Clay Science **5**, 313-318 (1981)

PARTICLE-PARTICLE AND PARTICLE-WATER INTERACTIONS IN AQUEOUS CLAY SUSPENSIONS. PART I. APPLICATION OF A MODIFIED ROBINSON EQUATION TO VISCOSITY DATA

KOJI WADA, YOSHIKAZU NITAWAKI and KAZUHIKO EGASHIRA

Faculty of Agriculture, Kyushu University 46, Fukuoka 812, Japan

(Received December 28, 1981)

ABSTRACT

The Robinson equation was modified and applied to the viscosity data of clay suspensions to which the Einstein equation was not applicable. The modified Robinson equation is:

$$\eta_{rel}-1=k'S'V/(1-S'V)$$

where η_{rel} is the relative viscosity, V the volume concentration of clay particles (cm^3/cm^3), S' a parameter for the ratio of the effective volume of clay particles to their actual volume and k' another parameter related to particle-particle interaction. The S' value increased from about 10 for spherical halloysite suspensions to allophane, kaolinite, montmorillonite and up to 1900 for fibrous imogolite suspensions. The k' value increased from about 1 for deflocculated suspensions to 20 for flocculated suspensions.

INTRODUCTION

The understanding of particle-particle and particle-water interactions in aqueous clay suspensions is important in various aspects of clay and soil technology. These interactions are complex reflecting variations in the shape and size of clay particles and in the nature of their surfaces on which different electrical double layers develop. In suspensions of platelike clay particles, three types of particle-particle interactions, edge-to-edge, edge-to-face and face-to-face have been postulated (van Olphen, 1977). The terms "flocculation" and "deflocculation" have also been used to describe the edge-to-edge and edge-to-face association and dissociation, and the terms "aggregation" and "dispersion" to describe the face-to-face association and dissociation. The viscosities of concentrated clay suspensions with and without addition of salt and peptizing chemicals were used to analyze such particle-particle interactions. In most of these works, the magnitude of experimentally determined yield stress was related to the forces required to break the link between the particles and to the number of the links per unit volume of clay suspension. The conclusions of particle-particle and/or particle-water interactions were, however, drawn by inference supplemented by information from other sources rather than analyses of viscosity data.

In Part I, an equation proposed by Robinson (1949) was modified to interpret the viscosity data of clay suspensions to which the Einstein equation was not applicable. Two empirical parameters S' and k' in the modified equation were derived from the relationship between the viscosity and the particle concentration of clay suspension. They were related to the particle shape and particle-water interaction and particle-particle interaction, respectively. The validity of these parameters was discussed referring to the data on various clay suspensions at different NaCl concentrations, which will be presented in Part II.

DERIVATION OF TWO PARAMETERS k' AND S'

The Einstein equation states the theoretical relationship between the viscosity and the particle concentration of suspensions of spheres:

$$\eta_{\mathrm{rel}}-1=kV \tag{1}$$

where η_{rel} is the relative viscosity, V the volume concentration of spheres ($\mathrm{cm}^3/\mathrm{cm}^3$), and k the constant ($=2.5$). This equation is derived for very dilute suspensions of spheres, in which the volume occupied by spheres is negligible. Robinson (1949) extended the equation to higher particle concentrations by introducing the concept that the specific viscosity ($\eta_{\mathrm{rel}}-1$) is not only proportional to the volume concentration of spheres, but that it is also inversely proportional to the volume of free liquid in the suspension. He then defined the equation applicable to any concentration of the suspension

$$\eta_{\mathrm{rel}}-1=kV/(1-S'V) \tag{2}$$

where S' is the ratio of the "effective" volume of spheres to their "actual" volume and k a constant. He measured the viscosities of suspensions of glass spheres at different concentrations using a rotational viscosimeter. The applicability of Eq. (2) was then tested using it in a form

$$\frac{V}{\eta_{\mathrm{rel}}-1}=\frac{1}{k}-\frac{S'}{k}V \tag{3}$$

and plotting the measured $V/(\eta_{\mathrm{rel}}-1)$ against V. The linear plot proved the applicability of Eq. (2) and two intercepts gave $1/k$ and $1/S'$.

Robinson (1949) found that Eq.(2) was valid for the glass spheres of 10–20 μm diameters suspended in various media over the range of V from 0.1 to 0.4, where the effective volume of spheres was equated with their packed-sediment volume. He stated that the physical significance of k is conjectural, but it may be a frictional coefficient, which is influenced by factors such as particle roughness and shape and the presence or absence of shells around the particles derived from the suspension medium.

