# ELECTROMOBILITY OF MICA PARTICLES DISPERSED IN AQUEOUS SOLUTIONS

R. M. PASHLEy <sup>l</sup>

Department of Chemical Engineering, Princeton University Princeton, New Jersey 08544

Abstract-Mobility measurements were made for dry-ground mica particles dispersed in aqueous KCI,  $Cr(NO<sub>3</sub>)<sub>3</sub>$ , and cetyltrimethylammonium bromide (CTAB) solutions. In the latter solutions charge reversal occurred at about  $2 \times 10^{-6}$  M and  $3 \times 10^{-5}$  M, respectively. Negative zeta potentials in KCI solutions calculated using the Smoluchowski equation are about one third of the corresponding values obtained from streaming potentials and force measurements using mica sheets. Good agreement, however, was obtained when positively charged groups created during grinding were neutralized, and the zeta potentials were corrected accordmg to the procedure of O'Brien and White with an assumed average particle size of 0.25  $\mu$ m. When the zeta potentials of positively charged particles were corrected in this way, agreement with values calculated from force measurements was also improved.

Key Words-Electromobility, Force measurements, Mica, Smoluchowski equation, Streaming potential.

### INTRODUCTION

The properties of clay-size muscovite have come under increased scrutiny in recent years because of the use of large (square centimeter size) cleaved sheets in the direct measurement ofDerjaguin, Landau, Verwey, and Overbeek (DLVO) and "solvation forces" in aqueous solutions by Israelachvili and Adams (1978) and Pashley (1981a, 198Ib). The results of these force experiments show that the DLVO theory is generally accurate in dilute electrolyte solutions  $(\leq 10^{-2}$  M, depending on the electrolyte), but that at higher concentrations short-range  $(\leq 50 \text{ Å})$  non-DLVO forces arise. In such experiments the ion-exchange properties of the mica basal plane determined the nature of both the diffuse double-layer forces and the observed solvation forces (see Pashley, 1981a). In dilute solutions where the forces can be accurately fitted by diffuse double-layer theory, an apparent surface potential can be calculated, because the Debye length of the solution is known. The variation of this potential with concentration and type of electrolyte gives a measure of ion adsorption at the mica surface and has been successfully described using a simple mass-action model by Pashley and Quirk (1984).

This variation suggests that the mica basal plane is an almost ideal ion-exchange surface with only one type of surface site, a conclusion which was also reached by Goulding and Talibudeen (1980) from direct ionexchange measurements. Thus, the diffuse double-layer potential and charge observed on mica immersed in an aqueous electrolyte solution depend on the relative

concentrations and surface adsorption energies of hydronium ions and any other cations present in solution. These cations adsorb on the negative sites on the mica basal surface which are present at the high density of about 2.1  $\times$  10<sup>14</sup>/cm<sup>2</sup> (Gaines and Tabor, 1956). Hence, for complete neutralization a monovalent cation must adsorb at a coverage of one ion per  $48 \text{ Å}^2$ . Thus, even for quite a high surface potential ( $\sim$ 100 mV) in dilute monovalent electrolyte solution ( $\sim 10^{-5}$  M), nearly all of these sites must be filled with adsorbed ions, and, in general, the diffuse layer charge is much less than the mica lattice charge (see Pashley, 198Ia).

In addition to the force method of obtaining surface potentials on mica, Lyons *et a/.* (1981) used a radialflow streaming potential apparatus to obtain zeta potentials on large mica sheets immersed in KCl, HCl, and CaCl, solutions. The potentials measured in KCl and CaCl<sub>2</sub> solutions agree closely with those obtained from the force measurements, although in HCl solution the force method gave significantly higher potentials (Pashley, 1981 b). The results from these quite different methods generally indicate good agreement and show that the basal plane is indeed capable of ion-exchange with a wide range of cations, as was also observed by Gaines (1957) and by Mokma *et al.* (1970) from ionexchange studies on mica powders.

