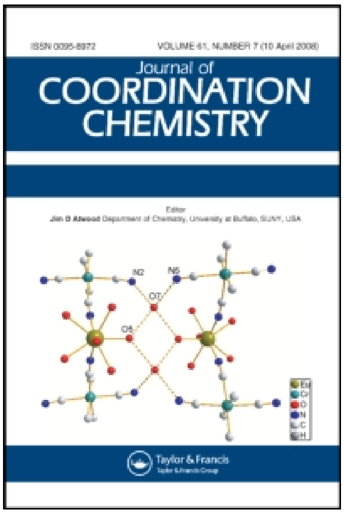

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Complexation of palladium(II) with chloride and hydroxide

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Complexation of palladium(II) with chloride and hydroxide

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Complex formation of Pd(II) with chloride and hydroxide has been investigated by spectrophotometry at 25°C and ionic strength 1.0 M. For the chloride complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n=0$–4), the formation constants, β_n, have been determined and the values are: $\log\beta_1 = 4.47$, $\log\beta_2 = 7.80$, $\log\beta_3 = 10.18$ and $\log\beta_4 = 11.53$. The formation of mixed chloro-hydroxo complexes, $[PdCl_p(OH)_q]^{2-}$, has been investigated at three chloride concentrations, 1.0, 0.5 and 0.2 M over the pH_c range 4–12. The average values determined for the formation constants, β_{pq}, where p and q refer to the number of chloride and hydroxide ions in the complex, are: $\log\beta_{31} = 16.48$, $\log\beta_{22} = 20.63$, $\log\beta_{13} = 24.02$ and $\log\beta_{04} = 26.23$. Molar absorption spectra for all the complexes in question have been obtained.

Keywords: Stability constants; Palladium(II) chloro complexes; Palladium(II) hydroxo complexes; Palladium(II) mixed chloro-hydroxo complexes

1. Introduction

It is well known that palladium(II) forms quite stable complexes with chloride. These complexes are assumed to be square planar and can be represented by the general formula $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n=0$–4). The complexation equilibria have been investigated by various authors and values for the formation constants have been determined [1–12]. Agreement between some stepwise equilibrium constants is excellent, e.g. 1.34 [3], 1.38 [7], and 1.38 [10] for $\log K_4$ at 25°C and ionic strength 1.0. However, values reported for some other constants differ considerably resulting in quite significant differences between the cumulative stability constants (β values). For the monochloro complex, for example, $\log K$ values ranging from 3.48 to 6.20 have been reported. The best agreement is between constants determined (25°C and $I = 1.0$) more than 30 years ago by Elding [10] and Weed [7] as can be seen from the successive $\log\beta$ values 4.47 (4.4), 7.76 (7.74), 10.17 (10.08) and 11.54 (11.46); the values of the latter authors are shown in parentheses. Despite this excellent agreement the deviations of other values led to a number of critical reviews speculating on the best set of constants as described by Boily and Seward [12]. In a thorough and comprehensive study these authors determined equilibrium constants at various temperatures from 5 to 125°C; the values $\log\beta_1 = 5.03$,

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$\log \beta_2 = 8.47$, $\log \beta_3 = 10.58$ and $\log \beta_4 = 11.46$ pertaining to 25°C and zero ionic strength (derived from the equations given) are not strictly comparable with the above because of the big difference in ionic strength. In a recent article [13] three different sets of constants have been used to demonstrate a linear relationship with the ΔH^0 values of the substitution of water molecules by chloride in $[Pd(H_2O)]^{2+}$.

Apart from some statistically predicted values [14] not so much is known about the stability of the mixed chloro-hydroxo complexes of Pd(II). There is agreement about the existence of the complex $[PdCl_3(OH)]^{2-}$, but some of the reported values for its formation from $[PdCl_4]^{2-}$ differ considerably, e.g., $\log K = 5.70$ [15], 4.45 [16] (both at 1.0 M ionic strength and 25°C), 4.8 [14] ($I = 0.7$ M; 25°C) and 6.45 [17] ($I = 1.0$ molal; 25°C). In the latter case the authors believed that an overestimation of the value of about 0.3 log units might be possible if significant quantities of the complexes $[PdCl_2(OH)_2]^{2-}$ and $[PdCl(OH)_3]^{2-}$ were present under the conditions of their solubility study. However, the $Pd(OH)_2$ species was also included in their reaction model and apparently becomes dominant at pH > 9. For the equilibrium constant expressed in terms of the hydrolysis reaction,

