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NMR study of lanthanide (III) nitrate complexes in CMPO/TBP systems

Y. Sano[a,*], J. Karino[b], T. Koyama[a], H. Funasaka[a]

[a] *Japan Nuclear Cycle Development Institute (JNC), Tokai, Ibaraki 319-1194, Japan*
[b] *Inspection Development Company, Tokai, Ibaraki 319-1194, Japan*

Abstract

The coordination properties of the lanthanide (Ln) (Ln; La~Eu) nitrate complexes in octyl (phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO)/tributylphosphate (TBP) systems were investigated using NMR techniques. In Ln/CMPO/TBP systems where the mole ratio of CMPO to the Ln ion ([CMPO]/[Ln]) is under 3, ^{13}C- and ^{31}P-NMR spectra show that several kinds of complexes are produced in which both CMPO and TBP coordinate to the Ln (III) ion. The contribution of CMPO to the coordination with the Ln (III) ion increases with [CMPO]/[Ln], and in the case where [CMPO]/[Ln]>3, only CMPO coordinates to the Ln (III) ion directly in the bidentate manner. The distances from the Ln (III) ion to phosphoryl P or carbonyl C are estimated to be 3.3~4.3 Å. In this system, TBP is absent from the first coordination sphere of the Ln (III) ion, but decreases the exchange rate constants, activation enthalpy and activation entropy in the CMPO exchange reaction between the free and coordinated states by the action from beyond the first coordination sphere. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nuclear resonances (E); Lanthanide; CMPO; TBP

1. Introduction

In a nuclear fuel cycle process, the TRUEX process was developed for use as one of the recovery methods of the trivalent metal ion from a wide concentration range of HNO_3 solutions. This process uses CMPO as an extractant and TBP as a phase modifier. There are many studies concerned with the extraction behavior of the trivalent metal ion in CMPO/TBP systems [1–5] and the coordination structures and kinetics of the complexes thus produced in the lanthanide/CMPO or lanthanide/TBP systems [6–9]. However, there are few investigations about the structures and kinetics of the complexes in the lanthanide/CMPO/TBP system, which leads to a deeper understanding of the extraction mechanism in the TRUEX process. Nuclear magnetic resonance (NMR) spectroscopy is useful for the elucidation of the structure and the dynamics of complexes in mixed liquid systems. In this study, the coordination properties of lanthanide (III) (these are the elements extracted in the TRUEX process) nitrate complexes in CMPO/TBP systems are investigated using ^{13}C and ^{31}P-NMR measurements.

2. Experimental

2.1. Materials

Hydrated lanthanide (III) nitrates (La, Ce, Pr, Nd, Sm and Eu) were purchased as starting materials from Soekawa Chemicals. These were reagent grade. TBP and CMPO purchased from Wako Pure Chemical Industries and Atochem North America, respectively, were used without further purification.

Samples for NMR measurements were prepared by mixing an appropriate amount of hydrated lanthanide (III) nitrate, TBP and CMPO in $CDCl_3$.

2.2. NMR measurements

NMR measurements for ^{13}C and ^{31}P were performed on a JEOL LA-400 NMR spectrometer with a deuterium lock ($CDCl_3$) at 100.4 MHz and 161.7 MHz for ^{13}C and ^{31}P, respectively. ^{13}C-NMR chemical shifts were measured with respect to TMS as an internal reference and ^{31}P-NMR chemical shifts were measured with respect to 85% H_3PO_4 solution as an external reference. ^{13}C and ^{31}P-NMR longitudinal relaxation times (T_1) were determined by using the inversion recovery method with a $180°–\tau–90°$

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*Corresponding author.

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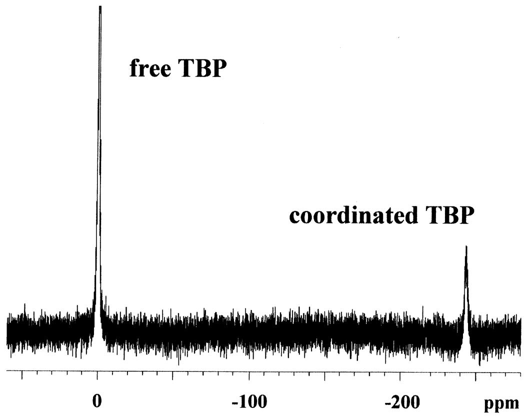
pulse sequence. The diamagnetic contributions to T_1 values in the systems containing the paramagnetic lanthanide (III) ions were corrected by using the T_1 value for the system in which La^{3+} ion was added, instead of the paramagnetic ions. All NMR measurements for the relaxation times were performed after bubbling argon gas through the sample for 5 min.

