

Extraction and separation of Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from hydrochloric acid solutions with selected cyanamides as novel extractants

E.A. Mowafy*, H.F. Aly

Hot Labs. Centre, Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt

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Abstract

Three structurally related novel extractants namely: *N,N*-dihexylcyanamide (DHCY), *N,N*-di(2-ethylhexyl)cyanamide (DEHCY) and *N,N*-di-octylcyanamide (DOCY) were synthesized in our laboratory and characterized by different techniques. The general method for synthesizing these extractants was based on the reaction of relevant secondary amines with cyanogen bromide in presence of sodium acetate anhydride. Their extracting ability in toluene as a diluent for Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from hydrochloric acid media has been studied. The extraction of hydrochloric acid was studied also. Pd(II) was strongly extracted by these extractants at low hydrochloric acid concentrations and the extraction decreased with increasing hydrochloric acid concentration while the reverse was obtained in the extraction of Pt(IV), Fe(III) and Zn(II). Under similar extraction conditions Cu(II) and Ag(I) were found poorly extracted. Hydrochloric acid was extracted only in its high concentration region. A systematic investigation has been carried out on the extraction of Pd(II) using two of the synthesized extractants. Pd(II) was extracted as a solvated complex with the composition, metal:chloride ion:extractant = 1:2:2. The extracted species were studied also using IR spectra.

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1. Introduction

Precious metals, which possess specific physical and chemical properties, are applied to many advanced industrial technology. Solvent extraction process of the precious metals and other accompanying base metals are already well established as more efficient alternatives to traditional precipitation techniques [1,2]. Chloride is the most common media into which all the precious metals, except silver, can be efficiently brought into solution [1]. Much attention has been paid to the distribution behavior of major radioactive fission products like strontium and cesium because of their high toxicity and half-life. On the other hand, some of less radioactive fission products have not attracted technological interest, even though imperfect decontamination of these fission products affects the reactor performance. Palladium is one of elements of this kind, thus there have been limited works on its distribution behaviors [3,4]. Dif-

ferent extractants have been developed and employed as solvent extraction reagents for precious metals for both commercial and analytical purpose include such diverse types as hydroxyoximes, alkyl derivative of 8-hydroxyquinoline, neutral organophosphorus compounds, hydrophobic amine and esters and so on [4–11]. Cyanide ion has been used for a long time for purification of gold and silver in the well known cyanide process and, consequently, nitrile compounds and soft bases, are considered to have high affinity for soft Lewis acid metals such as palladium, platinum, gold, silver and mercury [6,12]. Very limited information reported on their use as solvent extraction reagents. However, there was no information in the literature regarding the effect of structure of nitrile compounds on their extraction behavior towards different metal ions. The nature of alkyl chain substituents plays an important role for the coordination properties of amides (CHNO compounds) as extractants as reported in our previous works in Refs. [13–15]. This work is directed to synthesis and characterize three novel types of solvent extraction reagents (CHN compounds), *N,N*-dihexylcyanamide (DHCY), *N,N*-di(2-ethylhexyl)cyanamide (DEHCY) and *N,N*-di-octylcyanamide (DOCY), and to investigate their extraction

* Corresponding author. Tel.: +20 24 620780; fax: +20 24 620780.
E-mail address: mowafy69@yahoo.com (E.A. Mowafy).

ability in toluene as a diluent for Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from hydrochloric acid medium. In addition the extraction stoichiometry of Pd(II) by DHCY and DEHCY was also studied. The following effects were investigated namely: the length of alkyl group on nitrogen atom, hydrochloric acid concentration, salting-out agent, extractant concentration.

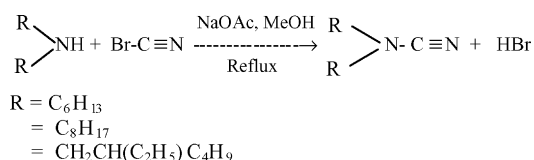
2. Experimental

All chemical used were of analytical grade purity and used without further purification.

2.1. Synthesis of extractants

The cyanamides chosen for this study are not commercially available. They were prepared by reaction of cyanogen bromide with the relevant secondary amine in presence of sodium acetate [6], according to Scheme 1.

