

FANFEI MIN*¹, CHENLIANG PENG*, SHAOXIAN SONG****HYDRATION LAYERS ON CLAY MINERAL SURFACES IN AQUEOUS SOLUTIONS: A REVIEW****WARSTWY UWODNIONE NA POWIERZCHNI MINERAŁÓW ILASTYCH
W ROZTWORACH WODNYCH: PRZEGLĄD**

Hydration layer on clay mineral surfaces is originated from the adsorption of polar water molecules and hydrated cations on the surfaces through unsaturated ionic bonds, hydrogen bonds and van der Waals bonds. It has attracted great attentions because of their important influences on the dispersive stability of the particles in aqueous solutions. This review highlighted the molecular structure of clay minerals, the origin of hydration layers on clay mineral surfaces, the hydration layer structural model, hydration force and the main parameters of affecting the hydration layers on clay minerals (crystal structure, cationic type and strength, and solution pH). Also, the research methods for hydration layers were briefly described, especially the determination of hydration layer thickness by the Einstein viscosity method and AFM method. In addition, the applications of the stability of fine clay mineral particles in aqueous suspensions were summarized.

Keywords: Hydration layers; clay minerals; dispersion; hydration force

Warstwa uwodniona na powierzchni minerałów ilastych (gliniastych) powstaje w wyniku adsorpcji polarnych cząsteczek wody i uwodnionych kationów powierzchniowych związanych za pomocą nienasyconych wiązań jonowych, wiązań wodorowych i wiązań van der Waalsa. Zagadnienie to wzbudza wiele uwagi ze względu na to, że w dużej mierze warunkuje stabilność dyspersyjną cząstek w roztworach wodnych. W pracy omówiono strukturę molekularną minerałów ilastych, powstawanie warstw uwodnionych na powierzchni minerałów ilastych i siły hydratacji; przedstawiono także model strukturalny warstwy uwodnionej oraz główne parametry warunkujące powstawanie warstwy uwodnionej na powierzchni materiałów ilastych (struktura krystaliczna, rodzaj występujących kationów, stężenie roztworu i jego pH). Ponadto, pokrótce przedstawiono metody badań, ze szczególnym uwzględnieniem badania grubości warstw uwodnionych przy zastosowaniu modelu lepkości Einsteina oraz metody AFM. Ponadto, zestawiono zagadnienia związane ze stabilnością cząstek drobnociąstkowych minerałów ilastych i ich potencjalne zastosowania.

Słowa kluczowe: warstwy uwodnione, minerały ilaste, dyspersja, siła hydratacji

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1. Introduction

Hydrophilic surfaces immersed in water have a strong attraction to the water molecules in the vicinity, resulting in the formation of ordered boundary layers on the surfaces. This phenomenon is termed as hydration, and the layer is termed as hydration layer (Israelachvili et al., 1988; Kendall et al., 2004; Pashley et al., 1984). Fig. 1 schematically represents hydration layer on a hydrophilic surface. The water in hydration layers has higher density and viscosity than bulk water. It has been found that hydration layers play a crucial role in many scientific and technological fields (Anderson et al., 2010; Acuna et al., 2011; Valle-Delgado et al., 2011). For instance, water in the vicinity of biological macromolecules, such as protein and DNA, is important for the structure, stability and function of the biological systems (Higgins et al., 2006; Molina-Bolívar et al., 1999, 1999). In nanoscale materials, hydration layers are in favor of the preparation and reservation of nanoparticles (Chang et al., 2002; Kotov et al., 2001).

