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Control of Fe³⁺ coordination by excess Cl[−] in alcohol solutions†

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We spectroscopically investigated coordination state of Fe³⁺ in methanol (MeOH) and ethanol (EtOH) solutions against Cl[−] concentration ([Cl[−]]). In both the system, we observed characteristic absorption bands due to the FeCl₄ complex at high-[Cl[−]] region. In the MeOH system, the proportion (*r*) of [FeCl₄][−] exhibits a stationary value of 0.2–0.3 in the intermediate region of 10 mM < [Cl[−]] < 50 mM, which is interpreted in terms of [FeCl_nL_{6−n}]^{3−n} (*n* = 1 and 2). In the EtOH system, *r* steeply increases from 0.1 at [Cl[−]] = 1.5 mM to 0.7 at [Cl[−]] = 3.5 mM, indicating direct transformation from [FeL₆]³⁺ to [FeCl₄][−]. We further found that the coordination change significantly decreases the redox potential of Fe²⁺/Fe³⁺.

Introduction

The coordination state around the redox pair in solution has a great influence on the redox potential (*V*) as well as its temperature coefficient (*S*_{EC}) because *V* is equivalent to $-\Delta G/e$, where ΔG and *e* are the variation in the Gibbs free energy associated with reduction reaction and elementary charge (>0). In a technological point of view, the electrochemical parameters can be used for energy harvesting device, such as liquid thermoelectric cell (LTE).^{1–6} In this sense, it is scientifically and technologically important to deeply comprehend and control the coordination state of redox pairs in solution. The Fe ion in solution is usually octahedrally coordinated by six solvent molecules (L) forming the FeL₆ complex. Inada *et al.*⁷ reported that Fe²⁺ is coordinated by six L in aqueous, methanol (MeOH), ethanol (EtOH), dimethyl sulfoxide (DMSO) solutions. If the aqueous solution contains Cl[−], however, it is reported that Fe³⁺ takes various coordination state,^{8,9} such as [FeCl_n(H₂O)_{6−n}]^{*n*−3} and [FeCl₄][−], reflecting a strong interaction between Fe³⁺ and Cl[−]. The Fe coordination in aqueous solution containing Cl[−] is still controversial.

Recently, there has been an interest in the electrochemistry of redox pairs not only in aqueous solutions but also in organic solutions. Especially, Inoue *et al.*¹⁰ reported that *S*_{EC} of Fe²⁺/Fe³⁺ in several organic solvents are much higher than *S*_{EC} in aqueous solution. For example, *S*_{EC} (= 3.6 mV K^{−10}) of Fe²⁺/Fe³⁺ in acetone is much larger than that (= 1.5 mV K^{−6}) in aqueous solution. In

addition, Wake *et al.*¹¹ reported that the dimensionless performance index (*ZT*) of LTE is much enhanced if aqueous solution of Fe²⁺/Fe³⁺ is replaced with acetone solution of Fe²⁺/Fe³⁺. In this situation, a comprehension of the coordination state of Fe ions in the organic solution is desired. In general, the formation of FeCl₄ in solution is governed by the equilibrium constant (*K*); $K = [\text{FeCl}_4^-]/[\text{Fe}^{3+}][\text{Cl}^-]^4$ for $\text{Fe}^{3+} + 4\text{Cl}^- \leftrightarrow \text{FeCl}_4^-$. Then, systematic investigation against Cl[−] concentration ([Cl[−]]) at a fixed Fe³⁺ concentration is effective for comprehension and control of the complex formation. We emphasized that the ultraviolet-visible (UV-vis) absorption spectroscopy is a sensitive probe for complex formation, because Fe³⁺ complex exhibits characteristic absorption bands in this region.¹² In addition, the spectroscopy is sensitive even in a dilute Fe³⁺ solution of sub mM and is suitable for investigation of organic solution.