The spheres interacting in the suspension are, however, not those with the "actual" volume but those with the "effective" volume. Taking this into consideration, the Robinson equation is modified to

$$\eta_{\mathrm{rel}}-1=k'S'V/(1-S'V) \tag{4}$$

where the parameter k' evaluates that effect of increasing V on the specific viscosity $(\eta_{\mathrm{rel}}-1)$, which is unaccountable by S' and $1-S'V$. The applicability of Eq. (4) can be tested using it in a form

$$\frac{1}{\eta_{\mathrm{rel}}-1}=\frac{1}{k'}-\frac{1}{k'S'}\frac{1}{V} \tag{5}$$

and plotting the measured $1/(\eta_{\mathrm{rel}}-1)$ against $1/V$. The linear plot proves the applicability of Eq. (4) and two intercepts give $1/k'$ and S'.

VALIDITY AND SIGNIFICANCE OF TWO PARAMETERS k' AND S'

The application of the original Robinson equation to various clay suspensions was first tested to know whether the two parameters k and S' are obtainable or not. We measured the viscosity of suspensions of Na-saturated montmorillonite, kaolinite, halloysite, allophane and imogolite at NaCl concentrations ranging from 10^{-4} to 10^{-2} M using a rotational viscosimeter at different rates of rotation, and found that most data, which will be presented in Part II, fitted to Eq. (2). Figure 1 shows a summary of the range of the k and S' values, which are different depending on the clay mineral spe-

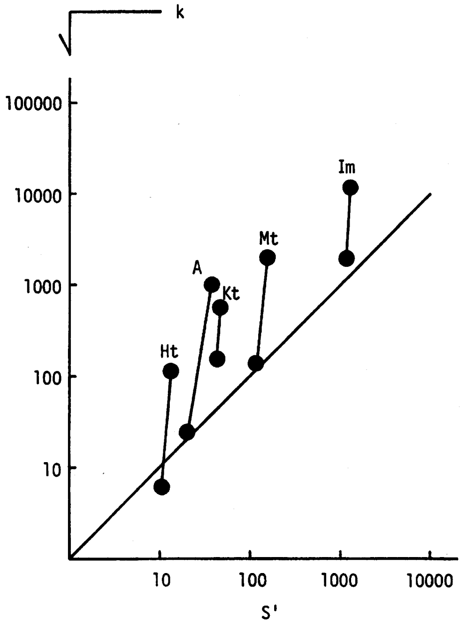

FIG. 1. The range of the pair of k and S' values found for various clay suspensions.

cies. The k and S' values generally increase with increasing NaCl concentration and with the decreasing rate of rotation. Only the pairs of the highest and lowest k and S' values are plotted for each mineral. All k and S' values are higher or much higher than the k (3–5) and S' (1.96) values found by Robinson (1949) for the glass spheres. There is a close correlation between the corresponding k and S' values, and the k value is always higher than the S' value. The former verifies the relationship $k=k'S'$, which can be found by comparison of the original Robinson equation (Eq. 2) with the modified equation (Eq. 4) and the latter indicates $k'>1$. When the particle-particle interaction is negligible, i.e. $S'V \ll 1$ and $k'=1$, Eq. (4) can be reduced to Eq. (1) and S' in Eq. (4) can be equated with k in Eq. (1). Actually, the S' values found for the montmorillonite, halloysite, allophane and imogolite suspensions at a NaCl concentration of about 10^{-4} M are close to the k values found by Egashira (1977) for the same but more dilute clay suspensions (Table 1).

Generally, the S' value increases in the order halloysite $<$ allophane $<$ kaolinite $<$ montmorillonite $<$ imogolite (Fig. 1), and is higher at higher NaCl concentration. The trend suggests that the parameter S' is influenced by two factors; the shape and size of clay particles, dissociated or associated, and the entrapment of water between and/or around the clay particles. Mehl *et al.* (1940) interpreted the viscosity data of protein in terms of the asymmetry of the molecules. They calculated the k value in Eq. (1) as a function of the axial ratio (ρ or $1/\rho$) of the molecule that is approximated by a flattened or an elongated ellipsoid of revolution, using an equation derived by Simha (1940). The ρ or $1/\rho$ values obtained from the measured k values by applying this functional relationship were generally in good agreement with those obtained from sedimentation velocity and diffusion data. The functional relationship between k and ρ or $1/\rho$ calculated by Mehl *et al.* (1940) was, therefore, used in Part II to calculate the S' value from the axial ratio of the clay particle which was approximated by an ellipsoid of revolution.

The retention of water by suspended particles has been considered in terms of their "hydration". In the study on protein, Mehl *et al.* (1940) calculated the ρ or $1/\rho$ values from viscosity, sedimentation velocity and diffusion data assuming that each protein carried varying amounts of water and found that hydration greater than 0.5 g of water per gram of protein is improbable. Egashira (1977) calculated the values corresponding to ρ or $1/\rho$ from the measured k values assuming that each clay mineral in Table 1 carried a certain amount of water and discussed the morphology and association of clay particles. The basis for the selection of the amount of hydration varied, however, from one mineral to another. In Part II of the present study, the S' values are calculated assuming the varying thickness of the water shell around the clay particle as well as its varying axial ratios. Comparison of the measured and calculated S' values, as supplemented by information from other sources, then indicates the probable ranges of

TABLE 1. Comparison of k and S' values found for Na-saturated clay suspensions at 10^{-4} M NaCl

Clay mineral	Particle size (μm)	k[1]	S'
Montmorillonite	<2	154	–
(Gunma Bentonite)	<0.5	—	156
Kaolinite (Iriki)	<2	—	72
Halloysite (VH)	<2	7.6	11
Allophane (KiP)	<0.2	42	—
	<0.5	—	37
Imogolite (KiG)	<2	1677	1450

[1] Egashira (1977).

the axial ratio and the thickness of water shell characteristic to each mineral species.