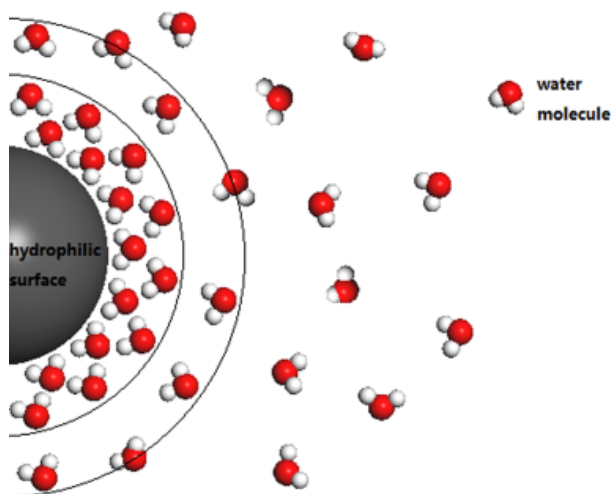


Fig. 1. Schematic view of hydration layer on hydrophilic surface. Water molecules in the small concentric circles can be attracted to vicinity of hydrophilic surface to form ordered layers. The order degree of the water molecules would be decrease with the increase of the distance between water molecule and surface. Outside the great concentric circles water molecules are disordered and less associated (Peng et al., 2005)

Clay minerals, such as mica, kaolinite and smectite, are common gangue minerals in mineral and coal processing. In coal washing plants, the separation of colloidal clay minerals from recycled water is a challenging problem, resulting in a high-solid concentration in the water and thus a detrimental effect on the coal washing circuit. In hydrometallurgical plants, it is difficult to remove colloidal clay minerals from metal-leaching solutions, leading to a poor-quality metal product. The problem is mainly due to the thick hydration layers on clay mineral particle surfaces in aqueous solutions, resulting in a high stability of the dispersions.

During last decades, numerous reports have concerned hydration layers on hydrophilic surfaces in aqueous solutions (Chatterjee et al., 2011; Fukuma et al., 2007; Manciu et al., 2004,

2006; Parsons et al., 2011; Song et al., 2005; Virtanen et al., 2010). In this paper, an attempt has been made to highlight the hydration layers on clay mineral surfaces in aqueous solutions, as well as hydration forces. It included the origin and structural model of hydration layers, hydration force, main parameters of affecting the hydration layers on clay minerals, research methods, dispersion of colloidal particles by hydration force and hydrophobic agglomeration.

2. Origin of Hydration Layers on Clay Mineral Surfaces

Clay minerals are distinguished by layered structures composed of polymeric SiO_4 tetrahedra sheets linked to $(\text{Al, Mg, Fe})(\text{O, OH})_6$ octahedra sheets, either 1:1 (e.g. kaolin group and serpentine group) or 2:1 (e.g. pyrophyllite, talc, mica, illite, smectite, vermiculite and chlorite etc.). These sheets form pseudo-3-D crystals consisting of regular stacks of parallel platelets (face-to-face association) held together. Particularly chlorite may be taken for 2:1:1 mineral, but we can regard it as a 2:1 layer mineral with an interlayer brucite sheet $\text{Mg}(\text{OH})_2$ (Theng, 2012).

There is a fundamental difference between the 1:1 and the 2:1 layers. The 2:1 layer is bounded on both sides by basal oxygen planes whereas the 1:1 layer has basal oxygens on one surface and hydroxyls on the other surface. The interlayer bonding for the 1:1 layer silicates, whether dioctahedral or trioctahedral, is by hydrogen bonds from one hydroxyl surface to the adjacent oxygen surface of the neighboring 1:1 layer. Although they are long hydrogen bonds, there are many of them and the contribution to the interlayer bonding is strong. The 2:1 layer is more complex because it is possible to have a net layer charge as a result of isomorphous substitution. Al for Si in the tetrahedral sheet and Mg for Al in the octahedral sheet are most common. Such a situation would be unstable due to the electrostatic repulsion between all the layers, so the charge must be balanced by extra positive charge (Yin et al., 2012).

For example, Fig. 2(a) shows smectite which belongs to 2:1 clay mineral with isomorphous substitution. The negative charge that results from isomorphous substitution is balanced by the presence of exchangeable cations in the interlayer space of which Ca^{2+} and Na^+ ions are the most common, and the basal spacing c is 0.96-4 nm dependent on the degree of hydration of smectite (Zheng et al., 2011). These cations are capable of acquiring complete or partial hydration layers, resulting in imparting an overall hydrophilic nature to the clay mineral. However, as shown in Fig. 2(b), kaolinite which belongs to 1:1 clay minerals that the bilayers structure are bonded together by hydrogen bonds between the hydroxyl ions of the octahedral sheet and the oxygen atoms of the silica tetrahedral sheet. Therefore, it is difficult for water molecules and hydrated cations to enter into the interlayer, and the basal spacing c is only 0.72 nm (Solc et al., 2011).