In this work, we spectroscopically investigated coordination state of Fe³⁺ against [Cl[−]] in the MeOH and EtOH solutions. In MeOH solution, with increases in [Cl[−]], octahedral [FeL₆]³⁺ gradually transforms to tetrahedral [FeCl₄][−] via mixed [FeCl_nL_{6−n}]^{3−n} state. In EtOH solution, [FeL₆]³⁺ directly transforms to [FeCl₄][−] with increase in [Cl[−]]. The variation of the Fe coordination significantly decreases *V* of Fe²⁺/Fe³⁺.

Experiment

UV-vis absorption

The UV-vis absorption spectra of Fe³⁺ solutions were investigated with a spectrometer (V750, Jasco) at room temperature. Absorption spectra were obtained by dividing the transmission intensity spectra (*I*) of the solution by that (*I*₀) without cell. The molar absorption coefficient (ϵ) was defined by $-\ln(I/I_0)/cd$, where *c* (= 0.5 mM) and *d* (= 1 cm) are the molar concentration of Fe³⁺ and thickness of the optical cell, respectively.

The solvents investigated were water (H₂O), MeOH (FUJIFILM Wako corp.), EtOH (FUJIFILM Wako corp.). The solvents

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are purchased and used as received. The solutions contain 0.5 mM Fe^{3+} . The $[\text{Cl}^-]$ value was controlled by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (FUJIFILM Wako corp.), $\text{Fe}(\text{ClO}_4)_3 \cdot 6.9\text{H}_2\text{O}$ (FUJIFILM Wako corp.), and NaCl (FUJIFILM Wako corp.) in appropriate molar ratios. At several $[\text{Cl}^-]$ in MeOH and EtOH solutions, we confirmed that the crystal water in solution does not affect the spectra. The intensity and shape of the spectra of anhydrous FeCl_3 (FUJIFILM Wako corp.) solutions are essentially the same as that of the corresponding hydrous FeCl_3 solution. In aqueous solution, LiCl (FUJIFILM Wako corp.) was used instead of NaCl , because LiCl shows higher solubility in water. We further investigated the solutions containing 0.5 mM $\text{Fe}(\text{ClO}_4)_3 \cdot 6.9\text{H}_2\text{O}$ (FUJIFILM Wako corp.). The ClO_4^- concentration ($[\text{ClO}_4^-]$) was controlled by dissolving extra NaClO_4 (FUJIFILM Wako corp.).

Variation of redox potential V

We systematically investigated variation in V of $\text{Fe}^{2+}/\text{Fe}^{3+}$ against $[\text{Cl}^-]$. We define ΔV as $V_{\text{sample}} - V_{\text{ref}}$, where V_{sample} and V_{ref} are V of the sample and reference cells, respectively. The reference and sample cells were beaker cells which were connected by a salt bridge. The salt bridge was made as follows. NaClO_4 (10 g per 100 mL) and agar (4 g per 100 mL) were added to water. Then, the solution was heated, dissolved, poured into a U-shaped tube, and cooled to harden. A Pt electrode was inserted into each cell.

The electrolyte in the reference cell was MeOH (or EtOH) solution containing 0.5 mM $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (FUJIFILM Wako corp.) and 0.5 mM $\text{Fe}(\text{ClO}_4)_3 \cdot 6.9\text{H}_2\text{O}$. The electrolytes in the sample cell were $[\text{Cl}^-]$ controlled MeOH (or EtOH) solution containing 0.5 mM Fe^{2+} and 0.5 mM Fe^{3+} . The $[\text{Cl}^-]$ value was controlled by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{ClO}_4)_3 \cdot 6.9\text{H}_2\text{O}$, and NaCl in appropriate molar ratios. ΔV between the cells were carefully investigated with confirming stabilization of the voltage. At several $[\text{Cl}^-]$ in MeOH and EtOH solutions, we confirmed that the crystal water in solution does not affect the redox potential. The redox potentials of anhydrous FeCl_2 (FUJIFILM Wako corp.)/ FeCl_3 (nacalai tesque) solutions are the same as that of the corresponding hydrous $\text{FeCl}_2/\text{FeCl}_3$ solutions within the experimental error (<6 mV).

