Size Selective Extraction of *N*,*N*,*N*′,*N*′-Tetraoctyldiglycolamide and the Structure of Its Divalent Metal Complex

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Using a new extractant, *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA), the dependence of the distribution ratio on the ionic radii for M^{II} was investigated, and their relation with the structures of metal complexes were discussed. Ca^{II} (ionic radius: 100 pm) shows the highest *D* values, and the *D* values decrease with increase and decrease of ionic radius from 100 pm. The geometrical optimization by density functional theory (DFT) of M^{II}–TODGA complex suggests that the carbonyl oxygen has more affinity with metal than the ether oxygen, and the distance between the center of oxygen donor and the edge of cation corresponds to the van der Waals radius of oxygen atom. The most stable complex, as 1:1 complex, can be formed with Mg^{II} from DFT calculation, the complex becomes unstable with increase of ionic radius of M^{II}. This order is good agreement with the magnitude of *D* for Ca^{II}, Sr^{II}, and Ba^{II}.

Coordination of the organic ligand with the metal ion gives a chemical behavior in solutions, many researchers have studied on the structures of metal–ligand complexes. The solvent extraction is a technique to see the chemical reaction between ligand and metal. Extractants have been widely developed in the field of not only the fundamental study but also the applied research. Most of the ligands have their specific size-selectivity, especially the crown ethers and the β-diketones were used to see the selective extraction of lanthanides and actinides.[1–3]

Recently, diglycolamide (DGA) compounds (general formula: $O(CH_2CON(R_1R_2)_2)_2$), neutral ligands, were developed for the actinides recovery from the spent nuclear fuel.[4] DGA compounds have a strong extraction ability for An^{III} and An^{IV}.[5,6] *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide, TODGA, four octyl-groups are attached to N atoms, has a high lipophilic property and high solubility in hydrocarbon diluents. The behavior of seventy-five metals against HNO_3 concentration was revealed. It was obvious that di-, tri-, and tetravalent metals are extracted effectively and that the *D* values by TODGA show the strong dependence of the ionic radii (IR) of metals.[7] The aim of this work is to clarify the size effect and confirm the relation with the chemical structures obtained by DFT calculation.

The purity of TODGA, which was supplied from Kanto Kagaku Co., is more than 98%. The solvent extraction method is as follows; pre-equilibrated TODGA/*n*-dodecane phase was shaken with HNO_3 or $HClO_4$ solution containing metal ions at 25 °C for 60 min. After centrifugation, aliquot of the aqueous phase was diluted to a suitable concentration for ICP-AES or ICP-MS spectrometry. Aliquot of the organic phase was used for the backward-extraction, the condition of the back-extraction was referred by the previous paper.[7] Then, the aqueous solution was diluted to a suitable concentration for ICP-AES and ICP-MS measurements. The distribution ratios (*D*, defined as the ratio of $[M]_o$ in an organic phase vs. $[M]_a$ in an aqueous phase) were obtained.

In order to obtain the information on the structure of M^{II}–TODGA complex, we performed the geometrical optimization by the preliminary DFT calculation at B3LYP/LanL2DZ level of theory. The program used was GAUSSIAN03. The stability at the optimized geometry was checked by a harmonic frequency analysis.[8] All the computations were carried out at the Research Center for Computational Science, Okazaki, Japan.

The *D*(M) values obtained under 0.1 M TODGA/*n*-dodecane and 3 M HNO_3 and 3 M $HClO_4$ are plotted against their ionic radii of the metal ions (Figure 1). The ionic radii of the divalent metals were used from the reference.[9] Some *D* values were obtained from the extrapolation using the log *D* vs. log [TODGA] relations. Figure 1 indicates that 1) metals with the ionic radii of 80–120 pm show very high *D* values, and the metals with smaller than 80 pm and bigger than 120 pm show negligibly small *D* values. The *D* value of Mg^{II}, which is one of the alkaline-earth metals and whose ionic radius is 72 pm, is lower than the detection limit ($D < 10^{-3}$). As shown in Figure 1, TODGA exhibits the size-selective extraction. 2) Ca^{II}, of which the ionic radius is 100 pm, has the highest *D* from both aqueous HNO_3 and $HClO_4$ media. 3) The perchlorate ion can accelerate the ion-pair extraction by the neutral donor, TODGA; however, this effect is hardly observed from Figure 1.

