2,2′-Dipyridyl-6,6′-dicarboxylic acid diamides: Synthesis, complexation and extraction properties

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ABSTRACT

New ligands for complexing of the post-transition metals – diamides of 2,2′-bipyridyl-6,6′-dicarboxylic acid were developed, synthesised and characterised. They were proposed to be effective extractants towards americium. The structures of the amides were studied in solid as well as in solution. The extraction of Am and lanthanides depending on diamide structure, chlorinated cobalt dicarbollide (CCD) – diamide ratio, type of diluent was studied. The optimal conditions for Am/REE separation were determined. The properties of new potentiometric sensors on the base of 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides were studied. The correlation structure vs. properties of ionophores (i.e. extractants), their sensitivity and selectivity in sensor analysis and extraction are discussed.

1. Introduction

Separation of minor actinides (particularly americium and curium) from rare earth elements is very important for reducing of actinide waste volume. The most powerful ligands for this purpose are poly-nitrogen compounds. Nitrogen is a "soft donor" and has strong affinity for actinides complexation over lanthanides. There are a lot of poly-nitrogen compounds that extract americium many times better than europium [1,2]. The majority of N-donors investigated are derivatives of pyridine. The usual drawbacks of such extractants are either low stability in nitric acid solutions or narrow working range. For instance, TPEN (N,N,N′,N′-tetrakis-(2-pyridylmethyl)-ethylene-diamine) possesses high hydrolytic stability but provides effective Am/Eu separation only from very diluted nitric acid solutions (pH = 4–6) [3]. Contrary iPr-BTP (2,6-bis(5,6-isopropyl-1,2,4-triazin-3,4-yl)pyridine) effectively separates Am from Eu at $\leqslant$1M HNO$_3$ but rapidly degrades by hydrolysis and radiolysis [4,5].

Diamides of dicarboxylic acids, for instance amides of diglycolic acid [6–8], are one of the most powerful extractants for actinide and lanthanide recovery. Such compounds complex the extracted metal via "hard donor" atoms – oxygens of carboxylic and ether groups. The presence of the "hard donor" in the extractant molecule provides very good extraction of trivalent lanthanides and actinides, and lanthanides are extracted slightly better than americium.

Diamides of dipicolinic acid (DPA) were also proposed as promising extractants for minor actinides (MA) extraction [9,10]. DPA belong to "soft-hard hybrid donor" ligands: they have two oxygens of carboxylic groups and nitrogen of pyridine ring. The solutions of DPA in polar fluorinates diluents effectively extract actinides (III, IV, VI) and lanthanides(III) form nitric acid solutions, and for some of them Am/Eu separation factor is about 6 [10].

DPA were also tested as solid extractants [11,12]. Very interesting new compounds – amides of phenanthroline carboxylic acid – were studied as potential extractants of actinides [13]. In all cases the ligands bearing "soft-donor" atoms show better extraction of MA if compare with lanthanides.

At the same time the extraction ability of neutral extractant can be increased by addition of bulky hydrophobic anion such as chlorinated cobalt dicarbollide (CCD). Many ligands were studied as synergistic additives to CCD [14]. For CCD-based systems lanthanides and Am distribution ratios are usually close to each other, but for some poly-nitrogen compounds in the presence of dicarbollide very high separation factors can be achieved. Heretofore some extraction systems on the base of CCD and poly-nitrogen ligands

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were proposed for Am/lanthanides separation from acidic solutions [15,16]. Diamides of dipicolinic acid were also tested in the presence of CCD. It was found that DPA–CCD system selectively extract Am over lanthanides from 1 to 5 M nitric acid with high separation factors of Am from light lanthanides (La–Gd). The selectivity of extraction tends to decrease with increasing of metal atomic number: D_{Am}/D_{La} is >100; while D_{Am}/D_{Eu} does not exceed 4 [17].

New selective sensors for rare earths elements determination have been nowadays widely developed and tested [18,19]. The ion–ligand interaction in the liquid–liquid extraction system has much in common with an interaction of metal ion with ionophore in the sensor membrane, so it is worth to use the ligands studied in liquid-liquid extraction as ionophores. It was shown in some papers [20,21] and also in our previous works [22–24] that such approach allows to reach good results in many cases.

The present work is devoted to the new type of "soft-hard hybrid donor" ligands – diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid. If compare with DPA, diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid possess in their structure additional pyridine ring, and should complex metal as tetradentate compounds. Moreover the introducing of the additional "soft donor" (nitrogen of pyridine ring) to the structure is to increase the selectivity of the ligand toward americium.

The aim of the present work was the study of extraction and separation of Am and lanthanides from nitric acid solution with new diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid both alone and in the presence of CCD, and development of new ion selective sensors on the base of studied diamides.

2. Experimental

2.1. Synthesis of Dyp-1 and Dyp-2

10 ml of $SOCl_2$, 2.0 g (8.2 mmol) of 2,2′-dipyridyl-6,6′-dicarboxylic acid and one drop of DMF were refluxed for 3 h. Excess of $SOCl_2$ was removed under reduced pressure and the resulting solid finely dried. The solid residue was dissolved in dry THF (120 ml). This solution was added dropwise to a mixture of 2.22 ml (17.2 mmol) HNR′R″ (HNR′R″: N-ethylaniline for **Dyp-1**; dibutylamine for **Dyp-2**), 8.3 ml (59 mmol) NEt_3 and THF (20 ml) at 50 °C. The resulting mixture was stirred overnight at this temperature, then poured into water (70 ml) and extracted with $CHCl_3$ (2 × 150 ml). The combined organic extracts were washed with water (2 × 120 ml) and dried over $NaSO_4$. Rotary evaporation of the organic solution yielded 74% **Dyp-1** or 80% **Dyp-2**.