Results and discussion

Overall feature of spectra

Fig. 1(a) shows molar absorption coefficient (ϵ) spectra of $\text{Fe}(\text{ClO}_4)_3$ dissolved in H_2O , MeOH, and EtOH. Thick and thin curves represent for the spectra without and with excess ClO_4^- , respectively. In all solutions, the spectra with excess ClO_4^- are the same as those without excess ClO_4^- . This observation indicates that the Fe^{3+} complex is stable even with excess ClO_4^- . In MeOH and EtOH solutions, the spectra exhibit two absorption bands at 360 nm and 260 nm. We ascribed the spectral feature to formation of $[\text{FeL}_6]^{3+}$. We calculated the absorption spectra of $[\text{Fe}(\text{MeOH})_6]^{3+}$ cluster with Gaussian 16W program¹³ (Fig. S1†). The calculated spectrum shows two-band structure at 190 nm and 370 nm due to the ligand to metal charge transfer

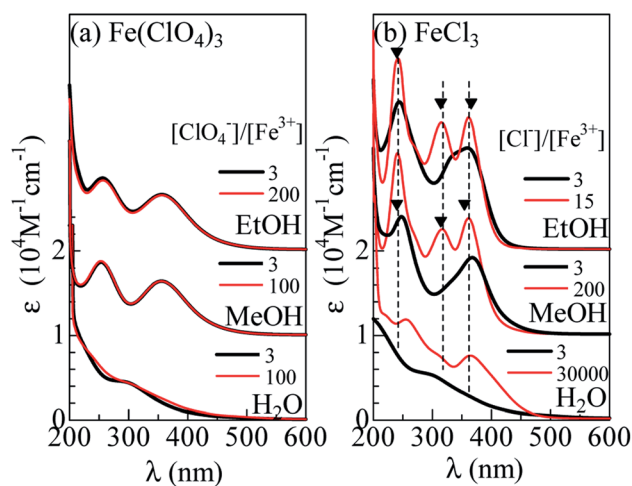


Fig. 1 Molar absorption coefficient (ϵ) spectra of (a) $\text{Fe}(\text{ClO}_4)_3$ and (b) FeCl_3 dissolved in H_2O , methanol (MeOH) and ethanol (EtOH). Thin curves (a) and (b) are the spectra with excess ClO_4^- and Cl^- , respectively. Filled triangles in (b) represent the absorption bands due to $[\text{FeCl}_4]^-$.

(LMCT) transition and qualitatively reproduces the observed spectra [Fig. 1(a)]. In aqueous solution, traces of absorption bands are discernible at 300 nm, which is ascribed to $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.^{14,15}

Fig. 1(b) shows the ϵ spectra of FeCl_3 dissolved in H_2O , MeOH, and EtOH. Thick curves represent for the spectra without excess Cl^- . The spectrum of the MeOH and EtOH solutions without excess Cl^- still exhibit two-band structure at 250 nm and 370 nm. The spectral weight of the 260 nm band is higher than that of the $\text{Fe}(\text{ClO}_4)_3$ solutions [(a)]. We ascribed the spectral feature to formation of $[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$ ($n = 1$ and 2), because the oscillator strength (f) of an electron transfer from Cl to Fe^{3+} is larger than that from O to Fe^{3+} . We calculated the absorption spectra of $[\text{FeClMeOH}_5]^{2+}$, *trans* $[\text{FeCl}_2\text{MeOH}_4]^+$, and *cis* $[\text{FeCl}_2\text{MeOH}_4]^+$ clusters with Gaussian 16W program¹³ (Fig. S1†). The total oscillator strength (f_{tot}) of transitions forming the higher energy band is larger in the Cl-substituted clusters than f_{tot} ($= 0.42$) in $[\text{FeMeOH}_6]^{3+}$; f_{tot} is 0.56 in $[\text{FeClMeOH}_5]^{2+}$, 0.73 in *trans* $[\text{FeCl}_2\text{MeOH}_4]^+$, and 0.74 in *cis* $[\text{FeCl}_2\text{MeOH}_4]^+$. The spectral shape of the FeCl_3 aqueous solution without excess Cl^- is the same as that of the $\text{Fe}(\text{ClO}_4)_3$ aqueous solution, indicating that the Fe coordination state remains $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.^{14,15}

