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### Study and Modeling of Metal Oxide Solubilization in (w/o) Microemulsions

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# Study and Modeling of Metal Oxide Solubilization in (w/o) Microemulsions

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Water-in-oil (w/o) microemulsions are very appealing reaction media due to their ability to provide huge surface of contact between water-soluble and oil-soluble reactants. Their application as reaction media, including the preparation of nanoparticles, is, however, limited to water soluble precursors. In this study, we present a first step scheme in a two-step process for the preparation of metal oxide nanoparticles starting from their water-insoluble metal oxide bulk powder. This step involves solubilizing the metal oxide in the water pools of the microemulsion with the aid of a solubilizing agent. The variables affecting the solubilizing capacity of iron and copper oxides, as examples of important metal oxides, in single HCl-containing AOT/water/isooctane microemulsions were investigated. The effect of the following variables on the solubilization capacity is reported, namely, mixing time, surfactant concentration, water to surfactant mole ratio ( $R$ ), and the nominal concentration of HCl in the water pool. At 300-rpm, time-invariant concentration of the metals in the microemulsions was achieved in about 6 hours. These values were quoted as the solubilization capacity of the metal oxide at the corresponding conditions. Solubilization capacity increased linearly with the surfactant concentration and  $R$ , and portrait a power function with the nominal concentration of HCl in the water pool. A mathematical model previously derived to describe nanoparticle uptake by single microemulsion accurately accounted for the effect of the aforementioned variables on the solubilization capacity.

**Keywords** Catalysts, metal oxide, microemulsion, model, nanoparticle, solubilization, surfactant

## 1. INTRODUCTION

Microemulsions have been widely used to carry out reactions between water-soluble and oil-soluble reactants.<sup>[1–3]</sup> These systems provide a huge surface of contact between the reacting species and help catalyzing the reaction by virtue of compartmentalization.<sup>[1,2,4]</sup> Moreover, water-in-oil (w/o) microemulsions have been extensively employed to prepare different kinds of nanoparticles from their water soluble precursors.<sup>[4–19]</sup> The application of microemulsion systems as reaction media is restricted to at least one water-soluble precursor. The preparation of nanoparticles starting from their insoluble salts in (w/o) microemulsions is a new approach aimed at extending the scope of application of microemulsion techniques. Recently, Husein et al.<sup>[10–12]</sup> have prepared silver halides nanoparticles by exposing the corresponding bulk powder to a single microemulsion with reactive surfactant counterion. The surfactant counterion, a halide, reacted with the

solid surface to form water-soluble higher halides, which then precipitated upon migration to the bulk water pool. Narrower size distribution and smaller particle size were obtained when employing the single microemulsion technique.<sup>[10–12]</sup> While this technique looks promising for *in-situ* preparation of nanoparticles it is, however, limited to specific nanoparticle/microemulsion combination. The current work aims at generalizing the single microemulsion approach to other water-insoluble ionic precursor with the aid of a solubilizing agent added to the water pool. Precipitation of the nanoparticles commences at later stage with the aid of a precipitating agent. The solubilization of two metal oxides, namely iron and copper, was demonstrated by mixing their powder with a (w/o) microemulsion consisting of AOT, isooctane, and aqueous solution of HCl. The effect of the following variables on the solubilization capacity of metal oxide was investigated; including surfactant concentration, water to surfactant mole ratio ( $R$ ) and the nominal concentration of solubilizing agent in the water pool. All experiments were carried out by changing one variable at a time and keeping the others constants. The solubilization capacity was taken as time-invariant concentration of the metal in the microemulsions as measured by the inductively coupled plasma-atomic

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emissions spectroscopy (ICP-AES). A mathematical model developed earlier by our group to describe the nanoparticle uptake by the same microemulsions was employed to describe the solubilization capacity of the metal oxides.<sup>[7,8]</sup>

