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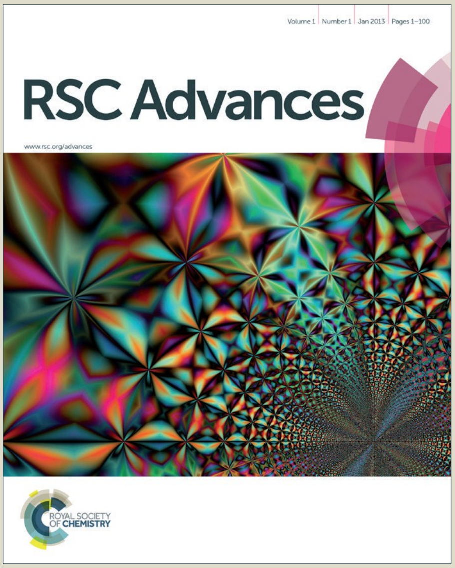

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ARTICLE

# Complexation of arsenate with ferric ion in aqueous solutions†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Interactions between arsenic and iron play an important role in arsenic removal from water. For the purpose of understanding the complexation of arsenate with ferric ion, arsenate solutions were prepared to react with ferric ion under various pH and temperature conditions. The formation of ferric-arsenate complex was examined using UV-Vis spectroscopy. The complex substance was proposed to exist as $FeH_2AsO_4^{2+}$ and $FeHAsO_4^{+}$, which transformed into gel-like material under higher pH (pH $\geqslant$ 2.38) or higher temperature (T $\geqslant$ 90 ℃). The solid phase of gel-like material was verified as poorly crystallized ferric arsenate by XRF, XRD and FTIR. Moreover, the competitive complexation of ferric between sulfate and arsenate was also concerned. This study is beneficial for the better understanding of the fate and solubility of arsenic and ferric in water.

## Introduction

The elevated level arsenic (As) in surface and ground waters due to geological processes and industrial activities pose a threat to environment and human health.[1] It is therefore a matter of urgency to prevent arsenic pollution. Iron (Fe) plays an important role in the removal of arsenic in different processes such as oxidation-reduction[2] and precipitation-dissolution[3], as well as adsorption-desorption on iron mineral surfaces[4]. Arsenic behaviour in these processes is closely related to its chemical species and determines its removal efficiency.

Actually, arsenic species have attracted increasing attention. The distribution of $H_3AsO_4$, $H_2AsO_4^{-}$, $HAsO_4^{2-}$, $AsO_4^{3-}$, $H_3AsO_3$, $H_2AsO_3^{-}$, $HAsO_3^{2-}$, $AsO_3^{3-}$ has been noticed by most researchers[5] because As(III) exists as neutral, uncharged molecular state ($H_3AsO_3$) in wider pH range so it is more difficult than As(V) to be removed by iron (hydro)oxides[6]. As and Fe generally occur in water system as arsenite As(III), arsenate As(V), ferrous Fe(II) and ferric Fe(III). Therefore arsenic species are closely related to iron species in the systems of Fe(III)-As(III)-$H_2O$, Fe(II)-As(III)-$H_2O$, Fe(III)-As(V)-$H_2O$, Fe(II)-As(V)-$H_2O$. For example, surface complexation of arsenic to iron (hydro)oxides were proposed as inner-sphere and outer-sphere complexes models[4c,7], and the surface complexation will transform into surface precipitate[8]. However, there is a little report about the complexation between arsenic and iron in solutions. The consideration of metal arsenate complexes is important in the solubility calculations but has been neglected by most previous researchers. Langmuir, D. et al.[9] performed solubility product calculations based on published solubility data for amorphous ferric arsenate and scorodite taking into account ferric arsenate complexes. In their paper, 14 data points of Nishimura, T. et al.[10] between pH 1.74 and 2.79 were chosen in which concentrations of dissolved As(V) greatly exceeded those of Fe(III) at equilibrium, with an Fe/As ratio in solution near $10^{-5}$. The solution speciation calculations indicates that more than 99% of dissolved Fe(III) occurs as the $FeHAsO_4^{+}$ and $FeH_2AsO_4^{2+}$ complexes. Unfortunately, there are few actual measurements of these ferric arsenate complexes so their stabilities were estimated using correlation estimation techniques.[11] The significant consistency between predicted association constants[12] and the measured one[13] indicates that $FeH_2AsO_4^{2+}$, $FeHAsO_4^{+}$, $FeAsO_4$ do exist and are significant in the solubility study. For example, Lee et al.[14] found that previous studies overestimated the solubility of metal arsenates because aqueous complexes of arsenic were not considered.

As mentioned above, the ferric arsenate complexes are meaningful for understanding the arsenic species and behaviours in Fe(III)-As(V)-$H_2O$ system. But they were investigated mostly in solubility study of arsenate solids. Our objective is to investigate the complexation between ferric and arsenate under different pH values and temperatures. Moreover, the competitive complexation with ferric between sulfate and arsenate was also targeted. UV-Vis spectroscopy was chosen as major method. It is because that UV-Vis spectroscopy has been used to study the thioarsenite species[15] and Fe(III) hydroxo complexes[16]. It has also been used for studying the complexation of As(V) in aqueous solutions in the presence of Fe(III), and been proved to be a liable method[17].

## Experimental section

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† Electronic Supplementary Information (ESI) available: Tables, Figures, characterization data, some spectral data and experimental apparatus. See DOI: 10.1039/x0xx00000x

### Materials and the preparation of experimental solutions

All chemicals used in this study were of analytical grade and used without further purification. Ferric nitrate ($Fe(NO_3)_3·9H_2O$) and sodium sulfate ($Na_2SO_4$) were purchased from GuangFu Fine Chemical Research Institute and KemiouCorp., TianJin, China, respectively. Perchlorate acid ($HClO_4$) and sodium arsenate ($Na_3AsO_4·12H_2O$) were both purchased from Sinopharm chemical reagent co. Ltd.

