

Hydrolysis–Precipitation Studies of Iron Solutions

III. Application of Growth Models to the Formation of Colloidal αFeOOH from Acid Solutions

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The development of a colloidal αFeOOH phase has been followed experimentally by measuring the dependence of the induction time on the OH/Fe ratio and by recording the pH relaxation of samples of known initial OH/Fe ratio. These results suggest that the growth of the solid phase is largely controlled by surface-nucleation processes. Two growth models are applied in the analysis of the kinetic data. This analysis permits an estimation of the interfacial tension of the solid to be made in acid solutions.

INTRODUCTION

In two earlier publications (1, 2) we reported on our study of the formation of iron oxyhydroxide from an acidified Fe(III) nitrate solution by titration with a base in a vessel of special design (3). The aging behavior of samples drawn at different stages (OH/Fe ratios) in a titration experiment was followed by recording changes in pH and optical density (OD).

A characteristic feature of the aging process was the observance of an induction period during which no change in either pH or OD could be detected. This behavior was also noted by Hsu (4). In this publication¹ we wish to present the results of a series of measurements of induction times and additional pH relaxation curves. These data will be analyzed by the application of surface nucleation-controlled growth models developed by Nielsen (5) and used by Lieser (6).

¹ Part of this work was orally presented at the Conference on Electrolyte Precipitation in Aqueous Solution (CEPAS), Copenhagen, August 1978.

EXPERIMENTAL

Continuous titrations were carried out by adding a base (NaOH) to acidified (pH = 1.0) iron(III) nitrate solutions ($6.25 \times 10^{-2} M$). The details of the experimental procedure have already been reported (1–3). A total of five separate titration experiments was done and during each run a number of samples was taken at different initial OH/Fe ratios for further study. These samples were kept in a thermostated bath at 24°C and changes in pH and OD (at 330 nm) were recorded. The gradual development of the solid phase was also followed in the ultracentrifuge.

RESULTS

Induction Times

The induction times derived from pH relaxation and from OD measurements on samples of the same initial composition were of similar magnitude. Stirring the samples during the measurement did not influence the length of the observed induc-

tion time. This observation suggests that the aging process is not diffusion controlled. Freshly prepared samples were also filtered through Millipore filters ($\sim 0.1 \mu\text{m}$) but the measured induction time was found to be equal to its value in unfiltered solutions. This finding is contrary to observations of Feenstra and de Bruyn (7). These investigators observed that the induction times in their study of the formation of hydroxyapatite from aqueous solution are markedly increased by prior filtration. Light scattering measurements (2, 8), however, indicated a small increase in the scattering signal during the induction period.

In Table I we list the observed induction times, the pH of the solution, and the calculated OH/Fe ratios. The total iron concentration of these samples was $(5.85 \pm 0.05) \times 10^{-2} M$. The OH/Fe ratios were calculated from the experimental titration curve corrected for the dilution due to addition of base.

We note from this table a decrease in induction time with increasing pH (increasing OH/Fe ratio). Apparent deviations from this general trend are to be ascribed to the accuracy with which the pH can be measured. This accuracy is about 0.33 pH unit.

TABLE I
Induction Times

pH	Induction time	OH/Fe	pH	Induction time (days)	OH/Fe
2.22	7 min	0.89	1.98	3	0.60
2.20	8 min	0.86	1.98	7	0.60
2.19	8 min	0.85	1.96	4	0.58
2.17	43 min	0.79	1.93	19	0.55
2.15	88 min	0.75	1.92	14	0.55
2.12	6.6 hr	0.71	1.91	6	0.54
2.06	24 hr	0.65	1.90	25	0.53
2.05	20 hr	0.65	1.86	21	0.50
2.02	24 hr	0.63	1.86	28	0.50
1.99	7 days	0.60	1.85	47	0.49

pH Relaxation or Growth Curves

At OH/Fe ratios greater than unity a sharp drop in pH is noted within 1 day and is generally followed by a further gentle decrease that extends over long periods. Previous studies (2) confirmed that in such samples growth of a solid phase occurred during this period of rapid pH change but was effectively stopped after 1 day. For our analysis longer growth periods are preferable so we restricted our pH relaxation studies to samples of which the initial OH/Fe range varied from 0.7 to 1.0 (pH 2.10 to 2.25). In this case the growth can be studied from the beginning. In these samples a less steep decrease in pH is noted as may be seen from Fig. 1 which plots a typical pH relaxation curve. The growth process is seen to spread out over a period as long as 6 days.

