

MESUREMENT OF POINT OF ZERO CHARGE OF BENTONITE BY SOLUBILIZATION TECHNIQUE AND ITS DEPENDENCE OF SURFACE POTENTIAL ON pH

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Abstract : The applicability of bentonite as a pollution-controlling medium has been widely recognized due to its high specific surface area and peculiar molecular structure. Therefore, understanding its interfacial characteristics is essential for a more efficient use of bentonite in relation with environmental application. The aim of this communication is focused on the development of a method for measuring the point of zero charge of bentonite, which is one of the most critical interfacial factors governing macroscopic behavior of bentonite in aqueous environment, using solubilization technique and its theoretical aspects are discussed. Also, from the measured point of zero charge, an equation predicting the variation of surface potential of bentonite depending on pH has been derived based on thermodynamic relationship. The results obtained show that the point of zero charge of bentonite is established at around pH 8.0 and its dependence of surface potential according to pH followed the equation of $\Psi_0 = 0.472 - 0.059 \text{ pH}$ at 25°C.

Key Words : Bentonite, Point of Zero Charge, Solubilization Technique, Surface Potential, pH

INTRODUCTION

Clay minerals are composed of very fine particles and they are abundant in natural environments. They are usually categorized depending on their crystallographic structure and amount and location of charges in the lattice.^{1,2)} Major species of clay minerals are kaolins, serpentines, montmorillonites, and illites or micas.^{3~5)} All of these have their own characteristic crystal lattice structure, however, there is also an amorphous clay such as allophane.⁶⁾ Because the particle size of clay minerals are

fine and as a result their specific surface area is generally very high, they have been widely utilized as the raw material in various industries, e.g., production of ceramics, adhesives, desiccant, absorbent, stabilizing agent, fillers, pharmaceuticals and cosmetics, polishing compounds, and clarification of beverage, etc.^{7, 11)} Even for the catalyst production, clay mineral has its wide applicability, therefore, it is rather difficult to find out some industrial fields where clay minerals are not consumed as a raw material.

Clay is the so-called layer structured mineral. In the case of mica, a quarter of Si^{4+} is substituted by Al^{3+} ions, creating a net negative charge in the layer. This charge is counterbalanced by the interstitial cations. When the crystal is placed in water, interstitial cations like

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K^+ or Na^+ go into solution, leaving net negative charge behind. Thus, the basal planes of these crystals are negatively charged, independent of pH. This charge is called as the intrinsic structural charge and it is directly related with the ion exchange capacity of clay minerals.^{12,13)} Among several clay minerals, montmorillonite, which is often called as bentonite commercially, has the highest ion exchange capacity and it sometimes reaches greater than 100 mequiv/100 g. Due to its high ion exchange capacity, bentonite has been widely employed as a clarifying agent in water and wastewater treatment and also as a molecular sieve especially for the removal of ammonium ions.¹⁴⁾ Recently, it has broadened its application to the protection of ground water being used as a blocking material for pollutants transferral, simultaneously working as an adsorbent.^{15,16)}

The first reason for the wide applicability of clay minerals including bentonite in the field of environmental engineering can be found in their fine particle size and peculiar molecular structure. Since the size of particles which composing the clay minerals is very fine, they easily form a colloidal state in aqueous environment. Therefore, especially in relation with water/wastewater treatment and employment as the lining material, it is very important to understand their surface properties in aqueous system such as surface potential and point of zero charge (pzc), etc. These parameters play the basic role in governing the macroscopic behavior of colloids so that they should be figured out to enhance the efficiency of pollution management by clay minerals.

In this communication, the measurement of pzc of bentonite has been attempted using solubilization technique and its theoretical background is discussed. Also, from the measured pzc, the equation describing the effect of pH on the surface potential, Ψ_0 , of bentonite has been derived by applying the Nernst equation. This thermodynamically derived equation is thought to be meaningful in the control of the stability of bentonite particles in aqueous environment and

accordingly its application to pollutant-treatment agent. The aspects considered in this study are expected to be of some help to enhance our understanding in the fundamentals of surface and colloidal features of bentonite and also attract further in-depth studies for the utilization of this material in relation with environmental application.