The three cyanamide extractants *N,N*-dihexylcyanamide, *N,N*-di(2-ethylhexyl)cyanamide and *N,N*-dioctylcyanamide were synthesized by mixing (0.1 mol) of the corresponding secondary amines, *N,N*-dihexyl amine, *N,N*-di(2-ethylhexyl)amine and *N,N*-dioctylamine, respectively, with (0.2 mol) of cyanogen bromide and excess of sodium acetate anhydride in methanol. The mixture reaction was overnight refluxed at 60 °C. After filtration to remove sodium acetate, methanol was removed by distillation under reduced pressure. The crude product was dissolved in benzene and washed first by distilled water followed by 4% by weight sodium carbonate solution and 5% hydrochloric acid solution and finally again with distilled water to a neutral pH. The organic layer obtained was dried overnight over an excess of anhydrous sodium sulphate. The residue obtained after evaporation of benzene, was purified under reduced pressure. The final products were characterized by elemental analysis, IR and H NMR spectra. The purity of the three synthesized extractants was higher than 98% and the analytical data of the products are shown in Table 1.



Scheme 1.

Table 1
Some analytical and IR spectroscopic data for the synthesized extractants and its complex

Name	Acronym	No. of C atoms	Structure	MW	Yield (%)	C (%)	H (%)	N (%)	$\nu_{\text{C}\equiv\text{N}} \text{ cm}^{-1}$	
									Free	Pd-complex
<i>N,N</i> -di-hexylcyanamide	DHCY	13	(C ₆ H ₁₃) ₂ NCN	210	94	74.11 (74.28)	12.31 (12.38)	13.39 (13.33)	2247	2189
<i>N,N</i> -di-(2-ethylhexyl)cyanamide	DEHCY	17	[CH ₂ CH(C ₂ H ₅)C ₄ H ₉] ₂ NCN	266	91	76.59 (76.69)	12.65 (12.78)	10.32 (10.52)	2245	2195
<i>N,N</i> -di-octylcyanamide	DOCY	17	(C ₈ H ₁₇) ₂ NCN	266	89	76.31 (76.69)	12.21 (12.78)	10.19 (10.52)	2246	2208

Values in the parentheses indicate expected values.

2.2. Extraction

Equal volumes of organic and aqueous phases were equilibrated for 24 h under vigorous mechanical shaking in a thermostated water bath (25 ± 1 °C). The equilibrium period used is much less than that reported by Inoue et al. [6], who found that 200 h are required for equilibrium extraction. This may be related to the type of shaking of the two phases.

After phase separation by centrifugation, known aliquots of each phase were sampled for analysis. The distribution ratio (D_M) was measured as the ratio between the concentration of an element in the organic and its concentration in the aqueous phases. Aqueous metal solutions were prepared by dissolving the corresponding metal chlorides in hydrochloric acid solution except for the case of silver, which prepared from silver nitrate. A 0.15 M solutions of *N,N*-dialkylcyanamide in toluene were used as an organic phase. In all cases aqueous feed contained about 100 ppm of metal chloride or nitrate in HCl solution. Metal concentrations in the aqueous phase was determined by a spectrophotometric method [16] using a Shimadzu UV-vis spectrophotometer model UV-160-A. Pd(II), Zn(II), Cu(II) and Ag(I) were measured by the dithizone method at $\lambda_{\text{max}} = 450, 495, 550$ and 462 nm, respectively, while Fe(III) and Pt(IV) concentrations were determined by thiocyanate ($\lambda_{\text{max}} = 495$ nm) and stannous chloride ($\lambda_{\text{max}} = 403$ nm) methods, alternatively. The acidity of the organic phase was determined as reported earlier in Ref. [15].

