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Surface pressure-area isotherms of PVS have been reported by several workers.^{7,13,20} They all obtained more expanded and flatter isotherms of PVS monolayers than those of VS. No details of compression techniques are given by Fort and Alexander,⁷ but the others^{13,20} used continuous compression by a single barrier at respectively 0.02 and 0.028 nm² molecule⁻¹ min⁻¹, and their surface pressure data were taken from a horizontal float at the fixed end of the trough. The implications of this mode of operation are clear from the data in Figures 1 and 7.

Furthermore, because of the serious gradient of surface pressure formed during compression, as shown in Figures 1 and 3, the film in the region close to the barrier will begin to collapse well before the surface pressure near the fixed end of the trough reaches a high value. Malcolm¹⁸ has pointed to an analogous situation in polypeptide monolayers. It is therefore likely that the isotherms of PVS monolayers reported in these earlier publications^{7,13,20} refer to films that are partially collapsed at moderate and high surface pressures.

The dependence of the surface pressure of PVS on the spreading method indicates that the macromolecules tend to remain in or near the region where they are spread because of the very slow diffusion in the film. This observation can also explain the apparent annealing effect observed by O'Brien, Long, and Lando.¹³ They reported that when a PVS film was compressed and held at 33 mN m⁻¹ for 3 h, the areas in a subsequent compression isotherm were considerably lower than for an unannealed film. It now seems likely that this was caused by the failure of the compressed film to expand properly

when the barrier was moved back. The distribution of film on the surface would thus have been similar to that in Figure 4 where the film was spread near the fixed end of the trough, and indeed there is reasonable agreement between the two isotherms after some allowance for the different measuring positions.

The present observations also provide an explanation for the reported difficulty in depositing Langmuir-Blodgett films of PVS.²⁰

Conclusions

During compression there is no appreciable inhomogeneity in the monolayers of VS, whereas large surface pressure gradients form in PVS monolayers. With PVS, the surface pressure is approximately a linear function of the distance along the trough, decreasing with distance from the compression barrier and with the gradient increasing as the compression proceeds. Such an inhomogeneity in the film depends on both the technique of spreading and the method of compression (symmetric, asymmetric, compression rate). It cannot be eliminated in PVS monolayers even though some improvement in the homogeneity would be gained by using both symmetric compression and even spreading. The surface pressure gradient does decay with time but did not reduce to an acceptable value even after 90 min of relaxation.

Acknowledgment. Financial support from the Australian Research Council is gratefully acknowledged. We also thank Dr. K. Milne for the molecular weight determination.

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Electrokinetics of the Muscovite Mica-Aqueous Solution Interface

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The electrokinetic characteristics of muscovite mica in contact with monovalent, divalent, and trivalent aqueous ions have been measured with an apparatus specially designed for measuring streaming potentials of flat surfaces. Modeling the data obtained by using a Gouy-Chapman-Stern-Grahame model shows that although a triple-layer model can describe the observed experimental trends there are some obvious limitations with the model. A comparison of the ζ potentials measured on the mica system with force balance derived potentials is also made. A good correlation between the two types of measurements exists for systems with 1:1 electrolytes; however, considerable differences are noted for 2:1 and 3:1 electrolyte systems.

Introduction

The colloid chemistry of clays has been extensively investigated and has centered on the most industrially and

agriculturally important types. However, the large variety of clays and their differences in structure have made most studies unique to the clay system under investigation. Even clays with few structural differences often show unique and relatively dissimilar swelling and elec-

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trokinetic behavior under controlled conditions of pH and electrolyte concentration. Therefore, to fully investigate even a small aspect of clay chemistry is often difficult.

The aim of this study was to characterize through electrokinetic measurements the sheet-like illite, muscovite mica. This material has many qualities that make its use as a base solid for electrokinetic measurements favorable. Not the least of these qualities is its sheet-like structure, which allows cleavage along a basal plane into a "molecularly smooth" surface of sufficient size for use in a flat plate streaming potential measurement.¹⁻³ It is just this same property that allows mica to be used in direct force measurements between two surfaces.⁴

To characterize the charge-potential behavior of mica, an electrokinetic investigation of the surface in the presence of monovalent, divalent, and trivalent cations was undertaken. Theoretical modeling of the observed electrokinetic behavior using the Gouy-Chapman-Stern-Grahame (GCSG) model of the electrical double layer (edl) and a single-site dissociation analysis were then used to develop physical concepts of the interaction and exchange of ionic species with the mica surface.

To model the charge-pH behavior of muscovite mica requires an analysis of the mode of charge generation in this system. The charging of the interface is generally assumed to have contributions from free (unneutralized) lattice charge and the hydrolysis in water of surface silicate species. The theoretical analysis of some clay systems⁴ has thus been based on the assumption of two specific adsorption (exchange) sites, each with its own exchange equilibria. More recent studies of the exchange equilibria of metal ions on mica^{2,5} suggests this to be unnecessary for the mica surface since it shows no evidence of a stepped adsorption isotherm and, hence, only one adsorption site. Although it is difficult to delineate the contributions from each charge generation source, James and Parks,⁶ Marshall et al.,⁷ Pashley,^{5,8,9} and Lyons et al.² have all proposed that mica may be modeled as the equivalent of a surface of weak acid sites. The proposed metal ion exchange equilibria for these sites may then be represented by a single-site dissociation model.

