Isotope Fractionation of Iron(III) in Chemical Exchange Reactions Using Solvent Extraction with Crown Ether

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This work reports on the chemical isotope fractionation of Fe(III) by a solvent extraction method with a crown ether of dicyclohexano-18-crown-6. The $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios were analyzed by multiple-collector inductively coupled plasma mass spectrometry. We determined the dependence of the isotope enrichment factors (ϵ) on the strength of HCl. The relative deviation of the $^{56}Fe/^{54}Fe$ ratios relative to the unprocessed material ($10^4\ \epsilon_{56}$) increases from −15.3 to −6.3 with [HCl] increasing from 1.6 to 3.5 mol/L. Likewise, $10^4\ \epsilon_{57}$ increases from −22.8 to −9.6 under the same conditions. The correlation between ϵ_{56} and ϵ_{57} is mass dependent within the errors. The observed fractionation was broken down into the effects of competing extraction reactions and of a reaction between Fe(III) species ($FeCl_2^+$ and $FeCl_3$) in the aqueous phase. We found that the isotope fractionation between the Fe(III) species is mass dependent, which we confirmed by calculating the reduced partition function ratios.

Introduction

Mass-dependent fractionation on ion-exchange columns is a well-known process (e.g., for Ca).[1] Chemical isotope fractionation of Fe(III) has been studied by liquid chromatography,[2] and this study was expanded by Roe et al[3] (the issue of Fe isotope fractionation in nature has recently been reviewed by Dauphas and Rouxel).[4] Precise analyses of iron isotope ratios are now routinely permitted by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). So far, mass-independent isotope fractionation of Fe has not been observed in nature.[4] In contrast, for other elements, a number of mass-independent isotope fractionations, which are explained by Bigeleisen's nuclear field shift theory,[5] have been found using chemical-exchange methods (mainly solvent extraction methods and liquid chromatography) (see references in ref 6). In a preliminary study,[7] we investigated chemical isotope fractionation of Fe(III) during liquid extraction experiments with crown ethers, in which the isotopic compositions were analyzed by thermal-ionization mass spectrometry (TIMS). We used a single collector (the Faraday collector could be switched with a secondary electron collector) with analogue output. Although we showed that isotope fractionation was present, the precision and accuracy of the data were inadequate for discussing mass-independent isotope effects. The experiments were therefore repeated with the more precise method of MC-ICP-MS. Iron isotopes were fractionated by the solvent extraction technique with a macrocyclic compound (the so-called crown ether), which is effective for separating isotopes.[8] The interpretation separates non-mass-dependent from mass-dependent effects using quantum mechanics simulations of the vibrational energy levels of the coexisting compounds. Although similar previous attempts exist in the literature,[9−11] we found it useful to complement the existing models with a simulation based on the Hartree−Fock approximation that would substantiate mass-dependent effects and therefore place the non-mass-dependent fractionation contribution on solid ground.

Experimental

We used dicyclohexano-18-crown-6 (DC18C6) (over 97% purity) and 1,2-dichloroethane (over 99.8% purity) from Fluka Chemie GmbH and a standard solution of 1000 ppm $Fe(NO_3)_3\cdot 9H_2O$ in 0.5 mol/L (M) HNO_3 from Merck KGaA. Hydrochloric and nitric acids (Merck KGaA, analytical grade) were purified by sub-boiling distillation. The other chemicals were reagent grade from Sigma-Aldrich Co.

Two milliliters of Fe standard solution were evaporated in a Teflon beaker on a hot plate, and the chemical form was converted to chloride by repeatedly dissolving the residue in concentrated HCl and evaporating the liquid. The final solid was redissolved in HCl to obtain 0.018 M Fe(III) solutions of various HCl molalities (1.6−4.0 M). We will refer to these solutions as the aqueous phase. The organic phase was a solution of 0.1 M DC18C6 in 1,2-dichloroethane. The experiments were carried out at room temperature (295 ± 0.5) K.

