Temperature Dependence of Mixed-Valence States in Solvated and Non-Solvated Trinuclear Iron Stearates

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Solvated and non-solvated mixed-valence trinuclear iron
stearates were prepared and their Mössbauer spectra were de-
termined. XRD patterns of the compounds show that they have
layer structures having different inter-layer distances. A
temperature-dependent mixed-valence state was observed in the
non-solvated compound, while not in the solvated compound.

It has been pointed out by Oh et al. that the interstitial solvate
molecule, S, in trinuclear iron acetates, $[Fe_3O(CH_3CO_2)_6(L)_3]S$, plays an
important role in the valence delocalization.[1] However, it was reported
recently by us that the temperature dependent valence delocalization was
found in the trinuclear iron complexes, $[Fe_3O(RCO_2)_6(py)_3]$, with long chain
fatty acid anions, such as myristate, palmitate, and stearate anions, which
were synthesized without interstitial solvate molecules.[2] Based on the
results it was tentatively concluded that the long alkyl chain in these
complexes also plays an important role in the valence-delocalization,
although each the crystal included a very small portion of another layer
phase with a little longer inter-layer distance.[2] On the other hand, it
has been also reported that 1',1'''-ditetradecyl-biferrocenium triiodide
having a long alkyl chain shows a temperature-dependent valence state
depending upon the crystal structures.[3] In order to define the effect of
alkyl groups, the present paper describes the temperature dependence of the
mixed-valence state of iron atoms in the pure crystals of the non-solvated
stearate complex, $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]$, and the pure crystals of the
pyridine-solvated complex, $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]py$, which were prepared
by revising the condition of recrystallization used in the previous method.
     The crude oxo-centered trinuclear iron stearate was prepared by the
method previously reported.[2] Dark green colored precipitates were fil-
tered and then recrystallized by two ways. Recrystallization from ethanol-

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pyridine (1:1) at 50 °C, instead of the recrystallization at 80 °C from the same solvent, gave a "single phase non-solvated" compound, $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]$, while recrystallization from hot pyridine instead of the mixed solvent gave a single phase "solvated" compound, $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]py$. The purity of the products was checked by elemental analysis. Found : C, 69.90; H, 11.07; N, 2.60%. Calcd for the solvated compound $(C_{128}H_{230}N_4O_{13}Fe_3)$: C, 69.85; H, 10.53; N, 2.55%. Found : C, 69.59; H, 10.84; N, 1.87%. Calcd for the non-solvated compound $(C_{123}H_{225}N_3O_{13}Fe_3)$: C, 69.63; H, 10.69; N, 1.98%.

X-Ray diffraction patterns were taken by using Cu K_α radiations. Mössbauer spectra of the samples kept at various temperatures were determined in a Mössbauer spectrometer against a $^{57}Co(Rh)$ source moving at room temperature in a constant acceleration mode. The spectra were least-squares fit with Lorenzian lines. Velocity calibration was carried out by determining the magnetic splitting of natural iron foil and experimental errors were estimated within ± 0.01 mm s^{-1}. All the data of isomer shifts were referred with respect to metallic iron.

X-Ray diffraction patterns of the samples are shown in Fig. 1. No reflection line suggesting impurity phases is observed for both the samples in the present study. The reflection lines observed in the small angle region with an equal interval suggest a layer structure, and the interlayer distances are estimated to be 25.4 Å in the non-solvated compound, and 23.6 Å in the solvated compound. Other weak reflections in the range 20-25 degree, which are slightly different from each other, are ascribed to orientation of alkyl chains. Because the intensity of reflections in the small angle region decreases monotonously with increasing 2θ, it has been concluded that non-solvated stearate has a single layer struc-

Fig. 1. XRD patterns of a) non-solvated, and b) solvated stearates.

ture in a solid state. The solvated stearate also seems to have a similar single layer structure, but not a bilayer structure, because any alternatively changes are not found in the intensity of reflections, although only the first reflection of the solvated stearate (marked with an arrow in Fig. 1) shows an irregularly lower intensity. The reason for the irregularity will be solved by means of single crystal X-ray structure analyses.

