Chapter 8

Hydrothermal Precipitation of β-FeOOH Nanoparticles in Mixed Water/Alcohol Solvent

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Additional information is available at the end of the chapter

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Abstract

In this research, synthesis of β-FeOOH nanoparticles was carried out using different alcohol/water mixed solvents. Four different alcohols were mixed with water to form solution of different surface tension. A relationship between particle size and surface tension has been drawn from theoretical analysis. A linear relationship was shown to exist between surface tension and particle size under the reported conditions. Statistically designed experiments were conducted to evaluate the interactions of process parameters on the particle growth. A generic correlation has also been developed empirically to predict particle size.

Keywords: β-FeOOH, nanorod, crystal growth, surface tension, generic correlation

1. Introduction

Akaganeite, β-FeOOH, a type of iron oxy hydroxide has been studied intensively not only because of its great technological and scientific interest but also for many applications [1]. β-FeOOH is a promising electrode material that has potential in rechargeable batteries due to its hollandite-like crystal structure with tunnel-like cavities [2]. β-FeOOH has also found applications in hydroprocessing of coal, removal of arsenate/arsenite [3] and phosphate from water [4]. Due to these intriguing applications, numerous works have investigated the methods of akaganeite synthesis [2]. Surface tension of solvent plays an important role in the formation of 1D β-FeOOH nanorods. A low surface tension of solvent can promote the growth of β-FeOOH nanorods [5]. Addition of medium that can lower the surface tension of precursor solution can alter the thermodynamic properties of the reaction system and subsequently affect the nucleation kinetics, which would result in various morphology and particle sizes. The application of alcohol/water mixture during the synthesis of different metal oxide nanoparticles can be found in the literature. Submicrometer ZrO_2 nanomaterial was synthesised by Hu and Chen [6] using alcohol/water mixture. Fang and Chen [7] used a mixed solvent of water/n-propanol to synthesise titania powders. $ZrO_2(Y_2O_3)$ nanoparticles were synthesised by Li and Gao [8] using ethanol/water mixture. So far, the effect of mixed solvent properties on the growth of 1D β-FeOOH nanorods were not evaluated despite of its numerical industrial and scientific applications. In our previous work, we have demonstrated that alcohol played an important role in controlling nucleation rate and particle size of 1D β-FeOOH nanoparticles [9, 10]. Previously reported work in the literature considered the dielectric constant, ε, properties of the water/alcohol mixture to be of significance in controlling particle growth, discarding the effect of surface tension, γ. However, it is interesting to note that the Coulomb interaction is very weak in water and solvent with high ε [11] and Coulomb interaction is directly related to ε of the solvent. This simple phenomenon makes the application of the ε of solvent only to relate to particle growths as described in the literature susceptible.

The application of mixed solvent is a new approach in the synthesis and processing of materials [12]. However, the role of surface tension is neglected when relating particle growth with solvent properties. Tuning the surface tension of the water/alcohol can affect the colloidal interaction between solid particles. Most of the literature reported on the use of alcohol/water mixture on the precipitation of submicro meter-sized TiO_2, ZrO_2, SiO_2 and CeO_2 particles. Published literature provides evidence that the formation of nanoparticles strongly related to the solution pH, precursor salt concentration, time and temperature, etc. However, very few attempts have been made in the literature to describe the interaction between the process parameters from statistically designed experiments. Moreover, only one work was done to describe the effect of process variables on particle size [13]. However, the empirical correlation reported can only predict spherical shape particles and the experiments were not designed statistically to evaluate the actual relationship between process variables.

Development of mathematical relationship that combines fundamental properties and empirical quantities derived from statistical analysis can be very useful in understanding the actual effect of process interactions on the particle growth. In a previous work [9], mathematical relation between solvent surface tension and particle growth was reported. However, the effect of various process parameters on the particle growth was not accounted in that model. Hence, in this chapter, an evaluation of the fundamental relationship between solvent surface tension, precursor concentration, time and β-FeOOH nanorod growth is presented via statistically designed experiments.