Two milliliters of the aqueous solution and 2 mL of the organic solution were poured into a glass vial with a Teflon-coated magnetic bar, and the glass vial was sealed with a stopcock. The two phases were agitated with a magnetic stirrer for 30 min. In our previous experiments,[7] we recognized that extraction equilibrium is attained at this point, and the two phases were then separated by centrifugation (2000 rpm, 1 min). An aliquot of the aqueous supernatant was taken for analysis. The iron concentrations in the equilibrated aqueous phase were analyzed by ICP-QMS (Thermo Elemental X7).

To minimize matrix effects, possible traces of organic material from DC18C6 were removed by ashing. The aqueous phase was

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transferred into a quartz crucible and dried on a hot plate. The chloride was converted back to nitrate by evaporation in concentrated nitric acid. The crucible was then heated at 1073 K in an electric furnace for 8 h, which turns Fe into iron oxide. This in turn was dissolved in 6 M HCl by gentle heating of the crucible on a hot plate for 24 h. No substantial loss of Fe could be observed from this procedure. The HCl solution was dried on a hot plate, and again, the chloride was converted back to nitrate by evaporation in concentrated nitric acid.

A 500 ppb solution of Fe in 0.05 M HNO_3 was prepared for isotopic analysis and introduced into the Nu Plasma 500 HR via a desolvating nebulizer Nu DSN-100. The mass spectrometer was operated in pseudo-high-resolution mode (closed source slits and open collector slits), which allows interferences, notably $^{40}Ar^{14}N$ at mass 54 and $^{40}Ar^{16}O$ at mass 56, to be resolved. Forty ratios in 2 blocks of 20 ratios each, for which the integration time of each scan was 10 s, were measured for each sample. The instrumental mass bias was controlled by bracketing each sample with standards. For the present experiment, the choice of standard is immaterial to the results. We confirmed that the potential interferences with Cr at mass 54 remained below detection levels. The uncertainties on $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ are 0.10 and 0.19‰, respectively, at the 2σ level. Because of the very low abundance of ^{58}Fe (0.282%), we could not obtain precise enough $^{58}Fe/^{54}Fe$ data for assessment of isotope fractionation.

Computational Details

We calculated the orbital geometries and vibrational frequencies of aqueous Fe(III) chlorides using the conventional Hartree−Fock (HF) approximation and density functional theory (DFT) as implemented by the Gaussian 03 code.[12] The DFT method employed here is a hybrid density functional consisting of Becke's[13] three-parameter nonlocal hybrid exchange potential (B3) with Lee, Yang, and Parr (LYP)[14] nonlocal functionals. The ++6-31G** basis set was chosen for H, O, and Cl, and LanL2DZ[15−18] was chosen for iron. The former is an all-electron basis set, while the latter is an effective-core potential basis set.

Results and Discussion

Extraction Reactions for the Fe(III)−Crown Ether System. The species of Fe(III) in HCl media considered here are Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, and $FeCl_4^-$, which are related through the following set of reactions

$$Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+} \tag{1}$$

$$FeCl^{2+} + Cl^- \leftrightarrow FeCl_2^+ \tag{2}$$

$$FeCl_2^+ + Cl^- \leftrightarrow FeCl_3 \tag{3}$$

$$FeCl_3 + Cl^- \leftrightarrow FeCl_4^- \tag{4}$$

The apparent stability constants of equilibria 1−4 are $K_1 = 30$, $K_2 = 4.5$, $K_3 = 0.15$, and $K_4 = 0.0078$, respectively,[19] in which the mean activity of HCl is treated as the activity of Cl^- and the activity coefficients of Fe species are set to unity. From these K values and the mean activity of HCl,[20] the mole fractions of the Fe species can be estimated (Figure 1). In the concentration domain considered in the present work ([HCl] = 1.6−4.0 M), the major species are $FeCl_2^+$ and $FeCl_3$.