$$[PdCl_4]^{2-} + H_2O \Leftrightarrow [PdCl_3(OH)]^{2-} + H^+ + Cl^- \tag{1}$$

the following values have recently been determined, $\log K_h = -8.98$ [18], −8.97 [19] (both in 0.5 M NaCl at 25°C) and −8.98 [19] at 25°C and ionic strength 1.0 M. For comparison the latter value can be converted using $pK_w = 13.71$ for 1.0 M NaCl and 25°C [20] to obtain $\log K = 4.73$.

In view of some of the above uncertainties as well as the lack of knowledge about the occurrence and stability of any other mixed chloro-hydroxo complexes of palladium(II), a spectrophotometric investigation of its hydrolysis in chloride medium has been undertaken. Also, in an investigation of the photocatalytic reduction of Pd(II) (and some other platinum group metals) we found a dependence of the reduction on the hydroxide concentration of the solution [21]. For a meaningful interpretation of the results it is important to know the relative stability of chloro- and possible mixed chloro-hydroxo complexes occurring under the conditions of the photoreduction experiments. As the Pd(II)–chloride system was taken as a starting-point and considering uncertainties regarding the values of the stability constants of the chloro-complexes, a re-investigation seems justified. Absorption spectra of these complexes were also needed.

2. Experimental

All reagents were of analytical grade (Merck and PGM Chemicals) and solutions were prepared with water obtained from a Millipore Milli-Q system. Hydrochloric acid and perchloric acid were standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Palladium chloride solution was prepared from $PdCl_2$.

For determination of the equilibrium constants of the Pd(II)–chloride complexes a series of 24 solutions was prepared of which the chloride concentration was varied from 6×10^{-5} to 0.69 M by addition of hydrochloric acid. The Pd(II) concentration of the solutions was 3×10^{-5} M while the acid concentration was kept constant at 1.0 M by addition of the appropriate amount of perchloric acid. A GBC 920 UV-Vis double beam spectrophotometer equipped with a peltier thermocell was used for the absorption measurements at 25°C. Spectra were recorded in the wavelength range 200–325 nm at intervals of 3 nm using quartz cuvettes of path length 1.00 cm.

For investigation of the formation of mixed complexes a 3×10^{-5} M solution of $PdCl_2$ was titrated with sodium hydroxide. Both the palladium and chloride concentrations were kept constant by adding simultaneously the same volume of a solution 6×10^{-5} M $PdCl_2$ and 2.0 M NaCl. The ionic medium of the solution was kept constant at 1.0 M (H)Cl. The solution in the titration cell, kept in a thermostatted water bath at 25°C, was stirred with a non-electric immersion magnetic stirrer. Absorbances were measured in the wavelength range 210–325 nm against water as reference. A similar blank titration was carried out to correct the spectra. The experiment was repeated at two other chloride concentrations, namely 0.50 and 0.20 M using $NaClO_4$ to keep the ionic strength at 1.0 M.

The free hydrogen concentration was determined by measuring the potential, E, to ±0.2 mV using a Ross combination electrode (Orion) with a 1.0 M $NaClO_4$ bridge solution. Equation (1) was used to calculate the hydrogen ion concentration from the measured potential at each titration point:

$$E = E^{\circ} + 59.16 \log[H^+] + E_j \tag{2}$$

Values for E° and E_j (the liquid junction potential) were determined from titrations of 1.0 M $NaClO_4$ with $HClO_4$ as described previously [22, 23]. For brevity $-\log[H^+]$ is denoted by pH_c.

3. Results and discussion

3.1. *Pd(II)–chloride complexation*

The change in absorption with chloride concentration is shown in figure 1.

