Paper I

SELECTIVE LIQUID-LIQUID EXTRACTION OF PALLADIUM(II) FROM HYDROCHLORIC ACID MEDIA BY DI-(2-ETHYLHEXYL) THIOPHOSPHORIC ACID (DEHTPA)

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ABSTRACT

Liquid-liquid extraction of Pd(II) from hydrochloric acid solutions using di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) dissolved in kerosene has been studied. Firstly the distribution equilibrium of DEHTPA between the aqueous phase and the organic phase was investigated by treating the data with the computer program LETAGROP-DISTR. The extraction of Pd(II) from HCl solutions by DEHTPA was studied as a function of several variables: equilibration time, organic phase diluent, HCl and DEHTPA concentrations as well as temperature. Experimental equilibrium data were analyzed numerically using the program LETAGROP-DISTR and the results showed that Pd(II) extraction can be explained assuming the formation of PdL_2 complexes in the organic phase. DEHTPA was found to be selective for Pd(II) against Pt(IV), Rh(III), Cu(II), Fe(III) and Zn(II). The back-extraction of Pd(II) loaded on the organic phase using different strippants is also reported.

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INTRODUCTION

At present there is a growing demand of precious metals for technological applications due to their outstanding physical and chemical properties. Palladium is one of the most important precious metals, consequently the development of processes for the recovery of palladium is necessary.

Traditional refining of precious metals was achieved through an extensive series of precipitation steps which are no longer considered efficient in terms of degree of separation. In the last twenty years, liquid-liquid extraction technology has been presented as one of the most suitable and powerful technique for the separation and purification of precious metals (1, 2).

In recent years various reagents have been studied for liquid-liquid extraction of Pd(II): long chain amines (3, 4), 7-substituted-8-hydroxyquinoleine derivatives (5, 6), tri-isobutylphosphine sulphide (7), bis(2-ethylhexyl) sulphoxide (8) as well as organothiphosphorous extractants (9-11). Sulphur-containing extractants, soft Lewis bases, are known to be highly selective for extraction of metals classified as soft Lewis acids. In fact, soft metals such as Ag(I), Hg(II) and Pd(II) are efficiently extracted by dialkyl thiophosphoric acids (12-14). Moreover, dialkyl thiophosphoric acids are much more resistant to hydrolysis than their dithio analogues. Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) is a new member of this class of extractants, and in previous works has been used for the selective extraction of Pd(II) by means of impregnated resins (15, 16) and supported liquid membranes (17). In the present work, the results obtained in the liquid-liquid extraction studies of Pd(II) by DEHTPA are presented.

EXPERIMENTAL

Reagents and Solutions

Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) was kindly supplied by Bayer and was purified through a procedure consisting in the formation of its potassium salt as described elsewhere obtaining a product with a purity of 96.9% (15).

Kerosene, cumene and toluene (Fluka) were employed as organic diluents for DEHTPA.

Stock metal solutions were prepared by dissolving the required amount of $PdCl_2$, $PtCl_4$, $RhCl_3.3H_2O$ (Johnson Matthey), $CuCl_2.2H_2O$, $ZnCl_2$ and $FeCl_3.6H_2O$ (Panreac) in hydrochloric acid solution.

All the other chemicals used in this work were of reagent grade.

Distribution of DEHTPA between the Aqueous Phase and the Organic Phase

The distribution experiments were carried out by shaking mechanically 10 ml of organic phase with an equal volume of aqueous phase for 24 hours to ensure that equilibrium was attained. Organic solutions of different extractant concentrations were prepared by dissolving DEHTPA in kerosene. Aqueous solutions with the following composition were prepared: 0.1 M (Na^+, H^+) Cl^-, and pH was varied. After phase separation, the equilibrium pH was measured and the total DEHTPA concentration in the aqueous phase was determined by analyzing the total phosphorus concentration by ICP (Spectroflame of Spectro Analytical Instruments). H_3PO_4 was used for the preparation of phosphorus standard solutions. The ligand concentrations in the organic phase after the distribution tests were calculated from a mass balance taking into account the phosphorus concentration in the aqueous phase.

Metal Extraction

The metal extraction experiments were carried out in batch experiments at room temperature if not otherwise stated. Equal volumes, 10 ml, of aqueous and organic solutions prepared as mentioned above, were shaken vigorously for 2 hours, except in the case of kinetic tests. After phase separation, metal concentrations in the aqueous phase were determined by ICP.

Metal Stripping

Metal stripping tests were carried out in batch experiments at room temperature. Firstly, 10 ml of Pd(II) solution were contacted with 10 ml of organic solution containing DEHTPA dissolved in kerosene for 2 hours in order to load the metal on the organic phase. Then, immediately after separating both phases, 10 ml of strippant reagent were added to the rich metal organic phase and were shaken vigorously for 2 hours. The metal concentrations after the extraction and stripping steps in the aqueous phase were determined by ICP.