According to classical electrostatic model, the chemical potential of two phases are equal in equilibrium and can be written as [11, 12]:

$$\mu^o{}_s + KT\ln C_S = \mu^o{}_L + KT\ln C_L \qquad (1)$$

where μ^o is the standard chemical potential, C is the concentration of solute (S and L represent solid and liquid phases, respectively), T is the temperature expressed in Kelvin and K is Boltzmann constant. Eq. (2) also known as Coulombs interaction can be used to express the energy required to separate the charged ions from the solid state [11, 12]:

$$\Delta\mu^o = \frac{Z_+ Z_- e^2}{4\pi\varepsilon_o\varepsilon(r_+ + r_-)} \tag{2}$$

where ε_o represents the permittivity in vacuum and ε is dielectric constant of a given solution. r_+ and r_- present the radii of ions charged. Based on Eqs. (1) and (2), Chen and Chang [12] proposed the below equation:

$$\frac{2\gamma}{rkT\rho} = \ln C + \frac{Z_+ Z_- e^2}{4\pi\varepsilon_o\varepsilon KT(r_+ + r_-)} \tag{3}$$

where m is the weight of the solute molecule; γ is the interfacial energy in J/m^2, the term interfacial energy can also be written as nm^{-1}; r is the particle size of a spherical particle and C is the solute concentration. The author linearized Eq. (3) in terms of particle size r(Y) and dielectric constant ε(X). It was assumed that only dielectric constant is significant and other properties are insignificant. However, according to Israelachvili [11], Coulombic interaction is much weakened in water. So, it can be postulated that, for homologous mixture of water and alcohol, the Coulombic interaction will be very weak. Hence, it can also be hypothesised that the surface tension of solvent will directly affect the nucleation and growth of particles.

2. Experimental

2.1. Materials and method

Analytical-grade $FeCl_3{\cdot}6H_2O$ and NH_4OH (B & M Scientific, Cape Town, R.S.A) were used as they are without any further purification. Deionised water and alcohol (methanol, ethanol and propanol) were mixed together with different ratios to vary the surface tension of solvent. Ammonium hydroxide, NH_4OH, was added drop wise until the mixture pH reached a value of 10. A certain amount of $FeCl_3{\cdot}6H_2O$ was added to the solution to make up 0.05 M solution (unless stated otherwise), and the solution was stirred until the iron salt was dissolved. The pH of the final solution (prior to heating) was recorded. The pH was always kept constant at ~2 to isolate the effect of pH on the particle growth in each case. The solution was replaced in a teflon-lined pressure autoclave. The temperature was 100°C. A reaction time of 2 h was used to synthesise the particles.

3. Results and discussion

3.1. Correlation between particle size and alcohol surface tension

Three different alcohols (methanol, ethanol and propanol) were used to tune the surface tension of the solvent. If the hypothesis conceived earlier is true, then there will be a qualitative relationship between particle size, D_e, and surface tension of solvent, γ. The particles synthesised in this study were rod-shaped particles. The length and diameter of the particles were measured from TEM images. A minimum number of 250 particles was counted for

