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Cationic Modification of Muscovite Mica: An Electrokinetic Study

Satoshi Nishimura,[†] Peter J. Scales,^{*,‡} Hiroshi Tateyama,[†]
Kinue Tsunematsu,[†] and Thomas W. Healy[‡]

Government Industrial Research Institute, Kyushu, Agency of Industrial Science and Technology (MITI), Shuku-machi, Tosu, Saga 841, Japan, and Advanced Mineral Products Research Centre, School of Chemistry, University of Melbourne, Parkville 3052, Australia

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The muscovite mica–electrolyte interface was investigated using an electrokinetic (electro-osmosis) technique after ion exchange and low temperature calcination at 300 °C. Samples calcined after ion exchange with H⁺ and K⁺ showed similar electrokinetic properties to the freshly cleaved sample whereas those calcined after ion exchange with either Li⁺ or Mg²⁺ ions showed a significant reduction in the magnitude of the zeta potential. This reduction was attributed to an irreversible fixation during calcination of Li⁺ and Mg²⁺ ions respectively to the basal plane of the muscovite mica. Modeling of the electrical double layer properties using a Gouy–Chapman–Stern–Grahame approach indicated that greater than 90% of the charge in the lattice had been neutralized by the calcination procedure.

Introduction

Clay colloid chemistry has been extensively investigated due to its importance in both industry and agriculture. In particular, phenomena such as clay swelling, colloidal stability, and rheological behavior are of interest. The electrical double layer properties of the clay solution interface are of central importance to these phenomena but the clay basal plane is difficult to characterize for all but macroscopic layered minerals such as muscovite mica. This mineral has therefore been extensively studied by clay and soil scientists. In addition, it is analogous in both crystal structure and chemical composition to many other layered clay minerals.

A wealth of knowledge of the double layer characteristics of the molecularly smooth basal plane of muscovite mica is now available. This has been achieved through the interpretation of direct force measurements,^{1–3} streaming potential measurements,^{4,5} and electro-osmosis measurements.^{6,7}

The origins of the surface charge in muscovite mica are correlated to a structural imbalance of charge due to isomorphous replacement of cations in the tetrahedral and octahedral layers of the mineral. The specific localization of this charge is, then, of interest. The charge imbalance is neutralized in the solid state by interlayer cations such as potassium and sodium but in aqueous solution, these cations are replaced by the dominant aqueous hydrated cation. Numerous studies have shown the order of effectiveness of neutralization of the lattice charge in aqueous solution for monovalent cations is Cs⁺ > K⁺ > Na⁺ ≈ Li⁺.^{3,5,8} Speculation as to the mechanism

of ion adsorption to the muscovite mica basal plane in aqueous solution leads to the conclusion that this ionic series reflects the ease with which cations are dehydrated and subsequently adsorbed to the Stern plane of the surface. Indeed, modeling of the electrical double layer properties of the muscovite mica surface as well as ESCA studies⁹ supports these conclusions. It is important to note that the bare cation size is the reverse of the above series.¹⁰

In terms of absorption into, rather than onto, the muscovite mica surface, only the bare Na⁺ and Li⁺ ions (of the monovalent series) are of small enough dimensions to pass easily into a hexagonal cavity formed by oxygen atoms in the tetrahedral layer of the mica. If the divalent cationic series is considered, only the Mg²⁺ cation of the series Ba²⁺, Sr²⁺, Ca²⁺, and Mg²⁺ is of small enough bare dimensions to pass easily into a hexagonal cavity. All the other cations in the quoted series are either of equivalent size or larger than the cavity.¹⁰ As to whether the dehydrated Na⁺, Li⁺, and Mg²⁺ ions could indeed be absorbed to the octahedral layer of a 2:1 layer clay mineral is not clear although there are no apparent physical constraints to this happening. According to the concept invoked by Hoffman and Klemen¹¹ and Greene-Kelly,^{12,13} ions that are irreversibly fixed in 2:1 type sheet silicates could migrate into a vacant site in the octahedral layer of a smectite, whereas studies by Tettenhorst¹⁴ and Farmer and Russell¹⁵ argue their IR data indicate that Li⁺ ions react with structural hydroxy groups to release protons. More recently, Jaynes and Bigham¹⁶ indicated the cation exchange capacity (CEC) decreases with the fixation of Li⁺ ions in smectites. If the fixation of cations occurs on the muscovite mica basal plane, a reduction in surface charge could be expected similar to the CEC reduction in Li-smectite. This will change the metal ion exchange equilibria of the surface. Electrokinetic measurements are expected to be sensitive to changes of this type.

