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Extraction–Spectrophotometric Determination of Pd(II) with 4-(3,5-Dichloro-2-pyridylazo)-1,3-diaminobenzene and Trichloroacetate. I

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In acid acqueous ethanol solutions Pd(II) reacts with 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene (3,5-Cl2PADAB=L) making up three colored complex species. The three complexes have a 1 : 1 metal–ligand molar ratio and they differ from each other only in their protonation degree. In solutions with H_2SO_4 or $HClO_4$ concentrations higher than 10 or 8 M, respectively, the complex species is yellow, and in less acid solutions (pH 0.80 to 2 M H_2SO_4 or pH 0.8 to 3 M $HClO_4$ range) it changes in a reversible way to a violet color while its intensity increases (molar absorptivity 8.2×10^4 dm^3 mol^{-1} cm^{-1} at 588 nm and 5.2×10^4 dm^3 mol^{-1} cm^{-1} at 545 nm). The red purple complex formed in the pH range 3—4 are insoluble in 10% (v/v) ethanol-water solutions. The complex species were given the formulation $PdH_nL^{(n+2)+}$ ($n>1$) ($H_2SO_4>10$ M, or $HClO_4>8$ M), $PdHL^{3+}$ (pH 0.8 to 2 M H_2SO_4 or pH 0.8 to 3 M $HClO_4$ range) and PdL^{2+} (pH 3—4), and the existence of one or another depends exclusively upon the acidity of the reaction medium. In 10% (v/v) ethanol–water solutions acidified with H_2SO_4 or $HClO_4$, only the last two species are extracted into benzene as $PdL^{2+}\cdot(TCA^-)_2$ and $PdHL^{3+}(TCA^-)_3$ (TCA^-=trichloroacetate) ion-associations. The composition of the complexes formed in aqueous solutions was estimated by the composition of the ion-association complexes transferred to the organic phase.

4-2(-Pyridylazo)-1,3-diaminobenzene (PADAB), 5-(2-pyridylazo)-2,4-diaminotoluene (PADAT) and its halogen-substituted compounds constitute a relatively new type of *o*-amino azo analytical reagents. All of them react chromatically only with a few metallic ions (Co(II), Pd(II), Zn(II), Cu(II), Au(III), Fe(II), Fe(III), Ni(II), and Ag(I)). Several of them have been used for the spectrophotometric determination of Co(II)[1—6] and Pd(II).[7—13] Cobalt(II) reacts with these reagents to form CoL_2 complexes (pH range 3—11) which are changed into other deeply colored monoprotonated and diprotonated complexes by the addition of hydrochloric or other mineral acids. The CoL_2 complexes,[3] or their ion-association species formed with a suitable organic base, can be extracted into an organic solvent.[3,14]

In the course of a systematic investigation on the reaction between one of these pyridylazo reagents, 3,5-Cl2PADAB, and Pd(II),[12] and on the extraction of the complexes formed, we have found that the behavior of the Pd(II)–3,5-Cl2PADAB complexes resembles those of Co(II).

As we have not found detailed information about the reaction between Pd(II) and this type of reagents, this work is devoted to elucidate the mechanisms of formation of the Pd(II)–3,5-Cl2PADAB complexes and their extraction as ion-association species formed with trichloroacetate.

Bearing in mind that in the search of new sensitive and selective chromogenic reagents, a full knowledge of the reactions involved in the formation and extraction of metallic complexes yields important information, which can be used as the basis for the development of new spectrophotometric methods.

Experimental

Apparatus. pH was measured on a digital Orion Mod. 701-A pH-meter provided with a glass/Ag–AgCl combination electrode. Both absorbance measurements and spectral recordings were carried out on a Varian Mod. 634-UV spectrometer equipped with 10-mm glass cells.

For the extractions, 100×35 mm "Pyrex"-type glass tubes with polyethylene stoppers were used. Equilibrations were carried out by mechanical shaking of the tubes with longitudinal desplacements of 35—40 mm and a rate of 300 fluctuations per minute. Temperature was kept at 20±0.5 °C.

Reagents. 3,5-Cl2PADAB Solutions: The synthesis of the reagent was described earlier.[12] A 1×10^{-3} M solution (1 M=1 mol dm^{-3}) was prepared in 96% pure ethanol by using a purified and solid reagent. Other solutions having the concentration required for each particular test were prepared by means of dilutions, with the same solvent, of that solution.

