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Thermodynamic Modeling of Extraction Equilibria of Platinum and Palladium with Nonylthiourea from Hydrochloric Acid Media

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Thermodynamic Modeling of Extraction Equilibria of Platinum and Palladium with Nonylthiourea from Hydrochloric Acid Media

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ABSTRACT

Models of extraction equilibria of Pt(IV) and Pd(II) with Nonylthiourea (NTH) from HCl media have been studied. The conditional equilibrium constants and the stoichiometry of the extracted species of Pt(IV) with NTH at different ionic strengths obtained by numerical analysis using the LETAGROP-DISTR program are reported. The dependence of the extraction constant values on the ionic strength has been analysed using the Specific Interaction Theory (SIT), from which the respective thermodynamic equilibrium constants of the extraction of Pt(IV) and Pd(II) with NTH have been determined. The thermodynamic equilibrium constants determined for Pt(IV) are $\log K^{o}_{11} = 5 \pm 1$ and $\log K^{o}_{14} = 14.6 \pm 0.2$, while for Pd(II) $\log K^{o}_{11} = 4.9 \pm 0.1$ and $\log K^{o}_{12} = 9.17 \pm 0.08$.

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The interaction coefficients, ε, for the pairs (H^+, $PtCl_6^{2-}$) and (H^+, $PdCl_4^{2-}$) have also been estimated to be 0.30 ± 0.08 and 0.41 ± 0.02, respectively.

Key Words: Platinum; Palladium; Thermodynamic modeling.

INTRODUCTION

The extractions of Pd(II) and Pt(IV) from hydrochloric acid solutions with nonylthiourea (NTH) dissolved in chloroform have been reported in our earlier papers.[1,2] Their extraction mechanisms were interpreted with the determination of respective extraction constants for Pd(II) at 1.0 M HCl[1] and Pt(IV) at 4 M HCl.[2] However, the extraction constants obtained in these solvent extraction studies are typically conditional constants, as most of those in the literature. To make them usable in practical applications under other ionic conditions, the conditional constants of a chemical reaction in general, and extraction in particular, need to be correlated by a model of activity coefficients as a function of the ionic medium, and if possible, extrapolated to obtain a thermodynamic constant at infinite dilution reference state.

For this purpose, several approaches have been used to describe the dependency of activity coefficients of solutes on ionic medium and concentrations. Among them the Pitzer equation,[3,4] the Bromley approach,[5] and the Brønsted-Guggenheim-Scatchard Specific Interaction Theory (SIT)[6,7] are worth mentioning. In these models, the deviation from ideal behaviour of the ions is considered to depend on two factors. The first factor takes into account long range electrostatic interactions (Debye-Hückel term) which is dependent only on the ionic strength. The second factor considers short range interactions (specific interactions between the different ions). The model proposed by Pitzer takes into account the interactions between the ions of different charge and between the ions of the same charge, in the short range interactions. Bromley proposed a “trial and error” method based on the empirical adjustable parameters. The SIT model is a simplified alternative of the Pitzer model, in which the interactions between ions of the same sign in the short range interaction are neglected.

Due to its simplicity, the SIT model has been applied in several solvent extraction studies to analyse the dependence of the equilibrium constants on ionic strength. It was reported that the formation constants of Pt(IV)-alamine obtained vary linearly with the ionic strength, and the interaction coefficient between $PtCl_6^{2-}$ and H^+ was estimated to be 0.46.[8] In the literature available, there is very limited information on the application of the SIT model to platinum group metals. Therefore, the purpose of the present work is to extend the applicability of the SIT model to the extraction of platinum group metals such as Pt(IV) and Pd(II) with NTH.

EXPERIMENTAL

Chemicals and Reagents

All of the chemicals and reagents used were of analytical grade, unless otherwise denoted. NTH was used as the organic reagent. The details of synthesis have been described elsewhere.[9] Different aqueous solutions of Pt(IV) or Pd(II) at given HCl concentrations were prepared from their respective stock solutions. The proton concentration was determined by potentiometric titration using 0.1 M NaOH.

