

BULLETIN OF THE KOREAN CHEMICAL SOCIETY

VOLUME 3, NUMBER 3, SEPTEMBER 30, 1982

Effect of Zeta-Potential on the Viscosity of Clay-Water Suspension

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(Received April 7, 1982)

Viscosity and zeta-potential of 11.0 wt. % aqueous bentonite suspension containing various electrolytes and hydrogen-ion concentration were measured by using a Couette type automatic rotational viscometer and Zeta Meter, respectively. The effects of pH and electrolytes on the rheological properties of the suspension were investigated. A system, which has a large zeta-potential, has a small intrinsic relaxation time β and a small intrinsic shear modulus $1/\alpha$ in the Ree-Eyring generalized viscosity equation, *i.e.*, such a system has a small viscosity value, since $\eta = \beta/\alpha$. In general, a stable suspension system has large zeta-potential. The stability condition of clay-water suspension can be estimated by viscometric method since stable suspension generally has small viscosity. The correlation between the stability, viscosity and zeta-potential has been explained by the Ree-Eyring theory of viscous flow.

Introduction

The rheological properties of clay-water suspension are complex, and not fully understood in spite of their scientific and technical importance. This complexity arises from the sign and magnitude of surface potential of the crystal face where an electric double layer is developed. The impurities in the clay also play an important role in the complexity since the impurities are different even in the same kind of the clay.¹

The stability theory of lyophobic colloids was developed by Verwey and Overbeek,² they considered that the particle-particle interactions are contributed by the two factors, the attraction term due to London dispersion force and the repulsion term arising from electrical double layer interaction. The experimental methods for studying the electrical double layer and the measurements of electrophoretic properties of clay particles were extensively studied.³

Van Olphen⁴ considered that the particle-particle interactions are divided into the three modes; edge-face, edge-edge and face-face, and that the interaction modes change with electrolytic environment. Rand *et al.*⁵ studied commercial kaoline suspension in water, interpreted the effect of electrolytes and pH on the Bingham yield stress, and also studied the sedimentation volume by using the Van Olphen clay colloid model. Park and Ree⁶ investigated the kinetics of

aqueous bentonite suspension, and developed a theory of thixotropy. The effect of electrolytes on flow properties of aqueous bentonite suspension was studied by Park *et al.*,⁷ the authors explained their experimental results by using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory² in conjunction with the Ree-Eyring generalized theory of viscosity.⁸ Lee *et al.*⁹ studied the flocculation of Veegum suspension, and Gabrysh *et al.*¹⁰ investigated the flow properties of attapulgite suspension in water, and found that the latter shows dilatancy.

In this study, the viscosity η and zeta-potential of aqueous clay suspension have been measured. The Ree-Eyring generalized viscosity equation⁸ was applied to the viscosity data, and the flow parameters involved in the equation were evaluated. We found that the variations of η and of the flow parameters with pH and electrolyte concentration are related to the zeta-potential of the clay suspension, in return, to the stability of the suspension system.

Theory

Viscosity. The Ree-Eyring generalized viscosity equation based on absolute reaction rate theory is given by the equation:⁸

$$\eta = \sum_{i=1}^n \frac{X_i \beta_i}{\alpha_i} \frac{\sinh^{-1} \beta_i \dot{\gamma}}{\beta_i \dot{\gamma}} \quad (1)$$

where \dot{s} is shear rate, X_i is the fraction of area occupied by the i th type of flow units on a shear surface, and $\alpha_i = (\lambda_2 \lambda_3 \lambda) / kT$, $\beta_i^{-1} = (2k' / \lambda_1)_{i1}$, k is the Boltzmann constant, T is absolute temperature, λ , λ_1 , λ_2 , and λ_3 are molecular dimensions in Eyring's theory of flow,¹¹ k' is the rate constant or the jumping frequency of the flow unit, β_i and $1/\alpha_i$ are the quantities proportional to the relaxation time and shear modulus of the i th type of flow units, respectively, and the subscript i outside parentheses indicates that the inside quantities belong to the i th type of units.