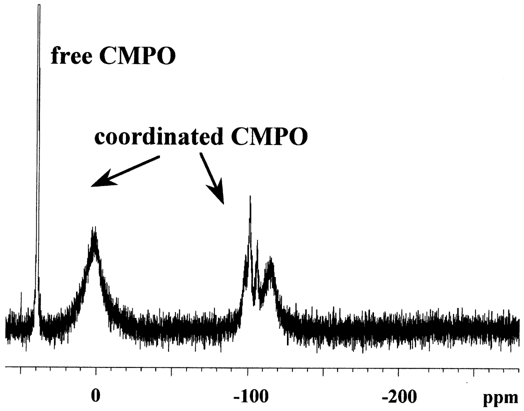
3. Results and discussion

Fig. 1 shows the ^{31}P-NMR spectra observed in Eu/TBP (a), Eu/CMPO (b) and Eu/CMPO/TBP (c) systems at –40°C. The mole ratio of the reagents in each system is noted in the figure, respectively. In the Eu/TBP system, two peaks assigned to free and coordinated TBP are

(a) Eu/TBP system ([Eu]:[TBP] $\cong$ 1:11)



(b) Eu/CMPO sytem ([Eu]:[CMPO] $\cong$ 1:7.5)



(c) Eu/CMPO/TBP system ([Eu]:[CMPO]:[TBP] $\cong$ 1:1.5:5.5)

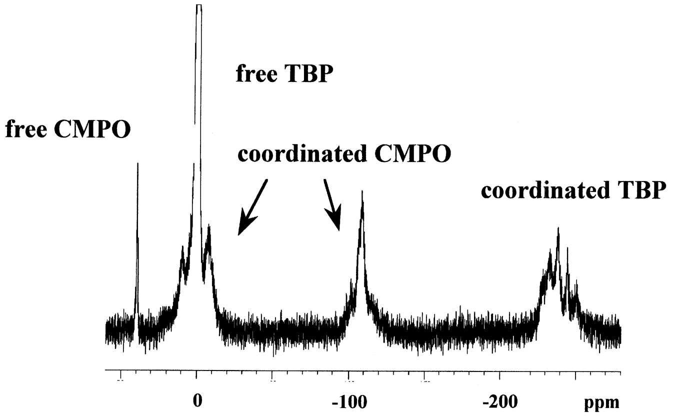
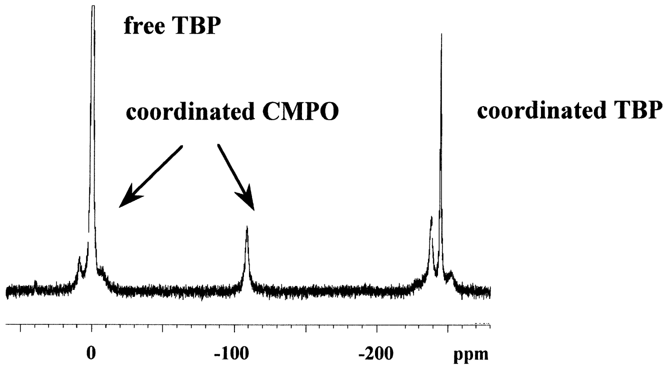


Fig. 1. ^{31}P-NMR spectra in Eu/TBP, Eu/CMPO and Eu/CMPO/TBP system at −40°C.

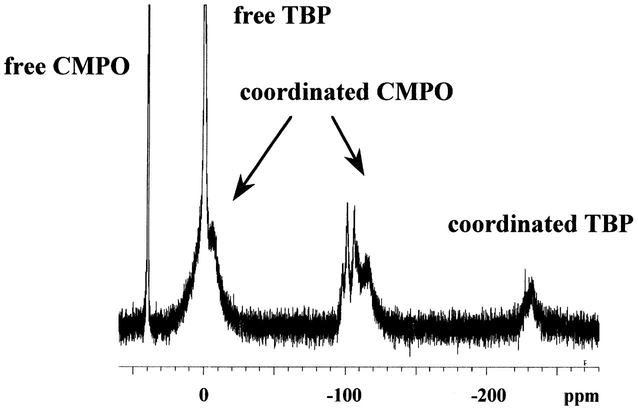
observed. In the Eu/CMPO system, one peak assigned to free CMPO and several peaks for the various isomers of Eu–CMPO complexes [8] are obtained. In the Eu/CMPO/TBP system, signals are observed at almost same position as those assigned to coordinated ligands in the Eu/TBP and the Eu/CMPO systems, which suggests that both TBP and CMPO coordinate to Eu^{3+} ion together in this system. However, several new peaks assigned to coordinated ligands appear, so it is considered that several complexes are produced in which the coordination manner of TBP and CMPO with Eu^{3+} ion is different from those in the Eu/TBP and the Eu/CMPO systems.