Dyp-1: mp. 182–184 °C. *Anal* Calc. for $C_{28}H_{26}N_4O_2$: C, 74.65; H, 5.82; N, 12.44. Found: C, 74.50; H, 5.90; N, 12.32%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, 1H), 7.46 (t, 1H), 7.17 (d, 1H), 7.07 (m, 5H, Ph), 4.01 (q, 4H, CH_2), 1.24 (t, 6H, CH_3). ^1H NMR (400 MHz, ACETONITRILE-d3) δ ppm: 1.18 (t, J = 6.97 Hz, 3H) 3.94 (d, J = 6.97 Hz, 2H) 7.04–7.34 (m, 5H) 7.57 (d, J = 7.34 Hz, 2H) 7.74 (t, J = 7.34 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 153.57, 143.43, 136.88, 128.77, 127.55, 126.44, 124.21, 121.53, 45.51, 12.77. IR (KBr), cm^{-1}: 1639 (amide I).

Dyp-2: m.p. 66–68 °C. *Anal.* Calc. for $C_{28}H_{42}N_4O_2$: C, 72.07; H, 9.07; N, 12.01. Found: C, 72.15; H, 9.18; N, 12.19%. ^1H NMR ($CDCl_3$) δ: 8.42 (d, 1H), 7.89 (t, 1H), 7.60 (d, 2H), 3.54 (t, 2H, cis-CH_2), 3.36 (t, 2H, trans-CH_2), 1.69 (m, 4H), 1.44 (q, 2H, cis-CH_2), 1.11 (q, 2H, trans-CH_2), 1.00 (t, 3H, cis-CH_3), 0.74 (t, 3H, trans-CH_3). ^1H NMR (400 MHz, TOLUENE-d8) δ ppm: 0.67 (t, J = 7.34 Hz, 3H) 0.86–1.05 (m, 5H) 1.35 (tq, J = 7.43 Hz, 2H) 1.54 (tt, J = 7.80, 7.58 Hz, 2H) 1.67 (tt, J = 7.80, 7.58 Hz, 2H) 3.14–3.32 (m, J = 7.58, 7.58 Hz, 2H) 3.50 (t, J = 7.34 Hz, 2H) 7.30 (t, J = 7.70 Hz, 1H) 7.55 (dd, J = 7.82, 0.98 Hz, 1H) 8.31 (dd, J = 7.83, 0.98 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 168.68, 154.63, 153.92, 137.65, 123.45, 121.30, 48.69, 45.66, 31.11, 29.63, 20.29, 19.76, 13.90, 13.55.

2.2. Dynamic NMR experiments

The ^1H NMR spectra were recorded at 400.13 MHz on a BRUKER "Avance400" instrument in approximately 0.2 mol/l solutions in toluene-d8 and CD_3CN in 5 mm probe tubes at different temperatures (deuteriated solvent as internal lock).

2.3. Extraction experiments

1,2-Dichloroethane and polar fluorinated solvents (*meta*-nitrobenzotrifluoride (F-3) and phenyltrifluoromethyl sulfone (FS-13)) were used as diluents for synthesised diamides.

For the preparation of $H^+BCl_6^-$ solution, a cesium salt of chlorinated cobalt dicarbollide was used. The exact weighted amount of cesium salt of CCD dissolved in a desired diluent was contacted twice with 4 M perchloric acid solution. The aqueous phase and cesium perchlorate sediment were thrown away and a solution of $H^+BCl_6^-$ in a diluent was filtered through a paper filter. The concentration of CCD in the solution was determined by titration of the aliquots with NaOH solution using bromcresol green as an indicator and by Co-analysis.

The extraction experiments were carried out in 5 ml polypropylene vials. One ml of organic phase and one ml of aqueous phase were placed in vials. An aqueous phase contained 10^{-3} M europium nitrate in nitric acid of desired concentration spiked with either ^{241}Am or ^{152}Eu. The samples were vigorously agitated for 3 min at room temperature (21 ± 1 °C). Phases were separated after a short centrifugation for 5–10 min, and aliquots (0.4 ml) were taken for analysis. The distribution ratios were determined radiometrically using a DeskTop InSpector-1270 scintillation γ-spectrometer designed on the base of a well-type NaI-detector 51 × 51 mm "Canberra" Co. The measurement error was less than 15%.

The extraction of lanthanides and fission products was studied by ICP-MS method. The initial solution contained 22 metals (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Fe, Cu, Zn, Cd, Pb, Pd, Zr and Mo) in nitric acid of desired concentration. The concentration of each metal in initial solution was 1×10^{-4} M.

2.4. Sensors experiments

The new sensors on the base of Dyp-1 diamide were prepared and tested in accordance with the procedure described previously in [24]. Sensor membranes consist of high molecular weight polyvinyl chloride (PVC) as a polymer, o-nitrophenyloctyl ether (NPOE) as a solvent-plasticizer, potassium tetrakis[3,5-bis(trifluormethyl)phenyl] borate (KTFB) and chlorinated cobalt(III) dicarbollide (CCD) were used as an ion-exchanger, Dyp-1 was used as neutral ligand with cadmium selectivity. The polymeric sensor membranes were produced according to the following standard procedure. Weighed amounts of membrane components were dissolved in freshly distilled tetrahydrofuran (THF) and stirred for 20 min on a magnet stirrer. Once the components were dissolved in the THF, the membrane cocktail was poured into a flat bottom teflon beaker and allowed to stand overnight at room temperature to evaporate the solvent. Disks 8 mm in diameter and 0.5 mm thick were cut from the parent membranes and attached with PVC glue onto the end of PVC tubes (10 mm in diameter) used as electrode bodies.

