SURFACE CONDUCTANCE AND ELECTROKINETIC PROPERTIES OF KAOLINITE BEDS

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Abstract — A technique was developed for forming clay beds of uniform porosity between 48 and 62 per cent. The surface conductance and streaming potential of sodium kaolinite were determined over a range of values. Zeta potential as calculated from the classical formula was about - 30 mV at neutral pH and changed sign at pH 4. The surface conductivity of the sodium clay at various pH values was directly proportional to the zeta potential and from 12 to more than 30 times as large as the calculated electrokinetic surface conductivity. Similar measurements were made on kaolinite in the acid (hydrogen-aluminum) and calcium forms. The acid clay fitted the experimental correlation found for the sodium series, but the calcium clay, with less than one-tenth of the zeta potential of the sodium clay at neutral pH, had half its surface conductance. The results are interpreted as showing that exchangeable ions on kaolinite are mostly in a condensed layer on the surface where the mobility determines surface conductance. The surface mobilities for Na, Ca and H-Al are 20, 8 and 0 per cent of normal, respectively. Apparently hydrogen ion from the solution is very effective in replacing sodium, which exhibits its electrokinetic and conductive properties in proportion to its concentration on the surface.

INTRODUCTION

THE SURFACE conductance of clays and the streaming potentials they generate are important in petroleum production because of their influence on electric logs. The two properties are closely associated, but agreement has not been reached on how far the two can be quantitatively related. Experimental values of the surface conductance of clays and related materials are usually larger than the predictions of the classical theory involving zeta potential (Overbeek, 1952; Street, 1956, 1960; Holmes *et al.*, 1965; James, 1966).

This disagreement with theory has been explained in various ways. Bikerman (1942) suggested that materials such as clays, which are capable of swelling in aqueous media, form a gel layer on the surface that is conductive but electrokinetically inactive. Other theories have suggested mobility of ions in the Stern layer (Urban *et al.*, 1935) and conduction by ionizable surface hydroxyl groups (Holmes *et al.*, 1965). These ideas are not mutually exclusive. It should also be remembered that calculations of zeta potential depend on the dielectric constant and viscosity, which may have abnormal values near the surface; that the compression of double layers in fine pores (e.g., Oldman *et al*, 1963) is often not taken into account; and that the effect of surface conductance on streaming potential in randomly interconnected pores cannot be evaluated precisely (Overbeek and Wijga, 1946). The result of these uncertainites is to make calculated zeta potentials too low, which tends to accentuate the discrepancy between calculated and measured surface conductivities. This error is partly compensated for by the fact that measured surface conductivity values are also too low, since the tortuosity of the pores is usually assumed to be the tortuosity effective for the surface as well.

The present work was designed to study the functional relation between surface conductivity and zeta potential on kaolinite. Measurements made over a range of zeta potential indicate the form of the function, and comparison of this with the theory is more revealing than a comparison of individual values. It is of particular interest to determine whether surface conductance disappears when the zeta potential becomes zero. In this way, information should be gained about the properties of the kaolinite surface.

Rutgers and De Smet (1953), working with glass, and Street (1958), working with an ion exchange resin, varied the zeta potential and found a minimum in surface conductance at the isoelectric point. However, the results were not further analyzed.

EXPERIMENTAL

Preparation of clay beds

The kaolinite used was Peerless No. 2,*a product of R. T. Vanderbilt Co. It was converted by leaching with NaCl, CaCl₂, or HCl to the sodium,

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*Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