3. Results and discussion

3.1. Influence of structure

The extraction of Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from 0.1 M hydrochloric acid with 0.15 M of the different synthesized cyanamides in toluene are given in Table 2. DEHCY showed the highest tendency to extract Pd and Pt than the other two extractants. It was found that the nature of nitrogen atom substituents in the cyanamides is of importance for Pd, Pt or Fe extraction. This was verified by a significant decrease in the values of extraction of Pd, Pt and Fe as the alkyl group is varied from C₆H₁₃ to C₈H₁₇. The branched alkyl group, *bis*(2-ethylhexyl), in DEHCY was found to enhance the extraction of Pd and Pt compared to the long chain octyl group in DOCY, although both DEHCY and DOCY have the same number of carbon atoms (no.

Table 2

Influence of alkyl group (R) on the extraction % of Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from 0.1 M hydrochloric acid solution with 0.15 M different synthesized extractants in toluene at $25 \pm 1^\circ\text{C}$

$\text{R}_2\text{N}-\text{C}\equiv\text{N}$			Extraction (%)					
Name	Alkyl group (R)	No. of C atom	Pd	Pt	Fe	Zn	Cu	Ag
DHCY	<i>n</i> -C ₆ H ₁₃	13	90	29	23	0.4	0.1	0.2
DEHCY	CH ₂ CH(C ₂ H ₅)C ₄ H ₉	17	96	36	15	1	0.3	0.3
DOCY	<i>n</i> -C ₈ H ₁₇	17	73	3	6	0.9	NE	NE

NE: no extraction.

of carbon atoms = 17). These results indicate that the branching alkyl group has a great influence on metal extraction. So far, no detailed work was reported on the effect of the introduction of branched radicals on the N atom of cyanamides. However, the better extraction of branched cyanamide (DEHCY) than the normal cyanamide (DOCY) may be related to the electro-inductive effect as well as steric hindrance of DOCY, as the case of carboxylic acid amides [15]. In this concern, our previous work in Refs. [13,15] studied the extraction of selected actinide and lanthanides metal ions with diamides as a function of the length of amidic alkyl chain (from C₄H₉ to C₈H₁₇), it is found that the longer alkyl chain suppresses the extraction. Sasaki et al. [17], found similar relation which support the present research.

As shown in Table 2, Zn, Cu and Ag are poorly extracted by DHCY, DEHCY and DOCY in the entire range of acid concentrations. The very low values of extraction of Zn, Cu and Ag with all the synthesized extractants indicated that the change in structure have no effect on the extraction of these metal ions, Table 2.

3.2. Extraction of hydrochloric acid

Due to the nature of nitrogen atom of the nitrile group, cyanamides were found to extract hydrochloric acid into the organic phase. Fig. 1 shows the plot of concentration of hydrochloric acid extracted with DHCY, DEHCY and DOCY in toluene against that in the aqueous phase after extraction. It is

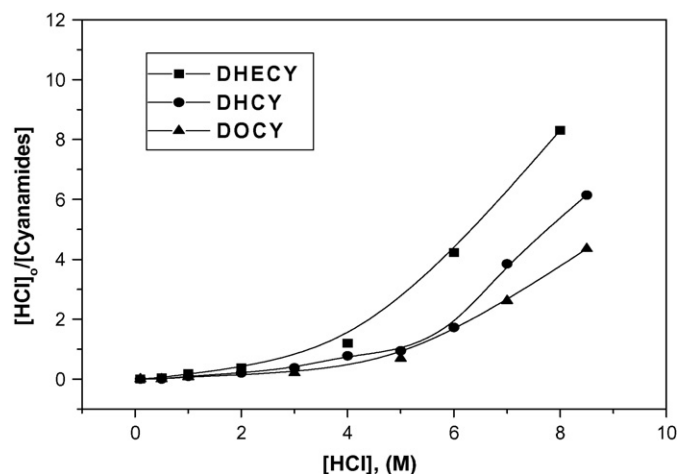


Fig. 1. Extraction of hydrochloric acid with 0.15 M of the cyanamides in toluene at $25 \pm 1^\circ\text{C}$.

clear that from low HCl medium, from 0.01 to 3 M, the extraction of HCl is rather limited. The extraction of hydrochloric acid was found to increase with increase of its concentration at acid molar concentration more than 3.0. This behavior is a typical characteristic of cyanamides and different from other organic extractants such as high molecular-weight amines, with which mineral acids may be extracted at very low acid concentration. This may be related to the expected basicity nature of the different cyanamides extractants investigated as a soft Lewis base [6], which has only low affinity for the hydrogen ion, a typical Lewis acid.

