ELECTROKINETIC STUDY ON CLAYS OF DIFFERENT MINERALOGICAL COMPOSITION BY MICROELECTROPHORESIS AND ELECTROOSMOSIS

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ABSTRACT

The electrokinetic behaviour of aqueous suspensions of naturally occurring clays with different mineralogical composition is reported as a function of pH and electrolyte concentration. The results indicate that the clay particles carry a net negative charge in the examined pH range. The estimated zeta (ζ) potential values have been interpreted in terms of the composition and structural characteristics of the clay minerals, nature and charge of the particle surfaces and properties of the electric double layers developed at the clay/electrolyte solution interface. The ζ potential values of the clays obtained using microelectrophoresis and electroosmosis techniques have also been compared.

Key Words: clays, electroosmosis, microelectrophoresis, zeta potential.

INTRODUCTION

In the study of colloid suspensions and other solid/liquid interfaces, the knowledge of the electrokinetic properties and in particular of the electrokinetic or zeta (ζ) potential, is of great interest in the structural characterisation of the electric double layer and in the analysis of the surface properties [1-3], and of considerable importance for understanding of many natural and industrial processes in the field of surface chemistry [4,5].

Although electrokinetic measurements on clay/aqueous electrolyte solution systems have been reported frequently [6-10], some difficulties can be encountered in the interpretation and prevision of results in terms of surface charge density or surface potential, reflecting a somewhat complex behaviour. Certain characteristics of the clay minerals such as the nature of the exposed surface to the surrounding medium, the heterogeneity on the electric charge distribution at the particle surface, the nature of the exchangeable ions or even the mineralogical composition, can all contribute for such behaviour.

The electrokinetic properties of aqueous suspensions of clays will depend among other factors on the interactions between the surface of the particles which have acid-base properties and the constituents of the liquid medium with which they contact, in particular the potential-determining ions (H^+ and OH^-). Therefore, the electric double layer developed at the particle surface should be influenced by the pH dependence of the ionic species in the solution

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as by the pH dependence of the nature of the surface. In such systems, the study of the variation of the ζ potential with parameters such as the pH or the ionic strength of the solution in contact with the clay can provide important information about its electrokinetic behaviour.

In this work we report some results obtained in an electrokinetic study of naturally occurring portuguese clays with several mineralogical composition suspended in solutions of different pH and electrolyte concentration. It has been used both microelectrophoresis and electroosmosis measurements for the determination of ζ potential.

EXPERIMENTAL

We used two different clays whose mineralogical composition characterised by X-ray diffraction and chemical methods showed to contain, by weight: clay A - 60 % kaolinite, 30 % illite, 10 % montmorillonite; clay B - 80 % montmorillonite, 15 % illite, 5 % kaolinite. All chemicals used except clays were of analar grade.

The suspensions of clays (size fraction smaller than 2 μm) were prepared with triply distilled water by dispersing each sample for an hour in an ultrasonic bath, in a concentration range varying from 1 g dm^{-3} to 5 g dm^{-3}. The concentration of each suspension was small enough to allow the quick location of particles in microelectrophoresis and high enough to yield the sedimentation in electroosmosis. The pH in the aqueous dispersions was controlled with HNO_3 or NaOH. The ionic strength of each suspension was adjusted between 10^{-4} and 10^{-2} mol dm^{-3} with $NaNO_3$. The suspensions were left to equilibrate for two days, being redispersed by shaking before the measurements were made. The temperature of the systems was maintained at 25±1 °C.

The ζ potential of the clays was estimated from values of the electrophoretic mobility operating a commercially available microelectrophoresis cell (Zeta Meter Inc.) and from the electroosmotic flow using an apparatus previously developed [11]. The experimental data were converted to ζ potentials by applying the Smoluchowski equation [3].

RESULTS AND DISCUSSION

The electrokinetic properties of materials like the clay minerals depend on the nature and charge of the surfaces in contact with the ionic medium and on the modes of particle-

particle association. It has been considered that on the crystal lattice of the clay minerals mainly constituted by inorganic oxides two types of exposed surfaces can coexist, the basal faces and the edges, whose chemical composition and charge can be appreciably different [4,7-9]. The contact of these surfaces with the surrounding liquid medium may develop different ionic distributions in the proximity of the particles and generate electric double layers whose potentials and charge densities can differ in magnitude and sign.