When minerals break, there are some degree of unsaturated bonds on the fracture surface of the mineral, so that the surfaces present a certain degree of polarity (Lu et al., 1996). Generally speaking, clay minerals are most commonly cleaved along basal surfaces, mainly the (001) plane. In the case of 1:1 clay minerals, such as kaolinite and serpentine, the unsaturated bonds exposed on basal surface are mainly hydrogen bonds. In the case of 2:1 clay minerals with a great degree of isomorphous substitution, such as illite, smectite and vermiculite, the unsaturated bonds mostly are ionic bonds due to the silica tetrahedron anions on the siloxane surface with electronegative layer charge. For 2:1 clay minerals which have little, if any, isomorphous substitution, e.g. talc and pyrophyllite, the exposed unsaturated bonds are basically van der Waals bonds resulted from the neutral siloxane surface. Among the unsaturated bonds the hydrogen bonds and ionic

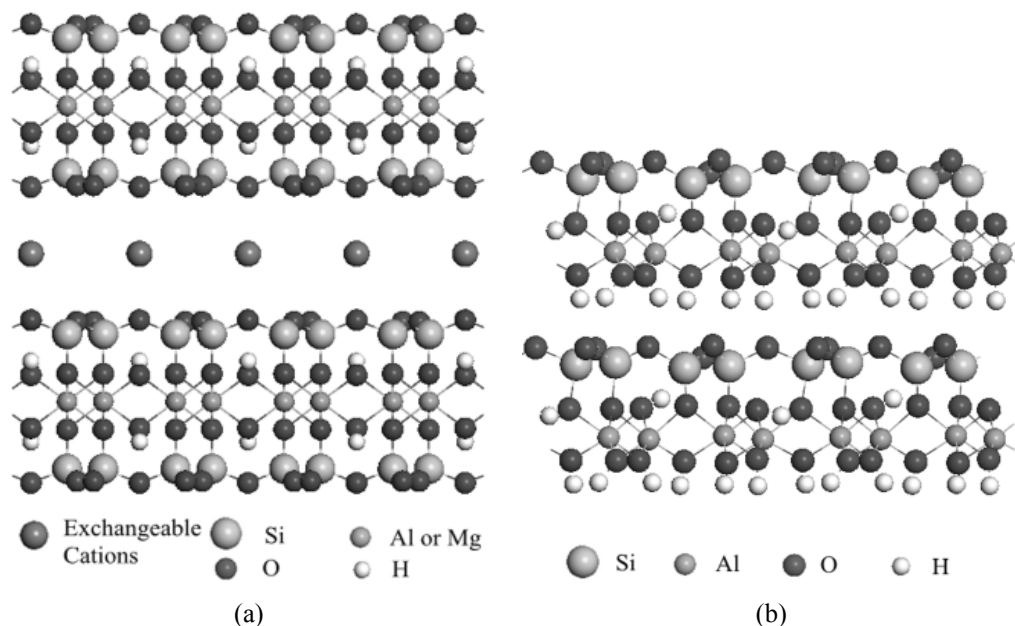


Fig. 2. Layered structures composed of silicon tetrahedron and aluminium octahedron sheets. (a) smectite which belongs to 2:1 clay mineral with isomorphous substitution. There are exchangeable cations in the interlayer space. (b) kaolinite which belongs to 1:1 clay mineral. There are not exchangeable cations in the interlayer space (Anderson et al., 2010)

bonds are relatively strong, whereas van der Waals bonds are very weak. So in aqueous solution in order to compensate the unsaturated bonds, the surfaces with the unsaturated hydrogen bonds and ionic bonds are capable of having strong interactions with water molecules and hydrated cations, such as kaolinite and smectite respectively, and strong hydration layers can easily form on these types of clay minerals surfaces, (Murray, 2000). In contrast the surfaces with unsaturated van der Waals bonds interact only weakly with water molecules. With this type of surface, the water molecules interact predominantly with each other but not with the surface, so there are only weak hydration layers on the surfaces, such as talc and pyrophyllite (Bergaya et al. 2006).