Metal Extraction

Equal volumes of aqueous and organic solutions with known concentrations were mixed using mechanical shaker (40 rpm) at 22°C for a given period. A preliminary experiment was carried out to determine the contact time required to attain equilibrium. The analysis of metal ions in aqueous phase, before and after the extraction, was carried out using an atomic absorption spectrometer (Varian AA Spectra-200, Varian, Australia) equipped with a graphite furnace (Varian GTA-A110, Varian, Australia). The metal concentration in the organic phase was calculated by mass balance.

RESULTS AND DISCUSSION

Treatment of the Distribution Data of Pt(VI) Extraction

In our previous study,[2] the extraction of Pt(IV) at 4.0 M HCl with NTH was investigated. It was concluded that the extraction of Pt(IV) with NTH proceeds through the formation of $PtCl_4(NTH)$ and $PtCl_4(NTH)_4$ species. In the present study, the extraction of Pt(IV) with NTH at 0.1 M and 2.0 M HCl has also been determined. Figure 1 shows the Pt(IV) distribution as a function of NTH concentration at a constant ionic strength of 0.1 M. Analysis of the experimental distribution data obtained at different ionic strength was performed using the computer program LETAGROP-DISTR.[10] This program

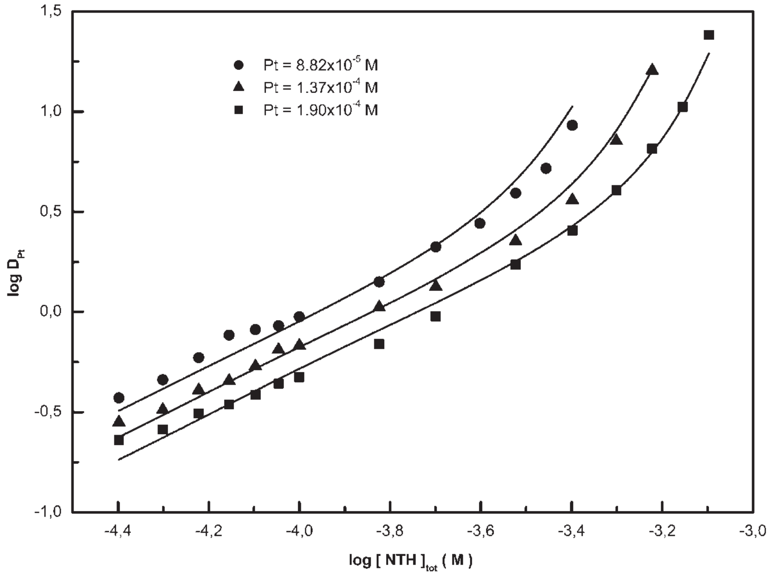

Figure 1. Distribution data for the extraction of Pt(IV) by NTH in chloroform from 0.1 M HCl solutions at 22°C. The points are experimental data while the solid lines are calculated using the model of 1 : 1 and 1 : 4 species and the equilibrium constants given in Table 2.

searches for the best equilibrium constant that minimizes the error squares sum defined by;

$$U(D) = \sum_{N_p} \left(\log D_{calc} - \log D_{\exp}\right)^2 \tag{1}$$

where $D_{\exp}$ is the distribution coefficient determined experimentally and D_{calc} is the value calculated by the program. This program also calculates the standard deviation $\sigma(\log D)$ defined by;

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

where N_p is the number of experimental points.

Several models have been tested for the best fit of the experimental distribution data. Table 1 summarizes the main results of the numerical treatment of the experimental distribution data for Pt(IV)-HCl-NTH extraction system at ionic strengths of 0.1 M and 2.0 M in comparison with the earlier reported data at 4.0 M HCl.[2] As can be seen, the results of numerical treatment agree well

Table 1. Summary of the numerical analysis of Pt(IV) distribution data at different ionic strength.

