Paper VI
Recovery of palladium(II) from hydrochloric acid solutions
using impregnated resins containing Alamine 336

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Abstract

Impregnated resins containing Alamine 336 were prepared by direct adsorption of the extractant onto Amberlite XAD2 and physico-chemical characterization was performed. The kinetics and equilibrium extraction of Pd(II) from hydrochloric acid media are also reported. The graphical and numerical analysis of the Pd(II) extraction data by resins containing Alamine 336 could be explained by the formation of \((\text{R}_2\text{NH})_2\text{PdCl}_4 \) complexes. The resins have also been tested for practical application by determining the loading isotherm.

Keywords: Metal extraction; Impregnated resin; Amberlite XAD2 polymer; Alamine 336 extractant

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1. Introduction

Palladium belongs to the Platinum Group Metals (PGM) and possesses specific physical, chemical and mechanical properties; therefore, the increasing demand of Palladium for technological applications is demanding the development of new extraction techniques. Recently, these techniques have been focusing on the palladium recovery from hydrochloric acid media solutions, originating from leaching steps of hydrometallurgical processes (1).

In preliminary studies by Dhara (2) long chain amines were introduced as extractants with high efficiency in liquid-liquid extraction processes for the refining of PGM. Taking into account these results, it was interesting the evaluation of these extracants adsorbed or impregnated into a polymeric carrier acting as a stationary phase in solid-liquid extraction schemes.

In the last few years, the study of impregnated resins has been a major field of research in separation science and they could be considered as a link between solvent extraction and ion-exchange technologies (3). Impregnated resins show an attractive number of properties when are applied in metal separation on both fixed bed columns and fluidized bed technology. In this sense fluidized bed technology, which allows for continuous work and good levels of control, has been combined with impregnated resins carrying Alamine 336 for the recovery of Pd(II) (4).

High molecular weight amines impregnated with resin beads have been used in the extraction of base metals as well as precious metals. By loading tri-n-octylamine (TOA) onto a macromolecular resin, the separation of Zn(II) and Cu(II) (5) and the adsorption of Pd(II) (6), Au(III), Pt(IV)) and Pd(II) (7) from hydrochloric acid media have been reported. Selective extraction of Au(III) in the presence of base metals Zn(II) and Cu(II) has been achieved by using tri-n-dodecylammonium chloride (TOMACl) impregnated in Amberlite XAD2 resin (8).

In this work impregnated resins containing a commercial extractant, Alamine 336 (C₈-C₁₀ tertiary amine), have been prepared, characterized and applied to the recovery of palladium from hydrochloric acid media.
2. Experimental

2.1. Reagents and solutions

Alamine 336 (R₃,N) was kindly supplied by Henkel and used as extractant without further purification. Its purity was determined, as will be described in the next section, to be 92.2%. Alamine 336 is a mixture of saturated and straight chain trialkylamines with carbon chains C₈ and C₁₀, in which the proportion of the carbon chain C₈ is about 2 to 1.

Amberlite XAD2 (Rohm and Hass) with particle diameter between 0.3 and 0.9 mm, unless otherwise stated, was used as a macroporous polymer adsorbent. To remove impurities, the resin was kept in contact with a 50% methanol-water solution containing HCl 4 M for 12 hours. Then the polymer was washed with water until chloride was not detected, and dried at 50°C.

Stock Pd(II) solution was prepared by dissolving an appropriate amount of PdCl₂ (Johnson Matthey) in hydrochloric acid solution.

HClO₄ 72%, glacial acetic acid 99.5%, and pure acetic anhydride (Carlo Erba) were used for the amine titration. All the other chemicals used in this work were of reagent grade.

2.2. Titrimetric determination of amine content in Alamine 336

Quantification of the amine content in Alamine 336 and in the impregnated sorbent was conducted by titration, with HClO₄, of the corresponding sample which was dissolved in glacial acetic acid.

