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Investigation on hydration layers of fine clay mineral particles in different electrolyte aqueous solutions

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ABSTRACT

The hydration of clay minerals due to adsorption of water molecules and hydrated cations in electrolyte aqueous solutions would affect the stability of dispersions, resulting in some detrimental effect in mineral processing and hydrometallurgy. A parameter, called as hydration index *I*, was presented to evaluate hydration layers on fine clay mineral surfaces in different electrolyte aqueous solutions through measurements of the relative viscosities of fine mineral dispersions as a function of the volume fractions of dry particles. The effect of type and concentration of electrolyte on hydration of fine clay mineral particles in aqueous solutions was investigated. The results showed that both hydration index *I* of montmorillonite and kaolinite in Na^+ aqueous solutions were larger than that in Ca^{2+} aqueous solutions at the concentration of 0.001 mol/L; either in Na^+ or Ca^{2+} aqueous solutions, the hydration index *I* of montmorillonite increased firstly with increasing concentration of electrolyte in aqueous solutions, then decreased when being above a certain concentration, whereas the hydration index *I* of kaolinite decreased with increasing electrolyte concentration when it being above 0.001 mol/L.

1. Introduction

Clay suspensions are the first step to obtain commercial products that have diverse size, shape, material composition and cost. The stability and flow properties of clay suspensions are of great importance in the manufacturing of various products. Hydration properties of clay particles in an aqueous solution play a significant role in understanding the dispersion. These properties govern the flotation, coagulation and dispersion properties in suspension systems and also identify the optimal conditions of a well dispersed system [1].

The most typical property of clay minerals is their ability to adsorb water molecules and hydrated cations in aqueous solutions, resulting in hydration on the external surface and internal surface. There are numerous evidences of the existence of ice-like structure water on clay minerals [2–5]. Hydration characteristics of different clay may be related to their chemical composition and crystal structure, to the kind and degree of isomorphous replacements in their structure, and the amount and nature of their associated exchangeable cations. After that clay hydration studies were conducted since 1933, a lot of experimental and simulation studies have been done to understand the clay hydration [6–10]. Hydration plays a significant role in dispersion and sedimentation of clay minerals in aqueous solutions. Recently, removing common gangue minerals which are mainly clay minerals, such as illite, kaolinite and smectite, from recycled water and metal-leaching solutions become a growing problem in mineral processing and hydrometallurgy. For instance, 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 sometimes difficult to remove colloidal clay minerals from metal-leaching solutions, leading to a poor-quality metal product. The problem is primarily due to the strong hydration on clay mineral particle surfaces in aqueous solutions, resulting in a high stability of the dispersions [11,12].

The purpose of our investigation is to understand the effect of Na^+ and Ca^{2+} on hydration of clay minerals in aqueous solutions by the method of viscosity measurement. The method was used to study the hydration degree of clay minerals in aqueous solutions by calculating hydration index *I*, based on measurements of the relative viscosities of the clay mineral dispersions in aqueous solutions as a function of volume fractions of dry particles.

2. Theory

The viscosity of liquid would increase after adding the colloidal particles owing to the effect on the flow pattern. Einstein viscosity equation, which was put forward by Albert Einstein in 1906, expresses the viscosity of a dilute dispersion of solid spheres as follows [13]:

$$\eta/\eta_o = 1 + 2.5\phi_p \tag{1}$$

where the quantity η/η_o is termed relative viscosity, η and η_o are the viscosity of the dispersion and liquid medium, respectively, ϕ_p is the

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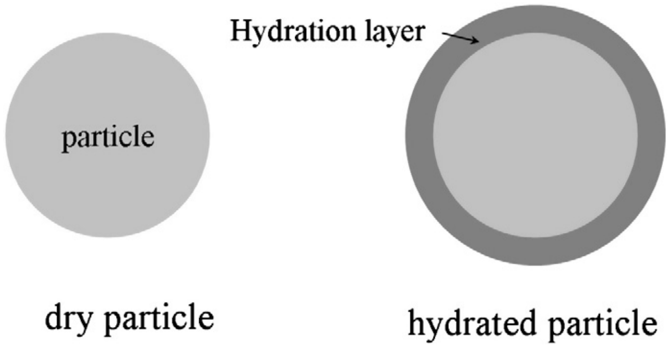

Fig. 1. Schematic diagram of dry particle and hydrated particle.

volume fraction of dispersed particles. In Eq. (1) the relative viscosity linearly increases with increasing volume fractions of dispersed particles with a slope of 2.5. The equation is limited to the concentration below $\phi_p = 3\%$.