Electrochemical measurements were carried out in the following galvanic cell (in case of liquid contact sensors):

Cu | Ag | Agcl,KCl_sat | sample solution | membrane |
CdCl₂, 0.01 M | Agcl | Ag | Cu
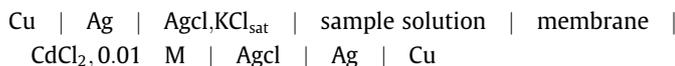
Electromotive force (sensor potential) values were measured with 0.1 mV precision against the standard reference electrode using a custom made 32-channel digital high impedance voltmeter connected to a PC for data acquisition. A glass pH electrode was used to monitor and control the acidity of sample solutions.

Calibration of the sensors was performed in a cadmium concentration range between 1×10^{-7} and 1×10^{-3} M to study the sensitivity. Both pure water solutions and 0.5 M NaCl were studied as a calibration medium and no any significant difference in sensors performance was observed. The data presented below were averaged over at least five replicate measurements. Measurement time in each solution was 2 min, which was found to be enough for the sensors to reach the steady readings.

2.5. Quantum-chemical calculations details

All calculations were performed using the resources of the Joint Supercomputer Center (JSC) supercomputer MVS-1000M (www.jscc.ru). The calculations have been done at the DFT level of theory. The geometry optimizations have been carried out using the PBE generalized gradient functional [25]. Geometries have been optimized using TZ2P valence basis set and tripleζ effective core potentials for C, N, O atoms [26]. Vibration frequencies have

been used to characterize stationary point as minima. All calculations were performed using the PRIRODA program [27,28].

3. Discussion

3.1. NMR-study

The amides of 2,2′-dipyridyl-6,6′-dicarboxylic acid was prepared with high yields according the following procedure starting from 2-bromo-6-picoline (Scheme 1) 6-Bromo-2-picolin and 6,6′-dimethyl-2,2′-bipyridyl were obtained in accordance with [29] and [30], correspondingly. Oxidation of 6,6′-dimethyl-2,2′-bipyridyl to 2,2′-bipyridyl-6,6′-dicarboxylic acid was described in our previous work [31].

The NMR spectra of the amides are quite similar in the aromatic region, while the aliphatic regions are different for both compounds. Due to the hindered rotations at room temperature about the C–N bonds of the carboxamides, two groups of signals corresponding to the *cis*- and *trans*-orientations of the two butyl-substituents with respect to the oxygen atom are observed for Dyp-2 (Fig. 1). (*Cis*- and *trans*- orientations correspond to the Z and E isomers respectively, when we consider the double bonds between nitrogen and carbon atoms of the amide-group.)

Heating the solution of Dyp-2 in toluene-d_8 allows determining the coalescence temperature for the signals of the α-methylene protons which is found to be near to 341 K. Since both the *cis*- and *trans*-positions are equally occupied, it is possible to calculate
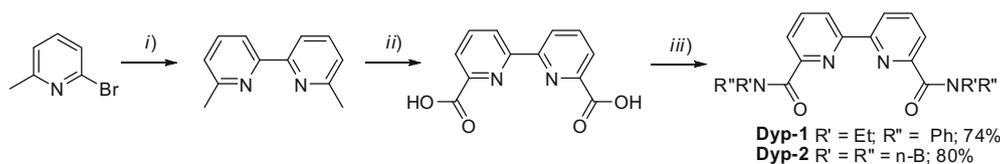
Scheme 1. The scheme of synthesis of 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides; (i) (1) Reney Ni, toluene, 110 °C, 22 h; (2) H₂O; (ii) CrO₃, H₂SO₄, 70 °C 1 h, 92%; (iii) (1) SOCl₂, Δ, 3 h, (2) HNR′R″, Et₃N, THF, 50 °C, overnight.
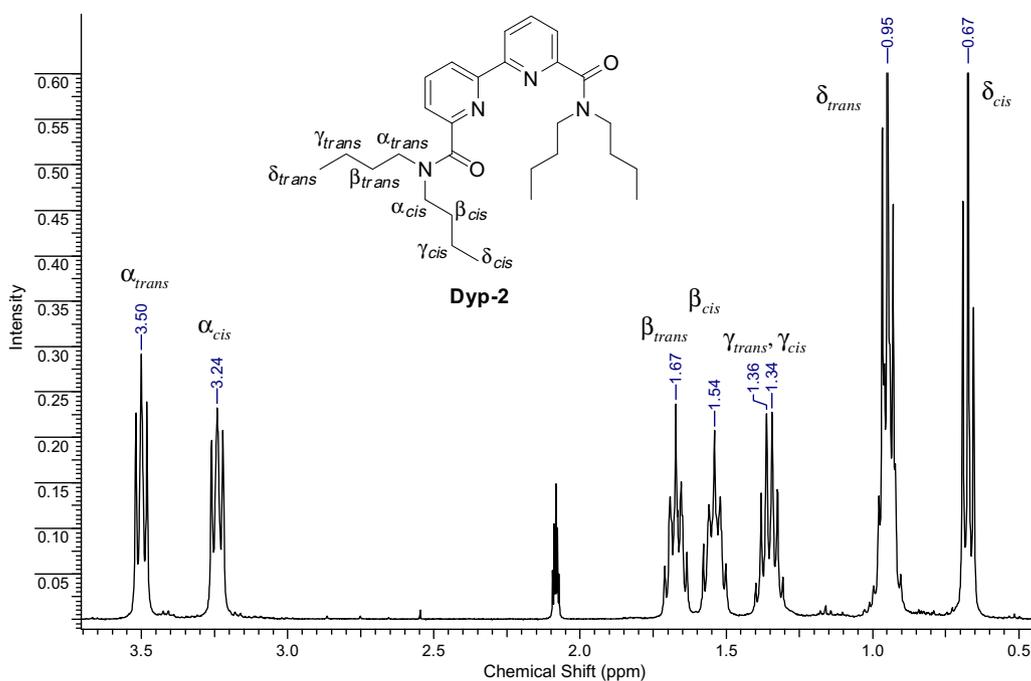
Fig. 1. Representative view of aliphatic region in typical ¹H NMR spectrum of Dyp-2 in toluene-d_8 and correlation of the aliphatic protons with the structure of Dyp-2.