RESULTS AND DISCUSSION

Study of DEHTPA Distribution between the Aqueous and the Organic Phase

The distribution of the extractant from the organic phase into the aqueous phase was studied at different pH for the aqueous solution and as a function of ligand concentration in the organic phase.

The distribution coefficient of the extractant between the organic phase and the aqueous phase was defined as:

$$D = \frac{[HL]_{org}}{[HL]_{aq}} \quad (1)$$

where $[HL]_{org}$ and $[HL]_{aq}$ are the total equilibrium concentration of DEHTPA, expressed in M, in the organic and in the aqueous phase respectively.

The dependence of DEHTPA distribution on pH for four different extractant concentrations is shown in Figure 1, where it can be seen that the distribution of the ligand in the aqueous phase is independent of pH at low pH values, approximately up to pH=3, and then decreasing as pH increases. In addition, the distribution ratio is not strongly dependent on the amount of extractant adsorbed on the resin, and consequently the presence of DEHTPA aggregates on the organic phase can be presumed to be not very significant.

The distribution data obtained could be explained assuming the following set of chemical reactions for the extractant molecules, HL, between the organic and the aqueous phase.

- Distribution of ligand between the organic and the aqueous phase:

$$HL_{aq} \Leftrightarrow HL_{org} \qquad K_D = \frac{[HL]_{org}}{[HL]_{aq}} \tag{2}$$

- Aggregation of DEHTPA in the organic phase:

$$nHL_{org} \Leftrightarrow (HL)_{n,org} \qquad K_n = \frac{[(HL)_n]_{org}}{[HL]^n_{org}} \tag{3}$$

- Dissociation of ligand in the aqueous phase:

$$HL_{aq} \Leftrightarrow H^+_{aq} + L^-_{aq} \qquad K_a = \frac{[H^+]_{aq}[L^-]_{aq}}{[HL]_{aq}} \tag{4}$$

where K_D, K_n and K_a are the distribution, aggregation and acidity constants respectively. The experimental distribution data were evaluated by the computer program LETAGROP-DISTR (18). In this program, for a given model, the computer searches for the best set of equilibrium constants that would minimize the error squares summatory defined by:

$$U = \sum (\log D_{exp} - \log D_{calc})^2 \tag{5}$$

where D_{exp} is the distribution ratio of the organothiophosphoric acid determined experimentally and D_{calc} is the value calculated by the program. The program also

calculates the standard deviation σ defined as:

$$\sigma(\log D) = \left(\frac{U}{N_p} \right)^{1/2} \qquad (6)$$

where N_p is the total number of experimental points. Several models with different aggregation numbers for the ligand HL were tried, in order to investigate the possibility of finding species which could improve the fit with the experimental results. The constants calculated are given in Table 1 and these values were used to calculate the solid lines in Figure 1, where good fitting of data is observed and which gives us great confidence in the proposed model. On the basis of the constants listed in Table 1 several points can be discussed. The high value of K_D indicates that the equilibrium distribution of DEHTPA between the kerosene and the aqueous phase is displaced toward the organic phase. The low aggregation constant found, confirms that the tendency of DEHTPA to form dimers in the organic phase is very limited. Nevertheless, some dimers can be expected to exist in the organic phase probably due to hydrogen bonding between the P=S and P-OH groups on adjacent DEHTPA molecules. Concerning the pK_a value found, it confirms the weak acidic character of DEHTPA. Taking into account the pK_a of DEHTPA and observing Figure 1, it can be concluded that the use of DEHTPA in highly acidic media will minimize the extractant loss from the organic to the aqueous phase, consequently DEHTPA can be an adequate extractant for precious metal recovery from highly charged mineral acid effluents.

A comparison between the distribution data obtained in this work and data available in the literature is also given in Table 1. The value of the K_D for DEHTPA on Amberlite XAD2 resins (15) is greater than that for DEHTPA in kerosene. This indicates that the equilibrium of DEHTPA is more shifted to the resin phase, and it seems that the interaction of DEHTPA with the resin phase acts to drive further the displacement of DEHTPA molecules from solution towards the macroporous polymer. The fact that the value of the distribution constant for

extractants adsorbed on resins is higher than the corresponding value for the same extractants in organic solvents has been reported (19, 20). Whereas the dimerization constant of DEHTPA in Amberlite XAD2 is rather low (15), in kerosene the aggregation is even lower than that found in the case of impregnated resins. The pk_a determined in this work, is in good agreement with values obtained by linearized pH-metric titration of DEHTPA in water with 16.7% ethanol (21) and with XAD2/DEHTPA resins distribution studies (15).