## 2. EXPERIMENTAL

### 2.1. Chemicals

AOT, dioctylsulfosuccinate sodium salt (98%, Sigma-Aldrich Fine Chemical, ON, Canada) was used as the surfactant; and isooctane (HPLC grade, Fisher Scientific, ON, Canada) was used as the oil phase in all the experiments. FeOOH powder (50–80 mesh, laboratory grade, Sigma-Aldrich Fine Chemical, ON, Canada) was used as the precursor salt for iron, CuO powder (~50 mesh, 99.99%, Sigma-Aldrich Fine Chemical, ON, Canada) was used as the precursor salt for copper, and hydrochloric acid (5.0 N, Alfa Aesar, ON, Canada) was used as the solubilizing agent. Deionized water was used for the aqueous solution of the microemulsion. All chemicals were used without further purification.

### 2.2. Sample Preparation

Deionized water or an aqueous HCl solution was added directly into AOT-isooctane solution under vigorous stirring at 25°C to achieve the required mole ratio of water to surfactant,  $R$ . Upon addition of HCl solution the system became cloudy. Cloudiness disappeared after shaking for 2 minutes. All microemulsion solutions were optically clear before introducing metal oxide powder and were freshly prepared. The microemulsion was then mixed with 10 times the stoichiometric amount of the metal oxide powder at 300 rpm and 25°C for 6 hours, unless otherwise noted. The use of 10 times of the stoichiometric amount was to ensure attaining time-invariant concentrations of the metals within reasonable time frame. After 6 hours of mixing, a complete transparent yellowish solution was obtained for FeOOH and a transparent bluish solution for CuO precursor. Excess precursor was made available in all the samples to ensure reaching equilibrium. Volumes of 1 mL were collected from the experimental samples at specified times, and the concentration of the metal in the microemulsion system was measured using the ICP-AES (IRIS Intrepid IIXDL, ThermoInstruments Canada Inc., Mississauga, ON, Canada). A standard containing 5 ppm was prepared by diluting 80 ppm Fe stock standard in the form of FeCl<sub>3</sub>-containing microemulsions with PermiSolv ICP solvent (CONOSTAN Oil Analysis Standards, Ponca City, OK, USA). The stock standard was prepared by dissolving 5 mg FeCl<sub>3</sub> in 0.2 M AOT microemulsions at  $R=4.0$ . For copper, CuCl<sub>2</sub> was used instead. During the standard preparation all the added salt was solubilized and no excess precipitate existed. Volumes of the

experimental samples were diluted with PermiSolv to concentrations around 2 to 5 ppm. Three replicates were prepared for some samples, and the 95% confidence intervals were calculated accordingly.

## 3. RESULTS AND DISCUSSION

The solubilization capacity of the metal oxide was taken as the time-invariant molar concentration of the metal based on the microemulsion volume.

### 3.1. Solubilizing Mechanism

The solubilization of FeOOH and CuO in HCl-containing microemulsions is believed to proceed according to the following steps. First, the metal oxide powder is exposed to HCl-containing microemulsions. Due to the dynamic nature of microemulsions, the HCl-containing reverse micelles migrate to the surface of the solid powder (metal oxide),<sup>[11,12]</sup> where, depending on the rigidity of the surfactant layer, they collapse. The following reactions then take place



The reverse micelles reform near the surface and migrate back to the bulk organic phase carrying the solubilized metal in their water pool. Once reaching the water pool, these metal ions exchange with the surfactant counterion, Na<sup>+</sup> or H<sup>+</sup>, and become bound in the Stern layer.<sup>[15,20–22]</sup> The ion exchange reaction is presented below:



where  $\text{AOTY}$  is the sodium and/or the acidic forms of the surfactant and  $M^{z+}$  is the cation with  $z$  oxidation state. This reaction contributes to releasing more of the H<sup>+</sup> from the Stern layer, hence, enhancing the solubilization capacity. It is worth noting here that only free H<sup>+</sup> ions are believed to react with the water-insoluble precursor as opposed to the mechanism proposed by Husein et al.<sup>[11,12]</sup> to explain the solubilization of the silver halides.