The basal face surfaces carry a negative and approximately constant charge not dependent on the pH variation of the liquid medium. This charge can be associated with lattice defects, or with a positive charge deficit caused by isomorphous substitution of metal ions within the aluminosilicate lattice by cations of lower charge (Si^{4+} for Al^{3+} in the silica tetrahedral sheets, or Al^{3+} for Mg^{2+} or Fe^{2+} in the alumina octahedral sheets) [6,7]. Conversely, the charge on the edge surfaces depends on the pH of the suspensions. In acidic media the charge can become positive in three ways: by protonation of groups on the solid surface specially hydroxyl groups, or by breaking of the bonds at the external surfaces leading to positive lattice sites which are usually associated with aluminium atoms, or by adsorption of H^+ ions [4,7,12]. The particle edges can acquire negative charge in basic media by a preferential adsorption of OH^- ions where the exposed atoms on the surfaces generate centres of positive charge, or due to the ionisation of surface groups of acidic nature [12,13].

The influence of pH on the ζ potential of the clays A and B at constant ionic strength is presented in Figure 1. The electrokinetic data indicate that their behaviour is not similar, although over the pH range from 3 to 12 both clays carry a net negative charge. This charge will be balanced by adsorption, either of exchangeable counter-ions dissociated from the surface layers, or of hydrated counter-ions originated from the surrounding solution. These cations will be held on the external surfaces of the particle aggregates or between the unit layers, most of them localised in Stern layers and a smaller fraction in diffuse layers [10]. The observed behaviour appears to reflect the conditions on the exposed surfaces of the two clays which chemically behave as inorganic oxides and the mode of aggregation of their particles.

The electrokinetic behaviour of clay A with 60 % of kaolinite differs only slightly from a clay having 97 % of kaolinite which indicates that the other mineral constituents have a smaller influence in its behaviour. The clay A exhibits a relatively low specific surface area and cation exchange capacity, 49.7 m^2/g and 10 meq/100 g of clay, respectively, in agreement with the properties of its major mineral constituent and should have a small fraction of exposed

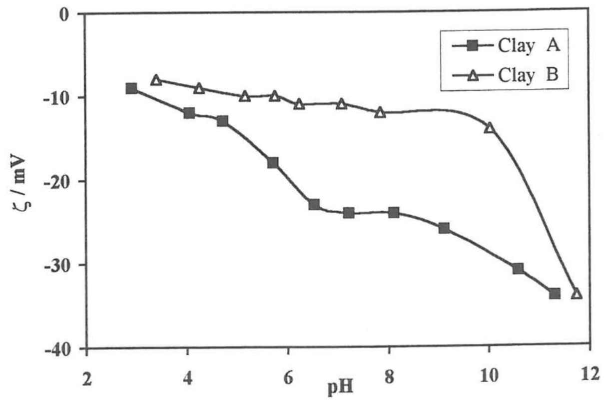

Figure 1. ζ potential of clays A and B as a function of pH at a constant ionic strength of 10^{-4} mol dm^{-3} in sodium nitrate.

surfaces to the solution per structural unit. These characteristics restrict the adsorption in the diffuse layer and reduce the fraction of exchangeable counter-ions which can only be taken up and adsorbed on the external surfaces of the particles [7,14].

At pH values below 6 the net charge on clay A, although remaining negative, is decreased as the pH is lowered mainly due to the increase of the positive charge on the edge surfaces by interaction or adsorption of H^+ ions at the surfaces, which will contribute to reduce the magnitude of the effective charge on the particles resulting on a lower mobility. The effects due to the mode of interaction of the unit layers should also be considered an important factor [14,15]. The edge-to-face association is probably dominant and the strength of interaction between the edges and the faces is promoted as the pH is decreased, therefore reducing the Stern layer potential and consequently the negative mobility. The results obtained still indicate that the proportion of positively charged edges exposed to the ionic medium is smaller in absolute value when compared to the negatively charged faces, due to the larger area occupied by the faces in the kaolinite crystals relatively to the area occupied by the edges. Over the pH range 6-8, the ζ potential remains approximately independent of the pH because the charges on the positive edges are almost or completely neutralised by adsorption or reaction with OH^- ions. So, the negative levelling of ζ in the pH range from 6 to 8 is consistent with a negative charge on the faces which is independent of pH and with a change on the edge charge from positive to neutral. The further rise of pH (pH > 8) which leads to an increase in the negative zeta potential, reflects the influence of the OH^- ions. In effect, the reaction of OH^- with the

neutral edge surfaces [14], or the preferential adsorption of OH^- on certain active sites located at the edge surfaces [9], increases the effective negative charge on the particles, thus contributing to a more negative ζ potential. The change on the edge-to-face electrostatic interactions may also affect the zeta potential, because as both surfaces have a negative charge there should be an increase on the repulsive interactions and a decrease on the attractive interactions between adjacent particles as the pH is increased.

