

## FORMATION OF COLLOIDAL DISPERSIONS FROM SUPERSATURATED IRON(III) NITRATE SOLUTIONS. IV. ANALYSIS OF SLOW FLOCCULATION OF GOETHITE

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### ABSTRACT

Slow flocculation of columnar-shaped goethite crystals (elongated along the *c*-axis) featuring very flat (110) faces is characterized (a) by an extreme sensitivity to ionic strength; (b) by a preferential side-by-side orientation of the (110) faces of the particles to yield linear arrays in the flocculated state.

The dependence of sol stability on ionic strength is explained by applying the DLVO theory in conjunction with electrophoretic measurements at a pH of 2 and varying ionic strength ( $10^{-2}$ – $10^{-1}$  M). A mechanism is proposed whereby the particles are allowed to approach each other in an orientation so as to minimize the repulsive interactions and to realize in the near-flocculated state the characteristic floc orientation by a rotational movement.

### INTRODUCTION

Recently, we reported on some aspects of the precipitation of goethite ( $\alpha$ -FeOOH) from partially neutralized iron(III) solutions [1–3]. It was shown that the crystalline phase developed from a colloidal solution of amorphous particles with a diameter of about 5 nm. We also tried to suggest a mechanism by which goethite grows from this precursor phase [3]. Goethite crystallizes in the orthorhombic system with unit cell dimensions  $a_0 = 4.6$  Å,  $b_0 = 9.96$  Å and  $c_0 = 3.02$  Å [4]. In a previous paper [3], we concluded from a detailed electron-microscopic study that the colloidal goethite crystals were elongated in the [001] direction and bounded by very flat (120) and (010) faces. On reviewing the experimental evidence, we are now convinced that (110) faces have mistakenly been interpreted as (010) and (120) faces and that they in fact account for the diamond-shaped cross-section (see, for example, Fig. 6, Ref. [3]). Lattice imaging in the electron microscope shows the individual particles to be monocrystalline. The initial degree of neutralization determines the concentration of the amorphous phase with respect to the total Fe(III) concentration and this concentration ratio is seen to control the size of the goethite particles in the aged precipitate. The sol stability is influenced by the total

Fe(III) concentration and is very sensitive to changes in ionic strength. The flocculated state of the goethite dispersion is characterized by linear arrays of crystals perpendicular to the [001] direction. This peculiar flocculation behaviour prompted the present study.

## EXPERIMENTAL

The preparation and characterization of the sol used in this investigation were discussed in a previous paper [3]. In the latter publication, it was referred to as an A-type sol and was prepared by free relaxation of a  $6.25 \times 10^{-3} M$  total Fe(III) solution at an initial pH of 2.22 and an OH/Fe ratio of 0.35. After preparation the sol was kept at room temperature for more than 2 y. An electron-microscopic (EM) study of the stable sol in a Philips EM 301 unit revealed the sol particles to be rod-like, 73 nm long and 20 nm along the sides of the diamond-like cross-section. No flocculated aggregates were observed in this EM study.

The diffusion coefficient of the sol particles was measured by dynamic light scattering or photon correlation spectroscopy [5]. These experiments were performed with an argon ion laser (Spectra Physics model 165) operating at 514.5 nm at a power of about 50 mW. The laser beam was focused in a sample cell which was placed in a double-walled thermostatic sample holder at a temperature of  $25.0 \pm 0.1^\circ\text{C}$ . The scattered light was detected by an EMI 9558 photomultiplier at angles varying from 60 to  $135^\circ$ . The output of the photomultiplier was amplified, discriminated and analysed by a Malvern K7025 64 point correlator. A hydrodynamic radius equal to 23 nm was calculated from these measurements on the assumption of spherical shape and by using the Stokes—Einstein relation.

The electrophoretic mobility (e.m.) of the sol particles was measured at several pH values and with varying ionic strength. The aged sol was first dialysed against a  $10^{-2} M$  nitric acid solution to lower the ionic strength and thus safeguard it against spurious flocculation. Just before starting the mobility measurements, aliquots were taken and dialysed against nitric acid and sodium nitrate solutions of ionic strength 0.1, 0.01 and 0.001 *M* and various pH values ( $1 < \text{pH} \leq 6$ ). At a pH of 2, e.m. measurements were also performed at ionic strengths of 0.075, 0.05 and 0.025 *M*. Visking membranes were used in the dialysis. The electrophoresis measurements were performed in a Mark II microelectrophoresis apparatus (Rank Brothers) equipped with a dark field illumination system and with cylindrical cells.

