Flocculation and Coagulation of Ca- and K-Saturated Montmorillonite in the Presence of Polyethylene Oxide

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ABSTRACT: The objective of this work is to study the flocculation of Ca- and K-montmorillonite in the presence of some coagulant ($CaCl_2$ and KCl) and mixtures of coagulants and polyethylene oxide (600,000 mol wt) through measuring the zeta potential. The action of Ca^{2+} was more effective than K^+ in decreasing the zeta potential of Ca-montmorillonite; consequently, the electrical double layer of the clay particles has been reduced. On the other hand, the action of K^+ was more pronounced than Ca^{2+} in decreasing the zeta potential of K-montmorillonite. This contradicting result was attributed to the change of the partial molal volume of Ca- and K-montmorillonite. The flocculation of Ca- and K-montmorillonite by polyethylene oxide was enhanced when the clay was initially treated with electrolyte. This electrolyte reduces the thickness of the electrical double layer. Under this condition, the polymer segments collapse on the clay surfaces, leaving polymer loops and tails available for contacting adjacent clay particles. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 659–662, 1999

Key words: flocculation; coagulation; montmorillonite; polyethylene oxide; adsorption

INTRODUCTION

Physicochemical properties of suspended particles and sediments in natural environments are dominated by properties of clay minerals. Due to their surface chemical properties, that is, large specific surface area, cation exchange capacity, and adsorptive affinity for organic and inorganic compounds and clay minerals are held responsible for scavenging contaminants from natural water bodies and for their deposition through sedimentation.[1–4]

Clay minerals are known to exhibit variable zeta potentials according to the type of clay as well as to the size and charge of the adsorbed cation. These potentials are the primary factor in the dispersion and flocculation of clays. Also, it is the real physical quantity determining floatability and sedimentation of clays.[5] Therefore, our attention in this work is focused on montmorillonite with Ca^{2+} and K^+ as the dominant interlayer cations.

Montmorillonite $[Na(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O]$ has a large cation exchange capacity and high specific surface area and swells (lattice expansion) in the presence of water or polar organic molecules such as polymers. The presence of polymeric materials on clay surface facilitate clay flocculation and formation of stable clay suspension. This property is a key role in soil structure, paint, drug, and other technological processes.

The objective of this work is to study flocculation of Ca- and K-montmorillonite in the presence of coagulants ($CaCl_2$ and KCl) and mixtures of coagulant and polyethylene oxide (600,000 mol wt) through measuring the zeta potential.

MATERIALS AND METHODS

The montmorillonite sample was obtained from (Union carbide, New York USA). The clay samples were saturated with potassium or calcium chloride to produce homionic clay, Ca-montmorillonite, and K-montmorillonite. The clays were brought into contact with $0.5N$ solution of the electrolyte (CaCl or KCl) and then left to settle for some days in order to decant as much of the clear supernatant liquid as possible. The supernatant liquid was decanted, and the above-mentioned steps were repeated for many times until the supernatant and the added solution had the same composition.

Three experiments were carried out. In the first, Ca-montmorillonite–$CaCl_2$ (Ca-M-$CaCl_2$) or K-montmorillonite KCl–(K-M-KCl) systems were prepared by adding different amounts of $CaCl_2$ or KCl to a series of dialyzed suspensions, thereby covering a wide range of salinities (10^{-4} to $10^{-1}N/$L). The free electrolyte suspension as well as the electrolyte suspension were adjusted to 2% solids by weight and the electrophoretic mobility of the particles were determined in duplicate. In the second experiment, Ca- and K-montmorillonite were used to study the effect of a cation rather than the originally saturated electrolyte on the mobility; that is, $CaCl_2$ was used on K-montmorillonite, while KCl was used on Ca-montmorillonite, at various electrolyte concentrations. In the third experiment, polyethylene oxide (600,000 mol wt) was mixed with the corresponding $CaCl_2$ or KCl to study the effect of different electrolyte and polymer fractions on the flocculation of Ca- and K-montmorillonite.

The electrophoretic mobility of the clay particles was determined with microelectrophoresis apparatus (zeta meter) using a cylinderical cell manufactured from Plexiglas. Prior to the measurement, the suspensions were shaken in a thermostat shaker for 24 hours at room temperature. To measure the particles velocity, 30 particles were timed at least in each experiment for both direction of the applied electric field, and the value of mobility assigned to each suspension was the average of the data obtained from 3 experiments carried out on different days. For the estimation of zeta potential (ξ), the values of the absolute viscosity and dielectric constant of the dispersing liquid have to be known.

$$\xi = \frac{3.6 \times 10^{-4} \eta V_E}{D}$$

Figure 1 Zeta potential of Ca-montmorillonite at different electrolyte concentrations.