It is stressed that the Einstein viscosity equation is based on the most essential postulate that dispersed particles are rigid spheres with no hydration layers on their surfaces [13]. But the fact is that the hydration layers could form on the surface of some mineral solid particles when dispersed in aqueous solutions [14]. The hydration of particles can expand the particle volume through bringing in the volume of hydration layers, as shown in Fig. 1. The expanding of the volume enhances the viscosity of the dispersion [15]. Though they would not increase the viscosity of dispersion in the same way as the rigid solid spheres described by the Einstein equation because hydration layers are not rigid, we could assume that the volume contribution of hydration layers increases the viscosity of the dispersion in γ times as that of the rigid solid spheres does. Then Eq. (1) becomes:

$$\eta/\eta_o = 1 + 2.5\left(\phi_p + \gamma\phi_h\right) \tag{2}$$

where φ_p and φ_h are the volume fraction of the dry particles and the hydration layers in the dispersion, respectively, which can be expressed by

$$\phi_p = \frac{V_p}{V} \tag{3}$$

$$\phi_h = \frac{V_h}{V} \tag{4}$$

where V_p and V_h are the volumes of dry particles and hydration layers, respectively; V is the volume of the dispersion. From Eqs. (2), (3) and (4), we can obtain

$$\begin{aligned}\frac{\eta}{\eta_o} &= 1 + 2.5\left(\phi_p + \gamma\frac{V_h}{V}\right)\\ &= 1 + 2.5\left(\phi_p + \gamma\frac{V_h}{V_p}\phi_p\right)\\ &= 1 + 2.5\left(1 + \gamma\frac{V_h}{V_p}\right)\phi_p.\end{aligned} \tag{5}$$

If the particle concentration is not negligible in nanoscale particle dispersion, the ratio (V_h/V_p) of the volumes of hydration layers and dry particles could be independent of the volume fraction (ϕ_p) of the dry particles. Therefore, a graph of η/η_o against ϕ_p should yield a straight line with the intercept of 1 for a given dispersion, and

$$\mathrm{Slope} = \mathrm{k} = 2.5\left(1 + \gamma\frac{V_h}{V_p}\right). \tag{6}$$

Defined

$$k_h = \gamma\frac{V_h}{V_p} \tag{7}$$

where k_h is the contribution of hydration layer to the slope of spherical particle. However, the deviation of the experimental slopes from Einstein theoretical value might not only be due to the hydration layers, but also due to the ellipticity of the particles. Therefore, the slope of the straight line k can be expressed by

$$k = 2.5(1 + k_h + k_e) \tag{8}$$

where k_e is the contribution of particle ellipticity to the slope. The deduction from Eq. (2) to (8) derived from Ref. [14] and [15]. In our case, the montmorillonite and kaolinite particles are layered structure whose $k_e \neq 0$. At present there is not applicable model to calculate k_e, but we can obtain it from rod-like particle model,

$$k_e = \beta\left(\frac{a}{4b}\right)^2 \tag{9}$$

where β is the shape factor of clay minerals; a and b are the width and thickness, respectively. Therefore, Eq. (9) becomes

$$k = 2.5\left(1 + \gamma\frac{V_h}{V_p} + \beta\left(\frac{a}{4b}\right)^2\right). \tag{10}$$

Because montmorillonite samples used in the series of measurements were same, similarly for kaolinite samples, the slopes in Eq. (10) mainly varied with the contribution of hydration of clay minerals in different aqueous solutions. Therefore, we can search for the influence of electrolyte on the hydration of montmorillonite and kaolinite particles in different aqueous solutions. The hydration index I was defined as:

$$I = \gamma\frac{V_h}{V_p} + \beta\left(\frac{a}{4b}\right)^2 \tag{11}$$

where I is termed hydration index, which represents the hydration degree of clay minerals in different aqueous solutions. From Eqs. (10) and (11), the hydration index I was obtained:

$$I = 0.4k - 1. \tag{12}$$

Therefore, hydration index I can be calculated through measurements of the relative viscosities of colloidal dispersions as a function of volume fractions of the dry particles.

3. Experiment

3.1. Materials

The montmorillonite was obtained from Fenghong New Material CO., LTD. (Zhejiang, China). The kaolinite was obtained from Huaibei Jinyan Kaolinite CO., LTD. (Anhui, China). Both of the purity was more than 99%. The water used in this study was first distilled and then passed through resin beds and a filter (0.2 μm). The residual conductivity of the water was less than 1 μS/cm. pH of the aqueous solutions was adjusted by adding hydrochloric or sodium hydroxide solutions. All of electrolytes were analytical grade.

3.2. Experimental methods

In this work, a given weight of dry clay mineral powder was first put into a 100 ml measuring flask. The flask was then filled to the mark with aqueous electrolyte solutions. The clay mineral dispersion was mildly stirred with a magnetic agitator at 180 rev/min for 10 h until it dispersed completely. All pH values of dispersions were 8