Solvent Isotope Effect in Ion-pair Extraction of Aqueous Lanthanoid(III) Picrates with a Crown Ether

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Lanthanoid-specific, global extractability doubling was achieved without changing the original cation-selectivity sequence by using D_2O, instead of water, as an aqueous phase in the solvent extraction of aqueous light lanthanoid(III) picrates (La^{3+}–Gd^{3+}) with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) in dichloromethane. Under comparable conditions, no appreciable effects were observed with alkali- and alkaline-earth-metal picrates. Quantitative solvent extraction studies using water, D_2O, and their 1 : 1 mixture revealed that the first extraction step, affording a 1 : 1 complex between partially hydrated lanthanoid and the ligand, is exclusively responsible for the solvent isotope effect, while the subsequent sandwich complexation of the 1 : 1 complex with another ligand molecule in the organic phase is not affected by the deuteriated aqueous phase. Thus, the lanthanoid-specific solvent isotope effect is attributed to hydrogen-bond breaking between hydrating water in the first solvation shell and bulk water upon the extraction of incompletely dehydrated lanthanoid ions into the dichloromethane phase.

Since the pioneering works on the complexation behaviour of crown ethers,[1,2] the solvent extraction technique has long been employed as a convenient and useful method for evaluating the cation-binding ability of various types of crown ethers.[3,4] However, there are some intrinsic differences in the cation-differentiation mechanisms operating in the solvent extraction and the similarly popular homogeneous-phase complexation, although both methods usually give consistent results at least for monovalent cations. In solvent extraction, since a metal salt is extracted by crown ether as an ion-pair complex, the lipophilicity of the counter anion plays a definitive role in determining the extractability, so that the highly lipophilic picrate is often employed. On the other hand, the anion effect is minimal in the homogeneous-phase complexation as far as the salt is dissociated. Another point of difference is the role of cation solvation. Since the ion-pair extraction of a metal salt from an aqueous to an organic phase is inherently highly dehydrating,[4,5] the extractability of a crown ether often depends significantly on the hydration energy of the metal ion to be extracted.[6] This becomes crucial with di- and, in particular, trivalent cations which possess much higher free energies of hydration than those of monovalent ones. Thus, the trivalent lanthanoid ions, as compared with mono- and di-valent ions, necessitate roughly ten times higher concentrations of crown ether to afford comparable extractabilities in the extraction of lanthanoid picrates in the water–dichloromethane system.[7] Furthermore, each lanthanoid ion extracted as a sandwich complex with two 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) has been demonstrated to carry three molecules of hydration water into the dichloromethane phase, as revealed by ^1H NMR measurement, and therefore the cation-selectivity sequence obtained in solvent extraction differs substantially from that observed in homogeneous-phase complexation.[7a] In this context, it is interesting to examine the solvent isotope effect on the solvent extraction of aqueous lanthanoid picrates with a crown ether.

In this paper we report our results on the solvent extraction of aqueous light lanthanoid(III) picrates (La^{3+}–Gd^{3+}) dissolved in water, D_2O, and their 1 : 1 mixture with 18-crown-6 in dichloromethane, and discuss the role and effect of hydration water in the extraction process. Part of this work has been communicated.[7b]

Experimental

Materials.—Commercially available 18-crown-6 (Nisso) was used without further purification. Alkali- and alkaline-earth-metal picrates were prepared from the corresponding metal hydroxides (Nakarai) and picric acid (Nakarai), as reported earlier.[6,8] Lanthanoid picrates were prepared in reactions of the corresponding carbonates or oxides (Mitsuwa, Nakarai, Wako, or Rare Metallic Co.) with picric acid, as reported previously.[7a,9] Deuterium oxide of 99.8% D content (Merck) was used as received. Distilled dichloromethane and deionized water were used throughout the study.