In order to avoid hydrolysis of ferric ion and keep ion strengths constant, 0.1 M perchlorate acid solution instead of ultrapure water was used to prepare all solutions if not specified. The concentration of ferric in all sample solutions was constant of 0.5 mM. Arsenate with concentration varied from 0 to 25 mM was prepared to study the complexation of arsenate with ferric in ferric-arsenate sample solutions. In addition, sulfate concentration was changed from 0 to 25 mM in ferric-sulfate sample solutions for comparison of the complexation with ferric between arsenate and sulfate.

Various amounts of concentrated perchlorate acids were added into ferric-arsenate sample solutions with 20 mM arsenate for studying the effect of pH values. For studying the effect of temperatures on the formation of ferric-arsenate complex, ferric-arsenate sample solutions with 10, 20, 30 mM arsenate were heated in water bath under 90 ℃ for 30 minutes and a continuous heating progress (Experimental apparatus see in Figure S1) was performed for ferric-arsenate sample solutions with 20 mM arsenate.

Figure 1 The UV-Vis spectra of (a) ferric-arsenate sample solutions and (b) ferric-sulfate sample solutions measured after 24-hours standing at 25 ± 0.1 ℃

The effect of sulfate anion was investigated by two ways for comparison: 1) keep arsenate and ferric concentration constant respectively at 20 mM and 0.5 mM, while sulfate concentration varied from 0 to 25 mM; 2) keep sulfate and ferric concentration constant respectively at 20 mM and 0.5 mM, while arsenate concentration varied from 0 to 25 mM.

### UV-Vis spectrophotometry

Spectrophotometric measurements were recorded at 1.0 nm intervals over the range of 200–400 nm using a HITACHI (Japan) UV-4100 double-beam spectrophotometer by wavelength scanning method. The dual-beam mode was used where the absorption of both two 1-cm quartz cells filled with deionized water were recorded before the sample solutions were placed in one of the cells. If not specified all measurements were at room temperature (25 ± 1 ℃). Time scan method was used at specified wavelength in a continuous heating progress.

### Gel-like material characterization methods

Gel-like material were separated from Ferric-arsenate sample solutions by centrifugal separation at 2650 g for 10 minutes and then dried at 60 ℃ for more than 24 hours. Scanning electron microscopy (SEM, JSM-6360) was used to characterize the morphology of the solid. The X-ray diffraction (XRD) pattern was obtained using Rigaku D/Max-RB diffractometer with Cu−Kα radiation (λ = 0.15406 nm, 35 kV, 40 mA). X-ray fluorescence (XRF, Shimadzu XRF-1800, operated at 40 kV, 95mA) analysis verified the molar ratio of ferric, arsenic and oxygen in gel-like material. Fourier transformed infrared spectroscopy (FTIR, Nicolet IS10) was employed to analyze the molecular structure of the yielded product at a resolution of 4 $cm^{-1}$.

## Results and discussion

### Spectroscopic evidence for ferric-arsenate complex

The complexation of arsenate with ferric ion was investigated spectrophotometrically in this study at room temperature 25 ± 1 ℃. A blank absorption curve of 0.1 M perchlorate solution with 0.5 mM ferric was measured against water and one major peak of ferric ion was located at $\lambda_{max}$ = 240 nm at 25 ℃.[18] Solutions of high acidity were used to prevent the formation of ferric hydroxide complex ions. This is because the absorption peak of $FeOH^{2+}$ ($\lambda_{max}$ = 205 nm & 297 nm)[16] was almost identical to the important wavelength of complex $FeHAsO_4^{2+}$ (λ = 290, 300 and 310 nm)[17]. When arsenate was incorporated into the solutions containing a constant amount of ferric, the absorbance of the solutions changed proportionally to the concentrations of arsenate (Figure 1(a)).

explained by the formation of ferric-arsenate complex. Moreover, when the blank absorbance was deducted from other spectrums, a peak at 280 nm was highlighted with the increase of arsenate concentration as shown in the inset in figure 1(a). It can be determined that the absorbance at 280 nm was not the hydrolysis of ferric ion because pH of all solutions is below 2.5 (Table S1).[17] In addition, it was verified that there was no spectral features due to the $Na_2SO_4$ and $Na_3AsO_4$ species in the wavelength range of interest (Figure S2).

In order to verify that the absorbance at 280 nm was due to ferric-arsenate complex, UV-Vis spectra (Figure 1(b)) of ferric-sulfate complex were measured with the same method. It was reported that a peak at 305 nm corresponded to ferric-sulfate complex $FeSO_4^+$.[19] The inset in figure 1(b) shows stronger absorbance at 305 nm with more sulfate provided, which is attributed to the formation of ferric-sulfate complex. According to the Beer–Lambert law, the relationship between the complex concentration and absorbance is linear. If ferric concentration remained constant, correlation of absorbance vs. sulfate or arsenate concentration was also linear within limits. Here the correlation curve of absorbance at 305 nm vs. sulfate was compared with that of absorbance at 280 nm vs. arsenate in figure 2. Linear correlation with negative deviation at higher sulfate and arsenate concentrations was observed for the two correlation curves. The similar correlation trends of two curves gave indirect evidence that a peak at 280 nm corresponded to ferric-arsenate complex. In conclusion, we believed that ferric-arsenate complex was formed when sodium arsenate was added into the sample solutions and they had a main absorbance peak at 280 nm.