Standard HClO₄ in acetic acid was prepared by adding 8.5 ml of HClO₄ 72% to 900 ml of glacial acetic acid, mixing, gradually adding 25ml of acetic anhydride and then diluting to 1 liter with glacial acetic acid. The obtained solution was standardized the next day against potassium hydrogen-phtalate in acetic acid with crystal violet indicator. Visual end-point was used in the case of high amine content but for the quantification of low amine concentrations we employed potentiometric end-point determination using an automatic Micro TT 2050 titrator connected to a glass electrode (Crison). The saturated KCl filling solution in the electrode was replaced with an aqueous LiCl 0.1M solution in order to avoid plugging its
junction capillary with KClO₄. When the temperature at the time of analysis differed from the standardization temperature of HClO₄, the molarity of the standardized HClO₄ was corrected, taking into account the coefficient of thermal expansion for glacial acetic acid (9).

2.3. Impregnation procedure

Impregnated resins were prepared using a dry impregnation method which consisted of mixing an appropriate amount of Alamine 336 dissolved in ethanol with dry XAD2 until total evaporation of the diluent was reached. Then the polymeric beads were washed several times with deionized water and dried at 50°C. The content of Alamine 336 absorbed on the resin was determined after contacting three times 0.2 g of impregnated resin with 20ml of glacial acetic acid, which completely elutes the ligand, and subsequent potentiometric titration of the sample with HClO₄ as previously described.

2.4. Determination of the specific surface area of the impregnated resins and distribution of Alamine 336 between the aqueous phase and XAD2

The free specific surface areas of the resins were measured using a Flowsorb II 2300 (Micrometrics) and applying the Brunauer, Emmet and Teller (BET) equation as described elsewhere (10).

Some efforts were made to determine the distribution of the ligand from the polymeric phase into the aqueous phase at different pH’s for the aqueous solution and for different ligand loadings on the resin. In order to analyse the samples, which contained very low amine concentrations in water, we used two methods: 1) a method based on the spectrophotometric measurement of the colored complex formed with amines and methyl orange (11) and 2) High Performance Liquid Chromatography (HPLC) using light-scattering detection. Unfortunately, in both cases non reproducible results were achieved.
2.5. Pd(II) extraction

The metal extraction was carried out in batch experiments at room temperature. Samples containing 0.1 g of impregnated resin were shaken vigorously with 20 ml of metal aqueous phase during different time periods, depending on the purpose of the experiment: variable time for kinetics tests and in order to reach equilibrium, 48 hours in Pd(II) extraction at different HCl concentrations, and 90 hours for adsorption isotherm determination. After phase separation, metal concentrations in the aqueous phase were determined by ICP (Spectroflame of Spectro Analytical Instruments).

3. Results and discussion

3.1. XAD2/Alamine 336 impregnation

The measurements of free specific surface areas for non impregnated Amberlite XAD2 having different particle diameters are reported in Table 1. There is no dependence between the free specific surface area and the diameter of the particle. This result could be explained for the fact that XAD2 is a highly porous polymeric support with a large internal surface area compared to its external surface area. The specific external area, $S_{ext}$, for a particle with diameter $d$, shape factor $\phi$, and density $\rho$, is expressed as (12):

$$S_{ext} = \frac{6}{\phi \rho d}$$

(1)

Theoretical values of external surface area for XAD2, $\phi=0.7$ and $\rho=740$ kg/m$^3$ (13), with different particle diameters are reported in Table 1. The external surface area is negligible in comparison to the total superficial free area. On the basis of this observation, presumably the efficiency of the impregnation of the resin with an extractant is independent of the particle’s size. This hypothesis was proved by impregnating different size fractions of XAD2 resin with Alamine 336, 1.5 mol/kg dry XAD2 resin; no variations with the particle diameter were observed in the final ligand content.

The data on the impregnation of XAD2, with 0.3-0.9 mm particle diameters, with different amounts of Alamine 336 are illustrated in Figure 1. The efficiency of the
impregnation was close to 100% in all cases, indicating that almost all of the ligand was retained on the polymeric bead. Although saturation plateau was not observed, the impregnated resins with extractant concentrations over 1.5 mol/kg were greasy. This was probably due to the saturation of the support; thus the resin's ligand content could not be determined precisely. Comparing these results with those obtained for the impregnation of XAD2 with di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) (10), using the same impregnation procedure, we achieved a 50% of efficiency in terms of extractant retention. Thus, it can be concluded that the major presence of hydrocarbon chains in Alamine 336, compared to DEHTPA, plays a determinant role in the adsorption of the extractant. The retention of ligands by Amberlite XAD2 is due to adsorption phenomena that could be explained by the interaction between alkyl groups of the extractant with the vinyl and styrene groups of the polymeric matrix (3).