$\Delta G^{\#}$ for the intramolecular rotation using Eiring equation. The calculated value is equal to 16.37 kcal/mol at the coalescence temperature for the toluene-d_8 solution and 16.02 kcal/mol at the coalescence temperature for the acetonitrile-d_3 solution. Therefore, we can conclude that the solvation has minimal effect on the intramolecular rotation for amide Dyp-2.

Contrary to the solution dynamics of the amide Dyp-2, the phenyl-ethyl-substituted 2,2′-dipicolinate Dyp-1 shows only one conformer at room temperature in all of the solvent tested (CDCl$_3$, toluene-d_8 or acetonitrile-d_3). (Fig. 2).

To elucidate the conformation isomerism of the amides quantum-chemical DFT calculations of the potential energy surface (PES) was carried out for both molecules (Fig. 3). Scanning for the amide torsion angle (angle O=C–N–C$_{(substituent)}$ of amide group)

shows that both amides possess a significant potential rotation barriers ($\Delta H^{\#}$ = 17.52 kcal/mol for Dyp-2 and 14.36 kcal/mol for Dyp-1). The rotation of the Bu$_2$N-group around the amide C(O)–N bond is a degenerative transformation due to identity of both substituents, so there are two equal minima with equal population on PES of amide Dyp-2.

The calculated rotation barrier is in close proximity to $\Delta G^{\#}$ value found by NMR. This supports that the entropy has minimal contribution to Gibbs energy of the intramolecular rotations. Contrary to the conformation dynamic of Dyp-2 the rotation of the PhEtN-group is more complex. The global minimum of PES of Dyp-1 corresponds to the *cis*-orientation of the ethyl-group, so the conformer with the *trans*-arrangement of the ethyl-group lies 2.81 kcal/mol higher in energy. The relative population of these
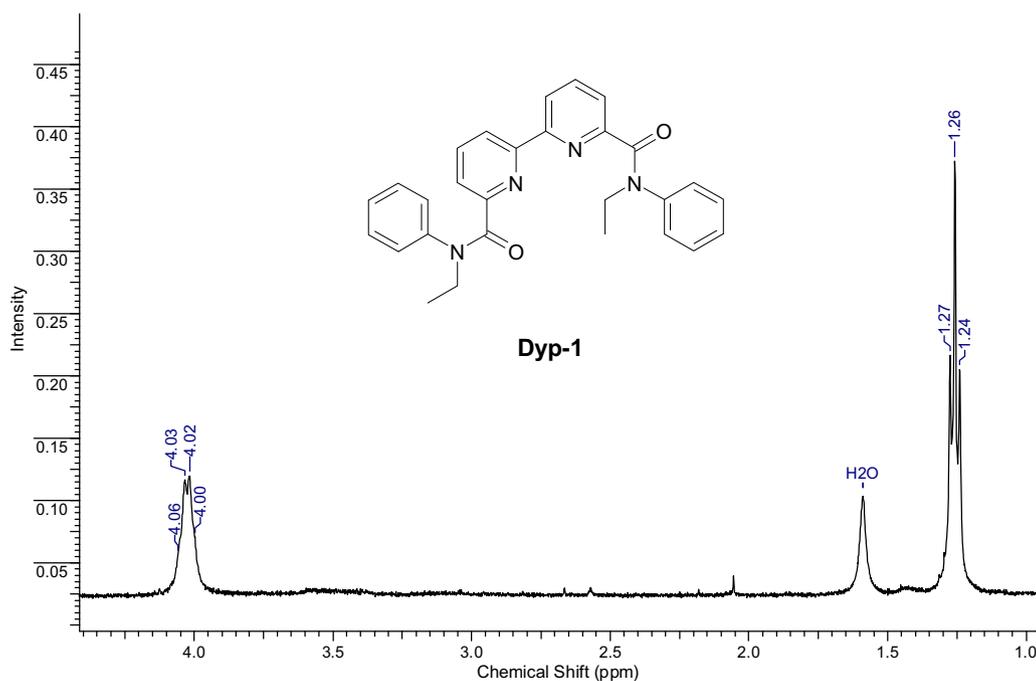
Fig. 2. Representative view of aliphatic region in typical ^{1}H NMR spectrum of Dyp-1 in CDCl$_3$.
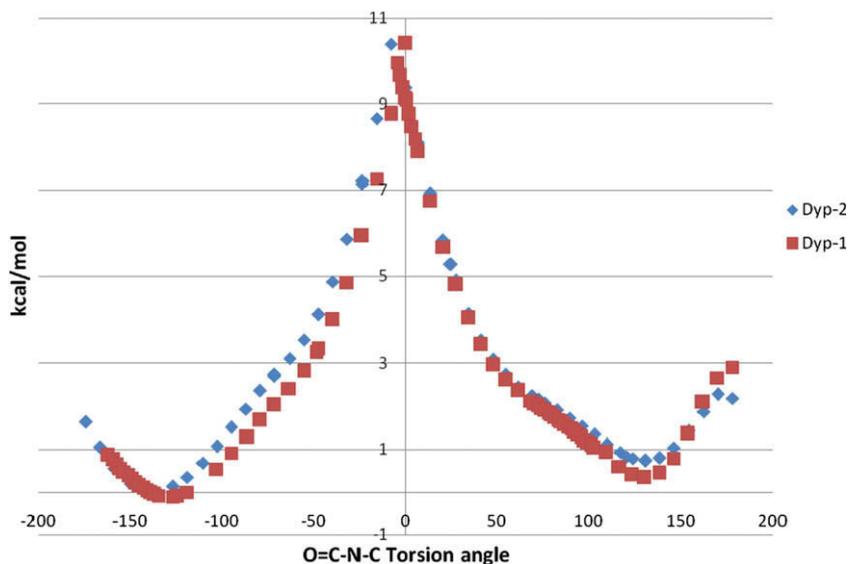
Fig. 3. Intramolecular rotation around the amide bond in Dyp-1 (rhombs) and Dyp-2 (squares) amides.