Figure 2 The correlation between absorbance and sulfate/arenate concentration based on the datas in inset of figure 1

Table 1 Delta H and G of relative reaction

| No. | Reaction Equations | $\Delta_rH^0$ (kJ/mol) | $\Delta_rG^0$ (kJ/mol) |
|---|---|---|---|
| (1) | $Fe^{3+} + H_2AsO_4^- \leftrightarrow FeH_2AsO_4^{2+}$ | -25.53 | -28.5 |
| (2) | $Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$ | -14.63 | -55.77 |
| (3) | $FeOH^{2+} + H_3AsO_4 \leftrightarrow FeH_2AsO_4^{2+} + H_2O$ | -58.6 | -25.87 |
| (4) | $FeOH^{2+} + H_2AsO_4^- \leftrightarrow FeHAsO_4^+ + H_2O$ | -36.72 | -29.49 |
| (5) | $FeOH^{2+} + HAsO_4^{2-} \leftrightarrow FeAsO_4 + H_2O$ | 17.48 | -24.92 |
| (6) | $FeH_2AsO_4^{2+} + OH^- \leftrightarrow FeHAsO_4^+ + H_2O$ | -271.92 | -225.77 |
| (7) | $FeHAsO_4^+ + OH^- \leftrightarrow FeAsO_4 + H_2O$ | -228.62 | -193.93 |
| (10) | $Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+$ | 26.7 | -11.06 |

Figure 3 UV-Vis spectra of ferric-arsenate sample solutions at different pH values measured after 24-hours standing at 25 ± 0.1 ℃ (Fe: 0.5 mM; As: 20 mM)

## Effect of pH values

The pH value is one of the key parameters for the formation of ferric arsenate solid (pitticit, kaňkite, scorodite and symplesite et al.) from Fe(III)-As(V)-$H_2O$ system. In order to study the role of pH values, the concentration of ferric and arsenate were constant of 0.5 mM and 20 mM, respectively. Different concentrations of perchlorate acid were added to control pH values in the range of 0.35 to 6.81.

Sample solutions were limpid at pH ≤ 1.57, and turned turbid at higher pH of 2.38 because gel-like material was formed. These findings by naked eye were in accordance with the results of UV-Vis spectra (Figure 3). Sample solutions absorbed both ultraviolet light and visual light at pH ≥ 2.38. Only ultraviolet light was absorbed at solution pH ≤ 1.57. It can be inferred that the absorbance of sample solutions for ultraviolet light was due to the formation of ferric-arsenate complex and the new-formed gel-like material contributed to the absorbance for visual light. It is well known that the hydrolysis of ferric ion and deprotonation of arsenate acid were closely related to pH values. Arsenate existed as $H_3AsO_4$ in acidic, $H_2AsO_4^-$ in weak acidic and $HAsO_4^{2-}$ in nearly neutral solutions due to $pK_1 = 2.2$ and $pK_2 = 6.96$. Thus a small amount of negatively charged $H_2AsO_4^-$ can react with positively charged ferric ion to form $FeH_2AsO_4^{2+}$ complex ion as equation (1). The first hydrolysis constant of ferric ion at 0.1 M $NaClO_4$ was 2.54.[20] $FeOH^{2+}$ was formed by the hydrolysis of ferric ion as shown in equation (2), and then reacted with $H_3AsO_4$, $H_2AsO_4^-$ and $HAsO_4^{2-}$ to form $FeH_2AsO_4^{2+}$, $FeHAsO_4^+$ and $FeAsO_4$ as shown in equation (3) to (5), respectively. It also can be found that the formation of $FeAsO_4$ through the deprotonation of complex ions $FeH_2AsO_4^{2+}$ and $FeHAsO_4^+$ as equation (6) and (7) with the increase of pH. Therefore increasing the solution pH untill 2.38, the formed gel-like material was speculated as ferric arsenate[21] and was further discussed below.

Figure 4 UV-Vis spectra of ferric-arsenate sample solutions before and after heated measured at 25 ± 0.1 ℃ (Heating time: 20 min)

Figure 5 UV-Vis spectrum of ferric-arsenate sample solutions measured in a continuous heating process (Fe: 0.5 mM; As: 20 mM; Temperature: 25-90 ℃ )

## Effect of temperature

The sample solution was prepared by respectively introducing arsenate of 10, 20 and 30 mM into three 0.5 mM ferric solutions. These three solutions were heated at 90 ℃ for 30 min and all of them became turbid. All of the three absorbance curves (Figure 4) showed that ultraviolet light was absorbed whether the solution being heated or not, and only visual light was absorbed after being heated. As mentioned above, the absorbance for visual light was attributed to the gel-like material. Thus, it can be concluded that higher temperature (T ≥ 90 ℃) benefit for the formation of gel-like material.

We made a bold conjecture that the formation of gel-like material was an endothermic reaction and the formation of ferric-arsenate complex was an exothermic process. For confirming, standard molar reaction enthalpies of involved reactions were calculated directly from enthalpies of reactants and products.

The standard molar enthalpy of $Fe^{3+}$ formation was - 49.0 ± 1.5 kJ $mol^{-1}$.[22] The molar enthalpy change of each hydrolysis reaction of ferric can be got from the database of Visual MINTEQ software (version 3.0) as shown in Table S2. Therefore the standard molar enthalpy of ferric species formation was derived and shown in table S3. The standard molar enthalpies of water and arsenate species formation were collected from reported paper.[23] All thermodynamic data of ferric-arsenate complex including aqueous $FeAsO_4$ were estimated by Marini et al.[24] The enthalpy and Gibbs free energy of ferric arsenate solid measured by experiments[25] were different from aqueous $FeAsO_4$ used here. Other data were all gathered from HSC software (version 7.1). All of these data were listed in table S3.

The calculated molar enthalpy change and Gibbs free energy change of possible reactions (Table 1) were in consistent with our postulate that the formation of ferric-arenate complexes ($FeHAsO_4^{+}$ and $FeH_2AsO_4^{2+}$) was exothermic with negative enthalpies and the formation of gel-like material was endothermic with the positive enthalpy change of 17.48 kJ/mol.

The endothermic nature of the reaction of equation (5) was also demonstrated by the time scan method in a continuous heating process in the solution containing 0.5 mM ferric and 20 mM arsenate. The absorbance at 280 nm increased slightly at the early stage and increased dramatically later as shown in figure 5. An obvious boundary of the time was about 3000 second and the temperature was about 90 ℃. This provided good evidence that enough heat was helpful to form the gel-like material.