Pd(II) Standard Solution (5×10^{-3} M). $Pd(NO_3)_2\cdot2H_2O$ (0.2665 g) was dissolved in 50 cm^3 of (4+6) H_2SO_4. The solution was heated to guarantee complete dissolution. Once cold, it was put in a volumetric flask and distilled water was added up to 200 cm^3. The effective concentration of the metal was complexometrically determined.[15] More diluted solutions were daily prepared from the previous one. Pd(II) solutions remain unaltered during 5 days if kept in glass vessels.

Trichloroacetic Acid (HTCA) Solution. The acid solution (500 cm^3, 5 M) was prepared from the solid drug. The exact content of the trichloroacetic acid was alkalimetrically determined on aliquot portions of the previous solution.[16]

General Procedures. Color Development. Aliquots of conveniently diluted Pd(II) solutions were diluted with distilled water up to about 15 cm^3. Acidity was adjusted to the value required for each test by adding concentrated

H_2SO_4 or $HClO_4$. When the medium acidity corresponded to the pH values higher than 0, the concentration of Na_2SO_4 or $NaClO_4$ was kept at 1 or 2 M, respectively. In these cases the pH of the solutions was adjusted at the required values by the addition of the diluted solution of H_2SO_4, $HClO_4$, or NaOH. The solutions were transferred to 25 cm^3 volumetric flasks, and 2.5 cm^3 of the ethanolic solution of the reagent were added. The absorbance of the solutions, as well as the absorption spectra of the solutes dissolved in them, were recorded when the color of each test reached its maximum insensity and remained, at least for ten minutes, unchanged.

Extractions. The complexation reactions were promoted on Pd(II) solutions (10—15 cm^3), put in extractions tubes and conditioned in the above-described way. The total initial HTCA concentration was kept constant at 1 M in all tests. Once the complexation was finished, a volume of pure benzene equal to that of the aqueous solution contained in the tubes was added, and the whole was mechanically shaken from 40min to 1 h. Then the organic phases were transferred to 25 cm^3 dried volumetric flask. The aqueous phases were washed twice, each time with 3 cm^3 portions of pure benzene, and the washing liquids were put together with the bulk of each benzenic extract, adding, in the end, benzene until completing 25 cm^3. After reaching the equilibrium, the pH of the aqueous phases was potentiometrically measured. The percentage of palladium extracted was spectrophotometrically determined by using 3,5-Cl2PADAB as chromogenic reagent.

Results and Discussion

In a previous paper,[12] we showed that in aqueous ethanol solutions Pd(II) reacts slowly with 3,5-Cl2PADAB in a wide range of concentrations of H_2SO_4 or $HClO_4$. The spectra of the palladium(II) chelates were measured for the 10% (v/v) ethanol-water solutions containing various concentrations of the components at different acidity conditions.

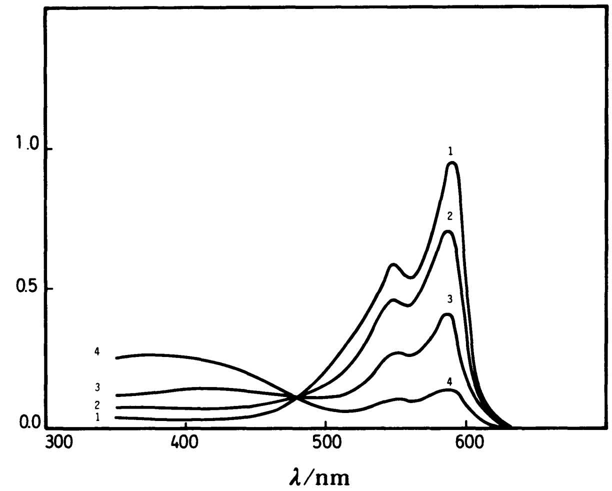


Fig. 1. Absorption spectra of Pd(II)-3,5-Cl2PADAB complexes in aqueous ethanol acid solution with 1.20×10^{-5} M reagent. Sulfuric acid concentration: (1) 2 M; (2) 7 M; (3) 8.30 M; (4) 9.80 M. Ethanol 10% (v/v).