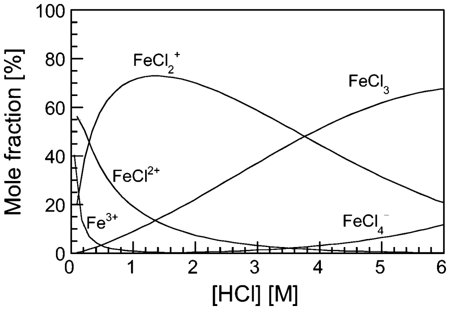

Figure 1. Formations of the Fe(III) species in HCl solutions. The mole fractions were calculated from the reported stability constants[19] and the mean activity of HCl. The mean activity of HCl was calculated from the semiempirical theory.[20]

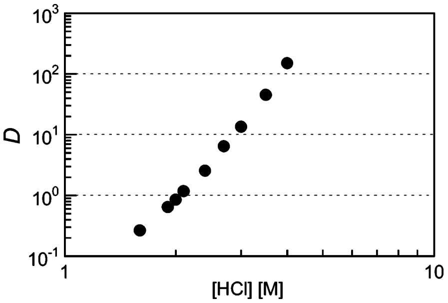

Figure 2. Distribution ratio of Fe(III). $D = [Fe(III)]_{org}/[Fe(III)]_{aq}$, in which $[Fe(III)]_{org}$ was determined as $[Fe(III)]_{init} - [Fe(III)]aq$.

The measured distribution ratios $D = \sum[Fe(III)]_{org}/\sum[Fe(III)]_{aq}$ are shown in Figure 2 as a function of [HCl]. The D value steeply increases with acid strength. Since DC18C6 is a neutral ligand, which preceeds ion association extraction, the extraction reaction of Fe(III) in the crown ether system may be written as

$$Fe^{3+} + 3Cl^- + L \leftrightarrow FeLCl_3 \tag{5}$$

where L stands for DC18C6. This equation predicts that the slope of log D versus log [HCl] should be 3, but the observed slope exceeds this value and thus requiring a different explanation. An association of $FeLCl_2^+$ with $FeCl_4^-$ in the organic phase has been suggested,[21] but the extraction stoichiometry of $FeLCl_2^+{-}FeCl_4^-$ does not result in this slope. We instead suggest that the strong dependence of D on acid strength can be attributed to a simultaneous extraction of the iron compounds and HCl, a phenomenon which will be referred to as coextraction. To describe this process, the extraction reaction can be rewritten as

$$nH^+ + FeCl_3 + nCl^- + L \leftrightarrow FeLCl_3{\cdot}nHCl \tag{6}$$

With the stability constant of reaction 6 defined as K_L, the equilibrium equation now reads

$$K_1K_2K_3K_L = \frac{[FeLCl_3{\cdot}nHCl]}{[H^+]^n[Fe^{3+}][Cl^-]^{n+3}[L]} \tag{7}$$

where $[FeLCl_3{\cdot}nHCl] = [Fe(III)]_{org}$ The total concentration of all Fe(III) species in the aqueous phase is

$$\begin{aligned}\sum[Fe(III)]_{aq} &= [Fe^{3+}] + [FeCl^{2+}] + [FeCl_2^+] + [FeCl_3] + [FeCl_4^-] \\ &= [Fe^{3+}](1 + K_1[Cl^-] + K_1K_2[Cl^-]^2 + K_1K_2K_3[Cl^-]^3 + K_1K_2K_3K_4[Cl^-]^4)\end{aligned} \tag{8}$$

TABLE 1: Isotope Enrichment Factors (in 10^{-4} or ϵ units)[a]

[HCl] (M)	D	$10^4\,\epsilon_{56}$	$10^4\,\epsilon_{57}$
1.6	0.263	−15.3	−22.8
2.0	0.855	−11.2	−18.7
2.1	1.16	−12.6	−18.7
2.7	6.44	−10.2	−16.9
3.0	13.7	−6.9	−11.9
3.5	45.2	−6.3	−9.6

[a] The 2σ uncertainties are 1.0 for $10^4\,\epsilon_{56}$ and 1.9 for $10^4\,\epsilon_{57}$.