calcium, or acid form, and equilibrated at the desired concentration and pH. The equilibrated suspension was centrifuged in small batches to form a paste. After the batches were mixed, the clay was placed in the side chamber, No. 11 in the apparatus shown in Fig. 1. The cell portion (No. 1), made of Plexiglas, was evacuated with an aspirator down to the vapor pressure of water (about 25 mm of mercury). The clay was extruded through a
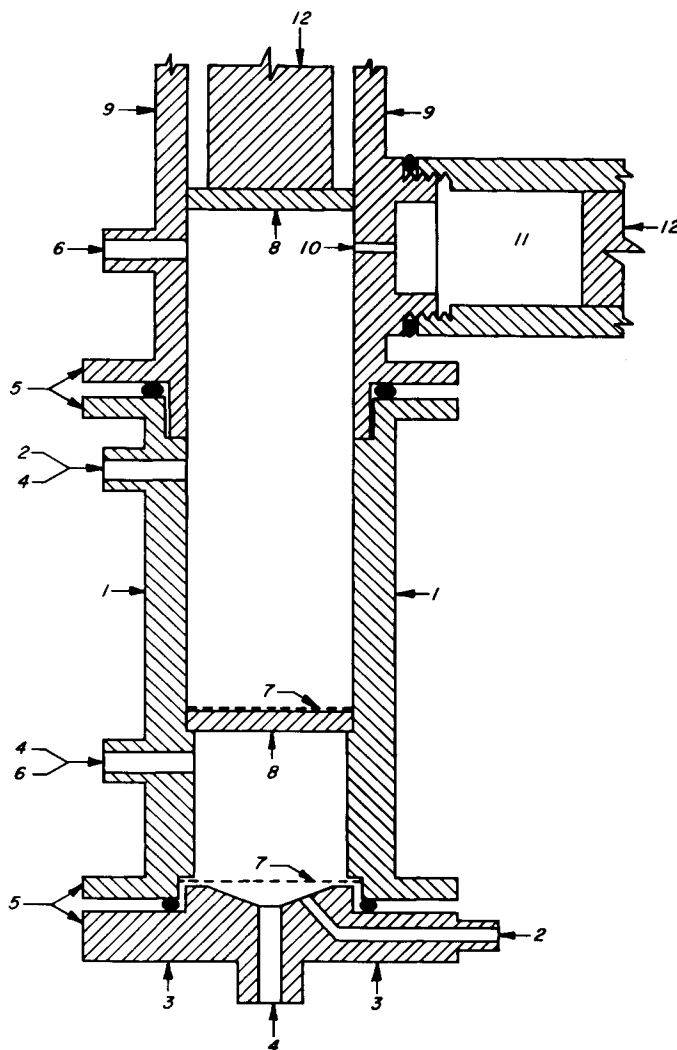

Fig. 1. Schematic section of cylindrical Plexiglas cell and filling apparatus. 1. Measuring cell with lower electrodes in place; 2. Tap for solution access; 3. Lower cap; 4. Tap for electrode lead; 5. Flanges, bolted together and sealed by O-ring; 6. Tap for vacuum; 7. Electrode; 8. Perforated Plexiglas disk (with filter paper); 9. Extrusion attachment. Replaced after extrusion by upper cap and electrode; 10. ⅛″ hole for extrusion; 11. Clay reservoir; 12. Piston, screw-driven (with sliding O-ring seal).

$\frac{1}{8}$ in. hole, No. 10, into the evacuated region. The vertical piston, No. 12, was used to apply just enough pressure to compress the clay into beds free of visible voids. Bed thicknesses varied from 1·2 to 2·4 cm. The cell had cross section of 35 cm². The vacuum was broken by admitting equilibrium solutions. Beds were permeated by several pore volumes of solutions, with a head of about 2 m of water upstream before measurements were made. It is assumed that during the equilibration period (several weeks) the acid clay exchange sites acquired a substantial population of aluminum ions.

Fractional pore volumes ranging from 0·48 to 0·62 were obtained by using different speeds on the centrifuge. With the sodium clay, measurements were made with solutions of NaCl in two series of concentrations, 0·6 and 2·0 meq/1. Within each series the pH was varied between 4 and 11 by substituting HCl or NaOH for part of the NaCl without significantly changing the ionic strength. After measurements on the beds, the solution conductivity and pH values were measured and used to calculate the final actual concentrations of Na⁺, Cl⁻, H⁺, OH⁻, and sometimes HCO_3^-. The calcium clay was measured in equilibrium with $CaCl_2$ at concentration 1·4 meq/1, and the hydrogen-aluminum clay in 0·01 meq/1 of HCl. All measurements were made with the cell maintained at 25·00°C in an oil bath.

Surface area

Fractional pore volume (porosity) and hydraulic permeability were measured for use in calculating surface area from the Kozeny-Carman equation. Permeability was measured by the pressure-decline technique (Dodd et al., 1951) with a maximum pressure of 30 cm of water. Linear uniformity of the beds was tested by slicing the beds into sections and measuring the porosity of the sections. The maximum variation in porosity was only 4 per cent of the overall bed porosity. Therefore, the present technique of preparing the clay beds avoids the pitfall of nonuniform beds, a condition generated when clay is compacted to different porosities with a piston. Separate beds formed from the same clay preparation were identical in porosity, and differed by about 1 per cent in permeability. The standard deviation of the calculated surface areas for samples of sodium clay at the same pH was 7 per cent.

Particle-size distributions were measured with a Coulter Counter on the most dispersed and the most flocculated clay. The peaks of the curves were at 1·5 and 2·5 μ, respectively.