Model species	I = 0.1 M (HCl)			I = 2.0 M (HCl)			I = 4.0 M (HCl)		
	Log *K*	U	σ	Log *K*	U	σ	Log *K*	U	σ
1 : 1	2.3 ± 0.09	0.7	0.1	4.59 ± 0.02	2.1	0.2	5.15 ± 0.09	0.8	0.2
1 : 2	6.4 max 8.7	5.5	0.4	8.5 ± 0.1	1.2	0.2	8.31 ± 0.01	1.5	0.2
1 : 4	14.7 max 16.9	21.3	0.8	15.1 ± 0.2	28.5	0.9	14.8 max 13.9	12.2	0.8
1 : 1	2.26 ± 0.06	0.3	0.1	4.5 ± 0.1	0.4	0.1	5.06 ± 0.01	0.02	0.02
1 : 4	14.43 ± 0.02			14.5 ± 0.2			14.12 ± 0.04		
1 : 1	2.2 ± 0.09	0.5	0.1	4.1 ± 0.1	0.5	0.1	5.05 ± 0.01	0.02	0.03
1 : 2	5.3 max 7.8			8.3 ± 0.2			6.67 ± 0.03		
1 : 4	12.8 max 15.1			13.3 max 13.1			14.09 ± 0.01		

The error in the constants values is given as $\pm\sigma(\log K)$.

with the earlier results. The best fit of the experimental data is shown by a model, as reported earlier,[2] of the following reaction mechanism:

$$PtCl_6^{2-} + q\overline{NTH} \Longleftrightarrow \overline{PtCl_4(NTH)_q} + 2Cl^- \tag{3}$$

where $q = 1$ and 4, and the bar denotes the organic phase. The equilibrium constant of the extraction reaction in Eq. (3) is therefore:

$$K_{1q} = \frac{\overline{[PtCl_4(NTH)_q]}[Cl^-]^2}{[PtCl_6^{2-}]\overline{[NTH]^q}} \tag{4}$$

Table 2 summarizes the corresponding conditional constants at ionic strengths of 0.1 M, 2.0 M and 4.0 M. As shown in Fig. 1, the solid lines calculated using the constants obtained at ionic strength of 0.1 M HCl, have a good fit to the experimental points, though there is a little increased deviation in the very low range of NTH concentrations.

Dependence of Extraction Constants of Pt(IV) on Ionic Media

As can be seen in Table 2, the obtained values of the conditional equilibrium constants vary with the ionic strength of the aqueous phase. The constants can be correlated to the ionic medium and extrapolated to the corresponding thermodynamic constants ($\log K^o$) at infinite dilution based on the SIT model. According to the SIT model, the activity coefficient γ_i of an ion of charge Z_i in a solution of ionic strength I (in molality) can be expressed by:

$$\log \gamma_i = -\frac{AZ_i^2 I^{1/2}}{1 + 1.5I^{1/2}} + \sum_j \varepsilon(i,j)m_j \tag{5}$$

where A is the Debye-Hückel parameter, 0.51 at 25°C and 1 atm, and ε (i,j) is the specific interaction coefficient between i and j, and has a value of zero

Table 2. The values of log K for Pt(IV) determined at different ionic strength and log K^o estimated using the SIT method.

