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Study of the zeta potential of Fe(O)OH colloids

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Zeta potentials of colloidal particles were used to study the influence of anions on the formation of ferric oxide hydroxides [Fe(O)OH]. This anion effect, complexation with ferric ions and adsorption on the resulting particle surface, correlated well with the determined zeta potentials. The greater anion effect in ferric ion solution decreased the measured zeta potential of colloidal particles. This effect increased with increasing size, charge and complexation of anions. The results indicated that the composition and morphology of Fe(O)OH precipitates were affected by the presence of anions in solution.

1. Introduction

Many studies have been reported on the properties of colloidal ferric oxide hydroxides, in relation to industrial applications [1]. These properties and applications are dependent on the parameters (e.g. pH, temperature, solvents and the concentration of ferric ions) of the preparation method [2]. Moreover, the nature of anions in solution is also an important parameter for the formation of ferric oxide hydroxide. For example, Ishikawa *et al.* [3] reported that the presence of tartarate ions influences the formation of ferric oxide hydroxide. However, the precise mechanism of anion effect on the formation of Fe(O)OH is far from clear. In order to reveal this anion effect, it was investigated closely by zeta potential determination of colloidal particles in this work.

Precipitation with sodium hydroxide from ferric ion solutions was selected to prepare ferric oxide hydroxides. The formation of Fe(O)OH precipitates begins with nucleation and proceeds through particle growth. Both nucleation and particle growth are affected by the complexation and adsorption of anions on to the ferric ions and colloidal surface in the solution. During ageing, large Fe(O)OH particles with more significant mass settle to form precipitates, whereas the very finely divided colloidal particles remain in the clear layer of the settling solution. The surface charge of Fe(O)OH precipitates is related to that of the Fe(O)OH colloids. Thus a close study of the influence of the sign of the electric charge on the colloidal particles will predict the effect of the anions on the formation of Fe(O)OH precipitates. Because it has now become accepted that the zeta potential, Z_p, measures the electrostatic potential at, or near to, the beginning of the diffusion double layer of colloidal particles [4], Z_p can be used to study the influence of anions on the formation of ferric oxide hydroxide. Anions with greater complexing and adsorbing abilities have greater influence on both the Z_p value and the formation of ferric oxide hydroxides. In addition to the influence on the formation of ferric oxide hydroxides, some properties of reduced iron powders are also affected by the nature of anions.

With better understanding of the mechanism of the anion effect, the results of this study will enable better selection of anions for the preparation of ferric oxide hydroxides and iron powders.

2. Experimental procedure

Precipitation of ferric oxide hydroxide was carried out by adding 1 M sodium hydroxide solution to 0.018 M ferric ion solution at room temperature. After 10 min agitation and 1 h settling, the zeta potential of residual colloids in the clear layer of the settling solutions was measured immediately using an electrophoretic light-scattering spectrophotometer (Otsuka, ELS-800), in which zeta potential values were calculated from mobility values, using the Smoluchowski equation [5]. The Stokes diameter of the colloidal particles [6] was also determined using the electrophoretic light-scattering spectrophotometer. During Z_p determination, the studied pH was varied over a range of 1–10 by changing the amount of sodium hydroxide solution added.

After settling, the solutions passed through 0.45 μm filters to remove Fe(O)OH precipitates, which were washed with distilled water and then dried in a desiccator for 1 week. Although the exact composition of Fe(O)OH precipitates always depends on the preparative method, at least a part of such precipitates seems to be the composition of Fe(O)OH. Therefore, the red–brown precipitates commonly called ferric hydroxide are described as ferric oxide hydroxide [Fe(O)OH] in this work.

In the ferric ion solutions, the studied anions were chloride, sulphate, fluoride, sulphamate, acetate, formate, oxalate and citrate ions. The added amount of studied anion was 100% combining weight to the ferric ion, that is 3 mol chloride ion or 1.5 mol sulphate ion per mole of ferric ion. The origins of these anions were, respectively, sodium salts or acids, because the sodium ion is an indifferent ion [7] and not specifically adsorbed at the colloidal interface, thus the Z_p value was only influenced by pH and anions in this work.

