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ELECTRICAL CONDUCTIVITY AND THE SURFACE CHARACTERISTICS OF KAOLINITIC CLAYS AND CLAY–HUMIC ACID COMPLEXES

N. C. LOCKHART

CSIRO Institute of Earth Resources, Physical Technology Unit, 338 Blaxland Road
Ryde, New South Wales, 2112, Australia

Abstract—The conductivites of the Na and H ion-exchanged forms of kaolinitic clay rejects from sand-washing operations, both purified and as found naturally as a complex with soil organic matter, were examined. The two Na-clays showed linear conductivity-concentration characteristics, each having two regions with different slopes intersecting at ~3.3% by weight of clay, which probably reflect a structural change from sol to gel. In the gel region, only the Na-counterions conducted, the reduction in conductivity with concentration being due to a smaller proportion of these ions in the Gouy layer and/or a decrease in their mobilities. In the sol, an additional, concentration-dependent conductivity arose from the electrophoretic motion of clusters of clay particles which gradually broke down on dilution. The two acid clays showed curved conductivity-concentration characteristics consistent with a weak acid dissociation equilibrium; the pK_a values of 6.37 to 6.56 are close to those determined independently from titration with alkali. A stronger acid species detected in the titrations was not seen in the conductivity. The $MOH_2^+/MOH/MO^-$ model of the clay-surface species and one set of the predicted concentrations of each species (see preceding paper) are consistent with the observed conductivities. The MOH_2^+ species probably bridged the edges and faces of clay particles so that the H atoms were identical, but became different when alkali was added.

Key Words—Electrical conductivity, Electrophoresis, Humic acid, Kaolinite, Surface properties.

INTRODUCTION

The preceding paper (Lockhart, 1981) presented data on the potentiometric and conductometric titration of the hydrogen and sodium forms of aqueous clay rejects from a sand-washing operation, with and without the organic matter complexed to the clay. Models for the acidic species which reacted with the alkali were suggested, and predictions were made for the concentrations of each species from the end points of the titrations. The results of the present study of the conductivity and electrophoretic mobility are ideal for testing these models and predictions.

EXPERIMENTAL

Samples

The untreated and NaCl-, HCl/H_2O_2-, and $NaCl/H_2O_2$-treated samples from batch A of the clay rejects described in Lockhart (1981) were examined. The peroxide treatment removed the organic matter, whereas the salt or acid treatment provided Na^+ or H^+ exhangeable cations. The untreated sample from batch B was also studied. Details of the preparations are given in the preceding paper (Lockhart, 1981).

Methods.

The dielectric cell and a.c. bridge used to measure the conductivity are described elsewhere (Lockhart and Snaith, 1978). The samples were prepared by successive dilution with conductivity water in the cell itself, stirring at intervals until the conductivity became nearly constant. The more concentrated samples required several hours to come to equilibrium. Also, for the untreated and HCl/H_2O_2 samples in dilute dispersion, it was necessary to stir every few minutes during the measurements to prevent settling. The resistance of the cell filled with each clay dispersion was measured at 100 Hz (where it is nearly equivalent to the dc conductivity) as a function of electrode separation (d) over the concentration range 0.05 to 75 g solids/100 ml dispersion. A correction for the electrode polarization resistance (Lockhart, 1979) was made where appropriate. The corrected resistance R was converted to specific conductivity $\kappa = d/AR$, where A is the area of the sample in the central electrode region of the cell, and thence to 'equivalent' conductance $\Lambda = 1000\,\kappa/c$ (Ω^{-1} cm^2 per unit-cell formula weight of the clay).

The (electrophoretic) mobility of the clay particles was measured independently using a glass microscope slide to which two parallel strips of gold foil were attached 2 mm apart to serve as electrodes. The motion of the particles in dilute dispersion was observed at 50 to 90× magnification, and the average time over a fixed distance was found for several particles in each sample using two different electric field strengths. The microscope was focused at the electroosmotic stationary level.