Mössbauer spectra of the solvated stearate at various temperatures are shown in Fig. 2. The Mössbauer parameters are summarized in Table 1. The spectrum of the solvated compound at 78 K consists of two quadrupole-split doublets characteristic of high-spin Fe(II) and high-spin Fe(III), respectively. Without showing any additional quadrupole-split doublets,
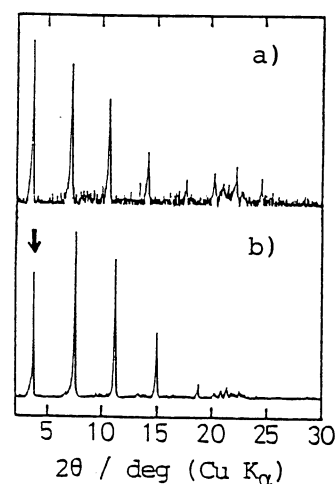
the two doublets remain up to room temperature. This is the first case
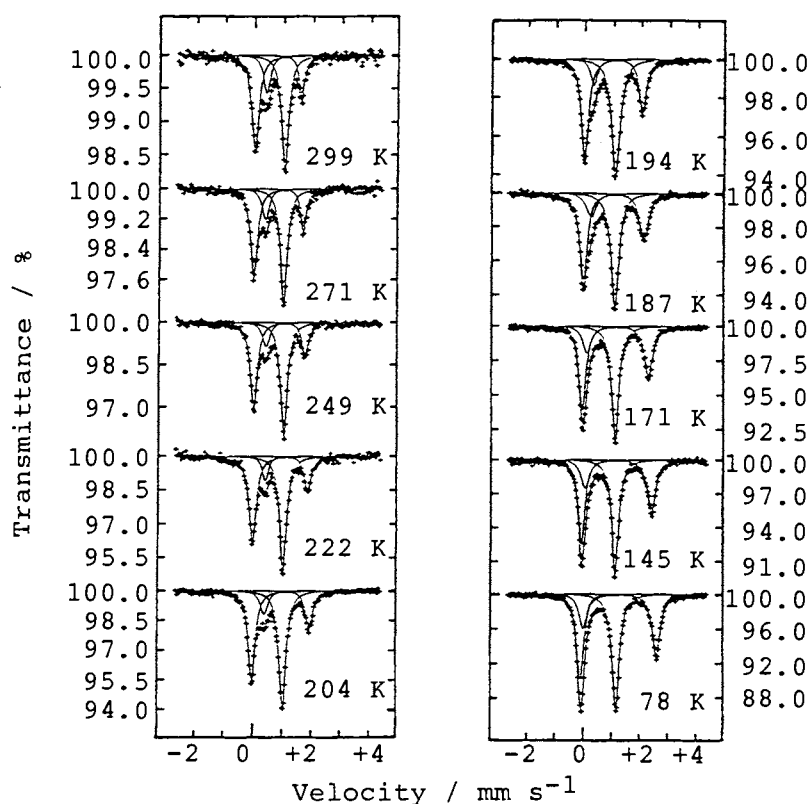where a temperature-independent mixed-valence state is observed for tri-

nuclear iron
carboxylates.
having a long
alkyl chain.
On the other hand,
the Mössbauer
spectra of non-
solvated compound
prepared in the
present study show
a temperature-
dependent mixed-
valence state as
reported for the
sample which
includes a small
portion of another
layer phase.[2]

Fig. 2. Mössbauer spectra of $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]py$.

Table 1. Mössbauer parameters of mixed-valence trinuclear iron stearates

| Sample | Temperature K | Fe(II) | | Fe(III) | |
		I.S. mm s^{-1}	Q.S. mm s^{-1}	I.S. mm s^{-1}	Q.S. mm s^{-1}
Non-solvated[a]	297	0.66[b]	0.99	——	——
	78	1.20	2.07	0.54	1.05
Solvated	299	1.01	1.20	0.52	1.03
	271	1.05	1.32	0.51	1.03
	249	1.09	1.36	0.51	1.04
	222	1.15	1.47	0.51	1.05
	204	1.18	1.55	0.51	1.06
	194	1.16	1.75	0.53	1.09
	187	1.19	1.90	0.53	1.12
	171	1.21	2.20	0.53	1.15
	145	1.25	2.37	0.53	1.18
	96	1.29	2.59	0.53	1.23
	78	1.31	2.62	0.54	1.24

a) A good agreement of the data for the non-solvated compound with those
for the previous data.[2] b) Intermediate valence state.

The spectrum at room temperature consists of only one quadrupole-split doublet showing an intermediate isomer-shift (I.S.) value of Fe(II) and Fe(III), as listed in Table 1. It is concluded that the coexistence of another phase, found as an impurity in the previous report, is not indispensable for the valence-delocalization, but that the long alkyl chain plays an important role. The asymmetric intensity of each doublet is attributed to the preferential orientation of the plate-like crystalline samples mounted on a sample holder.

According to the Debye approximation at high temperatures, the logarithmic value of recoil-free fraction of Mössbauer atoms is expected to decrease linearly with the increasing temperature.[4] However, as seen in Fig. 3, the temperature dependence of recoil-free fraction in both the samples is found to deviate from the linearity, probably because of the increasing motions of the alkyl chains in a solid, as in the case of $(C_nH_{2n+1}NH_3)_2SnCl_6$ (n=6, 8, 10, 12).[5] It is also seen in Fig. 3, the decrease of recoil-free fraction is larger in the non-solvated compound than that of the solvated compound, suggesting that the packing arrangement for the former is less closed than that for the latter. This suggestion seems to contradict the experimental results obtained in the studies of dialkylbiferrocenium indicating that the intermolecular interaction should be stronger in the same compound which has a shorter inter-layer distance.[3] Both the results lead us to conclude that an adequate intermolecular interaction is needed for the valence delocalization in the temperature-depending valence-delocalization compounds. It is also concluded that the solvate molecule in $[Fe_3O(C_{17}H_{35}CO_2)_6(py)_3]py$ rather inhibits the intermolecular interaction through the long alkyl chains.
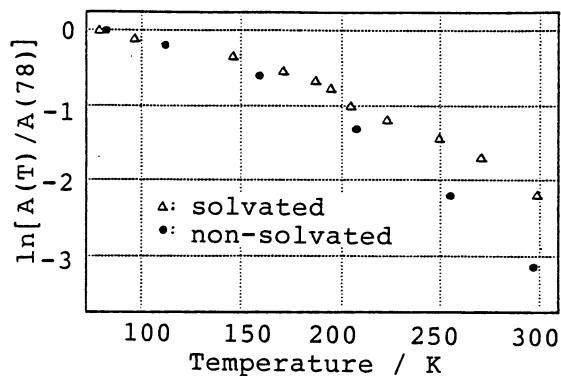

Fig. 3. Temperature dependence of recoil-free fraction in stearate compounds.

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