In addition, clay minerals can be cleaved along (100), (010) and (110) plane to some extent, the exposed fresh surface are the edge surface with unsaturated broken Si-O and Al-O bonds, which can strongly interact with water molecules. The result is that the under-coordinated OH groups come to being on the edge surface, and have strong affinity with water molecules by hydrogen bonds and with the hydrated cations by electrostatic attraction to facilitate the formation of hydration layers on the edge surfaces of clay minerals depending on the pH of the solution (Yin et al., 2012).

Hydration layers have been proved to exist on clay mineral surfaces by many experimental evidences. By means of neutron diffraction and quasielastic neutron scattering, Sobolev et al. (2010) found that water molecules form strong hydrogen bonds with the oxygen atoms of nontronite surfaces, and obtained that the diffusion activation energy (E_a) was about 29 ± 3 kJ/mol for water molecules hydrating the surfaces. Salles et al. (2008) studied the hydration sequence on solid

Na-montmorillonite at variable relative humidity (RH) by using thermoporometry, a calorimetric technique combined with XRD. It was shown that the hydration layers on montmorillonite surfaces mainly were due to RH, about 80%. At a high RH, water molecules enter into the interlamellar spaces, producing interlamellar osmotic swelling.

3. Structural Model of Hydration Layers

Most clay minerals are hydrophilic, except for talc and pyrophyllite whose edge surfaces also become hydrophilic depending on the pH of the ambient medium. The typical model of hydration layer for hydrophilic surfaces in pure water, three-structure model, was presented by Drost-Hansen et al. (1971, 1977), as shown in Fig. 3(a). The model shows that there are three types of water layers around the hydrophilic surface including ordered layer, transition layer and bulk water, of which the first two belong to hydration layer. In the ordered layer, water molecules are orderly oriented and in direct contact to the hydrophilic surface. The transition layer is located between the ordered layer and bulk water. The bulk water occupy the outermost space, which does not belong to the hydration layer and in which water molecules are disordered and less associated.

However, the model does not include the role of hydrated cations. Because the permanent

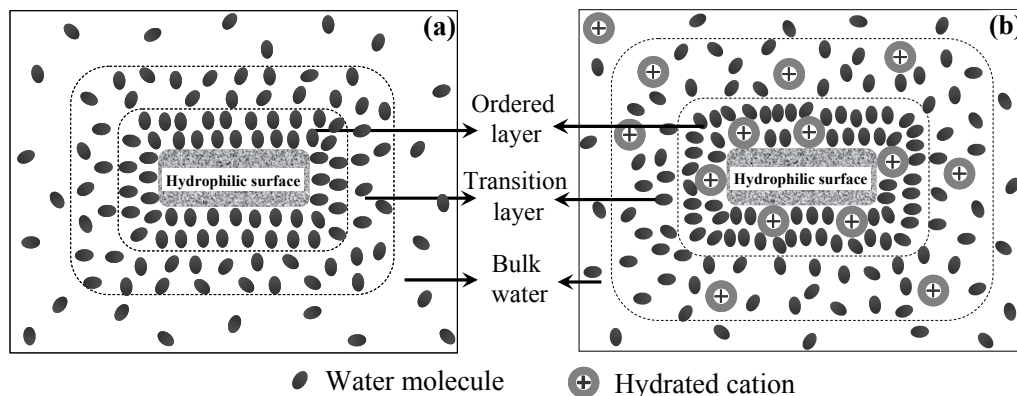


Fig. 3. Three-structure model of hydration layer on hydrophilic surface in pure water (a) and in presence of hydrated cations (b) (Song et al., 2005)

negative charge on the basal surface due to the isomorphous substitution in unit layer and the variable negative charge on edge surface depending on solution pH should be balanced by the metal cations, such as Ca^{2+} , Mg^{2+} , K^+ and Na^+ . The initial sorption of water on the clay minerals is influenced mainly by the hydration of metal cations (Cancela et al., 1997). These cations serve as strong hydrophilic sites for water sorption, and also can participate in the formation of the hydration layers around the clay minerals, as shown in Fig. 3(b). The effect of hydrated cations on hydration layers were also found in other works about silica by Song et al. (2005) and about silica and protein by Valle Delgado et al. (2011).