RESULTS AND ANALYSIS

Electrophoretic mobility

The particles were always repelled from the cathode and were attracted to the anode if the voltage was not

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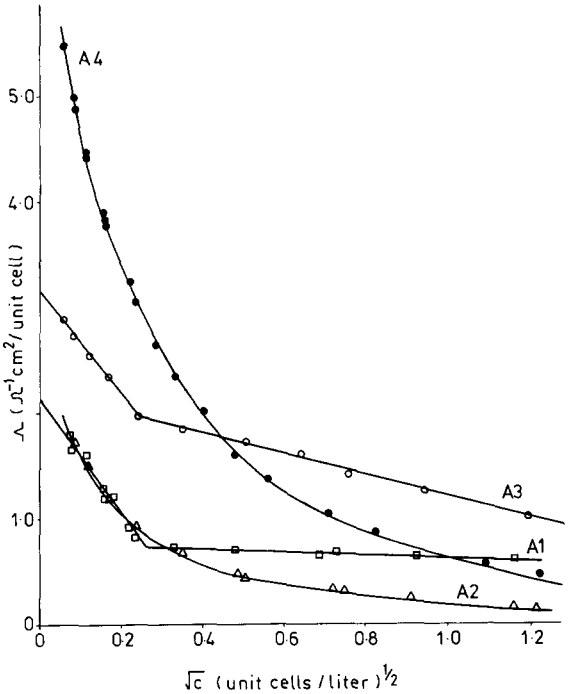

Figure 1. Equivalent conductivity vs. clay concentration for batch A: A1 = $NaCl/H_2O_2$, A2 = HCl/H_2O_2, A3 = NaCl, A4 = untreated. Note that the cation-exchange capacity (expressed as a square root of concentration) is located at 0.334 on A3 and 0.265 on A1.

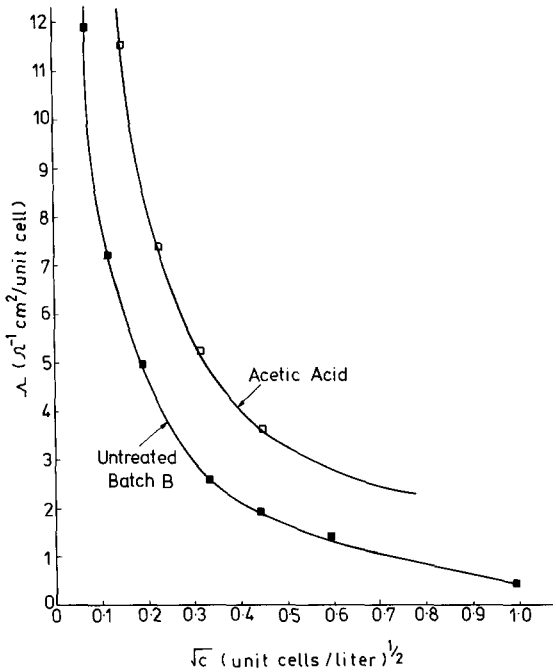

Figure 2. Equivalent conductivity vs. clay concentration for the untreated sample of batch B; acetic acid is shown for comparison.

so high as to cause charge injection. Thus the clay particles in all samples possessed a net negative surface charge. The calculated mobilities are (in 10^{-4} cm^2/v sec) 3.0 ± 0.4 for the NaCl sample, 2.5 ± 0.4 for the $NaCl/H_2O_2$ sample, 1.1 ± 0.3 for the untreated sample, and 0.9 ± 0.3 for the HCl/H_2O_2 sample. The error represents one standard deviation over about ten readings in each case; it is partly due to the difficulty of measuring exactly at the stationary level. The similarity of the latter two values tends to confirm that the 'untreated' sample is naturally acid treated.