MATERIALS AND METHOD

Bentonite which obtained from Ward's Earth Science was used in the experiment. After grinding slightly using agate mortar, it was sieved and the portion sized with 400 mesh was collected. To clean the surface of bentonite and remove possibly contained impurities, the fines were dispersed and stirred in 0.1 N HNO_3 solution for at least 2 hrs. Then, it was rinsed with deionized-distilled water ($>18 M\Omega$) more than 3 times following the same manner as cleaning and separated from solution by a centrifuge. The dried bentonite was stored in a desiccator filled with pure N_2 gas ($>99.99\%$) before experiment to prevent surface contamination. 100 g of prepared sample was taken in 1000 mL beaker containing 500 mL of deionized-distilled water which was previously adjusted at highly acidic pH and desired ionic strength. After stirring for *ca.* 20 min., the variation in the pH of suspension as alkaline material adds has been investigated using pH meter. The whole titration system was immersed in a water bath which was controlled at 25°C. Potassium chloride (KCl, Aldrich Co.) was employed as the swamping electrolyte and highly pure HCl and NaOH both purchased from Fisher Co. were used to adjust the solution pH. The crystal structure of bentonite was investigated by X-ray diffraction spectroscopy (Philips, PW1700) and every solution used in the experiments was prepared using deionized-distilled water.

RESULTS AND DISCUSSION

Figure 1 shows the result of X-ray diffraction

analysis for bentonite and it can be seen that the major species which comprising the bentonite are aluminium and silicon oxides. This can be taken for granted because bentonite is crystallographically composed of units made of two silicon-oxide tetrahedral sheets with a central aluminium-oxide octahedral sheet. The pattern also represents that magnesium and sodium atoms are contained in the lattice. The reason for this may be explained by the supplement of deficient positive charge by these atoms, which arising from the steric substitution of silicon atoms with aluminium atoms.

Figure 2 shows the variations in $\Gamma_{H^+} - \Gamma_{OH^-}$ of bentonite with pH at different concentrations of swamping electrolyte. Here, Γ_{H^+} and Γ_{OH^-} means the surface adsorption densities of H^+ and OH^- ions on bentonite, respectively. The absolute value of $\Gamma_{H^+} - \Gamma_{OH^-}$ for bentonite can be obtained by estimating its surface charge (σ_0)¹⁷ using Eq. (1) and dividing with Faraday's constant. In this estimation, the surface potential of bentonite cannot be directly measured, therefore, its electrokinetic potential can be employed instead without provoking a significant error.

$$\sigma_0 = (8n_0\epsilon kT)^{1/2} \sinh(Ze\Psi_0/2kT) \quad (1)$$

in which, n_0 ; corresponding bulk concentration of ionic species

ϵ ; permittivity of solution

k ; Boltzmann constant

$(1.381 \times 10^{-23} \text{ J/K})$

T ; absolute temperature (k)

Z ; valence of the ionic species

e ; elementary charge ($1.602 \times 10^{-19} \text{ C}$)

Ψ_0 ; surface potential of particles

Since the unit cell of bentonite is metal oxide, i.e., silicon-oxide and aluminium-oxide, when bentonite is placed in water the surface oxide groups turn into silanol (Si-OH) or aluminol group (Al-OH) as a result of hydrolysis reaction. At pzc, these neutral sites predominate at the surface of bentonite and they are considered to be electrically neutral. However, as

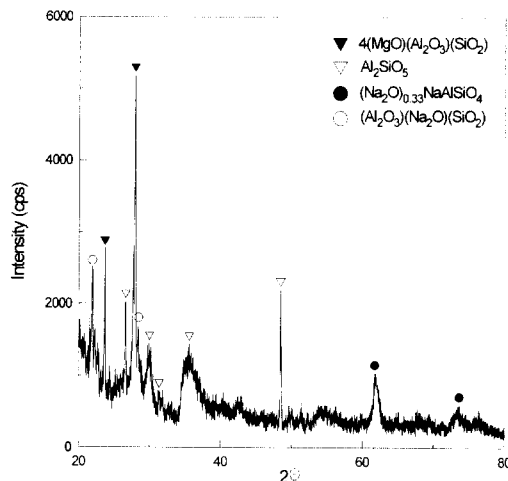


Figure 1. X-Ray diffraction spectrum of bentonite.