Crystallographic data for muscovite mica shows the idealized structure to be that of a potassium neutralized layer structure with a silicate unit area of 45.8 Å².^{10,11} This area per silicate corresponds to the lattice charge per unit area in the unneutralized case. Analysis of natural samples from Bihar (India) shows variations of only a few percent from the idealized structure. Israelachvili and Adams⁴ and Lyons¹² report typical structural data of the form $K_{0.84}Na_{0.12}(Al_{1.93}Fe^{2+}_{0.06}Mg_{0.04})(Si_{3.04}Al_{0.96}O_{10})(OH)_2$. The former workers were able to show through force balance measurements that small variations in this

structure produce large variations in calculated double-layer potentials. Lyons et al.^{2,12} also showed through electrokinetic measurements that similar results could be expected in trying to compare ruby and green mica.

Therefore, for a worthwhile characterization of this clay mineral, a mica sample of consistent structure was required. Pashley et al.,^{5,8,9} in their study of metal ion adsorption (exchange) on mica, overcame this problem by cleaving all experimental samples from the same base mica sheet. This procedure was adopted for this study.

Materials and Methods

Electrokinetic measurements were made by using a flat plate streaming potential apparatus that has been fully described in a previous publication.¹ Briefly, a capillary was formed between two mica sheets separated by a Teflon gasket. Streaming potentials were recorded for flow in both directions, and a ζ potential was calculated by using the Smoluchowski relationship¹³

$$\zeta = \left[\frac{\eta \lambda}{D \epsilon_0} \left(\frac{\Delta E}{\Delta P} \right) \right] \quad (1)$$

In this expression, D is the dielectric constant of the solution, λ the conductivity of the capillary, η the bulk viscosity, ΔP the pressure drop across the capillary, and ΔE the streaming potential. The measurements were adjusted for the effects of capillary surface conduction, as previously described.¹ Streaming potential plates of dimensions 7.5 × 2.5 cm were glued to pre-sized borosilicate microscope slides with a low melting point ($\approx 80^\circ\text{C}$) inert wax (Shell-Epikote Resin 1002). A small amount of wax was placed on a glass slide and the slide heated to $\approx 100^\circ\text{C}$. A piece of mica was then placed on the slide and pressed firmly. Cooling produced a firm bond that is chemically inert in aqueous systems.⁴ The mica was then trimmed to the exact dimensions of the glass slide and cleaved to produce a fresh surface for use in streaming potential measurements. A fresh mica sample was prepared for each experiment.

Water used in this study was purified by distillation followed by percolation through charcoal and mixed bed ion-exchange resins (Millipore, "Milli-Q"). The final conductivity of the water was less than $1 \times 10^{-6} \text{ S cm}^{-1}$ at 20°C . Sheets of mica were from Bahir, India, and were kindly supplied by Dr. R. Pashley, Australian National University, Canberra, Australia. Experiments were performed at $20 \pm 1^\circ\text{C}$. Electrolytes were analytical grade reagents. Electrodes were replatinized if the coating deteriorated or if the asymmetry potential in streaming potential measurements increased to a significant level.

Electrolyte pH was measured by using a Titron combined blue glass electrode and Radiometer Model pHm84 research pH meter. The bulk conductivity was measured by using a Titron conductivity probe and Philips Model PW 9526 digital conductivity meter.

Results and Discussion

ζ Potential of Mica in Aqueous 1:1 Electrolyte Solutions. The ζ potentials as a function of 1:1 electrolyte concentration for aqueous solutions of CsCl, KCl, NaCl, and LiCl at pH 5.8 ± 0.3 are shown in Figure 1. This pH regime was chosen since it represented the pH of the aqueous solutions after equilibration with atmospheric CO₂. It is also a pH regime in which aging effects at the mica-solution interface were expected to be minimal.^{2,12}

The difference in potential between the various 1:1 electrolyte ions at concentrations $\geq 1 \times 10^{-3} \text{ mol dm}^{-3}$ shows that the original potassium and sodium ions neutralizing the lattice charge of mica are exchanged for the more

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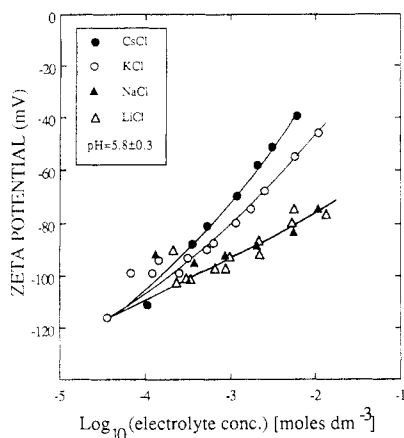


Figure 1. ζ potential of muscovite mica versus background electrolyte concentration at pH 5.8 ± 0.3 for various 1:1 electrolytes.