Iron powder was obtained by heating and reducing Fe(O)OH precipitates for 30 min at 680 °C by blowing hydrogen into them at 500 ml min^{-1}. The morphology of the precipitated Fe(O)OH particles and iron powders was examined using a scanning electron microscope (SEM). Infrared spectra of the precipitated ferric oxide hydroxides were also examined.

3. Results and discussion

3.1. Titration curves of ferric ion solutions

Hydroxide precipitation of the acidic ferric ion is a typical neutralization process; therefore, at a fixed titration rate, agitation speed and constant concentrations of alkali and ferric ion, the inflexion point of titration curve of ferric chloride solution should be same as ferric sulphate solution. However, as shown in Fig. 1, different inflexion points were obtained but only the existing anions were different. Because the inflexion points of sodium sulphate and sodium chloride solutions are zero, Fig. 1 indicates that different acidic ferric reactants and therefore different Fe(O)OH precipitates, were formed due to the presence of different anions.

In order to obtain a solution containing mainly ferric ions (say 99%) in the form of the pale purple hexa-aquo ion, the pH must be around zero [8]. Because the pH of all the studied ferric ion solutions was equal to or greater than 1, more highly condensed species of ferric ions were formed. These condensed species contain anions that are present in the solution. Therefore, during the titration process, both complexation and adsorption of ferric ions and condensed species by anions should be considered. The ferric ion has a greater affinity for anions that coordinate with oxygen, resulting in the sulphate ions having a greater affinity with ferric ions than chloride ions.

Therefore, ferric ions were more easily combined and charge-neutralized by the negative sulphate ion than that of the chloride ion, causing a lower amount of alkali to be needed to attain the inflexion point in the nickel sulphate solution than that of nickel chloride solution (Fig. 1).

The inflexion points of the titration curve of ferric chloride solutions were also changed when other anions were present in the nickel ion solutions. As a result, different anions produce different ferric reactants for neutralization and then different Fe(O)OH precipitates will be obtained.

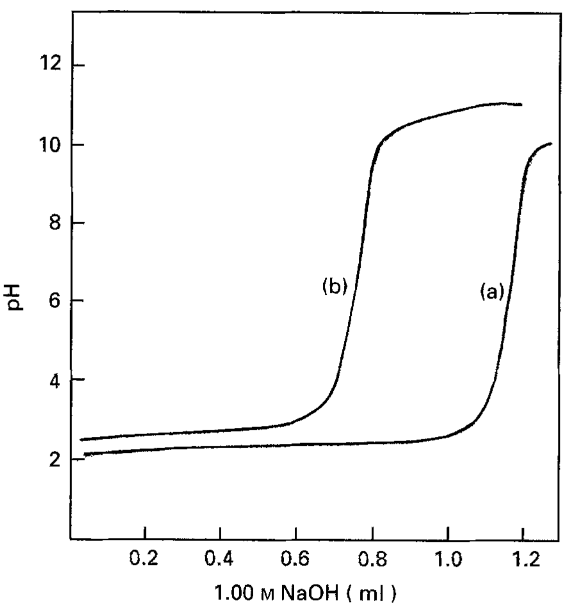

Figure 1 Titration curves of 50 ml 0.018 M Fe(III) electrolytes with 1.00 M NaOH. Ferric electrolytes were (a) ferric chloride and (b) ferric sulphate. The titration rate was 0.01 ml min^{-1}.

3.2. Z_p of chloride and sulphate solutions.

From the results of the inflexion points of the titration curves of ferric ion solutions, the formation of ferric oxide hydroxide was affected by the presence of anions. As the precipitation of ferric ion is a kinetically controlled process, different titration rates have different inflexion points on the titration curve, with the result that the explanation of the anion effect from the titration curves is very complicated. It has now become accepted that the zeta potential measures the electrostatic potential at, or very near to, the beginning of the diffusion double layer of colloids. Thus Z_p values were changed by the affinity of foreign ions in the compact layer of the double layer of the Fe(O)OH colloids. In this work, zeta potential was determined after 1 h ageing of colloids, which were thus near complete reaction, and more reliable results were obtained. Because the surface charge of Fe(O)OH precipitates is related to that of the Fe(O)OH colloids, Z_p determination can be used to study the influence of anions on the formation of Fe(O)OH precipitates.

