Journal of the Serbian Chemical Society

Distribution of micro-amounts of europium in the two-phase water–HCl–nitrobenzene–*N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide–hydrogen dicarbollylcobaltate extraction system

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Abstract: Extraction of micro-amounts of europium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of *N,N'*-dimethyl--*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA, L) was investigated. The equilibrium data were explained assuming that the species HL^+, HL_2^+, EuL_2^{3+} and EuL_3^{3+} are extracted into the organic phase. The values of the extraction and stability constants of the species in nitrobenzene saturated with water were determined.

Keywords: europium; hydrogen dicarbollylcobaltate; *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide; water–nitrobenzene system; extraction and stability constants.

INTRODUCTION

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs^+), and also, in the presence of polyoxyethylene compounds, for the extraction of Sr^{2+} and Ba^{2+} from aqueous solution into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes,[1] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[2–4]

Dicarboxylic acid diamides are the subject of active research as potential extractants of actinides (in particular of minor actinides) from radioactive wastes. Important information concerning substituted malonic diamides was reported.[5,6]

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Lately, interest has shifted to the properties of tetra-alkyl-diglycolamides,[7–10] with emphasis on tetra-octyl-diglycolamide (TODGA) as an extractant of Pu(IV), Np(IV), Am(III) and Cm(III) in solutions with hydrocarbon diluents.[7–9] The ability of TODGA to extract many other metals was discussed[10,11] and the very high extractive capacity of this agent was shown to allow its application as a solid extractant.[12]

Recently, the extraction properties of some 2,6-dipicolinamides were investigated.[13–16] In the present work, the solvent extraction of micro-amounts of europium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[1] in the presence of *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA, L) (see Scheme 1) was studied. The intention was to find the composition of the species in the nitrobenzene phase and to determine the corresponding equilibrium constants.
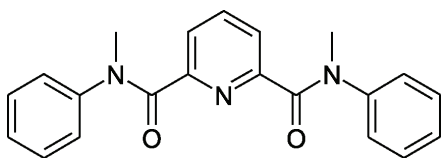
Scheme 1. Structural formula of *N,N'*-dimethyl--*N,N'*-diphenyl -2,6-dipicolinamide (MePhDPA).

EXPERIMENTAL

N,N'-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA) was prepared as described in the literature.[17,18] Cesium dicarbollylcobaltate (Cs^+B^-) was synthesized by the method published by Hawthorne *et al.*[19] A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[1] was prepared from Cs^+B^- by the procedure described elsewhere.[20] The other chemicals used (Lachema, Czech Republic) were of reagent grade purity. The radionuclide $^{152,154}Eu^{3+}$ (Polatom, Poland) was of standard radiochemical purity.

The extraction experiments in the two-phase water–HCl–Eu^{3+} (micro-amounts)–nitrobenzene–MePhDPA–H^+B^- systems were performed in 10 ml glass test-tubes closed with polyethylene stoppers, using 2 ml of each phase. The test-tubes filled with the solutions were shaken for 2 h at 25±1 °C using a laboratory shaker. Under these conditions, the equilibria in the system under study were established after approximately 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1 ml samples were taken from each phase and their *γ*-activities were measured using a well-type NaI(Tl) scintillation detector connected to a *γ*-analyzer, NK/350 (Gamma, Hungary).

The equilibrium distribution ratios, *D*, of europium were determined as the ratios of the corresponding radioactivities of $^{152,154}Eu^{3+}$ measured in the nitrobenzene and aqueous samples.