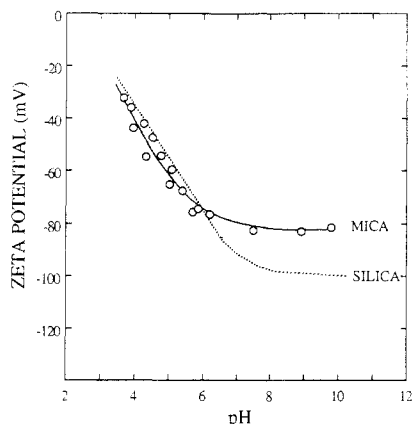


Figure 2. ζ potential of mica versus pH in an aqueous solution of KCl at $0.001 \text{ mol dm}^{-3}$. Dashed line is for fused silica under the same experimental conditions.

active solution ions in each case. At pH 5.8, the exchange equilibria proceeds as $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ \approx \text{Li}^+$. This series is based on the observation that at constant pH a higher solution activity results in a higher (less negative) value for ζ . Lyons et al.² observed (electrokinetically) a similar lyotropic series for the exchange of metal ions on mica at constant pH. A possible difference in their data was that the Na^+ ion was observed to produce a slightly lower value of ζ than for the Li^+ species. This is identical with the observation of Pashley⁵ for the same series of ions on mica as calculated from the interaction of crossed mica cylinders in their force balance apparatus.⁴

The ζ potential of mica as a function of pH in the presence and the absence of a $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous solution of KCl is shown in Figures 2 and 3, respectively. The effect of the hydrogen ion in decreasing the magnitude of the ζ potential of mica is clearly seen in both figures. Extrapolation of Figure 3 to low acid gives an indication of the magnitude of the ζ potential for a mica surface in the sole presence of H^+ cations and Cl^- anions at pH 5.8. A comparison with the ζ potential of fused silica under identical experimental conditions is also shown in Figure 2. The similarities in the shapes of the curves are quite striking, as is the comparison of the ζ potential of mica and silica in aqueous solutions of KCl at pH 5.8 ± 0.2 as shown in Figure 4. However, the absence of an isoelectric point (iep) in the mica case is a point of difference between the two interfaces. This observation is highlighted in Figure 3 by an insensitivity of the ζ potential to the addition of acid at concentrations $\geq 1 \times 10^{-3} \text{ mol dm}^{-3}$.

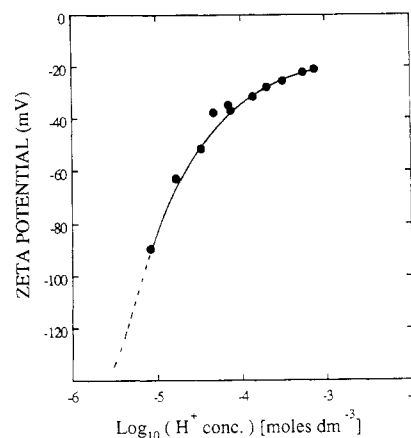


Figure 3. ζ potential of mica versus the concentration of HCl.

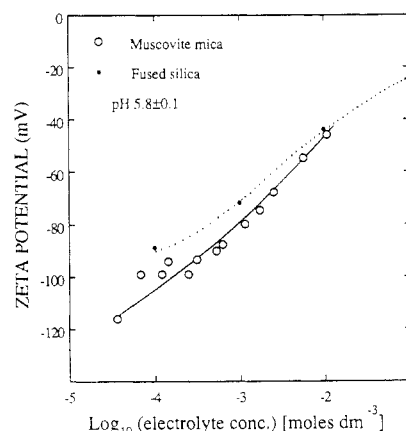


Figure 4. ζ potential of mica in the presence of aqueous solutions of KCl. Dotted line is the equivalent experiment on fused silica.

Studies of the aging of mica by Lyons et al.² show a possible reason for this behavior is the increased solubility (exchangeability) of lattice aluminium ions at pH extremes. Such a phenomenon produces a vast increase in lattice charge at both high and low pH, the process being accentuated at low pH, where the aluminium ion is more soluble in aqueous solution. Adsorption of the ion to the mica surface at higher pH values results in a reversal in the sign of the electrokinetic potential. The ion is also less likely to specifically readsorb to the surface at low pH. A similar study by Wiese et al.¹⁴ for trivalent metal ions adsorbed at the silica-solution interface also highlights the high adsorption specificity of aluminium ion species.

The structural and charge generation properties of mica are quite different from those of the silica system, but on the basis of the results in Figures 2-4, the surfaces show many similar ionization trends, particularly in the pH 4-8 regime. On purely structural grounds, this is unexpected, since the mica surface should act as a surface of constant charge. To justify these similarities, the observed ionization properties are attributed to the hydrolysis of the Si-O-Si groups at the surface to yield a form of ionizable surface silanol groups.

ζ Potential of Mica in Aqueous Solutions of CaCl_2 . The divalent calcium ion is also known to show a strong exchange equilibrium with mica.¹⁵ Therefore, it is of interest to characterize the electrokinetic behavior of the interface in the presence of this ion. The ζ

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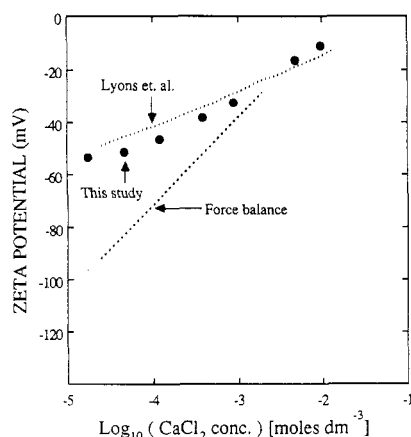


Figure 5. ζ potential of mica versus the aqueous concentration of calcium chloride. The data of Lyons et al.² for a sample of green mica and the force balance results of Pashley and Israelachvili⁸ for a brown mica sample are included for comparison. The pH was 5.8.

potential of mica as a function of CaCl_2 concentration at $\text{pH } 5.8 \pm 0.2$ is shown in Figure 5. Results were corrected for the effects of surface conductance, as are all results for the 1:1 electrolyte system.¹ This correction was minimal for mica-Ca systems compared with the 1:1 electrolyte case. The results of a previous study by Lyons et al.¹² for green mica in the presence of CaCl_2 solutions at pH 5.8 are shown as a dashed line on the same figure. The potentials as calculated by Pashley and Israelachvili⁸ from force balance measurements are also shown to compare the two techniques.