For aqueous bentonite suspension, Eq. (1) is reduced to Eq. (2):

$$\eta = \frac{X_1 \beta_1}{\alpha_1} + \frac{X_2 \beta_2}{\alpha_2} \frac{\sinh^{-1} \beta_2 \dot{s}}{\beta_2 \dot{s}} \quad (2)$$

where subscript 1 refers to a Newtonian type of flow units, and 2 to a non-Newtonian type. The details of Eq. (2) are referred to the reference.⁸

The DLVO Theory. For lyophobic colloids, Verwey and Overbeek² proposed the following equations:

$$V_a = -\frac{A}{48} \left(\frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{(d+\delta/2)^2} \right) \quad (3)$$

and

$$V_r = \frac{64n\kappa T}{\kappa} \gamma^2 \exp(-2\kappa d) \quad (4)$$

where $A (= \pi q^2 \lambda_L)$ is the Hamaker constant, q is the number of atoms per cm^3 of a colloid particle, λ_L is a factor involved in the London formula $V = \lambda_L / r^6$, d is the half distance between two parallel plates to which two particles are simulated, δ is the thickness of the plate, n is the ionic concentration in the suspension medium. The factors κ , γ and y_0 in Eqs. (3) and (4) are given by the following equations:

$$\kappa = \left(\frac{8\pi n v^2 e^2}{\epsilon k T} \right)^{1/2} \quad (5)$$

$$\gamma = \frac{\exp(y_0/2) - 1}{\exp(y_0/2) + 1} \quad (6)$$

and

$$y_0 = \frac{v e \phi_0}{k T} \quad (7)$$

where v is the valency of the ion, e is the electronic charge, ϵ is the dielectric constant of the medium, and ϕ_0 is the surface potential. One notices that the attractive potential V_a is independent of the ionic concentration in the dispersion medium, whereas V_r decreases with increasing ionic concentration since κ in Eq. (4) increases with the concentration of counter-ions n by Eq. (5).

Zeta-Potential. The zeta-potential is not directly related to the repulsive term V_r of the DLVO theory, but it is an experimental measure of repulsion between colloid particles.

When a particle moves with uniform velocity \bar{v} in a medium of dielectric constant ϵ under electrical potential gradient χ , the zeta-potential is given by

$$\zeta = \frac{6\pi\eta\bar{v}}{\epsilon\chi} \quad (8)$$

where η is the viscosity of medium. For more details of the theory and practice of zeta-potential, reference is made to the literature.^{3,12}

Experiment

Sample. The clay studied was Kyungju bentonite (produced in Kyeong-Nam, Korea) with white-gray color, and its chemical composition in weight percent was SiO_2 60.2, Al_2O_3 14.4, Fe_2O_3 3.04, MgO 4.10, CaO 1.49, Na_2O 1.93, K_2O 0.50 and the ignition loss was 13.7%.

The clay suspension was prepared by the following procedure. The native sample was swelled with distilled water for two weeks, after that sand and insoluble impurities were removed by a 325-mesh U.S.A. standard sieve. Then the sample was diluted to a proper concentration, and was mixed by a blender mixer for 45 minutes. The pH of a fresh sample was 8.4 and not changed with aging time. The concentration of bentonite in the aqueous suspension used in this study was 11.0 wt. percent.

In order to study the effect of pH, some amount of 2N HCl or 2N NaOH aqueous solution was added to the fresh sample, and for the study of the effect of electrolytes, a required amount of one equivalent aqueous solution of NaCl, MgCl_2 or AlCl_3 was added to 1l of the fresh sample. Letting these samples stand still for a week, the pH, viscosity and zeta-potential were measured.

Viscometer. The viscosity data were obtained with a Couette type automatic rotational viscometer at 25°C. In this experiment, the ratio of radii of the bob and cup, $S (= R_b/R_c)$, was 0.9421, and the maximum shear rate was 1300 sec^{-1} .

Zeta Meter. The velocity \bar{v} data were obtained at 25°C by a zeta-meter (Zeta-Meter, Inc., New York), the electrical potential gradient χ was 50V/10 cm, and the magnification of the microscope was 6. The zeta-potential was calculated from Eq. (8) by using the measured mobility $u (= \bar{v}/\chi)$.