and the distribution coefficient, K_D ($\sim D$)

$$K_D = \frac{K_1K_2K_3K_L[H^+]^n[Cl^-]^{n+3}[L]}{1 + K_1[Cl^-] + K_1K_2[Cl^-]^2 + K_1K_2K_3[Cl^-]^3 + K_1K_2K_3K_4[Cl^-]^4} \qquad (9)$$

With the use of Bjerrum's[19] K values and the assumption that $[H^+] \approx [Cl^-]$, the values of K_L and n can be calculated by regression of K_D against [HCl] as $K_L = 1.26$ and $n = 1.7$ with a squared correlation coefficient of $R^2 = 0.9997$. The value $n = 1.7$ suggests that one or two HCl molecules participate in extraction reaction 6. Bjerrum et al.[19] reported that, upon extraction from HCl solutions by ethers, Fe(III) is accompanied by one HCl molecule. We speculate that Fe(III) is extracted as $HFeCl_4$, likely as an ion pair of H_3O^+ (or H^+) and $FeCl_4^-$.[19,21] The following extraction may therefore compete with reaction 6

$$H^+ + FeCl_4^- + L \leftrightarrow HFeLCl_4 \qquad (10)$$

Isotope Fractionation during Extraction. The isotope separation factor, α_m, between the aqueous and the organic phases is defined as

$$\alpha_m = \frac{(\sum[^mFe]/\sum[^{54}Fe])_{org}}{(\sum[^mFe]/\sum[^{54}Fe])_{aq}} \qquad (11)$$

where the subscript m indicates the mass of a particular isotope ($m = 56$ or 57) and $(\sum[^mFe]/\sum[^{54}Fe])_{org}$ and $(\sum[^mFe]/\sum[^{54}Fe])_{aq}$ are the isotopic ratios of ^mFe relative to ^{54}Fe found in the organic and aqueous phases, respectively, summed over all the species present in each phase. The isotope enrichment factor, ϵ_m, is defined as

$$\epsilon_m = \alpha_m - 1 \qquad (12)$$

Since α is close to one, we will repeatedly use the approximation $\alpha - 1 \approx \ln \alpha$.

The experimental values of ϵ_m are shown in Table 1 and Figure 3, which shows the line of mass-dependent fractionation (ϵ is defined as 10^{-4} units). In the standard mass-dependent theory,[22,23] the isotope enrichment factor is proportional to $\delta m/mm'$, where m' stands for the light isotope, m for the heavy isotope, and δm for the difference, $m - m'$. The straight-line in Figure 3 shows the theoretical mass-dependent correlation ($\propto \delta m/mm'$) between ϵ_{56} and ϵ_{57}. The ϵ_m values plot on the mass fractionation line within experimental errors and increase with acid strength from −15.3 to −6.3 for $10^4\,\epsilon_{56}$ and from −22.8 to −9.6 for $10^4\,\epsilon_{57}$.

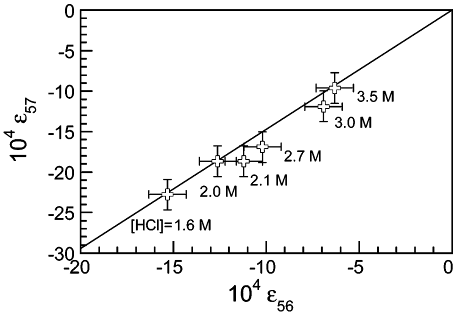

Figure 3. Isotope enrichment factor of Fe(III). $([^mFe]/[^{54}Fe])_{org}$ was determined from $([^mFe]/[^{54}Fe])_{init}$, $([^mFe]/[^{54}Fe])_{aq}$, and D. The linear line is a correlation of the mass dependent low ($\propto \delta m/mm'$), $\epsilon_{56}(56 - 54/56 \times 54)^{-1}$ vs $\epsilon_{57}(57 - 54/57 \times 54)^{-1}$.

