

Effect of Electrolytes on Rheological Properties of Young-II Bentonite Suspension

Wha Woo Shin* and Kwang Pyo Lee

*College of Pharmacy, Won-Kwang University, Iri 510 and
College of Pharmacy, Chung-Ang University, Seoul 151, Korea

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Abstract □ Dependence of the flow behavior of aqueous suspension of Young-II bentonite on the concentration and the type of electrolytes was studied. Viscosity measurements were made with Rion Viscotester, using No. 3 rotor at 62.5 R.P.M. at 25°C. As electrolyte concentration increased, the apparent viscosity was observed to increase. Changes in viscosity were in general agreement with predicted results based on the Hofmeister sequence and the Schulze-Hardy rule.

The observed electrolyte effect on the apparent viscosity was discussed in terms of the Verwey-Overbeek theory.

Keywords □ Young-il bentonite-montmorillonite □ Flocculation by electrolytes-monovalent cations, divalent cations, multivalent cations, anions □ Rheological properties-thixotropy □ Schulze-Hardy rule □ Hofmeister series □ Verwey-Overbeek theory

It is well known that thixotropy preferentially occurs in sols or suspensions containing plate-shaped or rod-shaped particles such as ferric oxide, vanadium pentoxide and many clay minerals. The montmorillonites to which the bentonite clay belongs have a layer structure composed of extremely small platelets,¹⁻³⁾ and their aqueous suspension exhibits pronounced thixotropic properties. Thus the thixotropy of bentonite suspension has been a frequent subject of experimental investigations.⁴⁻⁶⁾ Bentonite is drastically different from the other clay minerals in that it consists of thin submicroscopic flakes with high area-to-thickness ratio (as large as 100) and

that it swells extensively in the presence of water.^{2,3)} Consequently, the relationship between its colloidal stability and flow properties is far more complex than that of any other clay suspensions.

Due to the technological importance of bentonite, particularly in drilling-fluid applications and in the pharmaceutical industry as an emulsifying-suspending agent, the peptization and flocculation in relation with rheological properties of bentonite suspension have been extensively investigated.⁶⁻⁹⁾ However, the mechanism in which the electrolytes of various ionic charges influence the rheological behavior of bentonite suspension is not clearly understood.

In the present work, rheological properties of 8 wt. % Young-II bentonite suspension containing electrolytes of various charge types were measured. The experimental results were analyzed and rationalized in terms of Hofmeister sequence, Schulze-Hardy rule, and Verwey-Overbeek theory.

EXPERIMENTAL METHODS

1. Preparation of the Sample

(a) *Sample Studied* The bentonite sample studied was Young-II (Kyung-Buk Province, Korea) bentonite. The chemical composition of the sample was in weight percent SiO₂(66.34), MgO (2.20), Al₂O₃(16.00), Fe₂O₃(2.42), CaO(2.31), Na₂O(2.36), K₂O(0.66) and ig.loss(7.68

%). The bentonite sample was pulverized into the powder of ASTM 200~270 mesh using an iron mortar and dried at 110°C for a week prior to use.

(b) *Preparation of Aqueous Bentonite Suspension* A 16 wt.% aqueous suspension was prepared in 500 gm. portion by adding 80 gm. of bentonite to 420 ml. of distilled water, and by mixing for 10 minutes in a Waring Blender, Model No. 1120. The suspension was then weighted, and water lost by evaporation was replaced. The prepared gel was allowed to stand overnight for sufficient hydration to occur, and then used for the study. Aqueous bentonite suspensions of 16 wt.% were used for all tests in this work.

(c) *Preparation of the Suspensions Containing a Final Concentration of Electrolytes* Let the final concentration be x wt.% clay and y meq./l electrolyte. One hundred ml. of $2x$ wt.% clay was pipetted into the blender and 100 ml. of $2y$ meq./l electrolyte was then added slowly with constant stirring at moderate speed for 3 minutes. By this means, high local concentrations of electrolyte were avoided in preparing the samples. The concentrations of electrolyte ranged from 0.2 to 2000 meq./l.