RESULTS AND DISCUSSION

The dependence of the logarithm of the europium distribution ratios (log *D*) on the logarithm of the numerical value of the total (analytical) concentration of the MePhDPA ligand in the initial nitrobenzene phase, log *c*(L), is shown in Fig. 1. The initial concentration of hydrogen dicarbollylcobaltate in the nitrobenzene phase, *c*(B) = 0.010 mol/l, as well as the initial concentration of HCl in the aqueous phase, *c*(HCl) = 0.20 mol/l, are always related to the volume of one phase.
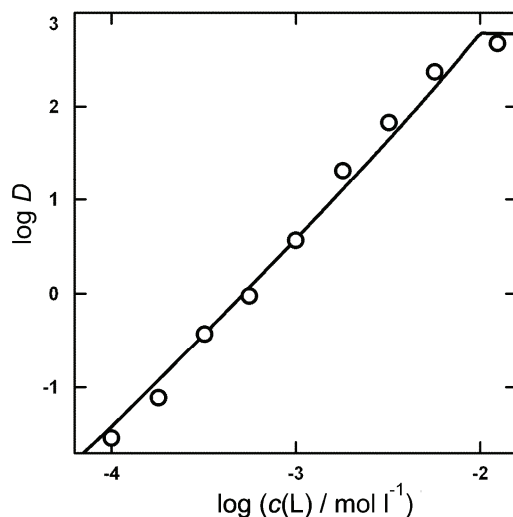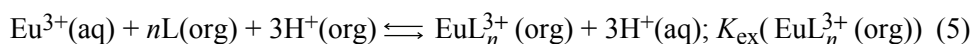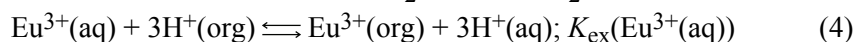
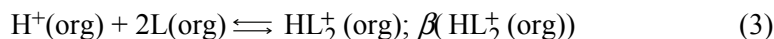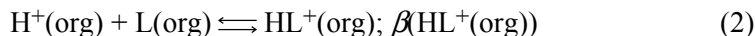Fig. 1. Log D as a function of log c(L), where L = MePhDPA, for the system water–HCl–Eu^{3+} (micro-amounts)–nitrobenzene–MePhDPA–H$^+$B$^-$. c(HCl) = 0.20 mol/l, c(B) = 0.010 mol/l. The curve was calculated using the constants given in Table I.

Regarding previous results,[21–26] the considered water–HCl–Eu^{3+} (micro-amounts)–nitrobenzene–MePhDPA(L)–H$^+$B$^-$ system can be described by the set of reactions:

$$L(aq) \rightleftharpoons L(org); K_D \quad (1)$$

$$H^+(org) + L(org) \rightleftharpoons HL^+(org); \beta(HL^+(org)) \quad (2)$$

$$H^+(org) + 2L(org) \rightleftharpoons HL_2^+(org); \beta(HL_2^+(org)) \quad (3)$$

$$Eu^{3+}(aq) + 3H^+(org) \rightleftharpoons Eu^{3+}(org) + 3H^+(aq); K_{ex}(Eu^{3+}(aq)) \quad (4)$$

$$Eu^{3+}(aq) + nL(org) + 3H^+(org) \rightleftharpoons EuL_n^{3+}(org) + 3H^+(aq); K_{ex}(EuL_n^{3+}(org)) \quad (5)$$

to which the equilibrium constants: K_D, $\beta(HL^+(org))$, $\beta(HL_2^+(org))$, $K_{ex}(Eu^{3+}(aq))$ and $K_{ex}(EuL_n^+(org))$ correspond.

TABLE I. Equilibrium constants in the water–HCl–Eu^{3+} (micro-amounts)–nitrobenzene––MePhDPA–H$^+$B$^-$ system

Equilibrium	log K
(1)	1.29[a]
(2)	9.30[b]
(3)	10.7[b]
(4)	1.30[c]
(5), $n = 2$	25.0
(5), $n = 3$	34.6
Eu^{3+}(org) + 2L(org) $\rightleftharpoons$ EuL$_2^{3+}$(org)	23.8
Eu^{3+}(org) + 3L(org) $\rightleftharpoons$ EuL$_3^{3+}$(org)	33.3

[a]Determined by the concentration dependent distribution method described in ref. 21; [b]determined by the method described in details in ref. 22; [c]ref. 23

A subroutine UBBE, based on the relations given above, the mass balance of the MePhDPA ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated[27,28] and introduced into a more general least-squares minimizing program LETAGROP[29] used for the determination of the "best" values of the extraction constants $K_{ex}(\mathrm{EuL}_n^{3+}$ (org)). The minimum of the sum of the errors in log D, *i.e.*, the minimum of the expression:

$$U = \Sigma(\log D_{calc} - \log D_{exp})^2 \tag{6}$$

was sought.