* To whom correspondence should be addressed.

[†] Government Industrial Research Institute.

[‡] University of Melbourne.

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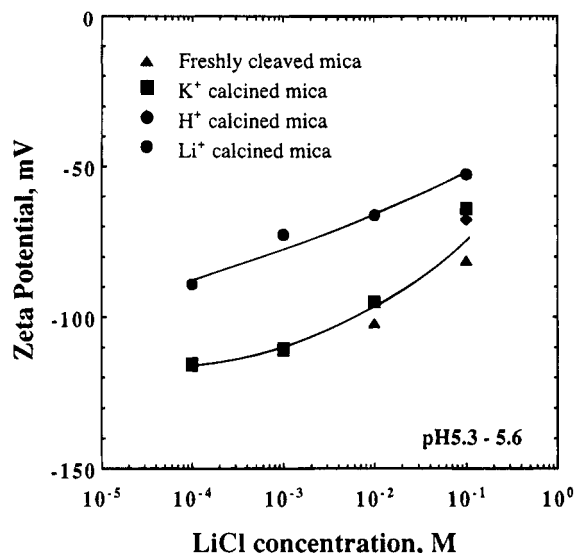


Figure 1. Zeta potential of the muscovite mica interface as a function of LiCl concentration at pH 5.6 ± 0.3 for freshly cleaved mica and after ion exchange and calcination to produce K^+ , H^+ , and Li^+ fixed micas.

The aim of this study was therefore to test using an electrokinetic technique the concept that a cation with sufficiently small bare size could be absorbed or "fixed" irreversibly into the mica basal plane and that this procedure would significantly effect the electrokinetics of the resultant mica–water interface. The results of the electrokinetic measurements (i.e., zeta potential measurements) are discussed in terms of a Gouy–Chapman–Stern–Grahame (GCSG) model of the electrical double layer assuming the irreversible fixation of a cation reduces the effective lattice charge of the substrate.

Experimental Section

All reagents used in this study were AR grade and water was from a Milli-Q water purification system. Measurements were made at $25 \pm 0.5^\circ\text{C}$.

Zeta potential measurements were performed using a plane interface electro-osmosis technique that has previously been described by Nishimura et al.⁶ In brief, electroosmotic mobilities at the mica–water interface were determined by extrapolation of a parabolic profile of electro-osmotic flow in a rectangular silica cell to the interface, and then zeta potentials were calculated from the mobilities using the Helmholtz–Smoluchowski equation.

Large pieces of muscovite mica (Bihar, India) were cut to fit the measurement cell. Prior to each measurement, a mica sheet was freshly cleaved in air along the basal plane. Polystyrene latex colloid with a diameter of $0.42\ \mu\text{m}$ was used as a probe particle for measuring the electro-osmosis in the cell. The pH of the aqueous solution was adjusted using HCl and KOH. KCl or LiCl (0.001 M) was used for a background electrolyte.

The mica interface was prepared as follows. The freshly cleaved surface was repeatedly rinsed in a Milli-Q water (pH ≈ 5.8) to produce a H^+ exchanged mica. A sample of this mica was retained and separate samples were then immersed in a 0.1 M KCl, LiCl, or $MgCl_2$ solution for 12 h. This produced respectively a K^+ , Li^+ , or Mg^{2+} exchanged mica. The Mg^{2+} , Li^+ , K^+ , and H^+ exchanged micas were then calcined in an oven at 300°C and cooled, and the surface was rinsed with distilled water. The electrokinetics of the interfaces so produced were determined in the presence of 0.001 M KCl solution as a function of pH using dilute solutions of HCl and KOH for pH adjustment and for the monovalent calcined samples at LiCl concentrations from 10^{-4} to 10^{-1} M at constant pH.

Results and Discussion

Figure 1 shows the electrokinetic response of muscovite mica at pH 5.6 ± 0.3 as a function of LiCl concentration.