The ion-exchange properties of clays in general make them of some interest with respect to the effect of the diffuse double-layer potential on their water-swelling properties. Friend and Hunter (1970) measured electromobilities of Li<sup>+</sup>-vermiculite particles in an attempt to relate the observed zeta potential with the doublelayer swelling pressures observed by Norrish and Rausell-Colom (1963). The mobilities were found to vary in a complex manner with concentration and gave zeta potentials of much lower magnitude ( $\sim$  -75 mV) than

<sup>&</sup>lt;sup>1</sup> On leave from Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra, ACT 2601, Australia.

required to explain the observed swelling pressures, even though the pressures decayed with separation as expected from double-layer theory. In earlier work, Low (quoted by Friend and Hunter, 1970) also reported that mobilities of Na<sup>+</sup>-montmorillonite particles are not a simple function of concentration.

More recently Low (1981) measured mobilities of a wide range of Na<sup>+</sup>-montmorillonite samples in  $10^{-4}$ M NaCl. The zeta potentials calculated from these results using the Smoluchowski equation were mostly about  $-60 \pm 10$  mV. Low compared these potentials with measurements on the swelling of Na-montmorillonite (Viana *et al.,* 1983) and concluded that even at quite large water-film thicknesses ( $\geq$ 100 Å) the pressures are substantially higher than could be explained by a double-layer interaction using these potentials.

In addition to the observation that the magnitude of zeta potentials obtained from mobility measurements on montmorillonite and vermiculite particles are much lower than expected from swelling studies, the potentials also do not decrease in magnitude as the adsorbing cation concentration is increased, contrary to what is expected for an ion-exchange type surface. Also, coion exclusion measurements on montmorillonite and illite clays for a wide range of cations indicate quite constant surface potentials over a concentration range of 0.3 to 0.003 M (see Chan *et aI.,* 1984). Callaghan and Ottewill (1974) obtained constant zeta potentials  $(-47 \pm 3 \text{ mV})$  from mobility measurements on Na<sup>+</sup>montmorillonite particles in NaCl solutions from  $10^{-1}$ to  $10^{-4}$  M. If only cations adsorb at the basal plane surface, as shown by Bolt and Wakentin (1958), then in order for the potential to remain constant these adsorbed ions must de-sorb as their concentration in bulk solution increases, in contradiction with the laws of mass action.

Clearly the charging properties of clay particles have so far eluded any simple interpretation in terms of ionexchange models and, in addition, are at variance with the pressures observed during clay swelling. In an attempt to solve some of these problems for mica, mobilities in a range of electrolyte solutions were measured and the calculated zeta potentials were compared with those obtained by the force and streaming potential methods.

Fundamental differences exist, of course, between the investigation of the basal plane surface and of mica particles. One difference is that the particles have edges which are likely to influence the overall mobility. Also, during the grinding process different surface sites may be created on the basal plane which might affect the charge of the particle. In an earlier investigation of the mobility of wet-ground mica, Lyons *et al.* (1981) concluded that at high and low  $pHs$  (3 and 10) mica particles aged quite rapidly  $($  < 1 day), whereas in neutral solutions aging was very slow. The aging effects were most likely due to the presence of hydrolyzable  $Al^{3+}$ 



Figure I. Scanning electron micrograph of coarse, dry-ground mica flakes. A wide size distribution of plate-like particles was observed.

presumably created from dissolution of the edges and from damage during wet grinding. To reduce these problems in the present study, the mica was dry ground and all measurements were carried out in solutions at  $pH \sim 5.7$ .

### MATERIALS AND METHODS

The mica particles were produced by dry grinding clean sheets of freshly cleaved, brown muscovite from Bihir, India, using a porcelain mortar and pestle. A typical composition of this mica was given by Israelachvili and Adams (1978). The brown mica became slightly grey-white on grinding. The dry-grinding procedure produced a polydisperse powder as shown by scanning electron microscopy (SEM) (Figure 1). It is clear from electron microscopic examination that the grinding process produced a wide size range of platelike particles. The ground mica was dispersed in water  $(-0.05\% \text{ wt./vol.})$ , and after 2 hr, a droplet was removed from the dispersion and slowly allowed to evaporate to dryness on an adhesive support. Typical SEMs of the sedimented and dried powder are shown in Figures 2 and 3. It is clear from these photographs that the size range of the dispersed particles was much narrower than for the dry ground powder and that the particles were mostly in the sub-micrometer size range. Also, although the clarity is not as sharp as for the dry ground sample (presumably because of concentration of solution contaminants and clumping on evaporating to dryness), the particles are generally plate-like with



