Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type

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Summary

The effect of changing pH and electrolyte concentration on the dispersion and zeta potential of Na- and Ca-forms of kaolinite, illite and smectite was investigated in relation to changes in their net negative charge.

The percentage of dispersible Na-clay and the percentage increase in net negative charge was positively correlated with pH, but the slopes varied from clay to clay. In general, the net negative charge was the primary factor in clay dispersion, and the pH affected clay dispersion by changing the net charge on clay particles. Na-smectite had larger net charge at all pHs than Na-illite and Na-kaolinite, and it always had larger flocculation values. The role of electrolyte concentration could be due to its effect both on flocculation and variable charge component of the clay minerals. The zeta potential at different pHs also reflected the same trend of clay dispersion with net particle charge.

In Ca-clays the trends were similar to Na-clays up to pH 7.0. In more alkaline solution $CaCO_3$ formation led to charge reduction on clay particles, resulting in flocculation and reduction of zeta potential. At similar pHs the electrophoretic mobilities of all the clays showed constant potential behaviour. However, the zeta potentials of Ca-clays were always smaller than those of sodic clays because the clays were more aggregated. Net particle charge was the most important factor in controlling clay dispersion for the whole range of pH and ionic strength and for all types of cations.

Introduction

Studies on dispersion and flocculation behaviour of sodium and calcium clay minerals are regarded as important because these clays have been considered as models for the behaviour of sodic and calcareous soils. Clay dispersion is governed by the attractive and repulsive forces in the electrical double layer at the surface of charged colloids. The balance between these forces is determined by factors such as exchangeable cation and ionic strength of the soil solution (Rengasamy & Olsson, 1991). The behaviour of calcium-clay is very different from that of sodium-clay, and electrostatic forces in addition to those normally in diffuse double layers are thought to operate. When calcium ions dominate the exchange phase, they probably have an orienting effect on clay platelets, and under such conditions quasi-crystals or tactoids have been reported to develop,

particularly in smectite clay minerals (Emerson, 1962; O'Connor & Kemper, 1969; Greene *et al.*, 1978).

Variations in pH have been found to affect dispersion in many pure clay minerals (Schofield & Samson, 1954; Arora & Coleman, 1979; Goldberg & Forster, 1990; Thellier *et al.*, 1992) and in soils (Gupta *et al.*, 1984; Suarez *et al.*, 1984). Depending on clay mineralogy and oxide contents, soil may exhibit a net negative charge or positive charge at high or low pH respectively. For example, Suarez *et al.* (1984) showed that at constant sodium adsorption ratio (SAR) and electrolyte concentration, clay dispersion increased with increasing pH for two arid-zone soils, one predominantly kaolinitic and the other smectitic. The particle charge of sodium-saturated clays depends on the degree of protonation of aluminol and silanol groups as affected by pH, and as a result, clay dispersion–flocculation behaviour is also altered (Thellier *et al.*, 1992). Although the influence of pH on clay dispersion is widely known, flocculation experiments have reported highly variable flocculation values for clay minerals and soil clays (see Sumner,

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1993), without emphasizing the effect of varying pH. The study of the influence of pH is of great interest in the analysis of the electrokinetic properties of clays because of its effect on the charge distribution of the particle surface. The effect of pH on the electrical potential of the sodium saturated clay surface can be related to the amount of variable charge available on the external surface of the particle. Therefore, the variable charge in single clay particles is expected to be greater than in aggregates of clay particles (domains). Lebron *et al.* (1993) found that changes in pH affect the electrophoretic mobility of individual crystals more than the mobility of domains.

Dixit (1982) showed that increase or decrease in electrophoretic mobility (EM) of Na-clays depended on pH, which in turn was responsible for the development of surface charge. Lebron *et al.* (1993) found that the EM of the Silver Hill illite was doubled when the pH increased from 5 to 9 at SAR > 15. The influence of the exchangeable cation on the zeta potential has been studied by several workers (Delgado *et al.*, 1985; Lebron *et al.*, 1993). The distribution of sodium and calcium ions on particle surface affects the electrical potential because the thickness of diffuse double layer is affected by the type of the cation.

While all these studies indicate the importance of individual factors such as sodicity, ionic strength, pH and the cationic effects on the clay dispersibility, it has not clearly been shown what is the common factor of clay dispersion and how the forces involved in the electrical double layer change. The repulsive forces in the electrical double layer responsible for clay dispersion are affected mainly by the charge characteristics on clay surfaces. Our studies on soil clays (Chorom *et al.*, 1994) have shown that the net negative charge is the primary factor in clay dispersion, and that the pH affects clay dispersion by changing the net charge on clay particles. Soil clays are heterogeneous, and the association of organic molecules make it difficult to interpret the experimental results on dispersion. It is highly desirable to use pure clay systems and study how the net charge is altered under different conditions such as pH, ionic strength and cation type to show that net particle charge is the primary factor influencing clay dispersion.