In the determination of \bar{v} , we found that our sample of 11.0 wt. % bentonite suspension was too thick for the zeta-meter since the particle did not move at all. Thus the sample was diluted 1000-times by adding distilled water, and used immediately for determining \bar{v} , from which ζ was found from a table attached to the zeta-meter. The η in Eq. (8) is the viscosity of the medium of very diluted aqueous suspension, thus $\eta \approx$ viscosity of water at 25°C.

Experimental Results

Typical Flow Curve and Flow Parameters. In Figure 1, curve A represents a typical flow curve (shear rate vs. shear stress) obtained for 11.0 wt. % aqueous bentonite suspension at 25°C. Curve A shows a thixotropic loop, where the dotted curve indicates the up-curve obtained while \dot{s} increases from zero to \dot{s}_{max} (the maximum shear rate), and the full curve is the down-curve obtained while \dot{s} decreases from \dot{s}_{max} to zero. In Figure 1, curves B to H express only the down-curves, the up-curves corresponding to these curves have been omitted for simplicity. Thus the shape of the thixotropic loops are not represented in Figure 1. The size of the loop and the position, where the loop appears in the figure of \dot{s} vs. f , change

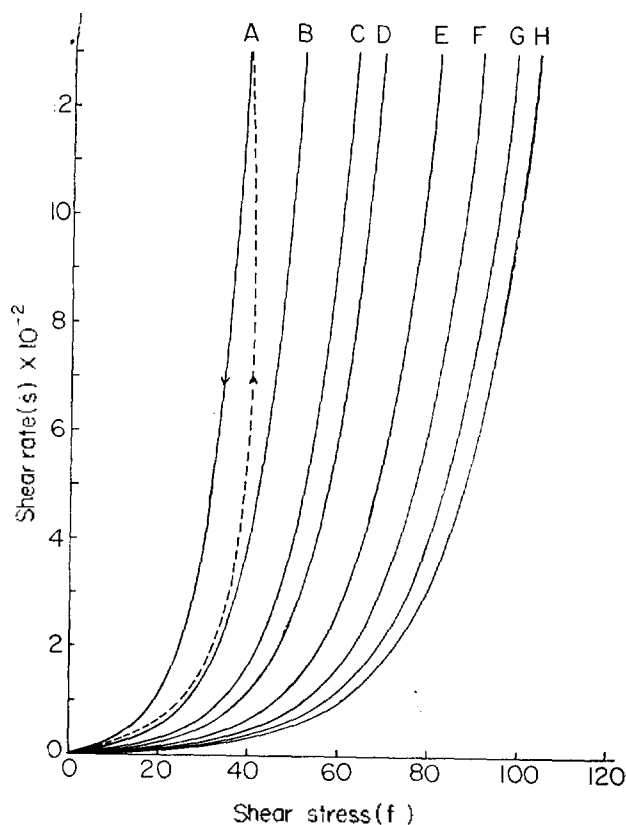


Figure 1. Typical reproducible flow curves at 25°C of 11.0 wt. % aqueous bentonite suspension with varying concentration of NaCl in m -equiv. per liter of the sample. (A) 0.25 (B) 0.50 (C) 0.75 (D) 1.0 (E) 1.5 (F) 2.0 (G) 2.5 (H) 3.0 In curve A, the upward arrow indicates the up-curve, and the downward arrow indicates the down-curve.

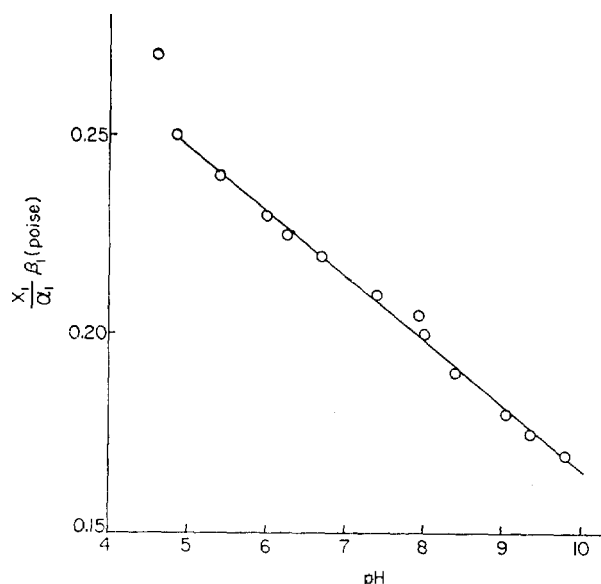


Figure 2. Dependence of the parametric value, $X_1\beta_1/\alpha_1$, on pH. Sample: 11.0 wt. % aq. bentonite suspension at 25°C.