Fig. 2 shows the change of the ^{31}P-NMR spectra with the increase of CMPO mole ratio in the Eu/CMPO/TBP system at −40°C. When the mole ratio of CMPO to the Eu^{3+} ion ([CMPO]/[Eu]) is under 3, the intensities and

(a) [Eu]:[CMPO]:[TBP] ≅ 1:0.8:5.5



(b) [Eu]:[CMPO]:[TBP] ≅ 1:3:5.5



(c) Eu/CMPO/TBP system ([Eu]:[CMPO]:[TBP] ≅ 1:7.5:11)

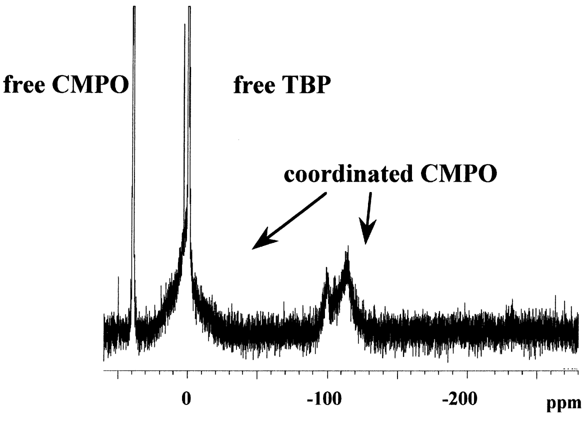


Fig. 2. CMPO concentration dependence of ^{31}P-NMR spectra in Eu/CMPO/TBP system at −40°C.

positions of the peaks for the coordinated TBP and CMPO change with the increase of [CMPO]/[Eu]. It shows that the structures of Eu–CMPO–TBP complexes produced in the Eu/CMPO/TBP system change with [CMPO]/[Eu]. It is also considered that the number of the coordinated TBP with Eu^{3+} ion decreases with the increase of [CMPO]/[Eu] because the intensities of the peaks assigned to the coordinated TBP become smaller.

In the Eu/CMPO/TBP system where [CMPO]/[Eu] is over 3, only the signals for the coordinated CMPO are obtained, and the peaks for the coordinated TBP disappear. These signals are similar to those in the Eu/CMPO system, which suggests that CMPO coordinates to Eu^{3+} ion in the bidentate mode [8]. Therefore, it is considered that in this system only CMPO coordinates to Eu^{3+} ion directly in the bidentate manner and TBP is absent from the first coordination sphere. In order to obtain the detailed information on the structure of Ln complexes in this system, we calculated the Ln–P (phosphoryl) and Ln–C (carbonyl, bridging) distances using the reduced Solomon–Bloembergen equation.

Assuming that the contact contribution to the Ln(III)-induced relaxation rate enhancements is negligible, the longitudinal relaxation time for the paramagnetic Ln (III) complex (T_{1p}), which is corrected for any diamagnetic contributions, can be related to the distances (r) between the Ln (III) ion and the other nucleus in the complex using the following reduced Solomon–Bloembergen equation [10]:

$$\frac{1}{T_{1p}}=\frac{1}{T_{1\mathrm{comp}}}-\frac{1}{T_{1\mathrm{La}}}=\frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)\left(\frac{{\mu_{\mathrm{eff}}}^2\gamma^2\beta^2T_{1e}}{r^6}\right) \qquad (1)$$