Surface conductance

Conductance (or resistance) was measured by the two-electrode method with a Foy-Martell conductance bridge (Foy and Martell, 1948) and checked by Eastman's (1920) four-electrode method. The current through the bed never exceeded 30 μ-amp/cm².

Silver gauze electrodes, lightly chloridized before each run, were used in all of the experiments. One pair was in contact with the bed (separated from the clay by filter paper). Electrode polarization corrections were obtained after each run by measuring the resistance of the cell filled with a solution of known conductivity.

Measurements were made at eight frequencies between 83 and 500 c/s. As usually observed with such systems, the resistance decreased continuously with increasing frequency. The total spread of values amounted to several per cent of the resistance in many cases. The resistance at zero frequency (R_o) was estimated by extrapolation by use of the impedance function of an analog circuit shown in Fig. 2. The data fitted this function empirically with a standard deviation of 0·3 per cent.

The surface conductance is evaluated from the measured conductance of the bed by a comparison with that expected from the conductivity of the permeant solution. The expected ratio of solution conductivity to bed conductivity was computed from the porosity, ϕ, by means of the empirical expression $1·76 \phi^{-1·17}$ (Winsauer et al., 1952). The constants in this expression were obtained by measurement over the experimental range of porosity on beds permeated by 0·1 N NaCl solutions. At this concentration the surface conductance is negligible. The standard deviation of the data from the expression was 1·6 per cent.

Electrokinetic properties

Figures 3 and 4 show examples of streaming potential and electroosmosis measurements. Figure 3 is a tracing of data plotted directly by an X–Y recorder, with the output of a pressure transducer on the X-axis and the output from electrodes in the cell on the Y-axis. The input impedance of the recorder was 1 $M\Omega$; the beds ranged from 150 to 1200 Ω. Pressure ($\pm$ 20 cm of water) was cali-
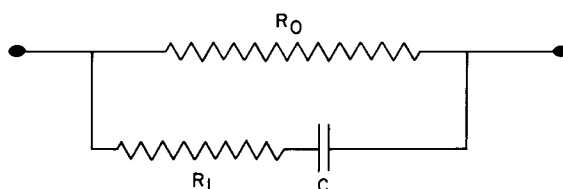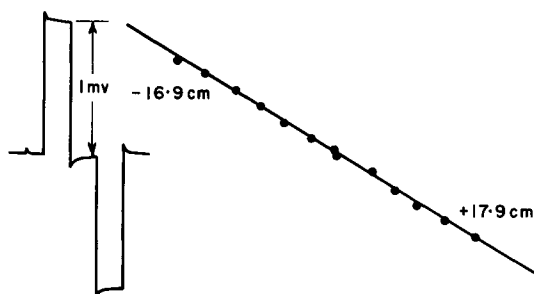

Fig. 2. Circuit analogue for clay bed.

Fig. 3. A streaming potential measurement.

The numerical agreement is within the reproducibility of the two sets of measurements. (The factor of 10^7 occurs because of the use of practical electrical units). Both streaming potential and electroosmosis have the same value for flow in either direction, which is another indication of the uniformity of the beds (Tikhomolova, 1960; Kedem and Katchalsky, 1963).

RESULTS

Surface areas

The area, S_o, in m^2/cm^3 of solid was calculated
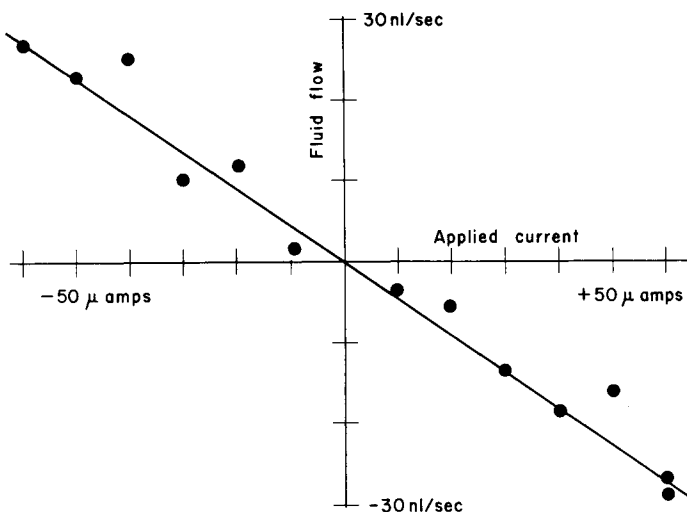

Fig. 4. An Electroosmosis measurement.

brated with a manometer in the line, and potential was calibrated by inserting a 1-mV signal from the potentiometer used to oppose the asymmetry potential of the electrodes.