Surprisingly, addition of excess Cl^- completely changes the spectra. Thin curves in Fig. 1(b) represent for the spectra with excess Cl^- . In the MeOH and EtOH solutions, excess Cl^- causes sharp absorption bands at 362, 318, and 242 nm, as indicated by filled triangles. We emphasize that the spectral profile of the MeOH solution is the same as that of the EtOH solution. The sameness of the two spectra indicates that Fe^{3+} is not coordinated by L, but Cl^- . In Fig. 2, we compared the spectra of the MeOH solution containing 0.5 mM Fe^{3+} with excess at $[\text{Cl}^-] = 101.5$ mM with that of nitromethane solution of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{FeCl}_4]$.³ Concerning to the lower-lying two absorption bands, the spectral profiles are essentially the same. This clearly

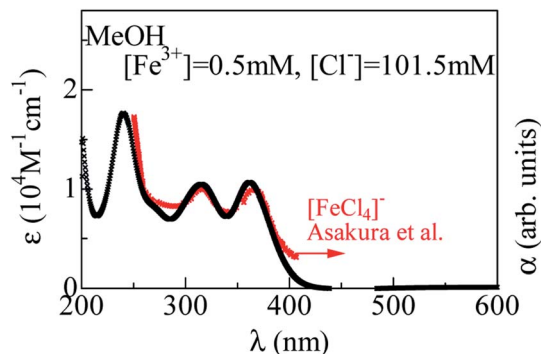


Fig. 2 Molar absorption coefficient (ϵ) spectra of MeOH solution containing 0.5 mM Fe^{3+} at $[\text{Cl}^-] = 101.5$ mM. Red symbols show the ϵ spectra of nitromethane solution of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{FeCl}_4]$ (cited from ref. 8).

indicates formation of $[\text{FeCl}_4]^-$ in the MeOH and EtOH solutions with excess Cl^- . On the other hands, the spectrum of aqueous solution at $[\text{Cl}^-]/[\text{Fe}^{3+}] = 30\,000$ exhibits two-band structure. The spectral profile is consistent with the spectra at $[\text{Cl}^-] = 15$ M reported by Liu *et al.*,¹² who ascribed the spectral feature to $[\text{FeCl}_3(\text{H}_2\text{O})_3]$ and/or $[\text{FeCl}_4]^-$. We emphasize that the 260 nm band is located at higher wavelength side than the 242 nm band due to $[\text{FeCl}_4]^-$, as indicated by broken straight lines. This clearly indicates that $[\text{FeCl}_4]^-$ is not the dominant species even at the highest $[\text{Cl}^-]$.

Spectral change against $[\text{Cl}^-]$

Now, let us investigate in detail how the ϵ spectrum changes with increase in $[\text{Cl}^-]$. Fig. 3(a) shows the ϵ spectra of the MeOH solution containing 0.5 mM Fe^{3+} against $[\text{Cl}^-]$. At $[\text{Cl}^-] = 0.0$ mM, the spectrum exhibits two broad absorption bands at 360 nm and 260 nm, which are due to an electron transfer from L to Fe^{3+} within the FeL_6 complex. At $[\text{Cl}^-] = 1.5$ mM, the spectra still show two-band structure, but the spectral weight of the higher energy band is much higher than those at $[\text{Cl}^-] = 0.0$ mM. As discussed in the previous subsection, the spectral change is interpreted in terms of the formation of $[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$ ($n = 1$ and 2). At $[\text{Cl}^-] = 11.5$ mM, trace of an additional absorption band is discernible, as indicated by an open triangle. Its spectral weight gradually increases as $[\text{Cl}^-]$ increases. At $[\text{Cl}^-] = 71.5$ mM, the spectrum shows characteristic three band structure due to FeCl_4^- (Fig. 2). The spectra remain unchanged in the $[\text{Cl}^-]$ region above 71.5 mM. This means that all Fe^{3+} form the $[\text{FeCl}_4]^-$ complex, because the equilibrium does not move with increase in $[\text{Cl}^-]$. Hereafter, we will call the absorption band at 318 nm as “ FeCl_4 band”. A detailed investigation revealed three isosbestic points at 225 nm, 255 nm, and 385 nm above $[\text{Cl}^-] = 11.5$ mM [Fig. S2(a)†]. The isosbestic point reflects the reaction between octahedral ($[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$) to tetrahedral ($[\text{FeCl}_4]^-$) complexes with increase in $[\text{Cl}^-]$.