Absorbance data at every third wavelength in the range 203 to 325 nm were treated with the program HYPERQUAD 2000 [24] to calculate equilibrium constants and absorption spectra for the complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). The values of the cumulative formation constants $\log\beta_1 = 4.47$ (4.47), $\log\beta_2 = 7.80$ (7.76), $\log\beta_3 = 10.18$ (10.17) and $\log\beta_4 = 11.53$ (11.54) are almost identical to those reported by Elding [10] shown in parentheses. There can now be little doubt about the reliability of these constants pertaining to 25°C and ionic strength 1.0 M (table 1).

The molar absorption spectra for the species are shown in figure 2 from which it is seen that the $[PdCl_4]^{2-}$ complex has the strongest absorption band with maximum absorption at 222 nm and a weaker band at 280 nm. These charge transfer bands, caused by the transition of electrons from the chloride ligands to molecular orbitals localized mainly on palladium, are shifted towards shorter wavelengths (higher energies) when chloride is substituted by water in the complexes. The characteristics of these bands have been discussed previously [10]. The absorption of the $[Pd(H_2O)_4]^{2+}$ species is very low and becomes significant only at very short wavelengths, i.e. below ~220 nm. As to be expected these spectra agree very well with those reported by Elding [10] and more recently (at the time of writing) by Boily and Seward [12].

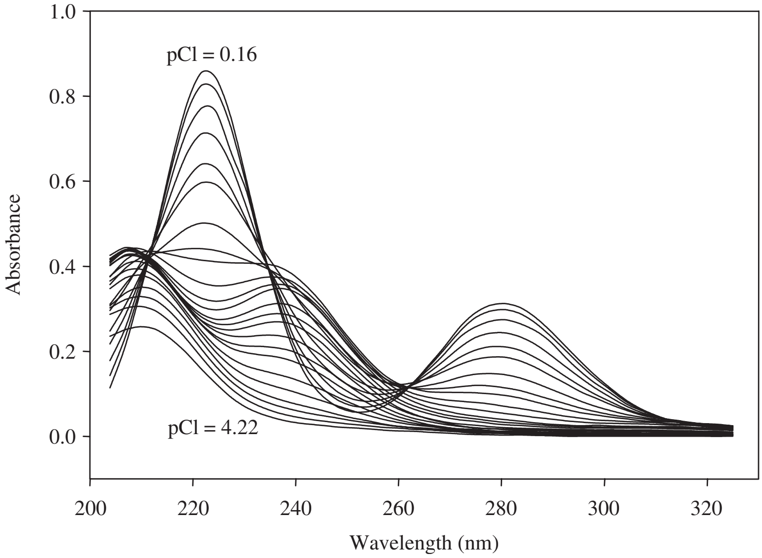

Figure 1. Change in absorption spectra with change in chloride concentration from 6×10^{-5} (pCl = 4.22) to 0.69 M (pCl = 0.16) of 3.5×10^{-5} M Pd(II) solutions.

Table 1. Formation constants for $[PdCl_n(H_2O)_{4-n}]^{2-n}$-complexes at 1 M ionic strength and 25°C.

Complex	$\log \beta_n \pm \sigma$			
$[PdCl(H_2O)_3]^+$	4.47 ± 0.07	4.47 ± 0.01	4.4	4.45 ± 0.04
$[PdCl_2(H_2O)_2]$	7.80 ± 0.11	7.76 ± 0.04	7.74	7.77 ± 0.03
$[PdCl_3(H_2O)]^-$	10.18 ± 0.14	10.17 ± 0.07	10.08	10.14 ± 0.06
$[PdCl_4]^{2-}$	11.53 ± 0.15	11.54 ± 0.09	11.46	11.51 ± 0.04
Reference	This work	[10]	[7]	Average

