Scientific Paper

Complex Formation Between Pd(II) and Immobilized Imidazol-Azo-Chromotropic Acid†

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Abstract

1,8-Dihydroxy-2-(imidazol-2-ylazo)-naphthalene-3,6-disulphonic acid (imidazol-azo-chromotropic acid - IACA) was immobilized onto the anion exchange resin Dowex 1-X8, 50-100 mesh. The aim of this work was to investigate the mechanism of the complex formation between Pd(II) and immobilized IACA by following the absorption spectra of the solid phase. The reaction between Pd(II) and immobilized azo-dye was followed in the acidity range from pH 1 to pH 7. Pd(II) and IACA form 1:1 complex with the absorption maximum at 650 nm. The kinetics of complex formation was followed in pH range from 1 to 6, as the function of Pd(II) in excess. The effective forward (k_f) and reverse (k_b) pH dependent rate constants for complex formation were obtained from the linear dependence of k_{obs} *vs.* Pd(II) concentration. Bell shaped pH profile (k_f *vs.* pH) indicated that both ligand and metal ion, were included in acidic - basic equilibrium with H^+ ion.

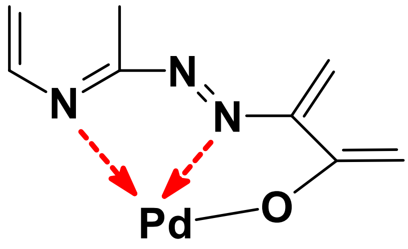
Key words: azo dye, immobilization, ion-exchange resin, Pd(II), determination.

Introduction

Azo-dyes with the heterocyclic diazo-component form coloured complexes with many metal ions in solution.[1–5] Great number of the spectrophotometric methods based on these reactions were developed and used in analytical chemistry. In recent years, a lot of publications deal with the investigations of the mechanism of azo-dyes adsorption onto the solid supports,[3] such as ion-exchangers, PVC, fabrics, silica gel or celulose. The reactions between the immobilized reagents and metal ions in solution have been widely investigated[1,6–12] because of their potentially use in the design of chemical optical sensors.[1,6–9]

Derivatives of mono- and bis-azo-chromotropic acid with pyrazole or imidazole as the heterocyclic diazo-component belong to class of organic reagents that contain four nitrogen atoms coupled in conjugated system of π-bonds.[13,14] In contrast to great number of heterocyclic azo-dyes, such as 2-(2-pyridylazo)-naphtol (PAN), 4-(2-pyridylazo)-resorcinol (PAR), 4-(2-tiazolylazo)-resorcinol (TAR) and their derivatives, sulphonated azo-dyes have good solubility and stability in water.[15–20] Besides, their spectral properties depend strongly on the media acidity, due to the protonation and dissociation of azo-group, heterocyclic >NH- and naphthalene -OH group.

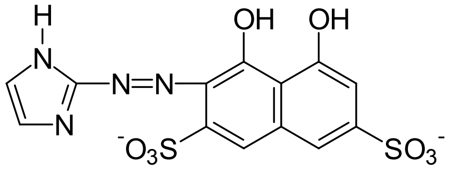
The heterocyclic azo-dyes usually react with the metal ions as tridentate ligands,[5,21] forming coordinative bonds with heterocyclic moiety, -OH group and azo-group (Scheme 1). The reactions between chromotropic acid derivatives with pyrazole or imidazole, as the heterocyclic diazo-component and Pd(II) are very sensitive and selective.[21–24]



Scheme 1

Pd(II) forms 1:1 complex even in strongly acidic media,[5,14] but the stoichiometry of the complexes and their spectral characteristics change with pH. The investigation of the kinetics of the complex formation suggested, that protonated and unprotonated forms of the ligands participate in the reaction with Pd(II), since the reaction rate decreased due to hydrolysis of metal ion.[25] Recently, pyrazole-azo-chromotropic acid was immobilized onto anionic resin Dowex 1-X8.[26,27] The immobilization increased the sensitivity and selectivity of the reaction with Pd(II).[1,28]

The present paper deals with the investigations of the complex formation between Pd(II) and 1,8-dihydroxy-2-(imidazol-2-ylazo)-naphthalene-3,6-disulphonic acid (IACA) whose structure is represented on Scheme 2, immobilized onto ion-exchange resin Dowex 1-X8, 50-100 mesh. In addition, the kinetics and mechanism of this reaction on the solid support was examined as the function of the media acidity.