Surface area measurements have been used as a powerful tool in the morphological characterization of impregnated resins (10, 14, 15). In Figure 2, free and occupied specific surface areas of the impregnated resins are plotted against the Alamine 336 concentration of the polymeric support. The tendency observed is similar to those reported in the literature and suggests that in the adsorption process of the extractant, the ligand molecules fill the pore space gradually from the smallest pores of the resin up to the pores with large diameters (10, 14). This can be justified by taking the approximate diameter of tertiary amine molecules present in Alamine 336 to be 1.15 nm, calculated assuming spherical molecules as the simplest model, and most of the pores of Amberlite XAD2 having a diameter between 1.5 nm and 30 nm. If at a low ligand concentration in the resin, the extractant molecules began filling pores with small diameters as mentioned above, one would expect a non-efficient filling of these pores due to steric exclusion effect because of the similarity of the molecular diameter to the diameter of the smallest pores in the resin. Moreover, owing to geometrical considerations, pores with small volumes have relatively large areas. Consequently, small amounts of extractant will be responsible for a major decrease in specific surface area. The opposite behaviour is expected and observed for highly concentrated resins (10, 14).

The experimental data for free surface area presented in Figure 2 were successfully fitted by linear regression analysis to obtain the following equation:

\[ \ln [R_2N] = 0.23(\pm 0.05) - 0.0139(\pm 0.0006)S, \]  

(2)
where \([R_2N]_i\) is the total concentration of Alamine 336 in the resin phase in mol/kg and \(S_i\) is the total free specific surface area in \(m^2/g\), both parameters referring to dry XAD2 resin. The goodness of the adjustment, shown in Figure 3, with a correlation factor \(r = 0.994\), suggests that the measurement of free surface areas can be used as an analytical method for the determination of ligand content on the resin, following calibration of the method with impregnated resins of known concentrations. For resins with a concentration of over 1.5 mol/kg, this measurement was not possible due to the almost nil free surface area value.

3.2. Extraction Kinetics of Pd(II)

Qualitative assessments of the kinetics of metal uptake as a function of the initial Pd(II) concentration and the extractant loading in the resin, were carried-out on the basis of the extraction half time, \(t_{1/2}\), defined as the time necessary to achieve 50% of the resin’s final extraction.

The palladium percentage extraction ratio at different times was calculated as follows:

\[
E(\%) = 100 \frac{[\text{Pd}]_i - [\text{Pd}]_{eq}}{[\text{Pd}]_i}
\]  
\[
(3)
\]

where \([\text{Pd}]_i\) and \([\text{Pd}]_{eq}\) in M units, are the initial and equilibrium concentration of metal in the aqueous phase, respectively.

The results of the extraction kinetics when the metal concentrations were varied are shown in Figure 4 and Table 2. It was found that systems with low Pd(II) concentrations had faster extractions, and when the metal concentration was increased, the time to achieve the extraction equilibrium dramatically increased. From a practical point of view, in experimental work with impregnated resins, such as isotherm determination, this phenomena should be taken into account especially when determining the contact time necessary for reaching the final equilibrium. On the other hand, the data corresponding to the extraction kinetics of Pd(II) at different concentrations of Alamine 336 in the resin are reported in Figure 5 and Table 3. The times needed to reach the equilibrium decrease significantly by increasing the ligand content in the polymeric support.

Although the kinetic data presented in this study is not enough for a complete interpretation of the results, an attempt to draw conclusions was made. Assuming that the
chemical exchange reaction between the metal and the extractant is very fast and therefore is not the controlling step, metal extraction rates in impregnated resins could be explained in terms of diffusion control. Moreover, the rate-determining mechanism could either be diffusion across the externally adherent stationary liquid film, film diffusion control, or diffusion within the particle, particle diffusion control (3). If it is assumed that due to the vigorous agitation used in the experiments, film diffusion was probably destroyed, the diffusion inside the pores was the limiting step. This could explain the fact that by increasing the metal concentration or reducing the extractant content in the resin, the diffusion in the pores and consequently the rate of extraction, became slow. This is in agreement with recent experiments performed using impregnated resins reacting with base metals (16). Moreover, it has been reported that a large pore diameter allows a faster diffusion inside the resins (17). Assuming that the ligand molecules fill the pore space gradually from the smallest pores of the resin to pores with large diameters, as mentioned before in the case of resins with low extractant loading, the ligand predominantly occupies the smallest pores; thus low extraction rates can be expected.