### 3.2. Effect of Mixing Time

Mixing is an important parameter affecting the rate of solubilization, since it exposes more of the solid surface and enhances mass transfer rate of the migrating reverse micelles.<sup>[11,12]</sup> The effect of mixing time on the concentration of the solubilized metal, iron or copper, in the microemulsions was investigated at 200 mM AOT, and  $R$  of 4.0 having a nominal HCl concentration of 1.5 M. Samples from the microemulsion-metal oxide mixture were collected at different time intervals, while mixing at

300 rpm. Figure 1 presents the variation of iron and copper concentrations with respect to time.

As can be seen in Figure 1 the solubilization of metal oxides increased with time and leveled off after 6 hours of mixing. This time-invariant concentration was considered as the ultimate solubilization capacity of the metal oxide in the microemulsions. Hence, for the subsequent experiments a 6-hour mixing time was considered sufficient to ensure attaining the solubilization capacity for a given metal oxide.

### 3.3. Effect of Surfactant Concentration

At fixed  $R$ , increasing the surfactant concentration will increase the population of the reverse micelles<sup>[7,8,11,15]</sup> and consequently, the solubilizing capacity is expected to increase. The effect of increasing AOT concentration from 0.12 to 0.3 for every value of  $R$  between 2.0 and 8.0 was studied. The concentration of HCl in the water pool was maintained constant at 1.5 M and 10 times of the stoichiometric amount of the metal oxide powder was added. Figure 2a presents the FeOOH solubilization capacity as a function of AOT concentration for various  $R$  values. Figure 2b shows CuO solubilizing capacity as a function of AOT concentration, at  $R = 4.0$ .

Figures 2a and 2b show that, for a given  $R$ , the solubilizing capacity increased linearly with AOT concentration and all lines pass through the origin. The linear increase in the solubilization capacity is attributed to a probable linear increase in the population of reverse micelles having the same nature and concentration of ions in the water pools. The increase in the solubilization capacity with surfactant

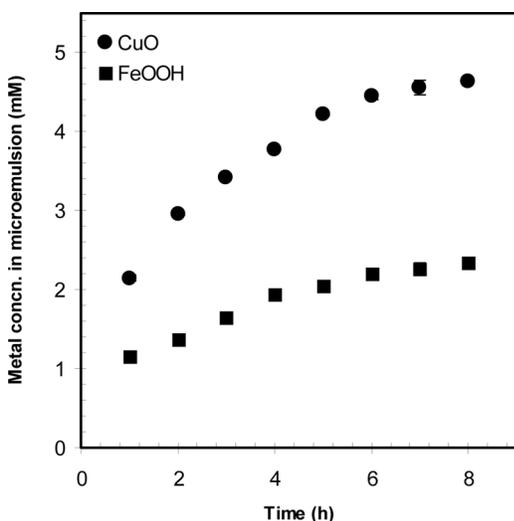


FIG. 1. Metal concentration in the microemulsion as a function of time obtained when mixing HCl-containing microemulsions  $\{[AOT]=0.2\text{ M}, R=4.0, [HCl]=1.5\text{ M}\}$  with 10 times the stoichiometric amount of metal oxide powder for different times at 300 rpm and 25°C.