Some flocculation experiments were done either by addition of sodium nitrate solutions or by dialysis against nitrate solutions of varying concentration. The onset of flocculation was determined from the appearance of a visible sediment.

## RESULTS

The e.m. as a function of pH at three ionic strengths is plotted in Fig. 1. All measurements were performed in duplicate. A few hundred particles were followed in each experiment. We note that the mobility varies in a quite complicated way with pH and ionic strength.

The results of the flocculation studies are summarized in Table 1. The stability of the sol is seen to change quite drastically with a five-fold increase in ionic strength or sodium nitrate concentration. At an ionic strength of 0.5 *M* the sol is seen to flocculate immediately, whereas it remains stable almost indefinitely at an ionic strength of 0.09 *M*. The flocs are observed to favour a typical string-like ordering at all ionic strengths although, at high ionic strength, the arrangement is somewhat less ordered. Figure 2 gives a typical example of the ordered structure of the floc formed by slow flocculation. The particles in the floc line up with their *c*-axes (the long dimension) parallel, through face-to-face contact between their (110) faces.

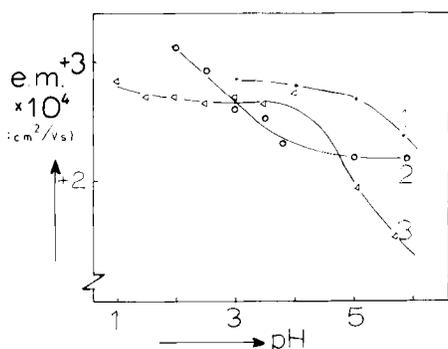


Fig. 1. The electrophoretic mobility as a function of pH. For curves 1, 2 and 3 the ionic strengths (*M*) are  $10^{-3}$ ,  $10^{-2}$  and  $10^{-1}$ , respectively.

TABLE 1

Observed formation of flocs at a pH of 2 for the A sol (see text)

Ionic strength ( <i>M</i> )	0.09	0.1	0.2	0.5
Flocculation time	$\geq 2$ y	2 weeks	$\leq 1$ min	$< 1$ s

## DISCUSSION

Our objective is to find an explanation for the pronounced dependence of the stability of the goethite sol on electrolyte concentration and the preferential side-by-side orientation of the particles in the flocs. We believe that this near-perfect orientation is related to the characteristic morphology of the goethite particles.

