Deuterium Oxide-enhanced Extraction of Aqueous Lanthanoid Picrates with Crown Ether

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Extractabilities of lanthanoid picrates are doubled by the use of D_2O, instead of H_2O, as an aqueous phase in the solvent extraction with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), whereas no appreciable enhancement is found in the extractabilities of alkali and alkaline earth picrates.

Solvent extraction has long been employed as a convenient and useful method for evaluating the cation-binding ability of crown ethers.[1] The extraction of a metal salt, mostly picrate, from aqueous to organic phase is inherently dehydrating, and, therefore, the extractability of crown ether significantly depends on the hydration energy of metal ion to be extracted.[2] This is especially remarkable with di- and tri-valent cations possessing high free energies of hydration; ΔG^0 values are 60–90 and 300–450 kcal mol^{-1} (1 cal = 4.184 J) for common alkali and alkaline earth ions, but soar up to 750–850 kcal mol^{-1} for lanthanoid(III) ions.[3] Thus, the tri-valent lanthanoids, as compared with the mono- and di-valent metals, demand roughly ten times higher concentrations of crown ether to afford moderate extractabilities in the extraction of lanthanoid picrates in the water–dichloromethane system.[4] Furthermore, each lanthanum ion extracted as a sandwich complex with two 18-crown-6 was demonstrated to carry three water molecules into the dichloromethane phase by the ^{1}H NMR measurement. In this context, it is interesting to perform the solvent extraction of lanthanoid picrates dissolved in heavy water and discuss the role and effect of hydration water in the extraction process.

The solvent extractions of aqueous lanthanoid (La^{3+}–Gd^{3+}) picrates (3 mmol dm^{-3}) with 18-crown-6 (30 mmol dm^{-3}) were performed comparatively in light and heavy water–dichloromethane systems at 25 °C, according to the established procedures.[4–6] For comparison, some alkali (Na^+ and K^+) and alkaline earth (Mg^{2+} and Ca^{2+}) picrates 3 mmol dm^{-3}) in H_2O and D_2O were similarly extracted with 18-crown-6 (3 mmol dm^{-3}) in dichloromethane under comparable extraction conditions except for the ligand concentration; note that a ten times higher ligand concentration was employed for the lanthanoids due to their extremely low extractabilities around 1% at 3 mmol dm^{-3} of the ligand.[4] The % extractabilities (% Ex) and the metal distribution coefficients (D_M) between organic and aqueous phases are listed in Table 1.

In sharp contrast to the practically identical % Ex, or D_M, values obtained in the solvent extractions of aqueous alkali and alkaline earth picrates from the H_2O and D_2O solutions,

Table 1 Percent extractability (% Ex)[a] and metal distribution coefficient (D_M)[b] in solvent extraction of alkali, alkaline earth and lanthanoid picrates in H_2O or D_2O with 18-crown-6[c]

Aqueous phase	Binding constant	Alkali		Alkaline earth		Lanthanoid						
		Na^+	K^+	Mg^{2+}	Ca^{2+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
H_2O	% Ex	6.3[d]	69.0[d]	0.5	28.5	12.7	13.9	13.2	11.7	11.1	10.0	7.4
	D_M	0.07	2.23	0.005	0.40	0.15	0.16	0.15	0.13	0.13	0.11	0.08
D_2O	% Ex	6.0	72.1	0.7	29.9	23.9	25.7	24.1	20.1	19.9	18.1	15.1
	D_M	0.06	2.58	0.007	0.43	0.31	0.35	0.32	0.25	0.25	0.22	0.18

[a] Defined as % picrate extracted into organic phase; error ±0.5%. [b] Defined as % Ex/(1 − % Ex). [c] Temperature 25.0 ± 0.2 °C; aqueous phase (10 cm^3): [picrate] = 3.0 mmol dm^{-3}; organic phase (CH_2Cl_2, 10 cm^3): [18-crown-6] = 3.0 mmol dm^{-3} for alkali and alkaline earth metals and 30 mmol dm^{-3} for lanthanoids. [d] Ref. 5.

the use of heavy water as an aqueous phase dramatically enhances the % Ex values for the lanthanoids. The distribution coefficient D_M, as a more quantitative measure of the extraction equilibrium constant,[4,5] increases by a factor of two for all light lanthanoids examined without any appreciable change of the original cation selectivity sequence in H_2O.

The identical % Ex values for alkali picrates in H_2O and D_2O seem reasonable in view of their low energies of hydration[3] and the same relative cation selectivities exhibited in the homogeneous solution and in the heterogeneous solvent extraction reported previously.[2,5] However, the similarly invariant % Ex for alkaline earths are somewhat unexpected, since they show a different cation selectivity sequence in the homogeneous and heterogeneous systems,[2] which has been rationalized in terms of the higher energies of hydration for divalent alkaline earths. The present result is probably due to the trivial difference between light and heavy water in the hydration energy of alkali and alkaline earth metal ions; the enthalpy of transfer from H_2O to D_2O is 0.6–0.7 kcal mol^{-1} for alkalis and 1.3–1.5 kcal mol^{-1} for alkaline earths.[7]

Pending further studies, the specific enhancement for lanthanoids may for the moment be accounted for in terms of their high energies of hydration around 800 kcal mol^{-1}.[3] In addition, the incomplete dehydration upon extraction into the dichloromethane phase,[4] which is also specific to lanthanoid ions, must play a significant role, since in such a case the extraction accompanies the break of hydrogen bonds between the hydrating water in the first solvation shell and the bulk water. Although further mechanistic and quantitative studies may be needed, practically, the use of heavy water as an aqueous phase may serve as a useful and powerful tool to enhance the extraction efficiency of trivalent metal ions like lanthanoids and actinoids, keeping extractabilities for mono- and di-valent ions invariant.

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