The number, size, structure and morphology of precipitated particles are primarily controlled by nucleation and particle growth. However, these two processes are not well understood. The extremely small size of nuclei and colloids make physical observation even more difficult. Z_p is a proper method to observe the adsorption of foreign ions on these very finely divided particles. For the Fe(O)OH system, the sodium ion is said to be an indifferent ion and it is not significantly adsorbed at the colloidal particles interface. On the other hand, H^+, OH^- and anions are potential-determining ions; therefore, the Z_p of Fe(O)OH colloids is controlled by anions and the pH of the solution in which it is immersed. Thus, Z_p was studied as a function of both pH and the anions existing in the studied solutions.

Ferric ions in aqueous solution have a tendency to hydrolyse and/or to form complexes [9]. When considering only the most hydroxocomplex formation constants of the ferric ion, the point of zero charge (PZC) [10] is pH 8.55. Thus the net charge of all ferric complexes is negative when the pH value exceeds 8.55, whereas the net charge is positive when the pH is lower than 8.55. These formation constants of ferric ion are thermodynamical and neglect the existence of anions; therefore, after considering the influences of anions, the PZC values of the studied solutions were different from 8.55. With the greater liability of the iron–chlorine bond [11], as shown in Fig. 2, ferric chloride solution has a behaviour most like that of free ferric ion solution, resulting in its PZC being near pH 8.55. On the other hand, a lower PZC and more negative Z_p values were obtained in the ferric sulphate solution. Like the results in Fig. 1, a possible explanation for this PZC shift and lower Z_p values in ferric sulphate solution may be that the anionic sulphate ions have greater complexation and adsorption on to the ferric ion and colloidal surface. The anionic affinity sequence at the colloidal Fe(O)OH could be deduced from the PZC and Z_p values and found to be sulphate ion > chloride ion. As a result, PZC and Z_p values are found to be fundamental properties of Fe(O)OH colloids [12], the greater difference between the measured PZC and pH 8.55 means a greater anion effect on the formation of ferric oxide hydroxide.

Compared to a chloride ion, a sulphate ion contains coordinated oxygen atoms and has greater complexation, as well as a greater size and charge of sulphate ions which increases the adsorption on the colloids in the ferric ion solution. This is the reason why a sulphate ion has a greater anion effect than a chloride ion in the ferric ion solution. During neutralization, the positive charge of the ferric ions and colloids was easily combined and charge-neutralized by the sulphate ions, thus a smaller amount of alkali is needed to neutralize and precipitate the ferric species, resulting in a lower pH of mass precipitation in the ferric sulphate solution than in the ferric chloride solution. The mass precipitation of the ferric sulphate solution is about pH 2.9, whereas in the ferric chloride solution it is about 5.8. Besides the Z_p measurement, as shown in Table 1, the existence of the studied dispersed colloidal particles was also indicated by the Stokes diameter, d, of the colloids obtained in these ferric ion solutions.

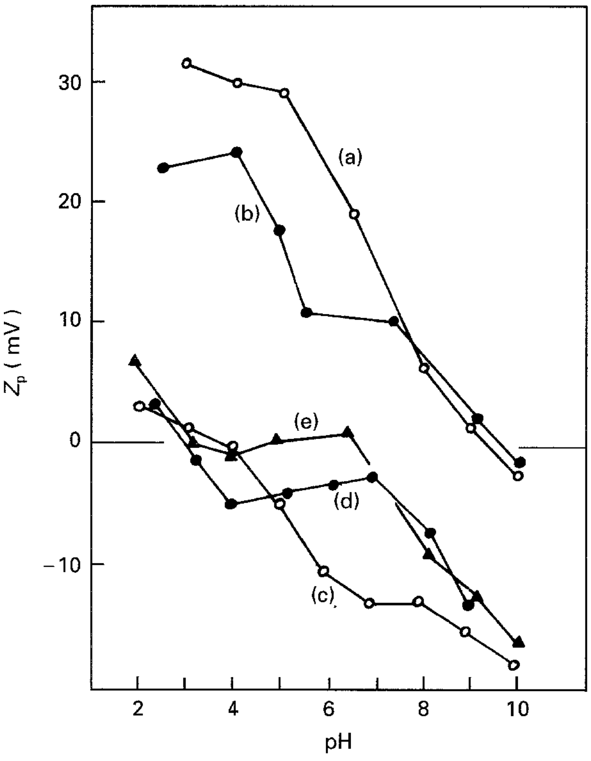

Figure 2 Zeta potentials of Fe(O)OH colloids obtained from 0.018 M Fe(III) solutions. Anions of ferric electrolytes: (a) 0.054 M chloride ions, (b) 0.108 M chloride ions, (c) 0.027 M sulphate ions, (d) 0.054 M sulphate ions, (e) 0.027 M sulphate ions and 0.054 M chloride ions.