The results of calculation on the structures of metal com-

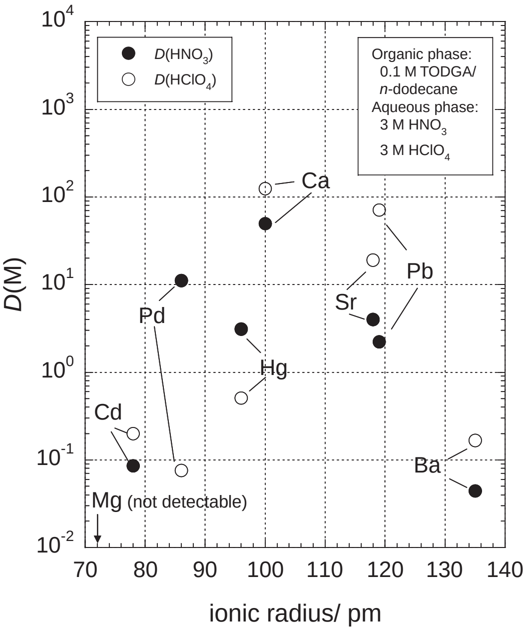

Figure 1. Relation of *D* values with the ionic radii of divalent metals.

Table 1. Bond length of TODGA complex for alkali-earth metals

	Bond length/pm						
	M–O(1)	M–O(4)	O(1)–O(4)	O(1)–O(7)	O(1)–C(2)	C(2)–C(3)	C(3)–O(4)
TODGA (+ Mg)	190.4	200.9	249.8	374.1	131.6	154.9	146.9
TODGA (+ Ca)	224.7	240.2	255.5	412.3	130.1	154.4	146.9
TODGA (+ Sr)	239.5	257.4	257.8	424.4	129.7	154.2	146.8
TODGA (+ Ba)	256.1	278.0	259.1	434.4	129.3	154.0	146.0
TODGA			271.3	469.0	125.3	154.0	144.5

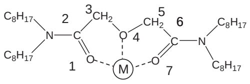

Table 2. Bond angles of TODGA complexes for alkali-earth metals

	Bond angle/°			
	O(1)–C(2)–C(3)	C(2)–C(3)–O(4)	C(3)–O(4)–C(5)	O(1)–O(4)–O(7)
TODGA (+ Mg)	116.2	104.0	122.1	97.0
TODGA (+ Ca)	116.9	106.2	116.1	107.6
TODGA (+ Sr)	117.3	107.0	114.3	110.8
TODGA (+ Ba)	117.7	107.6	113.0	113.4
TODGA	122.2	109.1	111.5	119.6

plexes are summarized, the data on the bond lengths of two atoms and the angles for three atoms are shown in Tables 1 and 2. Preliminary calculation of the alkaline-earth metals in the absence of d- and f electrons was performed, the results were used for discussion. The optimized geometry of metal–TODGA complex belongs to C_s point group. As shown in Table 1, the bond lengths of C(2)–C(3) and C(3)–O(4) are approximately the same, even after the metals are exchanged. On the other hand, the length of O(1)=C(2) is contracted, and those of O(1)–O(4) and O(1)–O(7) are spread out with increase of ionic radii (IR) of metals. As a reference,[10] the related bond lengths, C–C ($C(CH_3)_4$), C=O (HCHO), and C–O (CH_3OCH_3), were reported to be: 154.0, 120.8, and 141.0 pm, respectively. The interatomic distance containing oxygen atom is longer than the reference values. It is clear that the bite size between two oxygen donors increases with IR, the coordinated metals expand the central frame of TODGA. The distance of M–O(1) or M–O(4) depends on IR of metals. IRs of Mg, Ca, Sr, and Ba are 72, 100, 113, and 136 pm (6 coordination), the subtraction of IR from M–O(1) equal to 118.4 (Mg), 124.7 (Ca), 126.5 (Sr), and 120.1 pm (Ba), those for M–O(4) are 128.9 (Mg), 140.2 (Ca), 144.4 (Sr), and 142.0 (Ba), these values except Mg correspond to van der Waals radius of oxygen (140 pm). All of the length of M–O(1) are shorter than M–O(4), which suggests the carbonyl oxygen has more effective coordination than the ether oxygen.