We report in this paper the dispersive behaviour of three Na- and Ca-clay minerals, namely kaolinite, smectite and illite, as influenced by pH and the associated changes in particle charge. We also examine the relation between zeta potential (ζ-potential) derived from electrophoretic mobility and the dispersive behaviour of these clays.

Materials and methods

Characteristics of clays

The <2 μm fractions of Georgia kaolinite contained about 5% smectite, as shown by X-ray diffraction. The samples of Grundite illite (<2 μm) contained traces of quartz and about 5% kaolinite. No impurities could be detected by X-ray diffraction in Wyoming bentonite samples.

Clay preparation

Samples of Georgia kaolinite, Wyoming bentonite and Grundite illite were pre-treated to remove organic matter, free iron oxides and amorphous materials (Jackson, 1974). The clays were fractionated by allowing larger particles to settle out of suspension and then collection of the <2 μm fraction. This fraction was used to prepare homoionic Na and Ca-clays by washing the clays with NaCl or $CaCl_2$ (1 mol dm^{-3}) solutions, respectively. Before use, samples were dialysed against distilled water until free from chloride. The salt-free clay samples were freeze-dried and stored at room temperature. The homoionic clays were resuspended at 10 g dm^{-3} in distilled water when ready for laboratory tests and adjusted to the desired pH values with dilute HCl or NaOH for Na-clays and $Ca(OH)_2$ for Ca-clays. After shaking for 24 h, the suspension pH was measured and the proportion of clay remaining in suspension was determined turbidimetrically using an HACH turbidimeter (Barzegar *et al.*, 1994). A calibration curve was used to convert turbidity to amounts of dispersed clay. The sedimentation time was set for 16 h for all measurements. This time was chosen to avoid the effect of time on the kinetics of coagulation (Hersterberg & Page, 1990). Salt-free clay when suspended in water for 24 h released small quantity of electrolytes, and the electrical conductivity of the suspension was always less than 0.01 dS m^{-1}.

Flocculation of dispersed clay

The Na-clay suspensions were used to determine the flocculation values (Rengasamy, 1983) using NaCl solutions of different concentrations.

Determination of electrical charge on pure clay minerals

A 1% suspension of the clay (10 cm^3) was equilibrated with 0.1 mol dm^{-3} calcium chloride solution of known pH and converted to calcium clay by repeated washings with 0.1 mol dm^{-3} calcium chloride. The excess calcium chloride was removed by washing with 0.005 mol dm^{-3} calcium chloride once and then with A.R. methanol. The retained Ca^{2+} and Cl^- in the clay were exchanged with 0.1 mol dm^{-3} potassium nitrate solutions of the same pH. The negative charge was calculated on the basis of Ca^{2+} in potassium nitrate solutions, estimated by atomic adsorption spectrophotometry, and positive charge on the basis of Cl^- estimated by using on Orion chloride electrode (Model 94-17) in combination with a double junction reference electrode (Model 90-02).

Scanning electron micrographs

Scanning electron microscopy was used to examine individual and aggregated particles as affected by exchangeable cations. Each sample was coated with 40 nm of gold. Micrographs were

Table 1. Effect of changing pH (with H^+ or OH^-) on dispersible clay.

	Na-Kaolinite			Na-Illite			Na-Smectite	
pH	EC^b /dS m^{-1}	Clay^c /%	pH	EC^b /dS m^{-1}	Clay^c /%	pH	EC^b /dS m^{-1}	Clay^c /%
3.5[a]	0.23	0	2.6[a]	1.02	0	2.7	1.10	86
4.0	0.20	6	3.1	0.36	11	3.4	0.62	95
4.4	0.10	16	4.2	0.13	56	4.8	0.22	96
5.6	0.07	33	5.3	0.08	72	5.6	0.14	98
6.1	0.06	62	6.6	0.06	85	6.2	0.13	99
7.1	0.05	85	7.3	0.07	92	8.6	0.13	100
8.4	0.09	93	8.3	0.08	97	9.7	0.14	100
9.5	0.10	99						

[a]pH at which clays flocculated without adding an electrolyte.
[b]Without adding an electrolyte.
[c]Percentage of dispersed clay.

taken to show aggregated particles and individual particles using an SEM Cambridge type stereoscan 250.