Solvent Extraction.—The general procedures employed were described previously.[6,7] The solvents, dichloromethane and water (water, D_2O, or their mixture), were saturated with each other prior to use in order to minimize the volume change in both phases during extraction. Equal volumes (10 cm^3) of a dichloromethane solution of 18-crown-6 (1–150 mmol dm^{-3}) and an aqueous lanthanoid picrate (3 mmol dm^{-3}) were brought to equilibrium by shaking vigorously for 10 min in a Toyo incubator thermostatted at 25.0 ± 0.2 °C. Much lower ligand concentrations (0.5–6 mmol dm^{-3}) were used for most alkali- and alkaline-earth-metal picrates, except for Mg^{2+}, which requires very high ligand concentrations of 100–600 mmol dm^{-3}. The mixture was then allowed to stand for at least 2 h at that temperature in order to complete phase separation. A portion withdrawn from the equilibrated dichloromethane phase was evaporated to dryness *in vacuo*. After appropriate dilution of the residue with water or perchloric acid, both the picrate and metal concentrations were determined by means of UV/VIS spectrophotometry on a Hitachi 228 spectrophotometer and inductively coupled plasma (ICP) atomic emission analysis on a Shimadzu GVM 100P instrument, respectively. Both measurements gave consistent results in all cases.

Table 1 Solvent extraction of aqueous alkali-, alkaline-earth-metal, and lanthanoid picrates in water, water–D_2O (1 : 1), and D_2O solution with 18-crown-6 in dichloromethane[a] and ionic diameters and hydration energies ($-\Delta G_h^{\circ}$) of relevant metal ions

	Ionic diameter/Å				Extractability (%)[e]		
Cation	Crystal[b]	Hydrated[c]	$-G_h^{\circ}$[d]/kJ mol^{-1}	[Ligand]/mmol dm^{-3}	H_2O	H_2O–D_2O	D_2O
Li^+	1.52	7.64	481	3	1.1	f	1.6
Na^+	2.04	7.16	375	3	6.3	f	6.0
K^+	2.76	6.62	304	3	69.0	f	72.1
Rb^+	3.04	6.58	281	3	57.6	f	59.8
Cs^+	3.34	6.58	258	3	36.9	f	37.9
Mg^{2+}	1.44	8.56	1838	3	0.5	f	0.7
Ca^{2+}	2.00	8.24	1515	3	28.5	f	29.9
Sr^{2+}	2.36	8.24	1386	3	84.2	f	84.9
Ba^{2+}	2.70	8.08	1258	3	80.4	f	f
La^{3+}	2.06	9.04	3155	30	12.7	17.4	23.9
Ce^{3+}	2.02	9.04	3209	30	13.9	20.8	25.7
Pr^{3+}	1.98		3251	30	13.2	17.8	24.1
Nd^{3+}	1.97		3287	30	11.7	16.0	20.1
Sm^{3+}	1.92		3332	30	11.1	15.5	19.9
Eu^{3+}	1.89		3370	30	10.0	13.9	18.1
Gd^{3+}	1.88		3385	30	7.4	10.8	15.1

[a] Temperature 25.0 ± 0.2 °C; aqueous phase [water, water–D_2O (1 : 1), or D_2O, 10 cm^3], [picrate] = 3 mmol dm^{-3}; organic phase (CH_2Cl_2, 10 cm^3), [ligand] = 3 or 30 mmol dm^{-3}. [b] Ref. 10; co-ordination number = 6. [c] Ref. 11. [d] Ref. 12. [e] Defined as % picrate extracted into organic phase. [f] Not measured.

In control runs, only negligible amounts of lanthanoid picrates were extracted into the organic phase in the absence of the ligand (extractability < 0.3%), for which appropriate corrections were made.

Results and Discussion

Extraction Equilibria.—As has been demonstrated previously,[7] the lanthanoid picrates preferentially form sandwich complexes with 18-crown-6 through a two-step equilibrium between the aqueous lanthanoid picrate (LnA_3) and the ligand (L) in the organic phase. The stepwise complexation comprises the first extraction step giving the stoichiometric complex $[LnLA_3]$(org) [equation (1)] and the second sandwich complexation in the organic phase producing the 1 : 2 cation : ligand complex $[LnL_2A_3]$(org) [equation (2)].

$$Ln^{3+}(aq) + 3A^-(aq) + L(org) \xrightleftharpoons{K_1} [LnLA_3](org) \quad (1)$$

$$[LnLA_3](org) + L(org) \xrightleftharpoons{K_2} [LnL_2A_3](org) \quad (2)$$

Experimentally, the first (β_1) and overall (β_2) extraction equilibrium constants can be determined, where $\beta_1 = K_1$ and $\beta_2 = K_1K_2$. The overall extraction equilibrium is expressed by equation (3). The extraction equilibrium constants β_n (n = 1 or 2) are given by equation (4) where the distribution ratio (D) of lanthanoid ion between the organic and aqueous phases is given by equation (5). Modification of equation (4) leads to (6).