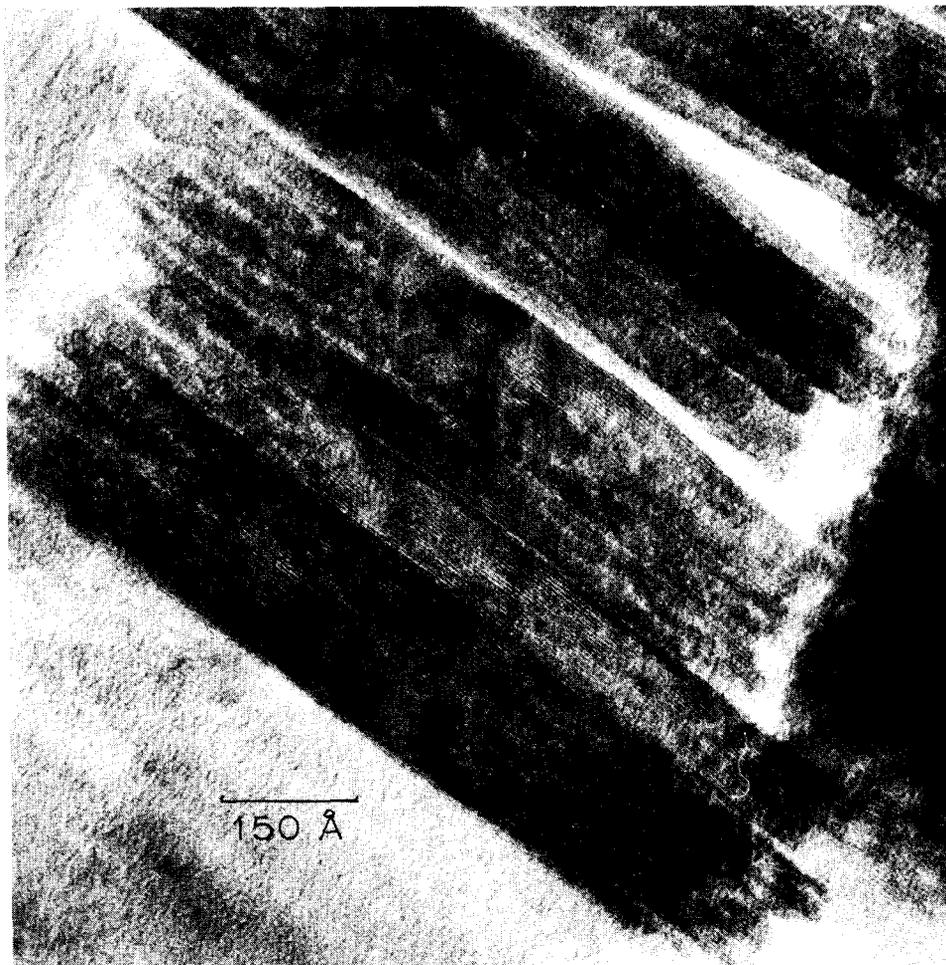


Fig. 2. Electron micrograph showing the ordered structure of the flocs formed by slow flocculation of the columnar-shaped goethite crystals.

We shall approach this problem by analysing the dependence of the flocculation rate on particle shape and size and on the surface potential. In order to relate the observed e.m. to a potential, we must know the charge distribution in the ionic atmosphere that surrounds a cylindrical or rod-like particle. Until now, such an analysis has not been attempted. The problem is even more complicated when this particle is in an applied electric field because of the nature of the hydrodynamic profile and the relaxation of the charge cloud [6,7]. Overbeek and Wiersema [7] reviewed analyses of the relation between the zeta potential and e.m. of cylindrical particles with large length:width ratios and for large values of  $\kappa b$ , where  $\kappa^{-1}$  is the characteristic Debye length and  $b$  is the radius of the cylinder. Later, Stigter

[8] derived expressions for the relation between e.m. and zeta potential for infinite rods. Sherwood [9] made similar analyses for rods in the limit  $\kappa l < 0.1$  and  $\kappa l > 10$ , where  $2l$  is the length of the rods. These calculations are, however, not directly applicable to our system because of the rather small ratio of particle length to width and because  $\kappa l$  commonly falls in the range 0.1–10.

These complications prevent a straightforward conversion of e.m. data to zeta potentials. We now propose to continue the analysis by assuming the particles to be spheres. For the radius of the sphere we choose the hydrodynamic radius (23 nm), as calculated from the measured diffusion coefficient in the dynamic light-scattering experiments. In making this assignment it is also assumed that the particles show no preferred orientation in the electric field. This assumption, which is quite reasonable, is nevertheless necessary because the calculation of a hydrodynamic radius from dynamic light-scattering measurements requires the non-spherical particle to show no preferred orientation while undergoing a Brownian motion. Having made these approximations, the calculation method of O'Brien and White [10] may now be applied to obtain zeta potentials from e.m. data. The results are plotted in Fig. 3 as a function of pH and ionic strength.

To justify the approximations made and to test the validity of the calculations, the e.m. of nearly spherical goethite particles with a hydrodynamic radius of 10 nm was measured. Quite monodisperse sols of these

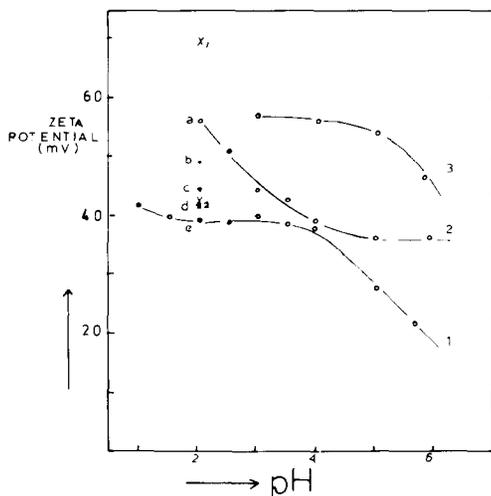


Fig. 3. Calculated zeta potential as a function of pH at different ionic strengths. For curves 3, 2 and 1 the ionic strengths ( $M$ ) are  $10^{-3}$ ,  $10^{-2}$  and  $10^{-1}$ , respectively. Points a–e give calculated zeta potentials at a pH of 2 but varying ionic strength; (a)  $10^{-2} M$ ; (b)  $0.025 M$ ; (c)  $0.050 M$ ; (d)  $0.075 M$ ; (e)  $0.10 M$ .  $x_1$  and  $x_2$  refer to the zeta potentials of nearly spherical goethite particles with a hydrodynamic radius of 10 nm at ionic strength  $10^{-2} M$  ( $x_1$ ) and  $10^{-1} M$  ( $x_2$ ). See text.