Zeta potential measurements

The ζ-potential is often considered as a remote effect of the surface charge of the particles. It is related to the electrophoretic mobility of the particles by the Smoluchowski equation (Pashley, 1985):

$$\zeta = 4\pi\eta\mu_e/\varepsilon,$$

where ζ is zeta potential in mV, μ_e is electrophoretic mobility (μm s^{-1} V^{-1} cm^{-1}), η is the viscosity of the medium, and ϵ is the dielectric constant. For aqueous media at 20°C, the relation between electrophoretic mobility and ζ-potential is 12.85 mV per mobility unit. The ζ-potential was measured by using a Malvern Zetasizer model 'Zetamaster particle electrophoresis analyser'. All ζ-potentials were measured at a constant 20°C and at a constant field strength of 80 V cm^{-1}. Measurements were conducted with a run time of 30 s, and final values were averaged over ten runs. Suspensions 0.1 g l^{-1} of Na and Ca-clays were prepared in deionized water, sonifying for 30 s and shaking for 2 h in a Spex mixer mill. The ζ-potential was determined at different electrolyte concentrations of the appropriate cation (expressed as electrical conductivity, EC) and at constant pH for Na- and Ca-clays. The influence of different suspension pH on the ζ-potential of Na- and Ca-clays was also measured by the Zetamaster. The ζ-potentials measured in this study were negative in sign, because the clay particles moved towards the cathode.

Results and discussion

Na-clays

Influence of pH on the dispersibility of pure clay minerals. The percentage of dispersed clay remaining in suspension, as influenced by the pH is given for kaolinite, illite and

smectite in Table 1. Adjustment of the pH resulted in the change in ionic strength, as shown by the different EC values. This change appeared greater at pH < 4 and at pH > 9. At high pHs the clay strongly dispersed, and the influence of electrolyte concentration (generated during addition of acid or alkali to change pH) was virtually nil. However, at pH < 4, kaolinite and illite suspensions tended to flocculate. Despite the fact that the released electrolytes may have caused some flocculation, the major influence is believed to have been due to the charge reduction at lower pHs, and this is discussed in detail below. In smectite suspensions, even at pH 2.7, 86% of the clay remained dispersed in spite of the EC of 1.1 dS m^{-1}. When the electrolyte concentrations were kept as small as possible, the clays completely flocculated at the pH of 3.5 for kaolinite and 2.6 for illite. Smectite did not flocculate even when the pH was lowered to 1.5. Smectite is unstable at this pH, forming a siliceous phase by incongruent dissolution (Churchman & Jackson, 1976). However, on standing, the whole suspension gelatinized with time, possibly because of the protonation of the remaining, mainly silanol and aluminol groups resulting in positive charge and cross linking between positive edges and negative faces. Oster *et al.* (1980) reported that the edge-to-face attraction plays a dominant role in the gel formation of Na-smectite. The gel formation in smectite and flocculation by edge-to-face attraction in kaolinite may complicate the quantitative analysis of flocculation values.

The mechanisms proposed to account for the dispersion or flocculation of sodium clays at high and low pH are as follows:
1 Low pH
At low pH, there is a replacement of adsorbed Na^+ by H^+ which has two effects: one is to increase the concentration of Na^+ in the solution and thus to increase the electrical conductivity of the suspension, and the other is to increase the concentration of H^+ on the surface. However, H^+ ions on the clay surface may slowly penetrate into the lattice (Shainberg, 1973). This attack by protons causes the clay to decompose and releases cations such as Al^{3+} and Mg^{2+}. The presence of di- or trivalent cations in the electric double layer

Na-Kaolinite			Na-Illite			Na-Smectite		
pH	EC /dS m^{-1}	Clay[b] /%	pH	EC /dS m^{-1}	Clay[b] /%	pH	EC /dS m^{-1}	Clay[b] /%
7.1	0.05	85	6.3	0.06	84	6.2	0.13	99
7.0	0.23	64	5.9	0.65	61	5.9	1.21	94
6.9	0.43	49	5.8	1.25	47	5.8	1.92	91
6.9	0.92	26	5.8	2.65	27	5.7	2.52	89
6.8	1.05	10	5.7	3.98	12	5.7	3.14	81
6.8	1.25[a]	0	5.6	4.55[a]	0	5.6	4.25	60
						5.5	5.85[a]	0

Table 2. Effect of changing NaCl concentration on clay dispersion of pure clay minerals at natural pH.

[a]CCC values for flocculation system.
[b]Percentage of dispersed clay.

can decrease zeta potential by reducing net negative charge due to the inner sphere complexation of these ions with clay surfaces (Sposito, 1989).

2   High pH

At high pH, OH$^-$ ions interact with the edges of the clay particles making them neutral or negatively charged. Laboratory studies have shown that the rate of dissolution of silicate minerals increases with increasing pH above 8 (Kohut *et al.*, 1994). In spite of increasing EC at high pHs, the clays dispersed because of the development of strong negative charge.