conformers at room temperature is higher than 100:1, therefore only one conformer is observed in the ^{1}H NMR-spectrum. The rotation energy barrier for amide Dyp-1 is less than that for the corresponding butyl-substituted amide Dyp-2.

3.2. Extraction study

The extraction properties of all diamide type extractants are strongly dependent on their structure. In the present work two diamides of different structure were studied. One of them Dyp-1 possess in its structure alkyl as well as aryl substituents on the amidic nitrogen. Dyp-2 has only alkyl substituents. The extraction behavior of the diamides of 2,2′-dipyridyl-6,6′-dicarboxilic acid in the absence of CCD is very similar to the one of DPA. First, the extraction of Am and Eu from nitric acid with a solution of 0.03 M Dyp-1 in F-3 (the maximum solubility in F-3) was studied. Americium distribution ratios for extraction from 0.2 M, 3 M and 5 M HNO$_3$ were 0.01, 0.33 and 0.76, correspondingly. Thus, as in the case of DPA, the extraction ability of Dyp increases with increasing of nitric acid concentration in an aqueous phase. The solubility of Dyp-2 in F-3 is much higher, however its extraction ability toward actinides and lanthanides is lower, e.g. for metal extraction from 3 M HNO$_3$ with 0.1 M Dyp-2 in F-3 americium and europium distribution ratios were 0.04 and 0.01, respectively. The better extraction ability of Dyp-1 comparing to Dyp-2 can be explained by so called "anomalous aryl strengthening" effect that was previously found first for bidentate phosphoryl extractants [32] and afterwards for DPA.

A high synergetic effect was found for diamides of 2,2′-dipyridyl-6,6′-dicarboxilic acid in the presence of CCD. The Dyp–CCD solutions in polar fluorinated diluents extract americium and lanthanides from nitric acid. As the data on the Fig. 4 shows systems Dyp–CCD selectively extract Am over Eu from acidic solutions with Am/Eu separation factors about −20 to 30. The distribution ratios decrease with increasing of nitric acid concentration. Such behavior is common for all CCD-based systems [33,34]. Chlorinated cobalt dicarbollide anion acts as a counter anion and increasing of nitric acid concentration leads to strengthening of competition between metal ion and extracted proton in creating of ion pair with CCD. However, the separation factors slightly change in the studied acidity range (0.3–1 M HNO$_3$).

The extraction of other lanthanides and some transition metals was also studied. The data on lanthanides extraction from 0.5 and 1 M nitric acid with Dyp-1- and Dyp-2-based solvents are presented on Figs. 5 and 6, correspondingly. In the case of Dyp-1–CCD system the distribution ratios decrease with increasing of atomic number. The lanthanide pattern is divided in two parts with the breakpoint on Gd: the distribution ratios decrease first from lanthanum to gadolinium and than from terbium to lutetium. Such breakpoint on gadolinium is usual for lanthanide extraction. Dyp-2–CCD-solvent extracts heavy lanthanides much better than lighter one. Neodymium and samarium are extracted worst of all other light lanthanides. This effect is noticeable best of all for the extraction from 0.5 M nitric acid (Fig. 6).

