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Am (III)/Eu (III) separation at low pH using synergistic mixtures composed of carboxylic acids and neutral nitrogen polydendate ligands

P.Y. Cordier[a,*], C. Hill[a], P. Baron[a], C. Madic[a], M.J. Hudson[b], J.O. Liljenzin[c]

[a]CEA-Valrhô DCC/DRDD/SEMP, Marcoule, BP 171, 30207 Bagnols-sur-Cèze, Cédex, France
[b]Department of Chemistry, University of Reading, Box 224, Whiteknights, Berkshire RG6 2AD, UK
[c]Department of Nuclear Chemistry, Chalmers University of Technology, S-41296 Göteborg, Sweden

Abstract

This paper deals with a potential An(III)/Ln(III) separation system based on the use of synergistic systems composed of α-substituted carboxylic acids and polydendate nitrogen soft donor ligands, 2,2′:6′,6″ terpyridine (Tpy) and 2,4,6-tri-2-pyridyl-1,3,5-triazine (TPTZ), and their respective lipophilic derivatives. The first experiments concern Am(III)/Eu(III) separation as a model for An(III)/Ln(III) group separation. © 1998 Elsevier Science S.A.

Keywords: Extraction; An(III)/Ln(III) separation; Synergistic systems

1. Introduction

It is well known that the An(III)/Ln(III) separation by liquid-liquid extraction is a difficult problem, owing to the similarities of the properties of these cations in solution [1]. For some years now [2], the possibility to use soft donor ligands (according to Hard and Soft Acid Base theory, HSAB [3]) for such separation was investigated, giving interesting results [4,5].

The goal of our work was to obtain An(III)/Ln(III) separation from nitric acid solutions (superior to 0.1 mol/l).

In this paper we report on results related to the study of synergistic mixtures made of α-bromodecanoic acid and polydendate nitrogen ligands for the separation of Am(III) over Eu(III). The nitrogen ligands selected are: (i) the 2,4,6-tri-2-pyridyl-1,3,5-triazine (TPTZ) [6], (ii) the 2,2′:6′,6″ terpyridine (Tpy) [7,8], and (iii) some of their lipophilic derivatives [9].

2. Experimental procedure

2.1. Chemicals

Acid, (HA): α-bromodecanoic acid (98% purity) was from Fluka.

Nitrogen polydendate ligands, (L): TPTZ and Tpy were Aldrich analytical grade reagents. Tritertiarybutyl-tripyridyltriazine (T^tBPTZ) was synthesised at Reading. The Tpy lipophilic derivatives, 4-*n*-octyl-terpyridine (C_8Tpy) and tritertiarybutyl-terpyridine (T^tBTpy) were synthesised by Panchim (Lisses, 91, France). Purity of the new molecules was determined by elemental analysis, gas chromatography, NMR and mass spectrometry.

Diluent: hydrogenated tetrapropene (TPH) from Prochrom (Champignols, 54, France), was used.

2.2. M(III) extraction procedure and measurement of L distribution ratio

Extractions of Am(III) and Eu(III) at tracer levels were performed using ^{241}Am and ^{152}Eu (γ counting at 59.54 keV and 121.78 keV for ^{241}Am and ^{152}Eu, respectively). Organic and aqueous phases were mixed for 30 min at 22°C. Distribution ratios D_M were calculated according to the equation $D_M=[\text{Activity}]_{org}/[\text{Activity}]_{aq}$; $[\text{Activity}]_{org}$ and $[\text{Activity}]_{aq}$ being the radioactivity (in counts/s) of ^{241}Am or ^{152}Eu at equilibrium for equal volumes of organic and aqueous phases, respectively. Separation factors $SF_{Am/Eu}$ were calculated as D_{Am}/D_{Eu} ratio for the same experimental conditions.

The measurements of the solubility in organic and aqueous phases and distribution of the nitrogen ligands L were carried out by spectrophotometry of the intensely coloured Fe(II) complexes with L. Absorbance measure-

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*Corresponding author. Tel.: +33 4 66791610; fax: +33 4 66791649.

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ments were carried out at 553 nm for Tpy-family complexes and 600 nm for TPTZ-family complexes.