3.3. Extraction of metal ions

The variation of the extraction (% E) of Pd(II), Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) with DHCY, DEHCY and DOCY as a function of hydrochloric acid concentrations is shown in Figs. 2–4. It was found that the extraction of Cu(II) and Ag(I) by the synthesized cyanamides is negligible over the whole concentration region of hydrochloric acid. The extraction behavior of palladium(II) with the three synthesized extractants from aqueous solutions at various concentrations of hydrochloric acid has a maximum at very low diluted hydrochloric acid (0.01 M) equal to 92, 98 and 71% for DHCY, DEHCY and DOCY, respectively. This is followed by gradually decrease in % E with increasing hydrochloric concentration up to 3 M. At higher HCl concen-

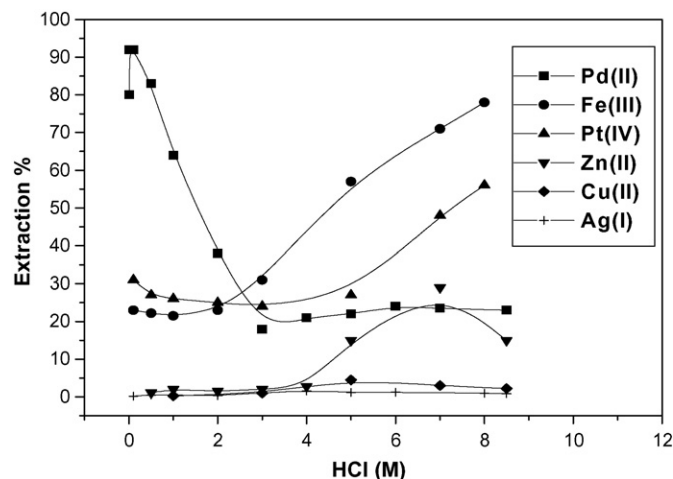


Fig. 2. Extraction of Pd(II), Fe(III), Pt(IV), Zn(II), Cu(II) and Ag(I) from hydrochloric acid solution with 0.15 M DHCY in toluene at $25 \pm 1^\circ\text{C}$.

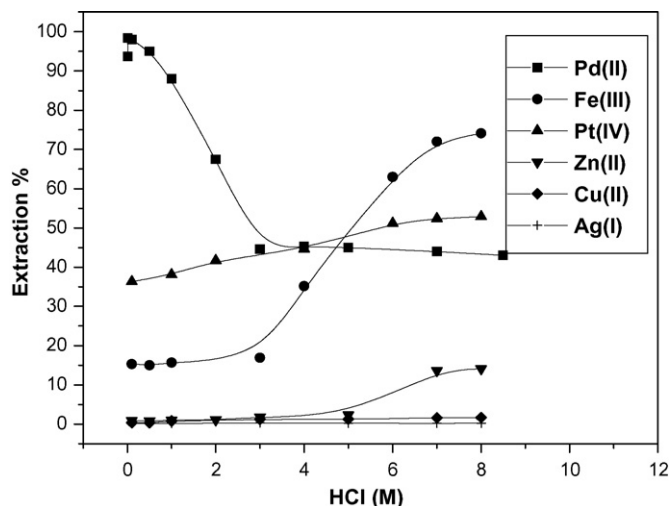


Fig. 3. Extraction of Pd(II), Fe(III), Pt(IV), Zn(II), Cu(II) and Ag(I) from hydrochloric acid solution with 0.15 M DEHCY in toluene at $25 \pm 1^\circ\text{C}$.