TABLE 2: Isotope Enrichment Factors, $\epsilon(3)_m$ and $\epsilon(L)_m$[a]

$10^4\,\epsilon(3)_{56}$	−31.6	$10^4\,\epsilon(L)_{56}$	11.4
$10^4\,\epsilon(3)_{57}$	−45.9	$10^4\,\epsilon(L)_{57}$	15.3
$\epsilon(3)_{57}/\epsilon(3)_{56}$	1.453	$\epsilon(L)_{57}/\epsilon(L)_{56}$	1.342

[a] The slope of the mass-dependent correlation is $(57 - 54/54 \times 57)/(56 - 54/54 \times 56) = 1.474$.

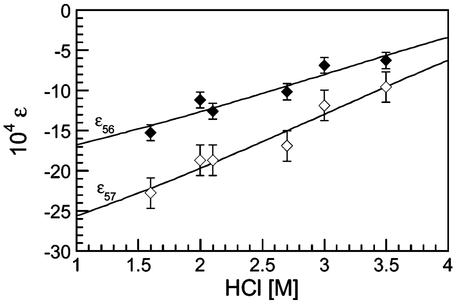

Figure 4. Acidity dependence of the isotope enrichment factor. Solid lines are calculated with eq 18. Determination factors of the analysis were $R^2 = 0.91$ for ϵ_{56} and $R^2 = 0.96$ for ϵ_{57}.

Since $FeCl_2^+$ and $FeCl_3$ are the dominant species at the HCl molarities used in this work (1.6 to 3.5 M), we will assume that reaction 3 is the only significant reaction taking place in the aqueous phase. The distribution coefficient ^mK_D for the isotope m is

$$^mK_D = \frac{^mK_3\,^mK_L[H^+]^n[Cl^-]^{n+1}[L]}{1 + {}^mK_3[Cl^-]} \qquad (13)$$

and the isotope separation factor, α_m, is

$$\alpha_m = \frac{^mK_D}{^{54}K_D} = \frac{^mK_3\,^mK_L}{^{54}K_3\,^{54}K_L} \times \frac{1 + {}^{54}K_3[Cl^-]}{1 + {}^mK_3[Cl^-]} \qquad (14)$$

We further define the new fractionation factors, $\alpha(3)_m = {}^mK_3/{}^{54}K_3$ and $\alpha(L)_m = {}^mK_L/{}^{54}K_L$, and substitute the values into eq 14 so that

$$\alpha_m = \alpha(3)_m\alpha(L)_m\left(\frac{1 + {}^{54}K_3[Cl^-]}{1 + \alpha(3)_m\,{}^{54}K_3[Cl^-]}\right) \qquad (15)$$

We set the value of $^{54}K_3$ at 0.15, here reported as K_3,[19] and treat $\alpha(3)_m$ and $\alpha(L)_m$ as unknown parameters. The values of $\alpha(3)_m$ and $\alpha(L)_m$ can be calculated by regressing α_m against $[Cl^-]$ (approximated by the concentration of HCl). By using the analytical results of Table 2, we can successfully estimate the values of ϵ_{56} and ϵ_{57} and their dependence on acid strength (Figure 4).

The ratios $\epsilon(3)_{57}/\epsilon(3)_{56}$ and $\epsilon(L)_{57}/\epsilon(L)_{56}$, in which $\epsilon(3) = \alpha(3)_m - 1$ and $\epsilon(L) = \alpha(L)_m - 1$, are also shown in Table 2.

TABLE 3: Bond Length (Å) Determined for $FeCl_2(H_2O)_4^+$ and $FeCl_4^-$

species	bond	HF	B3LYP	literature value
$FeCl_2(H_2O)_4^+$	Fe−O	2.104	2.129	2.02[a], 2.079[b], 2.07[c]
	Fe−Cl	2.307	2.267	2.30[a], 2.299[b], 2.30[c]
$FeCl_4^-$	Fe−Cl	2.289	2.259	2.22[a], 2.261[b]

[a] EXAFS.[31] [b] XRD.[30] We use the Fe-water molecule distance as a proxy for the length of the Fe−O bond. [c] X-ray scattering.[25] We use the Fe-water molecule distance as a proxy for the length of the Fe−O bond.