One can see that Dyp-1 and Dyp-2 extract light lanthanides (La–Gd) in the different ways and distribution ratios of heavy
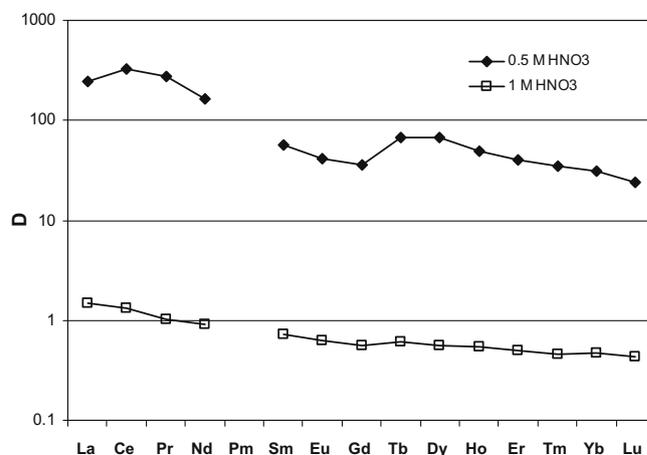
Fig. 5. Extraction data for lanthanides extraction by (0.01 M *Dyp-1* + 0.04 M CCD) in F-3 from 0.5 and 1 M nitric acid.
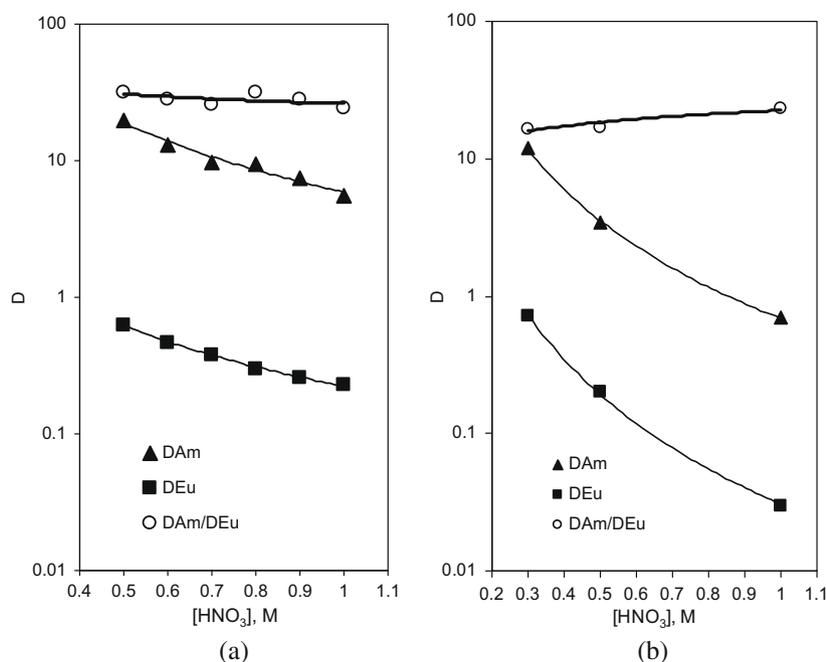
Fig. 4. The dependences of distribution ratios and Am/Eu separation factors on nitric acid concentration; solvent – (a) 0.03 M Dyp-1 + 0.01 M CCD in F-3; (b) 0.03 M Dyp-2 + 0.02 M CCD in F-3.

Fig. 6. Extraction data for lanthanides extraction with (0.01 M *Dyp-2* + 0.04 M CCD) in F-3 from 0.5 and 1 M nitric acid.

Fig. 7. Extraction of REE with (0.01 M Et(p)TDPA + 0.04 M CCD) in F-3 from 0.5 and 1.0 M nitric acid.

Fig. 8. Comparative data on lanthanide extraction with different diamides from 0.5 M HNO₃; Solvent – (0.01 M diamide + 0.04 M CCD) in F-3; Et(p)TDPA – N,N′diethyl-N,N′-di(*para*- tolyl) diamide of 2,6 pyridinedicarboxylic acid.

Concerning to diamides of 2,2′-dipyridyl-6,6′-dicarboxilic acid this row changed greatly: Cd > Pb Cu > Zr, Pd, Fe, Zn, Mo. Thus the difference in extraction ability is more noticeable for cadmium. The comparison of transition metal extraction from 0.5 M HNO₃ with different systems is presented in the Fig. 9.

3.3. Sensors experiments

Short preliminary experimental screening of the sensors made on the base of Dyp-1 was done. None of the sensors have shown any significant response towards RE metals (observed sensitivity values towards RE were lower than 5 mV/dec in the acidic media). Reasonable sensitivity (around 30 mV/dec) was found in the solutions of doubly charged metal cations, such as calcium, copper, zinc, lead; the most stable and reproducible results were found for cadmium. After this short preliminary experimental screening it was decided to use ligand Dyp-1 in further experiments as cadmium (II) ionophore.

Two types of inner electric contact were investigated: solid contact based on graphite conductive glue and ordinary liquid inner contact. In the latter case electrodes were filled in with 0.01 M CdCl₂ solution and all of the sensors were then immersed in the same solution for 48 h prior to measurements to equilibrate sensor membranes with aqueous solutions. Following sensors were prepared: with CCD and solid inner contact (*Dyp-1*-CCD-S), with KTFB and solid inner contact (*Dyp-1*-KTFB-S), with CCD and liquid inner filling (*Dyp-1*-CCD-L) and with KTFB and liquid inner filling (*Dyp-1*-KTFB-L). At least three replicate sensors of each composition were prepared.