As a check on the streaming potential, electroosmosis was measured on one bed with positive streaming potential and on another with negative. The rate of pressure-decline due to flow under a head of a few centimeters of water was observed in a vertical precision bore tube of inner diameter 0·2007 cm. The change in rate on application of a constant current was used to calculate electroosmosis. The results are compared with the streaming potential in Table 1.

Table 1. Electroosmosis and streaming potential

pH	Electro-osmosis (cm³sec⁻¹amp⁻¹)	Streaming potential volt · dyne⁻¹cm² × 10⁷
3·5	−0·22	−0·24
5	0·462	0·473

from the Kozeny-Carman equation in the form

$$S_o = [\phi/(1 - \phi)] \sqrt{(\phi/5 \cdot 00\, k)} \times 10^4$$

where k is the specific permeability in cm^2. Values ranged from 35 for the bed in the most basic solution to 20 in the most acid solution. The value for the hydrogen-aluminum clay was 21. Thus, flocculation in the acid solution reduced the surface effective in flow by 40 per cent. This corresponds with the particle sizes reported above which showed an equivalent increase. As shown in Fig. 5, there is a small variation with porosity, somewhat less than that found on beds compacted with a piston (Michaels and Lin, 1954; Ballou, 1955).

The Kozeny-Carman values of surface area were used to calculate surface conductivity. They were considered to be more representative of the areas in an aqueous medium than Brunauer-Emmett-Teller (B.E.T.) values from nitrogen adsorption, which are about 30 per cent higher and show little variation with ionic type (Johansen and Dunning, 1959; Keenan, Mooney, and Wood, 1951).
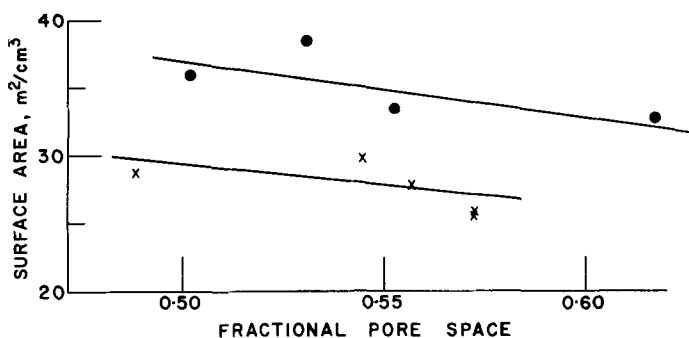
Fig. 5. S_o vs. ϕ: ● pH 11; × pH 6.

Zeta potentials

The electrokinetic properties of clay samples prepared in different ways were compared by converting streaming potentials, E_p, to "zeta potentials" as calculated from the classical Helmholtz-Smoluchowski expression $4\pi E_p \eta \kappa'/\epsilon$, where η is viscosity, ϵ is dielectric constant of the solutions, and κ' is the effective conductivity within the pores. The latter was calculated from $1.76\phi^{-1.17}L/RA$, where L is bed thickness, and A its cross sectional area. As discussed earlier, such "zeta potentials" are probably somewhat lower than the real zeta potential of the surface. In fact, it was expected that values calculated in this way would show a variation with porosity, since the mean hydraulic radius, $S_o(1-\phi)/\phi$, ranged from 0·033 to 0·071 μ, and its ratio to the Debye-Hückel radius ("double-layer thickness") ranged from 2·4 to 7·4 for the sodium clay. No such variation in "zeta potentials" was observed as long as pH was constant. In view of this, it did not seem appropriate to apply radius corrections.

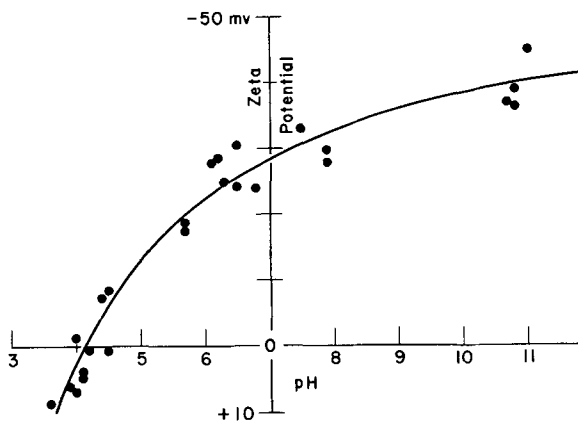The results were little affected by concentration