The streaming potential results of this study and those of Lyons et al.¹² for green mica show excellent correlation given the inherent differences in the type of mica used and the higher predicted lattice charge of the green mica sample. The neutralization of the mica lattice charge by the Ca^{2+} ion at concentrations $> 10^{-2} \text{ mol dm}^{-3}$ is also of interest. It is difficult to establish the exact point at which this occurs due to the high conductivity of CaCl_2 solutions limiting the accuracy of the streaming potential technique. Force balance measurements^{8,15} record no repulsive double layer forces at CaCl_2 concentrations $\leq 1 \times 10^{-2} \text{ mol dm}^{-3}$. This is consistent with streaming potential results presented here.

ζ Potential of Mica in Aqueous Solutions of LaCl_3 . The lattice charge of mica is reduced by the adsorption of ions at the surface, with the divalent calcium ion proving more effective than the monovalent metal ion series Cs^+ , K^+ , Na^+ , and Li^+ . This trend is further emphasized with the adsorption of La^{3+} ions. The ζ potential of mica as function of LaCl_3 concentration at $\text{pH } 5.8 \pm 0.4$ is shown in Figure 6. Slight hydrolysis of lanthanum occurs at concentrations $\geq 1 \times 10^{-3} \text{ mol dm}^{-3}$ at pH 5.8.¹⁴ This results in a small reduction in the pH of the solution. As with oxide systems¹⁴ and a previous study of the electrokinetic behavior of mica,⁹ the La^{3+} ion shows a strong adsorption to the surface. The result of this is a reversal in sign of the ζ potential at quite low concentrations of added LaCl_3 ($\leq 1 \times 10^{-5} \text{ mol dm}^{-3}$). An indication of the force balance results of Pashley⁹ is also shown in Figure 6 as a comparison of potentials obtained from an alternative technique. Both experiments predict a reversal in the sign of the potential at similar electrolyte concentrations.

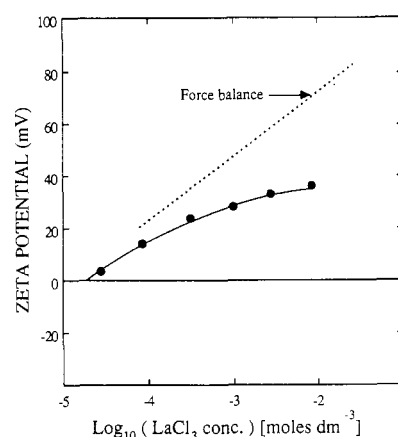


Figure 6. ζ potential of mica versus the concentration of lanthanum chloride at $\text{pH } 5.8 \pm 0.4$. The data of Pashley⁹ from force balance measurements is shown as a dashed line for comparison.

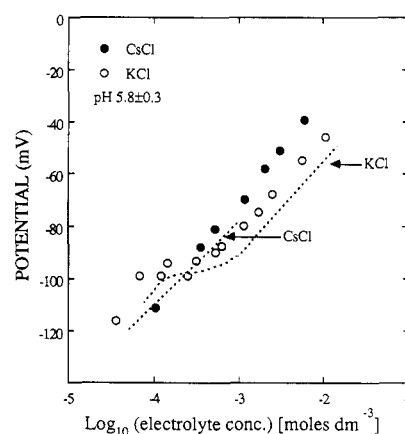


Figure 7. Comparison of the ζ potential of mica with potentials obtained from force balance measurements (ref 5). Dotted lines are force balance results.

A time-dependent variation in the ζ potential was observed at low additions of LaCl_3 , and because of this, 30 min of equilibration was allowed between measurements. Full equilibrium was probably not achieved in this time period, but this possibility was weighted against possible aging effects associated with mica experiments over extended periods.¹⁵

Comparison of Potentials Derived from Streaming Potential and Force Balance Techniques. The electrokinetic data presented are now compared with force balance derived potentials.^{5,8,9} To date, the relationship between data derived from both techniques has not been fully investigated.

Figures 7 and 8 compare the data of Pashley⁵ for 1:1 electrolyte ions exchanged to the mica surface with the electrokinetic data of this study. These data are for electrolyte concentrations between 1×10^{-5} and $1 \times 10^{-1} \text{ mol dm}^{-3}$ at pH 5.8 for aqueous solutions of CsCl and KCl and solutions of NaCl and LiCl , respectively. A similar comparison for aqueous solutions of CaCl_2 and LaCl_3 is shown in Figures 5 and 6, respectively.