Solvent Effect on Pd(II) Liquid-Liquid Extraction

The extraction percentage for a metal, M, can be calculated as follows:

$$E(\%) = 100\frac{[M]_i - [M]_{aq}}{[M]_i} \qquad (7)$$

where $[M]_i$ and $[M]_{aq}$ in M units, are the initial and equilibrium metal concentration in the aqueous phase, respectively.

The extractability of metals by organic extractants is greatly affected by the nature of the solvent. The liquid-liquid extraction of Pd(II) using DEHTPA dissolved in three different solvents: kerosene, cumene and toluene was tested. Table 2, reflects that highest Pd(II) extraction is obtained by using kerosene.

Extraction Kinetics of Pd(II) and Pt(IV)

Pd(II) and Pt(IV) extraction kinetics were studied with single metal solutions and employing the same conditions for each metal: initial metal concentration 2.35×10^{-4} M in 0.5 M HCl and DEHTPA concentration 0.0025 M in kerosene. The kinetics of Pd(II) extraction is very fast and after shaking the solutions for 30 minutes, Pd(II) was almost 100% extracted. Nevertheless, a shaking time of 2 hours was adopted in all the tests in order to ensure the attainment of the equilibrium. In the case of Pt(IV), after 4 days (96 hours) the extraction was only of 13% and moreover the equilibrium was still not reached.

TABLE 1
Equilibrium constants of DEHTPA on different mediums

Medium	log K_D	log K_2	pK_a	Reference
Kerosene	1.27±0.05	-0.36±0.54	3.72±0.11	This work
16.7% Ethanol-Water	-	-	3.62	(21)
Amberlite XAD2	2.65	0.04±0.06	3.64±0.07	(15)

TABLE 2
Effect of the solvent on Pd(II) extraction
Experimental conditions: Initial Pd(II) concentration $2.35x10^{-4}$ M in 1 M HCl, different initial DEHTPA concentrations ($[HL]_{i,org}$) and shaking time 2 h

	E(%)		
$[HL]_{i,org}$(M)	Kerosene	Toluene	Cumene
$1x10^{-4}$	17.6	9.6	6.3
$3x10^{-4}$	42.9	18.0	11.5
$6x10^{-4}$	82.7	30.9	15.0

Because of the great difference in the rates of extraction of Pt(IV) and Pd(II), a procedure was devised for separating these two metals ions from an aqueous hydrochloric acid solution containing both precious metals. Figure 2 illustrates the percentage of extraction for Pd(II) and Pt(IV) versus time, and it can be seen that it takes less than 60 minutes to attain complete extraction of Pd(II), whereas Pt(IV) extraction was nearly negligible during the experiment. These results demonstrate that the rapid extraction separation of Pd(II) from Pt(IV) using DEHTPA dissolved in kerosene is feasible.

Liquid-Liquid Distribution Studies of Pd(II)

The dependence of the percentage of Pd(II) extraction on initial aqueous HCl concentration as a function of DEHTPA concentration is shown in Figure 3. The results obtained illustrate that there is an increase in Pd(II) extraction as

DEHTPA concentration is increased and as [HCl] is diminished.

The distribution coefficient of palladium, D, is given by:

$$D = \frac{[Pd]_{org}}{[Pd]_{aq}} \tag{8}$$

were $[Pd]_{org}$ and $[Pd]_{aq}$ are the total palladium concentrations in the organic and aqueous phase respectively, expressed in M. Figure 4 shows the Pd(II) distribution dependency on HCl and ligand concentrations.

In order to determine the equilibrium extraction reaction of Pd(II) with DEHTPA, the distribution data was treated with the computer program LETAGROP-DISTR, being each ionic strength analyzed separately.

According to the experimental data the Pd(II) distribution could be explained by taking into account the following reaction:

$$PdCl_4^{-2}{}_{aq} + 2HL_{org} \Leftrightarrow PdL_{2\,org} + 4Cl^-{}_{aq} + 2H^+{}_{aq} \tag{9}$$

The stoichiometric equilibrium constant, K_{ex}, for this extraction reaction is defined:

$$K_{ex} = \frac{[PdL_2]_{org}[Cl^-]_{aq}^4[H^+]_{aq}^2}{[HL]_{org}^2[PdCl_4^{-2}]_{aq}} \tag{10}$$

The values of the equilibrium constants, which depend on the ionic strength, are given in Table 3 and by increasing the HCl concentration the equilibrium constants increase. These values were used to calculate the solid lines of Figure 4 by means of the program LETAPL (22).

Differently, the extraction of Pd(II) from HCl media with DEHTPA impregnated on Amberlite XAD2 resins, was explained by the formation of metal complexes $PdL_2(HL)_2$ (16).