		Ionic strength (M)			
Log K	Medium	0.1	2.0	4.0	0
Log K_{11}	HCl	2.26 ± 0.06	4.5 ± 0.1	5.06 ± 0.01	5 ± 1
Log K_{14}	HCl	14.43 ± 0.02	14.5 ± 0.2	14.12 ± 0.04	14.6 ± 0.2
Log K_4	HCl	12.17 ± 0.08	10.0 ± 0.3	9.06 ± 0.05	9.5 ± 0.8

when both ions are of the same charge sign. Based on the SIT model, the thermodynamic equilibrium constant ($\log K^o$) and the specific interaction coefficient $\varepsilon(H^+, PtCl_6^{2-})$ can be calculated according to the following equation:

$$\log K_{1q}^o = \log K_{1q} + \frac{2AI^{1/2}}{1 + 1.5I^{1/2}} + 2\varepsilon\left(H^+, Cl^-\right)m_{H^+} - \varepsilon\left(H^+, PtCl_6^{2-}\right)m_{H^+} \tag{6}$$

Where $q = 1$ and 4, $\varepsilon(H^+, Cl^-) = 0.12$,[6] and m_{H^+} is the proton concentration in molality.

Considering the reaction equilibrium in the organic phase;

$$\overline{PtCl_4(NTH)} + 3\overline{NTH} \Leftrightarrow \overline{PtCl_4(NTH)_4} \tag{7}$$

the equilibrium constant of Eq. (7) can be simply derived from the two extraction constants as follows;

$$K_4 = \frac{K_{14}}{K_{11}} = \frac{\left[PtCl_4(NTH)_4\right]}{[PtCl_4(NTH)][NTH]^3} \tag{8}$$

Since all the organic species have very low concentration in the present study, it is reasonable to assume that the equilibrium constant K_4 should not be affected by a concentration of any species, nor by the ionic medium in the aqueous phase. As shown in Table 2, however, three values of K_4 calculated from the respective constants of K_{11} and K_{14} at three different ionic strengths are not so consistent. The value of K_4 at 0.1 M HCl is too high, apparently due to a too low value of K_{11}, compared to other two which are in a reasonable agreement within 10% deviation of $\log K_4$. As pointed out above, the fit of the experimental data at 0.1 M HCl had the highest deviation in the region of low NTH concentrations, which significantly affects the reliability of the corresponding value of K_{11}. Therefore, the equilibrium constant in Eq. (8) can be assigned to be an average of two values at 2.0 and 4.0 M HCl, $\log K_4^o = \log K_4 = 9.5 \pm 0.8$ (Table 2).

By combining Eqs. (6) and (8), the SIT model can be re-expressed, having the unknown terms in Eq. (9) while the known terms in Eqs. (10) and (11), as follows:

$$Y = \log K_{14}^o + \varepsilon\left(H^+, PtCl_6^{2-}\right)m_{H^+} \tag{9}$$

$$= \log K_{14} + \frac{2AI^{1/2}}{1 + 1.5I^{1/2}} + 2\varepsilon\left(H^+, Cl^-\right)m_{H^+} \tag{10}$$

$$= \log K_{11} + \log K_4 + \frac{2AI^{1/2}}{1 + 1.5I^{1/2}} + 2\varepsilon\left(H^+, Cl^-\right)m_{H^+} \tag{11}$$

The evaluation of $\log K^o$ and $\varepsilon(H^+, PtCl_6^{2-})$ is then straightforward, since linear relationships are expected when plotting the Y values obtained from Eqs. (10) and (11) as a function of HCl concentration (in molality). As shown in Fig. 2, an intercept can be determined to be $\log K_{14}^o = 14.6 \pm 0.2$ and the slope to be $\varepsilon(H^+, PtCl_6^{2-}) = 0.30 \pm 0.08$. A value of $\log K_{11}^o = 5 \pm 1$ has been calculated according to Eq. (8) and listed in Tables 2 and 3. The value of the interaction coefficient $\varepsilon(H^+, PtCl_6^{2-})$ obtained in this study is comparable to another published value of 0.46.[8]