Figures 1 and 2 show the absorption spectra of a mixture containing an excess of Pd(II) compared with 3,5-Cl2PADAB. The wavelength of maximum absorbance and intensities at the maxima (Table 1) remained without changes for mixtures containing a 10 mole

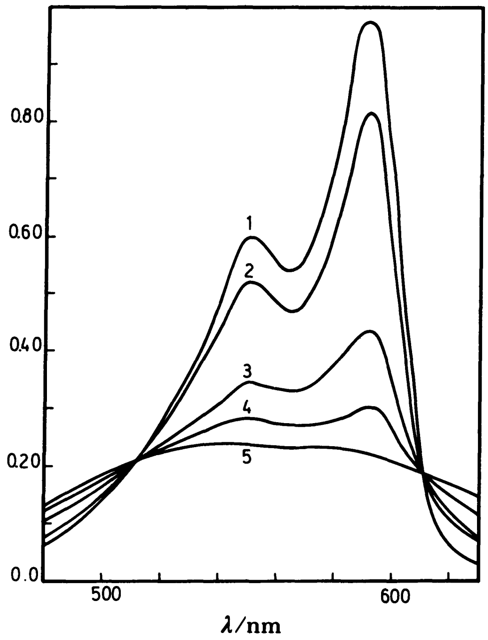


Fig. 2. Absorption spectra of Pd(II)-3,5-Cl2PADAB complexes in aqueous ethanol acid solution. Reagent, Pd(II) and ethanol concentrations as for Fig. 1. pH: (1) 1.00; (2) 1.70; (3) 2.30; (4) 2.80; (5) 3.20.

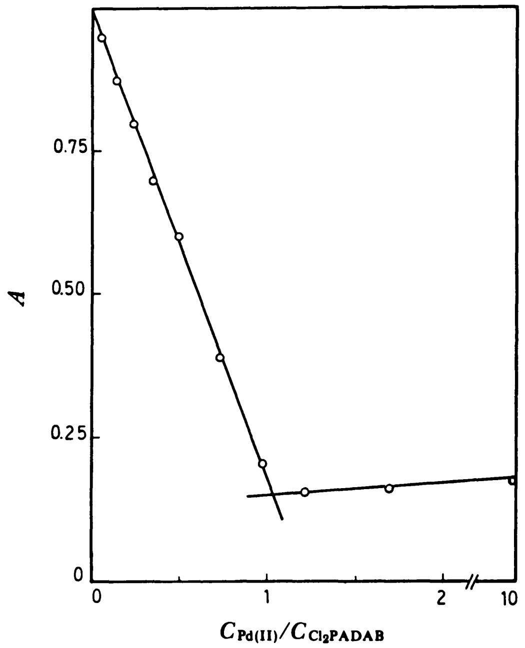
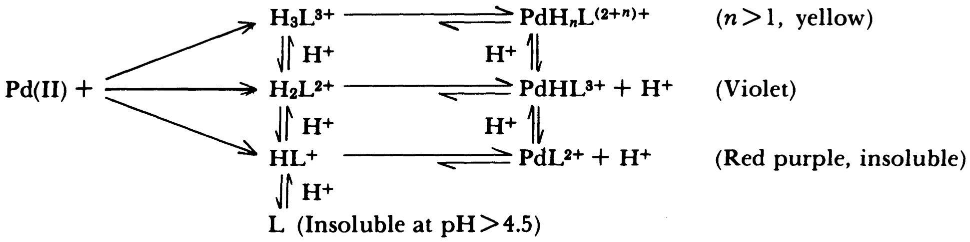


Fig. 3. Saturation curve of Pd(II)-3,5-Cl2PADAB complex in aqueous solution. 3,5-Cl2PADAB concentration was kept constant=3.50×10^{-5} M; Pd(II)=variable; 10% (v/v) ethanol; pH=3; λ=430 nm; water as blank.

excess of reagent. In these cases, the spectra were scanned with similar 3,5-Cl2PADAB solutions as reference because the mixtures showed a strong absorption due to of the great concentration of 3,5-Cl2PADAB.

As is evident from the comparison of the spectra in Figs. 1 and 2, two Pd(II)-3,5-Cl2PADAB complexes exist in aqueous ethanol, depending only on the acidity. The color of the complex formed in H_2SO_4>10 M solutions is yellow, similar to the reagent at this acidity, while the solutions containing the complex formed in the acidity range from pH 1 to 2 M H_2SO_4 or from pH 1 to 3 M $HClO_4$ showed a violet color. An insoluble red purple complex was precipitated in less acidic media (pH 3—4), starting from pH 1. Anyone of these comlexes was generated either by promoting the chelation reaction at the suitable acidity, or by conveniently adjusting the acidity of media of the solution containing any of them.