Ultracentrifuge studies revealed the presence of a second solid component after some time had elapsed. At an OH/Fe ratio of 0.9, for example, this heavier component was noted after 4 to 7 days of aging. In agreement with the findings of Murphy *et al.* (9) an increase in the sedimentation coefficient of the smaller component was measured during the first 4 days. As the heavy component was considered to form by flocculation (2) and not by growth, the growth analysis will be restricted to the first 4 days of the aging process.

DISCUSSION

The observed long induction times and their independence of the hydrodynamic conditions (stirring intensity) strongly indicate that a heterogeneous nucleation-controlled step is involved in the development of the solid colloidal phase. This conclusion is also in accord with the observation by Hsu (10) that samples seeded with iron(III) oxyhydroxide sols showed a spectacular decrease in the length of the induction times. Based on this evidence we propose an analy-

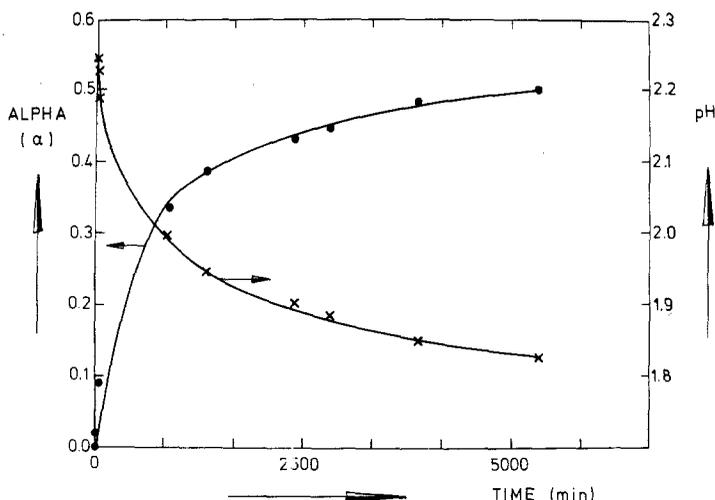


FIG. 1. pH vs aging time (a typical pH relaxation curve). Degree of reaction (α) vs aging time also illustrating a chromomal fit (I_0) to experimental data. Initial OH/Fe ratio = 0.96, $pK_c = 40.9$.

sis of our experimental data by the application of two growth models (A and B) devised by Nielsen (5).

The Growth Models

Both models describe the growth of particles and are not concerned with the initial birth or nucleation event. This system is furthermore assumed to be monodisperse and Ostwald ripening and coagulation processes are not allowed.

In model A, the so-called mononuclear model, the time elapsed between two surface-nucleation events is assumed to exceed greatly the time required for one surface nucleus to add, by growth, a complete new layer to the particle. The growth rate will therefore be controlled by the time necessary for the formation of the critical surface nucleus.

Nielsen (5) showed that the induction time τ_i may be written as

$$\tau_i = A \exp(\Delta G^*/kT), \quad [1]$$

where ΔG^* is the Gibbs free energy for the formation of a critical surface nucleus on a substrate of similar composition. Further-

more, it may be shown (5) that

$$\frac{\Delta G^*}{kT} = \frac{\beta \gamma^2 V^{4/3}}{(kT)^2 \ln S} = n^* \ln S, \quad [2]$$

where

- γ = the interfacial tension of the solid/solution interface,
- V = the mean molecular volume ($\sim 30 \text{ \AA}^3$ in our study) of the solid phase,
- β = a geometric factor (=4 for a square surface nucleus),
- S = the degree of supersaturation of the solution,
- n^* = the number of ions in the surface nucleus.

The preexponential factor A in Eq. [1] is not essential to our analysis. Its magnitude will be determined by the detailed description of the surface nucleation event. On taking the logarithm of Eq. [1] and combining the result with Eq. [2] we may write

$$\ln \tau_i = B + C(1/\ln S), \quad [3]$$

where B is a constant and C is a function of S because of the dependence of γ on the

supersaturation. Gindt and Kern (11) derived a similar expression except that their parameter B is also a function of the supersaturation. Over narrow ranges of the supersaturation they did find that plots of τ_i versus $\ln^{-1} S$ yield straight lines for some alkali-halide systems.