$$Ln^{3+}(aq) + 3A^-(aq) + nL(org) \xrightleftharpoons{\beta_n} [LnL_nA_3](org) \quad (3)$$

$$\beta_n = D/[A^-]_{aq}^3[L]_{org}^n \quad (4)$$

$$D = [LnL_nA_3]_{org}/[Ln^{3+}]_{aq} \quad (5)$$

$$\log(D/[A^-]_{aq}^3) = n \log [L]_{org} + \log \beta_n \quad (6)$$

Extractability and Extraction Equilibrium Constant.—Solvent extractions using water and D_2O as an aqueous phase were first performed at a given concentration of aqueous alkali-, alkaline-earth-metal, or light lanthanoid picrate (3 mmol dm^{-3}) and of 18-crown-6 (3 or 30 mmol dm^{-3}). The higher ligand concentration of 30 mmol dm^{-3} was needed for the lanthanoid picrates to give reproducible moderate extractabilities. The percent extractabilities obtained for alkali-, alkaline-earth-metal, and light lanthanoids in both water and D_2O are listed comparatively in Table 1, along with some relevant properties of the metal ions: crystal[10] and hydrated[11] diameters and free energies of hydration ($-\Delta G_h^{\circ}$).[12]

For more quantitative and comprehensive understanding of the solvent isotope effect, the complexation stoichiometry (n) and the extraction equilibrium constants (K_{ex} and β_n) for alkali-, alkaline-earth-metal, and lanthanoid picrates were determined for the solvent extractions using water and D_2O. The quantitative solvent extraction experiments were carried out in the dichloromethane–water system at 25 °C with a fixed picrate concentration and varying ligand concentrations. A set of percentage extractabilities obtained at different ligand concentrations were analysed by equation (6) according to the procedures reported previously[6–8] to give the equilibrium constants K_{ex} for the dinuclear 2 : 1 complexation[13] of Li^+ and the stoichiometric 1 : 1 complexations of Na^+–Cs^+ and Mg^{2+}–Sr^{2+}, and β_n (n = 1 or 2) for the stoichiometric 1 : 1 and sandwiching 1 : 2 complexation of lanthanoids. The results are listed in Tables 2 and 3.

Solvent Isotope Effects.—As can be readily recognized from the extraction data in Table 1, the use of D_2O as an aqueous phase dramatically facilitates the extraction of lanthanoid picrates, while essentially no solvent isotope effect is observed for alkali- and alkaline-earth-metal picrates. Thus, the extractabilities are doubled for all lanthanoids without any appreciable change in the original cation-selectivity sequence in water. The practically invariable extractabilities of all alkali-metal picrates in water and D_2O are readily justifiable and need no further explanation in view of their low energies of hydration[12] and the analogous relative cation selectivities observed in the solvent extraction and the homogeneous-phase complexation.[6,8b]

On the other hand, the similarly invariable extractabilities for alkaline-earth-metals in water and D_2O are somewhat unexpected, since the solvent extraction and the homogeneous-phase complexation give different cation selectivities for alkaline-earth-metals,[6] for which the much higher energies of

Table 2 Extraction equilibrium constants for stoichiometric 1:1 or dinuclear 2:1* complexation of aqueous alkali- and alkaline-earth-metal picrates in water and D_2O with 18-crown-6

	log K_{ex}							
Aqueous phase	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
H_2O	7.43[a]	3.89	6.20	5.96	5.17	3.99	7.16	10.1
D_2O	7.53[a]	3.83	6.38	5.95	5.17	4.07	7.38	9.69

* With lithium picrate, only the dinuclear 2:1 cation–ligand complex is extracted upon solvent extraction with 18-crown-6 in dichloromethane,[13] so that the K_{ex} values for Li^+, possessing a different dimension, should not be compared directly with those for other cations.