Dependence of Extraction Constants of Pd(II) on Ionic Media

Figure 3 shows the Pd(II) distribution as a function of ionic strength, i.e., HCl concentration, while both initial total concentrations of Pd(II) and NTH are constant. In our previous study,[1] the extraction of Pd(II) at 1.0 M HCl with NTH was interpreted to proceed through the formation of $PdCl_2(NTH)$ and $PdCl_2(NTH)_2$ species as follows;

$$PdCl_4^{2-} + q\overline{NTH} \Longleftrightarrow \overline{PdCl_2(NTH)_q} + 2Cl^- \tag{12}$$

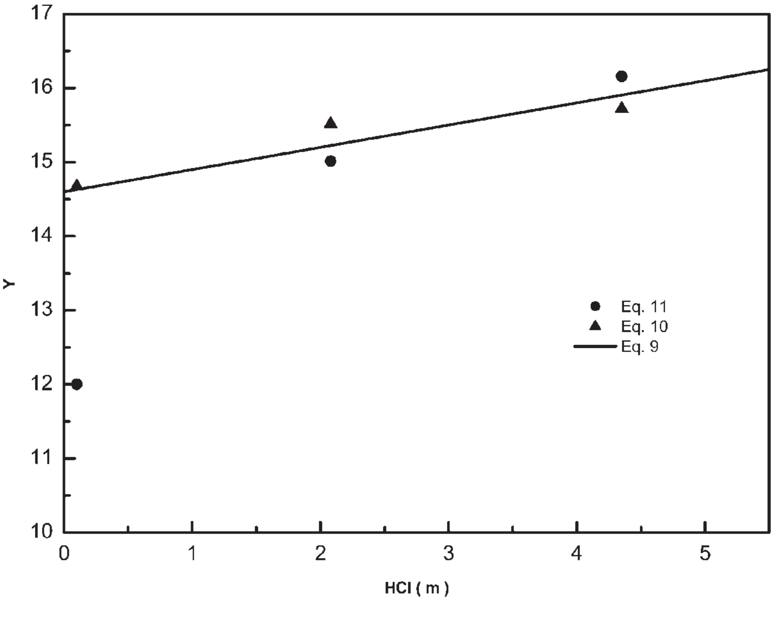

Figure 2. The SIT modeling for the determination of $\log K^o$ and ε for Pt(IV) extraction from HCl solutions.

Table 3. The value of log K^o and ε determined using the SIT model.

Metal ion	Log K^o_{11}	Log K^o_{12}	Log K^o_{13}	Log K^o_{14}	ε
Pt^{+4}	5 ± 1	—	—	14.6 ± 0.2	0.30 ± 0.08
Pd^{+2}	4.9 ± 0.1	9.17 ± 0.08	—	—	0.41 ± 0.02

where $q = 1$ and 2, with the respective equilibrium constants;

$$K_{1q} = \frac{\overline{[PdCl_2(NTH)_q]}[Cl^-]^2}{[PdCl_4^{2-}]\overline{[NTH]^q}} \tag{13}$$

Two constants of K_{11} and K_{12} can be correlated to the experimentally determined values of Pd(II) distribution, D, as a function of HCl concentration at