with the number of experiment by which the loop was obtained. When the cycling was repeated sufficiently, however, the size and the position of the loop do not change any more with cycling as Park *et al.* found,^{6,7} *i.e.*, we obtained a reproducible loop, curve A in Figure 1 represents the reproducible one. In this work, we treated only the flow curves obtained in this

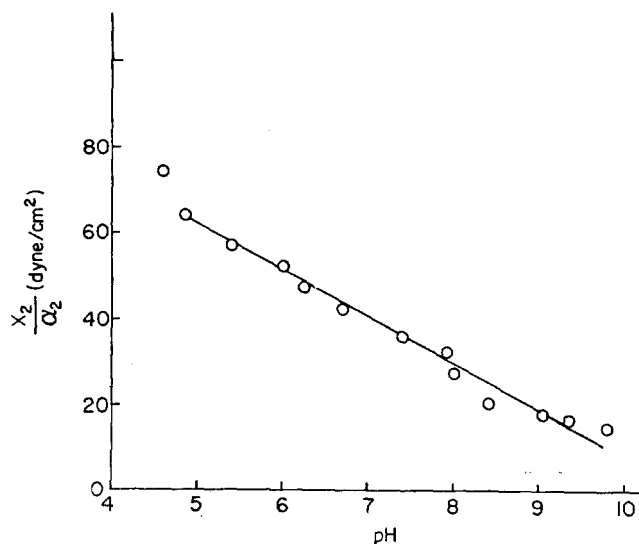


Figure 3. Dependence of the parametric value, X_2/α_2 , on pH. Sample: 11.0 wt. % aq. bentonite suspension at 25°C.

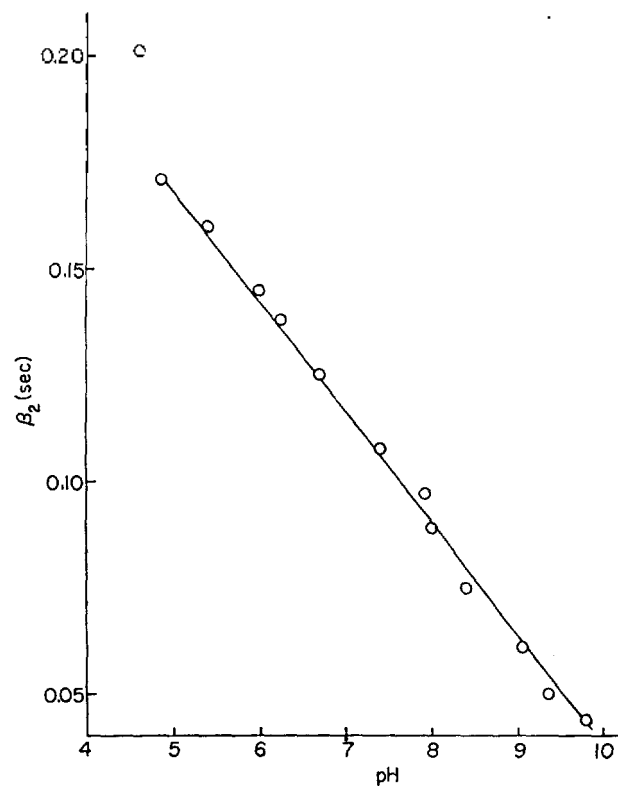


Figure 4. Dependence of the parametric value, β_2 , on pH. Sample: 11.0 wt. % aq. bentonite suspension at 25°C.

condition. Curves B to H represent only the down-curves obtained with varying NaCl concentrations. (See the foot note of Figure 1.) All the flow parameters appearing in the Ree-Eyring equation were obtained from these down-curves.

We have obtained similar flow curves as in Figure 1 by changing pH in the suspension medium, but the figure showing the flow curves has been omitted for simplicity. The flow parameters, $X_1\beta_1/\alpha_1$, X_2/α_2 and β_2 obtained by analysing the down-curves of the sample with varying pH are shown in Figures 2 to 4. We observed that all these parameters decrease monotonically with increasing pH.