particles were prepared from acid colloidal solutions in which only amorphous primary particles [1] were present via aggregation and recrystallization processes. There is no reason to expect the electrokinetic behaviour of these particles to differ significantly from that of the rod-like particles under consideration at identical pH and ionic strength. The calculated zeta potentials at a pH of 2 and ionic strengths 0.1 and 0.01 *M* are also shown in Fig. 3. At ionic strength 0.1 *M* the agreement is quite satisfactory. This correspondence is not too surprising, as under these conditions  $\kappa a > 10$  and the simple relation of Henry [11,12] will be obeyed. Given the experimental accuracy of the mobility measurements and the various approximations made, the agreement at the lower ionic strength is acceptable.

The apparent independence of the zeta potential from pH in the range  $1 \leq \text{pH} \leq 4$  at ionic strength 0.1 (see also Fig. 1) is quite remarkable. It implies that the flocculation rate in the low pH regime is quite insensitive to pH changes at this ionic strength.

We shall make use of the electrokinetic data at a pH of 2 (Fig. 3) in a further analysis of the flocculation process. It is at this pH that the dramatic variation in colloid stability has been most extensively studied (see Table 1).

The rate of slow flocculation is defined by the stability ratio *W*, the ratio between the rates of fast and slow flocculation. The expression for *W* given by Derjaguin and Müller [13] is

$$W = \int_2^{\infty} \frac{\beta(x)}{x^2} \exp(V/kT) dx / \int_2^{\infty} \frac{\beta(x)}{x^2} \exp(V_A/kT) dx \quad (1)$$

where *x* is the ratio between the centre-to-centre distance and the radius of the particles,  $V_A$  is the attractive potential, *V* is the total interaction potential, and  $\beta(x)$  is a hydrodynamic correction factor. For spheres having a radius of 23 nm and a zeta potential of about +40 mV, both theory and experiments [14,15] yield a value of about five for the differential quotient  $-d \log W/d \log c$ . If we let *W* be proportional to the observed flocculation time (see Table 1), then our experiments suggest that  $-d \log W/d \log c > 20$ . This large discrepancy would imply that the flocculation behaviour of this investigation cannot be accounted for by a model based on spherical particles.

Another extreme model to explain particle interaction is one in which the particles in the process of flocculating approach each other as parallel plates. This model has its merits in view of the observed preferential side-by-side orientation of the particles in the flocs and the flatness of the faces parallel to the *c*-axis.

We proceed now to a calculation of the complete energy of interaction between two sol particles according to this model. For the van der Waals

attraction energy as a function of half-distance  $d$  between parallel plates, we write [16]

$$V_A = - \frac{A \times O}{48\pi d^2} \quad (2)$$

This expression may be used if, as is true in our system, the distance of approach is small compared with the thickness of the plates.  $A$  is the Hamaker constant, which we set equal to  $3 \times 10^{-20}$  J, a typical value for salts in water [17,18];  $O$  is the area of an interacting surface, which for the goethite particles under consideration will be approximately equal to  $1.5 \times 10^{-15}$  m<sup>2</sup> (73 nm  $\times$  20 nm). For the repulsive energy of interaction we use the expression [16]

$$V_R = \frac{2nkT}{\kappa} O \left( \frac{e\psi_d}{kT} \right)^2 (1 - \tanh \kappa d) \quad (3)$$

which is derived by utilizing the Debye–Hückel approximation and therefore will be valid when the potential is small everywhere. The diffuse layer potential  $\psi_d$  is assumed to equal the zeta potential and  $n$  is the number concentration of the electrolyte. Hogg et al. [19] found the errors introduced by use of this expression for  $V_R$  to be quite small in their effects on  $W$ .

In Table 2 are summarized the important features of a series of calculated interaction curves for ionic strengths in the range  $10^{-2}$ – $10^{-1}$  M and at a pH of 2. The maximum in the free-energy barrier ( $V_{\max}$ ) is seen to drop quite drastically on increasing the ionic strength, corresponding well with our experimental observations. The results also suggest flocculation in the secondary minimum ( $V^*$ ) located at  $2d^*$  (see Table 2) to be possible. However, the relatively deep minimum is offset by the loss of entropy which at the low volume fractions involved will be about  $10kT$ . The formation of Schiller layers in the solution, as is observed in some old ironhydroxide sols [20], tungsten trioxide sols [21] and  $\beta$ -FeOOH sols [22], is therefore effectively prevented.