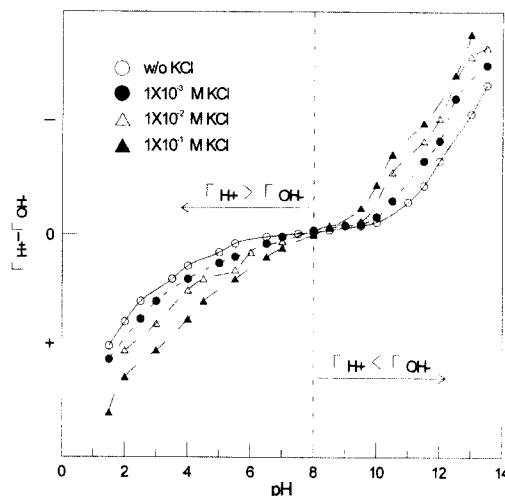


Figure 2. Plot of net Surface adsorption density of potential-determining ions versus pH for bentonite at different concentrations of KCl.

pH increases or decreases, these groups changes in their forms as $Si-(OH)_2^-$ (or $Al-(OH)_2^-$) or $Si-OH_2^+$ (or $Al-OH_2^+$) and due to these reactions H^+ and OH^- ions behave as the major potential-determining ions for oxide solids including bentonite in aqueous environment.

By definition, pzc means the pH for which the surface charge (σ_0) is zero and since σ_0 can be expressed as $F \times (\Gamma_{H^+} - \Gamma_{OH^-})$ for oxides $\Gamma_{H^+} - \Gamma_{OH^-}$ comes to be zero at pzc. In Figure 2, when there was no supporting electrolyte in solution,

$\Gamma_{H^+} - \Gamma_{OH^-}$ for bentonite was shown to increase gradually with pH. In the presence of 1×10^{-3} M KCl, the change in $\Gamma_{H^+} - \Gamma_{OH^-}$ with pH showed a nearly same trend with a slight increase of gradient, which resulted in making a point of intersection at around pH 8. As the concentration of KCl increased, the gradient increased further, however, the cross point was still formed at the vicinity of pH 8. Therefore, it was concluded that the pzc of bentonite determined by solubilization method was established at pH 8. Although not shown here, the isoelectric point (iep) of bentonite particles which measured by electrophoresis apparatus was observed at the almost same pH as pzc. The value of pzc for a given oxide must be same as its iep in the absence of specific adsorption and since KCl, which employed as a swamping electrolyte, does not adsorb onto the bentonite surface specifically the result obtained for pzc of bentonite by solubilization method could be substantiated.

The reason for the establishment of pzc at the cross point shown in Figure 2 can be explained by the so-called screening ion effect. Screening ion effect means that when certain ions have adsorbed specifically or non-specifically on the substrate in solution they come to provide in turn the sites of adsorption of ions with opposite charge for the substrate due to the electrostatic attraction between ion. That is, as shown in Figure 3(a), when the pH condition is below pzc for bentonite, the negatively charged Cl^- ions congregate firstly in the vicinity of bentonite surface because of the electrostatic attraction, which resulting in the non-specific adsorption of chloride ions. Then, the physically adsorbed Cl^- ions function as a screen for the adsorption of protons with the help of electrostatic interaction likewise. The adsorption of H^+ ions invokes a relative increase in $[OH^-]$ in solution, thus, the increase of solution pH. The screening ion effect will become more significant as the adsorption of Cl^- ion increases, which could be confirmed by the further shift of solution pH to the alkaline direction with the concentration of potassium chloride below pzc of bentonite (Figure 2).

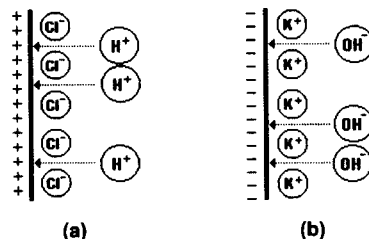


Figure 3. Screening ion effect by swamping electrolyte (a) below and (b) above pzc.

Exactly opposite argument can be applied to the case above pzc. This time, K^+ ions adsorb upon the surface of bentonite firstly, which results in more adsorption of hydroxide ions and, thus, the decrease of solution pH (Figure 3(b)). However, at pzc, Γ_{H^+} for bentonite is same as Γ_{OH^-} so that there will be no screening effect by swamping electrolyte regardless the existence and the concentration of potassium chloride in solution since σ_0 of bentonite is zero in this condition. Accordingly, the point of intersection of the plots of $\Gamma_{H^+} - \Gamma_{OH^-}$ vs. pH at different concentrations of KCl can be reasonably regarded as the pzc of bentonite.

The dependence of surface potential, Ψ_0 , of bentonite on solution pH has also been considered in this communication based upon the measured pzc. There are enough possibilities that pH conditions vary widely when bentonite is employed as the pollutant-controlling medium, therefore, it is very essential to understand the pH-dependence of Ψ_0 of bentonite, which is one of the most influential factors determining its interfacial properties, for a higher efficacy in the application of bentonite.