Here $\mu_0/4\pi$ is the magnetic permeability under vacuum, μ_{eff} is the effective number of the Bohr magneton, γ is the gyromagnetic ratio of the observed nucleus, β is the Bohr magneton, T_{1e} is the electron spin relaxation time, $T_{1\mathrm{comp}}$ is the longitudinal relaxation time of the nucleus in the complex and $T_{1\mathrm{La}}$ is that of the La^{3+} complex. Fig. 3 shows the ^{31}P-NMR spectra obtained with a 180°–τ– 90° pulse sequence in the Ce/CMPO/TBP system ([Ce]:[CMPO]:[TBP]$\cong$1:3:5). Under this condition, the CMPO exchange reaction between the free and the coordinated states is fast with respect to the ^{31}P-NMR timescale, resulting in the coalescence of the ^{31}P-NMR signals arising from CMPO in those states. In the system where such a fast ligand exchange occurs, the experimental longitudinal relaxation time ($T_{1\mathrm{exp}}$) is given approximately by MacLaughlin and Leigh using the following equation [11]:

$$\frac{1}{T_{1\mathrm{exp}}}=\frac{n\rho}{T_{1\mathrm{comp}}}+\frac{1-n\rho}{T_{1\mathrm{free}}} \qquad (2)$$

Here $T_{1\mathrm{free}}$ is the longitudinal relaxation time of the nucleus in the free ligand, n is the number of CMPO molecules coordinated to the Ln (III) ion and ρ is mole ratio of the Ln (III) ion to CMPO in the system.

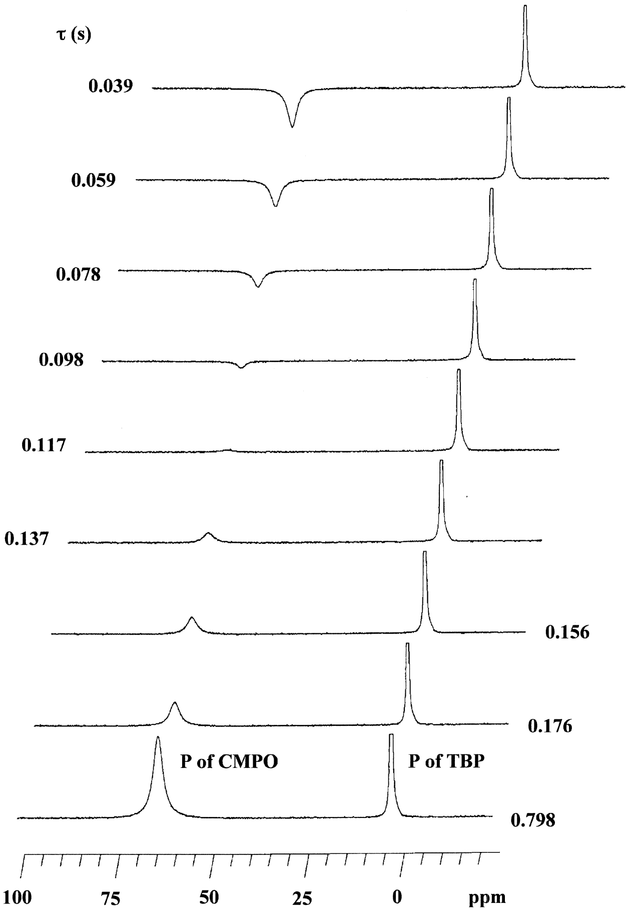


Fig. 3. ^{31}P-NMR spectra measured using the inversion recovery method with a 180°–τ–90° pulse sequence in Ce/CMPO/TBP system ([Ce]:[CMPO]:[TBP]$\cong$1:3:5) at room temperature.

The results of the calculation for r in the Ce/CMPO/TBP and Sm/CMPO/TBP systems are summarized in Table 1. These values were calculated by using $T_{1e}=1.1\times10^{-13}$ and 5.0×10^{-14} s for Ce^{3+} and Sm^{3+} ions, respectively, given by Alsaadi et al. for the Ln(III)–aquo cations [12] and $n=3$ which we previously reported for the condition [CMPO]/[Ln]$>$3 [13]. As shown in this table, the distances from the Ln (III) ion to the other nuclei in CMPO (phosphoryl P, carbonyl C and bridging C) do not differ much in the Ln/CMPO and Ln/CMPO/TBP systems, and it is confirmed that CMPO coordinates to the Ln (III) ion in the bidentate mode in these systems.

