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Macrocyclic Reagents for the Kinetic Control of Chelate Extraction Selectivities of Lanthanides

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In a search for new selectivities in metal complex formation, we have recently embarked on a systematic study of lanthanide (Ln) complexes of ionizable macrocyclic ligands. By varying the size of the macrocycle, novel complex formation selectivity has been observed [1, 2]. This thus allowed unique selectivity in chelate extraction of metal species at both low and relatively high pH [3]. In particular, a kinetic control of extraction selectivity can be envisaged at high pH and the preliminary information is reported in this communication.

Experimental

In competitive extraction experiments, aqueous phase comprised a mixture of either La and Yb or La and Eu at pH 7.5. Concentration of each lanthanide was maintained at 1.8×10^{-4} M and of DAPDA at 3.6×10^{-4} M. Ionic strength of the aqueous phase was adjusted to 0.2 with tris(hydroxymethyl) amino methane (Tris) buffer and tetramethyl ammonium chloride. The organic phase contained 3.3×10^{-3} M TTA in benzene. The volume of each phase was maintained at 6.0 ml and the mixing was carried out just before the shaking was started. Burrell wrist action shaker set at 280 oscillations per minute was used for equilibration experiments. The two phases were separated immediately after the required equilibration period and the aqueous phase was centrifuged to remove any suspended microdroplets of benzene from the aqueous phase. The aqueous phase was carefully separated and its pH was measured using a Fisher combination pH electrode and a Fisher model 825 mP pH meter. Acidity of the aqueous phase was adjusted to ~0.1 M before metal analysis by adding 0.05 ml of concentrated HCl to approximately 5.0 ml of the aqueous phase. Concentration of lanthanide ion in aqueous phase was measured by d.c. plasma emission spectroscopic technique as described earlier [3, 4].

Results and Discussion

Previous studies using thenoyltrifluoroacetone (HTTA) as the extractant for various lanthanide ions at low pH, e.g. pH 4, have shown that the tris complex, $Ln(TTA)_3$, is the extracted species [5, 6]. However, when an ionizable macrocyclic reagent such as 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (H_2L or K21DA) is used to form primary Ln complexes at pH 7.5, different results were obtained. For lighter lanthanides such as lanthanum, ternary complex, [La(L)(TTA)], is the major extracted species in the organic phase [4]. On the other hand, for heavy lanthanides such as ytterbium and lutetium, binary tris complex of the form $Ln(TTA)_3$ is dominant [3], presumably due to their smaller size which precludes the formation of strong ternary complex. The overall extraction is greater for the heavy lanthanides [3] which implies that under identical conditions, thermodynamic factors are not in favor of lighter lanthanides if competitive extractions are performed.

Figure 1 presents a simplified suggested distribution mechanism for the chelate extraction. It is obvious to conclude that the dissociation of the primary complex is the rate determining step for the extraction of heavy lanthanides for which equilibria are achieved in the order of several hours [7]. On the other hand, the extraction of the ternary lighter lanthanide species takes only minutes because formation of such complexes is in general very fast. (According to the Eigen's mechanism and data obtained [8], the pseudo-first-order rate constants for lanthanide complex formation with simple ligands are normally about 10^7–10^8 s^{-1}). Thus under suitable conditions, it is possible to alter chelate extraction selectivity by kinetic control. This is illustrated by the competitive extraction experiment described in Fig. 2 which shows the plots of % extraction (% *E*) of both La(III) and Yb(III) as a function of equilibration time. Indeed the extraction

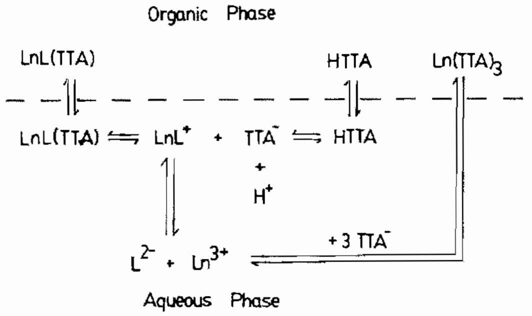

Fig. 1. A simplified suggested distribution mechanism for the chelate extraction involving ionizable macrocyclic ligands.

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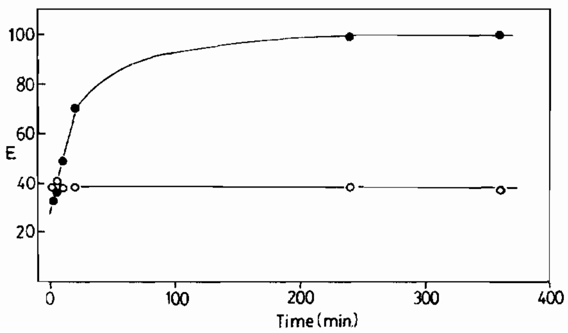

Fig. 2. Competitive extraction of La(III) and Yb(III) at pH 7.5 in the presence of 3.6×10^{-4} M K21DA. [HTTA] = 3.3×10^{-3} M, [La^{3+}] = 1.8×10^{-4} M (○), [Yb(III)] = 1.8×10^{-4} M (●).

reached equilibrium within twenty minutes for La(III) but it took roughly five hours for Yb(III). The extraction favored La(III) when less than ten minutes equilibration time was given and the selectivity approached the one predicted according to thermodynamic parameters after several hours. Similar observation on La(III)/Eu(III) system was also made in the present work.

The use of ionizable macrocyclic ligand such as 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (H_2L) in aqueous phase and extractant such as thenoyltrifluoroacetone (HTTA) in benzene has allowed the thermodynamically unfavored ternary complex, [La(L)(TTA)], to be extracted faster than the thermodynamically favored binary complex, [$Yb(TTA)_3$].

The present report on the kinetic control of chelate extraction selectivities of lanthanides is the first involving the use of macrocyclic ionophore. Earlier publications on the kinetic studies of lanthanides extraction in the presence of classic complexing agents like EDTA [9] and DTPA [10] in the aqueous phase did not involve the extraction of such ternary species. Consequently the rate of extraction of lanthanides increased only marginally with the decrease of atomic number in such studies. The application of the concept developed in this communication for extraction selectivity should be of great potential due to the significant difference in the rate of extraction of lighter and heavier lanthanides.

Acknowledgements

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