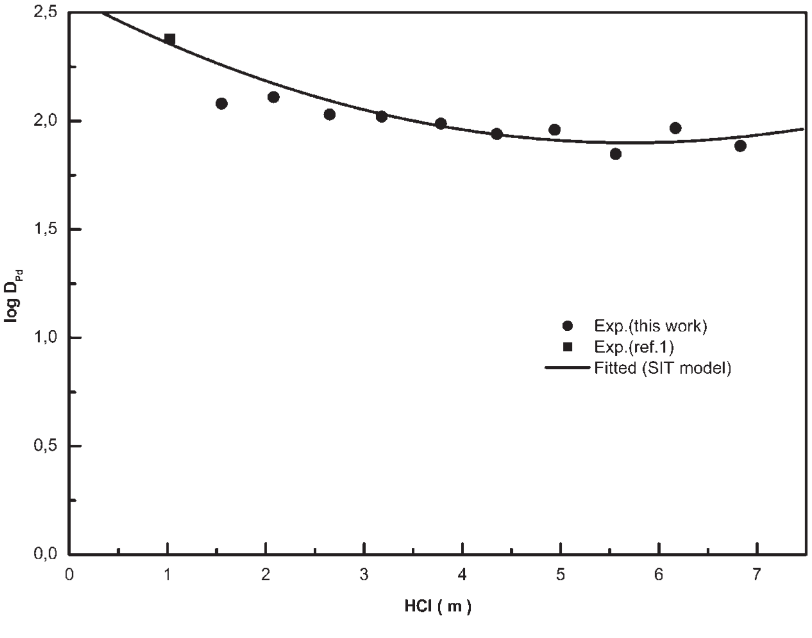

Figure 3. Distribution data for the extraction of Pd(II) by NTH in chloroform from 1–6 M HCl solutions at 22°C. The points are experimental data while the solid lines are calculated using the model of 1 : 1 and 1 : 2 species and the equilibrium constants given in Table 3.

the constant total concentrations of Pd(II) and NTH. These relationships can be described as follows;

$$D = \frac{\left[PdCl_4^{2-}\right]_{total} - \left[PdCl_4^{2-}\right]}{\left[PdCl_4^{2-}\right]} \tag{14}$$

$$= \frac{[PdCl_2(NTH)] + \left[PdCl_2(NTH)_2\right]}{\left[PdCl_4^{2-}\right]}$$

$$= \frac{K_{11}[NTH] + K_{12}[NTH]^2}{[Cl^-]^2} \tag{15}$$

$$[NTH]_{total} = [NTH] + [PdCl_2(NTH)] + 2\left[PdCl_2(NTH)_2\right]$$

$$= [NTH] + \frac{\left[PdCl_4^{2-}\right]\left(K_{11}[NTH] + 2K_{12}[NTH]^2\right)}{[Cl^-]^2} \tag{16}$$

On the other hand, the dependence of $\log K$ on the concentration of HCl as ionic medium can be expressed according to the SIT model,

$$\log K_{1q} = \log K_{1q}^{o} - \frac{2AI^{1/2}}{1 + 1.5I^{1/2}} - 2\varepsilon\left(H^+, Cl^-\right)m_{H^+} + \varepsilon\left(H^+, PdCl_4^{2-}\right)m_{H^+} \tag{17}$$

where $q = 1$ and 2.

By fitting the experimental data in Fig. 3 with Eqs. (14)–(17) in combination, two thermodynamic constants and interaction coefficient have been determined to be $\log K_{11}^{o} = 4.9 \pm 0.1$, $\log K_{12}^{o} = 9.17 \pm 0.08$ and $\varepsilon(H^+, PdCl_4^{2-}) = 0.41 \pm 0.02$ (Table 3). As shown in Fig. 3, the calculated values (solid curve) of log D present a good fit to the experimental data.

Simulation of Extraction of Pt(IV) and Pd(III) with NTH

Table 4 presents the calculated extraction constants of Pt(IV) and Pd(II) with NTH from two different solutions of 1 m and 6 m HCl, respectively,

Table 4. The calculated extraction constants of Pt(IV) and Pd(II) at 1 m and 6 m HCl using the SIT model.

Ionic strength (m)	Pt(IV)		Pd(II)	
	Log K_{11}	Log K_{14}	Log K_{11}	Log K_{12}
1	4.65	14.25	4.68	8.93
6	4.83	14.43	5.41	9.66

Based on these constants, the distribution diagrams of an extraction system of Pt(IV)-Pd(II)-HCl-H_2O-NTH can be obtained by using a computer program, MEDUSA, for the chemical equilibrium calculations, as presented in Figs. 4 and 5. The extraction percentage of Pd(II) and Pt(IV) at 1 m and 6 m HCl was calculated based on the distribution diagrams (Figs. 4 and 5). The selective extraction of Pd(II) and Pt(IV) as a function of NTH concentration at different HCl concentration is shown in Fig. 6. As can be seen from Fig. 6, the separation of Pd(II) and Pt(IV) is almost 5 times higher at 6 m HCl than at 1 m HCl, when NTH concentration is kept at 3.25 ± 0.5 mM. For instance at 6 m HCl, the extraction percentage of Pd(II) is 80%, while for Pt(IV) it is ~7% at NTH concentration of 3.25 ± 0.5 mM.