2. Apparatus and Procedures

Viscotester (RION VT-02 Type, Japan) is a commercial rotational viscometer. As the motor rotated, the viscous drag of the sample on the rotor is shown as a deflection on the dial of the instrument with a 0-100 scale. When analyzing Newtonian fluids, the absolute viscosity value is computed by the relation: viscosity (in poises) = RION factor \times dial readings. In the case of non-Newtonian fluids, the results are only of comparative value, and such experimental conditions as R.P.M., rotor number, temperature, and rotation time of the rotor should be specified.

All tests in this study were made at 25°C,

using a No. 3 rotor at 62.5 R.P.M. All viscosity readings were taken after 1 minute rotation of the rotor in the test samples which had been allowed to stand for 12 hours in the constant temperature bath at 25°C.

RESULTS

(a) Monovalent Cation Effect

Figure 1 represents the variation of the viscosity as a function of 1-1 valent electrolyte concentrations for 8 wt.% Young-II bentonite suspension. Various concentrations of 1-1 valent electrolytes were used to investigate the effect of concentration of the monovalent cations on the flocculation of the bentonite suspension. In Fig. 1, the following facts are observed:

(1) The flocculating power of monovalent cations decreases slightly in the order of $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ over the range of electrolyte concentration added. This sequence of the monovalent cations is called the lyotropic series or Hofmeister series in colloid chemistry. The "flocculation value" is defined as the minimum concentration of an electrolyte to cause the flocculation of a certain sol in a given time. That is, the lower the flocculation value of an elect-

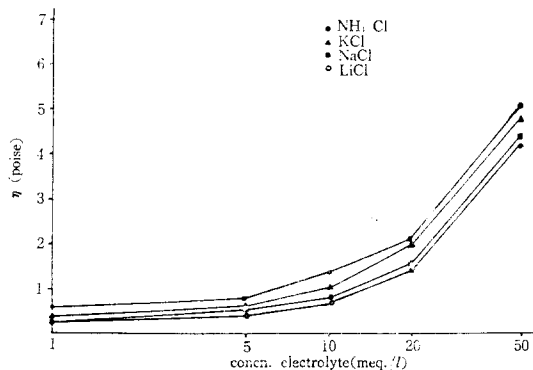


Fig. 1. Variation of the viscosity with 1-1 valent electrolyte concentrations for 8wt.% Young-II bentonite. Viscosity reading was taken after 1 minute rotation of No. 3 rotor at 62.5r.p.m. at 25°C.

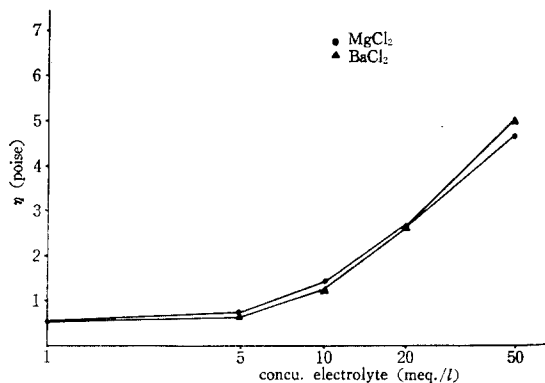


Fig. 2. Variation of the viscosity with 2-1 valent electrolyte concentration for 8wt.% Young-II bentonite. Viscosity reading was taken after 1 minute rotation of No. 3 rotor at 62.5r.p.m. at 25°C.

rolyte, the greater its flocculating power.

(2) The viscosity increases as the concentration of a 1-1 valent electrolyte increases. Other investigator⁷⁾ has shown that the decrease in viscosity occurred regardless of the type of monovalent cations in the range of extremely high concentration of electrolytes.

(b) Divalent Cation Effect

Figure 2 illustrates the effect of concentration of the divalent cation electrolytes on the viscosity of 8 wt.% Young-II bentonite suspension. Fig. 2 shows the following results:

(1) The flocculating power of Ca^{2+} and Ba^{2+} , and the degree of flocculation at a given concentration of both cations are similar to each other. These are in agreement with the Schulze-Hardy rule and the Verwey-Overbeek theory, i. e., the flocculation of clay suspension is not affected by the type of cations, but by the concentration and charge of cations.