When the pHs of the clay suspensions were at their natural values, the electrolyte concentration needed to flocculate the Na-clays (Table 2) was 1.25 and 4.54 dS m^{-1} respectively for kaolinite (pH~6.8) and illite (pH~5.6). For smectite, at pH~5.5, the flocculation EC was 5.85 dS m^{-1}.

It would be less confusing if the results were obtained at different electrolyte concentrations and keeping pH constant so as to enable splitting the two effects, namely, flocculation and variable charge due to potential determining ions. But in practice this is difficult to achieve in clay systems. In the present study electrolyte concentration changed during pH changes.

Influence of pH on net particle charge and dispersibility.   The changes in net negative charge as influenced by suspension pH are given for sodium forms of kaolinite, illite and smectite in Table 3. When the pH is changed from 2 to 9, the net negative charge on kaolinite particles increased from 62 to 94 mmol$_c$ kg^{-1}, on illite particles from 95 to 184 mmol$_c$ kg^{-1} and on smectite particles from 638 to 815 mmol$_c$ kg^{-1}. The kaolinite and illite had smaller net negative charge in this pH range, while smectite had values 6–8 times larger. This is clearly reflected in their flocculation values. For example, the flocculation value of smectite at pH 5.5 is 5.85 dS m^{-1}, and for illite at a comparable pH the flocculation EC is 4.54 dS m^{-1} (Table 2). However, many authors (e.g. Oster *et al.*, 1980; Goldberg & Forster, 1990) have reported that smectite clays have smaller flocculation values than illites. We found that the flocculation value at a given pH for smectite was always larger

than that for kaolinite and illite, reflecting the strong net negative charge on smectite particles. In the absence of particle charge characterization, the reports in the literature are difficult to interpret, even though the size and shape of illite particles have been invoked by some authors to explain the difference. Particularly, in variable charge systems, charge characterization should also be done at different ECs to separate the effects of pH.

In clay suspensions, regardless of the structure and shape of the particles, the charge (e.g. net negative or positive) gives rise to the electrostatic force responsible for particle repulsion. Charge density is used in the literature to account for the repulsive force. But, the reported flocculation values are generally not related to the calculated charge density of clay minerals. This is because of the surface heterogeneities due to non-uniform layer charge on clay particles and the variation of surface area from the conventionally measured N$_2$-adsorption values due to particle agglomeration. However, the results on sodic soil clays (Chorom *et al.*, 1994) showed that there was a good relation between net negative charge and the amount of dispersed clay. In the present study on pure clay minerals (Fig. 1) highly significant correlation was obtained between the percentage increase in net particle charge (based on the charge

Table 3. Effect of pH on net negative charge of Na-clays.

	Net negative charge/mmol$_c$ kg^{-1}		
pH	Na-Kaolinite	Na-Illite	Na-Smectite
2	62	95	638
2.5	64	95	656
3	67	102	683
3.5	69	—	—
4	73	120	711
5	78	130	771
6	81	143	782
7	85	156	797
8	89	173	802
9	94	184	815

Table 4. Some characteristics of the clays used.

| Clay minerals | Na-clay | | | Mean diameter[c] /μm | |
	A^a /m^2 kg^{-1}	CEC /$mmol_c$ kg^{-1}	Charge density[b] /$mmol_c$ m^{-2}	Na-clay	Ca-clay
Wyoming bentonite	68×10^4	810	1.2×10^{-3}	0.20	2
Grundite illite	11.5×10^4	180	1.5×10^{-3}	0.45	4
Georgia kaolinite	4.1×10^4	79	1.9×10^{-3}	0.60	8

[a]Specific surface of sodium clays as determined by ethylene glycol method (Mortland & Kemper, 1965).
[b]Charge density = CEC/A.
[c]Measured by sub-micron particle sizer Nicomp Model 370 as mean of an assumed Gaussian distribution.

of flocculated clays at low pH; data from Table 3) and the percentage of dispersed clay for the three pure clay mineral systems; this confirms that larger particle charge leads to more dispersion and hence larger flocculation values. Our calculation of increase in net particle charge for Na-smectite was based on the gel formation rather than complete flocculation. Goldberg & Forster (1990) found that the flocculation values for reference clays were much less than those for soil clays, indicating that extrapolation from the results on reference-clays is not possible, and that additional factors such as organic matter and Al- and Fe-oxide content influence the dispersion of soil clays.