Table 3 Overall and stepwise extraction equilibrium constants (β_n and K_n,* respectively) for stoichiometric 1:1 and sandwiching 1:2 complexations in solvent extraction of aqueous lanthanoid picrates in water or D_2O with 18-crown-6 in dichloromethane at 25 °C

Binding constant*	Aqueous phase	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
log β_1	Water	7.05	7.07	6.95	6.79	6.57	6.52	6.55
	D_2O	7.52	7.57	7.41	7.15	7.03	6.90	6.89
log β_2	Water	8.66	8.71	8.73	8.70	8.68	8.63	8.43
	D_2O	9.14	9.20	9.27	9.16	9.17	9.10	8.94
log (β_2/β_1)	Water	1.61	1.64	1.78	1.91	2.11	2.11	1.88
	D_2O	1.62	1.63	1.86	2.01	2.14	2.20	2.05

* $K_1 = \beta_1$, $K_2 = \beta_2/\beta_1$.

Table 4 Distribution ratios (*D*) of lanthanoid ions between organic and aqueous phases in solvent extraction of aqueous lanthanoid picrates in water, water–D_2O (1:1), and D_2O with 18-crown-6*

Aqueous phase	Distribution ratio	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
Water	D_{HH}	0.145	0.161	0.152	0.132	0.125	0.111	0.080
Water–D_2O	D_{HD}	0.211	0.263	0.217	0.190	0.183	0.161	0.121
D_2O	D_{DD}	0.314	0.348	0.318	0.252	0.248	0.221	0.178
	D_{HD}/D_{HH}	1.46	1.63	1.43	1.44	1.46	1.45	1.51
	D_{DD}/D_{HD}	1.49	1.32	1.47	1.33	1.36	1.37	1.47
	D_{DD}/D_{HH}	2.17	2.16	2.09	1.91	1.98	1.99	2.23

* $D = [Ln^{3+}]_{org}/[Ln^{3+}]_{aq}$.

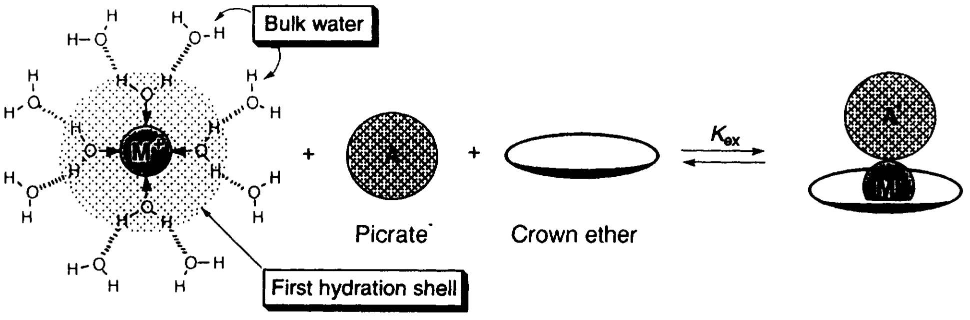
hydration,[14] especially for the smaller Mg^{2+} and Ca^{2+}, are thought to be responsible.[6] However, the deuterium isotope effect on the hydration energy of metal ions is trivial as judged from the enthalpies of transfer from water to D_2O (1.9–3.0 kJ mol^{-1} for Li^+–Cs^+ and 5.4–6.1 kJ mol^{-1} for Ca^{2+}–Ba^{2+})[14] which are almost negligible as compared with the absolute hydration enthalpy (522–274 kJ mol^{-1} for Li^+–Cs^+ and 1584–1314 kJ mol^{-1} for Ca^{2+}–Ba^{2+}).[12] Hence, the cation hydration is not considered to be affected significantly by the primary deuterium isotope effect, simply because a hydrated cation in water is co-ordinated by the oxygen atoms of hydrating water molecules in the first solvation shell, and their hydrogen/deuterium atoms do not directly interact with the cation but are rather hydrogen bonded to the surrounding bulk water. In conclusion, the negligible isotope effect on the extractabilities of alkali- and alkaline-earth-metal picrates indicates that the solvent extraction of these mono- and di-valent metal picrates does not involve any process(es) that cause extensive breaking/formation of the hydrogen-bond network around the hydrated cation, and further supports our belief that these and earth ions are dehydrated completely upon extraction.