(2) The viscosity increases over the range of a 2-1 valent electrolyte concentration added as the electrolyte concentration increases.

(c) Anion Effect

Figure 3 illustrates the variation of the viscosity as a function of the concentration of three

different types of anions for 8 wt. % Young-II bentonite suspension, i. e., the salt-flocculation curves for K_2CO_3 , KCl , and KI are shown.

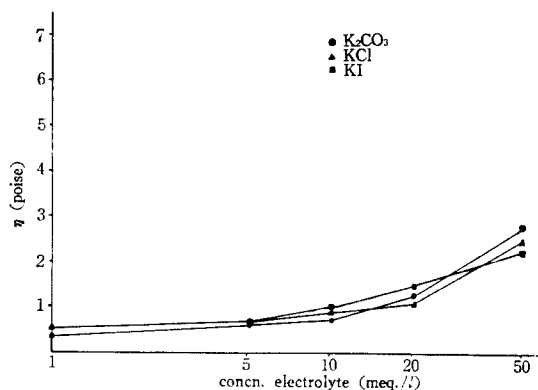


Fig. 3. Variation of the viscosity with K_2CO_3 , KCl and KI concentration for 8wt.% Young-II bentonite. Viscosity reading was taken after 1 minute rotation of No. 3 rotor at 62.5r.p.m. at 25°C.

The results in Fig. 3 does not reveal any significant difference in the viscosity due to the three different types of anions, i. e., CO_3^{2-} , Cl^- , and I^- . This phenomenon indicates that the Young-II bentonite suspension is not affected by anions, but by cations because of the fact that most clay particles are negatively charged.

(d) Effect of Cation Valence

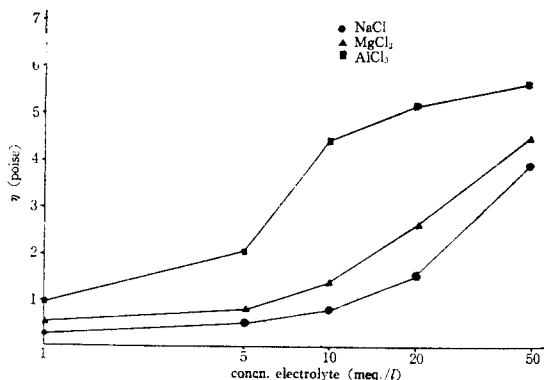


Fig. 4. Variation of the viscosity with 1-1, 2-1 and 3-1 valent electrolyte concentration for 8wt. % Young-II bentonite. Viscosity reading was taken after 1 minute rotation of No. 3 rotor at 62.5r.p.m. at 25°C.

In Figure 4, the variation of the viscosity with 1-1, 2-1, and 3-1 valent electrolyte concentrations for 8 wt. % Young-II bentonite suspension is shown. NaCl, MgCl_2 and AlCl_3 were used for the comparison of the effect of cation valence on flocculation of 8 wt.% Young-II bentonite suspension.

Figure 4 shows the following results:

(1) The flocculating power of the three cations (Na^+ , Ca^{2+} and Al^{3+}) of different charge follows the Schulze-hardy rule over the range of electrolyte concentrations added: $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$.

(2) The viscosity increases over the range of cation concentration added regardless of the cation valence as the cation concentration increases.

DISCUSSION

(a) *Verwey and Overbeek's Theory and its Application to Bentonite Suspension Flocculated by Electrolytes.*

Lyophobic colloids are characterized by the fact that their stability (peptization and flocculation), rheological properties, light-scattering and other physical properties are mainly determined by the electric double layer surrounding the particles. Theory of the interaction of the electric double-layers was offered by Verwey and Overbeek in relation to the stability of lyophobic colloids.¹⁰ They concluded that the stability must be associated with an increase in the free energy leading to a repulsion between the particles. The repulsive potential calculated from consideration of the free energy for certain special cases has been combined with London-van der Waals attractive potential calculated by Hamaker¹¹) to obtain net interparticle energy as a function of particle distance.