Scheme 2

Experimental

Chemicals

All chemicals used were of analytical grade. The 1×10^{-3} M Pd(II) stock solution, in 0.5 M $HClO_4$, was prepared according to standard procedure.[21,24] 1,8-dihydroxy-2-(imidazol-2-ylazo)-naphthalene-3,6-disulphonic acid (IACA) in the form of disodium salt was sintetized according to known procedure.[22–24] Purity of preparation was investigated chromatografically and confirmed by elemental analysis. IACA stock solutions (2×10^{-3}M) were passed through the cation exchange resin Dowex 50-X8 in order to be converted into acid form and kept at pH 4.5 until use. The acidity was controlled by addition of NaOH or $HClO_4$, or by using of Britton Robinson (BR) buffer.[29]

Immobilization support

Anion exchange resin Dowex 1-X8, 50-100 mesh, produced in Dow Chemical Company, was used as a support for IACA immobilization. Dowex 1-X8 is strong base anion exchange resin with active benzyltrimetil amonium groups. This resin is produced in Cl^- form and crosslinked with 8% divinylbenzen. Before use, resin was washed using distilled water and drain at room temperature.

Apparatus

Solution and solid phase absorption spectra were recorded using the cells of 1.0 and 0.2 cm on UV VIS spectrophotometer Beckman 5260 in wavelength range from 400 to 700 nm. Acidity of solutions was measured using the pH-meter Metrohm, model 713.

Immobilization procedure

IACA was immobilized onto resin Dowex 1-X8, 50-100 mesh in static conditions. The weighted amount of ion-exchanger was immersed into 10 mL of 5×10^{-5} M IACA solution and mixed at room temperature until the equilibration. The supernatant was decanted and the resin washed with distilled water, dried on air at room temperature and stored in glass containers until usage. The amount of adsorbed reagent q_t (mol of reagent/g of resin) was determined spectrophotometrically, according to the Equation 1:

$$q_t = \frac{(c_o - c_t)\cdot V}{m} \tag{1}$$

where c_o and c_t (mol/dm^3) are the initial concentration and concentration rested in solution after time t, V is the volume of the dye solution (dm^3) and m is sorbent mass (g). The average value of (0.78 ± 0.08) μmol IACA per gram of resin was obtained.

Absorbance measurements

Absorbance measurements on the resin phase in a 2 mm cell were carried out by the same procedure as that described earlier.[28,30] The mixture of the modified resin and sample solution was shaken mechanically. The resin beads were separated from the bulk solution and packed into a cell, by means of a pipette. A reference ion-exchanger layer was inserted in the reference beam to balance the light intensities. The overall absorbance of the sample layer is given by equation

$$A = A_{RC} + A_{RL} + A_R \tag{2}$$

where A_{RC} represents the net absorbance of the complex species in the solid phase, A_{RL} the absorbance of free dye in the solid phase and A_R the background absorbance due to light scattering and absorption by resin phase itself. A_R, A_{RC} and A_{RL} depended on the packing of modified resin in the cell. A_{RL} and A_{RC} were obtained directly by measuring the absorbance, with the reference layer containing no sample component and prepared under exactly the same conditions. To avoid the effect of resin packing (A_R) the spectrum of resin phase containing no coloured species was recorded against bidistilled water.[28,30] The absorbance at two different wavelengths, one corresponding to the absorption maximum of the coloured species (about

550 nm for ligand and 650 nm for complex) and the other in a region where the resin alone absorbs (750 nm) was measured. The absorbance difference was assumed to be constant under the similar packing coditions.[28,30] The absorbance of complex or ligand on the resin phase was obtained by subtracting of $A_R + A_{RL}$ or A_R, respectively, from the overall absorbance, A.

Results and discussion

Reaction between IACA and Pd(II) in solution and on the solid support

The absorption spectra of the solutions containing Pd(II) and IACA (both 4×10^{-5} M) were recorded in the acidity range from pH 1–13. The stoichiometry of the complex was determined by the molar ratio method, keeping the concentration of IACA 4×10^{-5} M. Figure 1 represents the absorption spectra of IACA and its Pd(II) complexes at various pH. The results on Figure 1 showed that complexes with molar ratios IACA: Pd(II) = 1:1 and 1:2 were formed at pH 1.6 and 12.9, respectively.