Model B, the polynuclear growth model of Nielsen, allows for the initiation of a large number of nucleation events on the particle surface. A correction must now be applied for the intergrowth of the various expanding surface nuclei. This model does not feature an induction time and will be applicable to growth systems in which the particles have sizes larger than those encountered with model A.

A mathematical description of the polynuclear growth mechanism is provided by the relation

$$t = KI_p(\alpha), \quad [4]$$

where

$$I_p(\alpha) = \int_0^\alpha x^{-2/3}(1-x)^{-p} dx, \quad [5]$$

and t = time of growth, K = a constant for a given experiment, α = the extent of the reaction, p = an integer equal to $(n^* + 2)/3$, where n^* is again the number of ions in the surface nucleus. For a certain value of p a plot of $I_p(\alpha)$ versus time should yield a straight line. This characteristic value of p can be evaluated by plotting the chronomal $I_p(\alpha)$ against time for different p values.

Application of the Mononuclear Growth Model

The induction time data may be analyzed with this model. We define the parameter π ,

$$\pi = \frac{c_{\text{Fe}^{3+}} \cdot c_{\text{OH}^-}^3}{K_c}, \quad [6]$$

and the degree of supersaturation S ,

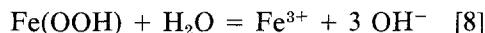
$$S = \pi^{1/4}, \quad [7]$$

where K_c is the (concentration) solubility product of the solid phase derived from the

equilibrium reaction



or



and is a function of the ionic strength of the solution phase which is constant in the pH region studied. The term c_j refers to the concentration of the free Fe^{3+} or OH^- ion in the supersaturated solution. S or π has been determined from the calculated free iron(III) concentration which can be computed from the known formation constants (1) of monomeric and dimeric iron-bearing species.

The solubility product K_c has been measured in 3 M NaClO_4 solutions. Biedermann and Schindler (12) determined a $\text{p}K_c$ value of 38.7 based on an aging time of 200 hr. Schindler *et al.* (13) reported a value of 39.1 after having aged a precipitate which they described as an "amorphous inactive hydroxide" for 1 year. The latter investigators also reported for αFeOOH a $\text{p}K_c$ value of 41.2. The variation in the literature values for $\text{p}K_c$ at 3 M is probably partly due to an increased solubility of very small particles. X-Ray analyses of the finely divided precipitates formed in our studies showed that the diffraction pattern resembled that of αFeOOH . Atkinson *et al.* (14) concluded that the diffraction patterns obtained by van der Giessen (15) also suggest the presence of goethite-like particles in his preparation. The so-called amorphous inactive hydroxide (13) consists most likely also of very small goethite-like particles. As the $\text{p}K_c$ at the ionic strength (~ 0.4 M) of our experiments is not known, we shall use in the analysis of our results a number of suitably chosen values.

In Fig. 2 we have plotted $\ln \tau_i$ versus $\ln^{-1} S$ for three different $\text{p}K_c$ values as suggested by Eq. [3]. The curvature in the plots may be accounted for by the pH dependence of the interfacial tension γ for this system. This effect is to be expected because of the important role of pH in the description of