CONCLUSIONS

The conditional equilibrium constants and the stoichiometry of the extracted species of Pt(IV) with NTH at different ionic strengths obtained by numerical analysis using the LETAGROP-DISTR program are reported. The variation of the ionic strength determines the variation of the extraction constants but does not influence the stoichiometry of the species formed

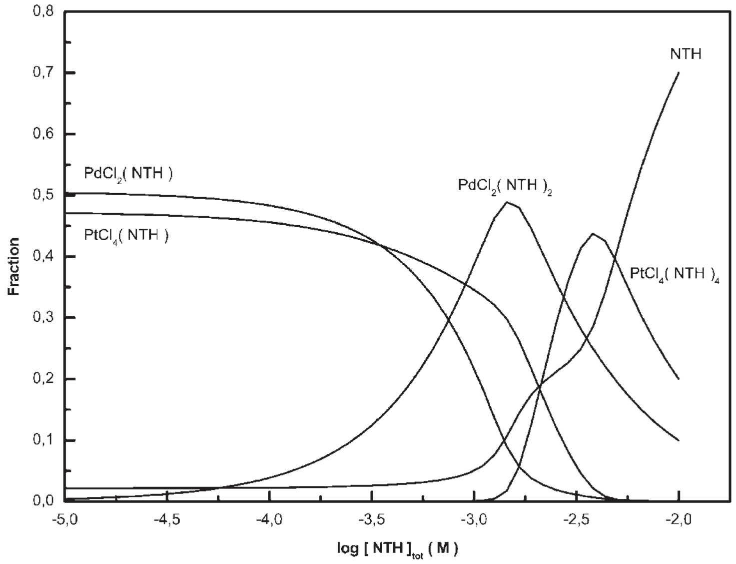

Figure 4. Fraction distribution of Pt(IV) and Pd(II) species in organic and aqueous phases at 1 m HCl.

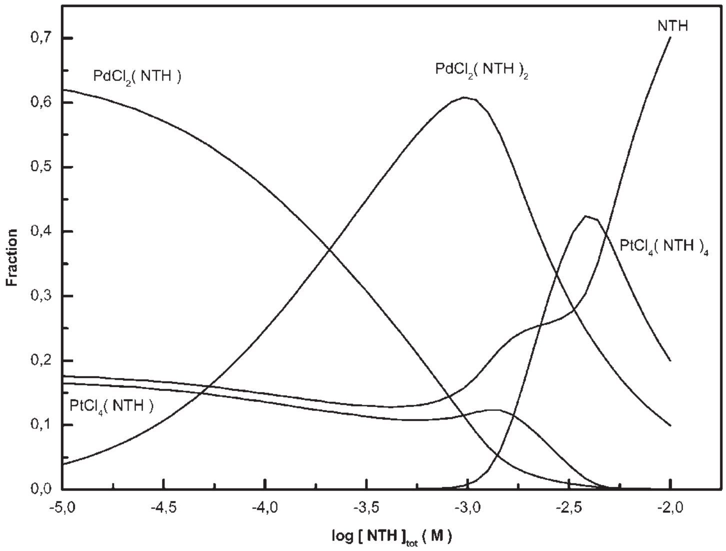

Figure 5. Fraction distribution of Pt(IV) and Pd(II) species in organic and aqueous phases at 6 m HCl.