3.3. Extraction equilibrium of Pd(II)

Figure 6 shows the Pd(II) percentage extraction E(%) at various concentrations of ligand as a function of the HCl concentration. The extraction of Pd(II) increases at low HCl concentrations and by increasing Alamine 336 content in the resin.

Pd(II) recovery by tertiary amines with solvent extraction (18) and impregnated resins (6) has been reported in the literature. The authors interpreted the extraction reaction in terms of an anion exchange mechanism. The tertiary amine forms an amine salt by reacting with HCl; because there is an excess of acid in the experimental conditions used in this work one can expect that this reaction takes place quantitatively. Two molecules of amine salt may react with the palladium tetrachlorocomplex $\text{PdCl}_4^{2-}$, which is the predominant specie of Pd(II) in hydrochloric acid solution, according to the following reaction:

$$2 \text{R}_3\text{NH}^+\text{Cl}^-_{\text{org}} + \text{PdCl}_4^{2-}_{\text{aq}} \Leftrightarrow (\text{R}_3\text{NH})_2\text{PdCl}_4^{2-}_{\text{org}} + 2\text{Cl}^-_{\text{aq}}$$  \hspace{1cm} (4)

where the subscripts "aq" and "org" denote species in the aqueous and resin phases, respectively.
In order to confirm that this reaction took place under the working conditions used in this study, slope analysis treatment was applied to the experimental data.

Analogous to solvent extraction, the distribution coefficient of the metal is defined as:

$$D = \frac{[\text{Pd}]_{\text{org}}}{[\text{Pd}]_{\text{aq}}} = \frac{([\text{Pd}]_i - [\text{Pd}]_{\text{aq}}) V}{[\text{Pd}]_{\text{aq}} m}$$  \hspace{1cm} (5)

where [Pd]_{org} and [Pd]_{aq} are the equilibrium metal concentrations in the resin and aqueous phase expressed in mol/kg dry impregnated resin and mol/l, respectively, [Pd]_i is the initial Pd(II) concentration in mol/l, V is the volume in l of the aqueous phase and m the mass of dry impregnated resin, in kg.

The extraction constant, \(K_{ex}\), for the reaction of the present system can be written as follows:

$$K_{ex} = \frac{\left[ (R_3 \text{NH}^+) \text{PdCl}_4^2 \right]_{\text{org}} \left[ \text{Cl}^- \right]^2_{\text{aq}}}{\left[ R_3 \text{NH}^+ \text{Cl}^- \right]_{\text{org}} \left[ \text{PdCl}_4^2 \right]_{\text{aq}}}$$  \hspace{1cm} (6)

By combining the definition of \(D\) and \(K_{ex}\), the following equation is deduced:

$$\log D = \log K + 2\log \left[ R_3 \text{NH}^+ \text{Cl}^- \right]_{\text{org}} - 2\log \left[ \text{Cl}^- \right]_{\text{aq}}$$  \hspace{1cm} (7)

Thus, for a determined ionic strength, plotting \(\log D\) versus \(\log [R_3\text{NH}^+\text{Cl}^-]_{\text{org}}\), as can be seen in Figure 7 a straight line with slope 2 should be obtained. While a good fit of the data is observed at high extractant concentrations of the resin, the distribution rate is remarkably lower than that expected at low Alamine 336 concentrations in the resin phase. In part, this phenomena could be explained due to lack of free extractant, because values of the total \([R_3\text{NH}^+\text{Cl}^-]_{\text{org}}\) instead free Alamine 336 concentrations in the resin were used to construct Figure 7, but it can not justify the fact that when Alamine 336 concentration was 0.19 mol/kg dry XAD2 resin, the Pd(II) extraction was almost completely suppressed as can be seen in Figure 6. As a first hypothesis, this loss of reactivity of Alamine 336 could be involved with the location of the amine molecules in pores with small diameter in the case of low extractant concentrations as mentioned before, and related to steric effects which influence the reaction between the metal and the extractant.