4. Hydration Forces

In the colloidal system, the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory has been proven to be very useful to explain the stability or aggregation from the assumption that the total interaction between two colloidal particles or surfaces can be divided into two independent portions: a repulsive force due to the overlap of the electrical double layers formed around the charged particles, and an attractive interaction due to van der Waals forces (Derjaguin et al., 1941; Verwey et al., 1948). The double layer repulsive force is affected by the ionic strength of the aqueous solution. The charge screening effect resulted from the ions in solution provokes the compression of the electrical double layers as the salt concentration in the medium increases. Generally, the double layer repulsive force decreases as the ionic strengths increase, quickly approaching zero at ionic strength above a certain value (Jacob et al., 2011). Although the long-range interactions observed in various systems, colloids and surfaces, e.g. at separations between surfaces $h > 10$ nm, are well expressed by the classical DLVO forces but it is inaccurate at very short distances (Grabbe et al., 1993).

Israelachvili et al. (1978) carried out the pioneer works to prove that an additional force acted between mica surfaces in aqueous electrolyte solutions at short separations. Valle-Delgado et al. (2005) measured the interactions between silica particles in aqueous solutions at 1 M NaCl and over the pH range from 3 to 9 with AFM. The results showed that a strong repulsive interaction exists at short distances (below 2 nm), which decayed exponentially with the distance between the particles, and the long-range double layer repulsion is negligible. Other studies on the determination of surface forces between silica surfaces by SFA and AFM suggested that hydration force was responsible for the non-DLVO short-range forces between particles (Meagher, 1992; Yoon et al., 1998). The overlapping of the hydration layers of two interacting surfaces causes an increase in the free energy of the system, provoking the short-range hydration repulsion. The experimental hydration forces (that exponentially decay on the separation distance) between hydrophilic surfaces (e.g. silica, mica, montmorillonite, lipids bilayers, etc.) was given by

$$U_H = \frac{a}{2} \left(C_1 D_1 \exp\left(-\frac{h}{D_1}\right) + C_2 D_2 \exp\left(-\frac{h}{D_2}\right) \right)$$

where C_1 , C_2 , D_1 and D_2 are empirical parameters; a is the particle radius, and h is the shortest separation between particles (Ho et al., 1998; Pashley et al., 1982; Valle-Delgado et al., 2005).

5. Main Parameters of Hydration Layers

5.1. Crystal structure of clay minerals

The hydration layers on clay minerals are mainly related to the crystal structure. Both of the basal surfaces of 2:1 minerals with trilayer structures are composed of oxygen atoms involved in Si–O bonds. When there are little isomorphous substitution and defect sites in crystal structure of 2:1 clay mineral, the Si–O bonds have considerable covalent character and the siloxane surface is neutral and hydrophobic (e.g. talc and pyrophyllite) (Giese et al., 1990; Michot et al., 1994). These surfaces are nonpolar and are not capable of forming hydrogen bonds with water molecules, the water molecules interact predominantly with each other and not with the surface, resulting in hardly any formation of hydration layer (Nulens et al., 1998). The study from molecular dynamics

simulation by Schrader et al. (1900) showed that very weak hydrogen bonds near the hydrophobic siloxane surface are spontaneously broken and created by the movement of water molecules, indicating little hydration layers on them. In addition to above, some extent of hydrophobicity for the siloxane surface of kaolinite and serpentine which are 1:1 clay minerals can be expected since they also have extremely small degree of isomorphous substitution relative to a perfect lattice. Using the method of molecular dynamics simulation (MDS), Du et al. (2007) suggest that the silica tetrahedral face of kaolinite should be hydrophobic, similar to pyrophyllite and talc.

However, in 2:1 clay minerals hydrophilicity can be introduced by isomorphous substitution inducing the presence of exchangeable cations, which are hydrophilic and can polarise the siloxane surface oxygen atoms (e.g., mica, illite, smectite and vermiculite etc.). So hydration layers can easily form on their basal surfaces (Nulens et al., 1998). In addition, hydrophilicity may also derive from the presence of hydroxyl groups at Al-octahedral or Mg-octahedral surfaces in 1:1 clay minerals such as kaolinite and serpentine. In this case water molecules are tightly bonded with hydroxyl groups which can provide plenty of hydrogen bonding sites and facilitate the formation of strong hydrogen bonds resulting in hydration layers on clay minerals (Kalinichev et al., 2007).