3. Results and discussion

For aliphatic diluents, where carboxylic acids exist as dimers, the M^{3+} extraction reaction can be written as in (1):

$$M^{3+}_{aq} + m\overline{(HA)_2} + n\overline{L} \overset{K_{ex}}{\leftrightarrow} \overline{ML_nA_3(HA)_{2m-3}} + 3H^+ \qquad (1)$$

with upper bars for organic phase bearing species.

To a certain extent, Eq. (1) is a simplified presentation of the system because L possibly exists into the organic phase as a hydrogen bound complex with HA molecules. Nevertheless, Eq. (1) was proven a good basis in particular for the reference system made of α-bromodecanoic acid and TPTZ [6].

According to Eq. (1), the distribution ratio D_M is strongly dependent on the acidity of the aqueous phases.

The main route to improve the system (α-bromodecanoic acid and TPTZ) studied by Vitorge [6] is to use more lipophilic ligands. This can be done by:

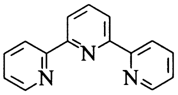
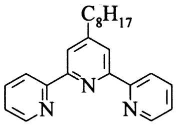
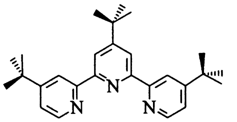
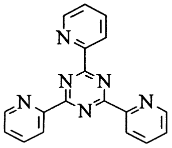
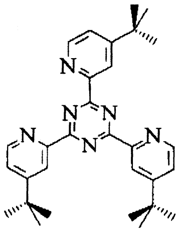
1. increasing the lipophilia of the terdendate TPTZ by branching alkyl groups within the structure of the TPTZ molecule. This will prevent important losses, certainly connected with the protonation of the molecule, in aqueous nitric acid phase;
2. replacing the TPTZ by another terdendate nitrogen ligand, with a similar coordination site for M(III) ions, the Tpy, of which the synthesis of lipophilic derivatives, by branching alkyl groups onto the Tpy structure, are easier than for TPTZ.

3.1. Solubility in solvents and distribution ratio of ligands (L)

It was necessary, preliminary to Am(III)/Eu(III) separation study, to determine the solubility limit of these L molecules in TPH and (TPH+HA) solution, firstly to determine the practical L concentration range, and secondly to study the effect of the lipophilisation of TPTZ and Tpy molecules on the washing out effect of these molecules from organic solutions, when contacted with acidic aqueous solutions. Table 1 presents the solubility of L in TPH and in 1 mol/l HA/TPH solution at room temperature.

All ligands L exhibit very low solubility in TPH (except C_8Tpy). Nevertheless, branching alkyl groups on the TPTZ and Tpy platforms induces definite increases in

Table 1
Solubility in TPH and HA (1 mol/l) TPH solution of some terdendate nitrogen ligands (room temperature)

Molecule	Acronym	MM (g/mol)	Solubility in TPH (mol/l)	Solubility in HA 1 mol/l in TPH (mol/l)
	Tpy	233.3	0.06	>0.5
	C_8Tpy	345.5	0.5	>0.7
	T^{t}BuTpy	401.6	0.02	>0.3
	TPTZ	312.3	0.0002	>0.1
	T^{t}BPTZ	480.7	0.002	0.05

these solubilities (except for T^{t}BTpy) (Table 1). The increase of L solubility in the presence of HA is certainly connected with the formation of adducts between L and HA molecules, possibly formed through hydrogen bonds between the OH group of the carboxylic acid and the nitrogen atoms of L.

Fig. 1 presents the variations of the overall distribution ratio D_L vs. the aqueous nitric acid concentration at equilibrium for TPTZ and Tpy families of molecules. The beneficial effect of the lipophilisation of the molecules is clearly shown: D_L values are increased by several orders of magnitude.

Considering that: (i) L and L/HA adducts are more lipophilic than the protonated L species formed through interactions of L with nitric acid, and (ii) D_L represents the overall distribution ratio of L in their different forms between the liquid phases, let us now try to propose a qualitative interpretation of these results.