TABLE 2

Calculated features of the interaction curves based on Eqns (2) and (3) with a Hamaker constant of  $3 \times 10^{-20}$  J

$c$ (M)	$\zeta$ (mV)	$V_{\max}/kT$	$2d_{\max}$ (nm)	$V^*/kT^a$	$2d^*$ (nm)
0.01	55	97	2.6	-0.3	25
0.025	49	83	2.1	-1.1	14
0.05	44.5	56	1.9	-2.6	8.5
0.075	42	35	1.8	-4.7	6.2
0.100	40	16	1.8	-7.2	4.9

<sup>a</sup> $V^*$  = interaction potential in secondary minimum.

Reerink and Overbeek [23] suggested that, in the case of slow flocculation, the differential quotient  $-d \log W/d \log c$  may be approximated by  $-d(V_{\max}/kT)/d \log c$ . This approximation makes an exact and very tedious calculation of  $W$  unnecessary. On applying this method of analysis to the results listed in Table 2 we find a limiting value of  $-d \log W/d \log c \approx 60$ . This is an extremely large value which exceeds the experimental indications (Table 1) by a factor of three. We may, however, suggest some modification of the flocculation model (parallel plate interactions) to account for the experimental observations. Table 2 illustrates that the most unfavourable situation during flocculation is the requirement that the particles maintain a "parallel" plate orientation at all times. The energy barrier will be lowered considerably if the particles initially make edge contact or point contact, as illustrated in Fig. 4a. The next step in realizing the final flocculated state would then involve a rotation or a gliding operation to increase the contact area. At low ionic strength, the repulsive energy will be relatively large and will increase with increasing contact area. Permanent contact will therefore be unlikely to occur, as is illustrated in Fig. 4b.

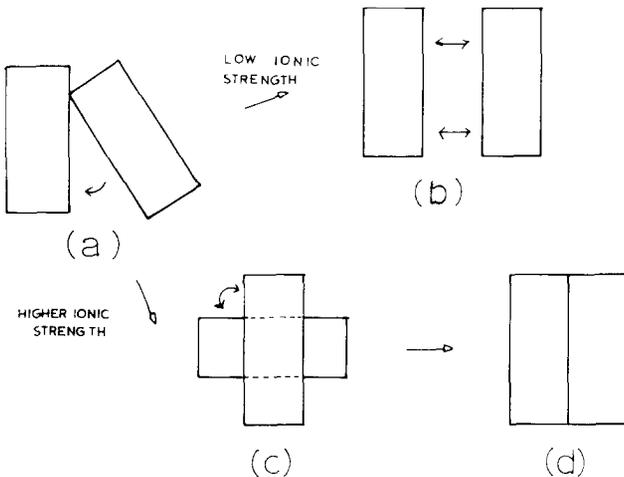


Fig. 4. Illustration of the particle contact on flocculation at low and higher ionic strength. (a) Edge or point contact of the particles on flocculation. (b) Strong repulsion at low ionic strength prevents permanent contact. (c) Energetically most favourable contact arrangement after having made edge contact. (d) After a rotation step in or near the primary minimum, the parallel orientation is reached.

Were the energy barrier to be surmounted, the contact surface area should be minimized. The energetically most favourable position to reach after having made edge contact would be that depicted in Fig. 4c. The two "plates" are superimposed in a cross-wise orientation. Compared to the parallel orientation state, in this orientation the barrier  $V_{\max}$  and the

quotient  $-d \log W/d \log c$  are reduced in magnitude to about 30% and therefore approach more nearly the experimental observation. Having reached the primary minimum, the parallel orientation is then reached by a rotation step. This step is possible because of the extreme flatness of the faces but will probably be retarded by the squeezing out of a thin water layer between the faces [24].

We have been able to give a semi-quantitative explanation of the observed dependence of the flocculation rate on ionic strength by utilizing measured electrophoretic mobilities and by taking into account the morphology of the colloidal goethite particles.

An added feature of the slow flocculation which needs further comment is preferential stacking of particles in the flocs with their (110) faces serving as interparticle contact planes. Formation of such anisotropic flocs has also been observed by other investigators in other systems. Gold sols [25] and thoria sols [26] are known to exhibit this behaviour. Thomas and McCorkle [26] applied the DLVO theory to account for the preferred formation of strings of flocs of spherical particles. In our case the reduction of  $V_{\max}$  to 30% of the value for a full crystal face is possible only for end-on flocculation. This would cause a very strong tendency towards linear flocculation in the slow regime, becoming much weaker near the coagulation value, as observed in our experiments.

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