Looking at the comparison of the 1:1 electrolyte data, and in particular, the data for CsCl and KCl , the agreement between the two techniques is excellent. This does not hold for the NaCl and LiCl data. A potential minimum in the force balance data at a concentration of $\approx 1 \times 10^{-3} \text{ mol dm}^{-3}$ for NaCl and of $\approx 1 \times 10^{-2} \text{ mol dm}^{-3}$ for LiCl is not observed in the streaming potential data. In general, the force balance technique predicts potentials

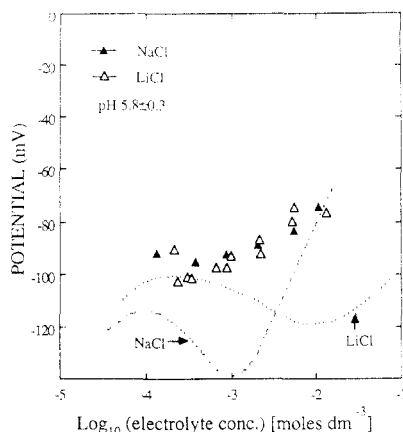


Figure 8. Comparison of the ζ potential of mica with potentials obtained from force balance measurements (ref 5). Dotted lines are force balance results.

of greater magnitude than the streaming potential technique. This is particularly the case at higher electrolyte concentrations. The difference is disturbing when one considers the similarities observed for the CsCl and KCl electrolyte species.

Speculation as to the reasons for the observed difference is warranted. The possibilities that come to mind are the viscoelectric effect proposed by Lyklema and Overbeek¹⁶ and insensitivities in the potential determination due to the highly charged nature of the mica surface.

For the viscoelectric effect, it was proposed that in the presence of high electric fields the viscosity of the solution at the surface of a particle is increased such that the position of the plane of shear is shifted outward from the surface. Under these circumstances, the analogy of $\Psi_d = \zeta$ is no longer valid. Lyklema and Overbeek¹⁶ proposed the existence of an observed electrokinetic potential, ζ_{obs} , that was different from the true electrokinetic potential, ζ . The relationship between these two potentials is controlled by a viscoelastic constant f . Lyklema and Overbeek proposed a value of the viscoelectric constant of $10.2 \times 10^{-16} \text{ V}^{-2} \text{ m}^2$; however, many workers believe their value to be an overestimate.¹⁷⁻²⁰ For the NaCl and LiCl ζ potential data, at low electrolyte concentrations ($\leq 1 \times 10^{-3} \text{ mol dm}^{-3}$), the magnitude of the potentials is such that the viscoelectric theory predicts an insignificant difference between ζ_{obs} and ζ , even for a value of f of the order of that proposed by Lyklema and Overbeek. At higher electrolyte concentrations, the force balance derived potentials are of a suitable magnitude to produce a difference between ζ_{obs} and ζ . By use of the LiCl force balance data as an example, good correlation is obtained between the force balance and the ζ potential data for a value of $f = 5 \times 10^{-16} \text{ V}^{-2} \text{ m}^2$.

Therefore, the viscoelectric theory produces agreement between the force balance and electrokinetic data for the LiCl electrolyte for a reasonable value of the viscoelectric constant, f . This same value of f predicts only minimal differences between ζ_{obs} and ζ for the CsCl and KCl electrolyte data. As noted, minimal differences are also predicted for all data at an electrolyte concentra-

tion of $1 \times 10^{-3} \text{ mol dm}^{-3}$. Since the minimum in the NaCl force balance data is at this electrolyte concentration, the agreement between the two techniques for these data is less encouraging.

The other possible cause of the difference in potentials is an insensitivity in the potential determination of both techniques to highly charged surfaces. Such a possibility cannot be ruled out, since breakdown in the Poisson-Boltzmann theory is expected for 1:1 electrolyte systems and surface charges greater than $\approx 20 \mu\text{C cm}^{-2}$.²¹ Nonetheless, any deviation between the two techniques should be systematic, and this is not the trend for the NaCl and LiCl data. Once again the NaCl force balance data are at odds with this analysis.

The data for the CaCl_2 and LaCl_3 solutions are shown in Figures 5 and 6, respectively. A divergence of the electrokinetic and force balance data is immediately obvious for potentials $\leq -20 \text{ mV}$ for the CaCl_2 solutions and $\geq 10 \text{ mV}$ for the LaCl_3 solutions.

The viscoelectric theory is of little help in resolving discrepancies in this case as the magnitude of the potentials is lower than for the 1:1 electrolyte case. Nonetheless, in support of the viscoelectric theory, the magnitude of the effect for divalent and trivalent electrolyte species has not been established. However, the divergence of the data is quite systematic, and this suggests a flaw in the analysis at a fundamental level for divalent and trivalent counterion species. In support of this statement, the correlation between the electrokinetic data of Lyons et al.² for CaCl_2 on mica and the data of this study appears too good to suggest major errors have occurred in the experimental electrokinetic analysis. The agreement of the data for both techniques at low potential is also too good to suggest the experiments were conducted under radically different experimental conditions. A breakdown in either or both of the techniques due to the highly charged nature of the surface is the most likely cause of the discrepancy.

Site Dissociation Model of the Mica-Solution Interface. The data presented in the preceding discussing reflect very well the ion-exchange nature of the mica surface, and a description of this behavior based on a single-site dissociation model is now considered. This idea has been put forward by numerous workers^{2,5-7} but has generally been complicated by aging effects² and the possibility of deposition of hydrolyzed silicon species from solution onto the mica surface.²² Since many of the predetermined constants required for a full theoretical description of the interface will change as a function of pH, perhaps irreversibly, such effects make a complete description as a function of both pH and electrolyte concentration impractical. However, an understanding of the charge-potential relationship for the interface may be obtained by looking at the present data where both aging and deposition effects are minimal.