By analysing the down-curves obtained for the samples

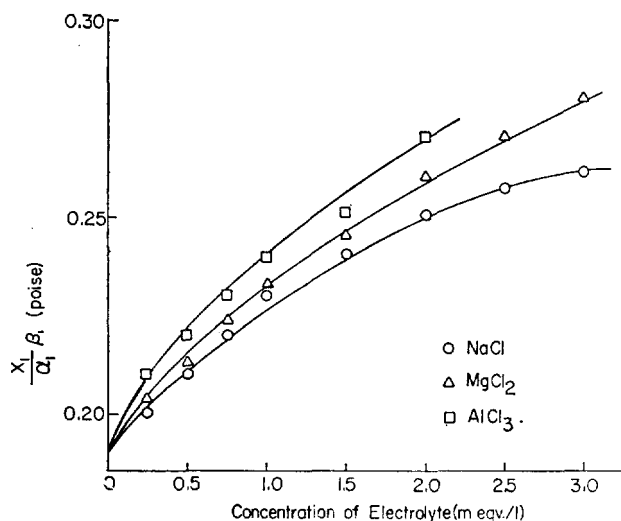


Figure 5. Variation of the parametric value, $X_1\beta_1/\alpha_1$, on concentration of electrolytes. Sample: 11.0 wt. % aq. bentonite suspension at 25 °C and pH 8.4.

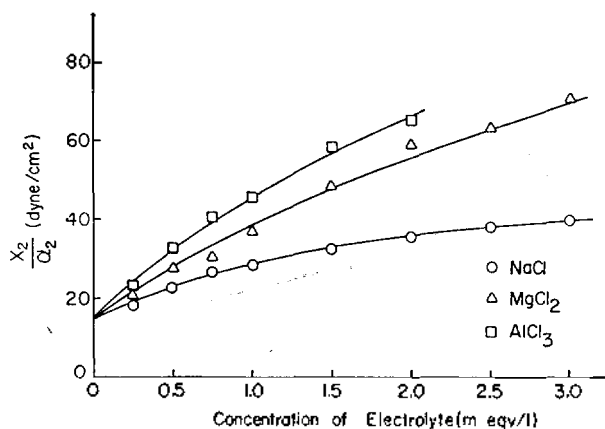


Figure 6. Dependence of the parametric value, X_2/α_2 , on concentration of electrolytes. Sample: 11.0 wt. % aq. bentonite suspension at 25 °C and pH 8.4.

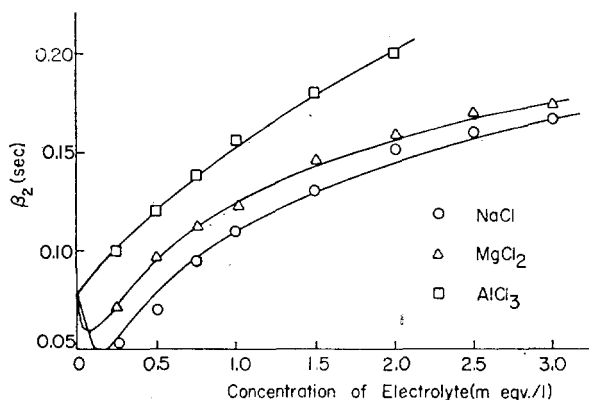


Figure 7. Dependence of the parametric value, β_2 , on concentration of electrolytes. Sample: 11.0 wt. % aq. bentonite suspension at 25 °C and pH 8.4

with different electrolyte concentrations the flow parameters, $X_1\beta_1/\alpha_1$, X_2/α_2 and β_2 were obtained. The variation of the parameters with electrolyte concentrations is shown in Figures 5 to 7. In this case, these parameters increase with increasing electrolyte concentration showing tendencies to reach maximum plateau values. We also note that the effect of the