## Competitive complexation between arsenate and sulfate with ferric

Based on the figure 2, the interaction was analysed according to Benesi–Hildebrand equations (equation (8)) to determine the equilibrium constant for Fe(III)-arsenate and Fe(III)-sulfate complexes.[26]

$$\frac{[Fe(III)]\times l}{\Delta A}=\frac{1}{C}\times\frac{1}{\varepsilon K_f}+\frac{1}{\varepsilon} \qquad (8)$$

where *[Fe(III)]* represents the concentration of the ferric ions, *l* is the length of quartz cuvette, Δ*A* is the difference in absorbance between the complex and ferric ion, *C* is the concentration of ligand; $\varepsilon$ and *K* are the molar absorptivity of the complex at $\lambda$ and the equilibrium constant for complex formation, respectively. The highly linear relationship ($R^2$ = 0.9969 and 0.9980) between *1/ΔA* and *1/C* indicated that the absorbance of the complex followed the Benesi–Hildebrand equation. As for Fe(III)-sulfate complex, further calculations showed that $\varepsilon_{305}$ = 1.716 × $10^3$ $M^{-1}$ $cm^{-1}$ and $K_f$ = 1.56 ×$10^2$ $M^{-1}$ (log $K_f$ = 2.2). Compared with complexation between Fe(III) and arsenate, $\varepsilon_{280}$ = 2.797 × $10^3$ $M^{-1}$ $cm^{-1}$ and $K_f$ =1.28 ×$10^2$ $M^{-1}$ (log $K_f$ = 2.1) were calculated and the value of log $K_f$ of Fe(III)-arsenate complex was a little lower than that of Fe(III)-sulfate complex. Therefore the stability of Fe(III)-arsenate complex was almost same to that of Fe(III)-sulfate complex.

The complexation of arsenate with ferric ion was obvious in perchlorate acid media. However, perchlorate is rare in arsenic wastewater while sulfate is common correlated with emissions of sulfur dioxide from anthropogenic sources.[27] We are curious about whether the complexation occurs in sulfate acid solutions or not. Jia, Y. et al.[28] found that sulfate was incorporated into the coprecipitates of arsenate with iron(III) in aqueous sulfate media at acidic pH, but was released completely when the pH was raised to 8. That maybe because sulfate complexed with ferric in acidic pH. In fact, the complexation between ferric and sulfate was reported, so there might be a competitive complexation between arsenate and sulfate with ferric in arsenate-sulfate-rich system. Langmuir, D. et al.[9] revaluated the solubility data of Nordstrom, D. K. et al.[23] and Tozawa, K. et al.[29] and found that $FeHAsO_4^{+}$, $FeSO_4^{+}$ and $Fe(SO_4)_2^{-}$ were all significant iron species. As mentioned above, the stability of Fe(III)-arsenate and Fe(III)-sulfate complexes were close but it can't declare what would happen in arsenate-sulfate-rich system. This is because the values of $log\ K_f$ were got in an independent system (arsenate-rich but sulfate-free or sulfate-rich but arsenate-free).

In order to understand the interaction of arsenate and ferric in sulfate media, a certain amount of sodium sulfate were introduced into the perchlorate acid solution. Sulfate of different concentrations ranged from 0 to 20 mM were added into the perchlorate solutions containing 0.5 mM ferric and 20 mM arsenate. A series of absorption curves of these solutions were shown in figure 7a. It is found that there is not obvious change. For comparison, the concentration of sulfate was kept constant and varied arsenate concentration. The same test was performed in solutions in which sulfate and ferric were respectively 0.5 mM and 20 mM and arsenate varied from 0 to 25 mM. The absorption curves changed greatly with increase of arsenate concentration as shown in figure 7b. Specifically, the absorbance increased significantly in the range of 240 - 300 nm and decreased significantly in the range of 300 - 380 nm.

It can be inferred from figure 7 that few ferric-sulfate complex was formed when sulfate was added into the perchlorate system containing a small amount of arsenate, while lots of ferric-arsenate complex was formed when arsenate was added into the sulfate system. We speculated that complexation of ferric with arsenate was stronger than that of sulfate. To confirm this point, we calculated enthalpy change and Gibbs free energy change of complexation reaction between ferric and sulfate as equation (9).

$$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^{+} \qquad (9)$$

Figure 6 The Benesi-Hildebrand fitting of Fe(III)-arsenate complex (circle) and Fe(III)-sulfate complex (square)

Figure 7 UV-Vis spectra of arsenate-sulfate-ferric sample solutions (a), Fe: 0.5 mM, arsenate: 20 mM & sulfate: 0-20 mM; (b), Fe: 0.5 mM, arsenate: 0-25 mM & sulfate: 20 mM

The standard molar enthalpy and Gibbs free energy of ferric-sulfate complex formation were also shown in table S3. The delta H and delta G of equation (9) were 26.7 and -11.06 kJ/mol, respectively. The delta G of aqueous ferric-arsenate complex was more negative. Thus $FeHAsO_4^{+}$ and $FeH_2AsO_4^{2+}$ were more easily formed than $FeSO_4^{+}$. Welham, N. J. et al. also concluded that arsenate ferric complexes being more favourable than sulphate ferric complexes in arsenate and sulfate mixed solutions.[30] This indicates the wide existence of aqueous ferric-arsenate complexes in sulfate-containing wastewaters.