Verwey and Overbeek derived the following

equation for the repulsion potential V_R between two electric double-layers, utilizing the theories of both Gouy and Stern, mainly Gouy's view because of its more simple mathematical treatment:

$$V_R = \left(\frac{64nkT}{\kappa} \right) \gamma^2 \exp(-2\kappa d) \quad (1)$$

$$\gamma = \frac{\exp(z/2) - 1}{\exp(z/2) + 1}$$

$$z = \frac{Ve\Phi_0}{kT} \quad (2)$$

$$\kappa = \left(\frac{8\pi ne^2 V^2}{\epsilon kT} \right)^{1/2}$$

It was assumed that no changes in surface potential or double-layer charge occurred. This relation is often a good approximation for large values of d comparison to $1/\kappa$ (i.e., $\kappa d \gg 1$).

Here,

n local ionic concentration in number of ions/cm³ (i.e., normality $\times 10^{-3} \times$ Avogadro's number)

kT Boltzmann's constant \times absolute temperature

Φ_0 surface potential

V valence of ion (number)

e elementary charge 4.77×10^{-10} e.s.u.

ϵ dielectric constant of the medium

d half-distance between surfaces

$1/\kappa$ is known as Debye characteristic length, and is an approximate measure of the thickness of the electric double-layer.

Eq. (1) for V_R is a useful equation as it confirms the facts that V_R for large distances declines exponentially, and the more rapidly, the smaller $1/\kappa$. Eq. (1) was used by Verwey and Overbeek for the explanation of a simple flocculation.

From Eq. (2) one can predict the effect of electrolytes on the configuration of an electric double-layer: the higher the concentration and the higher the valence of the ions of opposite sign, the more the double-layer will be comp-

ressed. This result will be important in the explanation of the Schulze-Hardy rule.

London-van der Waals attractive potential calculated by Hamaker is given by the equation.³⁾

$$V_A = -\frac{\pi q^2 \lambda}{48} \left[\frac{1}{d^2} + \frac{1}{(d+D)^2} - \frac{2}{\left(d + \frac{D}{2}\right)^2} \right] \quad (3)$$

According to Eq. (3) for V_A we may assume that London-van der Waals attractive potential is approximately independent of the electrolyte added, since the equation does not contain terms involving the concentration or valence of the ions of opposite sign. In Eq. (3), d is the half-distance between two parallel plates, D is the thickness of the plate and λ is a factor involved in the London formula. From the relation of the quantities q and λ , V_A can be expressed by the following formula:

$$V_A = -\frac{A}{48\pi} \left[\frac{1}{d^2} + \frac{1}{(d+D)^2} - \frac{2}{\left(d + \frac{D}{2}\right)^2} \right] \quad (4)$$

in which A is the London-van der Waals constant, being approximately equal to 10^{-12} .

Thus, one may see that the net interaction energy between particles is mainly governed by V_R . The net interaction-energy curves, or "potential curves of interaction", which involves both the repulsive and attractive energies, can be translated in terms of sol stability and flocculation by the following consideration.¹⁰⁾ Two particles may approach each other in a relative distance at which the deep minimum in the potential energy occurs, and become associated because of the prevailing attraction. The following three cases will appear:

1. In the case of very low electrolyte concentrations, where the particle separation is very large, the flocculation process is so retarded by the appreciable long-range repulsion that it may take a very long time before flocculation is

perceptible in the sol (stable sol). (Fig. 5)

2. At intermediate concentrations of electrolytes (Fig. 6), the flocculation process is slowed down by the long-range repulsion (slow flocculation).

3. On the other hand, in the case of a high electrolyte concentration the potential curve shows no repulsion at any particle distance (Fig. 7), and particle flocculation occurs at a maximum rate (fast flocculation).