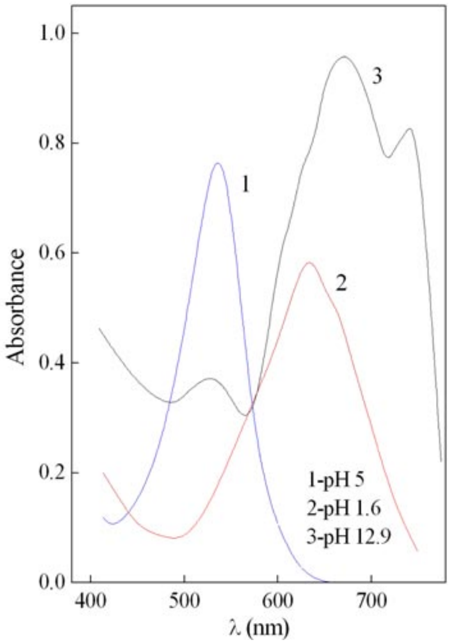


Figure 1. Absorption spectra of IACA and its Pd(II) complex at various pH; 1- $c_{IACA}=2\times10^{-5}$ M; 2 and 3- $c_{IACA} = c_{Pd} = 4\times10^{-5}$ M.

To investigate the reaction between Pd(II) and IACA on resin phase, 0.5 g of modified sorbent was immersed into 10 mL of 7×10^{-5} M Pd(II) solution. The acidity from pH 1–10 was controlled by using BR buffer. The absorption spectra of modified sorbent and its Pd(II) complex were recorded after 50–60 min equilibration, with occasionally mixing. Figure 2 represents the resin phase absorption spectra of IACA and its Pd(II) complex at pH 4.2 and pH 9.6.

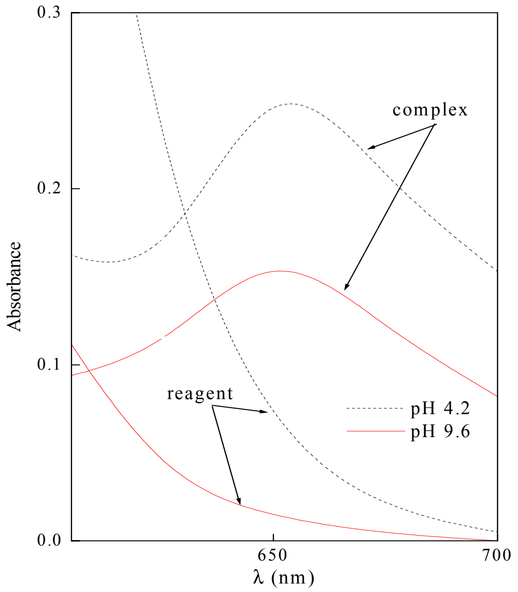


Figure 2. Absorption spectra of modified IACA (0.72 μmol IACA/g of resin Dowex 1-X8, 50–100 mesh) and the complex with Pd(II) ($c_{Pd} = 7\times10^{-5}$ M) at pH 4.2 and 9.6.

As can be seen at Figure 2, the immobilization of IACA did not influence the shape and position of absorption maximum, but it strongly affected its intensity. Figure 3 represents the dependence of absorbance of Pd(II)-IACA complex on resin phase at 650 nm on medium acidity.

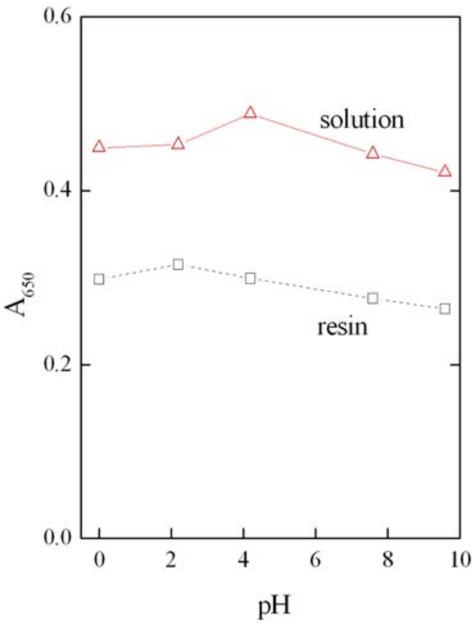


Figure 3. Dependence of absorbance of Pd(II)-IACA complex on acidity; resin Dowex 1-X8, 50-100 mesh (0.72–0.84 μmol of IACA/g of resin); acidity was controlled by adition of BR buffer; λ = 650 nm.