Clay B has a different behaviour from the observed with clay A, the negative zeta potential showing little change with the decreasing of pH below 10, but strongly increasing for pH > 10 (Figure 1). Electrokinetic measurements showed that clay B, with a specific surface area of 209.5 m^2/g and a cation exchange capacity of 86 meq/100 g, has a approximately similar behaviour to the montmorillonite in the same pH and electrolyte concentration, thus indicating that the montmorillonite the major constituent of the clay B is the main responsible for that behaviour.

The montmorillonite clay has some important structural characteristics which are relevant in its electrokinetic properties and should be reflected in the clay B properties: firstly, the surface charge is concentrated mainly on the basal faces because they represent the larger part of the exposed surfaces in contact with the solution, which have an approximately constant charge not dependent on the pH [4]; secondly, it can exchange and maintain more or less strongly adsorbed an important fraction of exchangeable cations released from the crystal lattice (specially Al^{3+} or yet Na^+) [9,16], which do not leave easily the Stern layer by influence of pH [10,17]; finally, its structural arrangements consist of separated unit layers between which hydrated counter-ions from the solution (H^+, Na^+) can be electrostaticly attracted [16,17]. Because of these reasons, the particles of clay B when compared to clay A will have a more strongly neutralised electrical charge and a consequently smaller zeta potential. On the other hand, due to the greater contribution of the face charges for the effective charge on the clay B, the influence of pH is minimised which accounts for the slight variation of the zeta potential observed when increasing the pH between 3 and 10. However, for pH > 10 the negative ζ potential of the clay B increases markedly with rising of pH due to the now significant contribution of the increasingly negative charge of the edge surfaces in the effective charge of the particles.

The available surface sites to adsorption and the cation exchange capacity of each one of the clays differ appreciably as was already referred. Thus, the higher exchange capacity

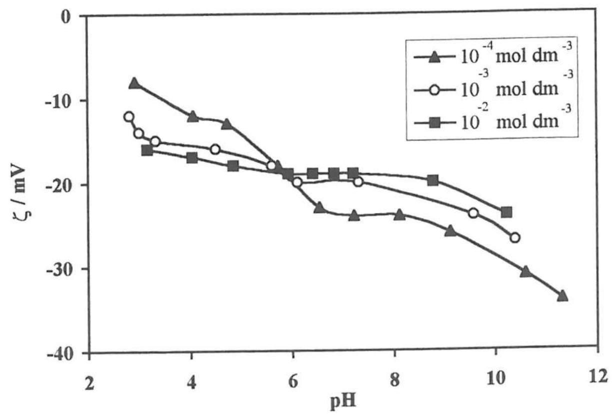

Figure 2. ζ potential of clay A as a function of pH at different ionic strengths in sodium nitrate.

associated with the larger specific surface of the clay B allows it to adsorb a larger amount of counter-ions on its surfaces and makes it more subject to particle charge reduction relatively to the clay A. In stronger acid media where the net negative charge on the particles is lesser, the counter-ions adsorbed on the surfaces are mainly H^+ ions originated from the bulk of the solution [17]. However, as the edges are positively charged at low pH, it is probable that there are negative ions from the electrolyte adsorbed on these surfaces resulting in a greater lowering of the Stern potential than at high pH values [15]. When pH is increased, Al^{3+} ions released from the clay lattice as exchangeable cations or Na^+ ions originated from the solution or from the solid particles, tend to replace the surface H^+ ions [9,17]. For the highest pH values, there will be tendency to a similar increase of adsorption in terms of counter-ions taken up by the surfaces of both the clays.

The effect of the ionic strength on the zeta potential of the clays A and B depends on pH and is shown in Figure 2 and 3, though at higher electrolyte concentrations the influence of pH becomes less important. At pH > 6, an increase in electrolyte concentration of the suspensions of the clay A (Figure 2), where the major constituent is kaolinite, reduces the electrokinetic charge and makes the zeta potential less negative, mainly by compression of the electrical double layers developed at both face surfaces (negative charge) and edge surfaces (neutral or negative charge). In addition, a reduction on the face-to-edge repulsive interactions and a promotion on the edge-to-edge and specially face-to-face associations among intercalated sheets will be expected, which also contributes to lower the negative ζ potential

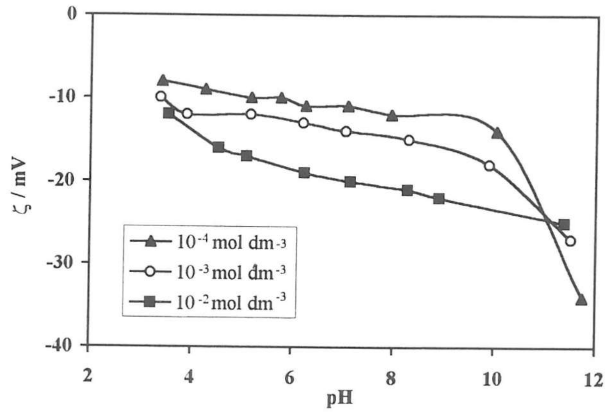

Figure 3. ζ potential of clay B as a function of pH at different ionic strengths in sodium nitrate.