The greater anion effect of a sulphate ion compared to a chloride ion was also verified by the results of curve (e) in Fig. 2. When 0.027 M sulphate ions were added to 0.018 M ferric chloride solution, the greater affinity of a sulphate ion compared to that of a chloride ion or a hydroxide ion, caused the Fe(O)OH colloids to be combined mainly by sulphate ions. Therefore, the PZC and Z_p values of curve (e) were nearer the curve of ferric sulphate solutions (curve c) than those of ferric chloride solutions (curve a). Owing to the fact that sulphate ions have greater affinity for ferric ions and ferric colloids, sulphate species were precipitated with the Fe(O)OH precipitates. The incorporated sulphate ions in precipitated particles were evinced by the infrared spectra. When ferric chloride solutions contain sulphate ions, the precipitates have very strong 1075 and 1120 cm^{-1} IR bands which can be assigned to sulphate groups in the Fe(O)OH precipitates. Infrared spectra also show that the precipitates prepared from ferric sulphate solution contain sulphate components. According to elementary analysis, the sulphur content of the Fe(O)OH precipitates obtained from sulphate-containing solutions is about 4%–5%. As a result, the existing anions was one of the most important considerations in the composition of ferric oxide hydroxide.

When 100% combining weight to ferric ions of sodium chloride or sodium sulphate was added to ferric chloride or ferric sulphate solution, respectively, as shown in curves (b) and (d) of Fig. 2, both the PZC and Z_p values were changed slightly from curves (a) and (c). These results indicate that the formation of Fe(O)OH precipitates was affected by the concentration of anions but with a saturation limit, thus doubling the concentration of anions (200% combining weight to ferric ions) could not give double changes of Z_p or PZC values.

3.3. Z_p of other anion solutions

Owing to the greater lability of a chloride ion, other anions could be added into the ferric chloride solution

TABLE I Stokes diameter of colloidal particles as a function of pH

Solution	pH	d values (μm)
Ferric chloride	2.7	0.14
	3.0	0.28
	4.0	10.06
	5.0	49.47
	6.0	66.68
Ferric sulphate	3.0	19.40

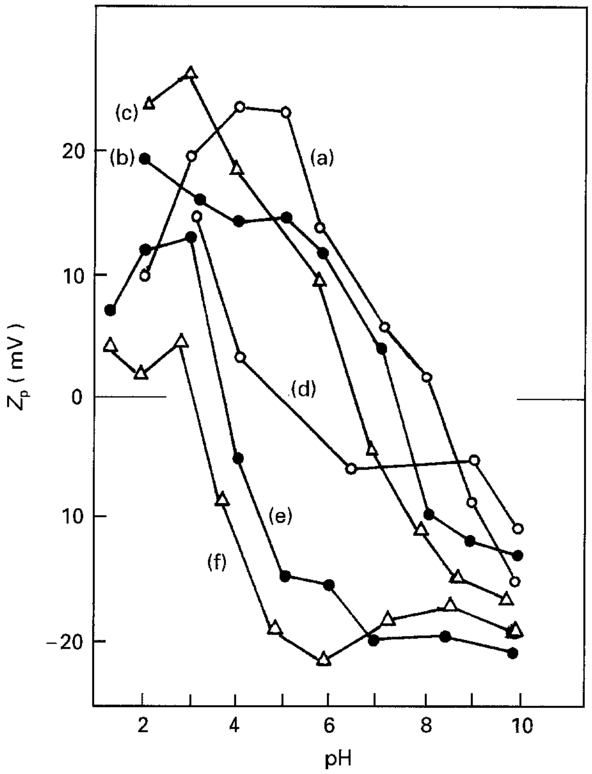

Figure 3 Zeta potentials of Fe(O)OH colloids obtained from 0.018 M ferric chloride solutions with following anions: (a) 0.054 M formate ions, (b) 0.054 M acetate ions, (c) 0.054 M sulphamate ions, (d) 0.054 M fluoride ions, (e) 0.027 M oxalate ions, (f) 0.018 M citrate ions.