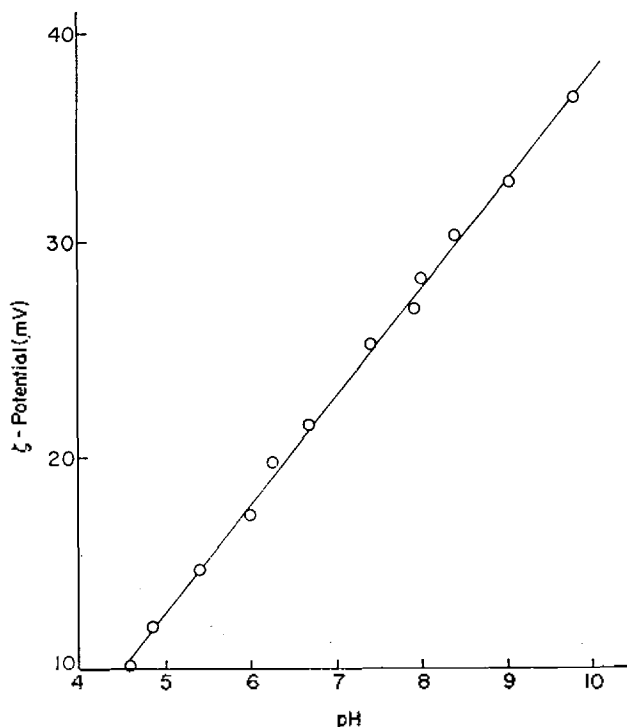


Figure 8. Dependence of the ζ -potential on pH at 25 °C. Sample: 11.0 wt. % aq. bentonite suspension diluted 1000 times.

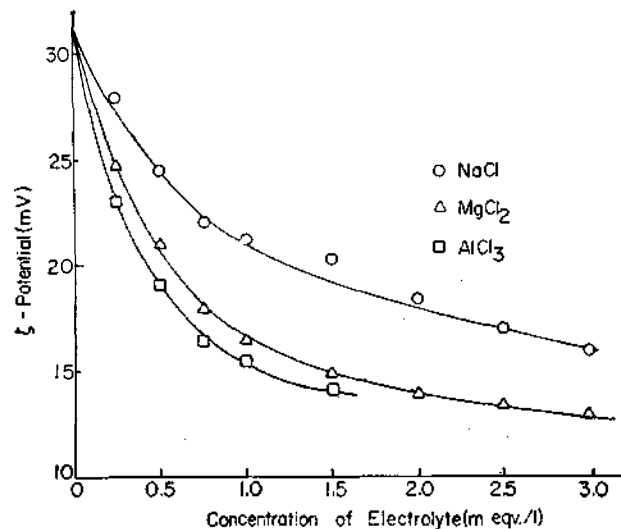


Figure 9. Dependence of the ζ -potential on concentration of electrolytes at 25 °C. Sample: 11.0 wt. % aq. bentonite suspension diluted 1000 times.

electrolytes to the flow parameters is the greater, the valence of the cation the larger.

Zeta-Potentials. The zeta-potentials which were obtained in our experiment are shown in Figures 8 and 9. We note that the zeta-potential increases monotonically with pH whereas it decreases with electrolyte concentration showing the tendencies leveling off. And it is also noted that the effect of electrolytes is the greater, the valence of the cation the larger.

Discussion

Correlation Between the Intrinsic Relaxation Time β and Zeta

Potential. In the Ree-Eyring generalized viscosity equation, the intrinsic relaxation time β is given by:

$$\beta^{-1} = \frac{\lambda}{\lambda_1} \left(2 \frac{kT}{h} \right) \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (9)$$

where

$$\Delta G^* = \Delta H^* - T\Delta S^* = \Delta E^* + P\Delta V^* - T\Delta S^* \quad (10)$$

Introducing Eq. (10) into (9), the following equation results:

$$\beta = C \exp(+\Delta E^*/RT) \quad (11)$$

where $C^{-1} = (\lambda/\lambda_1)(2kT/h)\exp[-(P\Delta V^* - T\Delta S^*)/RT]$. The activation energy for flow is represented by the following equation:

$$\Delta E^* = -(V_r + V_a) \quad (12)$$

where V_r and V_a are a positive and a negative quantity, respectively, and they are given by Eqs. (4) and (3). If Eq. (12) is introduced into Eq. (11), we obtain,

$$\beta = C \exp[-(V_r + V_a)/RT] \quad (13)$$

The attractive potential V_a is independent of the ionic concentration [see Eq. (3)] in the dispersion medium [see Eq. (3)], and thus it can be regarded as constant. The V_r represents the repulsion potential between two double layers, it can be regarded as proportional to the zeta-potential.¹² Thus intrinsic relaxation time β and zeta-potential has the following relation:

$$\beta = C' \exp(-C'' \zeta/kT) \quad (14)$$

where C' and C'' are the proportionality constants.