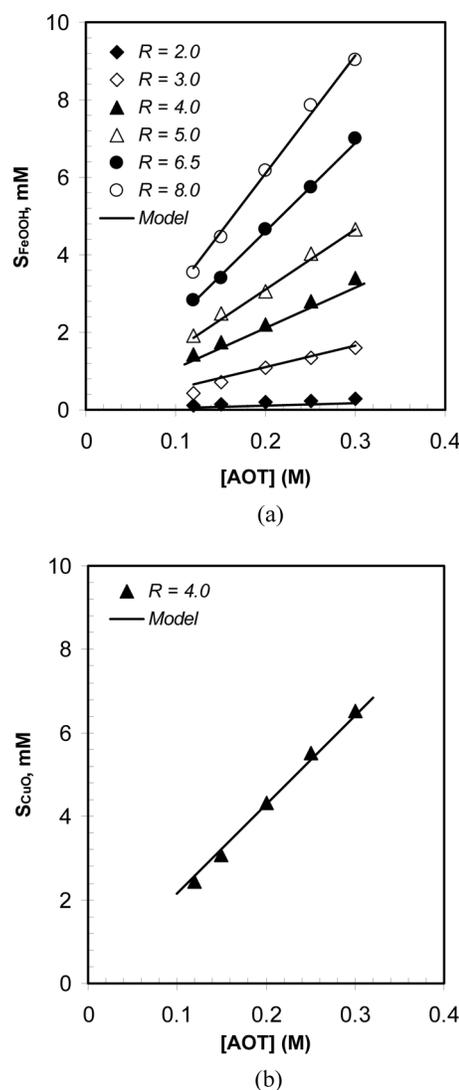


FIG. 2. Solubilization capacity as a function of AOT concentration obtained when mixing HCl-containing microemulsions  $\{[HCl]=1.5\text{ M}\}$  with 10 times the stoichiometric amount of (a) FeOOH powder, (b) CuO powder for 6 hours at 300 rpm 25°C.

concentration is higher at higher values of  $R$ , as evident from the slopes of the solid lines.

The solubilization capacity was higher for CuO compared to FeOOH. This can be attributed to the fact that, for the same moles of HCl, more moles of  $\text{Cu}^{2+}$  form than  $\text{Fe}^{3+}$  in accordance with the stoichiometric coefficient of reactions R1 and R2. Interestingly, when the stoichiometric coefficients were accounted for, it was found that the system is still able to solubilize more of the CuO. For example, after 6-hours mixing, at  $[AOT]=0.2\text{ M}$  and  $R=4.0$ , the solubilization capacity was 4.3 and 2.2 mM for copper and iron oxides, respectively. A multiplication of FeOOH solubilization capacity by 3/2 accounts for the difference introduced by the stoichiometric coefficients. The product,

3.3 mM, is still however, less than 4.3 mM. This suggests that another factor plays role in the solubilization process. It seems likely that the exchange between the solubilized metal ion and the surfactant counterion following reaction R3 had contributed to the release of more  $H^+$  ions from the Stern layer in the case of copper. Gurnule et al.<sup>[23]</sup> indicated that  $Fe^{3+}$  exchanges more favorably than  $Cu^{2+}$  at ion exchange resin surfaces. Nonetheless, it is the final equilibrium concentration of free  $H^+$  and free and bound  $Fe^{3+}$  or  $Cu^{2+}$  that dictate the solubilization capacity.

### 3.3. Effect of $R$ (Mole Water/Mole AOT)

The water uptake of Winsor type II microemulsions depends heavily on the type and concentrations of ions in the bulk water phase.<sup>[20–22,24]</sup> The water content of Winsor types II and/or IV has a significant effect on the activity of enzymes encapsulated in the water pools.<sup>[25–27]</sup> In addition,  $R$  is an important parameter which dictates the colloidal concentration of nanoparticles and their stability.<sup>[7,8,11,12]</sup> The value of  $R$  was increased in this experiment from 2.0 to 8.0 for every AOT concentration from 0.12 to 0.3 M. The nominal concentration of HCl was fixed at 1.5 M.

Figures 3a and 3b show a linear increase in the solubilizing capacity as  $R$  increased. The linear increase in the solubilization capacity is attributed to a linear increase in the free water content of the microemulsion. Since the nominal concentration of HCl was maintained constant, the number of moles of free  $H^+$  ions, available for the reaction, increases linearly as well. The figures show that all the straight lines intercept with x-axis at around  $R=2.0$ , independent of the surfactant concentration and the type of metal oxide. At low values of  $R$ ,  $\leq 2$ , all water contributed to the bound water and no free water was there to act as water of solvation.<sup>[7,8]</sup> Consequently, no free  $H^+$  was available for the reaction. In addition, the very rigid surfactant layer at low  $R$  value may have acted as an infinite kinetic barrier preventing the collapse of reverse micelles at the surface of metal oxide.