The charge densities of Na-clay minerals are similar (Table 4) irrespective of the type of the clay mineral. However, the flocculation values are very different for these three clays. Therefore, we suggest that total particle charge is more relevant in flocculation studies.
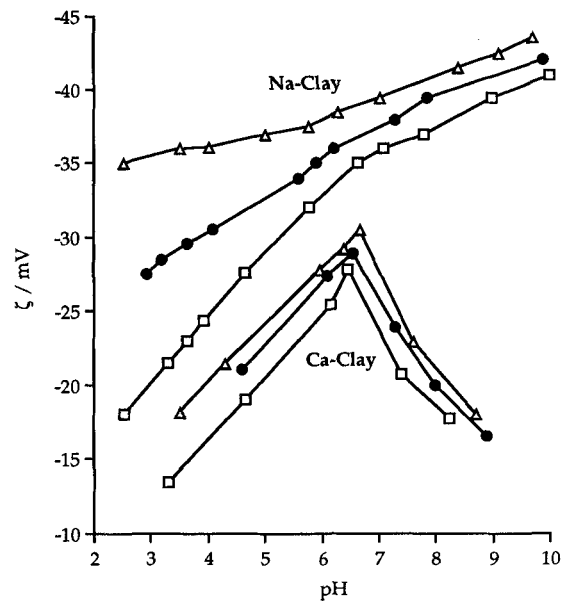
Zeta potential as a function of pH, EC, and dispersion. Figure 4 shows the variation of zeta potential (ζ-potential) with

the pH of the suspension, and Fig. 2 shows that the ζ-potential of Na-clays increases as the pH is increased. In general, the relation between pH and ζ-potential for Na-clays was positive in the pH range 2.5–9. If the adsorbed Na is concentrated on the external surface of the clay we can explain the rapid increase in ζ-potential caused by the increase in the negative charge, which is affected by pH. These results are in good agreement with our data on dispersion, and they confirm that with increasing pH net negative charge (or ζ-potential) will be increased.

The values of ζ-potential for Na-clay particles suspended in solutions of NaCl at different electrolyte concentrations but constant pH (~ 7) are shown in Fig. 3, which also shows that the ζ-potential increases when the electrolyte concentration (expressed as electrical conductivity, EC) of NaCl is logarithmically increased. The mechanism of this reaction is related to the thickness of the electrical double layer. When the

Fig. 1. Effect of increase in net particle charge (based on the charge at low pH) on dispersible clay of Na-clays: kaolinite $\square$; illite $\bullet$ and smectite $\triangle$.

Fig. 2. Zeta potential of Na-clays and Ca-clays as a function of the pH of the suspension: kaolinite $\square$; illite $\bullet$ and smectite $\triangle$.
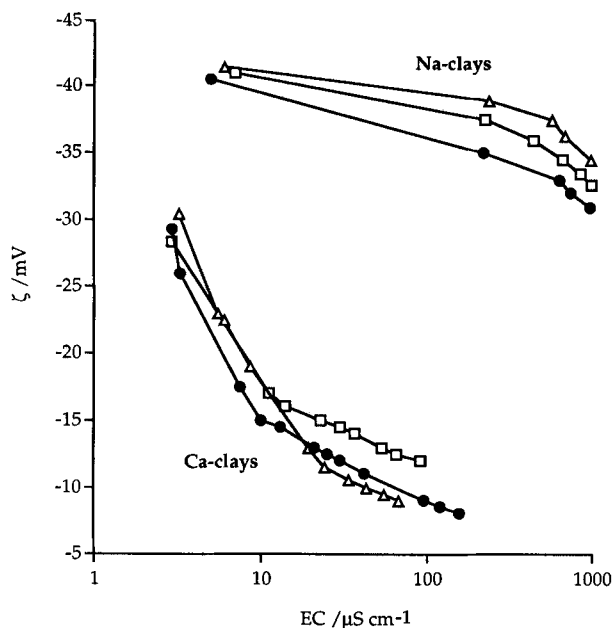
Fig. 3. Zeta potential of Na-clays and Ca-clays as a function of NaCl and CaCl$_2$ concentration: kaolinite $\square$; illite $\bullet$ and smectite $\triangle$.
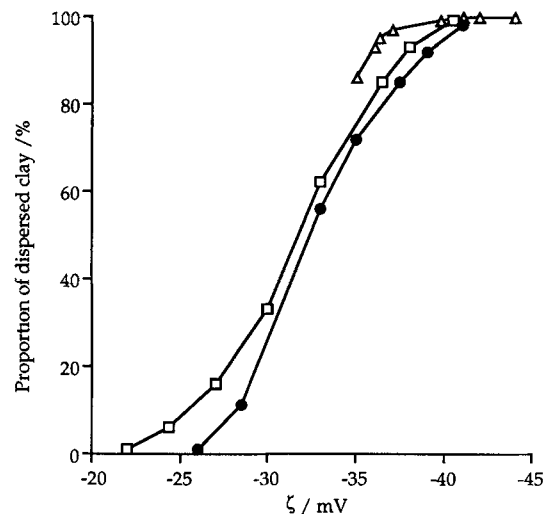