Influence of the temperature on Pd(II) extraction

The extraction of Pd(II) increases as the temperature increases as can be seen in Table 4. Treatment of these experimental data allows the estimation of the

enthalpy change, $\Delta H°$, for Pd(II) extraction assuming that Pd(II) is extracted only according to Reaction 9. Combining Equations 8 and 10 the following expression can be obtained:

$$\log K_{ex} = \log D + 4\log\left[Cl^-\right]_{aq} + 2\log\left[H^+\right]_{aq} - 2\log\left[HL\right]_{org} \quad (11)$$

Since $[Cl^-]_{aq}$, $[H^+]_{aq}$ and $[HL]_{org}$ were kept constant when the temperature effect was investigated, we can use log D in the place of log K_{ex} and analyze the data with the integrated Van't Hoff equation:

$$\log D = -\frac{\Delta H°}{2.3RT} + C \quad (12)$$

TABLE 3
Equilibrium constants for Pd(II) extraction by DEHTPA in kerosene from hydrochloric acid solutions

[HCl] (M)	log K_{ex}
0.5	6.5 ± 0.2
1	7.9 ± 0.2
3	10.3 ± 0.1

TABLE 4
Influence of temperature on Pd(II) extraction by DEHTPA
Experimental conditions: Initial Pd(II) concentration 2.35×10^{-4} M in HCl 1M
DEHTPA concentration 5×10^{-4} M in kerosene and shaking time 2h

T(°C)	E(%)
14	65.2
21	67.4
26	69.4
36	74.1
57	75.9
69	79.5

where R is the universal gas constant, 8.31 J/(K.mol), T is the temperature expressed in K and C is a constant value. In Figure 5, log D is plotted against 1/T and by fitting the data with linear regression analysis, an enthalpy change of +10 kJ/mol was determined indicating that the extraction of Pd(II) is an endothermic reaction.

Selective Pd(II) Extraction from Solutions containing Cu(II), Fe(III), Pt(IV), Rh(III) and Zn(II)

Figure 6 exhibits the extraction of Pd(II) by DEHTPA at different HCl concentrations from multimetal solutions containing some other precious metals: Pt(IV) and Rh(III), as well as some base metals: Cu(II), Fe(III) and Zn(II). Pd(II) is completely extracted in all the HCl concentrations range tested and among all the other metals, only Cu(II) and Fe(III) are significantly extracted at low acid concentrations. Thus, DEHTPA selectivity for Pd(II) extraction increases by increasing the acid concentration and over 3 M HCl only Pd(II) is extracted.

Metal Stripping

The stripping percentage of palladium was defined as the percentage of the Pd(II) loaded on the organic phase which was back-extracted to the aqueous phase.

Thiourea, Tu, and sodium thiocyanate, NaSCN were selected as stripping reagents. At first, the stripping of Pd(II) at different strippant concentrations in medium 1 M HCl was studied. Figure 7 shows the relation between the degree of Pd(II) stripping and the concentration of the stripping reagents. Back-extraction percentage increases with increasing the concentration of Tu and SCN^-. Although good results were obtained with thiocyanate, thiourea was found to be the reagent giving the best performance for Pd(II) re-extraction. The chemicals used in this work, which are soft ligands, act re-complexing the Pd(II) from the organic phase as a water soluble complexes: $Pd(Tu)_4^{+2}$ and $Pd(SNC)_4^{-2}$. The effect of HCl

concentration accompanying thiourea on metal stripping was also studied and the results are presented in Figure 8. When HCl was used as a unique strippant, almost nil stripping percentage was obtained, however in the case that HCl was combined with thiourea 0.005 M, the percentage stripping of Pd(II) increased gradually with increasing the HCl concentration, and a maximum value was attained around 3 M HCl. These results agree with those observed in the stripping of palladium loaded in bis(2,4,4-trimethylpentyl) monothiophosphinic acid, CYANEX 302 (11).

CONCLUSIONS

From the distribution studies of DEHTPA between the aqueous phase and kerosene it is concluded that the equilibrium distribution is displaced towards the organic phase, the extent of DEHTPA dimer formation in kerosene is not significant and the dissociation of the extractant in the aqueous phase becomes important approximately at pH>4, implicating that the use of DEHTPA in highly acidic media will minimize extractant loss.

The results obtained in the metal extraction sections show that DEHTPA is an effective extractant for Pd(II) from hydrochloric acid solutions, whereas Pt(IV) is extracted very slowly by DEHTPA. Pd(II) extraction with DEHTPA dissolved in kerosene, diluent which gives the highest extraction percentages, is an endothermic reaction which proceeds through the formation of the complex PdL_2. DEHTPA extracts selectively Pd(II) over other precious and base metals, and Pd(II) extraction is enhanced when the HCl concentration is reduced and when DEHTPA concentration is increased.

Complete stripping of Pd(II) from the organic phase is achieved using aqueous solutions of thiourea in HCl media.