### Gel-like material characterization

Gel-like material formed in 0.1 M perchlorate acid solutions containing 45 mM arsenate and 0.5 mM ferric was separated and dried at 60℃. The chemical composition of gel-like material in solid phase was determined by XRF (Table S4). The result showed that the molar ratio of As: Fe: O was 1: 1.11: 3.77 in this solid, which is close to the atomic ratio in $FeAsO_4$. This can be confirmed by XRD analysis, which indicated that the gel-like material was poorly crystalline ferric arsenate characterized by two broad peaks centered at 2θ values of 28° and 58° (Figure 8a).[31] Poorly crystalline ferric arsenate was reported as scorodite precursor with a formula of $FeAsO_4 \cdot (2 + x)\ H_2O$ ($0 < x < 1$).[32] The gel-like solid was further characterized using FTIR (Figure 8b). Result of FTIR exhibited a strong band at 1630-1636 $cm^{-1}$ and a broad band near 3445 $cm^{-1}$, which were attributed to the O–H bending and stretching vibration of water. The stretching vibration of As–O–Fe was located at 838 cm$^{-1}$ and generally with a shoulder at ~ 750 cm$^{-1}$, which is probably caused by the hydrogen bonding between $H_2O$ and $AsO_4$.[31] An important IR adsorption at 835 cm$^{-1}$ in our results also with a shoulder at ~ 750 cm$^{-1}$, belonged to the $\nu_3$ mode of $AsO_4$ (~ 833 cm$^{-1}$), identified as arsenate bonding structures of poorly crystalline ferric arsenate.[31] Other IR adsorption bands at about 2363, 1384 and 1088 cm$^{-1}$ were respectively antisymmetric stretching mode of carbon dioxide (−OH···O=C=O) adsorbed on hydroxyl groups[33], characteristic IR absorption of $NO_3^-$ (1384 cm$^{-1}$ / 1386 cm$^{-1}$) and $ClO_4^-$ (1088 cm$^{-1}$) anions[34]. These impurities were introduced by iron nitrate and perchloric acid. The results of XRF, XRD and FTIR demonstrated that gel-like material in our experiments was poorly crystallized ferric arsenate.

Scanning electron microscopy (SEM) was used for morphology characterization of gel-like material in solid phase. The SEM images showed that the sample was bulk and conchoidal (Figure 9). It was different from other reported precipitates in Fe(III)-As(V)-$H_2O$ system which were aggregated particles.[32] This is because the poorly crystalline ferric arsenate was formed from precursors of $FeHAsO_4^+$ and $FeH_2AsO_4^{2+}$, while other amorphous ferric arsenate was formed through transformation of the arsenate ions adsorption on the surface of the ferrihydrite.

Figure 8 (a) XRD patterns and (b) FTIR of the gel-like material in solid phase generated form ferric-arsenate sample solutions (Fe: 0.5 mM, arsenate: 45 mM)

Figure 9 SEM of the gel-like material in solid phase generated form ferric-arsenate sample solutions (Fe: 0.5 mM, arsenate: 45 mM)

## Conclusions

The complexation of arsenate with ferric was studied here by UV-Vis spectroscopy method. Ferric-arsenate complex with an absorption peak at about 280 nm was formed immediately when sodium arsenate was added into ferric-containing solutions. Ferric-arsenate complex ions were proposed with a formula of $FeHAsO_4^+$ and $FeH_2AsO_4^{2+}$. Both pH and temperature affected ferric-arsenate complex species. Poorly crystallized ferric arsenate occurred until pH value was higher than 2.38 or temperatures was above 90 ℃. In addition, sulfate had little effect on the formation of ferric-arsenate complex. The complexation of ferric with sulfate is weaker than with arsenate.

## Acknowledgements

This work was supported by National Natural Science Foundation of China (51304251, 51374237) and Special Program on Environmental Protection for Public Welfare (201509050).

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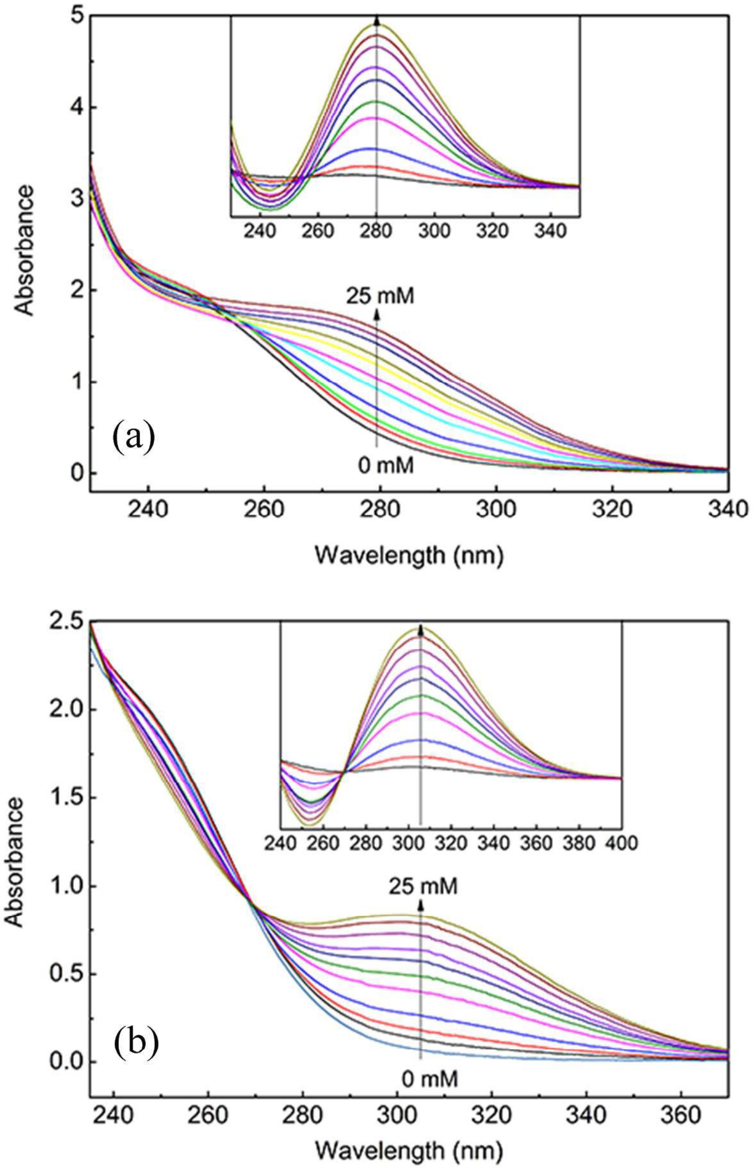