The Composition of the Complex and the Mechanism of Complex Formation. Earlier studies[12] have shown that the Pd(II): 3,5-Cl2PADAB ratio of the violet complex is 1:1. In spite of its low solubility in aqueous ethanol solutions, the composition of the complex prevailing in the pH range 3—4 was spectrophotometrically obtained by means of absorbance variations, measured at the reagent maximum absorption wavelength (420 nm), of the pH 3 solutions containing constant concentration of 3,5-Cl2PADAB and varied proportions of Pd(II) (Fig. 3). The molar ratio obtained was also 1:1. Because of its low molar absorptivity, no further studies were carried out on the yellow complex, but it is likely to have contain the same molar ratio as the others. Similar situations have been indicated by Shibata et al. with respect to the Co(II)-5-Cl2PADAB[3] and Co(II)-3,5-Cl2PADAT[6] complexes. In agreement with the above considerations, the spectral changes observed when the acidity of the Pd(II)-3,5-Cl2PADAB complex solutions was varied were due to protonation or acid dissociation of these complexes, rather than to a cange in the Pd(II):reagent molar ratio. Furthermore, knowing that the Pd(II) complex formed depends on the acidity of the reaction media and that in the pH 4 to 18 M H_2SO_4 or pH 4 to 10 M $HClO_4$ range three species of 3,5-Cl2PADAB,[12] H_3L^{3+}, H_2L^{2+}, and HL^+ are involved in its acid-base behavior, it can be assumed that the reaction between Pd(II) and 3,5-Cl2PADAB is described by the following equilibria:



The above scheme is in good agreement with the experimental facts observed. In order to prove, at least partially, the validity of the above equilibria, the number of protons released in the reaction as

$$PdHL^{3+} \rightleftharpoons PdL^{2+} + H^+ \qquad (1)$$

was spectrophotometrically examined for solutions containing excess of Pd(II). Studies in solutions showed that the $PdH_nL^{(2+n)+}$ and $PdHL^{3+}$ acid dissociation equilibria are sufficiently separated, so that they can be treated independently. If the acid dissociation constant for Eq. 1 is given by Eq. 2

$$K_a^{PdHL^{3+}} = [PdL^{2+}][H^+]/[PdHL^{3+}] \qquad (2)$$

the dependence of log{$[PdL^{2+}]/[PdHL^{3+}]$} is written as

$$pK_a^{PdHL^{3+}} = \log\{(A - A_{PdHL^{3+}})/(A_{PdL^{2+}} - A)\} + pH \qquad (3)$$

were A is the total absorbance of the solutions at a specified pH, and $A_{PdHL^{3+}}$ and $A_{PdL^{2+}}$ are the absorbance of solutions containing only the protonated complex and the soluble fraction of the non-protonated complex, respectively. The plot $\log\{(A-A_{PdHL^{3+}})/(A_{PdL^{2+}}-A)\}$ against pH gave a straight line with a slope of unity, value that is in good agreement with the supposition of Eq. 1. The $pK_a^{PdHL^{3+}}=2$ was calculated from the pH at which $\log\{(A-A_{PdHL^{3+}})/(A_{PdL^{2+}}-A)\}$ equals zero.

General Study of Extractable Pd(II)-3,5-Cl2PADAB-TCA⁻ Ion-Association Complexes. Considering that only positively charged Pd(II)-3,5-Cl2PADAB complexes can be formed, the extraction of such chelates can be carried out in the presence of suitable organic bases which form extractable ion-association complexes. In this sense, the best results were obtained for the trichloroacetate-benzene system. Pd(II) is quantitatively extracted into benzene in the presence of 3,5-Cl2PADAB, ethanol and high concentrations of trichloroacetate anion (TCA^-) within the acidity range from pH 4 to 2 M H_2SO_4 or from pH 4 to 1 M $HClO_4$ (Fig. 4). In strongly acidic solutions (pH 1 to 2 M H_2SO_4 or pH 1 to 1 M $HClO_4$ range), only a violet ion association complex is extracted into benzene.

Comparing the absorption spectra of this compound in benzene with those of the Pd(II)-3,5-Cl2PADAB complexes formed in aqueous solutions with the same mineral acid concentration, and in the presence or absence of trichloroacetate (Table 1) showed that the violet complex extracted was that stated as $\mathrm{PdHL^{3+}}$. Although some Pd(II) complexes were formed in aqueous solutions of $\mathrm{H_2SO_4}$ (C>10 M), they were not extracted into benzene, probably because under such conditions the HTCA dissociation is repressed to such