Fig. 4. Influence of zeta potential on dispersible clay of Na-clay minerals: kaolinite $\square$; illite $\bullet$ and smectite $\triangle$.

electrolyte concentration of the suspension is increased, the double layer is compressed, resulting in a smaller ζ-potential. Or, in other words, we can suggest that the flocculation due to the compression of the double layer is related to charge reduction in clay minerals as revealed by the diminished ζ-potential. But the increase in EC also has effects on the magnitude of the variable charge, and thus on the net particle charge. This also can have an effect on the ζ-potential, as shown by Lebron & Suarez (1992).

There is a positive relation between ζ-potential and the percentage of dispersed clay (Fig. 4). The change in ζ-potential has similar effects on the dispersion of Na-kaolinite and Na-illite. This observation agrees with previous data on pH effects on clay dispersion and confirms that by increasing the net particle charge (or ζ-potential), the percentage of dispersed clay increases.

Ca-clays

Influence of pH on the dispersibility of Ca-clay minerals. The pH of the resuspended Ca-clay minerals in distilled water was adjusted to the desired pH by adding either HCl or Ca(OH)$_2$ and, after allowing 24 h for equilibration the dispersible clay was determined. Figure 5 shows the percentage of dispersed clay, as influenced by the pH of the clay suspension. All Ca-clay minerals tended to disperse in the range of pH between 2 and 7, but, with increasing pH from 7 to 10, they tended to flocculate.

At low pH, exchange of Ca^{2+} by H$^+$ releases Ca^{2+} in solution, and at the same time net charge is also reduced due to
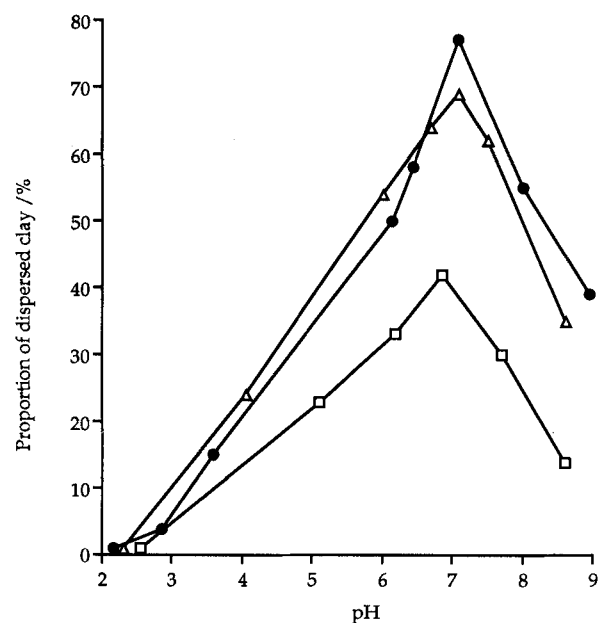

Fig. 5. Dispersible clay of Ca-clay minerals as a function of the pH of the suspension: kaolinite $\square$; illite $\bullet$ and smectite $\triangle$.

the effect of pH on surface charge. As a result, the clay is flocculated. However, at pH above 7, by adding Ca(OH)$_2$ in Ca-clays suspension, CaCO$_3$ formed (Table 5). Rengasamy (1982) reported that strong aggregate formation in calcium clay is possible due to either flocculation by specific adsorption of hydroxy calcium at pH > 10, as observed for iron polycations, or cementation by CaCO$_3$ precipitation. Our results suggest that CaCO$_3$ forms due to addition of Ca(OH)$_2$ in presence of atmospheric CO$_2$, and that clay particles are flocculated by charge reduction due to cementation or coating by CaCO$_3$.

Table 5. The formation of $CaCO_3$ in Ca-clay system at high pH values.

Ca-clay	pH	$CaCO_3$ /mg g^{-1} clay
Kaolinite	8.2	5
	10.0	11
Illite	8.2	9
	10.1	19
Smectite	8.0	11
	9.8	22

Zeta potential as a function of pH and EC. Figure 2 shows the changes in ζ-potential of Ca-clay minerals as related to changes in pH. There is an increase in the particle mobility (more negative) when the pH increases from about 2 to 7 for all Ca-clay minerals. From pH 7 to 9, increasing pH caused decrease in ζ-potential of Ca-clay minerals. This result agrees with the observations on flocculation. We suggest that $CaCO_3$ formation is responsible for the reduction in charge and diminishing of ζ-potential.