The values log $K_D = 1.29$ (see Table I, footnote a), log $(\beta(\mathrm{HL}^+(\mathrm{org}))) = 9.3$ (see Table I, footnote b), log $(\beta(\mathrm{HL}_2^+(\mathrm{org}))) = 10.7$ (see Table I, footnote b) and log $(K_{ex}(\mathrm{Eu}^{3+}(\mathrm{aq}))) = 1.3^{23}$ were used for the respective calculations. The results are listed in Table II, from which it is evident that the extraction data can be best explained assuming the complexes EuL_2^{3+} and EuL_3^{3+} are extracted into the nitrobenzene phase.

TABLE II. Comparison of three different models of europium extraction from an aqueous HCl solution by a nitrobenzene solution of $\mathrm{H^+B^-}$ in the presence of MePhDPA

Europium complexes in the organic phase	log K_{ex}[a]	U[b]
EuL_2^{3+}	25.60 (26.16)	10.40
EuL_3^{3+}	35.35 (35.73)	2.41
EuL_2^{3+}, EuL_3^{3+}	25.05 (25.32), 34.58 (34.99)	0.05

[a]The values of the extraction constants are given for each complex. The reliability interval of the constants is given as $3\sigma(K)$, where $\sigma(K)$ is the standard deviation of the constant K.[29] These values are given in the logarithmic scale using the approximate expression log $K \pm \{\log(K + 1.5\sigma(K)) - \log(K1.5\sigma(K))\}$. For $\sigma(K) > 0.2\,K$, the previous expression is not valid and then only the upper limit is given in the parentheses in the form of log $K(\log[K + 3\sigma(K)])$;[29] [b]the error-square sum $U = \Sigma(\log D_{calc} - \log D_{exp})^2$

Knowing the value log $K_{ex}(\mathrm{Eu}^{3+}(\mathrm{org})) = 1.30,^{23}$ as well as the extraction constants log $K_{ex}(\mathrm{EuL}_2^{3+}(\mathrm{org})) = 25.0$ and log $K_{ex}(\mathrm{EuL}_3^{3+}(\mathrm{org})) = 34.6$ determined here (Table II), the stability constants of the complexes EuL_2^{3+} and EuL_3^{3+} in the nitrobenzene phase defined as:

$$\beta(\mathrm{EuL}_2^{3+}(\mathrm{org})) = \frac{[\mathrm{EuL}_2^{3+}(\mathrm{org})]}{[\mathrm{Eu}^{3+}(\mathrm{org})][\mathrm{L}(\mathrm{org})]^2} \tag{7}$$

$$\beta(\mathrm{EuL}_3^{3+}(\mathrm{org})) = \frac{[\mathrm{EuL}_3^{3+}(\mathrm{org})]}{[\mathrm{Eu}^{3+}(\mathrm{org})][\mathrm{L}(\mathrm{org})]^3} \tag{8}$$

can be evaluated applying the simple relations:

$$\log \beta(\mathrm{EuL}_2^{3+}(\mathrm{org})) = \log K_{ex}(\mathrm{EuL}_2^{3+}(\mathrm{org})) - \log K_{ex}(\mathrm{Eu}^{3+}(\mathrm{org})) \tag{9}$$

$$\log \beta(\mathrm{EuL}_3^{3+}(\mathrm{org})) = \log K_{ex}(\mathrm{EuL}_3^{3+}(\mathrm{org})) - \log K_{ex}(\mathrm{Eu}^{3+}(\mathrm{org})) \tag{10}$$

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The respective equilibrium constants are summarized in Table I.

Furthermore, Fig. 2 depicts the contributions of the species $Eu^{3+}(org)$, $EuL_2^{3+}(org)$ and $EuL_3^{3+}(org)$ to the total europium concentration in the equilibrium organic phase. It follows from Fig. 2 that the complex $EuL_3^{3+}(org)$ is present in significant concentrations in the equilibrium nitrobenzene phase only at relatively high amounts of the MePhDPA ligand in the system under consideration.
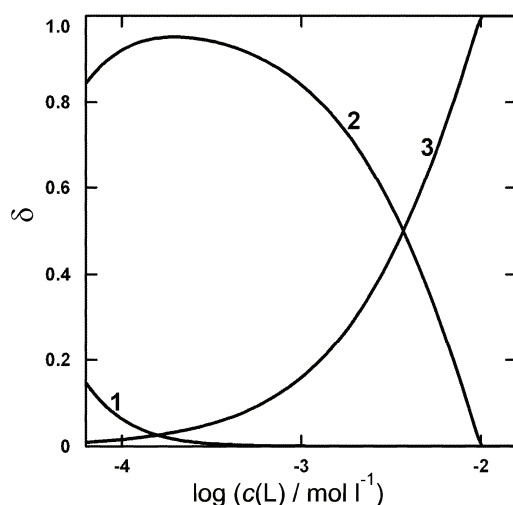

