is not appreciably different from the mobility of Na^{+}. Consequently, addition of Ca^{++} to Na^{+}-suspension does not change the γ factor. Addition of calcium in excess of 15 per cent of the total exchange cation results in a decrease in the fraction of ions participating in the electrical transport. This reduction is probably a result of demixing, tactoid formation and the fact that Ca^{++} inside these tactoids has a much lower mobility than Ca^{++} on external surfaces. This tactoid model may also be used to explain the changes in mobility at the higher range of

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Ca^{++}-saturation. When all the clay platelets have been condensed into tactoids, and most of the internal surfaces are satisfied with Ca^{++}, additional substitution of Ca^{++} for Na^{+} ions will be on external surfaces of the tactoids where the mobility of Na^{+} and Ca^{++} is about the same. Consequently, the γ factor would not change appreciably, as was noted in Fig. 1.

Addition of a small amount of Cs-clay to Na-clay reduces the fraction of adsorbed ions participating in the electrical transport considerably. Most of the Cs^{+} added to the system is "fixed" and is not mobile. Moreover, the Cs^{+} which is probably distributed randomly on the clay, increases the average distance between the exchange spots available to mobile Na ions (non Cs-saturated). Increase of this distance causes a marked increase in the energy of activation for movement of the remaining Na ions. This is consistent with the experimental results which show mobilities lower than would be expected if the ions had no effect on each other. This increase in average distance between dissociated exchange spots may also be a factor causing the low mobilities of Cs^{+} in Table 2.

APPLICATION

The deleterious effect of adsorbed sodium on the physical properties of agricultural soils and the favorable effect of calcium are well known. Saline-alkali soils are defined as soils in which the exchange sodium percentage is greater than 15 (U.S. Salinity Lab. Staff, 1954). It is difficult to visualize how sodium ion which constitutes only 15 per cent of the exchange capacity and is randomly distributed could have the ability to reduce the infiltration rate of the soil and to give the poor structure which is typical to alkali soils. However, if "demixing" is assumed the exchangeable sodium picture is altered. Aggregate formation consists of binding tactoids into larger units. The size of a tactoid is 4–15 elementary bentonite platelets, or an "effective radius" of less than 1 micron. The size of a small aggregate is 1 mm. It is the cementation of these packets that will form the aggregates. Most of the adsorbed sodium will be concentrated on the external surfaces of the tactoids which could be almost completely sodium saturated, when 15% of the total exchange capacity is satisfied with Na. Consequently, the repulsion forces between the individual tactoids could easily be strong enough to prevent aggregate formation.

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