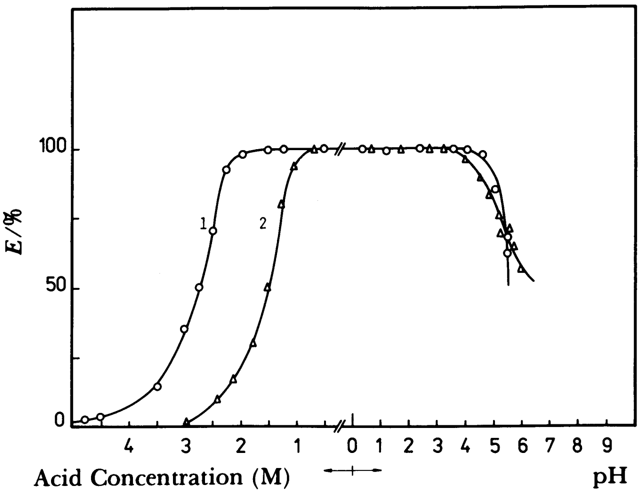


Fig. 4. Effect of pH or mineral acid concentration on extraction of the Pd(II)-3,5-Cl2PADAB-TCA$^-$ system. Extractions from aqueous 10% (v/v) ethanol solutions with 1.80×10^{-5} M Pd(II), 1.20×10^{-4} M 3,5-Cl2PADAB and 1 M HTCA. Curves: (1) $\mathrm{H_2SO_4}$; (2) $\mathrm{HClO_4}$. $V_o=V_w$. Time of full color development of the Pd(II)-3,5-Cl2PADAB complexes=period of equilibration=40 min.

Table 1. Absorption Maxima and Molar Absorptivity of Pd(II) Complexes in 10% Ethanol-Water Solutions and of Ion-Association Extracted into Benzene

Complex	λ_{max}/nm	Molar absorptivity/ $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
$\mathrm{PdL^{2+}}$	Insoluble	—
$\mathrm{PdHL^{3+}}$ a)	588 548	8.20×10^4 5.20×10^4
$\mathrm{PdH_nL^{(2+n)+}}$	380—400	2.00×10^4
$\mathrm{PdHL^{3+}}$ b)	594 560	8.40×10^4 5.90×10^4
$\mathrm{PdL^{2+}\cdot(TCA^-)_2}$	545 515—530	2.00×10^4 1.80×10^4
$\mathrm{PdHL^{3+}\cdot(TCA^-)_3}$ c)	600 555	8.60×10^4 5.50×10^4

L=3,5-Cl2PADAB. a) Complex formed in 1 M $\mathrm{H_2SO_4}$ aqueous solution with 10% (v/v) ethanol. b) Complex formed in 1 M $\mathrm{H_2SO_4}$ solution with 10% (v/v) ethanol and 1 M HTCA. c) Ion-association extracted into benzene from solution b).

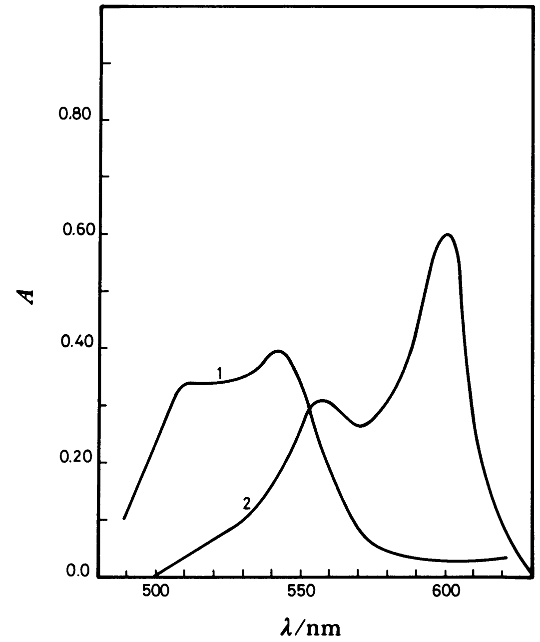


Fig. 5. Absorption spectra in benzene of the extracted ion-association compounds for the Pd(II)-3,5-Cl2PADAB-TCA$^-$ system. Concentrations in the aqueous phases: Pd(II)=1.90×10^{-5} M; 3,5-Cl2PADAB=2.00×10^{-4} M; HTCA=1 M; ethanol 10%. Acidity: (1) pH=4.00; (2) 1—2 M $\mathrm{H_2SO_4}$ with 7.00×10^{-6} M final concentration of Pd(II) in the organic extract. Measurements against corresponding reagents blanks in 10-nm cell. Time of full color development=period of equilibration=40 min. Organic extracts (10 cm^3) diluted to 25 cm^3 with pure benzene after extraction.