### 3.3. Effect of Nominal Concentration of the Solubilizing Agent

When an aqueous salt is added to a reverse micellar system, part of the water becomes bound to the surfactant head groups, which results in concentrating solutes in the water pool.<sup>[15,28]</sup> Moreover, in the current system,  $H^+$  ions migrate from the bulk water pool to the Stern layer as a result of an ion exchange reaction. This makes determination of  $H^+$  concentration in the water pool a challenging parameter to control. Therefore, the concentration of HCl in the added aqueous phase, nominal HCl concentration in the water pool, was used as the independent parameter.

Figures 4a and 4b show the effect of the nominal concentration of HCl in the water pool on the solubilization capacity of the metal oxides. This nominal concentration

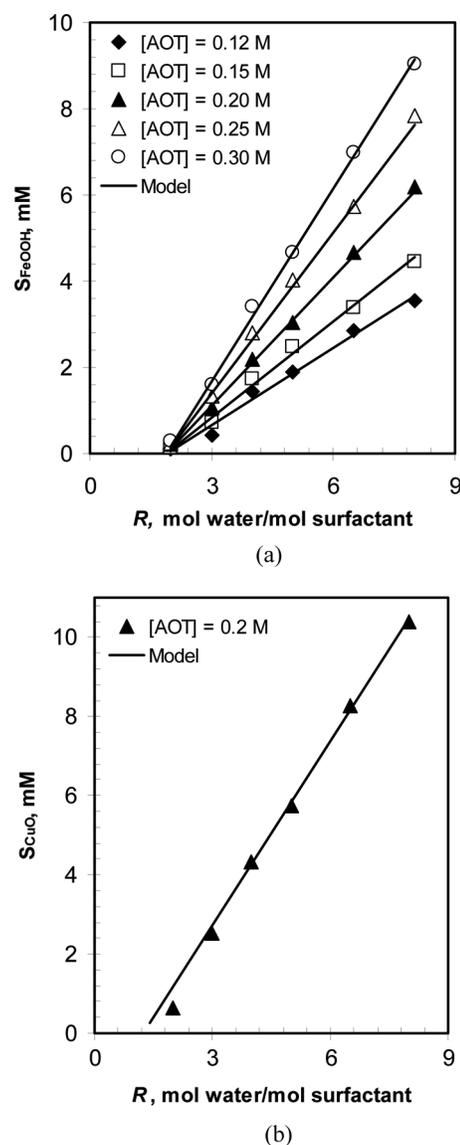


FIG. 3. Solubilization capacity as a function of water to surfactant mole ratio,  $R$ , obtained when mixing a stoichiometric amount of HCl-containing microemulsions  $\{[HCl]=1.5\text{ M}\}$  with 10 times the stoichiometric amount of (a) FeOOH powder, (b) CuO powder for 6 hours at 300 rpm 25°C.

was increased from 0.7 to 1.74 M for every AOT concentration between 0.12 and 0.3 M, at  $R=4.0$ , and 300 rpm of mixing. Figures 4a and 4b show that the solubilization capacity increased as the nominal concentration of HCl increased. At constant  $R$  and surfactant concentration, higher HCl concentration contributes to more free and bound  $H^+$ , and higher ionic strength. Hence, higher solubilization capacity is expected, however, in a non-linear manner due to the ion exchange reactions involved. Notably, the solubilization capacity took the form of a power function with respect to the nominal concentration