[15]. For pH < 6 the tendency is reversed because the edge and face surfaces will be oppositely charged. An increase in electrolyte concentration originates a compression of the electric double layers now at the positive edges and at the negative faces and the effect is a decrease in the absolute values of negative face and positive edge potentials. However, the reduction in the face potentials will not be compensated by changes in the edge potentials [9], thus resulting in an increasingly negative zeta potential. There will also be a decrease on the edge-to-face attraction and a reduction on the face-to-face and edge-to-edge association, favouring the increase of the absolute value of ζ potential [7,15].

Clay B does not behave exactly the same way as clay A under the influence of the ionic strength, although the tendency of variation of zeta potential with the electrolyte concentration was kept. The negative ζ potential of the clay B also increases with the rising of ionic strength but this time until about pH = 11 and decreases for larger values of pH (Figure 3). In view of the reasons previously indicated, the structural characteristics of the clay B surfaces must again be taken into account. Most of its specific surfaces are exposed to the electrolyte solution with the edge surfaces much less extensive than the face surfaces and the charge strongly localised on the basal face surfaces. In addition, the increasing of electrolyte concentration induces smaller interlayer spacing which restricts the adsorption of cations. Therefore, it is concluded that for pH < 11, the negative ζ potential is increased by increasing of the electrolyte concentration mainly due to the compression of the electric double layers and to the reduction of the fraction of adsorbed cations in the interlayer spacing. For pH > 11, in

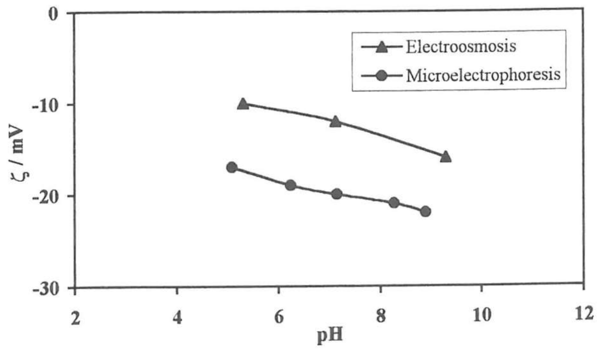

Figure 4. ζ potential of clay B as a function of pH at a constant ionic strength of 10^{-2} mol dm^{-3} in sodium nitrate, obtained by electroosmosis and microelectrophoresis.

addition to the double layer compression, other factors may explain the observed behaviour specially the effect of negative edge charge which is determinant in the inversion of the tendency of the zeta potential variation. The increase of electrolyte concentration now induces a decrease in the effective charge of the particles and a smaller negative potential.

The values of zeta potential obtained from electrophoretic mobility are more negative than the ones evaluated from electroosmotic flow measurements as is shown, for example for clay B, in Figure 4. However, there is a good qualitative agreement between the two curves which translates a similar electrokinetic behaviour.

The values of ζ potential should only depend on the characteristics of the phases in contact and be independent of the electrokinetic method used for its determination. The lack of concordance in the zeta potentials can be due to the applicability conditions of the Smoluchowski equation, which is subject to different limitations according to the applied electrokinetic technique. The heterogeneous distribution of the electric charge on the particle surfaces [9], the size and shape of the particles [8,18] and the influence of the particle surface and electrolyte conductivity [2], each can affect in a different way the calculated ζ values using the microelectrophoresis or electroosmosis.

In the deduction of the Smoluchowski formula when applied to the electroosmotic phenomenon it is supposed that each layer of liquid should be shifted within the capillary at a constant velocity. Meanwhile, only on the outside of the electric double layer where the electrolyte is neutral and is far from any charged surface, that is verified; the mobile part of the double layer near the shear plane moves more slowly due to the excess of ions close to the

surfaces [19]. As a consequence there will be a delay in the liquid movement and a consequent lesser value derived for zeta potential. The special orientation of the particles due to the heterogeneous charge distribution may also affect the geometry of the velocity profiles of the electroosmotic liquid movement through the clay [16] and contribute to its retardation. Therefore, these effects may have as a consequence an underestimate of the ζ potential obtained from this type of measurements relatively to the microelectrophoresis.

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