A large portion of the potential curve above the distance coordinate, or a large energy barrier, reduces the rate at which the sol particles associate by "jumping over the barrier". When the potential barrier becomes smaller, the rate of flocculation increases, and in the absence of a barrier, the rate is maximal. The height of the barrier is determined by the magnitude and range of the double-layer repulsion energy. The

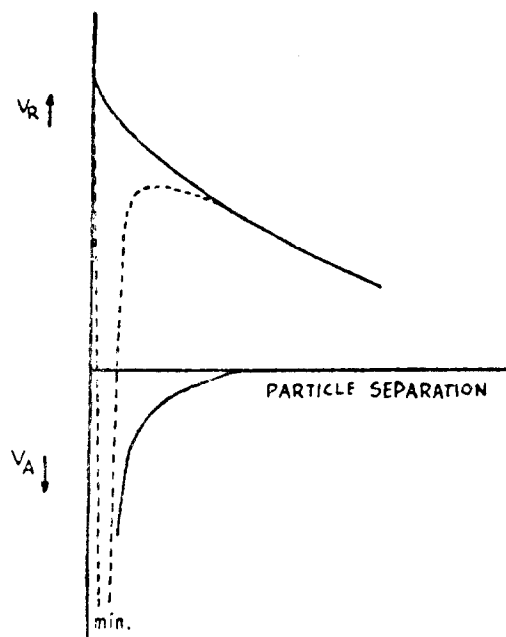


Fig. 5. Net interaction energy as a function of particle separation at low electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that the potential barrier is very high.

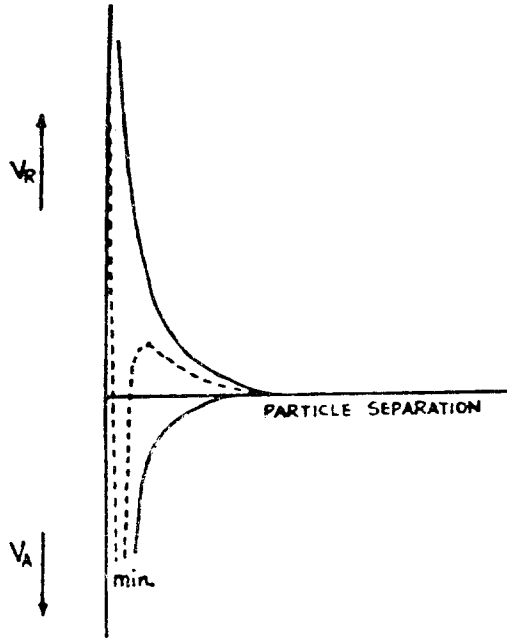


Fig. 6. Net interaction energy as a function of particle separation at intermediate electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that the potential barrier is remarkably reduced.

addition of electrolytes causes a compression of the double layer (a decrease in $1/\kappa$) and, therefore, a reduction of the range of repulsion and a reduction of the height of the energy barrier in the interaction curve. Since the compression of the double layer is determined by the concentration and valence of ions of opposite sign, the stability theory is able to explain the Schulze-Hardy rule [see Eq. (2)].

For plate-shaped particles oriented parallel to each other, the London-van der Waals potential for the relevant distance region can be represented by a d^{-2} law. Combining this with the approximate Eq. (1) for the repulsion potential, Verwey and Overbeek derived the following criterion for the transition between flocculating and stable sols:

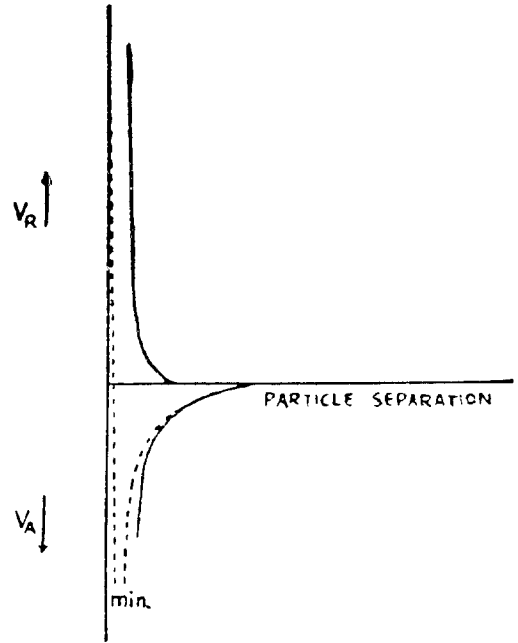


Fig. 7. Net interaction energy as a function of particle separation at high electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that there is no potential barrier.