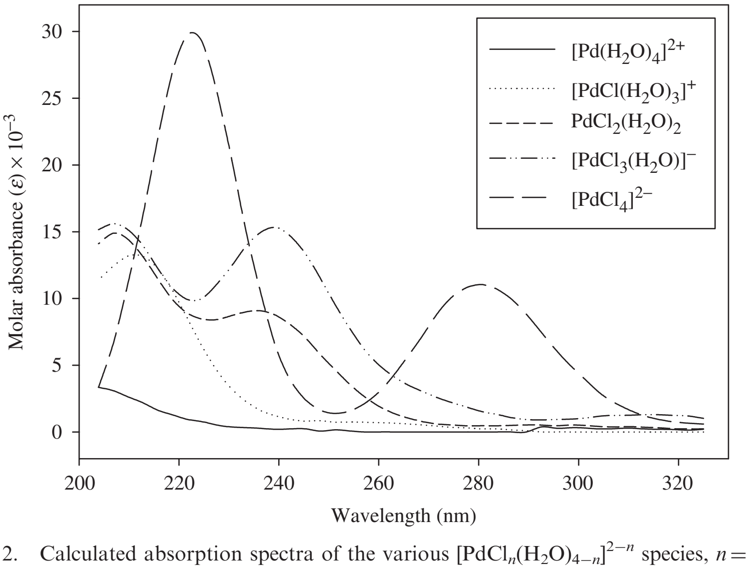

Figure 2. Calculated absorption spectra of the various $[PdCl_n(H_2O)_{4-n}]^{2-n}$ species, $n = 0$–4.

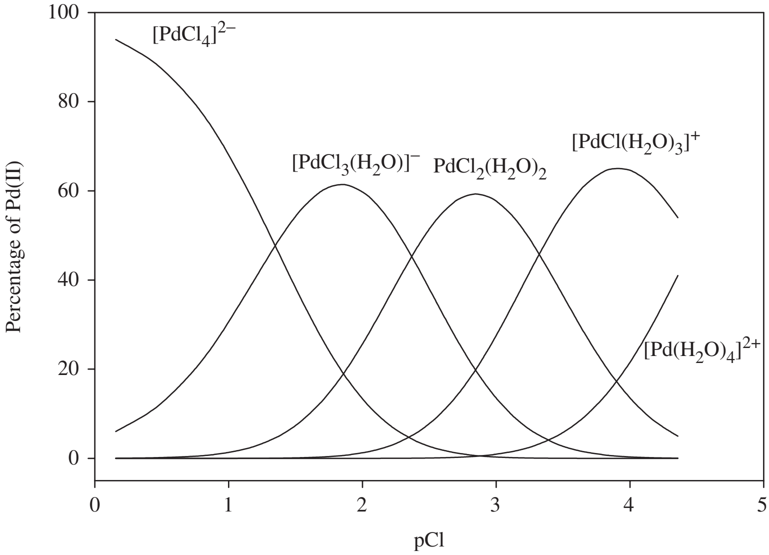

Figure 3. Distribution of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ species as a function of pCl.

The distribution of the complexes as a function of $-\log [Cl^-]$ is shown in figure 3. At a chloride concentration of 0.69 M, the highest under the experimental conditions, about 94% of the total palladium is in the form of the tetrachloro complex $[PdCl_4]^{2-}$. At the lowest chloride concentration (6×10^{-5} M) about 52% of the Pd(II) is already in the form of the monochloride complex $[PdCl(H_2O)_3]^+$.

3.2. *Complexation with hydroxide*

Due to the very low palladium concentration used in the experiments the presence of possible polynuclear palladium species was assumed to be negligible. The formation of chloro-hydroxo complexes was investigated at three chloride concentrations, 0.2, 0.5 and 1.0 M (ionic strength 1.0 M) by varying the pH_c over the range 2–12. The absorption spectra pertaining to 0.5 M Cl^- measured from 210 to 325 nm are shown in figure 4.

However, only measurements in the range 230 to 325 were regarded as reliable enough to be used in the calculations; at the shorter wavelengths the very strong absorption of the alkaline titrant necessitated a disproportionately high blank correction.

At each of the three chloride concentrations the $[PdCl_4]^{2-}$ complex is the major species (cf figure 3) with relatively small amounts of $[PdCl_3]^-$ present, the most (~17%) occurring at 0.20 M Cl^-. With increase in pH_c one would expect the successive replacement of chloride by hydroxide to form three mixed chloro-hydroxo complexes $[PdCl_3(OH)]^{2-}$, $[PdCl_2(OH)_2]^{2-}$, $[PdCl(OH)_3]^{2-}$ and finally the tetra-hydroxo complex $[Pd(OH)_4]^{2-}$ at high pH_c. This is seen in the change of the absorption spectra with change in pH_c (figure 4). The two prominent absorption bands of the $[PdCl_4]^{2-}$ complex gradually disappears to be replaced by spectral curves which indicate the formation