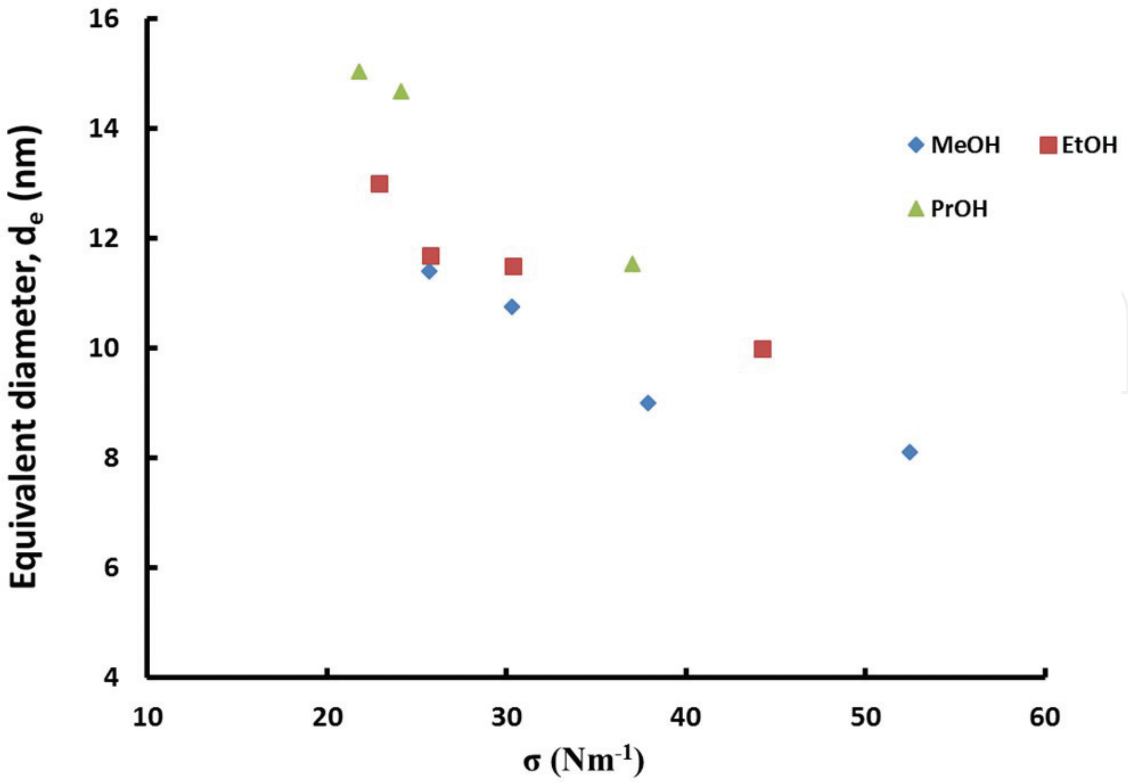

Figure 1. Correlation between particle size and solvent surface tension.

statistical purpose. The equivalent diameter of the rod-shaped particles was calculated using Huebscher formula to evaluate the role of surface tension on particle size [14]:

$$D_e = 1.30 \times \left[\frac{(a \times b)^{0.625}}{(a + b)^{0.25}} \right] \tag{4}$$

where a and b are the measured diameter and length of the particles in this study. It can be seen from **Figure 1** that there is a linear relationship that holds approximately independent of the nature of the alcohol used to synthesise the particles. This illustration proves the point that the surface tension of the mixed solvent can also be used to relate nucleation and growth.

3.2. A generic correlation to predict particle growth

Statistically designed experiments are effective optimising tools where the process is influenced by various external factors. In this chapter, a two level three factor factorial design was used to evaluate the effect of interaction of various parameters that have been manipulated during the synthesis of β-FeOOH particles. Previous work [9, 10] has shown that the particle phase is very sensitive to reaction temperatures and pH. Hence, reaction temperature and pH

Factors	Low level (−)	High level (+)
A: $FeCl_3$ concentration [M]	0.05	0.5
B: % solvent to water ratio	30	90
C: Time (h)	2	12

Table 1. Real amount of each factor used in the factorial trial experiments.

were omitted from the factorial trial for simplicity sake. Furthermore, butanol was used as solvent to synthesise β-FeOOH particles to validate the relations between particle growth and solvent surface tension. **Table 1** presents the real amount of each parameters that have been used at low and high levels, which is assigned by a positive (+) and negative (−) sign, respectively.

3.3. Evaluation of the effects of factors and the interaction between the factors on particle growth

Table 2 presents the obtained equivalent diameter at different experimental conditions according to the two level three factor factorial design. A Pareto chart is presented in **Figure 2** to assess the interaction between process parameters and obtained equivalent diameter of the particles. The factorial design can cover the main and interaction effects of the parameters within the whole range of selected parameters. Evaluation of the effect of principal factors revealed that these parameters have positive effects on the obtained equivalent diameters of the particles.

Based on the significance of effects from **Figure 2**, a generalised empirical correlation that takes solvent surface tension, precursor concentration and time into account is proposed:

Samples	$FeCl_3$ concentration [M]	% alcohol to water ratio used as solvent	Time (h)	D_e
1	0.5	90	2	17
2	0.05	30	12	17
3	0.5	30	12	90
4	0.05	30	2	16
5	0.5	90	12	43
6	0.05	90	12	16
7	0.05	90	2	15
8	0.50	90	2	7

Table 2. Results obtained for a two level factorial design.