The composition of complex, on resin phase, was determined using molar ratio method[28,30] at pH 2.3 and pH 4.2. 0.5 g of modified ion-exchanger with 0.51 μmol IACA/g of resin, was added to 10 mL of Pd(II) solution with the concentrations from 5×10^{-6} M to 1×10^{-4} M. Equilibration time was 50 min. From the changes of absorption spectra of modified sorbent with increase of Pd(II) concentration, it was noticed that complex formation was followed by the appearance of well defined isosbestic points at 470 and 615 nm, which indicated that equilibrium between two absorbing components onto solid phase was established.

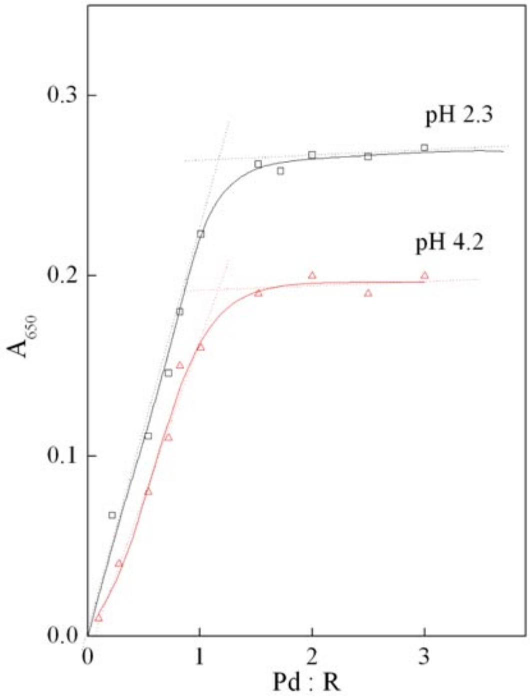


Figure 4. Determination of stoichiometry of Pd(II)–IACA complex by molar ratio method (Pd:R is the ratio between the concentrations of Pd(II) and IACA); resin Dowex 1-X8, 50–100 mesh, Cl^- form; contact time 50 min; *a* = 0.51 μmol IACA/g of resin; λ = 650 nm.

Figure 4 shows the dependence of absorbance at 650 nm (absorption maximum of complex) on molar ratio of Pd(II) in contact solution and adsorbed IACA (Pd:R). The dependence of A *vs*. Pd(II)/IACA has a plateau approximately at molar ratio of Pd(II) to immobilized IACA 1:1. According to the intersection of lines presented on Figure 4, the stoichiometry of complex was given as R:Me = 1:1 which confirms that complex of Pd(II) and IACA has the same stoichiometry for the solid phase as in the solution.[21,22,24]

The effect of acidity on complex formation in the pH range from 1–6 was followed in the solution and on the resin phase. The concentrations of Pd(II) and IACA in the solution were 4×10^{-5} M. The amount of IACA, adsorbed onto resin phase, (0.78 ± 0.08) μmol per gram of resin, corresponded to amount of Pd(II) ions in the solution, so the concentration ratio 1:1 was maintained in both cases. The results showed that there was no significant change of complex absorbance on medium acidities. This result pointed out that the acidity did not influence the change of structure or stoichiometry of the complex, as was noticed in the solution.

Effect of contact time

The effect of contact time between solid phase (modified resin) and Pd(II) solution on complexation reaction was followed at constant temperature. Two types of experiments were performed. In the first series, 0.5 g of modified resin containing 1.45 to 1.95×10^{-4} g of IACA was immersed into 10 mL 7×10^{-5} M Pd(II) (pH 1–6) for two minutes. The resin phase was separated from the bulk solution and the absorbance was measured as a function of time. The change of absorption spectra due to the complex formation was accompanied with two well defined isosbestic points, which indicated that two reacting components were in equilibrium. The complex formation was complete after more than 40 min.

In the second type of experiments the resin was in contact with Pd(II) solution for up to 50 min. The solution was decanted and absorption spectra were recorded. The kinetic curves of both series of experiments are presented on Figure 5.