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REFERENCES

1. M. Cox, in Principles and Practices of Solvent Extraction, J. Rydberg, C. Musikas and G. R. Choppin, Eds., Marcel Dekker, New York, 1992, p.357.
2. M. J. Cleare, P. Charlesworth and D. J. Bryson, J. Chem. Tech. Biotechnol., 29, 210 (1979).
3. K. Inoue, T. furusawa, I. Nagamatsu, Y. Baba and K. Yoshizuka, Solvent Extr. Ion Exch., 6, 755 (1988).
4. Y. Hasegawa, I. Kobayashi and S. Yoshimoto, Solvent Extr. Ion Exch., 9, 759 (1991).
5. B. Côté and G. P. Demopoulos, Solvent Extr. Ion Exch., 12, 393 (1994).
6. B. Côté and G. P. Demopoulos, Solvent Extr. Ion Exch., 13, 83 (1995).
7. M. Hidalgo, A. Masana, V. Salvadó, M. Muñoz and M. Valiente, Talanta, 38, 483 (1991).
8. J. P. Shukla, R. K. Singh, S. R. Sawant and N. Varadarajan, Anal. Chim. Acta, 276, 181 (1993).
9. K. Saito and H. Freiser, Anal. Sci., 5, 583 (1989).

10. T. Kakoi, K. Kondo, M. Goto and F. Nakashio, Solvent Extr. Ion Exch., 11, 627 (1993).
11. T. Kakoi, M. Goto and F. Nakashio, Solvent Extr. Ion Exch., 12, 541 (1994).
12. T. H. Handley, Anal. Chem., 35, 991 (1963).
13. I. P. Alimarin, T. V. Rodionova and V. M. Ivanov, Russian Chem. Reviews, 58, 863 (1989).
14. G. Cote and D. Bauer, Rev. Inorg. Chem., 10, 121 (1989).
15. M. Rovira, L. Hurtado, J. L. Cortina, J. Arnaldos and A. M. Sastre, Solvent Extr. Ion Exch., 16, (1998) in press.
16. M. Rovira, J. L. Cortina, J. Arnaldos and A. M. Sastre, Solvent Extr. Ion Exch., submitted for publication.
17. M. Rovira and A. M. Sastre, J. Membr. Sci., submitted for publication.
18. D. H. Liem, Acta Chem. Scand, 25, 1521 (1971).
19. J. L. Cortina, N. Miralles, A. Sastre, M. Aguilar, A. Profumo and M. Pesavento, React. Polym., 21, 89 (1993).
20. J. L. Cortina, N. Miralles, M. Aguilar and A. Sastre, Solvent Extr. Ion Exch., 12, 349 (1994).
21. A. Merkoci, A. Sastre, J. L. Cortina and C. Maccà, Fresnius J. Anal. Chem., 358, 489 (1997).
22. M. Petrich and J. L. Cortina, unpublished program.

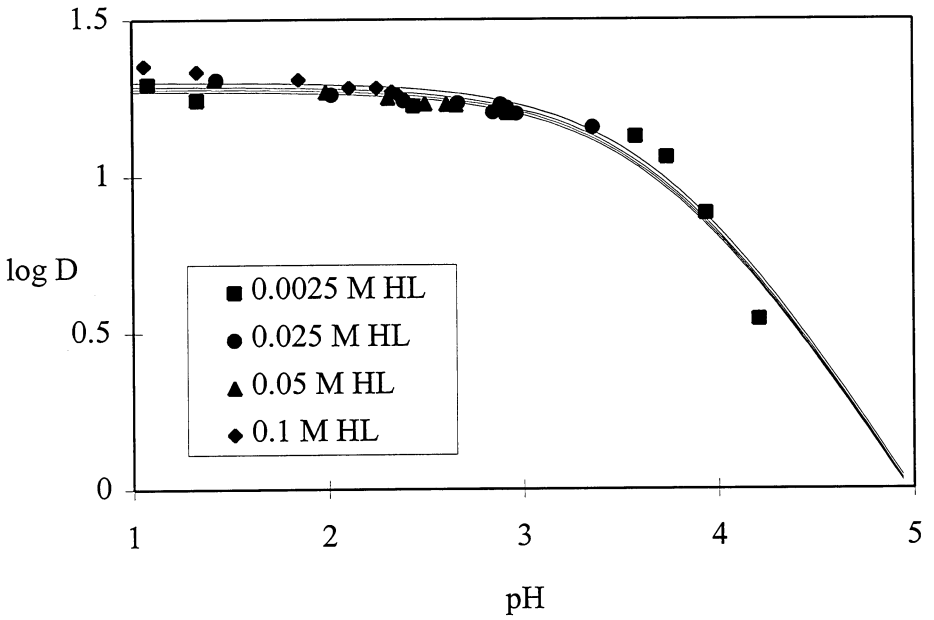

FIGURE 1. log D plotted as a function of pH for different DEHTPA concentrations in the organic phase being the composition of the aqueous phase: 0.1 M (Na^+, H^+) Cl^-. Full drawn lines calculated by the program LETAPL using constants given in Table 1 for DEHTPA in kerosene.