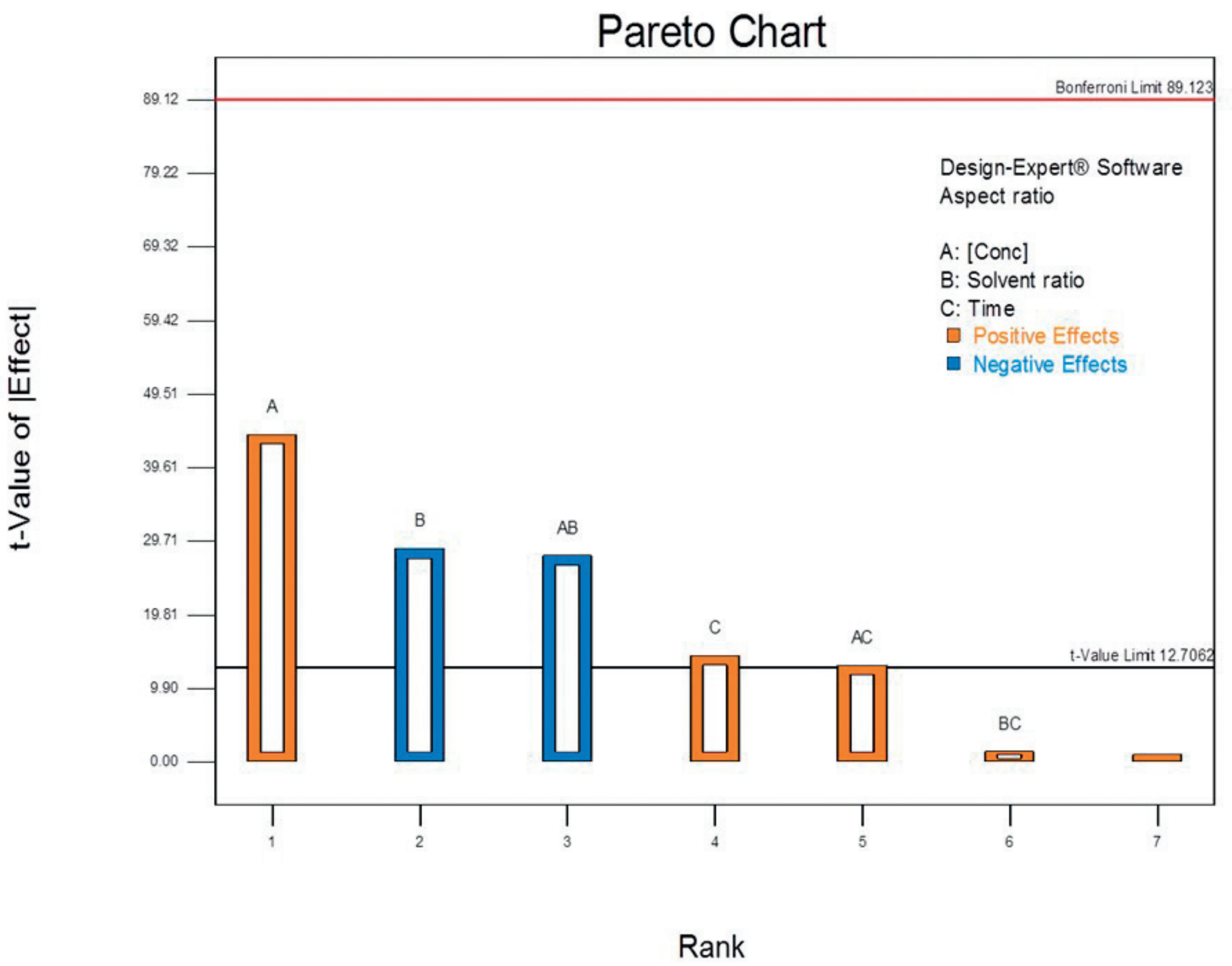

Figure 2. Estimated effects of factors on particle aspect ratio using factorial design.

$$Y = \beta_o \gamma + \sum_{i=A} \beta_i X_i + \sum_{i=A} \sum_{j=A \neq i} \beta_{ij} X_i X_j \tag{5}$$

where Y is the predicted response (D_e in this case), X_i is the un-coded or coded values of the factors ($FeCl_3$ concentration denoted by A, % alcohol to water ratio is denoted by B and time is denoted by C), β_o and β_i are constant and γ is the surface tension of alcohol used. The corresponding response model for the obtained aspect ratio of the particles, which are valid for un-coded factor, is:

$$\mathrm{Y} = 0.39\gamma + \beta i[A] + 0.047[B] - 0.38856[C] - 1.8[A^*B] + 5.05[A^*C] + 0.004[B^*C] \tag{6}$$

Linear regression can be used to obtain corresponding values of β_i. **Figure 3** presents typical comparison of experimental and predicted values using different β_i values. It can be seen from **Figure 3** that the comparison between experimental and predicted values agrees very well.