5.2. Cationic types and strength

5.2.1. Cationic types

Cationic types in aqueous solution will have an impact on structural properties and thickness of hydration layer on particles or surfaces (Li et al., 2005; Pashley et al., 1984; Turov et al., 1998). For clay minerals, the negative charge due to isomorphous substitution is balanced by the presence of metal cations. but the chemical nature of these metal cations (i.e. effective ionic radius, hydration energy, hydrolysis constant) determines many of the important chemical and physical properties of clay minerals, including the formation of hydration layers.

For swelling clays, e.g. smectite, the measurement of water adsorption isotherms of smectite intercalated with a variety of different monovalent cations (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) by Mooney et al. (1952) has revealed that for the larger cations, less water is adsorbed. Amorim et al. (2007) by XRD found that with increasing water content, the smectite with Li^+ and Na^+ , which have high hydration energy, formed one- then two- and finally three- layer hydration structures in the range of water contents considered. In contrast Liu et al. (2006) found that the smectite with K^+ and Cs^+ , which are weakly hydrated cations, only showed a single hydration structure even at 98% RH. However it is not true that swelling clays have higher extent of hydration with the hydration energies of cations increasing for polyvalent cations. This in part can be attributed to the lower dielectric constant experienced in the vicinity of polyvalent cations.

For non-swelling clays, e.g. kaolinite, the surface adsorbed water is caused by hydrogen bonding. Through enhancing and reducing the hydrogen bonding at the interface the cations can be classified as water structure makers and breakers respectively. FTIR-transmission experiments by Cao et al. (2011) revealed that water structure making cations, such as Mg^{2+} , can enhance the H-bonding of water molecules and increase the “ice-like” structure in solution also stabilize the hydration layer on the cation/solution interface. Water structure breaking cations, such as K^+ , tend to disrupt the organized water structure. Similar results can be found in the works about the role of cations in guar gum adsorption on kaolinite by Ma et al. (2007). The phenomenon of enhancing guar gum adsorption on kaolinite in KCl and CsCl solutions was attributed to the water structure

breaking properties of poorly hydrated K^+ and Cs^+ cations, which can reduce the stability of the hydration layer on kaolinite. Whereas Mg^{2+} and Na^+ even give a measurable decrease in guar adsorption, which indicate that they facilitate the stability of the hydration layer on kaolinite.

5.2.2. Cationic strength

There is a suitable range of cationic strength with respect to the hydration layer and dispersion of clay minerals. For instance Na^+ which is strongly hydrated can enhance the hydration layer thickness and stability of clay minerals in aqueous solution, but if the Na^+ strength is too strong, the dispersion of clay minerals would be converted into agglomeration. The cause might be that too large amount of cations would compete with water molecules on clay mineral surfaces, resulting in the reduction of the ability of water molecules adsorbed on the surfaces. In addition, it can partly be put down to the compression of the diffusion layer of the clay mineral surfaces negatively charged, which reduces the thickness of the diffusion layer and hydration layer.

5.2.3. Solution pH

For clay minerals the basal surfaces and edge surfaces behave differently with respect to their interaction with surrounding water molecules. It is extensively reported that the edge surfaces of clay minerals have broken bonds which give rise to under-coordinated OH groups in aqueous solution (Schrader et al., 1990; Malandrini et al., 1997). These groups are more reactive than the charge neutral OH groups on basal surfaces. So it would be expected that the edge surface will favor hydrogen bonding with water molecules to affect the formation of hydration layer on clay minerals. These OH groups carry either a positive or negative charge depending on the pH of the ambient aqueous solution. At pH values higher than the p.z.c of a mineral, the surface will have a net negative charge and will tend to accumulate hydrated cations. Similarly, the edge surface will have a net positive charge when the ambient pH is lower than the p.z.c, and will weaken the interaction between edge surface and hydrated cations or water molecules. Accordingly, hydration layer on clay mineral surface in alkaline solution is stronger than in acidic solution.