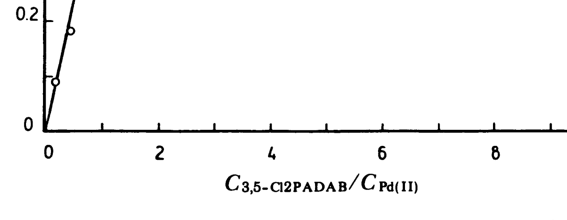


Fig. 6. Saturation curve of Pd(II)-3,5-Cl2PADAB complex extracted into benzene. Concentrations in the aqueous phase (10 cm^3): Pd(II) 6.00×10^{-5} M; HTCA 1 M; ethanol 10% (v/v); pH=3; λ=545 nm; Extracts (10 cm^3) dilute to 25 cm^3 with pure benzene after equilibrations.

an extent that practically no free anion occurs.

When the pH of the aqueous phases was increased from 1 to 4, the extraction was accompanied by a change in the absorption spectra of the extracts (Fig. 5), which is reversible with the acidity variations of the aqueous phases. In the pH range 3—4, only a red purple ion-association complex is extracted. This compound, and the reagent excess at pH 3—4, are not greatly soluble in benzene or in ethanol–benzene mixtures. In Table 1 are summarized the wavelength of maximum absorption and the molar absorptivities of the two ion-associations extracted.

The 1:1 Pd(II):3,5-Cl2PADAB molar ratio of the colored ion-association complexes in the organic phases were corroborated at 2 M H_2SO_4 by the molar ratio and slope-ratio methods, and at pH 3 by the molar ratio method (Fig. 6). The total Pd(II)-3,5-Cl2PADAB-TCA$^-$ composition was also spectrophotometrically studied. The knowledge of the number of trichloroacetate anion molecules associated to each of the complexes extracted confirmed their charge and, consequently, the $PdHL^{3+}$ and PdL^{2+} composition postulated in aqueous solutions. The expression applied to establish the total (Pd(II)-3,5-Cl2PADAB)-TCA$^-$ composition was derived as follows.

In some additional experiments on the extraction into organic solvents, it was established that Pd(II)-3,5-Cl2PADAB complexes are not extracted in the presence of the anions sulfate, perchlorate, nitrate, or chloride. They were extracted only in the presence of trichloroacetate anion. Therefore, it was concluded that this is the anion that takes part in the formulation of the extracted compound, and not any other. Bearing this in mind, as well as the 1:1 Pd(II):3,5-Cl2PADAB composition observed during complex formation and extraction, a general quantitative description of the complex extraction must consider the following ion-association reaction and distribution equilibria:

$$\mathrm{PdH}_n\mathrm{L}^{s+} + s\mathrm{TCA}^- \rightleftharpoons \mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s \qquad (4)$$

$$\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s \rightleftharpoons (\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s)_{\mathrm{org}} \qquad (5)$$

were the subscript org refers to the benzene phase, and the absence of a subscript indicates the aqueous phase. The ion-association formation constant and the distribution constant are given by:

$$K_{\mathrm{ass}} = [\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]/\{[\mathrm{PdH}_n\mathrm{L}^{s+}][\mathrm{TCA}^-]^s\}, \qquad (6)$$

$$K_{\mathrm{D}}^{\mathrm{ass}} = [\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]_{\mathrm{org}}/[\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]. \qquad (7)$$

The extraction constant of ion-association is given by:

$$K_{\mathrm{ex}} = K_{\mathrm{D}}^{\mathrm{ass}}\cdot K_{\mathrm{ass}} = [\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]_{\mathrm{org}}/ \{[\mathrm{PdH}_n\mathrm{L}^{s+}][\mathrm{TCA}^-]^s\} \qquad (8)$$

Introducing the HTCA acid association constant (K_a^{HTCA}) and distribution constant ($K_{\mathrm{D}}^{\mathrm{HTCA}}$) in material balance for HTCA after extraction, and taking into account that $C_{\mathrm{Pd(II)}} \lll C_{\mathrm{HTCA}}$, it can be shown that

$$[\mathrm{TCA}^-] = C_{\mathrm{HTCA}}/\{1 + [\mathrm{H}^+]/ (K_a^{\mathrm{HTCA}} + K_{\mathrm{D}}^{\mathrm{HTCA}}\cdot[\mathrm{H}^+]/K_a^{\mathrm{HTCA}})\} \qquad (9)$$