to investigate the influence of anions on the formation of Fe(O)OH precipitates. As shown in Fig. 3, due to their large size compared to a chloride ion and contained coordinated oxygen atoms, sulphamate, acetate and formate ions decreased the Z_p and PZC values of ferric chloride solution. Of these three monovalent anions (sulphamate, acetate and formate ions), a formate ion has a smaller size and so less adsorption on the colloid, resulting in less anion effect and has greater Z_p and PZC values. On the other hand, the sulphamate ion has a larger size and more coordinated oxygen and nitrogen atoms, resulting in a greater anion effect and less Z_p and PZC values.

Although a fluoride ion is smaller in size than a chloride ion, the formation constant for ferric ions with fluoride ions is greater than the corresponding constants for chloride or even acetate ions, causing greater complexation, and resulting in lower Z_p and PZC values when 0.054 M fluoride ions were added to the ferric chloride solution. The formation constants of the complex species of Fe^{3+}-fluoride, Fe^{3+}-acetate and Fe^{3+}-chloride are $10^{5.28}$, $10^{3.2}$ and $10^{1.48}$, respectively. Because the effect of the small size of the fluoride ion is overcome by its greater complexation, a fluoride ion has a greater anion effect than a chloride ion. This fact was also indicated by curve (a) of Fig. 4. Both the Z_p and PZC values of the ferric fluoride solution are smaller than those of the ferric chloride solution. Moreover, the fact that curve (d) of Fig. 3 is very near curve (a) of Fig. 4 also indicates that a fluoride ion has greater affinity for ferric ions than that of a chloride ion. The greater affinity of fluoride ions for ferric ions and the colloidal surface was also proved by the pH of mass precipitation. In contrast to the pH 5.8 of ferric chloride solution, due to the greater anion effect of the fluoride ion, the pH of the mass precipitation was about pH 5.3 in the ferric fluoride solution.

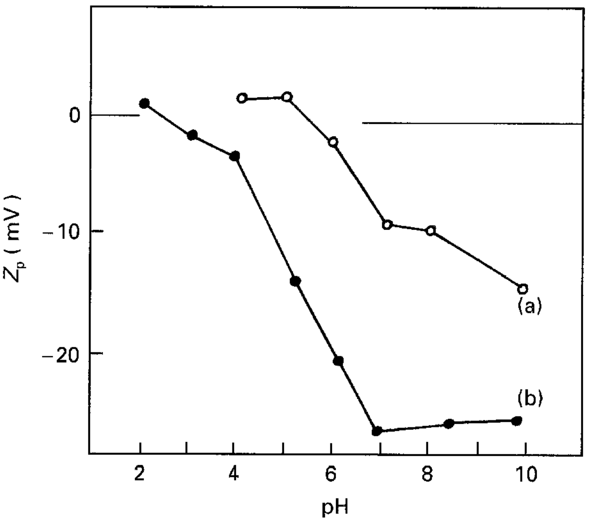

Figure 4 Zeta potentials of Fe(O)OH colloids obtained from (a) 0.018 M ferric fluoride and (b) saturated ferric citrate solutions.

Added to their greater charge and size, citrate or oxalate ions contain chelating oxygen atoms (e.g. trisoxalato complex, $[Fe(C_2O_4)_3]^{3-}$), resulting in these two ions possessing greater adsorbing and complexing abilities. Thus citrate or oxalate have a greater anionic affinity for the colloids than the other monovalent anions discussed in this work. As a result, when citrate or oxalate ions were added to the ferric chloride solutions, the obtained Z_p or PZC values were less than those of monovalent anion-containing solutions. Among these two anions, besides a greater formation constant (the formation constants of the complex species of Fe^{3+}-citrate and Fe^{3+}-oxalate are $10^{12.5}$ and $10^{9.4}$, respectively), a citrate ion also has greater charge and size than an oxalate ion. Therefore, the citrate anion has a greater affinity with colloidal particles than an oxalate ion, resulting in a lower Z_p or PZC value when the ferric chloride solution contains citrate ions. The result that curve (f) of Fig. 3 is very near curve (b) of Fig. 4 also indicates that a citrate ion has greater affinity for ferric ions than that of a chloride ion. As a result, in the ferric chloride solution, the anionic affinity sequence at the colloidal surface decreases according to the sequence citrate ion > oxalate ion > fluoride ion > sulphamate ion > acetate ion > formate ion.