6. Research Methods

There are numerous investigations for hydration layers on hydrophilic surfaces in aqueous solutions. Various techniques such as NMR, IR and X-ray scattering have been used to determine the ordering and mobility of the water molecules in the layers (Nickolov et al., 2005; Pouliquen et al., 2001; Slade et al., 1991; Turov et al., 2005). Molecular dynamics simulation that combines physics, mathematics and chemistry is an advanced research method to study the radial distribution of water molecules around particles. For example the molecular dynamics simulation for the relationship between hydration forces and water molecules polarization by Faraudo et al. (2011) indicated that a strong hydration force related to the polarized 2-3 layers of water molecules in the hydration layer on hydrophilic surface.

The hydration layer thickness is one of the most important parameters of hydration layer, but is one of the most difficult parameters that can be measured accurately. Recently, the Einstein viscosity method and the AFM method for the determination of the hydration layer thickness were presented. The first method was based on the Einstein theory of viscosity of dispersion,

which determined the thickness of hydration layer on solid particles in aqueous dispersions through measuring the relative viscosity of the dispersion as the function of solid concentration, the specific surface area and the density of particles. It was shown that the thickness of hydration layers on silica powders in water was around 12-18 nm by Song et al. (2005) with Einstein viscosity method. The AFM method used Atomic Force Microscope in contact mode to determinate the sum of the thickness of hydration layers on the sample surfaces and AFM tip immersed in aqueous solutions. It was reported that the sum for a silica surfaces and a silicon tip was around 29.6 nm in pure water, 33 nm in 1.5 mol/l NaCl solution and 37.4 nm in 3 mol/l NaCl solutions by Peng et al. (2004).

7. Stability of Colloidal Clay Minerals in Aqueous Solution

Aqueous clay mineral dispersions usually have a high dispersive stability, which might be mainly due to the thick hydration layers on the mineral surfaces and thus the strong hydration force between the particles (Kendall et al., 2004; Pashley et al., 1982). The stability control of the dispersions plays a crucial role in many industrial and technological fields. For instances, in water conservancy project, if the water-conservation dams are built with dispersive clays, the low-salinity water would enhance the dispersion of the clay minerals and bring about harmful effects on water conservancy engineering (Diaz-Perez et al., 2007). In petroleum industry, high-stability drilling fluids (which consist of dispersive clay minerals) would result in a very good rheology capacity and a much less filter loss (Bailey et al., 1994).

In the field of coal washing, fine clay mineral particles are greatly increasing in raw coals due to the increasing mechanization degree of coal extraction and poor raw-coal quality. These fine particles appear in coal-slurry water in a high stability, and are hard to be removed effectively. This phenomenon is very detrimental to the separation processes in coal washing plants, such as flotation and fine coal filtration (Atesok et al., 2002; Xia et al., 2007). In some cases, it is necessary to discharge this coal-slurry water into rivers, which will lead to serious pollution to the water bodies. Accordingly, it is important to study the hydration layers on clay minerals in coal-slurry water, and to develop an effective coagulation process for the clay mineral fines through the elimination of the hydration layers.

Hydrophobic agglomeration is an effective process for coal-slurry water treatment, which is originated from the hydrophobic attraction between hydrophobic particles in aqueous suspensions. The attraction was found to be 10-100 times stronger than van der Waals force. For hydrophilicity of clay minerals, the aggregation could be realized by rendering surfaces hydrophobic upon the adsorption of surfactants on the surfaces (Song et al., 2000). For example polyacrylamide could be also used to achieve the hydrophobic agglomeration of kaolinite fines in water through a hydrophobic modification (Ren et al., 2008).

8. Summary

The hydration layer plays a crucial role in the stability of clay minerals in aqueous solution. The clay mineral particle surface adsorbs polar water molecules mainly by the unsaturated ionic bonds, hydrogen bonds and van der Waals bonds. The crystal structure of clay minerals, cationic types and strength, and solution pH have influence on structural properties and thickness

of hydration layers near clay minerals surfaces. The research of hydration layers has good application prospects on the agglomeration and sedimentation of fine particles in coal slurry water.

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