Figure 2. Scanning electron micrograph of dispersed mica fraction after 2 hr in water. Solution was evaporated to dryness to obtain the photograph. Distribution of particle sizes is much narrower than in the original ground sample.

sharp, angular edges. Typical particle dimensions are  $\sim$ 0.5  $\mu$ m diameter and  $\leq$ 0.05  $\mu$ m thickness. The SEMs support the assumption that the basal plane surface accounts for most of the surface area of the powder.

The dispersions used for all of the mobility measurements (unless stated otherwise) were prepared by dispersing about 0.2 mg of mica powder in 20 ml of aqueous solution. This low concentration  $(\sim 0.001\%)$ wt./vol.) was used to reduce the possibility of contamination from the mica powder itself. Mobilities were measured at 25°C using a rectangular quartz cell in a Rank Brothers MKII microelectrophoresis apparatus with Ag/AgCl electrodes. Measurements were made after 2-4 hr and 24 hr. For the 24-hr measurements the dispersion was lightly shaken to increase the particle number density for measurement. About 20 particles were measured, which were not sedimenting during the time scale of the measurements, typically 5-10 min. The particles were observed using dark-field illumination, and the voltage was reversed for each measurement to prevent polarization effects. Unless stated otherwise, the aqueous solution was equilibrated with the  $CO<sub>2</sub>$  in the atmosphere and typically had a pH of  $\sim$  5.7. The dispersions were prepared in Pyrex glass testtubes with a coverlet to protect from dust, but still allowing  $CO<sub>2</sub>$  equilibrium. All salts used were of analytical grade, and the solutions were made up using water purified by treatment with activated charcoal and a mixed-bed ion-exchange resin.



Figure 3. Scanning electron micrograph of 2-hr-dispersed fraction at higher magnification. Particles are generally platelike; most are  $\sim$  0.5  $\mu$ m across.

### RESULTS AND ANALYSIS

# *KCI solutions*

Mobility measurements of mica particles in a range of KCl solutions at  $pH = 5.7$  are given in Figure 4. The mobilities are listed both in terms of a dimensionless mobility E and of the corresponding apparent zetapotential  $\langle \zeta \rangle$  calculated using the Smoluchowski equation:

$$
\zeta = 4\pi \eta \mu/\epsilon = 2EkT/3q, \qquad (1)
$$

where

$$
E = 6\pi \eta q \mu / \epsilon k T, \qquad (2)
$$

and  $\mu$  is the mobility of the particles,  $\eta$  is the viscosity,  $\epsilon$  the dielectric constant, and q the electronic charge. For aqueous solutions at  $25^{\circ}$ C, Eqs. (1) and (2) are simply:  $\zeta$  (mV) = 12.8 $\mu$  and E = 0.75 $\mu$ , where  $\mu$  is in units of  $\mu$ m/sec per volt/cm. The potential calculated by Eq. (1) is valid for spherical particles when  $\kappa a \geq$ 200 (where  $\kappa^{-1}$  is the Debye length and a is the radius of the particle), that is, where the surface is essentially flat relative to the thickness of the diffuse double layer.

The potentials calculated from the mobility measurements are compared in Figure 4 with those obtained from both force measurements and streaming potentials. The mobility potentials were within 3 mY over a period of 2-4 and 24 hr after dispersion in all the solutions studied, indicating no significant timedependent effects. The zeta potentials calculated for



Figure 4. Comparison of the zeta potentials calculated using the Smoluchowski equation with the values obtained from force measurements (Pashley, 1981a) and streaming potentials (Lyons *et al.*, 1981) for mica in KCl solutions. Dashed line corresponds to the expected behavior of an ion-exchange surface (see text).

the mica particles are much lower than those obtained from the other methods and, in addition, show a marked plateau from  $10^{-3}$  M to "pure water." The results obtained here agree quite closely to those reported by Leiner (1973). Although the mobility zeta potentials are consistently about one third of those determined by other methods, all three series of measurements seem to indicate charge neutralization at about the same concentration  $(\sim 0.1 - 0.2 \text{ M})$ .