A similar $[\text{Cl}^-]$ -dependent spectral change is observed in the EtOH solution [Fig. 3(b)]. At $[\text{Cl}^-] = 0.0$ and 0.9 mM, the spectra exhibit two-band structure. At $[\text{Cl}^-] = 2.5$ mM, an additional absorption band appears as indicated by an open triangle. Its

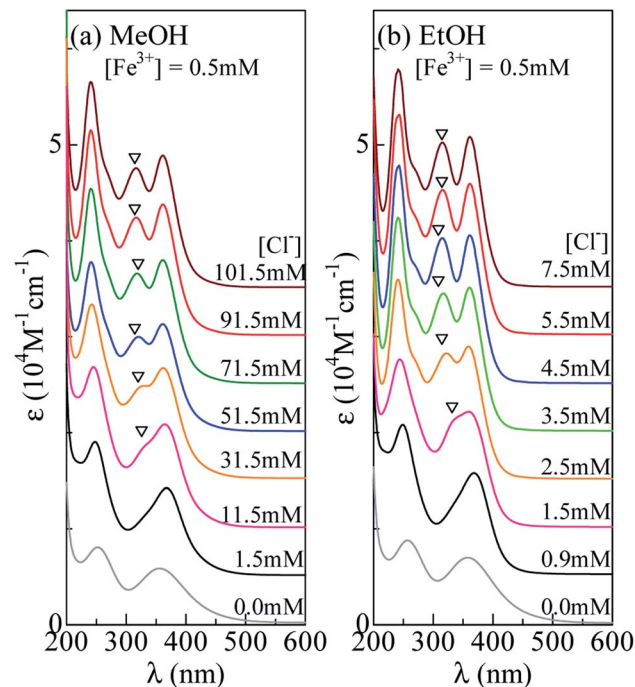


Fig. 3 Molar absorption coefficient (ϵ) spectra of (a) MeOH and (b) EtOH solution containing 0.5 mM Fe^{3+} against Cl^- concentration ($[\text{Cl}^-]$). Open triangles indicate FeCl_4 band (see text).

spectral weight steeply increases as $[\text{Cl}^-]$ increases. At $[\text{Cl}^-] = 4.5$ mM, the spectrum shows characteristic three band structure due to FeCl_4 (Fig. 2). The spectra remain unchanged in the $[\text{Cl}^-]$ region above 4.5 mM, indicating that all Fe^{3+} forms the FeCl_4 complex. We found three isosbestic points at 225 nm, 260 nm, and 385 nm above $[\text{Cl}^-] = 0.9$ mM [Fig. S2(b)†]. The isosbestic point reflects the reaction between octahedral ($[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$) to tetrahedral ($[\text{FeCl}_4]^-$) complexes with increase in $[\text{Cl}^-]$.

FeCl_4 formation against $[\text{Cl}^-]$

The solution system investigated contains multiple complex species, such as, $[\text{FeL}_6]^{3+}$, $[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$ ($n = 1$ and 2), $[\text{FeCl}_4]^-$. It is difficult to unambiguously decompose the spectrum into the respective components because there is no quantitative information on the spectra due to $[\text{FeCl}_n\text{L}_{6-n}]^{3-n}$. Fortunately, we know the spectrum of $[\text{Fe}^{\text{III}}\text{Cl}_4]^-$. In addition, the FeCl_4 band at 318 nm is well separated from the absorption bands due to other complexes. In the following, we focused our attention on the FeCl_4 formation against $[\text{Cl}^-]$. We evaluated the intensities and peak positions (λ_p) of the FeCl_4 band by least-squares fitting with three Gaussian functions (Fig. S3 and S4†). The intensities were normalized by the value at $[\text{Cl}^-] = 101.5$ mM (7.5 mM) for the MeOH (EtOH) solutions, where all Fe^{3+} is considered to form the FeCl_4 complex. Then, the proportion (r) of the FeCl_4 complex is the same value as the normalized intensity (I).