Conductivity

The conductivity results are summarized in Figures 1 and 2 as plots of Λ vs. the square root of concentration. Literature data (MacInnes and Shedlovsky, 1932) for the common weak acid, acetic acid, are also shown in Figure 2 for comparison. The curved plots for the untreated samples from each batch resemble that for the acetic acid, indicating that the conductivity in these samples is controlled largely by a dissociation equilibrium. The organic-free sample in acid form also has a curved Λ vs. $\sqrt{c}$ plot. The dissociation constant K_a for a weak acid is approximately $\alpha^2\chi$, where α is the degree of dissociation ($\ll 1$) and χ the molar concentration of the acid (strictly, the molar activity). According to the theory of weak electrolytes (Robinson and Stokes, 1970) α is given by Λ/Λ_0, where Λ_0 is the equivalent conductance at infinite dilution; also χ is equal to the clay concentration (c) for the HCl/H_2O_2 sample and about 6% of c for the two untreated samples, because the weight loss of 6–6.2% (see Lockhart, 1981) is probably synonymous with the organic acid content. Thus, K_a is proportional to Λ^2c and hence to $\Lambda\sqrt{c}$, so that for weak-acid behavior, the product $\Lambda\sqrt{c}$ should be a constant. In Table 1, Λ values taken from Figures 1 and 2 at convenient intervals of $\sqrt{c}$ are listed along with the products $\Lambda\sqrt{c}$. The acetic acid data do not extend beyond $\sqrt{c} \sim 0.4$, but the product $\Lambda\sqrt{c}$ should continue to decrease as $\sqrt{c}$ rises because neglect of the activity coefficient in $K_a = \alpha^2\chi$ become serious at higher concentrations (Robinson and Stokes, 1970). This variation in $\Lambda\sqrt{c}$ is also exected for the clays. In comparing the acetic acid data and the clay data, it is also worth noting that the conductivity of the clay particles themselves is concentration dependent because of the gradual association into edge-to-face and edge-to-edge clusters whereby the particles are eventually immobilized in a network structure. In these circumstances the approximate constancy of the $\Lambda\sqrt{c}$ products for each of the three clays is strong evidence for the weak acid picture.

The actual value of K_a may now be calculated from the averages of the $\Lambda\sqrt{c}$ products over the range $\sqrt{c}$ = 0.15 to 0.8, knowing that Λ_0 is the sum of the H^+ ion

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Table 1. Conductivity multiplied by the square root of the concentration.[1]

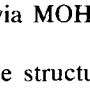
Concentration $\sqrt{c}$ (unit cells/liter)[1]	Conductivity Λ (Ω^{-1} cm²/unit cell)				Product $\Lambda \times \sqrt{c}$			
	Untreated Batch A	Untreated Batch B	HCl/H_2O_2 Batch A	Acetic acid	Untreated Batch A	Untreated Batch B	HCl/H_2O_2 Batch A	Acetic acid
0.1	4.69	7.70	1.63	15.1	0.469	0.77	0.163	1.51
0.15	3.92	6.00	1.29	11.1	0.558	0.90	0.194	1.65
0.2	3.42	4.71	1.07	8.13	0.684	0.942	0.214	1.64
0.3	2.61	2.95	0.77	5.40	0.783	0.885	0.231	1.62
0.4	2.01	2.13	0.59	4.02	0.804	0.852	0.236	1.61
0.5	1.59	1.66	0.47	—	0.795	0.830	0.235	—
0.6	1.28	1.37	0.39	—	0.768	0.822	0.234	—
0.8	0.90	0.83	0.28	—	0.720	0.664	0.224	—
1.0	0.67	0.42	0.22	—	0.670	0.42	0.220	—

[1] Data taken from Figures 1 and 2.

contribution of 332.4 Ω^{-1} cm²/eq (at 21.5°C in present experiments) and the clay contribution of 10.6 Ω^{-1} cm²/eq for the untreated and 8.7 Ω^{-1} cm²/eq for the HCl/H_2O_2 samples which are calculated from the measured mobilities. K_a ($\times 10^7$) is thus 2.77, 3.61, and 4.31 for the untreated batch A, untreated batch B, and HCl/H_2O_2 batch A, respectively. The corresponding pK_a values are 6.56, 6.44, and 6.37. These values suggest that a rather weak dissociation equilibrium (cf. acetic acid $K_a = 1.75 \times 10^{-5}$, $pK_a = 4.76$) controls the conductivity of the acid clays whether or not organic material is complexed to the clay. James and Parks (1981) used surface ionization constants in modeling colloidal dispersions in general.