By using the data of β_2 and ζ obtained in our experiment, the plot of $\ln \beta_2$ vs. ζ was obtained as shown in Figure 10. From this, one notes that Eq. (14) hold satisfactorily. It should be noted that the zeta-potential were obtained by using the 1000-times diluted samples as previously mentioned. One may, however, assume that the zeta-potential for a diluted sample ζ_{dil} is proportional to that for the undiluted sample ζ_u for which the β value was determined i.e., $\zeta_u = C''' \zeta_{dil}$, where C''' is another proportionality constant. Thus the relation $\ln \beta_u = \text{const} - \text{const}' \zeta_{dil}$ still holds. The good correlation shown in Figure 10 attests that the above assumption is right and also that the basic idea for deriving Eq. (14) is right.

The flow curve of the diluted sample of 11.0 wt. % sample showed that the diluted system is completely a Newtonian type, i.e., the second term of Eq. (2) does not appear. One cannot dissolve the Newtonian term of Eq. (2), $X_1\beta_1/\alpha_1$ (where $X_1 \approx 1$), into two factors, β_1 and α_1 i.e., β_1 is not able to be obtained for the diluted sample for which the ζ potential measurement is possible. Because of this situation, in testing Eq. (14) and explaining the linear relationship of $\ln \beta_2$ vs. ζ in Figure 10, we used the β_2 for undiluted system while the zeta potential obtained for the diluted system was used under the assumption that $\zeta_u = C''' \zeta_{dil}$ as mentioned previously.

According to the Ree-Eyring theory,⁸ viscosity is given by

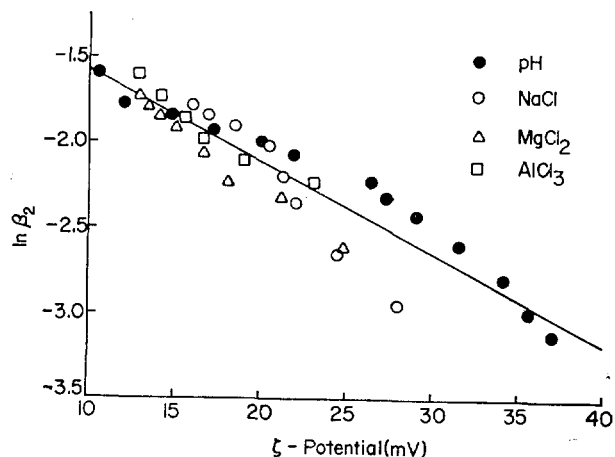


Figure 10. Plot of ζ , vs. $\ln \beta_2$. Sample: The aqueous bentonite suspension with different concentrations of NaCl, MgCl₂, AlCl₃ and with various pH. In the determination of the zeta-potentials, the sample of 11.0 wt. % aq. bentonite suspension diluted 1000 times was used.

$\eta = \beta/\alpha$. The β decreases with ζ [see Eq. (14) and Figure 10], i.e., η decreases with increasing ζ which in turn decreases with increasing electrolyte concentration. See Figure 9 and Eq. (8) where \bar{v} (velocity of the colloid particle) decreases with increasing electrolyte concentration.

Variation of α^{-1} with the Ion Atmosphere. The intrinsic shear modulus, $1/\alpha$, is given by:

$$\frac{1}{\alpha} = \frac{2kT}{\lambda_2\lambda_3\lambda} \quad (15)$$

where λ_2, λ_3 and λ are molecular dimensions as previously mentioned, i.e., $\lambda_2\lambda_3$ is the area occupied by a flow unit on a shear surface, and λ is the jumping distance. Thus, these parameters are related to the double layer thickness (Debye characteristic length), $1/\kappa$, of the colloid particle. If an electrolyte is added to a suspension system (i.e., if n increases), $1/\kappa$ decreases [see Eq. (5)], i.e., double layer contraction occurs, vice versa. By the double layer contraction, $\lambda_2\lambda_3\lambda$ becomes small, i.e., α^{-1} becomes large [see Eq. (15)], in other words, the intrinsic shear modulus increases with n as shown in Figure 6. [Note: X_2 may increase with electrolyte concentration or may be independent.] The increase in α^{-1} with the double layer contraction (i.e., with increasing n), however, seems to reach asymptotically a maximum plateau value (see Figure 6), i.e., more addition of electrolyte has no effect in causing the double layer contraction; that is, a saturation phenomenon appears.