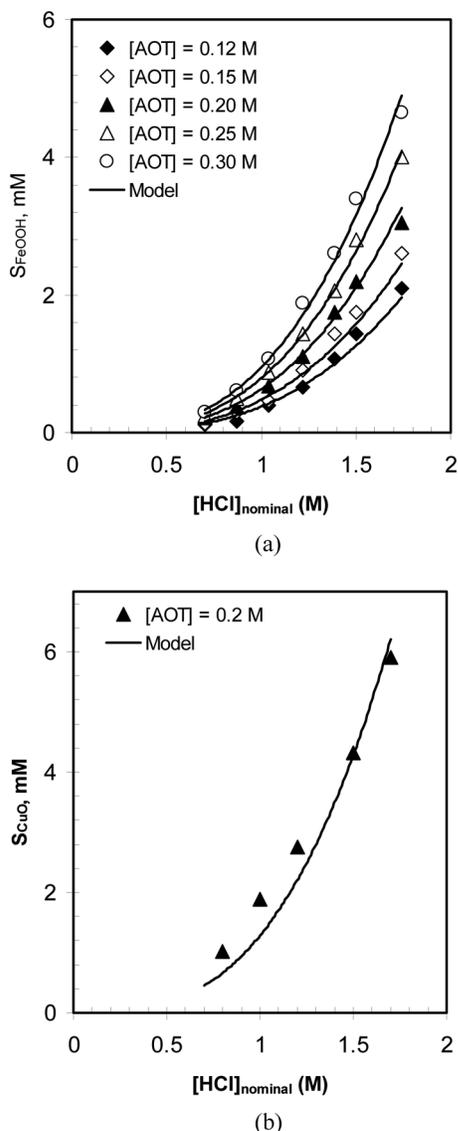


FIG. 4. Solubilization capacity as a function of the HCl nominal concentration obtained when mixing a stoichiometric amount of HCl-containing microemulsions  $\{R=4.0\}$  with 10 times the stoichiometric amount of (a) FeOOH powder, (b) CuO powder for 6 hours at 300 rpm 25°C.

of HCl. Rabie and Vera<sup>[20]</sup> reported a power function relationship between the water uptake by Winsor type II microemulsions and the ionic strength. Nassar and Husein<sup>[7,8]</sup> also reported the same trend between the nanoparticle uptake by single microemulsions and the ionic strength in the water pool.

#### 4. MODELING

This model is developed to describe the individual solubilization capacity of iron and copper oxides by HCl-containing AOT/isooctane/water single microemulsion.

The model is limited to the region where stable microemulsions is maintained, as was the case for all the experiments in this study, and all the surfactant molecules are assumed to participate at the reverse micellar interface.

Gobe et al.<sup>[29]</sup> reported a linear relationship between the solubilization capacity of  $\text{FeCl}_3$ , a water-soluble salt, and surfactant concentration in AOT/water/isooctane microemulsions. Fletcher<sup>[24]</sup> studied water uptake by Winsor type II microemulsions of AOT/water/n-heptane and reported a dependency of the water content in the oil phase on the concentration of NaCl in the bulk aqueous phase. This relationship was further developed by Rabie et al.<sup>[30]</sup> and Rabie and Vera<sup>[20]</sup>, who generalized Fletcher's results and concluded that the water uptake by Winsor type II microemulsions varies linearly with the surfactant concentration in the oil phase and takes the form of a power function with respect to the ionic strength. Husein et al.<sup>[11,12]</sup> concluded that the nanoparticle uptake by single microemulsions follow a similar trend to that of the water uptake by Winsor type II microemulsions as a function of surfactant concentration. In previous studies, Nassar and Husein<sup>[7,8]</sup> introduced a mathematical model to describe the nanoparticle uptake by single microemulsion. The model was based on the observations and correlations reported in the above literature, and it is successfully accounted for the effect of the microemulsion variables on the nanoparticle uptake. The current model finds its roots in our previous model. It starts from the observations that the solubilization capacity of the metal oxides increases linearly with the surfactant concentration. Equation 1 below was considered the starting point.