In the Fig. 10 general view of the calibration curve for sensors based on Dyp-1 and KTFB on the background of 0.5 M NaCl is presented. Sensitivity values (slopes of the linear part of the calibration curve) were calculated in the concentration range 10^{-5}–10^{-3} M of cadmium and for all of the studied sensors this value was in the range 28.5 ± 0.7 mV/pCd, which is in a good agreement with the theoretical values of the slope for doubly charged cations (29.5 mV/pMe). No valuable dependence of the slope on sensor composition was found.

Selectivity of the sensors was studied by mixed solutions method in a presence of 10^{-4} M background content of interfering ion (copper, zinc, lead). Results of the selectivity determination logarithm of selectivity coefficients units are shown in the Table 2.

All of the sensors have shown selectivity towards cadmium. Selectivity values were found to be strongly dependent on the sensor composition. Sensors with inner liquid contact have shown in general more selective behavior, but taking into account

lanthanides (Tb–Lu) are very close to each other for both ligands. Thus, the diamide structure, viz. the type of substituents on amidic nitrogen, exerts great influence on the extraction ability towards light lanthanides. For understanding of the nature of this effect the additional study is required.

As it was mentioned above diamides of 2,2′-dipyridyl-6,6′-dicarboxilic acid behave similar to diamides of dipicolinic acid. The data on lanthanides extraction with the solvent on the base of N,N′-diethyl-N,N′-di(*para*-tolyl) diamide of dipicolinic acid (Et(p)TDPA and chlorinated cobalt dicarbollide are presented in the Fig. 7. The lanthanides distribution ratios increase with increasing of atomic number of the element very sharply from La to Eu, with the breakpoint on Gd. The heavier lanthanides are extracted very close to each other. As one can see the extraction ability of Et(p)TDPA is much higher than that of Dyp-ligands. The difference in the extraction ability towards light and heavy lanthanides in the case of Dyp-solvents is also smaller than in the case of Et(p)TDPA (Fig. 8).

The data on transition metals extraction with different diamide solvents are presented in the Table 1. One can see that despite of diamide type iron, zirconium and molybdenum are weakly extracted form nitric acid solutions. At the same time, Dyp-ligands in contrast to Et(p)TDPA possess very high extraction ability towards cadmium. The metals distribution ratios in the case of Et(p)TDPA change in the row: Cu > Pb > Zr > Pd > Fe, Zn, Cd, Mo.

Table 1
Extraction of metals from nitric acid by (0.01 M Dyp-1 +0.04 M CCD) in F-3.

	[HNO$_3$] M	Fe	Cu	Zn	Cd	Pb	Pd	Zr	Mo
Dyp-1	0.5	0.50	73	1.4	730	80	1.6	1.5	0.13
	1	0.47	100	9.3	850	34	0.49	0.31	0.06
Dyp-2	0.5	<0.01	118	4.3	440	45	2.9	1.4	0.3
	1	0.05	101	1.9	260	6.1	1.2	0.52	0.12
Et(p)TDPA	0.5	0.024	68	0.82	0.19	8.1	2.5	0.57	0.14
	1	0.06	37	0.26	0.09	1.2	0.60	0.28	0.12
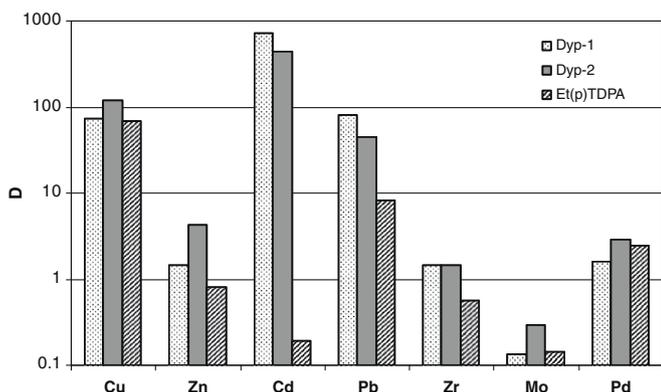
Fig. 9. Comparative data on transition metals extraction with different diamides from 0.5 M HNO$_3$; Solvent – (0.01 M diamide + 0.04 M CCD) in F-3.

Fig. 11. The comparative data on cadmium detection in the presence of copper.

Developed sensor composition P1-KTFB-S has high sensitivity and selectivity to cadmium, reasonable stability of the response, fast response time and can be used for further practical applications.

4. Conclusions

Diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid extract americium better than europium. The addition of chlorinated cobalt dicarbollide greatly increases the extraction ability of the mixture CCD–Dyp. Comparing with diamide of dipicolinic acid, the introduction of the second pyridine ring to the ligand molecule results in better extraction of "soft" cadmium ion. Two "soft" nitrogen atoms in Dyp molecule also change extraction ability towards lanthanides. The sensors on the base of 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides – new class of tetradentate ligands – provide very high sensitivity to cadmium.

Fig. 10. General view of the calibration curve for sensors based on *Dyp-1*-KTFB on the background of 0.5 M NaCl.

Table 2
Selectivity of the sensors, lgK$_{sel}$, ±0.1.

	P1-CCD-S	P1-KTFB-S	P1-CCD-L	P1-KTFB-L
Cu/Cd	−1.4	−1.8	−1.8	−2
Zn/Cd	−2.4	−2.5	−2.6	−2.6
Pb/Cd	−0.5	−1.4	−1.5	−1.6

convenience considerations solid contact sensors could be a better option for possible practical applications of the developed sensors. P1-KTFB-S possesses better selectivity values for cadmium (see Table 2), although sensitivity is the same as in case of P1-CCD-S. On the Fig. 11 experimental curves for detection of cadmium in presence of copper are shown for comparison of these two types solid contact sensors.