The effect of electrolyte concentration on ζ-potential of Ca-clay minerals is shown in Fig. 3. It is clear that the ζ-potential of Ca-clay minerals decreases when the electrolyte concentration of $CaCl_2$ is logarithmically increased. In general, the electrolyte concentration (expressed as electrical conductivity, EC) needed to flocculate or decrease the ζ-potential of Ca-clay minerals is much less than for Na-clay minerals. Although both Na^+ and Ca^{2+} ions tend to diminish the ζ-potential as their concentration in solution increases, the action of Ca^{2+} is much more pronounced than that of Na^+, in accordance with the valency difference.

The mechanism responsible for restricted swelling of calcium clays in water and in aqueous salt solutions was explained by Kjellander *et al.* (1988). They reported that for divalent ions the double-layer interaction is strongly attractive at fairly small surface separations, provided the density of surface charge is reasonably large. Sodium smectite in dilute suspensions exists largely as single platelets (van Olphen, 1977). Norrish & Quirk (1954) reported that calcium smectite exists as packets (tactoids or quasi crystals). The illites exist as quasi crystals or aggregates of domains in the Ca-system (Rengasamy *et al.*, 1984). Therefore, the particle charge is screened by the inner-sphere complexation of Ca ions with clays, responsible for the formation of domains and quasi

crystals. The average particle size for Na- and Ca-clays (Table 4) supports this hypothesis.

Scanning electron microscopy of Na- and Ca-clay minerals (Fig. 6) also shows this variation of aggregation to be present and is related to the treatment given. The aggregation is greater for the Ca treated samples, as evident in the kaolinite sample where 10 μm size aggregates are present in micrograph (Fig. 6a), which are absent in micrograph (b) of the Na treated sample. This trend is also evident for the illite [micrographs (c), Ca treated and (d) Na treated], and the smectite specimens [micrographs (e) Ca treated, and (f) Na treaated]. In micrograph (f) large surface undulations are present, but these are due to the shrinkage of the clay as it dried, and not due to aggregation.

The ζ-potential of the clays (kaolinite, illite and smectite) are similar when they are saturated by a given cation, Na or Ca (Table 6). They exhibit almost constant potential behaviour in the neutral solution. This is in agreement with the report by Horikawa *et al.* (1988). The ζ-potentials of Ca-clays are very much smaller than for Na-clays, confirming greater particle aggregation in the Ca-system.

Flocculation values of Na- and Ca-clay systems

The flocculation values for Na-clays in near neutral NaCl solution were 1.25 dS m^{-1} for Na-kaolinite, 4.45 dS m^{-1} for Na-illite and 5.85 dS m^{-1} for Na-smectite (Table 2). The electrolyte concentration (expressed as, EC) needed to flocculate the Ca-clays in $CaCl_2$ solution in the neutral pH values were 0.025 and 0.11 dS m^{-1} respectively for Ca-kaolinite and Ca-illite. For Ca-smectite the flocculation EC was 0.072 dS m^{-1}. These values are different with the Schulze–Hardy valency rule of flocculation which predicts that the monovalent and divalent colloids coagulate at concentration ratio of $(1/2)^6$ or $1:64$. The ratio of flocculation values of sodium and calcium clays was $1:50$ for kaolinite, $1:42$ for illite and $1:80$ for smectite. The different ratios for these clays are perhaps due to the difference in total charge of these clay minerals in suspension.

Conclusions

This study clearly shows that pH primarily affects dispersion of reference clays by changing the net negative charge on clay

Table 6. Constant ζ-potential of Na- and Ca-clays.