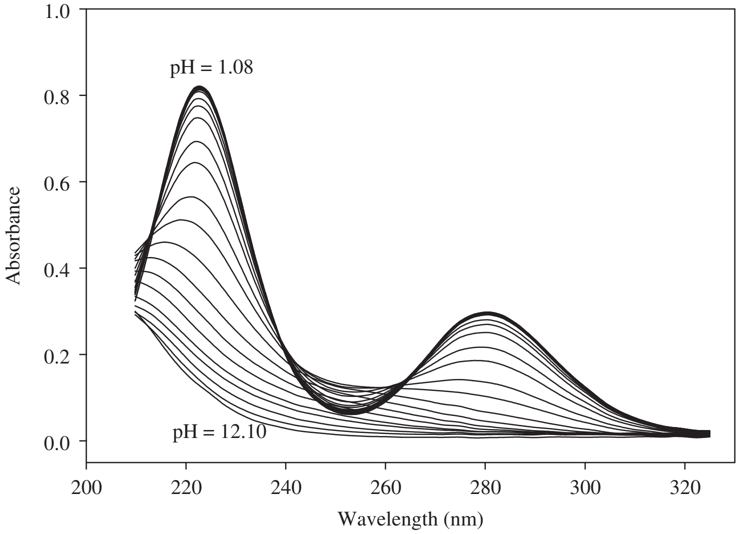

Figure 4. Change in absorption spectra with change in pH_c from 1.08 to 12.10 of a 3×10^{-5} M Pd(II) solution, 0.5 M in chloride at ionic strength 1.0 M.

Table 2. Values for the formation constants of the various $[PdCl_p(OH)_q]^{2-}$-complexes at three different chloride concentrations. Ionic strength of 1.0 M and temperature at 25°C.

	$\log \beta_{pq} \pm 3\sigma$			
	1.0 M Cl^-	0.50 M Cl^-	0.20 M Cl^-	Average
Model 1				
$[PdCl_3(OH)]^{2-}$	16.33 ± 0.04	16.43 ± 0.01	16.62 ± 0.05	16.46 ± 0.15
$[PdCl_2(OH)_2]^{2-}$	20.21 ± 0.07	20.45 ± 0.02	20.80 ± 0.01	20.49 ± 0.30
$[PdCl(OH)_3]^{2-}$	23.11 ± 0.12	22.98 ± 0.09	22.42 ± 0.05	22.84 ± 0.37
σ_A	0.00513	0.00294	0.00723	
$ss \times 10^3$	1.50	0.75	5.07	
Model 2				
$[PdCl_3(OH)]^{2-}$	16.34 ± 0.03	16.50 ± 0.01	16.61 ± 0.02	16.48 ± 0.14
$[PdCl_2(OH)_2]^{2-}$	20.19 ± 0.14	20.82 ± 0.03	20.87 ± 0.10	20.63 ± 0.38
$[PdCl(OH)_3]^{2-}$	23.04 ± 0.22	24.28 ± 0.03	24.74 ± 0.03	24.02 ± 0.88
$[Pd(OH)_4]^{2-}$	26.29 ± 0.12	26.28 ± 0.18	26.13 ± 0.07	26.23 ± 0.09
σ_A	0.00339	0.00206	0.00589	
$ss \times 10^3$	0.711	0.416	0.381	

of complexes having absorption bands at wavelengths below 210 nm. The formation constants of the above complexes are denoted by β_{pq} where the subscripts p and q refer to the number of chloride and hydroxide ions bound to Pd(II).

The spectrophotometric data were treated with the program EQUISPEC [25]. The two known formation constants of the complexes $[PdCl_4]^{2-}$ and $[PdCl_3]^-$ and the spectrum of the latter were supplied to the program. The relative concentrations of the $[PdCl_4]^{2-}$ complex were high enough to justify the calculation of its spectrum. In view of the rather high chloride concentrations used and the relatively small change in absorption at high pH_c, the $[Pd(OH)_4]^{2-}$ complex was not considered in the first reaction model. The results of the calculations are shown in table 2.