3.4. Ferric oxide hydroxide precipitates

Ferric ion solutions with different anions have different ionic strengths, titration curves, Z_p, and PZC. Therefore, the nucleation and particle growth and thus the morphology of Fe(O)OH precipitates should all be markedly affected by the existing anions, particularly complexing and adsorbing anions, in solutions.

Although most Fe(O)OH precipitates obtained from alkali neutralization were often gelatinous, other

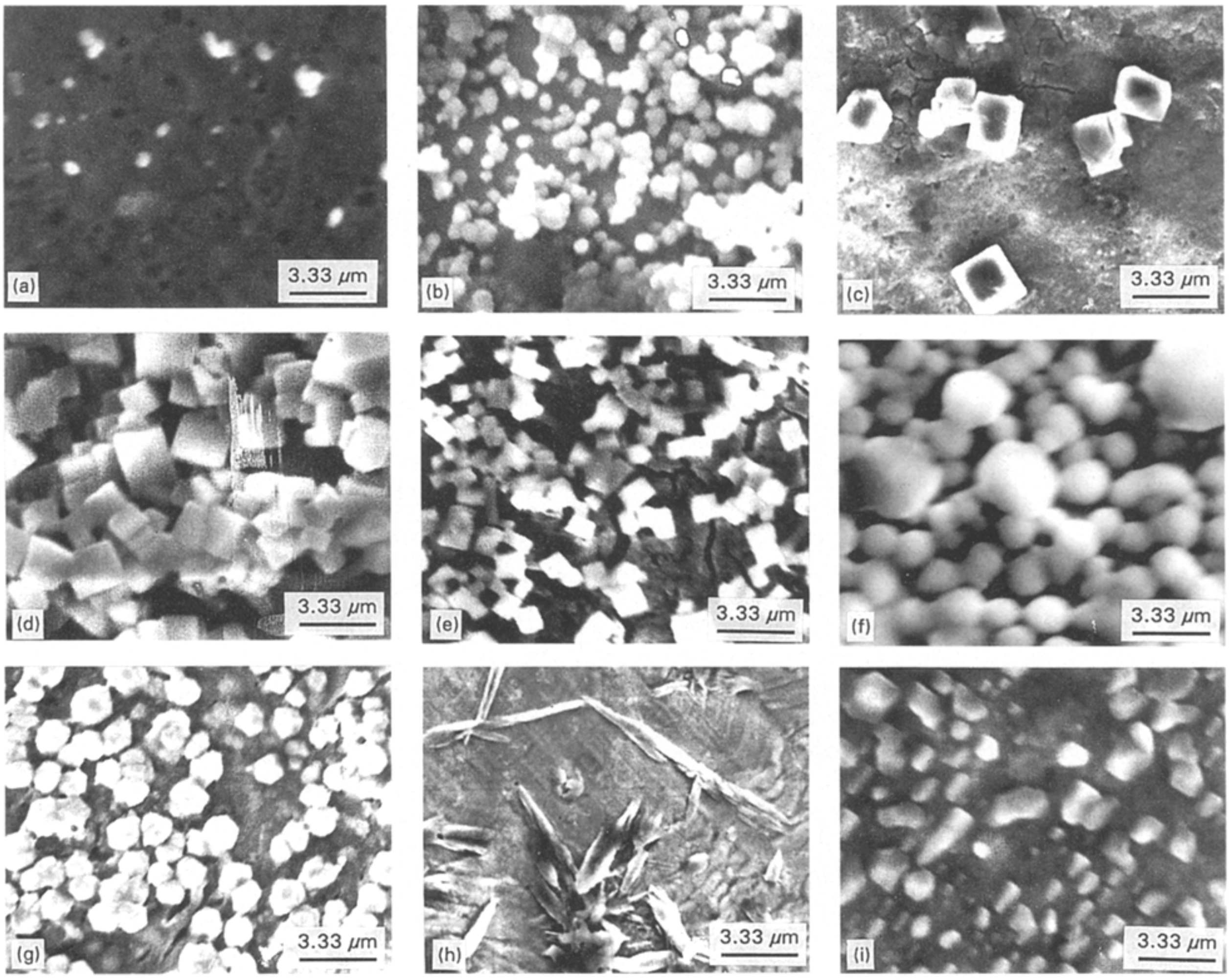

Figure 5 Scanning electron micrographs of Fe(O)OH precipitates obtained from following solutions: (a) 0.018 M ferric chloride solution, (b) 0.018 M ferric fluoride solution, (c) 0.018 M ferric chloride with 0.054 M acetate solution, (d) 0.018 M ferric chloride with 0.054 M formate solution, (e) 0.018 M ferric chloride with 0.027 M oxalate solution, (f) 0.018 M ferric chloride with 0.054 M sulphamate solution, (g) 0.018 M ferric chloride with 0.018 M citrate solution, (h) 0.018 M ferric sulphate solution, (i) 0.018 M ferric chloride with 0.027 M sulphate solution.

particles in several forms also exist simultaneously depending mainly on the nature of the anions in the testing solutions. On the other hand, no noticeable effects of the anions or pH are seen on the size of Fe(O)OH precipitates. The ferric oxide hydroxide precipitates obtained from ferric halide solutions were granular particles, fine granules from the chloride solution and larger circular granules from the fluoride solution (Fig. 5a and b). Possibly due to the carbonate group, when ferric chloride solution contains acetate, formate or oxalate ions, the Fe(O)OH precipitates obtained were in the cubic form (Fig. 5c–e). When ferric chloride solution contains sulphamate ions, the Fe(O)OH precipitates were circular granular particles (Fig. 5f). The presence of citrate ions in the ferric chloride solution produced Fe(O)OH precipitates with an irregular circular granular form (Fig. 5g). On the other hand, as shown in Fig. 5h, the acicular particles of Fe(O)OH precipitates evidently differed from those prepared from other ferric ion solutions. This may be due to the special coordination and adsorption of sulphate ions on the surface of the precipitated solids in ferric sulphate solution. Furthermore, when sulphate ions were added to the ferric chloride solution, the Fe(O)OH precipitates obtained (Fig. 5i) had a different form from those in Fig. 5a and h.