In addition to the close agreement between the force and streaming potential methods, these potentials are also well described by simple mass-action adsorption. Thus, the adsorption can be assumed to be given by the equations:

$$
K_{M+} = [S^-][M^+]_S/[SM]
$$
 (3)

and

$$
K_{H+} = [S^-][H^+]_S/[SH],
$$
 (4)

where  $K_{H+}$  and  $K_{M+}$  are the dissociation constants for adsorption of hydronium and potassium ions, respectively. [S-], [SM], and [SH] are the surface densities of unfilled negative adsorption sites and sites filled by  $K^+$ and  $H^+$  ions, respectively.  $[M^+]_S$  and  $[H^+]_S$  are the concentrations of the ions in solution just next to the mica surface. Combination of these equations with the Gouy-Chapman theory for the diffuse-layer charge, the equation

$$
\sigma_{\rm D} = -(\epsilon k T/2\pi q) \kappa \sinh(q\zeta/2kT), \qquad (5)
$$

gives an accurate description of the potential behavior (see Figure 4).

The fact that the simple ion-exchange model cannot explain the mobility results lends further support to

the suggestion that the properties of the particles do not correspond to the properties of the mica basal plane. This result may be due to: (1) the effects of adsorption of contaminants created by grinding, such as  $Al^{3+}$  and  $Fe<sup>3+</sup>$ , (2) the possibility of positively charged aluminatype sites on the face and edges of the particles, (3) the non-spherical shape of the particles, and (4) the assumption that  $k = 200$  is not valid. To test the first two possibilities, mobility measurements were carried out on mica particles treated in several ways. First, 0.1 to 0.01 times more dilute dispersions were made up in  $10^{-4}$  M KCl in an attempt to vary the degree of contamination. In each dispersion the mobilities were constant (to about  $\leq$ 2 mV). Second, mica powder was dispersed in water, then centrifuged, the clear solution run off, and the process repeated ten times. The potential of the final dispersion was within  $2 \text{ mV}$  of the original sample.

Clearly, no easily desorbed contaminants were present to reduce the mobility of the particles; however, positive sites in the basal plane and at the edges of the particles could have been present due to exposed AI-OH groups. Inasmuch as alumnina has a p.z.c. at pH  $\sim$ 9, the effect of these positively charged groups should have been removed at high pH. To test this possibility, mobility measurements were carried out in  $10^{-3}$  M KCl at a pH of 9.1 (by addition of KOH). The zeta potential at this pH was increased in magnitude from  $-37$  to  $-48 \pm 2$  mV. Although the increase was not sufficient to bring the potentials in line with the results from the other methods, it suggests that a small fraction of alumina-like sites must have existed on the particles. As a further test of this possibility, mobilities were measured in  $10^{-3}$  M KCl solutions containing  $10^{-4}$  M sodium dodecyl benzene sulphonate. Anionic surfactants do not adsorb on the basal planes of mica sheets (O'Connor and Saunders, 1956), but they may well adsorb on positively charged alumina sites. The zeta potential increased in magnitude from  $-37$  to  $-47$ mV, again indicative of a small but significant fraction of positive sites on the ground mica particles. These simple tests indicate that although there were most likely scattered positively charged sites on the particles (at pH  $\sim$  5.7), these sites were not solely responsible for the low apparent potential obtained from mobility measurements.