Fig. 4 shows the temperature dependence of ^{31}P-NMR spectra observed in the Sm/CMPO and Sm/CMPO/TBP systems. The peaks for the free and the coordinated CMPO coalesce with increasing temperature, which is caused by the exchange reaction between the free and the coordinated CMPO, but its speed in the Sm/CMPO system is faster than in the Sm/CMPO/TBP system. This means that CMPO exchanges more rapidly between the free and the coordinated states in the Sm/CMPO system than in the Sm/CMPO/TBP system. As mentioned above, using the condition [CMPO]/[Ln]$>$3 in the Ln/CMPO/TBP sys-

Table 1
Longitudinal relaxation time ($T_{1\mathrm{exp}}$) for the observed nuclei and distances between Ln^{3+} ion and those in Ln/CMPO and Ln/CMPO/TBP systems at room temperature

Ln/CMPO/TBP (mole ratio)	Nucleus	$T_{1\mathrm{exp}}$ (s)	Distance (Å)
Ce/CMPO (1:3)	Ce–P (phosphate)	0.199	3.82
	Ce–C (bridging)	0.12	3.80
	Ce–C (carbonyl)	0.269	3.31
Ce/CMPO/TBP (1:3:5)	Ce–P (phosphate)	0.192	3.79
	Ce–C (bridging)	0.1	3.66
	Ce–C (carbonyl)	0.34	3.48
Sm/CMPO (1:3)	Sm–P (phosphate)	0.477	4.08
	Sm–C (carbonyl)	1.205	4.06
Sm/CMPO/TBP (1:3:5)	Sm–P (phosphate)	0.486	4.27
	Sm–C (bridging)	0.114	3.43
	Sm–C (carbonyl)	0.97	3.53

tem, TBP does not exist in the first coordination sphere, so it is considered that TBP affects the CMPO exchange reaction from beyond the first coordination sphere. The activation parameters calculated using the CBS (complete bandshape) method for the CMPO exchange reaction in the Ln/CMPO/TBP systems are summarized in Table 2, which we have already reported in the previous paper [13]. The exchange rate constant, *k*, the activation enthalpy, $\Delta H^{\neq}$, and the activation entropy, $\Delta S^{\neq}$, decrease with the increase of TBP concentration in these systems. It shows

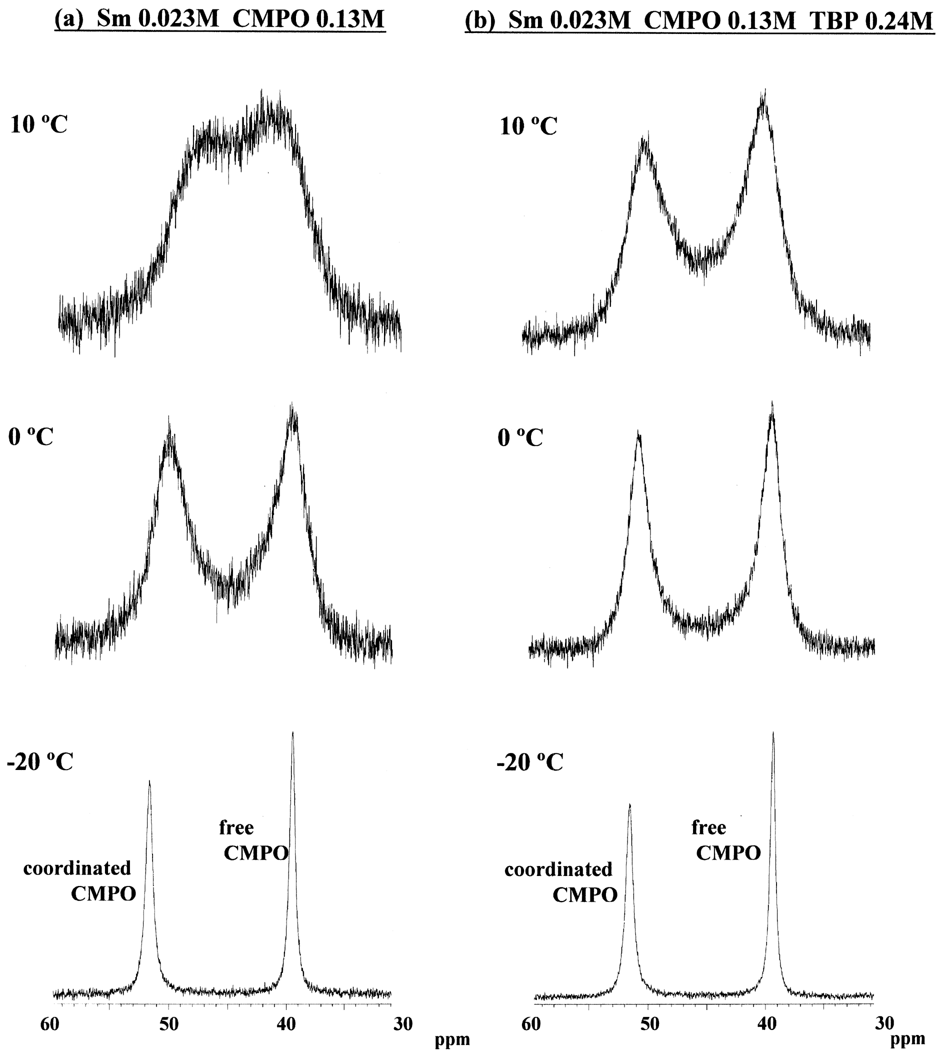


Fig. 4. Temperature dependence of ^{31}P-NMR spectra in Sm/CMPO and Sm/CMPO and Sm/CMPO/TBP systems.