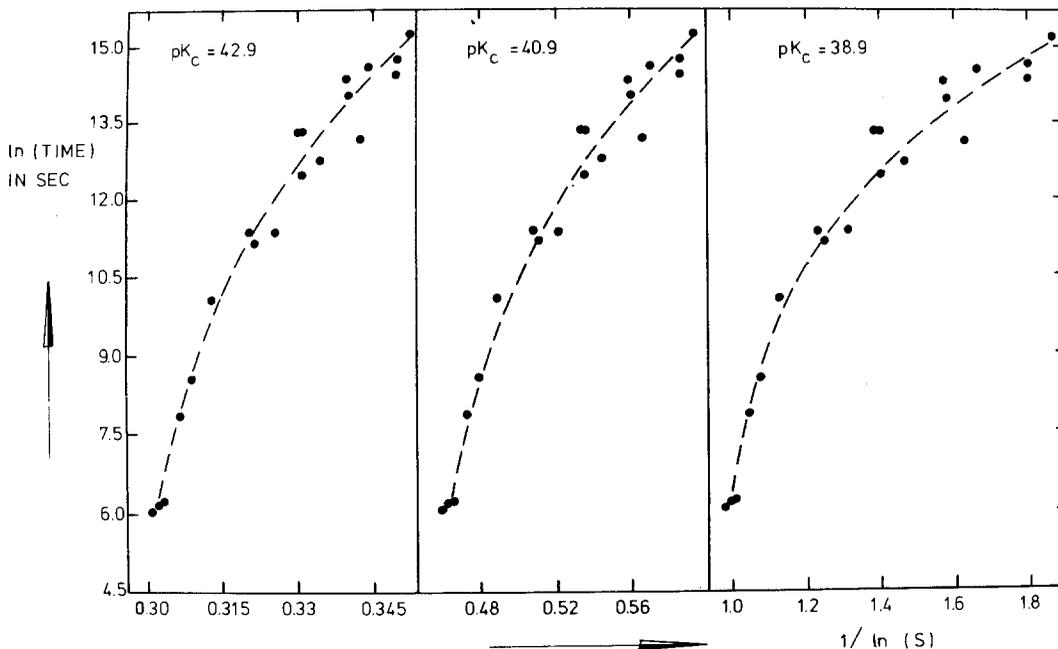


FIG. 2. Logarithm of induction time (sec) vs inverse logarithm of supersaturation at different pK_c values.

the electrical double layer at the oxide/solution interface (16). The dependence of γ on pH and therefore on the supersaturation (see Eq. [6]) may be stressed by rewriting Eq. [3] as

$$\ln \tau_i = B + C' \gamma^2(S) \ln^{-1} S, \quad [9]$$

where C' is a constant.

The interfacial tension γ at a given S may be derived from the slope of the curves in Fig. 2 if, according to Eq. [9],

$$\gamma^2 \gg \frac{1}{\ln S} \frac{d\gamma^2}{d(1/\ln S)}. \quad [10]$$

We have verified this condition and give in Fig. 3 a plot of the calculated γ as a function of pH for different K_c values. Remarkable is the relatively large increase in γ over this narrow pH range. If this trend were to persist at higher pH values then an unrealistically large value of γ will be indicated at the point of zero charge (pH \approx 8 (16)). We shall return to this questionable conclusion later on.

Application of the Polynuclear Growth Model

In Fig. 1 we also give a plot of α (the extent of reaction) as a function of time. This parameter is defined by the relation

$$\alpha = \frac{c_0 - c_t}{c_0 - c_\infty} = \frac{S_0 - S_t}{S_0 - 1}, \quad [11]$$

where c_0 equals the product $(c_{\text{Fe}^{3+}} \cdot c_{\text{OH}^-}^3)^{1/4}$ at $t = 0$ and c_∞ refers to the same product under equilibrium conditions. The latter parameter can therefore be derived from the solubility product. The magnitude of α was determined by an iterative procedure also used in evaluating the supersaturation.

The smooth curve which follows the experimental points quite closely is obtained by applying the I_9 chronomal to Eq. [4]. The constant K in this equation was evaluated from a plot of time against I_9 . In Table II we list the chronomal fits for two different pK_c values. We believe that the experimental conditions realized in our study

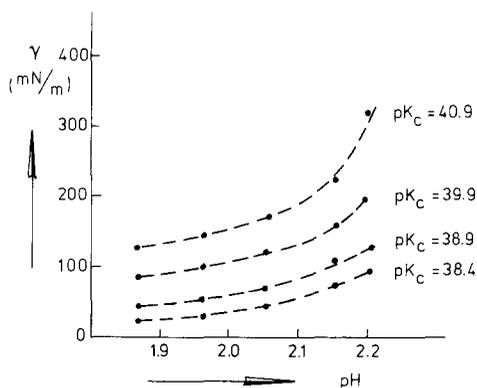


FIG. 3. Interfacial tension γ (mN/m) vs pH at different pK_c values (deduced from analysis of induction times).

(ionic strength 0.4 M) are reflected in this choice of pK_c values. From this table we note that the magnitude of the parameter p is practically independent of the choice of pK_c . The degree of supersaturation at the start of the growth period and after 4 days is also included in this table. A variation in p from 7 to 9 implies that the number of ions in the critical nucleus varies between 19 and 25, a result which suggests a degree of polymerization for the surface nucleus of 5 to 7 when expressed in terms of the number of iron atoms.