# *Cr(NO)j solutions*

The mobility measurements in  $Cr(NO<sub>3</sub>)<sub>3</sub>$  solutions are shown in Figure 5. Adsorption of  $Cr<sup>3+</sup>$  ions apparently caused charge-reversal at the low concentration of  $2 \times 10^{-6}$  M, presumably because of the substantially increased trivalent cation concentration next to a negatively charged surface. Potentials obtained from direct force measurements (Pashley, 1984) in  $Cr(NO<sub>3</sub>)<sub>3</sub>$  solutions are also given in Figure 5 for comparison. The two methods appear to agree much more



Figure 5. Zeta potentia1s calculated using the Smoluchowski equation from the electromobilities of mica particles in  $Cr(NO<sub>3</sub>)<sub>3</sub>$  solutions. Some values for the potentials obtained from the force method are also given. Dashed line corresponds to the expected behavior for an ion-exchange surface at a constant pH (see text).

closely than those conducted in KCl solutions, and at  $10^{-5}$  and  $10^{-3}$  M they differed by only about 10 mV. The dashed line in Figure 5 corresponds to a massaction model similar to that already discussed. At higher concentrations ( $\geq 10^{-3}$  M) the observed potentials should fall well below the theoretical curve because of hydrolysis effects which reduce the pH and hence increase hydronium adsorption at the mica surface.

# *Cetyltrimethylammonium bromide (CTAB) solutions*

Mobility measurements in CTAB solutions are given in Figure 6. CTA $+$  ions apparently adsorbed so as to neutralize the surface at a concentration of about 3  $\times$  $10^{-5}$  M. Pashley and Israelachvili (1981) measured adsorption layer thickness for CTA<sup>+</sup> ions on mica and found that monolayer adsorption occurred at concentrations between  $3 \times 10^{-5}$  and  $7 \times 10^{-5}$  M and bilayer adsorption at about the critical micelle concentration  $({\sim}10^{-3}$  M). The steeply rising mobilities on the positive side of the graph correspond well with such stepped adsorption.

Using the force method for the interaction of CTAB bilayers adsorbed on mica sheets, a potential of  $+60$ mV was measured in  $4 \times 10^{-3}$  CTAB solution, where the effect of the background electrolyte  $(\sim 10^{-3}$  M) should have been small (Pashley and Israelachvili, 1981). This value agrees closely with the zeta potential calculated from the mobility measurements using the Smoluchowski equation. From an analysis of diffuse double-layer interactions in CT AB soap films, Donners *et al.* (1977) obtained surface potentials in the range  $+60$  to  $+90$  mV for the bilayer surface.

# DISCUSSION

The above results indicate that positively charged mica particles have mobilities reasonably close to those



Figure 6. Zeta potentials calculated using the Smoluchowski equation from the electromobilities of mica particles dispersed in cetyitrimethylammonium bromide solutions. Some values obtained from the force method are also given. Stepped part of the curve at positive potentials appears to correspond to monolayer and bilayer adsorption.

expected from experiments on the basal plane of mica, whereas negatively charged particles have much lower mobilities. At first sight these observations point to the presence of positive (alumina-like) sites on the particles; however, attempts to neutralize these sites caused only a small increase in the magnitude of the low negative potential. Also, the concentration at which charge neutralization occurred for each of the electrolytes studied in the mobility measurements is similar to that obtained by the other methods, which suggests that the chemistry involved in charging the particle was similar to that on the basal plane surface. These observations suggest that the deviations for negatively charged particles may have been due to an incorrect assumption that  $\kappa a \geq 200$ .

O'Brien and White (1979) published numerical solutions relating observed particle mobilities to zeta potentials over the full range of ka values (i.e.,  $0 \rightarrow \infty$ ). For spherical particles in KCl solution with a  $\kappa a$  of about 2-5, a plateau was observed for potentials above  $\sim$ 100 mV. At higher values of  $\kappa$ a a maximum was always observed which had a significant effect even at  $\kappa a \sim 100$  for high potential surfaces. The results of this numerical analysis can be applied precisely only to spherical, mono-disperse colloids of known radius. In the present study the size and shape of the particles were roughly known; however, the appropriate mean value of the particle radius, (a), was not.

It is possible, of course, to estimate a value of  $\langle a \rangle$ which would give zeta potentials in good agreement with the other methods, if such a value exists. To test this possibility, the mobility data in KCl solutions must be re-examined, where SDBS adsorption has removed or reduced the effect of positively charged sites. For example, in  $10^{-2}$  M,  $10^{-3}$  M, and  $10^{-4}$  M KCl with added SDBS the reduced mobilities (E) are 2.05, 2.75,

and 2.75, respectively. Using Figure 4 from O'Brien and White (1979) and an estimated  $\langle a \rangle$  value of 0.12  $\mu$ m, the corresponding zeta potentials would be about  $-40$  mV at  $10^{-2}$  M,  $-65$  mV at  $10^{-3}$  M, and  $-85$  mV at  $10^{-4}$  M, which are in reasonable agreement with the values obtained by the other methods.