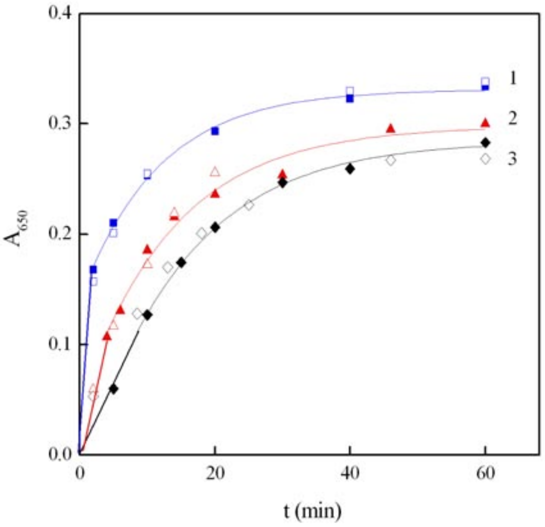


Figure 5. Time dependence of the colour development in the resin phase separated from 10 mL 7×10^{-5} M Pd(II) solution. Open symbols – solid phase separated after 2 min stirring; Solid symbols – solid phase stirred with the solutions till the measurement. 1- pH 2.2; 2- pH 4.2; 3- pH 5.9. Resin: Dowex 1-X8, 50–100 mesh, Cl^- form.

The absorption spectra of complex and kinetic curves obtained for both series of experiments after the equilibration were similar. The colour developement was completely terminated after 50 minutes. According to these results, the postulate was made, that in the first two minutes almost all Pd(II) present in the solution was adsorbed onto modified resin, and after that it reacts with immobilized IACA, i.e. that the reaction rate after 2 minute contact time didn't depend on time during which modified resin was in contact with Pd(II) solution.

Effect of acidity on reaction rate of Pd(II) with modified ion-exchanger

The rate of reaction of complex formation between IACA and Pd(II) was followed in the acidity range from pH 1–6, by measuring the solid phase absorbance at 650 nm as the function of time, Pd(II) concentrations in contact solutions (from 5×10^{-6} to 5×10^{-5} M), while the amount of IACA, adsorbed onto ion-exchange resin was 0.26 μmol per g of resin.

The kinetic curves revealed exponential dependence, which is typical for the pseudo-first order reactions. The rate constant was determined by fitting of experimental data with function:

$$ln\ (A_{eq} - A) = - k_{obs}\, t + ln\ (A_{eq} - A_o) \qquad (3)$$

where k_{obs} is the overall rate constant, A_o and A_{eq} are the absorbancies of complex, adsorbed onto solid phase at t = 0 and at equilibrium (plateau on kinetic curves), while A is the absorbance of solid phase at t min. Values of k_{obs} as the function of Pd(II) concentration at pH 2.2 and 4.2, are represented in Table 1.

Table 1. Dependence of k_{obs} at pH 2.2 and 4.2 on Pd(II) concentration.

	k_{obs} ($\times10^4$ s^{-1})				
c_{Me} ($\times10^5$ M) / pH	1	2	3	4	5
2.2	0.14	0.17	0.19	0.21	0.23
4.2	0.12	0.14	0.18	0.19	0.21

The pseudo-first order rate constants (k_{obs}) were dependent on Pd(II) concentration according the Equation 4, which is typical for substitution in square-planar and octahedral complexes:[25]

$$k_{obs} = k_f\,[Pd(II)] + k_b \qquad (4)$$

where k_f and k_b are forward and reverse rate constants. The dependence of k_{obs} on *[Pd(II)]* was linear in all cases. k_f and k_b, determined from the slope and the intercept of plots are represented in Table 2.

Table 2. Values of k_f and k_b for the complex formation between Pd(II) and IACA (0.26 μmol per g resin Dowex 1-X8, 50–100 mesh).

pH	k_f (mol^{-1}dm^{3}s^{-1})	k_b ($\times10^5$ s^{-1})
1.0	0.9 ± 0.1	0.20 ± 0.03
2.2	2.2 ± 0.3	1.2 ± 0.2
4.2	2.1 ± 0.3	1.0 ± 0.2
5.6	0.20 ± 0.03	0.30 ± 0.05

Mechanism of complexation reaction

The dependence of rate constants for complex formation k_f vs. pH in solution and on resin phase is presented on Figure 6. In both cases the bell shaped pH profile of complexation reaction was obtained. This result confirmed, that both reactants underwent to acid-base equilibria with H$^+$ ions.