where η is the viscosity of the medium (water), D is the dielectric constant of the medium, and V_E is the electrophoretic mobility of the suspension.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the zeta potential (ξ) and the electrolyte concentration for the first system (Ca-montmorillonite). The clay particles were suspended in solutions of $CaCl_2$ or KCl at a constant pH ($\sim$ 7). The results show that with increasing electrolyte concentration, the zeta potential decreased. Although both K^+ and Ca^{2+} ions tend to reduce the zeta potential, the action of Ca^{2+} was more effective than K^+, in accordance with the Schulz and Hardy rule.[6] For instance, a Ca^{2+} ion has a small hydrated ionic radii, a small distance of the closest approach a^o, and high polarizability compared to K^+.[6,7] These properties make Ca^{2+} ions approach the surface of clay more readily and become specifically adsorbed; consequently, the electrical double layer of the clay suspension was compressed. Therefore, the reducing of zeta potential of Ca-montmo-

Figure 2 Zeta potential of K-montmorillonite at different electrolyte concentrations.

rillonite could be much more pronounced in the presence of $CaCl_2$ solution than in the case of KCl.

Figure 2 shows the zeta potential of the second system (K-montmorillonite) in the presence of KCl or $CaCl_2$. The results show that the decrease in zeta potential of K-montmorillonite in presence of KCl was more than in the presence of $CaCl_2$. The expected result that might be obtained is the decrease in the zeta potential of K-montmorillonite with $CaCl_2$ must be more than with KCl according to the fact mentioned in the other system; Ca-montmorillonite. This contradicting result was attributed to the partial molal volume of K-montmorillonite, which is larger in the presence of KCl than $CaCl_2$.[8] This is consistent with the properties of K^+ and Ca^{2+} ions calculated from their partial molal volumes at infinite dilution and their intrinsic volumes.[9] Therefore, in montmorillonite and at infinite dilution, where the particle–particle interaction is eliminated, the properties of the adsorbed ions and its electrostrictive effect is the main factor in determining the partial molal volume of a clay. Similar results were found for koalinite by Helmy et al.,[10] indicating that there is more restrictive effect on molal volume of the clay at infinite dilution. The partial molal volumes follow the order Ca < Mg

< K, which is the reverse order of surface affinity in cation exchange and, consequently, the zeta potential. This behavior explains the importance of partial molal volumes in determining selectivity as well as suspension stability in cation exchange systems.

Figure 3 shows the zeta potential of Ca- and K-montmorillonite at a constant in different electrolyte concentrations (KCl or $CaCl_2$, 10^{-2} mol/L) and different polymer concentrations. It was found that the decreasing of zeta potential of Ca-montmorillonite was more than K-montmorillonite system. This behavior could be attributed to the polymer–clay interaction, which was affected by the original exchangeable cation.[11] The reason for this differences can be explained through the physicochemical properties of both the adsorbed ion and the polymer. The affinity of the polymer adsorption on the clay surface is reduced by the presence of the greater polarizing ion, potassium ion on the clay surfaces by making the displacement of water from the hydration shell of the exchangeable cations more difficult than in Ca-montmorillonite.[12] Generally, the decrease in Ca- and K-montmorillonite zeta potential was much more in the presence of a mixture between the

Figure 3 Zeta potential of Ca- and K-montmorillonite (constant) in different electrolyte concentrations (KCl or $CaCl_2$, 10^2 mol/L) and different polymer concentrations.

electrolyte and the polymer compared with zeta potential of the other 2 systems without the polymer. Consequently, flocculation of Ca- and K-montmorillonite by polyethylene oxide was enhanced when the clay had initially been coagulated by the addition of the electrolyte. This electrolyte (coagulant) acts to reduce the thickness of the diffuse double layer of adjacent clay particles, thus reducing the interparticle distances, whereas polyethylene oxide (a flocculent) is able to span the interparticle distances between these aggregated clay particles by the formation of bridges through the hydrogen bond mechanism.[13] These 2 process may act individually or together to affect the sedimentation of clays, leading to the initial stages of aggregation. Then a network structure could be produced through the polymer molecules attachment at many points of adsorption sites on the clay surface. This stage accompanied by the formation of large floces (that is, the minimum zeta potential) could be obtained.

CONCLUSION

1. The action of Ca^{2+} had a more pronounced effect on the zeta potential of Ca-montmorillonite than K^+.

2. The action of K^+ had a more pronounced effect on the zeta potential of K-montmorillonite than Ca^{2+}.

3. The decrease in the zeta potential of Ca-montmorillonite and K-montmorillonite was much greater in presence of mixtures of electrolyte and polymer solutions compared with the same system in the presence of the electrolyte.

4. The flocculation of Ca- and K-montmorillonite by polyethylene oxide was enhanced when the clay had initially been coagulated by the addition of the electrolyte.

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