At constant proton concentration and salt content, Eq. 9 becomes:

$$[\mathrm{TCA}^-] = C_{\mathrm{HTCA}}/\mathrm{cte} \qquad (10)$$

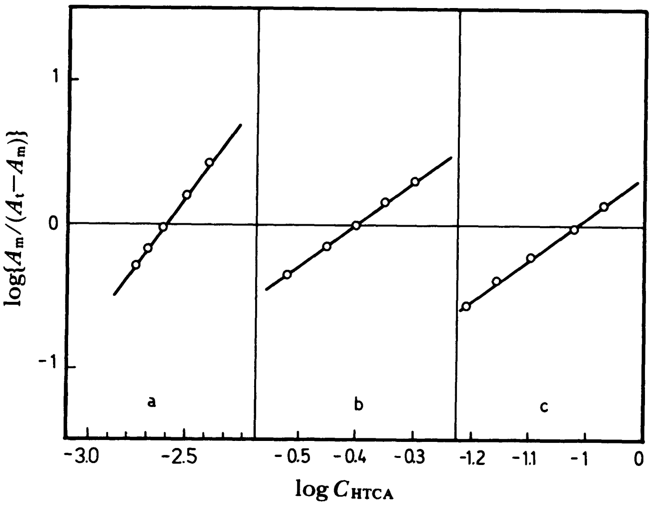


Fig. 7. log{$A_m/(A_t-A_m)$} vs. log C_{HTCA} curves for the Pd(II)-3,5-Cl2PADAB-TCA$^-$ system. See text.

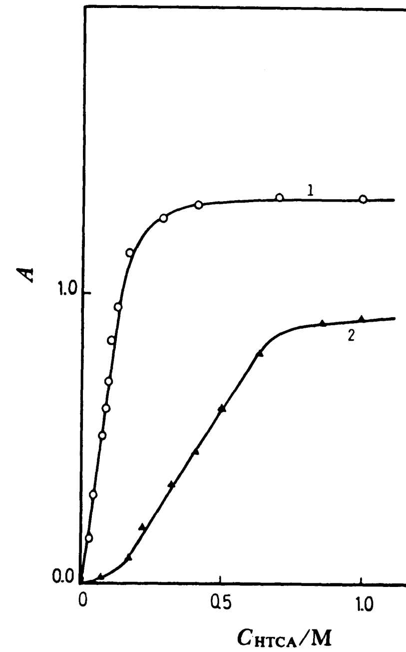


Fig. 8. Absorbance of Pd(II)-3,5-Cl2PADAB-TCA$^-$ compounds in benzene vs. HTCA concentration in the aqueous phases. Concentrations present in the aqueous phases (10 cm^3): 3.90×10^{-5} M Pd(II), 10% ethanol, (1) 4.00×10^{-4} M 3,5-Cl2PADAB, 1 M H_2SO_4, λ_{max}=600 nm; (2) pH 1.50 (H_2SO_4), 5.90×10^{-5} M 3,5-Cl2PADAB, λ_{max}=600 nm. Benzene as blank. Organic extracts (10 cm^3) diluted to 25 cm^3 with pure benzene after equilibration.

Introducing Eq. 10 in Eq. 8, rearranging and taking logarithm, the Eq. 8 takes the form:

$$\log[\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]_{\mathrm{org}}/[\mathrm{PdH}_n\mathrm{L}^{s+}] = \log K^*_{\mathrm{ex}} + s\log C_{\mathrm{HTCA}} \qquad (11)$$

where K^*_{ex} is the extraction constant based on total initial HTCA concentration in the aqueous phase:

$$K^*_{\mathrm{ex}} = K_{\mathrm{ex}}\cdot \mathrm{cte}^s \qquad (12)$$

where cte is defined by Eqs. 9 and 10.

For any C_{HTCA}, the ratio $[\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s]_{\mathrm{org}}/[\mathrm{PdH}_n\mathrm{L}^{2+}]$ could be calculated from absorbance of $\mathrm{PdH}_n\mathrm{L}^{s+}\cdot(\mathrm{TCA}^-)_s$ in benzene vs. C_{HTCA} curves. In this case, this ratio becomes equal to $A_{\mathrm{m}}/(A_{\mathrm{t}}-A_{\mathrm{m}})$, where A_{t} is the absorbance of extracts for the C_{HTCA} at which the extraction is quantitative, and A_{m} is the absorbance of extracts for any C_{HTCA} lower than the suitable for the quantitative extraction. Thus, the concentration of $\mathrm{PdH}_n\mathrm{L}^{s+}$ remaining in the aqueous phase will be $A_{\mathrm{t}}-A_{\mathrm{m}}$; Eq. 11, then, becomes,

$$\log\{A_{\mathrm{m}}/(A_{\mathrm{t}}-A_{\mathrm{m}})\} = \log K^*_{\mathrm{ex}} + s\cdot\log C_{\mathrm{HTCA}} \qquad (13)$$