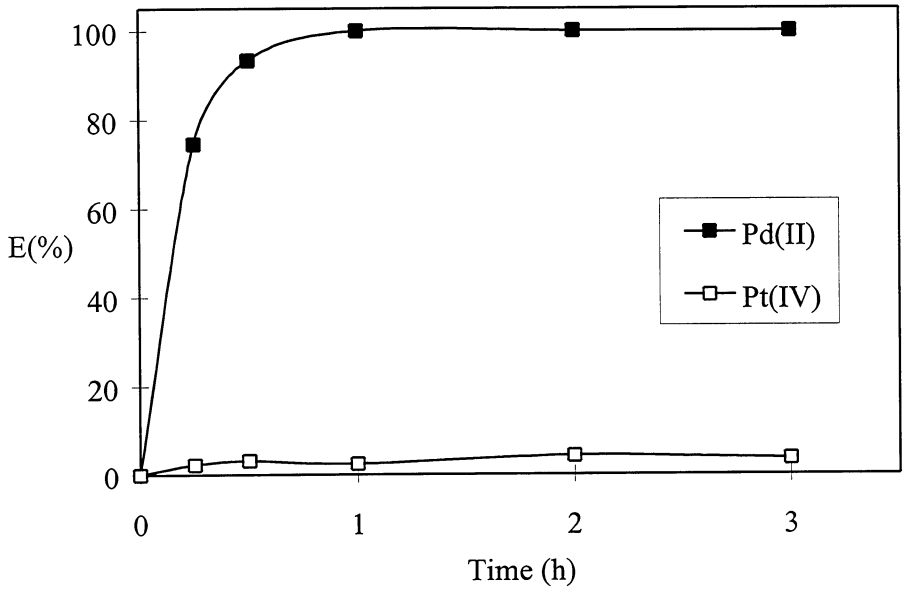

FIGURE 2. Percent extraction of Pd(II) and Pt(IV) against contact time. Experimental conditions: initial metal concentrations $[Pd]_i=[Pt]_i=2.35x10^{-4}$ M in 0.5 M HCl and DEHTPA concentration 0.0025 M in kerosene.

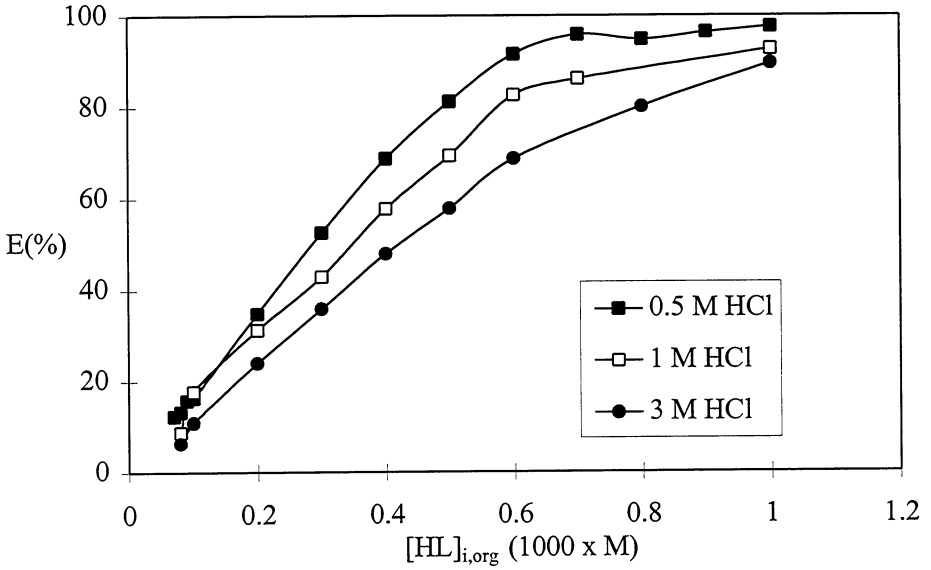

FIGURE 3. Effect of initial HL and HCl concentrations on percent extraction of Pd(II) resins. Experimental conditions: initial Pd(II) concentration 2.35×10^{-4} M and shaking time 2 h.