$$S = \alpha[\text{AOT}], \quad [\text{E1}]$$

where,  $S$  is the solubilization capacity of a given metal oxide based on the volume of the microemulsion system (mM),  $\alpha$  is a proportionality constant, and  $[\text{AOT}]$  is the concentration of the surfactant in the microemulsion system (mM). The experimental results showed that  $\alpha$  takes the form of a power function with respect to the nominal concentration of HCl and varies linearly, as per Equations (2) and (3), respectively.

$$\alpha(C) = \beta_1 C^{\beta_2}, \quad \text{at constant } R \quad [\text{E2}]$$

$$\alpha(R) = \beta_3 R - \beta_4, \quad \text{at constant } C. \quad [\text{E3}]$$

Hence, the value of  $\alpha$  in E1 was expressed as a multiplication of the two functions, as per Equation (4)

$$S = \beta_1 C^{\beta_2} (\beta_3 R - \beta_4) [\text{AOT}], \quad [\text{E4}]$$

where  $\beta$ 's are fitted parameters, and  $C$  is the nominal concentration of HCl in the water pool (mM). Equation (E4)

TABLE 1

Values of the fitted parameters for the solubilization capacity of iron and copper oxides

Material	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$
Iron oxide	2.15	2.97	0.7	1.32
Copper oxide	2.17	2.97	1.07	1.32

looks similar to our previous model which describes nanoparticle uptake by single microemulsions.<sup>[7,8]</sup> The parameters  $\beta_2$  and  $\beta_4$  were obtained from the least square fit of Equation (E4) to Figures 2a, 3a, and 4a, and were used to predict the behavior of CuO solubilization capacity. The parameters  $\beta_1$  and  $\beta_3$ , on the other hand, were allowed to vary for the two metal oxides. The values of  $\beta$ 's are listed in Table 1. It can be seen from Table 1 that  $\beta_1$  has almost the same value for the two metal oxides. The parameters  $\beta_1$ ,  $\beta_3$  and  $\beta_4$  can be thought of microemulsions and solubilizing agent specific, since they are independent of the metal

oxide. Interestingly, the ratio of  $\beta_3$  for FeOOH and CuO,  $\beta_{3(FeOOH)}/\beta_{3(CuO)}$ , was found to be equal to the stoichiometric ratio of HCl in reactions R1 and R2,  $v_{HCl,R1}/v_{HCl,R2}$ . Hence, one can think of  $\beta_3$  as related to the stoichiometric coefficient of the solubilizing agent. In our previous model  $\beta_2$  and  $\beta_4$  reflected the degree of interaction between the stabilized particles and the surfactant head group. As can be seen in Figures 2 to 4, the model fit is in well agreement with the experimental results.

## 5. SENSITIVITY ANALYSIS

In order to investigate the reliability “authenticity” of the model parameters a sensitivity analysis was performed. Figures 5a–5d show the effect of 10% increase or decrease in the values of the fitted parameters listed in Table 1 on the percentage of solubilization capacity of metal oxide for samples having  $[AOT] = 0.2$  M,  $[HCl] = 1.5$  M, and  $R = 4.0$ . Clearly, the sensitivity of these parameters on the model is critical.  $\beta_3$  is the most sensitive; while  $\beta_4$  is the lowest.