The interfacial tension γ may again be evaluated by utilizing an expression that re-

lates n^* , S , and γ (see Eq. [2]);

$$\gamma = 21.3 \ln S \cdot (n^*)^{1/2} mN/m. \quad [12]$$

The results of this calculation, performed with the aid of information included in Table II, are presented in Fig. 4 for two reasonable pK_c values. The dashed curves give the pH dependence of γ as derived from the mononuclear model and the experimental induction time data. An analysis of the growth curves based on the polynuclear model yields a less pronounced change of γ with pH and suggests that a more reasonable value of γ should be found at the point of zero charge. A similar dependence of γ on pH was also found from an analysis of some preliminary pH relaxation studies in solutions in the pH range 2.2 to 2.5 and an Fe(III) concentration of $5 \times 10^{-3} M$.

In the analysis of our experimental data we have ignored the dependence of γ on particle size. This dependence might have an important effect especially in the analysis of the induction time results. Under the conditions prevailing in the aging systems characterized by measurable induction times the particles must have been very small.

The discrepancy in the estimated γ values based on induction time measurements and pH relaxation studies may also be partly due to changes in the nature and structure of the growing particles. It is possible that

TABLE II
Chronomal Fits

OH/Fe	p		Log π for $pK_c = 39.9$	
	$pK_c = 39.9$	$pK_c = 40.9$	$t = 0$	$t = 4$ days
0.74	7	8	2.53	1.90
0.77	7	8	2.58	1.85
0.79	7	8	2.64	1.83
0.82	7	8	2.69	1.82
0.85	7	8	2.74	1.81
0.89	7	8 or 9	2.78	1.81
0.92	7	9	2.82	1.81
0.96	7 or 8	9	2.84	1.82
0.99	8	9	2.86	1.83
1.03	8	9	2.86	1.83
1.07	8	9	2.87	1.84

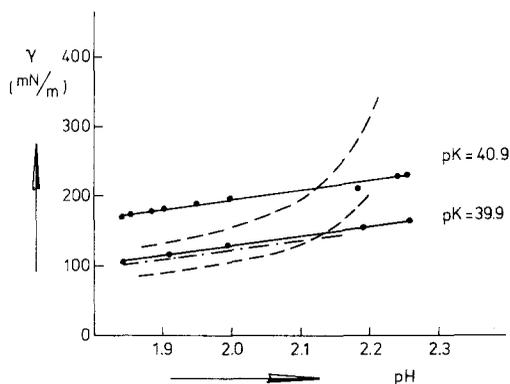


FIG. 4. Interfacial tension (mN/m) vs pH at two pK_c values. —, OH/Fe = 0.99; ---, OH/Fe = 0.77; - · -, taken from Fig. 3.

polymers obtained by olation reactions (1, 2) act as the substrate on which growth of the new phase initiates. This supposition is in accord with the observation that the same induction times were measured in filtered and unfiltered solutions. These polymers were too small to be filtered out. After the start of the growth (presumably mononuclear) an oxolation step probably takes place (2) which results in a structural change of the very small particles on which further growth (polynuclear model) of iron oxyhydroxide takes place.

CONCLUSION

In earlier publications (1, 2) we proposed that the formation of an iron oxyhydroxide phase by base titration of an acidified Fe(III) salt solution may be divided into four consecutive stages. Hydrolysis of Fe(III) to monomeric and dimeric species is followed by a reversible rapid growth to large polymers which, as suggested here, then act as the substrate for the formation via a surface nucleation-controlled growth process of a colloidal FeOOH phase which then tends to flocculate. From an analysis of the third step in this chain of events we were able to derive an order of magnitude value for the interfacial tension of the iron oxyhydroxide/solution interface in a decidedly acid environment. The crudeness of the growth models used in this analysis, our ignorance about the relation among γ , surface potential, and pH, and the uncertainty about the true solubility product of the small hydroxide particles do not allow a more detailed analysis to be attempted. We have, however, illustrated that in studying the formation and growth of a new phase, the effect of changing interfacial tension cannot be ignored.

One important feature of the formation of an iron oxyhydroxide phase at room temperature from acid solutions that still remains to be explained is the observed stop in the growth of the solid particles once they reach the size range 20–40 Å and have

undergone no change for more than a year. It is quite likely that a thermodynamically stable sol has been formed under the experimental conditions as suggested by Stol and de Bruyn (17, 18). According to these authors the thermodynamic stability of such a sol will be related to a drastic lowering of the interfacial tension by ionic adsorption in the electrical double layer at a pH far removed from the pH of the point of zero charge.

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