- For TPTZ and T^{t}BPTZ, a continuous decrease of D_L is observed between 0.01 and 1 mol/l HNO_3 aqueous concentration. Those data are consistent with the multiple protonations of TPTZ and its low basicities [6]; the less basic sites being not fully protonated when the organic phase is in contact with 1 mol/l nitric acid solution. This is also consistent with the slight difference in the basicities of the different basic sites of TPTZ (no apparent steps in the decreasing curve D_L vs. $[HNO_3]$). Without any quantitative treatment of those data, we cannot conclude regarding the modification of the basicity of the basic sites of TPTZ owing to branching of tertiarybutyl groups onto the TPTZ skeleton.
- For Tpy, a three orders of magnitude decrease of D_L is observed between 0.01 and 1 mol/l HNO_3 solutions. The same explanation as those for TPTZ can be proposed for these data; nevertheless, as the decrease of D_L is less for Tpy than for TPTZ, this possibly means that a fewer number of sites are protonated for the former molecule than for the latter. For C_8Tpy the patterns obtained are different. Decrease in D_L is observed between 0.008 and 0.1 mol/l aqueous HNO_3 concentrations, then D_L remains almost constant. This can mean that the last basic site is fully protonated for $[HNO_3]>0.5$ mol/l, and the constant D_L value thus corresponds to the most protonated unique LH_n^{n+} species. Comparing the data between Tpy and its alkylated derivative, we can conclude that the lipophilisation of Tpy has two consequences: first, a large increase of D_L value and second an increase of the basicity of the less basic site of the molecule. Note that we cannot conclude regarding the effect of the lipophilisation of Tpy on its more basic sites.

3.2. Am(III)/Eu(III) separation with the new synergistic systems

The new terdendate nitrogen ligands L were compared with TPTZ, in synergistic combination with HA, in their ability to extract selectively Am(III) over Eu(III) from aqueous acidic nitric solutions. Results related to TPTZ and Tpy families of molecules are presented in Fig. 2 and Fig. 3, respectively.

- For each new synergistic system studied, reasonably high (≈10) separation factors $SF_{Am/Eu}$ are observed (see Table 2). The almost identical values of $SF_{Am/Eu}$ observed for all systems suggest that the number of ligands L bound into the inner-sphere of M(III) ions is the same (one, as suggested by Vitorge [6]) and that their denticity, probably equal to 3, is maintained throughout the two series of molecules.
- Most of the curves $\log D_M = f(\log[HNO_3])$ correspond to straight lines with slopes close to -3. For most systems, one can conclude that Eq. (1) is verified, at

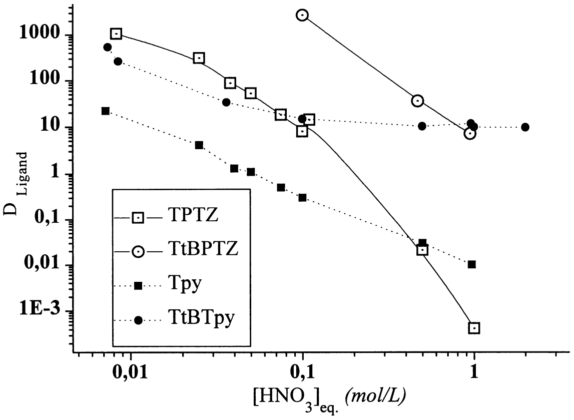


Fig. 1. D_L for TPTZ and Tpy ligands as a function of the acidity in aqueous phase at equilibrium. Organic phase: $[L]_{tot}=0.02$ M, [HA]=1 M, TPH. Aqueous phase: $[HNO_3]$=variable, room temperature.

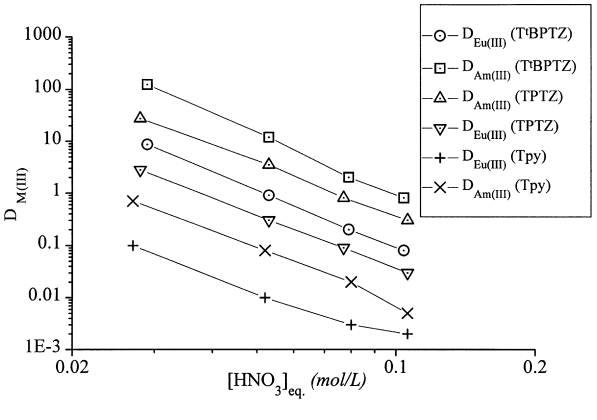


Fig. 2. Extraction of Am(III) and Eu(III) by (TPTZ+HA) synergistic mixtures as a function of the acidity in aqueous phase at equilibrium. Organic phase: [L]=0.02 M, [HA]=1 M, TPH. Aqueous phase: $[HNO_3]$=variable, room temperature. N.B.: data related to Tpy are shown here for comparison with those related to TPTZ molecules.