With different complexing and adsorbing abilities, different anions in the ferric ion solutions have different influences on the nucleation and particle growth of ferric oxide hydroxide. Therefore, different shapes of Fe(O)OH precipitates were observed when ferric ion solutions contained different anions.

3.5. Iron powders

The iron powders obtained from the reduction of Fe(O)OH precipitates were also affected by the presence of anions in the ferric ion solutions. Although all the reduced iron powders obtained from these tested ferric ion solutions were irregular elliptical or spherical particles, some properties of these iron powders were changed. Possibly due to the greatest complexation and adsorption of anions, when ferric chloride solutions contain oxalate or citrate ions, the obtained iron powders were very tough. When sulphamate ions were added to the ferric chloride solution, the iron powders obtained were also slightly toughened. On the other hand, brittle iron powders can be obtained when the ferric solutions contain nitrate ions. Typical

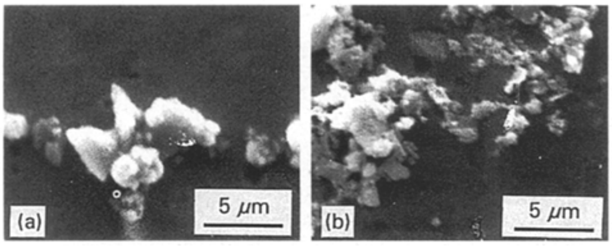

Figure 6 Scanning electron micrographs of iron powders obtained from (a) 0.018 M ferric chloride solution and (b) 0.018 M ferric sulphate solution.

iron powders obtained from the ferric chloride and ferric sulphate solutions are shown in Fig. 6.

4. Conclusion

The formation of Fe(O)OH and iron powder from the neutralization of ferric ion solutions depends, to a great extent, on the nature of the existing anions. Greater size and charge, together with greater complexation of anions, have a greater influence on the formation of Fe(O)OH. This anion effect can be measured by PZC and Z_p determinations. The results indicate that the composition and morphology of ferric oxide hydroxide could be controlled by the presence of anions in the ferric solutions. Some properties of iron powders were also dependent on the nature of the anions existing in the ferric ion solutions.

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