Clay minerals	pH	EC /dS m^{-1}	Dispersible clay /%	Negative ζ-potential /mV
Na-kaolinite	7.1	0.050	85	40.5
Na-illite	7.2	0.070	93	41.1
Na-smectite	7.0	0.090	100	42.3
Ca-kaolinite	6.6	0.010	39	27.3
Ca-illite	6.7	0.015	78	28.2
Ca-smectite	6.8	0.012	64	29.8
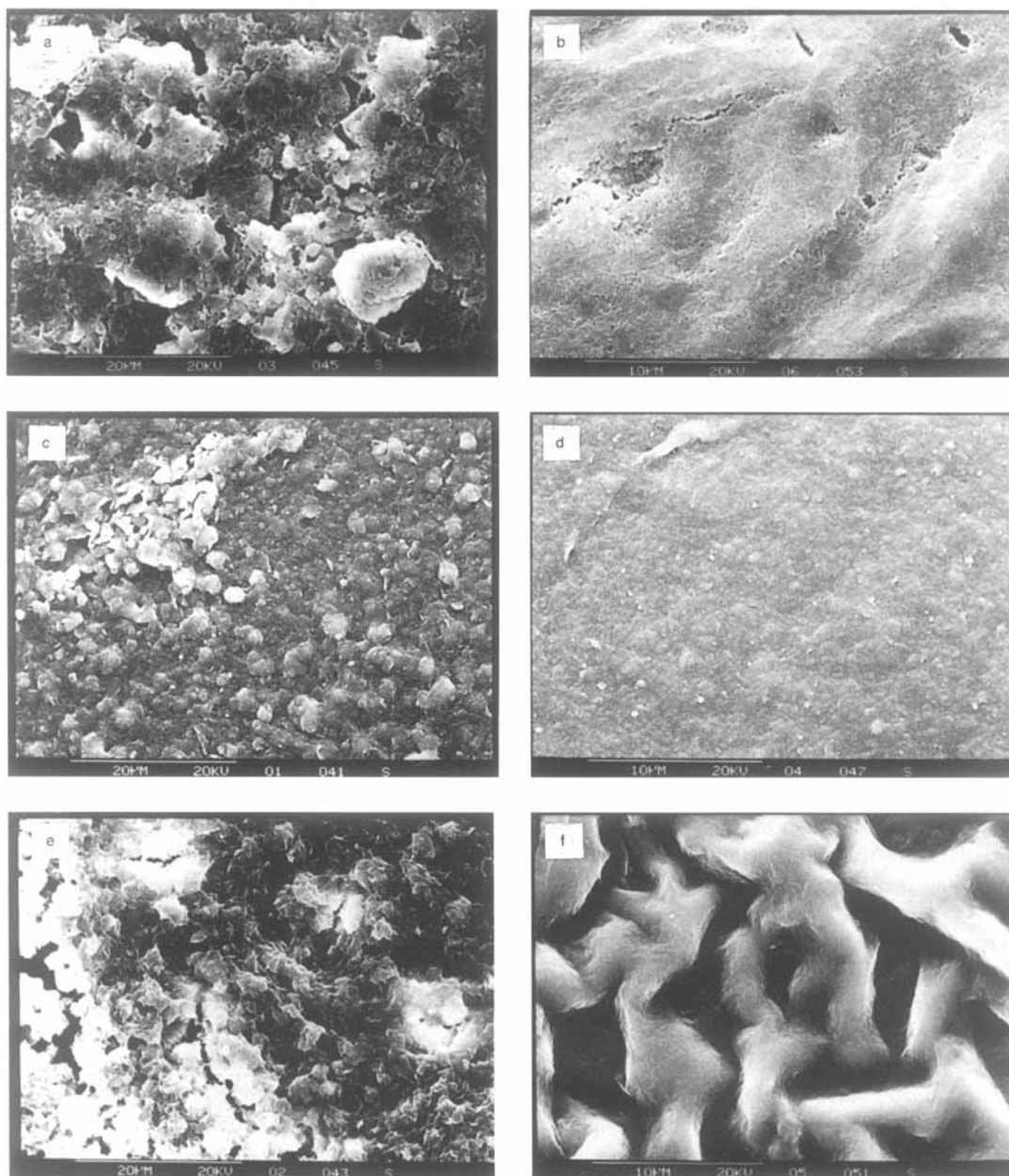
Fig. 6. Scanning electron micrographs of sodium and calcium clay minerals. (a) Ca-kaolinite, (b) Na-kaolinite, (c) Ca-illite, (d) Na-illite, (e) Ca-smectite and (f) Na-smectite.

particles. The slopes of the positive relation between pH and the percentage of dispersible clay decreased in the order kaolinite > illite ≫ smectite when they are sodium saturated. The percentage increase in net negative charge with an increase in pH is in the order illite > kaolinite > smectite. However, the amount of clay dispersed and flocculation values were related to net negative charge on the clay particles. Thus, smectite with larger net charge at all pHs, always had larger flocculation values than illite and kaolinite.

In general, while the changes in pH increase the net negative charge and zeta potential, increasing electrolyte concentration

at constant pH induces charge reduction and diminishes the ζ-potential, probably because there are more cations in the Stern layer. In Ca-clays, the trends were similar to the Na-clays up to pH 7. With further addition of $Ca(OH)_2$, the Ca-clays tended to flocculate, probably because of the formation of $CaCO_3$ and ζ-potential decreased. For Na-clays, the ζ-potential continued to increase. These results are reflected in the values of zeta potential at different pHs. The present study has clearly demonstrated that net particle charge is the common factor affecting clay dispersion under different conditions of pH, ionic strength and cation type.

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