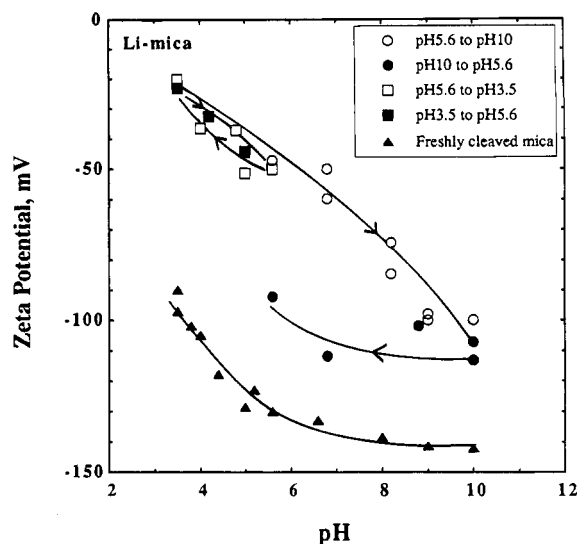


Figure 2. Zeta potential versus pH for freshly cleaved mica and Li^+ calcined mica in the presence of 0.001 M KCl. The data show hysteresis if the pH is cycled from low pH to high pH for the Li^+ calcined mica. To illustrate the pH sweeps, the drawn lines at low (<5.6) pH are slightly displaced from best fits. The points are plotted exactly.

The data clearly show the differences between the Li^+ exchanged and calcined muscovite mica and mica in the freshly cleaved, K^+ calcined, and H^+ calcined form. It should be acknowledged at this point that a mica immersed in a salt solution in the absence of irreversible fixation of ions would be expected to exchange freely with the dominant cation, in this case, Li^+ . Only a small difference in the magnitude of the zeta potential is observed for the freshly cleaved, K^+ calcined, and H^+ calcined forms at around a concentration of 0.1 M KCl. The reduction in the magnitude of the zeta potential for the Li^+ calcined mica is consistent with a reduction in the negative charge of the mica by the irreversible fixation of Li^+ ions. The electrokinetic response is explained by comparing the size of a bare ion with that of the hexagonal cavity. K^+ ions, by simple size considerations, cannot pass into the hexagonal cavity. It is concluded therefore that a K^+ ion is easily hydrated and released to the bulk water phase after calcination since the zeta potential showed little or no change from the freshly cleaved mica case.

Examination of the bare size of the Li^+ ion shows it is possible for this ion to pass into and be fixed in the hexagonal cavity. These observations are also supported by imaging of the same surfaces using atomic force microscopy (AFM).¹⁷ If this fixation process is accompanied by a reaction with structural hydroxy groups where the protons of the hydroxy groups are displaced by Li^+ ions, there will be no alteration in surface charge as a result of compensation for deprotonated hydroxy groups. The observation is that the Li^+ case showed a zeta potential of lower magnitude than freshly cleaved mica (i.e., a reduction of negative surface charge). It is concluded therefore that there is little reaction of Li^+ ions with the structural hydroxy groups. It is not surprising that the H^+ calcined mica is not significantly different from a freshly cleaved mica even if protons of the hydroxy groups were replaced by H^+ ions through calcination since the reaction of H^+ with the structural hydroxy groups is expected due to the small bare size of this ion.

Figure 2 shows the pH response of Li^+ calcined mica. The data for freshly cleaved mica in 0.001 M KCl are also

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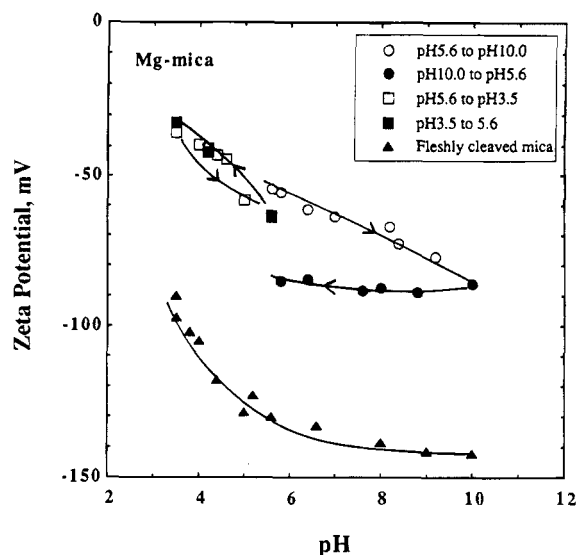