The two Na-clay samples with and without the organic material present have linear Λ vs. $\sqrt{c}$ plots, each comprising two regions with different slopes. Linear behavior is typical of strong electrolyte systems, with the value of Λ at $\sqrt{c} = 0$ (i.e., Λ_0) representing the sum of the equivalent conductivities of the contributing ions, while the concentration dependence of Λ reflects increasing ionic interactions that can be described in terms of activity coefficients (Robinson and Stokes, 1970). It is reasonable to suppose the linear components in Figure 1 represent the sol and gel regions of the clays, with the point of intersection being the minimum concentration of particles required to set up a continuous network structure. The decline in conductivity with concentration in the gel region, where only the Na counterions are mobile, must reflect a gradual reduction in this mobility and/or a steady decrease in the proportion of Na ions in the diffuse Gouy part of the double layer. In the sol region there is an additional contribution from the clay particles themselves, which must also be concentration dependent due to variation in the number and size (and hence the mobility) of edge-to-face and edge-to-edge associated clusters of particles. It is interesting that the gel region of the NaCl sample extrapolates to $\Lambda = 0$ at a $\sqrt{c}$ value equivalent to 100% clay solids. Another empirical observation is that the conductivity difference between the NaCl and $NaCl/H_2O_2$ samples is constant at 1.1 Ω^{-1} cm²/unit cell up to $\sqrt{c} = 0.4$, which is about 7.8% by weight of clay. This difference could represent the contribution from the *extra* cation-exchange capacity associated with the organic matter.

MODEL TESTING

In the accompanying paper dealing with conductometric and potentiometric titrations, models for the surface chemical species behaving as stronger and weaker acids in the various clay samples were proposed, and predictions were made of the concentrations of each species from the end points of the titrations. The present conductivity results provide independent tests of these models and predictions. The pK_a values of 6.37–6.56 from the curved Λ vs. $\sqrt{c}$ plots are remarkably close to the 6.48–6.85 range obtained quite independently for the weaker acid reaction in the titrations. There is no evidence from the conductivity results for the stronger acid species (pK_a 4–5) revealed in the titrations. The two species must have been basically the same, but became distinguishable when alkali was added to the clays. The model $MOH_2^+/MOH/MO^-$ (where M = Al and/or Fe) proposed in the accompanying paper allows 'bound' MOH_2^+ to behave similarly to MOH groups, whereas 'free' MOH_2^+ (exchanged with Na^+ from the alkali) can release a 'stronger acid' proton to react with the alkali. More specifically, two clay particles could associate via MOH_2^+ bridges as, for example, in an edge-to-face structure [edge MO  face⁻]

where the H atoms are clearly identical, but on alkali addition the particles disperse [edge MOH + H^+ face⁻], making the H atoms different.

A more quantitative assessment requires that the predicted concentrations of each species in Table 2 of

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Table 2. Conductivities (Ω^{-1} cm²/unit cell) calculated from the predicted concentrations (meq/100 g) of each species.[1]

	$NaCl/H_2O_2$		HCl/H_2O_2		NaCl		Untreated	
	Conc.ⁿ	Calc. λ_0	Conc.ⁿ	Calc. λ_0	Conc.ⁿ	Calc. λ_0	Conc.ⁿ	Calc. λ_0
Cl^-	0 ↓ 1.65	0 ↓ 0.61	0 ↓ 1.65	0 ↓ 0.61	0 ↓ 1.65	0 ↓ 0.61	0 ↓ 1.65	0 ↓ 0.61
Na^+ or MOH_2^+	11.05	2.65	1.65	2.83	19.0	4.55	4.0	6.87
$Clay^-$	11.05 ↓ 9.4	1.38 ↓ 1.17	1.65 ↓ 0	0.07 ↓ 0	19.0 ↓ 17.35	2.84 ↓ 2.59	4.0 ↓ 2.35	0.22 ↓ 0.13
		Sol Gel		Sol		Sol Gel		Sol
Λ_0 calculated		4.03 ↓ 4.43	2.65 ↓ 3.26	2.90 ↓ 3.44		7.39 ↓ 7.75	4.55 ↓ 5.16	7.09 ↓ 7.61
Λ_0 observed		2.14	0.78			3.17	2.22	

[1] Procedure described in text. Λ_0 is the sum of the λ_0 values.

Lockhart (1981) be consistent with the conductivities in Figure 1 of the present paper. It is understood that the values in meq/100 g clay listed in Table 2 of the preceding paper for the $NaCl/H_2O_2$ and HCl/H_2O_2 samples also apply to the NaCl and untreated samples, with (for batch A) an additional 7.95 meq/100 g of MO^-Na^+ weaker acid sites in the NaCl sample and an extra 2.35 meq/100 g of $clay^-MOH_2^+$ stronger acid sites in the untreated sample. The overall charge on the clay particles is the algebraic sum of the + and − sites in each case. The predicted net charge is strongly positive (14.0 and 11.65 meq/100 g) for the HCl/H_2O_2 and untreated samples when the one-step weaker acid situation is considered. The negative electrophoretic mobilities actually observed in the present study clearly eliminate this alternative. Even for the two-step weaker acid reaction, the predicted net charge is positive for $MOH_2^+Cl^- > 1.65$ meq, so that detailed comparisons which follow are restricted to the range $1.65 \rightarrow 0$ meq/100 g.