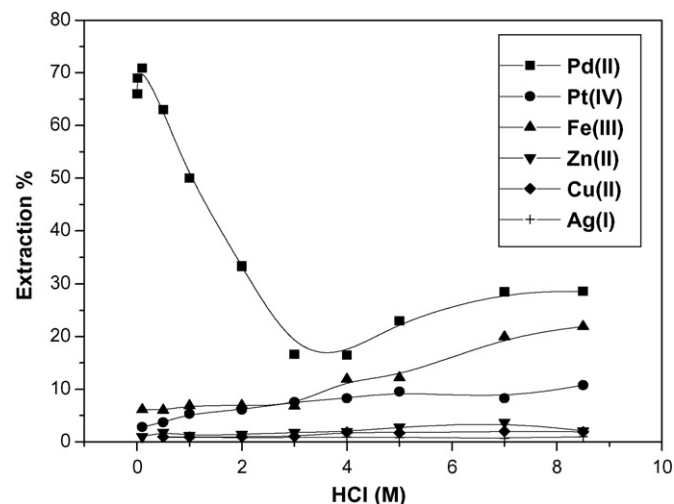


Fig. 4. Extraction of Pd(II), Fe(III), Pt(IV), Zn(II), Cu(II) and Ag(I) from hydrochloric acid solution with 0.15 M DOCY in toluene at $25 \pm 1^\circ\text{C}$.

tration the % E for palladium remained almost constant. The decrease in % E may be due to the protonation of the ligand at higher HCl concentration. The strong extraction of palladium only in the low concentration region of hydrochloric acid solution with these extractants permits an easy stripping of palladium with higher concentration of hydrochloric acid solution. The extraction of Fe(III) with DHCY and DEHCY was found independent of HCl concentration in the range 0.01–3.0 M, followed by a sharp increase up to the maximum acid concentration studied, Figs. 2 and 3. Similar behavior was obtained for the extraction of Pt(IV) with DHCY as shown in Fig. 2. The extraction of Pt(IV) and Fe(III) with DOCY was found to increase slightly with increasing HCl concentration as well as Pt(IV) with DEHCY, Figs. 3 and 4. The two extractants DEHCY and DOCY are similar in the atomic weight and the number of carbon atoms in the form of *n*-alkyl groups, however, DEHCY showed the highest tendency to extract the metal ions under investigations than DOCY, a behavior which was explained in previous section. The extraction data obtained suggesting that the extraction of palladium and platinum is governed by a different mecha-

nism even with the same extractant. These observations were also reported for other extractants [2,18]. The extraction of Zn by DHCY and DEHCY showed similar extraction behavior. Zn extraction by DHCY was found to slightly increase with the increase of acid concentration to reach maximum extraction of about 20% from 7 M HCl followed by slight decrease, Fig. 2.

As shown in Figs. 2–4, Cu and Ag are poorly extracted by the investigated extractants in the entire range of hydrochloric acid concentrations, while Zn shows a significant extraction especially from relatively high acid concentrations. Consequently, it appears to be very convenient to achieve effective separation of palladium from the other investigated elements in hydrochloric acid medium using the synthesized extractants as shown in Table 3.

It was found that good separation factors of Pd from Pt and Fe, can be obtained at the very low hydrochloric acid concentrations. On other hand, inclusive separation of Pd(II) from Zn(II), Cu(II) and Ag(I) can be completely achieved at ≥ 0.05 M HCl. As shown in Fig. 4 and Table 3, Pd(II) can be separated from Pt(IV), Fe(III) and Zn(II) at the whole range of hydrochloric

Table 3
Separation factors of Pd(II) from Pt(IV), Fe(III), Zn(II), Cu(II) and Ag(I) from various concentrations of hydrochloric acid with 0.15 M DHCY, DEHCY or DOCY in toluene at $25 \pm 1^\circ\text{C}$