TABLE 4: Logarithm of the Reduced Partition Function, ln(*S*/*s*′)*f*[a]

	HF		B3LYP	
	^{56}Fe	^{57}Fe	^{56}Fe	^{57}Fe
ln(*s*/*s*′)*f*, $FeCl_4^-$	0.00728	0.01074	0.00619	0.00913
ln(*s*/*s*′)*f*, $FeCl_2(H_2O)_4^+$	0.00858	0.01266	0.00673	0.00994
difference [10^{-4}]	−13.0	−19.2	−5.4	−8.1

[a] The difference $\ln(s/s')f_{FeCl_4^-} - \ln(s/s')f_{FeCl_2(H_2O)_4^+}$ is treated as $\epsilon(3)$ via the molecular vibration. *T*=295 K.

It is known that the crown ether system is efficient at revealing mass-independent isotope effects (see references in ref 6). The ratio $\epsilon(L)_{57}/\epsilon(L)_{56}$ (1.342) shows about 10% deviation from the mass-dependent correlation of $\delta m/mm'$ (i.e., $(57 - 54/54 \times 57)/(56 - 54/54 \times 56) = 1.474$). If the experimental uncertainty on $\epsilon(L)$ is similar to that on ϵ, a 10% deviation of the $\epsilon(L)_{57}/\epsilon(L)_{56}$ ratio with respect to the value expected from mass-dependent effects alone is not enough to reach conclusions about mass-independent effects. It should be noted that if the mass-independent isotope effect reported by Bigeleisen[5] is dominating, the $\epsilon_{57}/\epsilon_{56}$ ratio can be approximated by $\delta\langle r^2\rangle_{57}/\delta\langle r^2\rangle_{56}$ with $\delta\langle r^2\rangle_m = \langle r^2\rangle_m - \langle r^2\rangle_{54}$ ($m = 56$ or 57) standing for the isotopic change in the mean-square radius of nuclear charge distribution. For $\delta\langle r^2\rangle_{56} = 0.327$ fm^2 and $\delta\langle r^2\rangle_{57} = 0.447$ fm^2,[24] we obtain $\epsilon_{57}/\epsilon_{56} \approx 1.367$.

To further evaluate the respective strengths of the mass-dependent and mass-independent effects, we performed some quantum chemical analysis calculations of the vibrational energies of the aqueous Fe(III) chloride species.[12] Although literature data exist,[9−11] we reiterated the calculations using conditions close to those of our experiments. The aqueous Fe(III) chloride species are generally thought to be present as octahedral $FeCl_x(H_2O)_{6-x}$ ($x = 0\ 4$).[3] For example, $FeCl_2^+$ is known to have the configuration $FeCl_2(H_2O)_4^+$.[25] Different structures have been suggested for $FeCl_4^-$, either the octahedral anion $FeCl_4(H_2O)_2^-$[26] or the tetrahedral $FeCl_4^-$.[27−31] The tetrahedral $FeCl_4^-$ is considered to be the dominant species. For $FeCl_3$ in aqueous solutions, there is no structural data. A trigonal bipyramidal geometry has been suggested for $FeCl_3(H_2O)_2$,[32] but the coordination number of $FeCl_3$ has been reported to be four.[29] Both the coordination number of four and our extraction results (reaction 10) suggest that $FeCl_3$ may rather be present as $H^+{-}FeCl_4^-$. If the core structure of $HFeCl_4$ is $FeCl_4^-$, the isotope fractionation factor between $FeCl_2^+$ and $FeCl_3$ can be estimated through the fractionation between $FeCl_2(H_2O)_4^+$ and $FeCl_4^-$.