Ψ_0 is the potential difference across the double layer and is known to be obtainable by applying the Nernst Eq.¹⁸⁾;

$$\begin{aligned}
 \Psi_0 &= (kT / |Z^+| e) \times \ln(C^+ / C^+_{pzc}) \\
 &= (kT / |Z^-| e) \times \ln(C^-_{pzc} / C^-)
 \end{aligned} \quad (2)$$

in which, k; Boltzmann constant (1.381×10^{-23} J/K)
 T; absolute temperature
 Z^+ ; valence of the cationic potential-determining ion

- e; elementary charge (1.602×10^{-19} C)
- C^+ ; concentration of the cationic potential-determining ion (M)
- C^+_{pzc} ; C^+ at pzc (M)
- Z; valence of the anionic potential-determining ion
- C^- ; concentration of the anionic potential-determining ion (M)
- C^-_{pzc} ; C^- at pzc (M)

Since proton and hydroxide ion are the cationic and anionic potential-determining ions for oxides, hydroxides, and silicates in water, when Eq. (2) is applied to bentonite for the cationic case it can be represented as the following equation;

$$\Psi_0 = (kT/e) \times \ln([H^+]/[H^+]_{pzc}) \quad (3)$$

By substituting the numerical values for the variables in the pre-logarithmic factor in Eq. (3) and rearranging, the following Eq. can be obtained.

$$\begin{aligned} \Psi_0 &= 0.059 \times \log_{10}([H^+]/[H^+]_{pzc}) \\ &= 0.059 \times [pzc - pH] \text{ (Volts)} \end{aligned} \quad (4)$$

Eq. (4) implies that the surface potential of bentonite can be theoretically calculated for a specific pH condition when its pzc is known.

Figure 4 shows the change of the estimated Ψ_0 of bentonite as a function of pH and it is noticeable that Ψ_0 increases in the positive direction as pH decreases. This can be clearly reasoned considering that the value and sign of surface potential of a specific substrate is directly determined by the nature of specifically adsorbing ions, i.e., potential-determining ions. As the solution pH decreases, more protons are expected to adsorb on the surface of bentonite, which resulting in the increase of Ψ_0 positively. Eq. (4) also tells us that Ψ_0 of bentonite comes to be zero at pzc. This is explainable by recalling the definition of pzc, that is, there accomplishes no excessive adsorption of either cationic or anionic potential-determining ions at

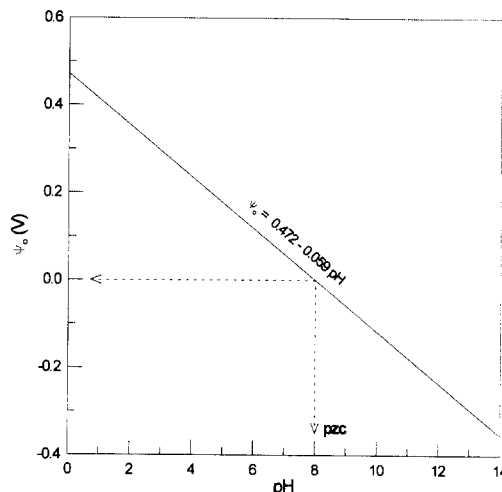


Figure 4. Variation of the surface potential of bentonite according to the pH at 25°C.

pzc so that the surface charge of bentonite is zero at this condition. Since there does not exist either positive or negative charge on the surface, its surface potential is justly zero.

CONCLUSIONS

Bentonite is a material with great potentials for the employment as pollution-preventing medium. The environmental applicability of bentonite can be even broadened when considering its inert and safe physicochemical properties and cheap prices. The purpose of this communication lies in the attempt of understanding of interfacial features of bentonite by measuring its pzc using solubilization technique and theoretically estimating its surface potential based on thermodynamic calculations. Since the calculated surface potential of bentonite can replace with the electrokinetic potential for most cases, it can be usefully employed in controlling the stability of bentonite particles in their application. The surfacial parameters considered are the chief factors determining the status and behavior of fine materials like bentonite, therefore, in relation with the application of bentonite for an efficient control of pollutants their systematic apprehension is indispensable. The results of present investigation are expected to provide a

meaningful information for an environmental utilization of bentonite and to provoke further studies for its enhanced applicability.

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