Figure 3. Zeta potential versus pH for freshly cleaved mica and Mg^{2+} calcined mica in the presence of 0.001 M KCl. The data show hysteresis if the pH is cycled from low pH to high pH for the Mg^{2+} calcined mica. To illustrate the pH sweeps, the drawn lines at low (<5.6) pH are slightly displaced from best fit. The points are plotted exactly.

shown. Hysteresis in the Li^+ calcined mica data is observed. The data are reproducible and no hysteresis is observed if the pH is cycled below pH 7; if the pH is raised to 10, the magnitude of the zeta potential increases. Cycling back from pH 10 exhibits hysteresis in the magnitude of the zeta potential. At no point do we measure a value of equal magnitude to the freshly cleaved case. It may be concluded nonetheless that the hysteresis is representative of an increase in the effective surface charge relative to the low pH calcined case and is associated with a partial release of the fixed cation when the pH is cycled above 7.

Figure 3 shows the pH response of Mg^{2+} calcined muscovite mica in the presence of 1×10^{-3} M KCl. The data for freshly cleaved mica under the same conditions are included for comparison. The data are similar in form to that observed for the Li^+ calcined case. Once again hysteresis is observed if the pH is cycled at values above 7. The magnitude of the potential both before and after pH cycling is lower than the Li^+ calcined mica case. The reduction in the magnitude of the zeta potential on calcination is attributed, as with the Li^+ calcined case, to the irreversible fixation of Mg^{2+} ions in the hexagonal cavity of the muscovite mica. AFM studies¹⁷ confirm the fixation process, as with the Li^+ case. However, the pH-cycling hysteresis of zeta potential in the Mg^{2+} calcined mica appeared to be less serious than that for the Li^+ calcined mica. This may be due to a more attractive Coulombic interaction as a result of the larger valence of the Mg^{2+} ion.

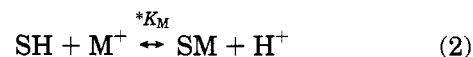
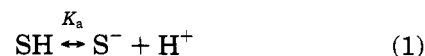
The pH dependence of the zeta potential shows hysteresis in alkaline solution for both Li^+ and Mg^{2+} calcined mica. This may be due to rehydration and some release of the fixed cations and/or dissolution of the Si-O-Si network forming the hexagonal holes.

Russel²⁰ observed that the structural hydroxy group to the Fe ion in the octahedral layer was deprotonated when dioctahedral smectites were treated with alkalis and again reprotonated when the clays were treated with acetic

acid. If such a deprotonation of structural hydroxy groups occurred in the present study, fixed cations in the muscovite mica would be replaced to H^+ ions and hysteresis of zeta potential curves for calcined mica would be observed in acid aqueous solution. There was no observed hysteresis in acid solution in either the Li^+ or Mg^{2+} calcined cases. This provides further support for the contention that there is little reaction of the fixed cations with the structural hydroxy groups in the octahedral layer.

To further understand the electrokinetic results, the freshly cleaved muscovite mica zeta potential data were modeled using a triple layer site binding model as initiated by Yates et al.¹⁸ and previously used to model the muscovite mica surface by Scales et al.⁵ A single acid dissociation site is assumed with binding of cations to the Stern plane. The variability in the zeta potential as a function of pH is postulated to be due to the formation of ionizable silanol groups as a result of hydrolysis of Si-O-Si in the tetrahedral layer. The number of surface sites per square meter (N_s) was taken as the theoretical lattice imbalance of 2×10^{18} sites/ m^2 of surface or one charged site per 46.8 \AA^2 of surface.^{18,19}

The surface equilibria of the mica basal plane is described by



$$N_s = [\text{S}^-] + [\text{SH}] + [\text{SM}] \quad (3)$$

where S^- is a surface site, H^+ is assumed to be a potential determining ion, M^+ represents an aqueous metal ion, K_a and $*K_M$ are the acid and metal ion dissociation constants, respectively, and $[\text{S}^-]$, $[\text{SH}]$, and $[\text{SM}]$ are concentrations of surface sites. It further follows from the triple-layer model and the condition of double layer electroneutrality that

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad (4)$$

$$\sigma_o = -e([\text{S}^-] + [\text{SM}]) = C_1(\Psi_o - \Psi_\beta) \quad (5)$$

$$\sigma_\beta = e([\text{SM}]) \quad (6)$$

$$\sigma_d = e([\text{S}^-]) = C_2(\Psi_d - \Psi_\beta) \quad (7)$$

where σ_o , σ_β , and σ_d are the charge densities at the mica surface and the inner and outer Helmholtz planes, respectively, and C_1 and C_2 are the capacitances of the inner and outer Helmholtz layers, respectively.