[HCl] (M)	DHCY					DEHCY					DOCY				
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₁	S ₂	S ₃	S ₄	S ₅	S ₁	S ₂	S ₃	S ₄	S ₅
0.01	25.6	38.4	–	–	–	90.3	8.7	4900	2450	9800	61	40.7	–	–	–
0.05	25.6	41.1	–	–	–	55	5.4	1650	3300	6600	85.3	38.8	–	–	–
0.1	21.9	32.1	–	–	–	37.5	4.3	2400	2400	2400	81.3	34.8	244	–	–
0.5	11.2	22.4	–	560	–	29.7	3.1	950	533	3800	42.5	24.3	85	170	170
1.0	5.2	6.1	170	170	–	16.4	2.1	1150	1150	1150	16.6	12.5	100	100	100
2.0	1.7	1.5	30	60	–	4.2	1.9	150	150	300	7.3	6.4	25.5	51	51
3.0	1.3	1.8	11.5	23	11.5	1.3	8.0	20	30	60	2.6	2.6	11.5	23	23
4.0	1.3	2.9	6.5	13	26	1.1	1.5	20.5	41	82	2.5	1.6	12.5	12.5	25
5.0	1.1	4.4	1.3	6	30	1.0	1.9	23.3	31	93	2.8	1.4	11	16.5	33
7.0	2.9	5.9	1.1	11	16.5	1.4	3.71	3.7	26	39	4.9	1.2	12.3	24.5	49
8.5	4.0	9.0	1.1	15	30	1.4	4.5	2.9	24	72	3.5	1.1	24.5	24.5	49

where, $S_1 = D_{Pd}/D_{Pt}$, $S_2 = D_{Pd}/D_{Fe}$, $S_3 = D_{Pd}/D_{Zn}$, $S_4 = D_{Pd}/D_{Cu}$ and $S_5 = D_{Pd}/D_{Ag}$.

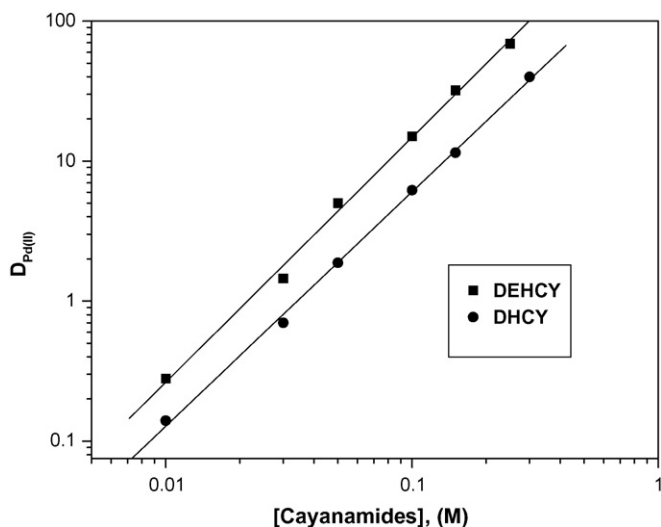


Fig. 5. Dependence of Pd(II) extraction on cyanamides concentration in toluene from 0.035 M HCl at $25 \pm 1^\circ\text{C}$.

acid concentrations using DOCY compared with DHCY and DEHCY.

To get an insight into the nature of the extracted species of palladium into the organic phase, the distribution ratios of Pd(II) from 0.035 M HCl were determined as a function of DHCY and DEHCY concentrations. The relation between $\log D_{\text{Pd}}$ versus $\log[\text{extractant}]$ gave a straight line having slopes nearly equal 2 with DHCY and DEHCY, Fig. 5.

The effect of presence of lithium chloride (salting-out agent) in the aqueous phase on the extraction of Pd(II) and keeping $[\text{H}^+]$ constant at 0.03 M HCl by DHCY and DEHCY was investigated. The relation between $[\text{Cl}^-]$ and distribution ratios of Pd(II) is given in Fig. 6. The log–log relations fit straight lines of slopes equal -1.7 and -1.8 for DHCY and DEHCY, respectively.

Based on these findings, we can suggest that the main extracted species of Pd(II) is in the form $\text{PdCl}_2 \cdot 2\text{L}$. Therefore, the extraction equilibrium of Pd, under the present experimen-