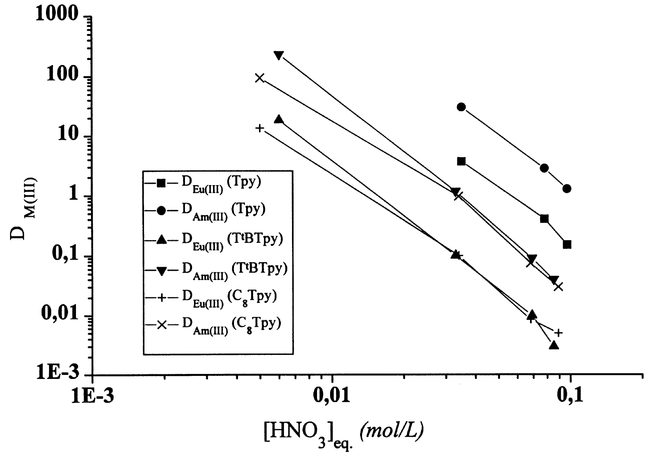


Fig. 3. Extraction of Am(III) and Eu(III) by (Tpy+HA) synergistic mixtures as a function of the acidity in aqueous phase at equilibrium. Organic phase: [L]=0.1 M, [HA]=1 M, TPH. Aqueous phase: $[HNO_3]$= variable.

least concerning the number of protons exchanged per M(III) extracted ion.

- The increase in lipophilia within the two series of L molecules induces opposite effects: while a beneficial increase of D_M is observed for M=Am and Eu when passing from TPTZ to T^tBPTZ, with an average D_M increasing factor equal to about 5, a definite decrease, by a factor of about 50 is observed for the Tpy family of molecules.

Some qualitative explanations can be tentatively proposed.

- The key parameter to explain the observed phenomenon relies certainly in the modification of the basicity of the nitrogen bonding sites of L molecules owing to branching of alkyl groups on the Tpy and TPTZ skeletons. Since this is an alkyl branching, the electronic density of the chelating nitrogen should increase, thus facilitating the interaction with the proton. The overall effect of this branching will be a balance between the positive effect of lipophilisation and the negative effect of proton competition.
- In case of TPTZ, the branching of tertiarybutyl groups on the molecule will have an effect on the lateral rings (direct branching), but almost no effect on the central triazinic ring. As this central triazine nitrogen, which plays a pivotal role in bonding of L with M(III), is not modified much between TPTZ and T^tBPTZ, the increasing lipophilia of T^tBPTZ compared to TPTZ overbalance the effect of the increase in the basicities of the two pyridine nitrogen atoms. Consequently, the increase in D_M is limited when T^tBPTZ data are compared with TPTZ ones.

Table 2
Separation factor $SF_{Am/Eu}$ for various (HA+L) synergistic systems

L	$SF_{Am/Eu}$
TPTZ[a]	10.1
T^tBPTZ[a]	11.9
Tpy[a,b]	7.2
C_8Tpy[b]	7.8
T^tBTpy[b]	11.6

[a] $[\overline{L}]$=0.02 mol/l in combination with HA 1 mol/l in TPH.
[b] $[\overline{L}]$=0.1 mol/l in combination with HA 1 mol/l in TPH.

- In case of the Tpy series of molecules, the branching of the alkyl groups directly affects all the pyridinic rings, including the central one. Thus, this increases competition between H^+ and M(III) for the nitrogen bonding sites, and overbalances the lipophilisation effect. So, this can explain the large decrease of D_M observed.

4. Conclusions

Synergistic mixtures made of carboxylic acid and polydendate nitrogen ligands are interesting systems to perform Am(III)/Eu(III) separation at low pH. Increasing the lipophilicity of nitrogen ligands induces beneficial increase of D_M if the basicity of the nitrogen atoms is preserved. This study is thus encouraging for the design of an efficient An(III)/Ln(III) group separation system.

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