The decrease of reaction rate with increasing of pH is the consequence of hydrolysis of Pd(II) ions. In the case of increasing acidity, protonation of heterocyclic diazo-component and azo-group which take place in formation of coordination bonds with Pd(II) decreased the reaction rate. Results showed that solid phase did not influence on reaction path. Also, according to obtained results, represented on Figure 6, the maximum od pH profile on resin phase was shifted toward higher pH values. Besides, it is noticable that reaction rate of modified sorbent with Pd(II) decreased comparing to reaction rate in solution for approximatelly 10 times. This result suggests that, IACA can be adsorbed on the polystiren matrix via dissociated sulpho-groups, as well as by surface interaction with heterocyclic and naphtalene rings. The sorption induced steric hidrances, since Pd(II) forms coordinative bonds with heterocyclic >N-, -OH group and nitrogen atom from azo-group which is closer to the heterocyclic ring.[31]

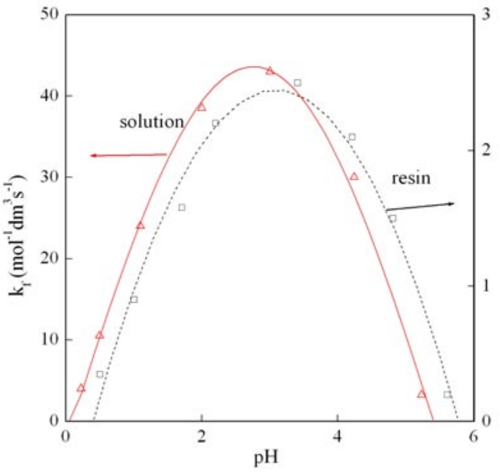
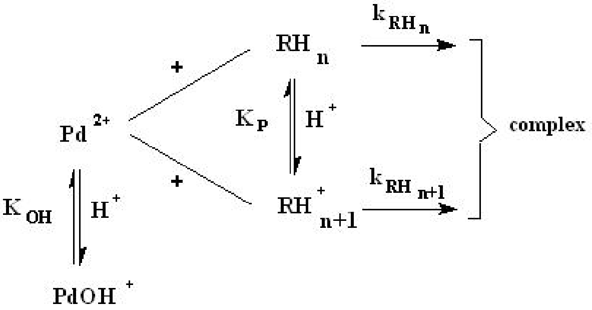


Figure 6. pH profile of reaction between IACA and Pd(II) in solution and on resin; $c_r = c_{Pd} = 1\times10^{-5}$ M.

Bell shape of the pH profile is in accordance with reaction scheme represented below,[32] that includes hydrolysis of Pd(II) ion with equilibrium constant pK_{OH} = 2.05 and protonation of heterocyclic diazo-component, pK_p = 1.86,[32,33] In given scheme, k_{RHn+1} and k_{RHn} are rate constants for the complexation reaction of protonated and unprotonated ionic form of the reagent.



Scheme 3

Conclusions

The reaction between Pd(II) and 1,8-dihydroxy-2-(imidazol-2-ylazo)-naphthalene-3,6-disulphonic acid (IACA), adsorbed onto Dowex resin, was investigated. The stoichiometry of the complex was 1:1 and it had absorption maximum at 650 nm. It was established that in investigated pH range, there was no shift in absorption maximum position on the solid phase on the contrary to solution.

Acknowledgements

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Povzetek

1,8-Dihidroksi-2-(imidazol-2-ilazo)-naftalen-3,6-disulfonsko kislino (imidazol-azo-chromotropic acid - IACA) smo imobilizirali na anionsko izmenjalno smolo Dowex 1-X8 (50-100 mesh). Namen našega dela je bil raziskati mehanizem tvorbe kompleksa med Pd(II) in imobilizirano IACA na podlagi absorpcijskega spektra trdne faze. Reakcijo med Pd(II) in imobiliziranim azo barvilom smo spremljali v kislem območju (pH = 1 do pH = 7). Pd(II) in IACA tvorita kompleks v molskem razmerju 1:1 z absorpcijskim maksimumom pri 650 nm. Kinetiko tvorbe kompleksa smo spremljali v odvisnosti od koncentracije Pd(II) pri vrednostih pH od 1 do 6. Efektivne konstante reakcijske hitrosti za tvorbo (k_f) in razpad (k_b) kompleksa, ki so odvisne od pH, smo izračunali iz linearne odvisnosti izmerjenih konstant reakcijskih hitrosti (k_{obs}) od koncentracije Pd(II). Zvonasta oblika funkcije k_f(pH) kaže, da sta tako ligand kot kovinski ion vključena v kislinsko-bazno ravnotežje s H^+ ionom.