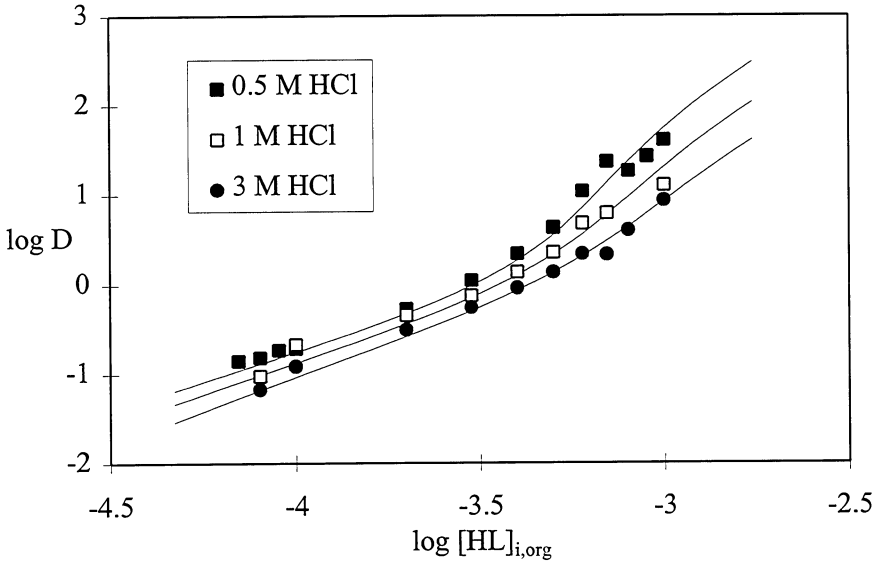

FIGURE 4. Effect of initial HL and HCl concentrations on the distribution ratio of Pd(II). Dashed lines have been calculated by the program LETAPL using the constants given in Table 1. Experimental conditions: as in Figure 3.

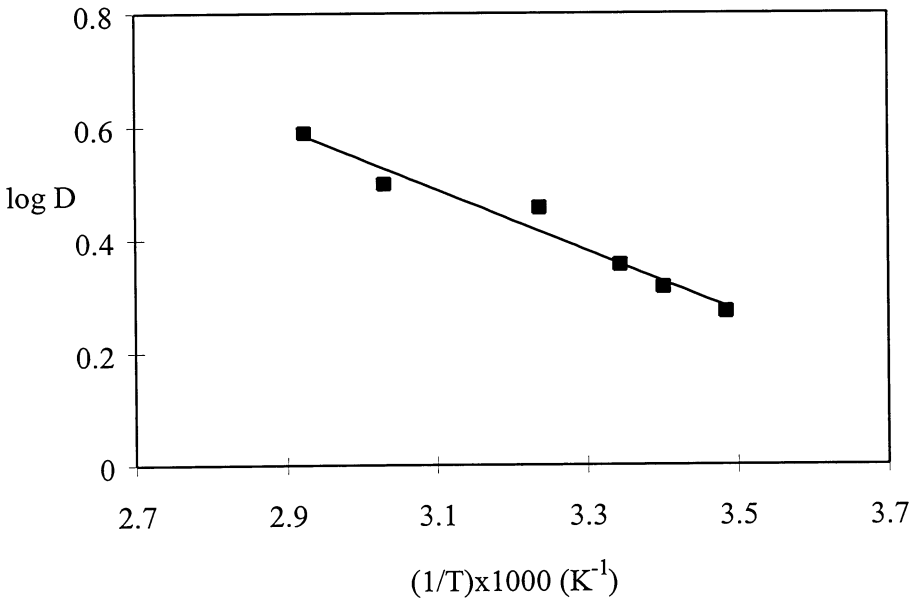

FIGURE 5. log D versus 1/T for Pd(II) extraction by DEHTPA. Solid line calculated by linear regression analysis. Experimental conditions: as in Table 4.