The calculated bond lengths of Fe−O and Fe−Cl are shown in Table 3. All calculated geometries were optimized within appropriate symmetries (i.e., octahedral symmetry for $FeCl_2(H_2O)_4^+$ and tetrahedral symmetry for $FeCl_4^-$). The bond lengths determined by X-ray spectroscopy[25,30,31] are also shown. Our calculations correctly reproduce the literature values of Fe−Cl bond lengths.[25,30,31] In contrast, the calculated Fe−O bond lengths are slightly, though marginally longer than literature values.[25,30,31] We speculate that including the second coordination sphere may have improved the agreement. The vibrational frequencies of the $FeCl_2(H_2O)_4^+$ and $FeCl_4^-$ isotopomers were calculated for each of the three Fe isotopes 54, 56, and 57.

The mass-dependent isotope effect is the result of the isotopic difference in the vibrational energies of isotopomers.[22,23] The isotope enrichment factor due to this effect can be evaluated from the reduced partition function,[23] $(s/s')f$,

$$\ln (s/s')f = \sum[\ln b(u_i') - \ln b(u_i)] \tag{16}$$

$$\ln b(u_i) = -\ln u_i + u_i/2 + \ln (1 - e^{-ui}) \tag{17}$$

where $u = h\nu_i/kT$. The subscript *i* stands for the *i*th molecular vibrational level with primed variables referring to the light isotopomer. The isotope enrichment factor resulting from the molecular vibration can be evaluated from the frequencies (ν) summed over all the different modes. For example, we can estimate $\epsilon_{56}(3)$ as $\{\sum[\ln b(^{54}u_i) - \ln {}^{56}b(u_i)]_{FeCl_4^-} - \sum[\ln b(^{54}u_i) - \ln {}^{56}b(u_i)]_{FeCl_2(H_2O)_4^+}\}$. The logarithm of the reduced partition function for each isotopomer is shown in Table 4. The calculation results show negative $\epsilon(3)$ values, which conform to our experimental values (Table 2). The absolute values of $\epsilon(3)$ calculated using HF are larger than those calculated using B3LYP (see Computational Details). Reduced partition functions have been calculated previously[11] for various iron complexes in aqueous solution using a combination of force-field modeling and literature vibrational frequencies. These authors reported that their calculations agree with predictions based on Mössbauer spectra[9,10] and experimental data.[2] The isotope fractionation factor ($10^4\ \epsilon_{56}$) between $FeCl_2(H_2O)_4^+$ and $FeCl_4^-$ at 298 K reported by Schauble et al.[11] is −13. This value is identical to the $\epsilon(3)_{56}$ calculated using HF (Table 4). The absolute values of both Schauble et al.'s[11] and the present results are still smaller than those of $\epsilon(3)_{56}$ shown in Table 2. This may be the result of the small fractions of $Fe(H_2O)_6^{3+}$ and $FeCl(H_2O)_5^+$ present in our aqueous solutions. For example, the isotope fractionation factor ($10^4\ \epsilon_{56}$) between $Fe(H_2O)_6^{3+}$ and $FeCl_4^-$ at 298 K is quite large, −44.[11] If such a strong fractionation actually occurred, the observed $10^4\ \epsilon(3)_{56}$ should be $\ll -13$. Our $10^4\ \epsilon(3)_{56} = -31.6$ value (Table 2) shows an intermediate value between −13 and −44, and we therefore consider that our simplified speciation and vibrational model provides a reasonable prediction of the magnitude of $\epsilon(3)$. The calculation results support that the isotope fractionation corresponding to the aqueous Fe(III) chlorides is mainly the mass-dependent isotope fractionation resulting from the molecular vibration.

Conclusions

Iron isotopes were fractionated in the chemical exchange reaction with DC18C6. The resulting observed isotope enrichment factors show no clear departure from the mass-dependent correlation within analytical and theoretical uncertainties. From the dependence of mass fractionation on acid strength, the isotope fractionation factors for the extraction reaction and the reaction between $FeCl_2^+$ and $FeCl_3$ were determined. The mass-dependent isotope fractionation from the reaction between $FeCl_2^+$ and $FeCl_3$ further was modeled successfully by the vibrational partition functions of the related molecules.

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