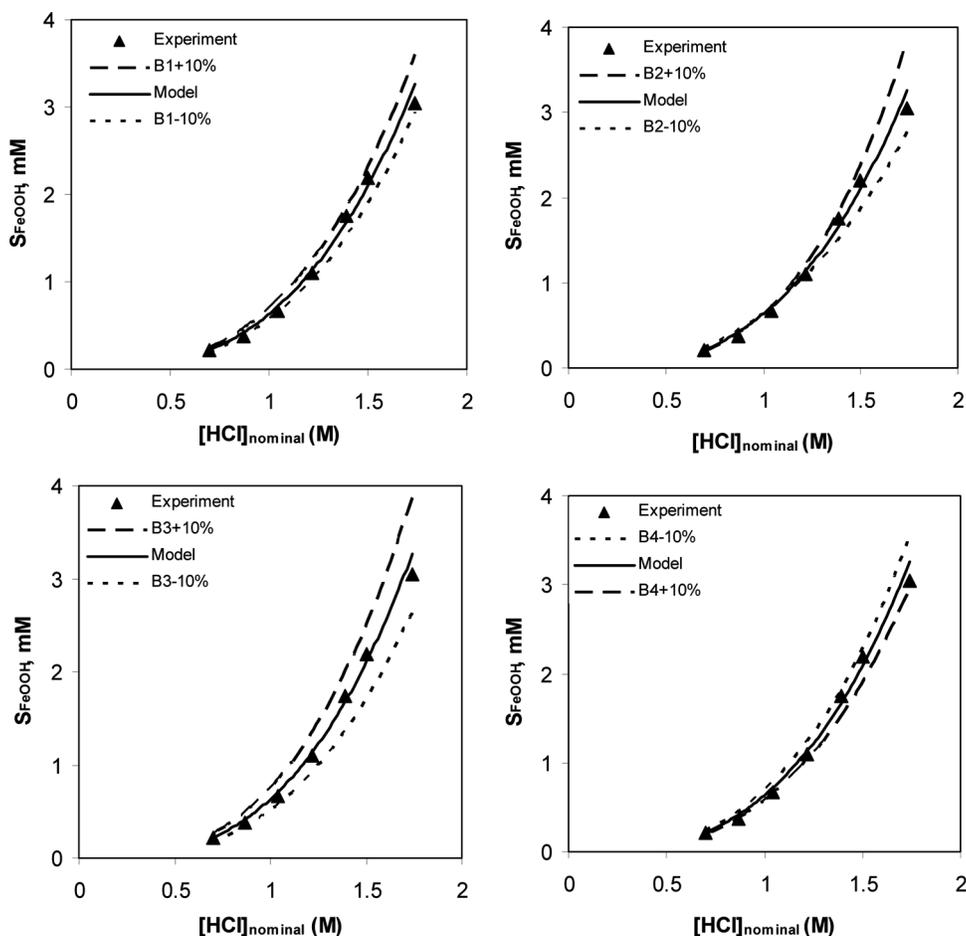


FIG. 5. Sensitivity analysis to the values of the fitted parameters. Microemulsion variables were  $[AOT] = 0.2$  M,  $R = 4.0$ , and 10 times the stoichiometric amount of FeOOH powder.

## 6. CONCLUSIONS

This work explores the use of single microemulsion approach for in-situ formation of colloidal metal oxide nanoparticles from its insoluble precursor. These colloidal particles find application in heavy oil upgrading and nano-fluids. At the experimental conditions considered, the effect of mixing time, surfactant concentration,  $R$ , and the nominal concentration of HCl on the solubilization capacity of metal oxides, was evaluated. Solubilization capacity increased with mixing and leveled off after 6 hours of mixing. A linear relationship between  $R$  and the solubilization capacity was obtained. This was attributed to the increase of the moles of  $H^+$  free ions in the water pool in addition to the decrease in the rigidity of the surfactant layer. The solubilization capacity also increased linearly with the surfactant concentration due to the increase of the number of reverse micelles, which resulted in higher solubilization capacity. In creasing the nominal concentration of HCl enhanced the solubilization capacity. This again was attributed to the increase in  $H^+$  free ions. High  $H^+$  free ions could solubilize more metal oxide. At the same experimental conditions, HCl-containing microemulsions can solubilize more copper oxide when compared with iron oxide. This may be attributed to the high ratio of the stoichiometric coefficient between HCl and iron oxide compared with copper oxide. In addition,  $Fe^{3+}$  ions caused an increase in the rigidity of the surfactant layer which led to a decrease in the solubilization capacity. A mathematical model, which accurately described the solubilization capacity as a function of  $R$ , HCl nominal concentration in the water pool, and surfactant concentration was tested. The model agreed well with the experimental results.

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