Lyons et al.² in their study of the properties of the mica solution interface noted the following points on the effects of surface aging: (i) Aging at pH 10 in silica vessels produced a surface very similar in electrokinetic behavior to a pure silica surface after a number of days. This observation reflects the deposition of hydrolyzed silicon species onto the mica surface.²² (ii) Aging at pH 3 produced a surface that, upon pH increase, showed electrokinetic behavior reflecting the adsorption of aqueous alu-

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minium species or other hydrolyzable metal ions from solution.^{23,24} This was more pronounced for crushed, as distinct from sheet, mica. (iii) Aging at pH 7 was minimal. (iv) Aging at pH 4 was less significant in the presence of aqueous 1:1 metal ions such as potassium.

One can conclude from these observations that it is possible to attempt a theoretical description of the mica solution interface in the pH 5–8 regime, but outside of these pH limits, an adequate description in terms of a single surface mechanism is not possible. The use of a single-site dissociation model is based on the work of Goulding and Talibudeen,²⁵ who found that mica, unlike many other clay surfaces, has only one type of surface-exchange site.

The most widely encountered model of the edl using a Poisson–Boltzmann distribution of ions in the diffuse double layer and a GCSG-type approach to the inner double-layer region is the triple-layer model proposed by Yates et al.²⁶ This model assumes the edl to be divided into a diffuse and compact region, the latter of which is further divided into an inner and outer capacitive layer having dielectric constants D_1 and D_2 , respectively. The point of closest approach of hydrated double-layer ions is then the edge of the outer layer at a distance d from the surface (commonly referred to as the outer Helmholtz plane or OHP) and to a distance β , the edge of the inner region (commonly referred to as the inner Helmholtz plane or IHP), for bound ionic species. This double-layer model has an electroneutrality condition of the form

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \quad (2)$$

where σ_0 , σ_β , and σ_d are the charge densities at the surface, IHP, and OHP, respectively.

The charge generation process may then be represented as a simple surface site equilibrium given by



where S is a surface site and H^+ is assumed to be a potential-determining ion (pdi). The surface acid dissociation constant for the reaction is then

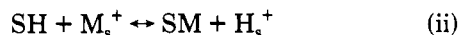
$$K_a = [\text{S}^-]a_s(\text{H}^+)/[\text{SH}] \quad (3)$$

where $a_s(\text{H}^+)$ is the activity of the hydrogen ion at the surface. Assuming a Poisson–Boltzmann distribution of ions, this may be related to the activity of similar species in the bulk by

$$a_s(\text{H}^+) = a_b(\text{H}^+) \exp(-e\psi_0/kT) \quad (4)$$

where $a_b(\text{H}^+)$ is the activity in the bulk and ψ_0 is the surface potential.

For the case of counterion binding, an additional surface equilibrium is proposed such that



where M^+ represents an aqueous metal ion and the surface binding constant is given by

$$*K_M = \left(\frac{[\text{SM}]a_s(\text{H}^+)}{a_s(\text{M}^+)[\text{SH}]} \right) \quad (5)$$

where as before

$$a_s(\text{M}^+) = a_b(\text{M}^+) \exp(-e\psi_\beta/kT) \quad (6)$$

where, as noted, ψ_β is the potential of the plane of closest approach of a counterion to the surface, obtained by using the analogy of James, Davis, and Leckie,²⁷ and $a_b(\text{M}^+)$ is the bulk electrolyte activity.

The surface charge is then given by

$$\sigma_0 = -e([\text{S}^-] + [\text{SM}]) \quad (7)$$

the charge at the IHP as

$$\sigma_\beta = e[\text{SM}] \quad (8)$$

and the total number of surface sites as

$$N_s = [\text{S}^-] + [\text{SH}] + [\text{SM}] \quad (9)$$

By use of the electroneutrality relationship of eq 5

$$\sigma_d = e[\text{S}^-] \quad (10)$$

If ions are bound such that any micropotential terms²⁸ can be neglected or are constant and assuming activities may be reasonably approximated by concentrations for dilute electrolyte systems, then

$$*K_M = \left(\frac{[\text{SM}][\text{H}^+]_b}{[\text{SH}][\text{M}^+]_b} \right) \exp\left(\frac{e\psi_\beta - e\psi_0}{kT}\right) \quad (11)$$

Then, by rearrangement, the surface concentrations of $[\text{SM}]$, $[\text{SH}]$, and $[\text{S}^-]$ may be found. From equations of Yates et al.²⁶ relating the potentials at the surface and using a suitable root-finding mechanism, the charge–potential relationship across the interface as a function of pH and electrolyte concentration may be computed.

A value of K_a , the acid dissociation constant, was obtained from a plot of the acidity quotient, $\text{p}Q_a$, versus pH by using the method of Sprycha and Szczypa.²⁹ The acidity quotient is given by

$$\text{p}Q_a =$$

$$\text{pH} + \log N_s - \log \left[\left(\frac{-2\kappa D\epsilon_0 kT}{e^2} \right) \sinh \left(\frac{e\zeta}{2kT} \right) \right] \quad (12)$$

where κ , D , and ϵ_0 have their usual meaning and ζ is equated to the OHP potential. This equation assumes N_s to be approximated by $[\text{SH}]$, the concentration of hydrogen-bound surface sites. For oxide surfaces with a high $\Delta\text{p}K_\pm$, this is a reasonable approximation, but for mica, this same assumption is equivocal and must first be tested before an unambiguous value of K_a can be obtained by the $\text{p}Q_a$ versus pH interpolation technique.