References

[1] S. Tachimori, Y. Morita, in: B.A. Moyer (Ed.), Ion Exchange and Solvent Extraction: A Series of Advances, vol. 19, CRC Press, New York, 2009, pp. 1–63.
[2] C. Hill, in: B.A. Moyer (Ed.), Ion Exchange and Solvent Extraction: A Series of Advances, vol. 19, CRC Press, New York, 2009, pp. 119–193.

[3] R. Mirvaliev, M. Watanabe, T. Matsumura, S. Tachimori, K. Takeshita, J. Nucl. Sci. Technol. 41 (2004) 1122.
[4] Z. Kolarik, U. Müllich, F. Gassner, Solvent Extr. Ion Exch. 17 (1999) 1155.
[5] C. Hill, L. Berthon, C. Madic, Proc. of Global 2005 Int. Conf., Tsukuba, Japan, October 9–13, 2005.
[6] Y. Sasaki, S. Tachimori, Solvent Extr. Ion Exch. 20 (2002) 21.
[7] S.A. Ansari, P.N. Pathak, V.K. Manchanda, M. Husain, A.K. Prasad, V.S. Parmar, Solvent Extr. Ion Exch. 23 (2005) 463.
[8] D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, C. Sorel, Solvent Extr. Ion Exch. 27 (2009) 26.
[9] A. Shimada, T. Yaita, H. Narita, S. Tachimori, K. Okuno, Solvent Extr. Ion Exch. 22 (2004) 147.
[10] V.A. Babain, M.Yu. Alyapyshev, R.N. Kiseleva, Radiochim. Acta 95 (2007) 217.
[11] M. Arisaka, M. Watanabe, T. Kimura, Proc. of Global 2007 Int. Conf., Boise, ID, United States, Sept. 9–13, 2007.
[12] N.P. Molochnikova, G.V. Myasoedova, I.I. Eliseev, M.Yu. Alyapyshev, Radiochemistry 52 (2010) 65.
[13] T. Yaita, H. Shiwaku, S. Suzuki, Y. Okamoto, Patent WO 2008/081814 (10.07.2008).
[14] J. Rais, B. Grüner, in: I. Marcus, A.K. Sengupta (Eds.), Ion Exchange and Solvent Extraction: A Series of Advances, vol. 17, CRC Press, New York, 2004, pp. 243–334.
[15] J. Rais, S. Tachimori, Sep. Sci. Technol. 29 (1994) 1347.
[16] I.V. Smirnov, A.V. Chirkov, V.A. Babain, E. Yu, E.Yu. Pokrovskaya, T.A. Artamonova, Radiochim. Acta 97 (2009) 593.
[17] A. Paulenova, M.Yu. Alyapyshev, V.A. Babain, R.S. Herbst, J.D. Law, T. Todd, Proc. on 7th Int. Conf. on Nucl. and Radiochem., NRC7, Budapest, Hungary, August 24–29, 2008.
[18] M. Shamsipur, M. Yousefi, M. Hosseini, M.R. Ganjali, Anal. Chem. 74 (2002) 5538.
[19] V.K. Gupta, S. Jain, S. Chandra, Anal. Chim. Acta 486 (2003) 199.
[20] P. Bühlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1593.
[21] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Hydrometallurgy 70 (2003) 63.
[22] A.V. Legin, D.O. Kirsanov, V.A. Babain, A.V. Borovoy, R.S. Herbst, Anal. Chim. Acta 572 (2 243-24) (2006).
[23] A.V. Legin, V.A. Babain, D.O. Kirsanov, O.V. Mednova, Sens. Actuators B 131 (2008) 29.
[24] D.O. Kirsanov, O.V. Mednova, E.N. Pol'shin, A.V. Legin, M.Yu. Alyapyshev, I.I. Eliseev, V.A. Babain, Yu.G. Vlasov, Russ. J. Appl. Chem. 82 (2009) 247.
[25] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[26] D.N. Laikov, Chem. Phys. Lett. 416 (2005) 116.
[27] D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151.
[28] D.N. Laikov, Yu.A. Ustynyuk, Russ. Chem. Bull. Int. Ed. 54 (2005) 820.
[29] R. Adams, S. Miyano, J. Am. Chem. Soc. 76 (1954) 3168.
[30] F. Vogtle, R. Hochberg, F. Kochendörfer, P.-M. Windscheif, M. Volkmann, M. Jansenb, Chem. Ber. 123 (1990) 2181.
[31] M.Yu. Alyapyshev, V.A. Babain, N.E. Borisova, R.N. Kiseleva, D.V. Safronov, M.D. Reshetova, Mendeleev Commun. 18 (2008) 336.
[32] M.K. Chmutova, L.A. Ivanova, N.E. Kochetkova, N.P. Nesterova, B.F. Myasoedov, A.M. Rozen, Radiochemistry 37 (1995) 427.
[33] J. Rais, P. Selucky, N.V. Šistkova, J. Alexova, Proc. of the 2nd NUCEF Int. Symp., NUCEF'98, 215–240, Hitachinaka, Ibaraki, Japan, 1999.
[34] T.A. Luther, R.S. Herbst, D.R. Peterman, R.D. Tillotson, T.G. Garn, V.A. Babain, I.V. Smirnov, E.S. Stoyanov, N.G. Antonov, J. Radioanal. Nucl. Chem. 267 (2006) 603.