Table 2 summarizes the concentrations in meq/100 g clay of the species concerned for the four samples of batch A. The ion conductivites λ_0 at infinite dilution for the present temperature of 21.5°C are (Robinson and Stokes, 1970) $H^+ = 332.4$; $Na^+ = 46.4$; $Cl^- = 71.2$; clay = 28.9, 24.1, 10.6, and 8.7 for NaCl, $NaCl/H_2O_2$, untreated, and HCl/H_2O_2 samples respectively, as obtained from the electrophoretic mobilities. The units of λ_0 are Ω^{-1} cm²/eq. Since the unit-cell formula weight of kaolinite is 516, the concentrations are first multiplied by 5.16 to obtain meq/unit cell of clay, and then by the appropriate λ_0 values to get Ω^{-1} cm²/unit cell. This allows direct comparison with the experimental Λ values in these units in Figures 1 and 2. The total predicted Λ_0 is the sum of the Cl^-, Na^+ or H^+, and $clay^-$ values for the sol, with the clay contribution being excluded from the gel totals. For the HCl/H_2O_2 and untreated samples the predicted values are close to the observed Λ values for the most dilute dispersions that were measured (the experimental Λ_0 itself is not available from the curved plots). In addition, the contribution of the clay to the total conductivity is predicted to be small, which explains why the weak acid type of dissociation equilibrium is adequate to explain the near constancy of the $\Lambda\sqrt{c}$ products in Table 1. The predicted Λ_0 for the untreated sample from batch B (not shown in Table 2) is 13.0 Ω^{-1} cm²/unit cell, which also compares well with the observed values at the lowest concentrations in Figure 2.

The predicted contribution of the clay to the conductivity of the NaCl and $NaCl/H_2O_2$ samples is, on the other hand, quite significant, and is also in accord with the observed results. The concentration dependence of the conductivity should indeed have quite different origins than in the two acid clays. The predicted Λ_0 values for the NaCl clay are nearly twice those for the $NaCl/H_2O_2$ clay, approximately reflecting the relative values actually observed. The ratio of 2–3 between the predicted and observed values for both the sol and gel regions of the two samples is also reasonable. This follows from the theoretical (Van Olphen, 1977) and experimental (Lockhart, 1980) observations that between two-fifths and two-thirds of the Na counterions are located in the Gouy layer and are able to contribute to the conductivity, whereas the remaining counterions bound in the Stern layer contribute only to the permitivity.

Therefore, the model and one set of predictions based on the end points of potentiometric and conductometric titrations are also quantitatively in agreement

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with the conductivity results for the organic-complexed and organic-free clays, in both the acid form and the sodium form.

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Резюме—Исследовались проводимости Na и H катионообменных форм каолинитовых глин, отбрасываемых после процесса промывания песков, в двух состояниях: чистом и естественном с присутствием почвенного органического материала. Две Na-глины показали линейные характеристики проводимость-концентрация, которые имели две области с разными наклонами, пересекающимися при ~3,3% веса глины, что, вероятно, указывает на перемену структуры из золя в гель. В области геля только Na-противоионы проводили, и уменьшение проводимости с концентрацией было результатом меньшей пропорции этих ионов в слое Гуи и/или уменьшения их мобильности. В золе добавочная проводимость, зависимая от концентрации, была результатом электрофорезной подвижности вкоплений глинистых частиц, которые постепенно разбавлялись. Две кислотные глины показали изогнутые характеристики проводимость-концентрация, согласованные с равновесием диссоциации слабой кислоты. Величины pK_a от 6,37 до 6,56 близки величинам, полученным независимо путём титрования щёлочами. Более сильные кислотные вещества, обнаруженные путём титрования, наблюдались во время процесса проводимости. Модель $MOH_2^+/MOH/MO^-$ веществ на поверхности глины, а также одна система предсказанной концентрации для каждого вещества (смотри предыдущую статью) находятся в согласии с наблюдаемыми проводимостями. Вещества MOH_2^+, вероятно, образовали мостики между краями и гранями глинистых частиц, так что атомы H были тождественные, но становились разными после добавления щёлочи. [E.C.]