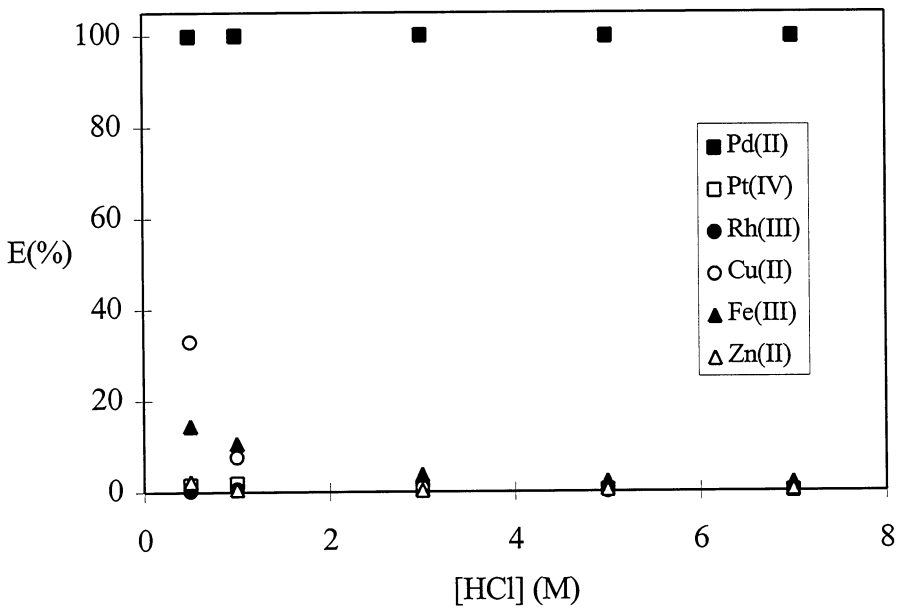

FIGURE 6. Effect of HCl concentration on percentage extraction of heavy metals. Experimental conditions: initial metal concentrations $[M]_i$=2.35x10^{-4} M, DEHTPA concentration 0.0025 M in kerosene and shaking time 2 h.

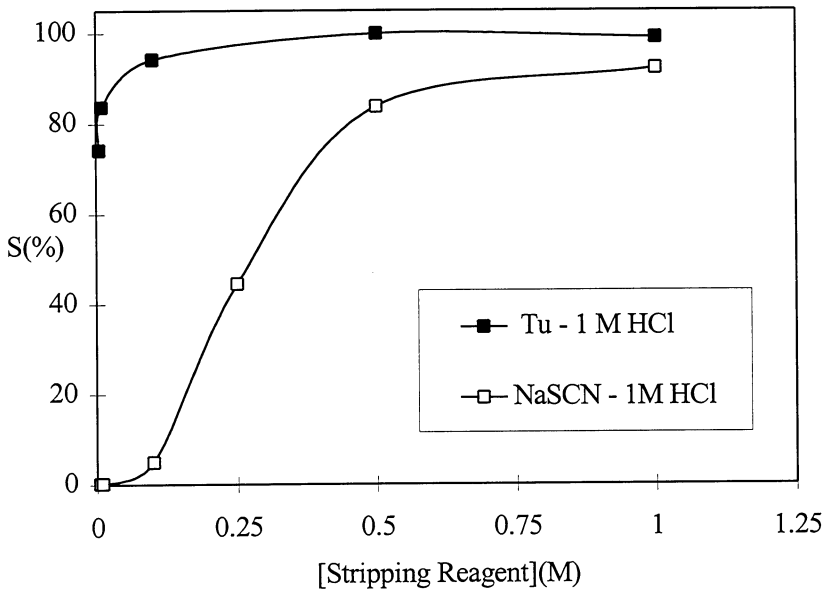

FIGURE 7. Effect of thiourea (Tu) and thiocyanate (SCN^-) concentration, in 1 M HCl, on the percent stripping of Pd(II) from the organic phase. Experimental conditions: metal concentration in the organic phase 2.35×10^{-4} M and shaking time 2 h.

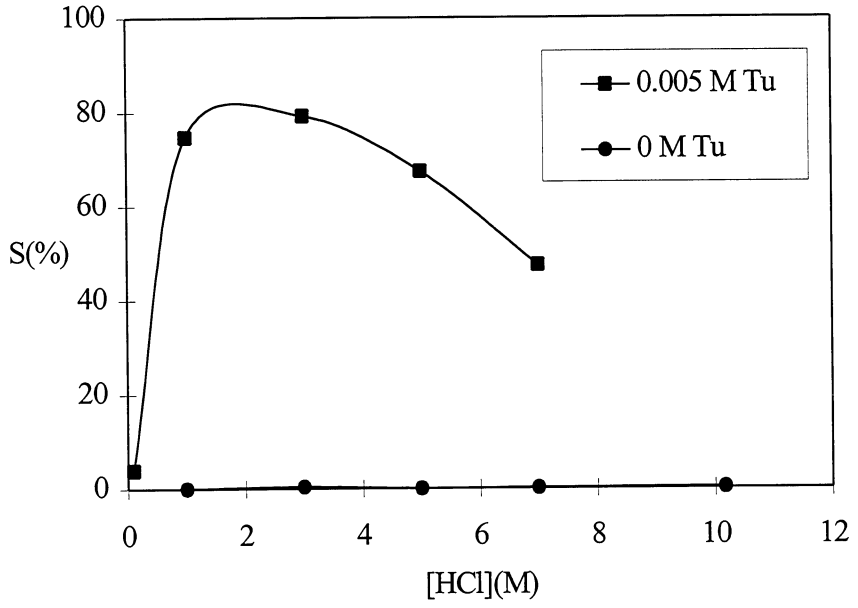

FIGURE 8. Effect of HCl concentration, in 0.005 M Tu, on the percent stripping of Pd(II) from the organic phase. Experimental conditions: metal concentration in the organic phase 2.35×10^{-4} M and shaking time 2 h.