It should be noted that the calculated curves of O'Brien and White are for a positively charged surface in KCI solution, whereas a negative surface has been used in the present experiments. Because the mobilities of  $K<sup>+</sup>$  and Cl<sup>-</sup> ions are almost identical, their use should have introduced only negligible error. Also, the solutions used in these experiments had a background electrolyte of about  $10^{-5}$  M due to dissolved  $CO<sub>2</sub>$  and ions from glassware and the ground particles themselves. Consequently, only concentrations of KCI at or greater than about  $10^{-4}$  M should have influenced the zeta potential of the particles. Hence, it is not surprising that the potential remained constant on diluting below  $10^{-5}$  M KCl.

Because the effective  $\langle a \rangle$  value should be roughly constant from solution to solution, it can be used to re-calculate the positively charged potentials where, in addition, no correction is needed for positively charged sites on the mica. Although the curves given by O'Brien and White (1979) refer only to KCI, because the counterion is most important one can at least estimate corrected positive zeta potentials in  $Cr(NO<sub>3</sub>)<sub>3</sub>$  and CTAB solutions. Using the  $\langle a \rangle$  value already derived, the potentials in  $Cr(NO<sub>3</sub>)<sub>3</sub>$  solutions increase between +5 and  $+10$  mV, which brings them much closer to those obtained from the force measurements. Similarly, in CT AB solutions the positive potentials increase uniformly by about  $+15$  mV with the curve still showing the stepped feature. The corrected potentials are then well within the range of values reported for CTAB soap films and close to the values obtained from the force measurements between adsorbed bilayers on mica.

Although the corrected potentials calculated using this value of  $\langle a \rangle$  are reasonable and consistent, the problem remains as to how one can independently justify its use. As mentioned above, the particles measured were non-settling and appeared from electron micrographs to be plate shaped with typical dimensions  $0.5 \times 0.05 \mu$ m. An effective diameter of  $\sim 0.25$  $\mu$ m is well within the size range of the asymmetric particles, but no adequate justification exists for its use other than that it leads to calculated zeta potentials that are in good agreement with those obtained from other independent methods. Indeed, for a perfectly flat, thin 'platelet the Smoluchowski equation should be valid and almost independent of the particle size. Hence, no theoretical justification exists for using an apparent spherical diameter related to the size of the particle; however, these comments apply only when the diffuse double-layer remains at equilibrium, perpendicular to the flat surface, which would not be the case if the

<https://doi.org/10.1346/CCMN.1985.0330304>Published online by Cambridge University Press

rotation of the particle approached the relaxation time for the double-layer. Such a dynamic effect may introduce an effective diameter related to the size of the particle.

Perrin (as discussed by Berne and Pecora, 1976) derived an equation for the rotational diffusion time of macroscopic plate-like particles, which for dry-ground mica in water will be of the order of  $1$  usec. Assuming that the ions in the diffuse double-layer will follow a rotation of the particle under a diffusion gradient similar to that in the double-layer, relaxation times of the order of  $1$  usec are achieved. These crude estimates indicate that an effective spherical diameter could be introduced because of the asymmetry of the particles. If this suggestion is correct, it follows that the mobilities of clay particles cannot be simply related to the potential obtained from clay swelling studies.

# **CONCLUSIONS**

Zeta potentials calculated from the electromobilities of dry-ground mica particles using the Smoluchowski equation are in reasonable agreement with potentials obtained by other methods only when the particles are positively charged. The much larger differences observed for negatively charged particles are, in part, due to the presence of positively charged sites. Once these sites have been neutralized, the remaining disagreement can be explained by assuming an effective particle diameter of about 0.25  $\mu$ m. It is apparent from these results that under certain conditions zeta potentials calculated using the Smoluchowski equation may not be valid for plate-like particles, an observation which will be of particular relevance to the study of clay minerals.