Fig. 6. Zeta potential of sodium kaolinite.

in this range, in agreement with the measurements of ζ on the same clay by the Cornell University Project (1951). Consequently, all the data for the sodium clay are plotted together in Fig. 6. The standard deviation of points from the curve is 3·6 mV. The value at pH 7 agrees with several published values of ζ for this kaolinite, based on streaming potential (M.I.T., 1953), electroosmosis (Michaels and Lin, 1955), and electrophoresis (Cornell University, 1951). It was indeed lower than some reported values (Ballou, 1955; Street and Buchanan, 1956), but such differences can easily be caused by differences in the conditions of preparation. Thus, there is considerable variation in the reported pH for the isoelectric point of kaolinite (e.g., Street and Buchanan, 1956; Smith and Narimatsu, 1967), which cannot be attributed to any particular assumptions in calculation. It is therefore believed that the "zeta potentials" reported here represent the true values within a factor of 3 or 4.

Surface conductivity

Street's (1956) formula for surface conductivity applied to the present system becomes

$$\kappa_s = (1.76 \, \phi^{-1.17}L/AR - \kappa) \sqrt{(5k/\phi)}$$

where κ is the conductivity of the solution outside the pores. As previously mentioned, this formula gives an underestimate of κ_s. Like ζ, the experimental value of κ_s was not significantly different at the two concentrations. The results on the sodium clay (solid circles in Fig. 7) indicate a linear relation between zeta potential and surface conductance. There is no residual surface conductance at the isoelectric point: the least-squares line passes within a distance less than 0·1 standard deviation from the origin. It was thought that the linear proportionality between κ_s and ζ might be spurious due to the influence of surface conductance on the calculation of zeta potentials from

streaming potentials. The correction implied in the use of κ' is not strictly correct in porous media (Overbeek and Wijga, 1946). Therefore, a test was made with the equation of Ghosh et al. (1954),

$$\zeta_t = \zeta_a(1 + B\mu_s/a\mu).$$

When the mean hydraulic radius was used for a, the values of the empirical geometrical factor B. necessary to convert apparent values ζ_a to theoretical values ζ_t, varied from 0·8 to 30, changing regularly with pH (but not with porosity). This would be inconsistent with the results on particle size and surface area. It is therefore believed that the linearity of Fig. 7 is real.

The open circle represents three determinations with a hydrogen-aluminum clay. It deviates from the line by only 0·5 standard deviation, and thus conforms with the low-pH values for the sodium form. The triangles, for calcium clay, are spaced about five standard deviations above the sodium-clay line. Probably this clay does have a residual surface conductance when the zeta potential is zero.

For comparison, a plot is included of κ_s calculated for 2 meq/l NaCl from the formula based on the Gouy theory, which for mixed electrolytes takes the form

$$10^9\kappa_s = 0·2653 \sqrt{c} \sinh^2 (\zeta/100)$$
$$+ (1·922 \times 10^{-3}/\sqrt{c}) \Sigma_i c_i u_i (e^{-z_i\zeta/50} - 1)$$

where c is total ionic concentration, c_i is the concentration of the i ion, in meq/l, u_i is the ionic mobility in cm²volt⁻¹sec⁻¹, and z_i is the algebraic value of the valence.

DISCUSSION

In Fig. 7 it is seen that the surface conductance of a "sodium" clay decreases linearly with zeta potential as the acidity is increased. The significant fact is that the behavior approaches that of the purely acid clay. This observation suggests that there is a changing composition of the surface ion population, from an all-sodium surface with relatively high electrokinetic activity and surface conductance, to hydrogen-aluminum, with almost none.

The linear trend of the data in Fig. 7 does not bear out the theoretical prediction of an exponential relation. Another evidence of nonclassical behavior is the results on calcium clay. They show about half the surface conductance but less than one-tenth the zeta potential of neutral sodium clay. Consequently, surface conductance is dependent on factors other than the variables c, ζ, and u_i of the theoretical equation.

The factor by which the experimental results exceed the theoretical varies from 12 for a basic sodium clay to more than 30 for an acid clay, and is even higher for the calcium clay. It is implausible that a discrepancy of this magnitude could be attributed to oversimplified calculations of zeta potential and surface conductance, especially as the two quantities are altered in the same direction by the approximations.