Table 2

Parameters for CMPO exchange reaction in Sm/CMPO/TBP and Pr/CMPO/TBP systems [13][a]

System	TBP (M)	k (300 K) (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})
Sm 0.023 M/CMPO 0.13 M	0.12	$(8.8\pm0.3)\times10^3$	49.7 ± 2.5	-4.1 ± 10.3
	0.24	$(4.0\pm0.3)\times10^3$	39.9 ± 0.8	-43.3 ± 3.1
	0.47	$(2.3\pm0.3)\times10^3$	36.6 ± 1.6	-58.7 ± 6.0
Pr 0.044 M/CMPO 0.24 M	0.24	$(1.6\pm0.03)\times10^4$	48.9 ± 0.7	-1.8 ± 2.8
	0.48	$(1.5\pm0.03)\times10^4$	48.1 ± 0.7	-4.7 ± 2.7
	0.95	$(1.2\pm0.03)\times10^4$	42.0 ± 0.6	-27.5 ± 2.3

[a] Quoted errors represent standard deviations obtained from a linear regression fit of the experimental data to the Eyring equation.

that the change of $\Delta S^{\#}$ with the addition of TBP slows the exchange reaction of CMPO in the Ln/CNPO/TBP systems. Such changes of these parameters seem to be caused by the interaction between the Ln (III) ion and TBP which exist in the second or higher coordination sphere; we consider the following:

$$\mathrm{Ln(NO_3)_3(CMPO)_3} \cdots n\mathrm{TBP} \rightarrow \mathrm{Ln(NO_3)_3(CMPO)_2} \cdots (n+m)\mathrm{TBP} + \mathrm{CMPO}$$

$$\mathrm{Ln(NO_3)_3(CMPO)_2} \cdots (n+m)\mathrm{TBP} + \mathrm{CMPO}^* \rightarrow \mathrm{Ln(NO_3)_3(CMPO)_2CMPO}^* \cdots n\mathrm{TBP}$$

Here an asterisk denotes the exchange species. In this CMPO exchange reaction, $\Delta H^{\#}$ decreases with the increase of TBP concentration because the interaction between the Ln (III) ion and TBP makes the electrostatic attraction between the Ln (III) ion and CMPO weaker. An ordering of the transition state with respect to the ground state increases with TBP, so $\Delta S^{\#}$ also decreases with the increase of TBP concentration.

Thus, in the Ln/CMPO/TBP system where [CMPO]/[Ln] is over 3, TBP does not exist in the first coordination sphere, but affects the CMPO exchange reaction between the Ln (III)–CMPO complex and free CMPO from beyond the first coordination sphere.

4. Conclusions

In the Ln/CMPO/TBP system, it was shown that the structure of the Ln (III) complex changed with the concentration ratio for the CMPO added to the Ln (III) ion, according to the NMR measurements.

When the mole ratio of CMPO to the Ln (III) ion ([CMPO]/[Ln]) is under 3, ^{13}C- and ^{31}P-NMR spectra show that several kinds of complexes are produced, in which both CMPO and TBP coordinate to the Ln (III) ion together, and the contribution of TBP to the coordination with the Ln (III) ion decreases with [CMPO]/[Ln].

In the system where [CMPO]/[Ln] is over 3, only CMPO coordinates to the Ln (III) ion directly in the bidentate manner. According to the calculation with the reduced Solomon–Bloembergen equation, the distances from the Ln (III) ion to phosphoryl P or carbonyl C are estimated to be 3.3~4.3 Å. These are the same coordination properties as those in the Ln/CMPO system. In this condition, TBP is absent from the first coordination sphere of the Ln (III) ion, but affects the CMPO exchange reaction from beyond the first coordination sphere. The rate of the exchange reaction of CMPO decreases with the increase of TBP concentration in the system, which is due to the decrease of the activation entropy. Namely, in this system, a CMPO exchange reaction proceeds via the mechanism with an ordering into the second coordination sphere, which is caused by TBP.

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