#### ACKNOWLEDGMENT

Partial support of this work by NSF grant CPE82- 12317 is hereby acknowledged.

### REFERENCES

- Berne, B. J. and Pecora, R. (1976) *Dynamic Light Scattering:* Wiley, New York, 143-144.
- Bolt, G. H. and Wakentin, B. P. (1958) The negative adsorption of anions from clay suspensions: *Colloids* 156, 41- 46.
- Callaghan, I. C. and Ottewill, R. H. (1974) Interparticulate forces in montmorillonite gels: *Farad. Disc. Chem. No.* 57, 110-118.
- Chan, D. Y. C., Pashley, R. M., and Quirk, J. P. (1984) Surface potentials derived from co-ion exclusion measurements on homonionic montmorillonite and illite: *Clays & Clay Minerals* 32, 131-138.
- Donners, W. B. A., Rinjbout, J. B., and Vrij, A. (1977) Light scattering from soap films: *J. Colloid Interface Sci. 61,*  249-260.
- Friend, J. P. and Hunter, R. J. (1970) Vermiculite as a model system in the testing of double-layer theory: *Clays* & *Clay Minerals* 18, 275-283.
- Gaines, G. L. (1957) The ion-exchange properties of muscovite mica: *J. Phys. Chem.* 61, 1408-1413.
- Gaines, G. L. and Tabor, D. (1956) Surface adhesion and elastic properties of mica: *Nature* 178,1304-1305.
- Goulding, K. W. T. and Talibudeen, O. (1980) Heterogeneity of cation-exchange sites for K-Ca exchange in aluminosilicates: *J. Colloid Interface Sci.* 78, 15-24.
- Israelachvili, J. N. and Adams, G. E. (1978) Measurement of forces between two mica surfaces in aqueous electrolyte solutions in the range 0-100 nm: *J. Chem. Soc. Faraday Trans. 174,975-1001.*
- Leiner, W. (1973) Bestimmung der Bindungsenergien der K+-Ionen in der Spaltflache von Muskovit aus elektrokinetischen Daten: in *6th Int. Congress on Surface Active Substances, Stuttgart, Germany,* 1972, Verlag, Munich, 45- 54.
- Low, P. F. (1981) The swelling of clay: Ill: *J. Soil Sci. Soc. A mer.* 45, 1074-1078.
- Lyons, J. S., Furlong, D. N., and Healy, T. W. (1981) The electrical double-layer properties of the mica (muscovite) aqueous electrolyte interface: *Aus. J. Chem.* 34,1177-1187.
- Mokma, D. L., Syers, J. K., and Jackson, M. L. (1970) Cation exchange capacity and weathering of muscovite macroflakes: *Soil Sci. Soc. Amer. Proc.* 34, 146-151.
- Norrish, K. and Rausell-Colom, J. A. (1963) Low angle X-ray diffraction studies of the swelling of montmorillonite and vermiculite: in *Clays and Clay Minerals, Proc. 10th Nat!. Con!, Austin, Texas,* 1961, Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 123-490.
- O'Brien, R. W. and White, L. T. (1978) Electrophoretic mobility of a spherical colloidal particle: *J. Chem. Soc., Faraday* //, 74, 1607-1626.
- O'Connor, D. J. and Saunders, J. V. (1956) Hydrophobic monolayers on platinum, mica, and silica: *J. Colloid Sci.*  11, 158-166.
- Pashley, R. M. (1981a) DLVO and hydration forces between mica surfaces in  $Li^+$ , Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> electrolyte solutions: *J. Colloid Interface Sci.* 83, 531-546.
- Pashley, R. M. (1981b) Hydration forces between mica surfaces in aqueous electrolyte solutions: *J. Colloid Interface Sci.80, 153-162.*
- Pashley, R. M. (1984) Forces between mica surfaces in  $La^{3+}$ and Cr<sup>3+</sup> electrolyte solutions: *J. Colloid Interface Sci.* (in press).
- Pashley, R. M. and Israelachvili, J. N. (1981) A comparison of surface forces and interfacial properties of mica in purified surfactant solutions: *Colloids and Surfaces* 2, 169- 187.
- Pashley, R. M. and Quirk, J. P. (1984) The effect of cation valency on DLVO and hydration forces between macroscopic sheets of muscovite mica in relation to clay swelling: *Colloids and Surfaces* 9, 1-17.
- Viani, B. E., Low, P. F., and Roth, C. B. (1983) Direct measurement of the relation between interlayer force and interlayer distance in the swelling of montmorillonite: *J. Colloid Interface Sci.* 96, 229-244.
- *(Received* 24 *April* 1984; *accepted* 12 *August* 1984; *Ms.*  1356)