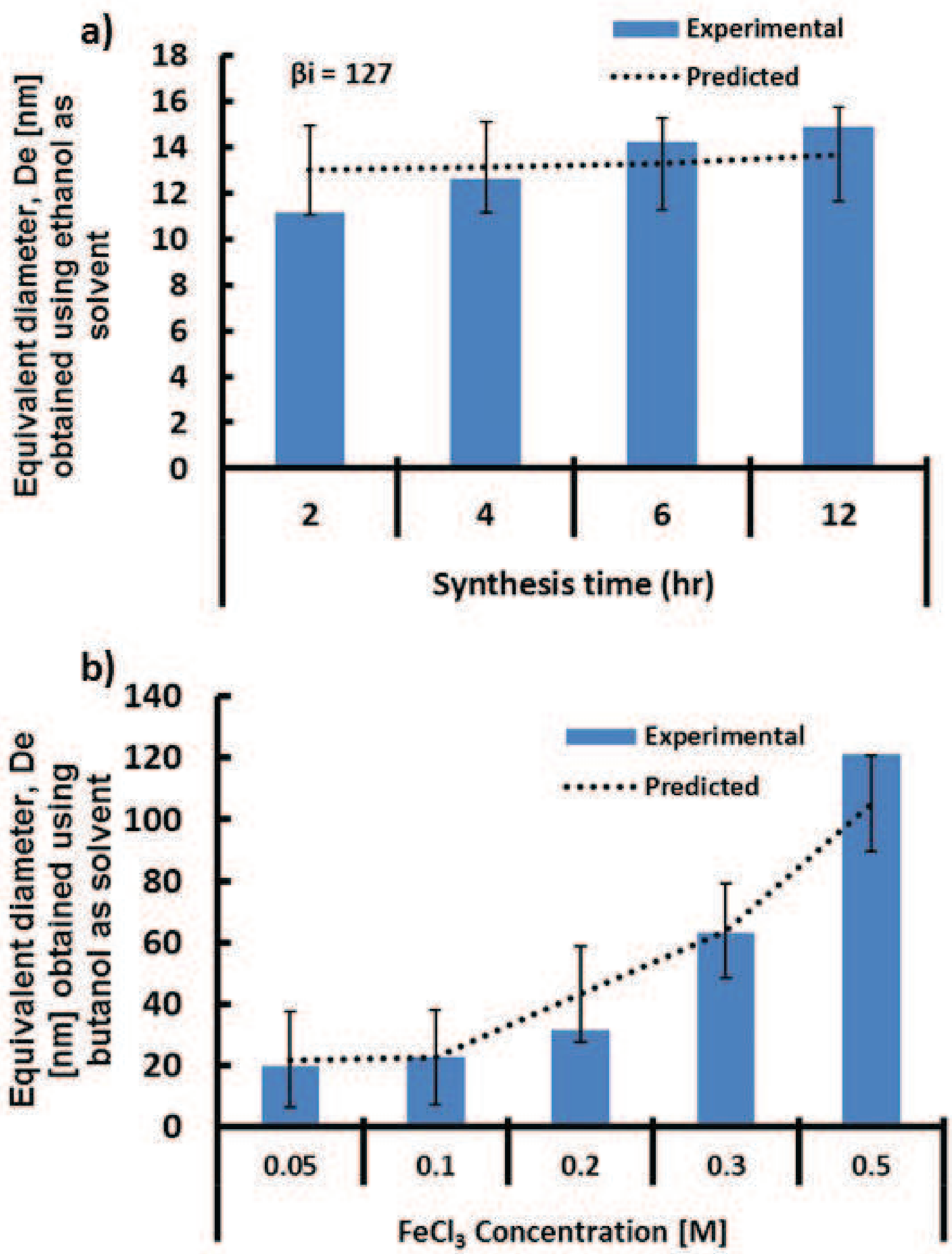

Figure 3. Typical comparison between experimental data and predicted value using different β_i constants for ethanol (a) and (b) butanol solvents.

4. Conclusion

Interaction between solvent surface tension and various process parameters on the synthesis of different β-FeOOH morphology has been evaluated for the first time assuming the presence of low Coulombic interaction. A linear relationship was found between particle size and surface tension of the solvent. Statistically designed experiments were performed to evaluate the interaction between particle growth and process parameters. A generic correlation has been developed to predict particle growth. The correlation can be extended further to predict particle size of other type of materials. The results obtained in this work clearly indicate that the application of only dielectric constant to relate particle nucleation and growth is not adequate. A combination of surface tension and dielectric constant together will be appropriate.

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Conflicts of interest

The author declares no conflicts of interest.

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