Considering the very low absorption of the solutions the agreement between the constants obtained at the three different chloride concentrations is quite good, the difference between the constants pertaining to 1.0 and 0.5 M Cl^- being only 0.1 to 0.2 log units. There is a small increasing trend in the values of β_{31} and β_{22} with decreasing chloride concentration which might partly reflect the change in the composition of the 1.0 M ionic medium due to the substitution of chloride by perchlorate. However, the trend is in the opposite direction for β_{13}, the formation constant of the complex $[PdCl(OH)_3]^{2-}$ that occurs in the higher pH_c range. The possibility that $[Pd(OH)_4]^{2-}$ might be present in this pH_c range was therefore investigated. Addition of this complex to the reaction model resulted in a significant improvement of the fit at each of the three chloride concentrations. For this model the agreement between the constants for the different chloride concentrations is also good, the best agreement now being between the constants pertaining to 0.5 and 0.2 M chloride. The values of β_{13} are the most affected by the inclusion of $[Pd(OH)_4]^{2-}$ as can be expected. The fact that the formation constants of $[Pd(OH)_4]^{2-}$ ($\log\beta_{04} = 26.29$, 26.28, 26.13) agree so well is a further indication that its inclusion is justified despite the small change in measured absorption and the absence of an absorption peak at high pH_c. These values are in good agreement with the literature values, $\log\beta_{04} = 26.43$ [26] and 26.5 ($0.5\,M \le I \le 1.0\,M$) [14] based on solubility and hydrolysis studies of Pd(II).

A value for $\log K = 4.8$ ($I = 0.7$ M NaCl at 25°C) deduced [14] from the results of Kump and Byrne [27] for the replacement of chloride by hydroxide according to the reaction

$$[PdCl_4]^{2-} + OH \Leftrightarrow [PdCl_3(OH)]^{2-} + Cl^- \qquad (3)$$

agrees with the value 4.81 ($\log\beta_{31}$–$\log\beta_{40}$) calculated from the data pertaining to 1.0 M Cl^- in this investigation. The average value of $\log K = (4.94 \pm 0.42)$ obtained in this investigation (3σ error limits) can be compared with some other literature values, i.e. 4.74 valid for ionic strengths 0.3–1.0 M [19], 4.73 determined in 0.5 M NaCl [18] and 4.45 in 1.0 M ionic medium [16] all at 25°C. The fact that the values of the equilibrium constants of both the first and last complexes in the series agree very well with literature values can be seen as a strong indication of the reliability of the constants of the two intermediate complexes $[PdCl_2(OH)_2]^{2-}$ and $[PdCl(OH)_3]^{2-}$, which are now reported for the first time, and indeed of the existence of these mixed complexes under the experimental conditions described. The only other values for these complexes that have been reported in the literature are a set of statistically predicted constants which were expected to be somewhat smaller than the directly observed values [14], $\log\beta_{31} = 15.69$ (16.48), $\log\beta_{22} = 19.66$ (20.63) and $\log\beta_{13} = 23.23$ (24.02) which can be compared with the average values obtained in this investigation, shown in parentheses.

An attempt to calculate a set of constants from the data for the three chloride concentrations grouped together was not successful. The absorptivities of the $[PdCl_2(OH)_2]^{2-}$ complex turned out to be negative and the formation constant about one log unit lower than the average of the previous calculations. Small inconsistencies among the data sets might be the reason for this result. Combination of the two data sets pertaining to chloride concentrations 0.2 and 0.5 M, however, resulted in acceptable spectra for all complexes and values for the formation constants agreeing within the error limits of the average values. The molar absorption spectra for the various complexes obtained from the data pertaining to 0.5 M Cl^- are shown in figure 5.