Figure 2 illustrates three types of combinations of the k'-Ω and S'-Ω relationships found for the clay suspensions where Ω is the rate of rotation at which the viscosity is measured. Table 2 lists the clay suspensions classified into three groups according to the combination of k'-Ω and S'-Ω relationships. The pH and NaCl concentration of the suspensions which are classified into the first type suggest that they are in the deflocculated state, whereas those of the suspensions which are classified into the second and third types suggest that they are in the flocculated state. The statement that k' measures particle-particle interaction is verified by comparison of the first type combination with the second and third type combinations of k'-Ω and S'-Ω relationships. In the first type combination, the k' value is close to 1 and both the k' and S' values show little or no change with Ω. This can be expected to occur under the condition that the particle-particle

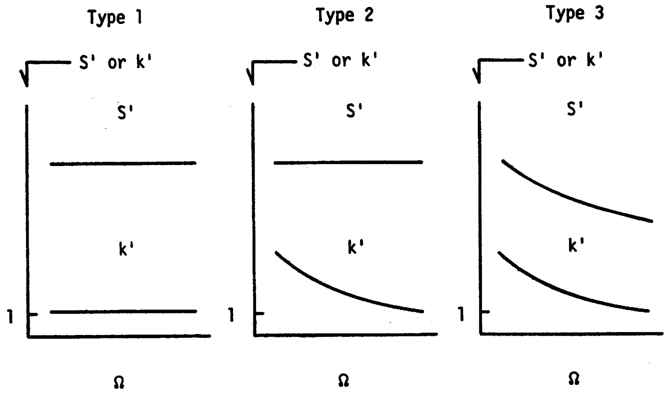

FIG. 2. Three types of combinations of the k'-Ω and S'-Ω relationships found for various clay suspensions.

TABLE 2. Classification of clay suspensions according to the combination of k'-Ω and S'-Ω relationship

Type	Clay mineral	pH	NaCl concentration (M)
I	Montmorillonite	6.1–6.6	10^{-4}–10^{-3}
	Halloysite	8.0–8.3	10^{-4}–10^{-3}
	Allophane	4.9–5.3	10^{-4}–10^{-3}
II	Kaolinite	6.7	5×10^{-3}
	Kaolinite	6.9–7.2	10^{-4}
	Halloysite	7.2	5×10^{-3}
	Allophane	5.5–5.6	2×10^{-3}
III	Montmorillonite	5.6–5.9	5×10^{-3}
	Imogolite	6.3–6.7	10^{-4}–10^{-3}
	Imogolite	6.0–6.3	2×10^{-2}

interaction is very weak or none. In the second and third type combinations, the k' value is larger and decreases with Ω. The change of the k' value with Ω can be interpreted in terms of the particle-particle interaction, which is maximum in a static state and decreases with accelerated rotation. Thus, we may conclude that the first type combination characterizes the state of deflocculation, whereas the second and third type combinations characterize the state of flocculation.

The fact that there is no change in S' with increasing Ω in the first type combination of k'-Ω and S'-Ω relationships (Fig. 2) deserves attention, because the S' value can then be used to assess the particle shape and the thickness of water shell around the clay particle. The situation is more complicated in the second and third type combinations, where orientation or dissociation of associated particles can occur with accelerated rotation. The orientation will not produce much change of S' with Ω unless the association is broken down, whereas the dissociation either decreases or increases S' with Ω according to whether or not the dissociation results in the decrease or increase of ρ and whether or not the dissociation results in the decrease of entrapped water. Possibly, the former orientation corresponds to the second type of combination, and the latter dissociation, either with or without orientation, corresponds to the third type of combination.

REFERENCES

EGASHIRA, K. (1977) *Clay Sci.*, **5**, 87–95.

MEHL. J. W., ONCLEY, J. L., and SIMHA, R. (1940) *Science*, **92**, 132–133.

ROBINSON, J. V. (1949) *J. Phys. Colloid Chem.*, **53**, 1042–1056.

SIMHA, R. (1940) *J. Phys. Chem.*, **44**, 25–34.

VAN OLPHEN, H. (1977) *An Introduction to Clay Colloid Chemistry* (2nd edition), John Wiley & Sons, Inc., New York, 95–98.