Fig. 2. Distribution diagram of europium in the equilibrium nitrobenzene phase of the water–HCl–Eu^{3+} (micro-amounts)–nitrobenzene–MePhDPA–H^+B^- extraction system in the forms of Eu^{3+}, EuL_2^{3+} and EuL_3^{3+}. $c(HCl) = 0.20$ mol/l; $c(B) = 0.010$ mol/l.
1: $\delta(Eu^{3+}) = [Eu^{3+}(org)]/c(Eu^{3+}(org))$;
2: $\delta(EuL_2^{3+}) = [EuL_2^{3+}(org)]/c(Eu^{3+}(org))$;
3: $\delta(EuL_3^{3+}) = [EuL_3^{3+}(org)]/c(Eu^{3+}(org))$,
where:

$$c(Eu^{3+}(org)) = [Eu^{3+}(org)] + [EuL_2^{3+}(org)] + [EuL_3^{3+}(org)].$$

The distribution curves were calculated using the constants given in Table I.

Finally, the stability constants of the EuL_2^{3+} and EuL_3^{3+} complexes in water saturated nitrobenzene at 25 °C for L = *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide, (MePhDPA), *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (EtPhDPA) are given in Table III. It is interesting that the stability constants of the EuL_2^{3+} complexes in the mentioned medium are comparable for both these ligands, whereas the stability of the species EuL_3^{3+} is somewhat higher for L = = MePhDPA than when L = EtPhDPA, as follows from Table III.

TABLE III. Stability constants of the complexes EuL_2^{3+} and EuL_3^{3+} for L = *N,N'*-dimethyl--*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA), *N,N'*-diethyl-*N,N'*-diphenyl-2,6-dipicolinamide (EtPhDPA) in water saturated nitrobenzene at 25 °C

L	$\log \beta(EuL_2^{3+}(org))$	$\log \beta(EuL_3^{3+}(org))$
MePhDPA	23.75	33.28
EtPhDPA[a]	23.54	32.36

[a]Ref. 30

In conclusion, it is necessary to emphasize that the stability constants of the complexes EuL_2^{3+} and EuL_3^{3+}, where L is *N,N'*-dibutyl-*N,N'*-dimethyl-2-(2-dodecyloxyethyl)malonamide (DBDMDDOEMA) in nitrobenzene saturated with water are $\log \beta(EuL_2^{3+}(org)) = 7.17$ and $\log \beta(EuL_3^{3+}(org)) = 9.18$.[31] From this

fact, it follows that the DBDMDDOEMA ligand is a less effective extraction agent for Eu^{3+} than the ligand MePhDPA in the two-phase water–nitrobenzene system.

ИЗВОД

РАСПОДЕЛА МИКРОКОЛИЧИНА ЕУРОПИЈУМА У ДВОФАЗНОМ ЕКСТРАКЦИОНОМ СИСТЕМУ ВОДА–HCl–НИТРОБЕНЗЕН–*N,N'*-ДИМЕТИЛ-*N,N'*-ДИФЕНИЛ-2,6- -ДИПИКОЛИНАМИД-ВОДОНИК-ДИКАРБОЛИЛКОБАЛТАТ

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Испитивана је екстракција микроколичина еуропијума водоник-карболилкобалтатом (H^+B^-) раствореним у нитробензену, у присуству *N,N'*-диметил-*N,N'*-дифенил-2,6-дипиколинамида (MePhDPA, L). Подаци за стање равнотеже објашњени су уз претпоставку да су јони HL^+, HL_2^+, EuL_2^{3+} и EuL_3^{3+} екстраховани органском фазом. Одређене су вредности константи екстракције и стабилности јона у водом засићеном нитробензену.

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