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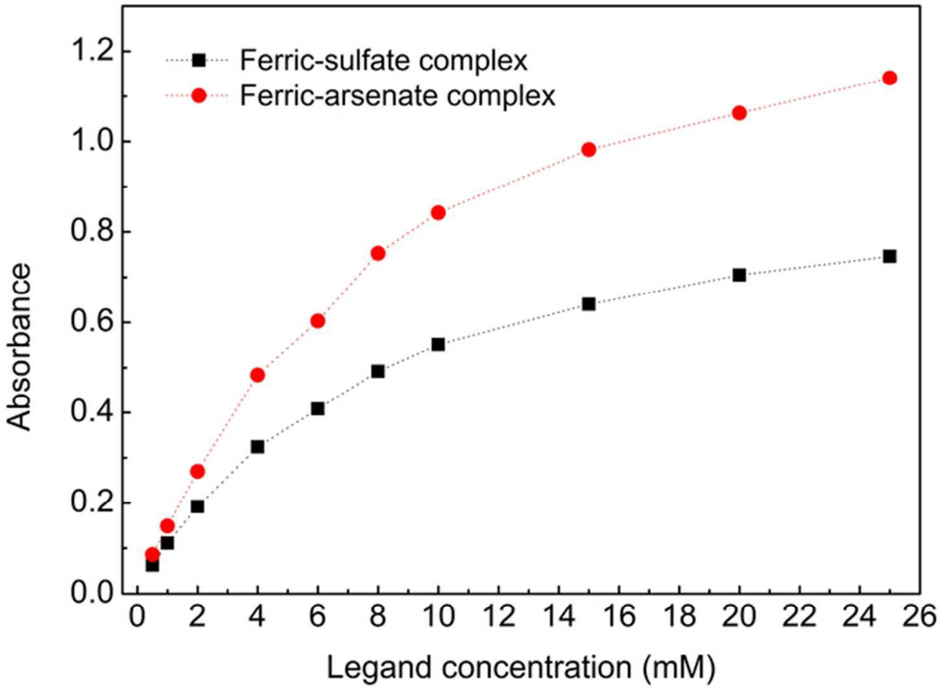

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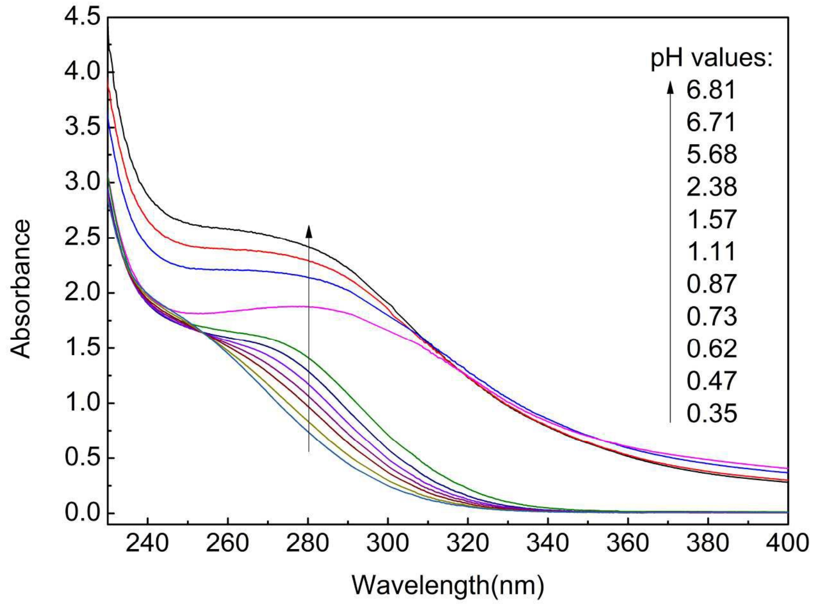

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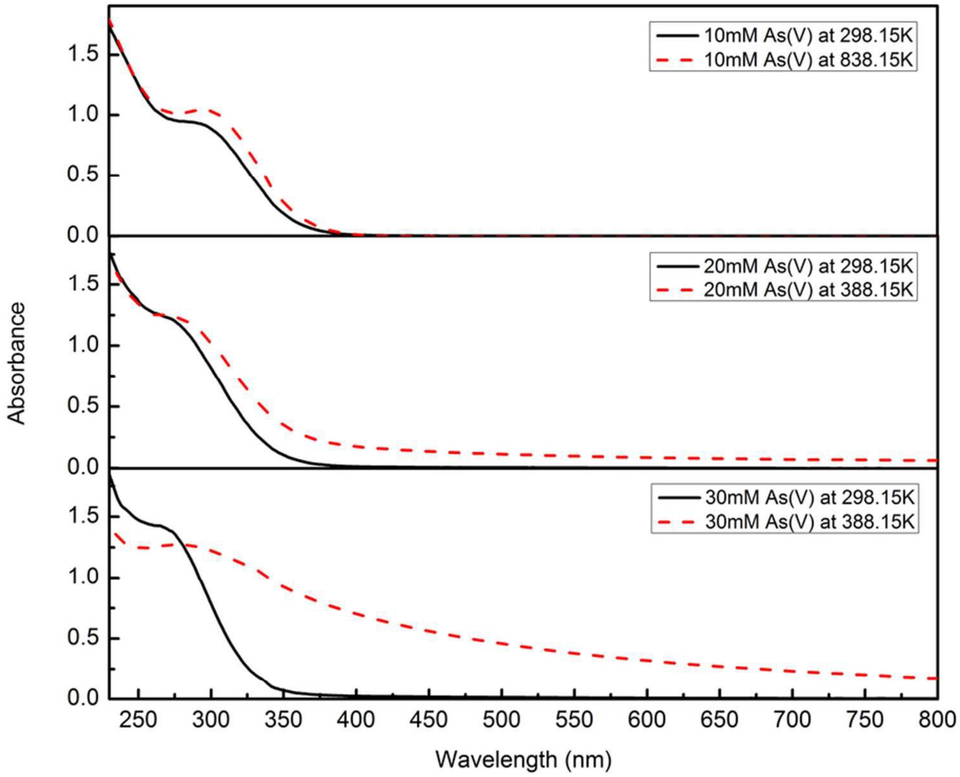