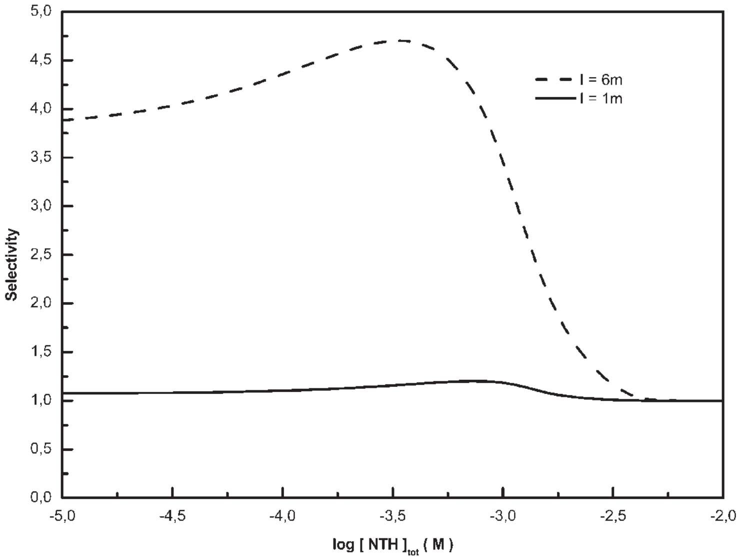

Figure 6. Simulation of the extraction of Pt(IV) and Pd(II) with NTH at 1 m and 6 m HCl.

during the extraction of Pt(IV) with NTH. The dependence of the extraction constant values on ionic strength was analysed by specific interaction theory (SIT). Using the SIT model, the respective thermodynamic equilibrium constants of the extraction of Pt(IV) and Pd(II) with NTH, and the interaction coefficients for the pairs (H^+, $PtCl_6^{2-}$) and (H^+, $PdCl_4^{2-}$) have also been determined.

REFERENCES

1. Uheida, A.; Zhang, Y.; Muhammed, M. Selective extraction of palladium (II) from chloride solutions with nonylthiourea dissolved in chloroform. Solv. Extr. Ion Exch. **2002**, *20* (6), 717–733.
2. Uheida, A.; Zhang, Y.; Muhammed, M. Extraction of platinum(IV) with nonylthiourea dissolved in chloroform from hydrochloric acid media. Solv. Extr. Ion Exch. **2003**, *21* (6), 827–840.
3. Pitzer, K.S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. **1973**, *77*, 268–277.
4. Pitzer, K.S., Ed.; Ion interaction approach; theory and data correlation. In *Activity Coefficients in Electrolyte Solution*, 2nd Ed.; CRC Press: Boca Raton, FL; 1991; 91–92.
5. Bromley, L.A. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE J. **1973**, *19*, 313–320.
6. Grenthe, I.; Puigdomenech, I. Modelling in aquatic chemistry. Nuclear Energy Agency, OECD: Paris; 1997.
7. Wang, M.; Zhang, Y.; Muhammed, M. Critical evaluation of thermodynamics of complex formation of metal ions in aqueous solutions: I. A description of evaluation methods. Hydrometallurgy **1997**, *45* (1–2), 21–36.
8. Alguacil, F.J.; Cobo, A.; Coedo, A.G.; Dorado, M.T.; Sastre, A. Extraction of platinum(IV) from hydrochloric acid solutions by amine alamine 304 in xylene. Estimation of the interaction coefficient between $PtCl_6^{2-}$ and H^+. Hydrometallurgy **1997**, *44* (1–2), 203–212.
9. Zuo, G.; Muhammed, M. Extraction of gold and silver by thiourea-based reagents. Sep. Sci. Technol. **1990**, *25* (13–15), 1785–1802.
10. Liem, D.H. High-speed computers as a supplement to graphical methods. Application of LETAGROP to data for liquid–liquid distribution equilibria. Acta Chem. Scand. **1971**, *25*, 1521–1534.

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