The bond angles are shown in Table 2. The bond angles are varied by metal complexation. The angles of O(1)–C(2)–C(3) and C(2)–C(3)–O(4) increase with IR of metals, on the other hand, C(3)–O(4)–C(5) decreases with IR. The reported values[10] of the atoms with sp^2 and sp^3 hybridized orbital are 121.9 (ethylmethylketone, ∠CCO) and 109.4° (ethylmethylether, ∠CCO). It is noticed that the angle, C(3)–O(4)–C(5), in Mg–TODGA complex is 122.1°, which shows the similar angle to sp^2 hybridized orbital, although these atoms has sp^3 orbitals. Moreover, the angle of O(1)–O(4)–O(7) for Mg–TODGA complex becomes considerably narrow (−22.6°) from the data of TODGA without metal. Because Mg^{II} has small IR, three oxygen donors are close to this metal, with a strong distortion of the central frame.

Table 3. Enthalpy of coordination (ΔH) and net atomic charge (in e) by Mulliken population analysis

	Mg	Ca	Sr	Ba	TODGA
ΔH (kcal/mol)[a]	−299.3	−214.71	−189.0	−164.7	
charge of M	1.419	1.758	1.818	1.844	
charge of O(1)	−0.603	−0.633	−0.620	−0.600	−0.267
charge of O(4)	−0.528	−0.510	−0.489	−0.463	−0.250

[a] $\Delta H = E[M(TODGA)^{2+}] - (E[M^{2+}] + E[TODGA])$.

Table 3 shows the enthalpy (ΔH) and the net atomic charge calculated for M^{II}–TODGA complex. ΔH was estimated from the equation,

$$\Delta H = E[M^{II}\text{–TODGA}] - (E[M^{II}] + E[\text{TODGA}]).$$

The electric energies of M^{II}–TODGA, M^{II}, and TODGA are expressed as $E[M^{II}$–TODGA$]$, $E[M^{II}]$, and E[TODGA], respectively. The ΔH values in Table 3 indicate that M–TODGA complex becomes unstable with increase of IR for M^{II}. The stability can be compared with the D values in Figure 1. Except Mg^{II}, D decreases with IR of alkaline-earth metals, the same order between IR and enthalpy (Table 3) can be seen. The calculation was performed as 1:1 complex of M^{II}:TODGA; however, M^{II} is formed with two TODGA in the organic phase.[7] The reason having the exception of Mg^{II} will be explained after the calculation on 1:2 complex.

The coordination mechanism of TODGA is discussed with the net atomic charge of M^{II} and the oxygen atoms in TODGA. The charges of M (Ch(M)) in Table 3 are lower than +2, the positive charge is partly neutralized by oxygen donation. Ch(M) of Mg^{II} appears to be low compared to other metals, because Mg^{II} has relatively high charge density and forces to be neutralized. The charges of O(1) (Ch(O1)) and O(4) (Ch(O4)) are lower than those for TODGA without metal. It is clear that the negative charge might be accumulated by the electron transfer after metal complexation. The negativity for Ch(O1) is lower than that for Ch(O4), which might be considered as the predominant electron transfer at C=O double bonds.

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