Eq. 13 indicates that the plot of $\log\{A_{\mathrm{m}}/(A_{\mathrm{t}}-A_{\mathrm{m}})\}$ against $\log C_{\mathrm{HTCA}}$ should give a straight line with a slope of s, that is the number of trichloroacetate anion associated to the complex. Figure 7c shows this plot for A_{t} and A_{m} values taken from the absorbance (600 nm) vs. C_{HTCA} curve (Fig. 8 curve 1) obtained at 1 M $\mathrm{H_2SO_4}$. The straight line has a slope of 3. Carrying out the extractions at pH 3—4, the value s calculated was not completely reliable owing to the very great absorbance even of a slight reagent excess, that disturbed seriously the absorbance measurements.

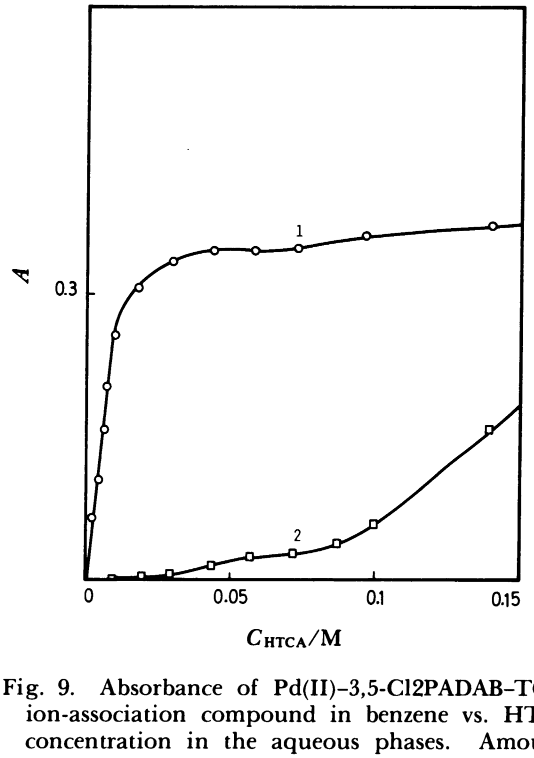


Fig. 9. Absorbance of Pd(II)-3,5-Cl2PADAB-TCA⁻ ion-association compound in benzene vs. HTCA concentration in the aqueous phases. Amounts present in the aqueous phases (10 cm³) 3.90×10⁻⁵ M Pd(II); 5.90×10⁻⁵ M 3,5-Cl2PADAB; 10% ethanol; pH 1.50. (1) λ_{max}=545 nm; (2) λ_{max}=600 nm. Benzene as blank. Organic extracts diluted to 25 cm³ with pure benzene after equilibrations.

The complex-to-TCA⁻ molar ratio of the red purple ion-association was established carrying out extractions at pH 1.5 in solutions containing a 1.5-fold molar excess of 3,5-Cl2PADAB with respect to Pd(II), and reading the absorbance against pure benzene. At pH 1.5 both complexes are formed and exracted. However, in the C_{HTCA} range from "0" to 0.07 M practically only the red purple ion-association complex is extracted (Fig. 9), while for C_{HTCA} higher than 0.07 M both ion-association complexes are simultaneous extracted. In the latter case, the absorbance measures at 600 nm were not disturbed by the presence of the red purple ion-association complex in the extracts (Fig. 8, curve 2).

According to what has been said above, it can be shown that, carrying out the extractions at pH 1.5 within the appropriate C_{HTCA} range and reading the absorbance of extracts at the suitable wavelength, Eq. 13 can be applied to establishing simultaneously the composition of the two ion-association complexes.

Figures 7a and 7b show the results obtained by applying Eq. 13 when the extractions were carried out in the C_{HTCA} ranges from "0" to 0.07 M and from 0.07 M to 1 M, respectively.

In the first case, the slope value of the straight line is 2, and in the second, such value is 3. This values agree with the essential electroneutrality of the extracted compound, assuming that the Pd(II) chelates have the composition PdL^{2+} and PdHL^{3+}, as suggested.

For the purpose of analytical applications, because of its very high molar absorptivity (600 nm) in benzene, the $\mathrm{PdHL}^{3+}\cdot(\mathrm{TCA}^-)_3$ ion-association complex is the most important.

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