One notices that in Figure 6 cations with higher valence shows higher efficiency for increasing α^{-1} , i.e., cations with higher valence have stronger power for causing the double layer contraction in agreement with the Schultz-Hardy rule in colloid chemistry.

Variation of β_2 with Electrolyte Concentration. The intrinsic relaxation time β_2 is related to the attractive V_a and repulsive potential V_r between two colloid particles by Eq. (13). The V_a is independent of electrolyte concentration n as previously mentioned [see Eq. (3)] whereas V_r , which appears between

TABLE 1: Viscosity of 11.0 wt.% aqueous Bentonite Suspension with Various Concentration of NaCl

Conc. of NaCl in m-eqv./l	η (cp)
0.25	3.08
0.50	4.02
0.75	4.90
1.00	5.38
1.50	6.34
2.00	7.06
2.50	7.66
3.00	8.06

* The viscosities were calculated at the apices of the down-curves in Figure 1.

two electrical double layers of the particles, changes with n . The double layer thickness $1/\kappa$ of the bentonite particle is contracted by counter ions, H^+ , Na^+ , Mg^{2+} , and Al^{3+} in the medium, *i.e.*, κ becomes large. With the increasing κ , V_r becomes small [see Eq. (4)], as a result, β increases in accordance with Eq. (13). This is experimentally true as shown in Figure 7.

Viscosity Variation with Electrolyte Concentration. Previously, it was mentioned that $\eta = \beta/\alpha$, where both β and $1/\alpha$ increase with increasing n as mentioned previously (see Figures 7 and 6). Thus, the second term of Eq. (2), the non-Newtonian viscosity part of the viscosity, increases with n , since the term $(\sinh^{-1} \beta_2 \dot{\gamma})/\beta_2 \dot{\gamma}$ is independent of n if $\dot{\gamma}$ is small, and since X_2 may increase with n or may be independent.

The first term of Eq. (2), $X_1 \beta_1/\alpha_1$, is the Newtonian part of the viscosity of the system. As shown in Figure 5, $X_1 \beta_1/\alpha_1$ increases with n . The increase is natural since in this case also, β_1 and $1/\alpha_1$ will behave similarly toward electrolytes as β_2 and $1/\alpha_2$. Thus β_1 and $1/\alpha_1$ both increase with n whereas X_1 may increase with n or be independent of it, *i.e.*, the Newtonian term increases with n as shown in Figure 5.

Since the first and second term in Eq. (2) both increase with n , the viscosity η of the system increases with electrolyte concentration. This is experimentally true as shown in Table 1 where η 's were calculated at the apices of curves A to H by using the equation $\eta = f/\dot{\gamma}$.

By varying pH of the medium of the bentonite suspension, a similar result is obtained as shown in Table 1, *i.e.*, n increases with $[H^+]$. The result, however, is not shown here.

The pH Effect. As mentioned above, the hydrogen ions in the medium of the suspension behave similarly as Na^+ , Mg^{2+} and

Al^{3+} , *i.e.*, the parameters, $X_1 \beta_1/\alpha_1$, X_2/α_2 and β_2 increase with $[H^+]$ (see Figures 2 to 4). But, the dependence of these parameters on $[H^+]$ is different from the metallic cation case, *i.e.*, in the case of $[H^+]$, the relation, $P = P_0 + C_h \ln [H^+]$, holds over the range of $[H^+] = 10^{-6}$ to 10^{-10} , where P represents the parameters $X_1 \beta_1/\alpha_1$, X_2/α_2 and β_2 , P_0 and C_h are constants. The reason for the relation is not clear at present; but it seems that because of small size of $[H^+]$, the latter behaves quite differently from other cations.

Acknowledgement. The authors wish to acknowledge the Korea Research Center for Theoretical Physics and Chemistry for a partial support of this research.

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