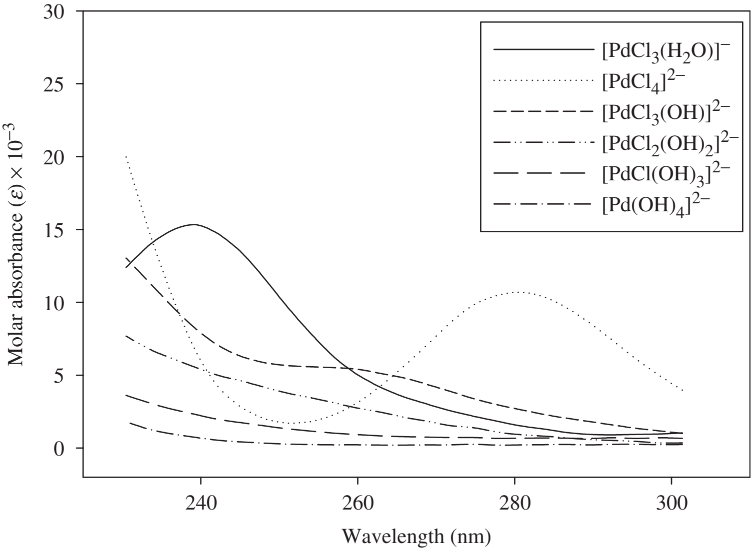

Figure 5. Absorption spectra of complexes calculated from the data pertaining to 0.5 M Cl^-.

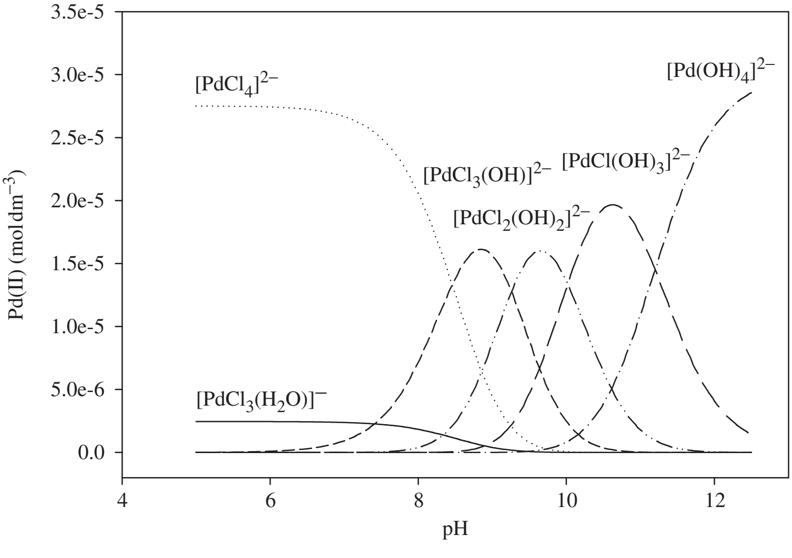

Figure 6. Distribution of complexes as a function of pH_c at chloride concentration 0.5 M.

The spectrum of $[PdCl_4]^{2-}$ is the same as that obtained from the work described in section 3.1. The $[PdCl_3(OH)]^{2-}$ complex exhibits a shoulder at 260 nm and apparently has an absorption peak at much lower wavelengths. Generally, replacement of Cl^- by OH^- in the coordination sphere of Pd(II) results in a decrease in absorption apparently caused by a shift of bands to shorter wavelengths.

The distribution of the complexes as a function of pH_c at chloride concentration 0.5 M is shown in figure 6.

It is seen that the hydroxo complexes occur at $pH_c > 7$ and that about 86% of the Pd(II) is already in the form of $[Pd(OH)_4]^{2-}$ at $pH = 12$. At lower chloride concentration the relative amounts of OH^- complexes increase at a given pH_c. At $pH_c = 12$, for instance, the relative concentrations of $[Pd(OH)_4]^{2-}$ at 0.2 and 1.0 M Cl^- are 94 and 75.6% respectively.

4. Conclusion

Values for the formation constants of the four chloro complexes of Pd(II), i.e., $[PdCl(H_2O)_3]^+$, $[PdCl_2(H_2O)_2]$, $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$ have been determined ($I = 1.0$ M and 25°C) which are in excellent agreement with two previous investigations, thereby removing all existing doubt about the reliability of these values. By using this system as starting point the chloro-hydroxide complexes $[PdCl_3(OH)]^{2-}$, $[PdCl_2(OH)_2]^{2-}$, $[PdCl(OH)_3]^{2-}$ as well as the tetra-hydroxo complex $[Pd(OH)_4]^{2-}$ could be characterized in terms of stability constants and absorption spectra. This is the first time that experimentally determined equilibrium constants and spectra for the mixed complexes $[PdCl_2(OH)_2]^{2-}$ and $[PdCl(OH)_3]^{2-}$ are reported.

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