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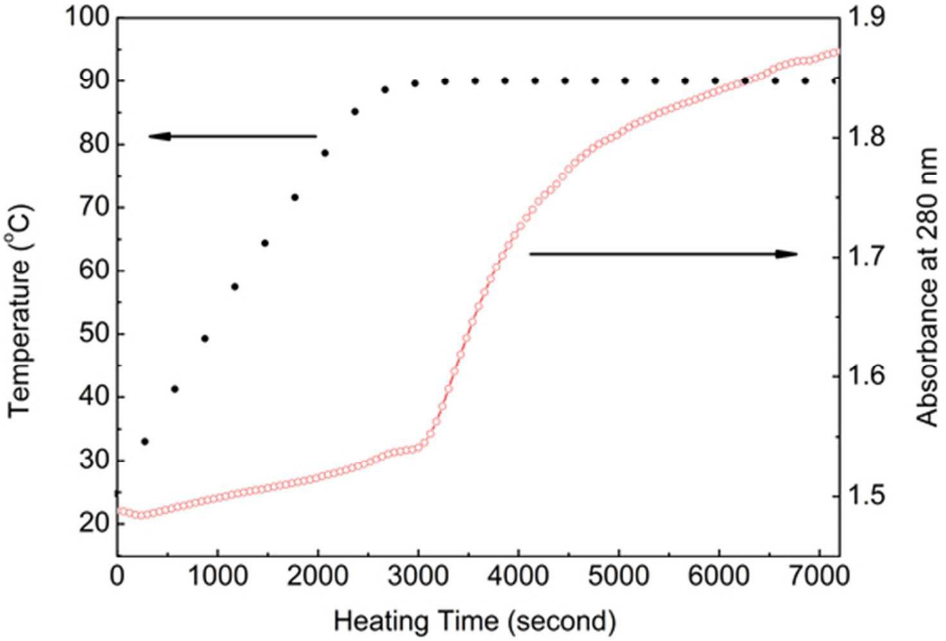

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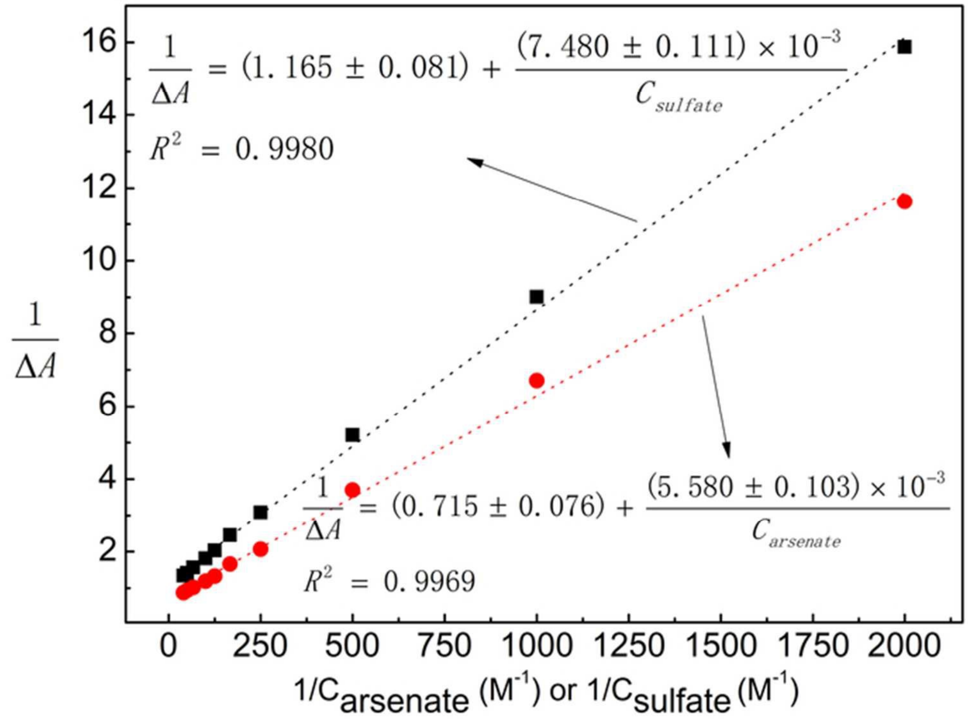