Experimental extraction data were also analyzed numerically with the program LETAGROP-DISTR (19) treating each ionic strength separately. This program searches for the best equilibrium constant that minimizes the error squares sum, defined by:
\[ U = \sum \left( \log D_{\text{exp}} - \log D_{\text{calc}} \right)^2 \]  

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

\[ \sigma(\log D) = \sqrt{\frac{U}{N_p}} \]

where \( N_p \) is the number of experimental points.

In order to investigate the possibility of finding other species which could improve the fit to the experimental results, several chemical reactions were attempted. However, the reaction expressed in Equation 4 provided the best fit. The values of the equilibrium constants at different ionic strengths are given in Table 4, stability constants for Pd(II) with Cl - found in the literature (20) were used in the calculations.

3.4. Extraction isotherm of Pd(II)

Figure 8 illustrates Pd(II) extraction isotherms at HCl 1 M and for different Alamine 336 loadings on the resin. The experimental data was fitted by means of a Langmuir isotherm:

\[ \Gamma = \Gamma_{\text{max}} \frac{K_{\text{ads}} [\text{Pd}]_{\text{sq}}}{1 + K_{\text{ads}} [\text{Pd}]_{\text{sq}}} \]  

where \( \Gamma \) and \( \Gamma_{\text{max}} \) are the equilibrium and maximum Pd concentration adsorbed in the resin expressed in mol/kg of dry impregnated resin, respectively, \( K_{\text{ads}} \) is the adsorption equilibrium constant in l/mol and \([\text{Pd}]_{\text{sq}}\) is the concentration of adsorbate in solution in mol/l. The results obtained for the fitting of experimental data are summarized in Table 5 and were used to construct the solid lines presented in Figure 8. At the saturation loading, the molar relationship between Alamine 336 and Pd(II) in the organic phase reached values very close to 2, indicating that all the molecules of the long chain amine in the sorbent are involved in the sorption reaction. This furthermore corroborates the extraction mechanism proposed.
4. Conclusions

The impregnation efficiency in terms of extractant retention is not affected by the particle size since the external surface area is negligible considering the total surface area. Almost 100% efficiency was obtained in the impregnation of Alamine 336 onto Amberlite XAD2 under the experimental conditions used in this work.

The free specific surface area measurements provide an alternative method for the determination of the extractant content of the resin. Furthermore, the adsorption mechanism of Alamine 336 filling the pore space gradually from the smallest pores up to larger pores was justified.

We were also able to determine some properties of the Pd(II) extraction. First of all, the extraction kinetics of Pd(II) became faster when the initial metal concentration was decreased and when the ligand content in the resin was increased. On the other hand, Pd(II) extraction increased at low HCl concentrations, and at high Alamine 336 loading in the resin, being metal uptake expressed by an anion exchange reaction. Finally, the extraction Pd(II) isotherm may be represented by the Langmuir isotherm.

Acknowledgments

This work was supported by the CIRIT Project QFN93-4414 (Autonomous Government of Catalonia) and the CICYT Project QUI 96-1025-C03 (Ministry of Science and Culture of Spain). Miquel Rovira gratefully acknowledges the Ministry of Science and Culture of Spain for a fellowship. We also thank Henkel for kindly donating Alamine 336. The authors are indebted to Dr. S. Akita, Nagoya Municipal Industrial Research Institute (Japan), for his helpful suggestions for this work.

References


TABLE 1
Values of measured total free specific surface areas ($S_t$) and calculated external free specific surface areas ($S_{ext}$) of Amberlite XAD2 with different particle diameters

<table>
<thead>
<tr>
<th>Particle diameter (mm)</th>
<th>$S_t$ (m$^2$/g)</th>
<th>$S_{ext}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3-0.9</td>
<td>305</td>
<td>-</td>
</tr>
<tr>
<td>0.3-0.4</td>
<td>311</td>
<td>0.033</td>
</tr>
<tr>
<td>0.4-0.5</td>
<td>308</td>
<td>0.026</td>
</tr>
<tr>
<td>0.5-0.63</td>
<td>314</td>
<td>0.021</td>
</tr>
<tr>
<td>0.63-0.75</td>
<td>312</td>
<td>0.017</td>
</tr>
</tbody>
</table>