A plot of $\text{p}Q_a$ versus pH for a 1×10^{-3} mol dm⁻³ KCl solution is shown in Figure 9. It has been extrapolated to a pH of 3.0, corresponding to the iep of a typical silica-solution interface.³⁰ Although mica does not achieve an iep as would an oxide system, this is assumed to be largely due to aging effects, which are not significant in the pH 4–8 regime. Therefore, the plot is assumed valid for the mica-solution interface. Curve-linear interpolation as described by Sprycha and Szczypa²⁹ gives a $\text{p}K_a$ of 5.6 ± 0.2 . This is in reasonable agreement with the value of 6.0 obtained by Pashley⁵ for a similar system using the force balance technique, the latter value being obtained by fitting a simple site dissociation model to

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(25) Goulding, K. W. T.; Talibudeen, O. *J. Colloid. Interface Sci.* **1980**, *78*, 15.

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(28) Levine, S.; Smith, A. L. *Discuss. Faraday Soc.* **1971**, *52*, 302.

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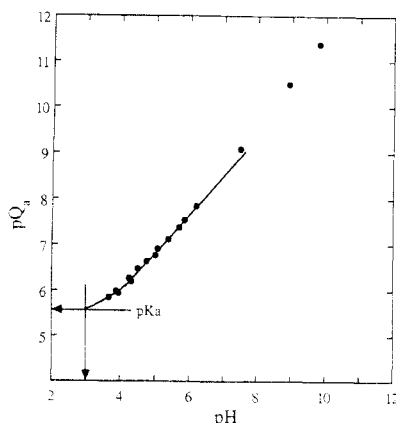


Figure 9. Plot of the acidity quotient (pQ_a) versus pH for mica in an aqueous solution of KCl at $0.001 \text{ mol dm}^{-3}$.

the data. The magnitude of the error in K_a is hard to judge in the absence of a full set of ζ potential data as a function of both concentration and pH. The validity of the assumption of $N_s \approx [\text{SH}]$ is discussed later.

Values for the counterion binding constant $*K_M$ and for the Cs^+ , K^+ , Na^+ , and Li^+ ions on mica have been proposed by Pashley.⁵ These were derived from the data of Goulding and Talibudeen²⁵ for K^+ ion displacement of Ca^{2+} ions on mica. Values of $p*K_M$ for Cs^+ , K^+ , Na^+ , and Li^+ were predicted to be 2.9, 2.5, 2.5, and 3.0, respectively. (These are in terms of $*K_M$, not K_M as quoted by Pashley.)

Interestingly, these values for $p*K_M$ are not in the same order of binding expected from the exchange of metal ions as noted in the measurement of the ζ potential. Pashley⁵ overcame this discrepancy by putting an ion size adsorption constraint on each ion to give the desired lyotropic series. This proved successful in the prediction of the shape of the observed potential versus electrolyte concentration curves at pH 5.8. Claesson et al.³¹ successfully used the same concept in their analysis of data for the adsorption of large organic ions to mica. The method, unfortunately, shows an extreme dependence on the value chosen for N_s , the number of ionizable sites per unit area. This might not seem an unreasonable constraint for a lattice charge system such as mica. After all, the value of N_s is well established, except that the pH dependence of the mica surface is predicted quite poorly.

An alternative theoretical method is to use the triple-layer model described earlier and obtain a fit to data through adjustments in the outer-plane capacitance. This same procedure was successful in the prediction, simultaneously, of both the charge and potential behavior of the silica-solution interface¹ and appears equally as valid as using an ion size parameter. The ion size parameter is related to a predicted ability of an ion to sit in a mica lattice hole, with hydrated ions larger than potassium excluded because of size constraints. On this basis, a model taking into account a different binding plane for small and large ions (i.e., a variable inner layer capacitance) seems more appropriate than constraining the area of each ion.

No values of $*K_M$ obtained by the double pQ_a extrapolation method of Davis and Leckie³² are available for mica. This has resulted in many values being obtained from simple fits to data and, therefore, a high model depen-

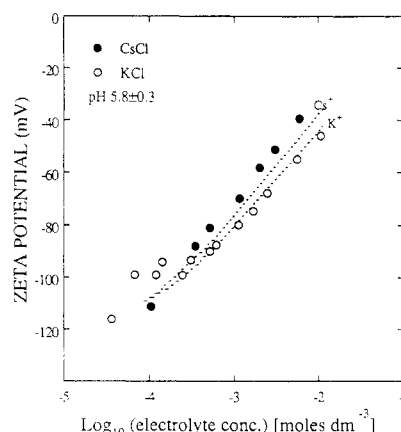


Figure 10. Comparison of the ζ potential of mica with potentials predicted by using a single-site dissociation model of the surface. Dotted lines are theory. Parameters used: $pK_a = 5.6$; pH 5.8; $p*K_M = 2.8(\text{Cs}^+)$, $3.2(\text{K}^+)$; $C_1 = 1000 \mu\text{F cm}^{-2}$; $C_2 = 200 \mu\text{F cm}^{-2}$.

dence. James and Parks⁶ calculated a $p*K_M$ for K^+ ions on a Putnam clay of 2.5. This is similar to the value obtained by Pashley.⁵ Yates et al.²⁶ showed that the free energy of adsorption (ΔG) of a counterion could be calculated as

$$\Delta G = -kT \ln *K_M \quad (13)$$

From ref 27, a $p*K_M$ value of 2.5 represents a free energy of adsorption of 14.0 kJ mol^{-1} at 20°C , a "disturbingly large value" as noted by Hunter.³³ He goes on to say that "this is more or less expected, considering the very high surface charge on clay minerals and the very low values of ζ -potential commonly measured." Nonetheless, there exists a mild dilemma as to the source of reasonable values for $p*K_M$ in the mica system.