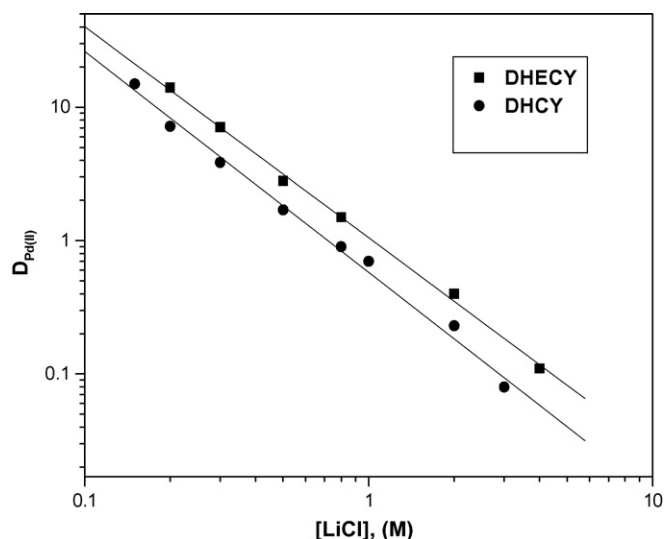
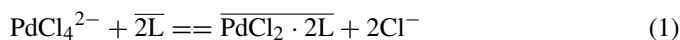


Fig. 6. Dependence of Pd(II) extraction on chloride ion concentration in the aqueous phase with 0.15 M cyanamides in toluene from $25 \pm 1^\circ\text{C}$.

tal conditions, from dilute hydrochloric acid medium can be represented as follows:



where bars denote organic phase species and L denotes the cyanamides DHCY and DEHCY.

To obtain an insight into the nature of the extracted species by DHCY and DEHCY, the IR spectra of the organic phase before and after Pd extraction from 0.5 M HCl were investigated in the range $4000\text{--}400\text{ cm}^{-1}$. The free nitrile group ($\text{C}\equiv\text{N}$) stretching vibration is at 2247 and 2245 cm^{-1} for DHCY and DEHCY, respectively. When the concentration of Pd in the organic phase equals half of the concentration of DHCY or DEHCY, the nitrile group stretching vibration vanishes and the coordinated $\text{C}\equiv\text{N}$ stretching vibration of DHCY and DEHCY with Pd occurs at 2189 and 2195 cm^{-1} , respectively. These results indicated that Pd may be mainly coordinated to the nitrile group and extracted as disolvate with DHCY or DEHCY.

These results may indicate that Pd(II) is coordinated to the nitrogen of the two cyanamides. The shift observed for the nitrile band was 50 cm^{-1} for DEHCY and 58 cm^{-1} for DHCY. The high shift for DHCY than DEHCY is expected if palladium species is more extracted by DHCY than DEHCY, if bonding is mainly to nitrogen atom. This contradicts the experimental results which indicate that Pd(II) is more extracted by DEHCY than DHCY. Therefore, bonding of Pd species to DEHCY should be different than its bonding with DHCY. This was explained by Inoue et al. [6] who illustrated the chemical structure and electron density at the functional group and donor atoms of branched cyanamides (*N,N*-di(2-ethylhexyl)cyanamide) as calculated by the PM3 type of semi-empirical molecular orbital method on the software, HyperChemTM Release 4 (Serial No. 51910006221). It was found that the negative charges are located on the nitrile group and not on the nitrogen atom in DEHCY. These studies have indicated that both hydrogen ion and metal ions on the extraction with DEHCY are not bonded to the nitrogen atom but to the nitrile group, a soft base. This can be the reason for the smaller shift of the $\text{C}\equiv\text{N}$ group of DEHCY than that of DHCY. These results are in parallel to that previously reported for amides-U(VI) complexes [14].

4. Conclusion

From the obtained data it is concluded that:

- Increasing the chain length of the alkyl substituted cyanamides on the nitrogen atom from C_6H_{13} to C_8H_{17} decreases the extraction of Pd, Pt and Fe.
- The very low values of extraction of Zn, Cu and Ag with all the synthesized extractants indicated that the change in structure have no effect on the extraction of these metal ions.
- The extraction of hydrochloric acid with cyanamides increase with an increase of its concentration in the aqueous phase.
- Pd is strongly extracted at low hydrochloric acid concentration (0.01 M) and shows a maximum around 0.01 M.

- Cu(II) and Ag(I) are poorly extracted by cyanamides in the entire range of aqueous acidity used while significant extraction, especially from relatively high hydrochloric acid concentrations, was observed for Pt(IV), Fe(III) and Zn(II).
- The general formula of palladium extracted species is $\text{PdCl}_2 \cdot 2\text{L}$ for the cyanamides used.
- The complexation of Pd (II) arises through the nitrile group of the cyanamides.