Resümee—Es wurden die Leitfähigkeiten von Na^+- und H^+-ausgetauschten Formen von Kaolinit-Tonen untersucht, die Abfallprodukte aus den Sandwaschvorgängen sind. Diese Proben wurden sowohl in gereinigter Form als auch in natürlicher Form—als Komplexe mit organischem Bodenmaterial—untersucht. Die beiden Na-Tone zeigten lineare Leitfähigkeit vs. Konzentration-Abhängigkeiten, wobei jeder zwei Bereiche mit verschiedenen Anstiegen hat, die sich bei etwa 3,3 Gew.-% Ton kreuzen, was wahrscheinlich einen strukturellen Übergang vom Sol zum Gel widerspiegelt. Im Gelbereich leiteten nur die Na-Gegenionen, wobei die Verringerung der Leitfähigkeit mit der Konzentration auf einen kleineren Anteil dieser Ionen in den Gouy-Schichten und/oder auf eine Abnahme ihrer Beweglichkeit zurückgeht. Im Solbereich entwickelte sich eine zusätzliche, Konzentrations-abhängige Leitfähigkeit aus der elektrophoretischen Bewegung von Aggregaten von Tonteilchen, die mit der Verdünnung allmählich zusammenbrach. Die beiden sauren Tone zeigten nichtlineare Leitfähigkeitskonzentrationsabhängigkeiten, was auf das Dissoziationsgleichgewicht einer schwachen Säure hinweist; die pK_a-Werte von 6,37 bis 6,56 liegen nahe bei den Werten, die unabhängig davon aus Titrationen mit Alkalien erhalten wurden. Eine stärker saure Spezies, die bei der Titration gefunden wurde, wurde bei der Leitfähigkeit nicht beobachtet. Das $MOH_2^+/MOH/MO^-$-Modell für die Arten der Tonoberfläche und die vorhergesagten Konzentrationen für jede Spezies (siehe vorhergehende Publikation) stimmen mit den beobachteten Leitfähigkeiten überein. Die MOH_2^+-Spezies überbrückten wahrscheinlich die Kanten und Flächen der Tonteilchen derart, daß die Wasserstoffatome strukturell gleichartig wurden sich aber trotzdem beim Zusatz von Alkalien unterschiedlich verhielten. [U.W.]

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Résumé—On a examiné les conductivités de formes échangées aux ions Na et H de rebuts d'argiles kaolinitiques d'opérations de lavage de sable, formes purifiées et aussi formes trouvées naturellement en tant que complexes avec de la matière de sol organique. Les deux argiles-Na ont montré des caractéristiques de conductivité-concentration linéaires, chacune ayant deux régions avec des inclinaisons différentes, ayant une intersection à 3,3% par poids d'argile, ce qui réflète probablement un changement structural de sol à gel. Dans la région de gel, seuls les contre-ions Na étaient conductifs, la réduction de la conductivité proportionelle à l'augmentation de la concentration étant due à la moindre proportions de ces ions dans la couche Gouy, et/ou à une diminution de leurs mobilités. Dans le sol, une conductivité additionelle, dépendante de la concentration, est survenue de la motion électrophorétique de grappes de particules d'argile, qui s'effondrent progressivement à la dilution. Les deux argiles acides ont montré des caractéristiques de conductivité-concentration courbées compatibles à un équilibre de dissociation d'acide faible; les valeurs pK_a de 6,37 à 6,56 sont proches de celles déterminées de manière indépendante de titration d'alkalins. Une espèce d'acide plus fort détectée dans les titrations n'a pas été trouvée dans la conductivité. Le modèle $MOH_2^+/MOH/MO^-$ de l'espèce de la surface de l'argile et une série des concentrations prédites de chaque espèce (voir article précédent) sont compatibles aux conductivités observées. L'espèce MOH_2^+ a probablement traversé les bords et les faces des particules d'argiles de sorte que les atomes H étaient identiques, mais devenaient différents quand un alkalin était ajouté. [D.J.]

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