Solving the above equations numerically, the zeta potential data for the freshly cleaved muscovite mica basal plane can be fitted to Ψ_d using the input parameters $\text{p}K_a = 3.7$, $\text{p}^*K_M = 2.5$, $C_1 = 1000 \text{ \mu F/cm}^2$, and $C_2 = 200 \text{ \mu F/cm}^2$. The value of $\text{p}K_a$ is substantially lower than the values of 6.0 estimated by an earlier surface force apparatus study³ and previous electrokinetic work (5.6).⁵ More recently, Shubin and Kekicheff²¹ calculated a $\text{p}K_a$ of 4.2, which is much closer to the value in the present study. They also recognized a discrepancy in the $\text{p}K_a$ between measurement methods but suggested that it could be due to different samples. Surface force work has shown a variation in Ψ_s between -50 and -130 mV for five different

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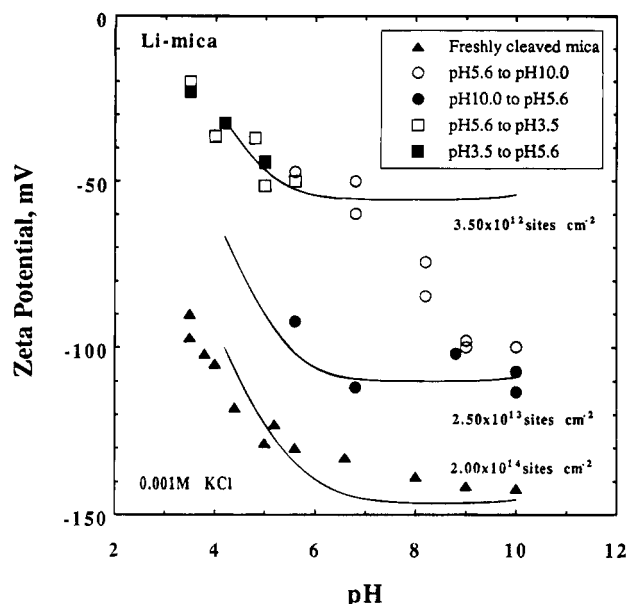


Figure 4. Fitting of the zeta potential versus pH data of Figure 2 using the site binding model of the electrical double layer. Solid lines are model predictions; points are experiment. Model parameters: $pK_a = 3.7$, $p^*K_M = 2.5$.

micas.²² The value of p^*K_M is similar to the value of 2.5 for K^+ ions on mica and Putnam clay calculated by Pashley⁵ and James and Parks,²³ respectively, but lower than other modeling of the muscovite mica-solution interface.^{3,5,7} These values all correspond to a large free energy of adsorption. Most values of p^*K_M for alkali ions on layered silicate minerals are in the range 2 to 4.^{3,5,7,22} The value of p^*K_M obtained here is not unreasonable although there still exists a dilemma as to the source of a reasonable value for p^*K_M . The inner layer capacitances (i.e., C_1 and C_2) are fitting parameters based on a previous study.⁵

The first modeling step was the case where Li^+ had been fixed to the muscovite mica basal plane. The main effect of the fixation process was assumed to be a reduction in the total number of charged sites with no proposed effect on either K_a or *K_M . As discussed above, this assumption is substantiated by the observation that the fixed cations compensate for negative lattice charges in the tetrahedral layer of muscovite mica but not for deprotonated hydroxyls in the octahedral layer. By adjustment of the value for N_s in the modeling program, a reasonable fit was obtained for both the low pH (fixed) and high to low pH (partially hydrated) data. The results of the analysis are shown in Figure 4. Values of N_s of 3.5×10^{16} and 2.5×10^{17} were required to fit the data both before and then after partial hydration, respectively. These values suggest that a significant number of sites on the muscovite mica basal plane are occupied by Li^+ ions after calcination (of order 98%) and that although this figure reduces on pH cycling, approximately 87% of sites remain occupied. The data are further evidence for the argument that the K^+ ion, although of apparently equivalent diameter to the hexagonal layer site on the muscovite mica basal plane, is weakly fixed and is removed or "washed out" relatively easily. This latter observation is consistent with AFM¹⁷ work that does not detect the presence of the K^+ ion in the hexagonal layer site after immersion in aqueous solution.