Fig. 4 shows I (upper panel) and λ_p (middle panel) against $[\text{Cl}^-]$ in (a) MeOH and (b) EtOH solutions. For convenience of explanation, we define regions I, II, and III as regions where $r (= I) < 0.2$, $0.2 < r < 0.7$, and $r > 0.7$, respectively. The region I and III are dominated by the $[\text{FeL}_6]^{3+}$ and $[\text{FeCl}_4]^-$ complexes,



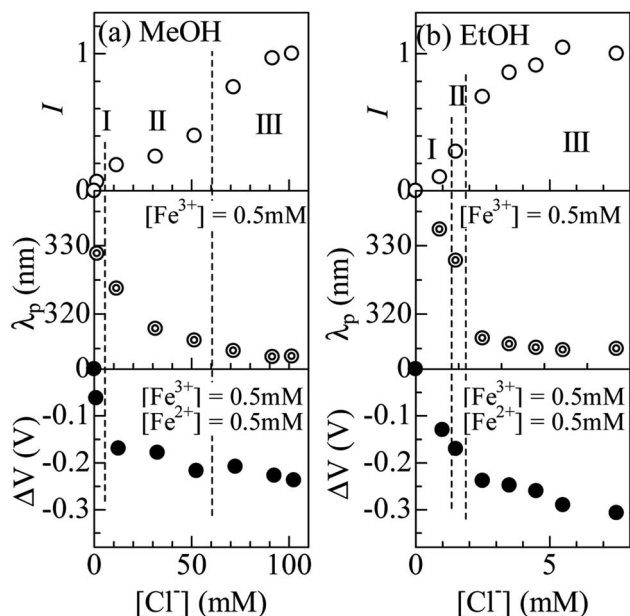


Fig. 4 (a) Normalized intensity (I ; upper panel) and wavelength (λ_p ; middle panel) at the peak of the $FeCl_4$ band, and variation (ΔV ; bottom panel) in V of Fe^{2+}/Fe^{3+} in MeOH solution against $[Cl^-]$. The intensity was normalized by the value at $[Cl^-] = 101.5\text{ mM}$. (b) I (upper panel) and λ_p (middle panel), and ΔV (bottom panel) in EtOH solution against $[Cl^-]$. The intensity was normalized by the value at $[Cl^-] = 7.5\text{ mM}$. For convenience of explanation, regions I, II, and III are defined (see text).

respectively. In (a) MeOH system, r exhibits a stationary value of 0.2–0.3 in the region of $10\text{ mM} < [Cl^-] < 50\text{ mM}$ (region II). The fact that r remains 0.2–0.3 indicates existence of a dominant species other than $[FeCl_4]^-$ and $[FeL_6]^{3+}$, that is, $[FeCl_nL_{6-n}]^{3-n}$ ($n = 1$ and 2). In (b) EtOH, r steeply increases from 0.5 at $[Cl^-] = 1\text{ mM}$ to 0.7 at $[Cl^-] = 2.5\text{ mM}$. The steep increase in r indicates that FeL_6 almost directly transfers to $FeCl_4$ with increases in $[Cl^-]$.