Резюме-Измерения мобильности были сделаны на сухо-растертых частицах слюды, диспергированных в водных растворах KCl, Cr(NO<sub>3</sub>)<sub>3</sub> и цетилтриметиламмиачного бромида (ЦТАБ). В последних растворах реверсирование заряда происходило при концентрациях  $2 \times 10^{-6}$  M и  $3 \times 10^{-5}$  M, соответственно. Отрицательные зета потенциалы в растворе KCl, вычисленные по уравнению Смолуговского, равны примерно одной трети соответствующих величин, полученных из текущих потенциалов и силовых измерений, используя пластинки слюды. Хорошее соответствие, однако, получалось, когда положительно заряженные группы, образованные в течение растирания, нейтрализовались, а потенциалы зета корректировались соответственно при помощи процедуры О'Браяна и Уайта, предполагая средний размер частиц равен 0,25 µm. После коррекции потенциалов зета положительно заряженных частиц при помощи этого метода, также улучшилось согласие с величинами, полученными по измерениям силы. [E.G.]

Resiimee-Mobilitatsmessungen wurden an trocken gemahlenen Glimmerpartikeln durchgeftihrt, die in wässrigen KCI-,  $Cr(NO<sub>3</sub>)<sub>3</sub>$ -, und Cetyltrimethylammoniumbromid-Lösungen (CTAB) dispergiert waren. In den letzteren Lösungen trat bei etwa  $2 \times 10^{-6}$  m bzw.  $3 \times 10^{-5}$  m, Ladungsumkehr auf. Negative Zeta-Potentiale in den KCI-Losungen, die mit der Smoluchowski-Gleichung berechnet wurden, betragen etwa *lh* der entsprechenden Werte, die aus den Stromungspotentialen und Kraftmessungen unter Verwendung von Glimmerbllittchen erhalten wurden. Eine gute Ubereinstimmung wurde jedoch erreicht, wenn man positiv geladene Gruppen, die wahrend des Mahlens entstanden sind, neutralisierte, und die Zetapotentiale nach der Methode von O'Brien und White korrigierte unter der Annahme, da8 die durchschnittliche Partikelgröße 0,25  $\mu$ m beträgt. Wenn die Potentiale der positiv geladenen Teilchen auf diese Art korrigiert wurden, dann wurde auch die Ubereinstimmung mit den aus den Kraftmessungen berechneten Werten verbessert. [U.W.)

Résumé-On a mesuré la mobilité de particules de mica moulues-sèches dispersées dans du KCl aqueux et dans des solutions de Cr(NO<sub>3</sub>)<sub>3</sub>, et de bromide cétyltriméthylammonium (CTAB). Dans ces dernières solutions, le renversement de charge s'est produit à à peu près  $2 \times 10^{-6}$  M, respectivement. Les potentiels zeta negatifs dans des solutions KCI calcules en employant l'equation Smoluchowski sont approximativement un tiers des valeurs correspondantes obtenues de potentiels coulants et de mesures de force utilisant des feuilles de mica. On a cependant obtenu un bon accord lorsque des groupes charges positivement crées lors du broyage ont été neutralisés et les potentiels zéta ont été corrigés selon le procédé d'O Brien et White avec une taille de particule moyenne de 0,25  $\mu$ m. Lorsque les potentiels zéta de particules chargees etaient corriges de cette maniere, l'accord avec des valeurs calculees a partir de mesures de force a été amélioré. [D.J.]