It is therefore evident in several ways that there is a mechanism for surface conductance that is not included in the classical theory. The nonconductive nature of the surface of the H-Al clay favors a surface hydroxyl theory over the idea of a conductive surface gel. While there may be such a physical structure, it cannot be considered as a
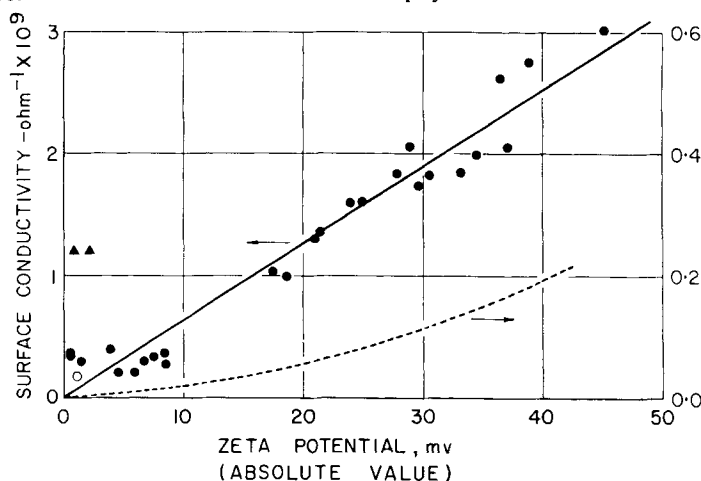

Fig. 7. κ_s vs. ζ for kaolinite: ● sodium form; ○ hydrogen-aluminum form; △ calcium form; ——— least squares line for sodium; ——— theoretical for sodium (chloride).

parallel path independent of the electrokinetic properties. It seems more fitting to speak simply of a condensed layer. Table 2 illustrates the distribution and mobility of ions on the surface of kaolinite, as calculated from Stern's model. Both the model and the data are approximations, but the calculations are of qualitative interest. Even for the sodium clay, most of the exchangeable ions are in a condensed layer; in the model only about 1 per cent are set in motion by the streaming of the liquid. The calculated adsorption potential is

Apart from the effect of continuous changes in surface composition, there is no direct correlation of surface conductivity of kaolinite with the zeta potential. The zeta potential regulates the mobile part of the double layer. The surface conductance is dominated by the condensed part of the double layer and the mobility of the ions there. Table 2 illustrates that these factors are independent. The surface conductance is therefore dependent on specific properties of the ions and not on the simple existence of a zeta potential.

Table 2. Calculations on homoionic kaolinites

	Sodium in 0·6 meq/1 NaCl	Calcium in 1·4 meq/1 CaCl₂
Cation exchange capacity, meq/l	3·1	3·1
Surface area, m²/g	13	9·3
Total surface charge density,* μC/cm²	23	
ion/unit cell area	0·66	
Zeta potential, mV	36	1
Ratio, (mobile/total) surface charge density	0·006	0·0005
Stern adsorption potential,† ev	0·23	0·24
Cation mobility on surface, ohm⁻¹cm²equiv⁻¹	9	4·6

*Calculated from exchange capacity and surface area for dispersed sodium clay and assumed to be the same for calcium clay.
†Based on 2 exchange site/unit cell area.

rather large, and the mobility of the adsorbed sodium ions is about 20 per cent of its normal value. For the calcium ions, the figure is about 8 per cent of normal.

Previous work has indicated that calcium is less mobile than sodium on the surface of montmorillonite (Van Olphen, 1957), and that sodium is somewhat less mobile on kaolinite than on montmorillonite (Cremers and Laudelot, 1966). The present work confirms the low mobility on kaolinite and shows that calcium is less mobile than sodium in this case too. Aluminum is not mobile at all, and the decrease of both conduction and electrokinetic effects in the order Na, Ca, Al is no doubt partly a valence effect.

The hydrogen does not fall into this valence sequence. In fact, it is unique in several ways, such as its influence on cation exchange capacity, and its role in the development of positive edge charges in competition with negative face charges. It also has a very high replacing power. In the experiments described above, the process of replacement of Na was virtually complete at pH 3·8, where the H : Na ratio was 1 : 2 for the dilute series and only 1 : 10 for the concentrated. Thus the low mobility and electrokinetic activity of hydrogen on kaolinite must be due to the nature of the bond to the surface rather than to a steric blocking by aluminum.

REFERENCES

Ballou, E. Vernon (1955) Electroosmotic flow in homoionic kaolinite: *J. Colloid Sci.* 10, 450–460.

Bikerman, J. J. (1942) Electrokinetic equations from gels and the absolute magnitude of electrokinetic potentials: *J. Phys. Chem.* 46, 724–730.