References

- [1] G. Kyuchoukov, L. Michaylov, A novel method for recovery of copper from hydrochloric acid solutions, *Hydrometallurgy* 27 (1991) 361–369.
- [2] I. Szczepanska, A. Borowiak-Resterna, M. Wisniewski, New pyridine caboxamides for rapid extraction of palladium from acidic chloride media, *Hydrometallurgy* 68 (2003) 159–170.
- [3] T. Fujii, H. Yamana, M. Watanabe, H. Moriyama, Extraction of palladium from nitric acid solutions by octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide, *J. Radioanal. Nucl. Chem.* 247 (2001) 435–437.
- [4] C. Yuan, H. Ma, J. Cao, L. Zhou, R. Luo, Studies on the structural effect of dialkyl(aryl)sulfides in gold and palladium extraction, *Solvent Extr. Ion Exch.* 6 (1988) 739–753.
- [5] M.J. Nicol, C.A. Fleming, J.S. Preston, in: G. Wilkinson (Ed.), *Comprehensive Coordination Chemistry*, vol. 6, Pergamon, Oxford, 1987, p. 779.
- [6] K. Inoue, K. Yoshizuka, A. Nakamura, S. Honda, Solvent extraction of palladium(II) with *N,N*-di(2-ethylhexyl)cyanamide, *Solvent Extr. Res. Dev. Jpn.* 2 (1995) 221–228.
- [7] R.A. Grant, R.F. Burnham, S. Collard, in: T. Sekine (Ed.), *Solvent Extraction*, Elsevier, Amsterdam, 1990, p. 961.
- [8] R.F. Dalton, R. Price, B.Q. Quan, B. Towson, in: M.J. Jones, R.I.T. Oblatt (Eds.), *Novel Solvent Extractants for Recovery of Copper from Chloride Leach Solutions Derived from Sulfide Ores*, Reagent in the Minerals Industry, Institute of Mining and Metallurgy, London, 1984, p. 181.
- [9] S. Daamach, G. Cote, D. Bauer, Extraction of palladium(II) by dialkyl-sulfides and trialkylphosphine sulfides: nature of extracted complexes in hydrochloric acid media and values of the extraction constants, *C.R. Acad. Sci., Paris, Ser. II* 304 (1987) 889–892.
- [10] J.S. Preston, A.C. du Preez, Solvent extraction of platinum—group metals from hydrochloric acid solutions by dialkyl sulphoxides, *Solvent Extr. Ion Exch.* 20 (2002) 359–374.
- [11] S.J. Al-Bazi, H. Freiser, Mechanistic studies on the extraction of palladium(II) with dioctylsulphide, *Solvent Extr. Ion Exch.* 5 (1987) 265–275.
- [12] R. Axen, J. Porath, S. Ernback, Chemical coupling of peptides and proteins to polysaccharides by means of cyanogens hilides, *Nature* 214 (1967) 1302–1304.
- [13] E.A. Mowafy, H.F. Aly, Extraction behaviors of trivalent lanthanides from nitrate medium by selected substituted malonamides, *Solvent Extr. Ion Exch.* 24 (2006) 677–692.
- [14] E.A. Mowafy, H.F. Aly, Extraction of actinides and selected fission products from nitric acid medium using long chain monoamides, *Solvent Extr. Ion Exch.* 19 (2001) 629–641.
- [15] E.A. Mowafy, H.F. Aly, Synthesis of some *N,N,N',N'*-tetraalkyl-3-oxapentane-1,5-diamide and their applications in solvent extraction, *Solvent Extr. Ion Exch.* 25 (2007) 205–224.
- [16] Z. Marczenko, *Spectrophotometric Determination of Elements*, John Wiley & Sons Inc., New York, USA, 1986.
- [17] Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3 -*n*-dodecane system, *Solvent Extr. Ion Exch.* 19 (2001) 91–103.
- [18] G.P. Demopoulos, Solvent extraction in precious metals refining, *J. Met.* 38 (1986) 13.