The difference in the complex formation between the MeOH and EtOH solutions is probably reflects the difference in solubility of Cl^- . The solubility ($= 6\text{ mM}$) of $NaCl$ in EtOH is much smaller than that ($= 100\text{ mM}$) in MeOH. In EtOH system, Cl^- in solution is unstable and tend to form the $[FeCl_4]^-$ complex if Fe^{3+} exists in solvent. The $[Cl^-]$ value ($= 2.0\text{ mM}$) at the boundary to region III is nearly the same value ($= 2.0\text{ mM}$) as required for all Fe^{3+} to become $FeCl_4$. In MeOH system, Cl^- in solution is stabler than in EtOH. This causes the stable $[FeL_6]^{3+}$ in small $[Cl^-]$ region ($< 10\text{ mM}$; region I) and $[FeCl_nL_{6-n}]^{3-n}$ formation in the intermediate $[Cl^-]$ region ($10\text{ mM} < [Cl^-] < 50\text{ mM}$; region II). In aqueous solution where Cl^- is much more stabler than in alcohol solutions, no trace of $[FeCl_4]^-$ is observed even at $[Cl^-] = 15\text{ M}$ [Fig. 1(b)]. Thus, our investigation revealed the solvent dependence in complex formation against $[Cl^-]$.

Coordination effect on V

Now, let us investigate the correlation between the Fe ion coordination and V of Fe^{2+}/Fe^{3+} . The bottom panel of Fig. 4 shows ΔV ($= V_{\text{sample}} - V_{\text{ref}}$) of Fe^{2+}/Fe^{3+} in (a) MeOH and (b) EtOH solutions. The electrolyte in the reference cell was MeOH

(or EtOH) solution containing $0.5\text{ mM } Fe^{2+}$ and $0.5\text{ mM } Fe^{3+}$ at $[Cl^-] = 0.0\text{ mM}$, where the FeL_6 complex is dominated. We must confess that we have no detailed information on the complex state of Fe^{2+} against $[Cl^-]$. Like Fe^{3+} , the complex state is considered to change from $[FeL_6]^{2+}$, $[FeCl_nL_{6-n}]^{2-n}$, to $[FeCl_4]^{2-}$ with increase in $[Cl^-]$. In the following argument, we assume that the redox reaction of the complex occurs without substitution of the coordinated molecules/ions.

In (a) MeOH system, ΔV is -0.16 V at the entrance of region II. The variation in V between $[FeL_6]^{2+}/[FeL_6]^{3+}$ (region I) and $[FeCl_nL_{6-n}]^{2-n}/[FeCl_nL_{6-n}]^{3-n}$ (region II) is well explained in terms of the crystal field splitting. We note that six d electrons in the octahedral $[FeL_6]^{2+}$ and $[FeCl_nL_{6-n}]^{2-n}$ takes high-spin (HS) configuration, similarly to the case of $[Fe(H_2O)_6]^{2+}$.^{16,17} The crystal field from Cl^- is weaker than that from oxygen in L. Then, V of $[FeCl_4]^{2-}/[FeCl_4]^-$ is expected to be lower, reflecting narrower crystal field splitting. In (b) EtOH system, ΔV is -0.24 V at the entrance of region III. Variation of V between $[FeL_6]^{2+}/[FeL_6]^{3+}$ (region I) and $[FeCl_4]^{2-}/[FeCl_4]^-$ (region III) is also explained in terms of the crystal field splitting. We note that six d electrons take the HS configuration in tetrahedral $[FeCl_4]^{2-}$, because the crystal field splitting ($= 10\text{ Dq}$) in octahedral complex is larger than that ($= 4.45\text{ Dq}$) in the tetrahedral complex.¹⁸ V of $[FeCl_4]^{2-}/[FeCl_4]^-$ is expected to be lower, reflecting narrower ligand field splitting.

Conclusions

We spectroscopically investigated variation of the Fe ion coordination against $[Cl^-]$ in MeOH and EtOH solutions. In MeOH solution, with increases in $[Cl^-]$, octahedral $[FeL_6]^{3+}$ gradually transforms to tetrahedral $[FeCl_4]^-$ via mixed $[FeCl_nL_{6-n}]^{3-n}$ ($n = 1$ and 2). In EtOH solution, $[FeL_6]^{3+}$ directly transforms to $[FeCl_4]^-$ with increase in $[Cl^-]$. We found that the coordination change significantly decreases V of Fe^{2+}/Fe^{3+} and interpreted the observation in terms of the ligand field splitting.

Author contributions

Y. N. performed spectroscopic and electrochemical experiment. D. I. have supported the experiment and analysis. D. I further performed quantum chemistry calculation. Y. M. made the experimental plan and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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