Cornell University (1951) Fundamental Properties, Clay–Water Systems: Soil Solidification Research, Final Report, Vol. II.

Cremers, A. E., and Laudelot, H. (1966) Surface mobilities of cations in clays: *Proc. Soil Sci. Soc. Am.* 30, 570–576.

Dodd, Charles G., Davis, James W., and Pidgeon, Frances D. (1951) Measurement of specific surface areas of nonporous powders by a pressure-decline liquid-permeability method: *J. Phys. Chem.* 55, 684–698.

Eastman, E. D. (1920) Conductivity and frequency: *J. Am. Chem. Soc.* 42, 1648–1655.

Foy, Walter L. and Martell, Arthur E. (1948) An improved conductance bridge: *Rev. Sci. Instrum.* 19, 628–632.

Ghosh, B. N., Choudbury, B. K., and De, P. K. (1954) Evaluation of true zeta potential of the particles of glass forming a diaphragm from measurements of

streaming potential: *Trans. Faraday Soc.* **50**, 955–958.

Holmes, H. F., Shoup, Charles S., Jr., and Secoy, C. H. (1965) Electrokinetic phenomena at the thorium oxide-aqueous solution interface: *J. Phys. Chem.* **69**, 3148–3155.

James, S. D. (1966) Electrochemistry of the interface between some aluminosilicate crystals and salt solutions. I. Surface conductivity: *J. Phys. Chem.* **70**, 3447–3454.

Johansen, Robert T., and Dunning, H. N. (1959) Water-vapor adsorption on clays: *Clays and Clay Minerals* **6**, 249–278.

Kedem, O., and Katchalsky, A., (1963) Permeability of composite membranes. Part 3. Series array of elements: *Trans. Faraday Soc.* **59**, 1941–1953.

Keenan, A. G., Mooney, R. W., and Wood, L. A. (1951) The relation between exchangeable ions and water adsorption on kaolinite: *J. Phys. Chem.* **55**, 1462–1474.

Michaels, Alan S., and Lin, C. S. (1954) Permeability of kaolinite: *Ind. Eng. Chem.* **46**, 1239–1246.

Michaels, A. S. and Lin, C. S. (1955) Effects of counter-electroosmosis and sodium ion exchange on permeability of kaolinite: *Ind. Eng. Chem.* **47**, 1249–1253.

M.I. T., Soil Stabilization Lab. Rep. VI, October 1953.

Oldham, I. B., Young, F. J., and Osterle, J. F. (1963) Streaming potential in small capillaries: *J. Colloid Sci.* **18**, 328–336.

Overbeek, J. Th. G. (1952) In H. R. Kruyt (Editor) *Colloid Science*, Vol. I., p. 235. Elsevier, Amsterdam.

Overbeek, J. Th. G., and Wijga, P. W. O. (1946) On electro-osmosis and streaming-potentials in diaphragms: *Rec. Trav. Chim.* **65**, 556-563.

Rutgers, A. J., and De Smet, M. (1953) *Nat. Bur. Std. Circular* 524, p. 263.

Smith, R. W., and Narimatsu, Y. (1967): *Mining Engr.* **19**, 34 (abstr.).

Street, N. (1956) The rheology of kaolinite suspensions: *Australian J. Chem.* **9**, 467–479.

Street, N., and Buchanan, A. S. (1958) The ζ-potential of kaolinite particles: *Australian J. Chem.* **9**, 450–466.

Street, Norman, J. (1958) Surface conductivity of an anion-exchange resin: *J. Phys. Chem.* **62**, 889–890.

Street, Norman J. (1960) Surface conductance of suspended particles: *J. Phys. Chem.* **64**, 173–174.

Tikhomolova, K. P., (1960) Electroosmosis and streaming potential on two-layer powder membranes: *Vestn. Leningr. Univ.* **15**, no. 4. *Ser. Fiz. i Khim.* no. 1, 106–116.

Urban, Frank, White, H. L., and Stassner, E. A. (1935) Contribution to the theory of surface conductivity at solid–liquid interfaces: *J. Phys. Chem.* **39**, 311–330.

Van Olphen, H. (1957) Surface conductance of various ion forms of bentonite in water and the electrical double layer: *J. Phys. Chem.* **61**, 1276–1280.

Winsauer, W. A., Shearin, H. M., Jr., Masson, P. H., and Williams, M. (1952) Resistivity of brine-saturated sands in relation to pore geometry: *Bull. Am. Assoc. Petrol. Geol.* **36**, 253–277.