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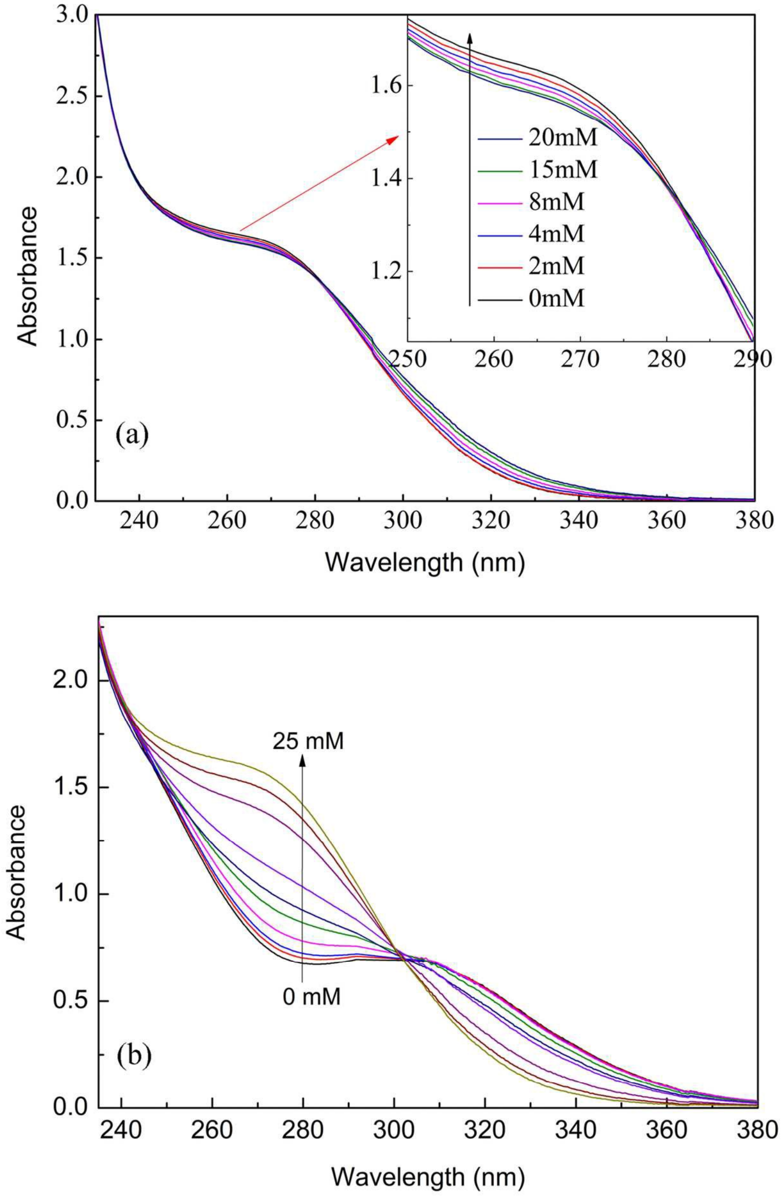

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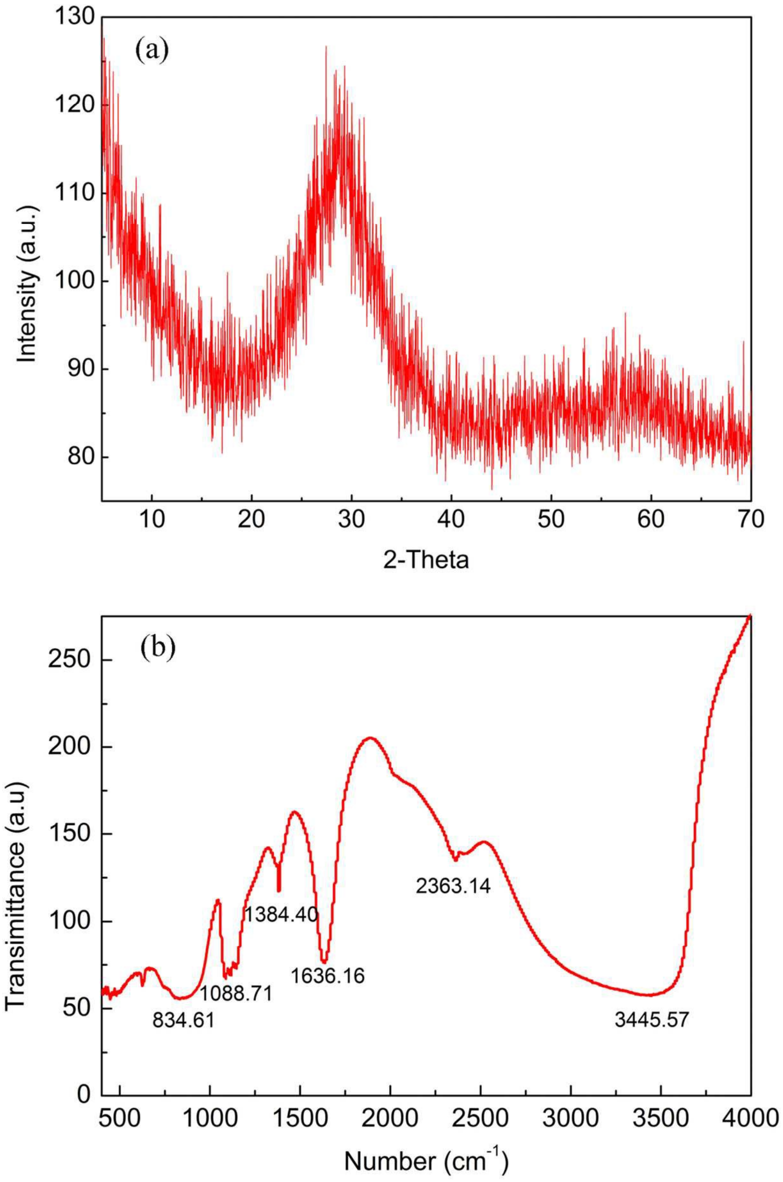

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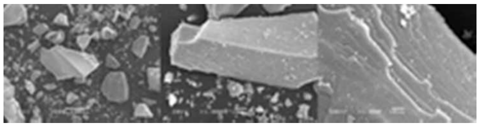

19x4mm (300 x 300 DPI)

# Complexation of arsenate with ferric ion in aqueous solutions†

Jinqin Yang,[a] Liyuan Chai,[a, b] Mengqing Yue[a] and Qingzhu Li[a, b, *]

Ferric arsenate complexes ($FeH_2AsO_4^{2+}$ and $FeHAsO_4^{+}$) formed in acidic solutions were confirmed by UV-Vis spectroscopic techniques, which transformed into gel-like material under higher pH (pH ⩾ 2.38) or higher temperature (T ⩾ 90 ℃) conditions.