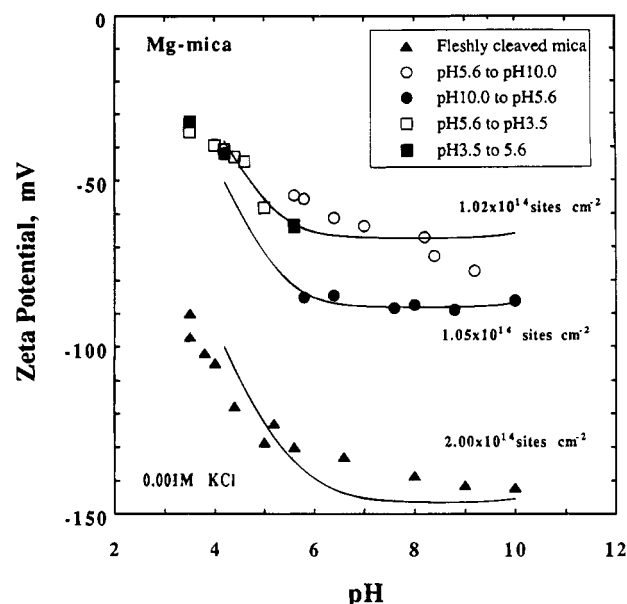


Figure 5. Fitting of the zeta potential versus pH data of Figure 3 using the site binding model of the electrical double layer. Solid lines are model predictions; points are experimental. Model parameters: $pK_a = 3.7$, $p^*K_M = 2.5$.

The Mg^{2+} data were modeled in the same manner as the Li^+ calcined case except the fixation of a Mg^{2+} ion was assumed to reduce the muscovite mica charge density in accordance with the divalent charge on the Mg^{2+} ion. A case where the Mg^{2+} was absorbed into the surface and then allowed to partially hydrate, without release from the interface, was also considered but perhaps, encouragingly, the simpler case proved the most successful in describing the data. Values of N_s (the free number of sites) of 1.02×10^{18} and 1.05×10^{18} were required to fit the data both before and then after partial hydration and release of the metal ion, respectively. The results of the analysis are shown in Figure 5. The values of the number of free sites for the Mg^{2+} modeling case are equivalent to 4.0×10^{16} and 1.0×10^{17} sites/m² when scaled to the monovalent cation case is compared.

The qualitative conclusion is therefore that the calcination of the Li^+ and Mg^{2+} ions neutralize about the same amount of charge on the muscovite mica surface but the Mg^{2+} is more difficult to hydrate. Previous work on the role and position of Mg^{2+} ions in the interlayer spacing of sodium and calcium vermiculites²⁴ suggests the Mg^{2+} ion to have a greater capacity to locate in both tetrahedral as well as octahedral interstitial sites. Analysis of AFM images¹⁷ of the calcined surfaces further supports the modeling analysis in that the number of vacant hexagonal layer sites observed for the Mg^{2+} exchanged and calcined micas is much reduced relative to the Li^+ exchanged and calcined samples. It should be noted that the above theoretical calculation using a triple double-layer model provided a good fit to all data in this study using only one $pK_a = 3.7$ and $p^*K_M = 2.5$ value. This implies that the negative lattice sites remaining on the Li^+ and Mg^{2+} calcined mica are chemically identical to those on the freshly cleaved mica basal plane.

Conclusions

The electrokinetic data for ion exchanged and calcined muscovite mica samples support the conclusion that only

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cations with a bare ion size substantially smaller than the dimensions of a hexagonal site on mica can be irreversibly fixed to the surface. Partial hydration and release of the fixed cations in the hexagonal layer sites were possible if the pH of the aqueous phase was cycled above 7. Modeling of the electrical double layer indicates that the calcination procedure results in a significant proportion of the lattice charge being neutralized.

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