This problem was partially solved by Claesson et al.,³⁴ who, taking the Cs^+ ion as an example, used a simple Gouy-Chapman model to fit the force balance derived potential data of Pashley⁵ and exchange data for the Cs^+ ion on mica. In so doing, they obtained a value for $p*K_M$ of 2.8. This value is probably a good starting point for the analysis, since no ion size constraint was used in its determination. Their use of a Gouy-Chapman model of the interface is the equivalent of assuming an infinite value for the inner- and outer-plane capacitances. Given the postulated ability of the less hydrated metal ions (i.e., cesium) to bind in close conjunction with the mica surface, possibly even in holes in the lattice structure, the plane of the surface and the plane of bound counterions are coincidental under these conditions, and a high value of the outer-plane capacitance (C_1) is considered reasonable. The outer-layer capacitance (C_2) may then be adjusted to obtain a fit to data and an estimate of the position of the shear plane relative to the surface. This is the only arbitrary fitting parameter used in the model.

A fit to the data for Cs^+ ion exchange on mica at pH 5.8 is shown in Figure 10. Values of $p*K_M = 2.8$, $C_1 = 1000 \mu\text{F cm}^{-2}$, and $C_2 = 200 \mu\text{F cm}^{-2}$ were used. Adjustment of the outer-layer capacitance has much the same effect as providing an ion size constraint, except that it has little or no effect on the theoretical degree of dissociation of the surface. A fit to the K^+ ion data was obtained

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(34) Claesson, P. M.; Herder, P.; Stenius, P.; Eriksson, J. C.; Pashley, R. M. *J. Colloid Interface Sci.* 1986, 109, 31.

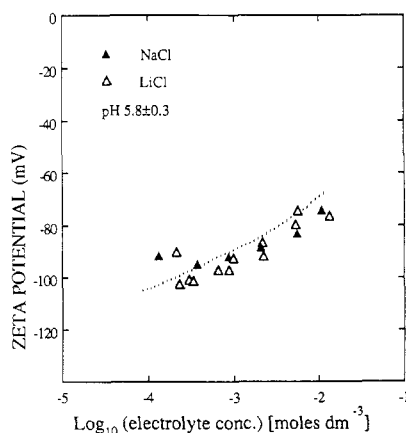


Figure 11. Comparison of the ζ potential of mica with potentials predicted by using a single-site dissociation model of the surface. Dotted lines are theory. Parameters used: $pK_a = 5.6$; $pH = 5.8$; $p^*K_M = 5.5$; $C_1 = 1000 \mu F cm^{-2}$; $C_2 = 200 \mu F cm^{-2}$.

with a p^*K_M value of 3.2 keeping all the other input parameters constant. This fit is also shown in Figure 10.

The data for Na^+ and Li^+ are not as easily analyzed if one considers the data of Claesson et al.³⁴ for the exchange of Na^+ ions on mica. To fit the potential data requires a p^*K_M value of 5.5, and in so doing, the exchange data of Claesson et al.³⁴ are underestimated. The fit to the data is shown in Figure 11. This p^*K_M value reflects less specificity of the Na^+ and Li^+ ions for the mica surface and a more positive free energy of adsorption. This supports the postulate that these ions are excluded from a close association with the surface sites. There is no suitable value of p^*K_M (using this model) to fit the force balance potential data of Pashley⁵ for the binding of the Li^+ counterion. As speculated, there are a number of reasons for the observed discrepancies in the data sets.

While the method of Pashley of invoking an ion size constraint does produce a fit to data at pH 5.8, the pH dependence and free energy of adsorption for the various 1:1 metal ions on mica are better considered by using

a GCSG model. The discrepancies between the electrokinetic and the force balance measurements may also be reconsidered in the light of the modeling data. Given that no value of p^*K_M is applicable to the Li^+ and Na^+ force balance data, one needs not only to question the possibility of a breakdown in the Poisson-Boltzmann theory but also the possibility that the force balance and streaming potential techniques predict the potential of different surface planes under conditions of very low counterion binding or where the hydrated ion is excluded from close association with the surface.

Conclusions

The mica surface, on the basis of this modeling exercise, does behave as a single-site dissociation (exchange) surface which may be adequately but not completely described by a constant set of input parameters to the triple-layer model. The difference between mica and many oxide surfaces is highlighted in the counterion binding constants required to obtain a fit to the electrokinetic data as a function of both pH and aqueous electrolyte concentration. The high specificity of the Cs^+ and K^+ ions for the surface is also highlighted. This specificity is assumed to be primarily due to an ability of these ions to fit into lattice holes. The data for Li^+ and Na^+ suggest a vastly lower specificity of these ions for the mica surface. This is equated to the more hydrated nature of these ions in solution and an inability, due to size constraints, to bind closely with surface lattice sites.

The comparison of the ζ potential data of this study with force balance derived potentials shows reasonable correlation for 1:1 electrolytes but divergence for 2:1 and 3:1 electrolyte systems. The solution to this problem may well be associated with self-atmosphere effects³¹ that are not accounted for in the Poisson-Boltzmann description of the ion distribution about a charged surface. As discussed, these effects are expected to be minimal for 1:1 electrolyte systems at low surface charge densities but may be important to the mica surface under specific ionic conditions. Included in these conditions are divalent and trivalent counterion systems.