The possible role of the selective solvation by water or D_2O was also examined semiquantitatively by performing solvent extraction of lanthanoid picrates in a 1:1 mixture of water and D_2O. As shown in Table 1, for each lanthanoid, the extractability obtained is approximately the average of those obtained with pure water and D_2O. For a more quantitative comparison, the metal distribution ratios between the organic and aqueous phases (D_{HH}, D_{HD} and D_{DD} for water, water–D_2O and D_2O, respectively) and their relative ratios (D_{HD}/D_{HH}, D_{DD}/D_{HD} and D_{DD}/D_{HH}) were calculated. As can be seen from Table 4, the overall isotope effect induced by the use of D_2O is quite similar for all lanthanoids, giving an average of $D_{DD}/D_{HH} = 2.08 \pm 0.12$. Interestingly, the overall isotope effect (D_{DD}/D_{HH}) is composed of stepwise isotope effects of the same magnitude within experimental error ($D_{HD}/D_{HH} = 1.48 \pm 0.07$ and $D_{DD}/D_{HD} = 1.40 \pm 0.07$) for stepwise increments in the deuterium content of aqueous phase from 0 to 50 and then to 100%. The coincidence of the stepwise isotope effects means that the distribution ratio *D* increases linearly with the solvent deuterium content to give the ultimate value at 100% D_2O. This in turn indicates that no selective solvation of the lanthanoid ions occurs in the mixed aqueous phase and the lanthanoid-specific enhancement of extractability cannot be attributed to selective solvation.

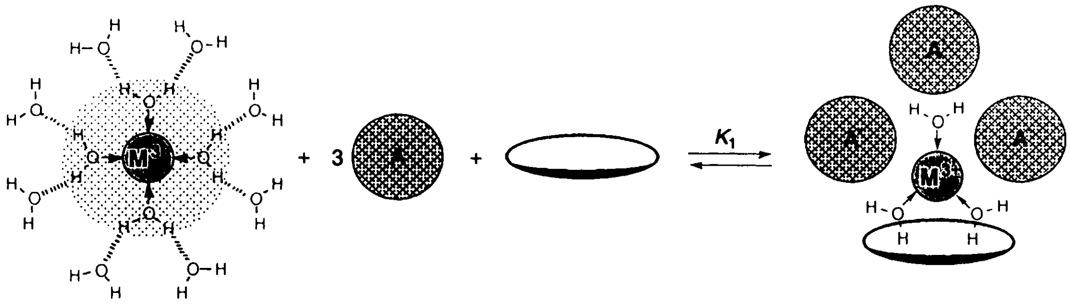
In this context, it is also inadequate to rationalize the lanthanoid-specific extractability enhancement in terms of the much higher hydration energies of trivalent lanthanoid ions: 3155–3385 kJ mol^{-1} (Table 1). Alternatively, the incomplete dehydration of lanthanoid ions upon extraction into the dichloromethane phase,[7a] which is also specific to the lanthanoids, is considered to play a significant role. As illustrated in Scheme 1, alkali- and alkaline-earth-metal picrates, which are completely dehydrated upon extraction with a crown ether, do not suffer from the primary deuterium isotope effect, since only the co-ordination of solvent oxygens to the metal ion is broken upon extraction. On the other hand, the extraction of more strongly hydrated lanthanoid ions occurs only through the partial dehydration which accompanies breakage of hydrogen bonds between the hydrating water in the first hydration shell and the bulk water (Scheme 1), which inevitably suffers from the primary isotope effect.

This scheme is further supported by the stepwise extraction equilibrium constants shown in Tables 2 and 3. As anticipated from the extractability data shown in Table 1, the K_{ex} values for alkali- and alkaline-earth-metal picrates show no appreciable

(a) Alkali-metal picrates



(b) Lanthanoid picrates



Scheme 1 Desolvation upon solvent extraction

solvent isotope effect. This result merely confirms the lack of hydrogen-bond cleavage upon ion-pair extraction of the mono- and di-valent metal picrates into the organic phase, and is no longer particularly interesting.

In contrast, the stepwise equilibrium constants for lanthanoid picrates provide us with further insights into the solvent isotope effect in the ion-pair extraction. The values in Table 3 unequivocally demonstrate that the lanthanoid-specific solvent isotope effect arises solely from the first extraction step [equation (1)] as discussed above using Scheme 1, while the second sandwich complexation in the organic phase [equation (2)] is absolutely independent of the solvent isotope effect. These results strongly support our incomplete dehydration model for the ion-pair extraction of heavily hydrated lanthanoid ions.

Finally, we would like to emphasize that the use of D_2O as an aqueous phase in solvent extraction may serve as a useful and general tool to enhance the extraction efficiency of trivalent metal ions like lanthanoids and actinoids, keeping both the original cation-selectivity sequence and the extractabilities for mono- and di-valent ions invariant.

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