$$n = \frac{107\epsilon^2 k^2 T^5 \gamma^4}{A^2 (Ve)^6} \quad (5)$$

Thus, they found for the flocculating concentration c (in millimoles per liter) of a V - V valent electrolyte at room temperature,

$$c = 8 \times 10^{-22} \frac{\gamma^4}{A^2 (Ve)^6} \quad (6)$$

As for $z/2 < 1$ we obtain an even simpler equation relating V and c at incipient flocculation:

$$\gamma = \frac{1 + \frac{z}{2} + \dots - 1}{1 + \frac{z}{2} + \dots + 1} \approx \frac{z}{4} = \frac{Ve\Phi_0}{4kT}$$

Hence, they found instead of Eq. (6)

$$c = \frac{10^{-22}}{32A^2 V^2} \left(\frac{e\Phi_0}{kT} \right)^4$$

and they obtained the very simple result that the flocculating concentration is approximately

proportional to the fourth power of the double-layer potential:

$$c = \text{constant} \cdot \frac{1}{V^2} \Phi_0^4 \quad (7)$$

For larger values of Φ_0 , however, especially for valences higher than 1, γ^4 approaches unity, and, therefore, the flocculation value is no longer very sensitive to the double-layer potential. This leads to a very simple limiting law which relates the influence of the valency of the electrolyte to the flocculation concentration. According to Eq. (6), if γ^4 approaches unity, the flocculating concentration of electrolytes is merely proportional to V^{-6} . Thus Verwey and Overbeek found in this case that the amounts of 1-1 valent, 2-2 valent and 3-3 valent electrolytes required to flocculate a lyophobic sol or suspension are in a ratio

$$1:(1/2)^6:(1/3)^6 \text{ or } 100:1.6:0.13.$$

This result of the approximate theory stands in very good agreement with colloid chemical experience as formulated long time ago in the well-known Schulze-Hardy rule. Good agreement between the theory and experiment has been found with sols containing asymmetric particles, e.g., with the sodium montmorillonite clays by Kahn.⁷⁾

(b) Effect of Monovalent Cations

In Fig. 1, one sees that the flocculating power of monovalent cations over the range of electrolyte concentration added follows the sequence of the Hofmeister series in the order of $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Monovalent cation effect on the flocculation of lyophobic sols such as bentonite suspension cannot be predicted from the Overbeek and Verwey theory, since the theory does not involve the type but the valence and concentration of ions of charge opposite to that of the particle surface. This indicates the fact that although these cations are all monovalent, their rates of ion exchange are different.

(c) Effect of Polyvalent Cations

Fig. 2 shows that both Mg^{2+} and Ba^{2+} have nearly the same effect on the flow property of 8 wt. % Young-II bentonite suspension. This fact is predicted from the Schulze-Hardy rule or the Verwey-Overbeek theory, since those cations are divalent. It is a well-known rule of colloid chemistry that ions of higher valence preferentially replace those of lower valence in electric double-layer. In the case of the bentonite system, it is probable that Na^+ in the double-layer of the particle will be replaced mainly by Mg^{2+} or Al^{3+} to form magnesium or aluminum bentonite,

Fig. 4 indicates that the flocculating power of cations follows well the Schulze-Hardy rule, which states that the flocculating power of electrolytes is predominantly governed by the valence rather than type of those ions with a charge opposite to that of the particle. The results of the flocculation do not, however, fit quantitatively into the Verwey-Overbeek theory, which predicts flocculation values in the ratio of 1: $(1/2)^6$: $(1/3)^6$ for mono-, di-, and trivalent cations. It may be due to two factors, i.e., the high concentration (8 wt. %) of Young-II bentonite suspension in this study and the effect of cation exchange which might occur.¹²⁾

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