TABLE 2
Half time dependency on initial Pd(II) concentration
(Experimental conditions are the same as those in Figure 4)

<table>
<thead>
<tr>
<th>[Pd]$\text{II}$ (M)</th>
<th>$t_{1/2}$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4x10$^{-4}$</td>
<td>0.4</td>
</tr>
<tr>
<td>4.7x10$^{-4}$</td>
<td>0.5</td>
</tr>
<tr>
<td>9.4x10$^{-4}$</td>
<td>2.3</td>
</tr>
<tr>
<td>1.7x10$^{-3}$</td>
<td>5.0</td>
</tr>
</tbody>
</table>

TABLE 3
Half time dependency on Alamine 336 content in the resin
(Experimental conditions are the same as those in Figure 5)

<table>
<thead>
<tr>
<th>[R$_2$N]$\text{III}$ (mol/kg)</th>
<th>$t_{1/2}$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>3.6</td>
</tr>
<tr>
<td>0.37</td>
<td>2.3</td>
</tr>
<tr>
<td>0.94</td>
<td>0.4</td>
</tr>
</tbody>
</table>
TABLE 4
Extraction constants for Pd(II) extraction by XAD2/Alamine 336 resins from hydrochloric acid solutions

<table>
<thead>
<tr>
<th><a href="M">HCl</a></th>
<th>log $K_{ex}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>2</td>
<td>4.86±0.06</td>
</tr>
<tr>
<td>3</td>
<td>4.83±0.05</td>
</tr>
<tr>
<td>4</td>
<td>4.70±0.03</td>
</tr>
<tr>
<td>5</td>
<td>4.54±0.07</td>
</tr>
<tr>
<td>6</td>
<td>4.28±0.03</td>
</tr>
<tr>
<td>8</td>
<td>3.8±0.1</td>
</tr>
</tbody>
</table>

TABLE 5
Parameter values obtained by fitting the data presented in Figure 8 by means of a Langmuir isotherm

| [R₂N]₀(mol/kg) dry XAD2 resin | 0.60 | 1.27 |
| [R₂N]₀(mol/kg) dry impregnated resin | 0.48 | 0.85 |
| $Γ_{max}$ (mol/kg) theoretical | 0.24 | 0.42 |
| $Γ_{max}$ (mol/kg) isotherm fitting | 0.22 | 0.43 |
| $K_{ads}$(l/mol) | $1.2\times10^4$ | $1.3\times10^4$ |
FIGURE 1. Concentration of extractant on dry XAD2 resin as a function of extractant mass used in the impregnation of 0.025 kg of dry XAD2. The line “Ideal Impregnation” was plotted assuming 92.2% purity for Alamine 336 and its complete adsorption on the resin.
FIGURE 2. Free and occupied specific surface areas as a function of extractant concentration on dry XAD2 resin.
FIGURE 3. Linear fit for the determination of Alamine 336 content on the resin from surface area measurements.
FIGURE 4. Effect of the initial Pd(II) concentration on extraction kinetics of Pd(II) by XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.05 g, volume of aqueous phase 20ml, HCl 0.5 M and extractant content in the resin 1.27 mol/kg dry XAD2 resin.
FIGURE 5. Effect of extractant content in the resin (expressed in mol/kg dry XAD2 resin) on extraction kinetics of Pd(II) by XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, HCl 0.5 M and initial Pd(II) concentration 4.7x10^{-4} M.
FIGURE 6. Effect of HCl concentration on the extraction of Pd(II) with XAD2/Alamine 336. Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, initial Pd(II) concentration $4.7 \times 10^{-4}$ M and variable extractant content in the resins (expressed in mol/kg dry XAD2 resin).
FIGURE 7. Effect of total Alamine 336 concentration (expressed in mol/kg dry impregnated resin) on the distribution ratio of Pd(II). Dashed lines were plotted taking into account slope 2. Experimental conditions: the same as those in Figure 6.
FIGURE 8. Effect of extractant content in the resin (expressed in mol/kg dry XAD2 resin) on the adsorption isotherm of Pd(II). Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, HCl 1 M and variable initial Pd(II) concentration.