Résumé – On a développé une technique pour former des couches d'argile de porosité uniforme, entre 48 et 62%. La conductance en surface et le potentiel d'écoulement de kaolinite au sodium ont été déterminés pour toute une gamme de valeurs. Le potentiel zéta, calculé d'après la formule classique, était d'environ − 30 mV pour pH neutre et changeait de signe pour pH 4. La conductivité en surface de l'argile de sodium à différentes valeurs de pH était directement proportionnelle au potentiel zéta et de 12 à plus de 30 fois aussi grandes que la conductivité en surface calculée par l'électrocinétique. Des mesures similaires ont été faites sur le kaolinite sous les formes d'acide (hydrogène-aluminium) et de calcium. L'argile acide correspondait exactement à la corrélation expérimentale trouvée pour la série sodium, mais la conductivité de surface de l'argile de calcium, avec moins d'un dizième du potentiel zéta de l'argile de sodium au pH neutre, était inférieure de moitié. L'interprétation des résultats montre que les ions d'échange du kaolinite se trouvent surtout dans une couche condensée de la surface où la mobilité détermine la conductivité. Les mobilités de surface pour Na, Ca, et H-Al sont respectivement de 20%, 8% et 0% de la normale. Apparemment, l'ion d'hydrogène de la solution est très efficace dans le remplacement du sodium, qui expose ses propriétés électrocinétiques et de conductivité par rapport à sa concentration en surface.

Kurzreferat – Es wurde eine Methode zur Bildung von Tonbetten gleichförmiger Porosität zwischen 48 und 62% entwickelt. Die Oberflächenleitung und das Strömungspotential von Natriumkaolinit wurden über einen weiten Bereich von Werten bestimmt. Das nach der herkömmlichen Formel berechnete Zetapotential war circa − 30 mV bei neutralem pH und wechselte Vorzeichen bei pH 4. Die Oberflächenleitung des Natriumtones bei verschiedenen pH Werten war dem Zetapotential direkt proportional and 12 bis mehr als 30 mal grösser als die berechnete elektrokinetische Oberflächenleitfähigkeit. Es wurden änliche Messungen an Kaolinit in der sauren (Wasserstoff–Aluminium) und Calciumform durchgeführt. Der saure Ton stimmte mit der für die Natriumserie gefundenen experimentellen Korrelation überein, der Calciumton dagegen, mit weniger als einem Zehntel des Zetapotentials des Natriumtones bei neutralem pH, wieshalb die Oberflächenleitfähigkeit desselben auf. Die Ergebnisse werden dahingehend ausgedeutet, dass austauschbare Ionen am Kaolinit meist in einer verdichteten Schicht an der Oberfläche sind, wo die Beweglichkeit die Oberflächenleitung bestimmt. Die Oberflächenbeweglichkeiten für Na, Ca und H-Al sind 20%, bzw, 8% und 0% des Normalwertes. Wasserstoffion aus der Lösung ist scheinbar sehr wirksam im Ersatz von Natrium, das seine elektrokinetischen und Leitfähigkeitseigenschaften im Verhältnis zu seiner Konzentration an der Oberfläche zum Ausdruck bringt.

Резюме—Разработана методика получения глинистых препаратов в виде слоев с однородной пористостью от 48 до 62%. Поверхностная проводимость и потенциал течения натриевого каолинита определялись в широких пределах их значений. Дзета-потенциал, вычисленный по классической формуле, составлял около– 30 *mv* при нейтральном значении pH и менял знак при pH 4. Поверхностная электропроводность натриевой глины при разных значениях pH была прямо пропорциональна дзета-потенциалу и превышала в 12–30 раз и более вычисленную электрокинетическую поверхностную электропроводность.

Аналогичные измерения были сделаны для кислой (водородно-алюминиевой) и кальциевой форм каолинита. Данные для кислой глины согласуются с экспериментальным соотношением, установленным для натриевых форм, но кальциевый каолинит, дзета-потенциал которого составлял менее чем 0,1 величины дзета-потенциала натриевой глины при нейтральном значении pH, обладает только половиной его поверхностной проводимости. По результатам экспериментов сделан вывод, что обменные ионы в каолините в основном находятся в конденсированном слое на поверхности, где их подвижность определяет поверхностную проводимость. Подвижности Na, Ca и H–Al поверхностного слоя соответственно составляют 20%, 8% и 0% от нормальной. Очевидно, ион водорода раствора очень эффективно замещает натрий, который обнаруживает электрокинетические свойства и свойство проводимости пропорционально его концентрации на поверхности.