3.6.14

Stepwise formation of Pd(II)-chloride complexes in hydrothermal solutions

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The stepwise formation constants of palladium(II)-chloride complexes in aqueous solutions up to 300°C were determined with uv-vis spectrophotometry. An objective treatment of spectra of solutions containing µmolal concentrations of Pd(II) at HCl concentrations ranging from 0 to 0.1 m HCl was used to extract the temperature-dependent stepwise formation constants for the reaction:

$PdCl_{n-1}^{2-(n-1)} + nCl^- \rightleftharpoons PdCl_n^{2-n}$

where $1 \leq n \leq 4$.

The complexes were also identified with EXAFS spectroscopic measurements in the same range of temperatures and are likely to possess a square planar geometry with Pd-Cl distances ranging from 2.26 to 2.30 Å and Pd-OH_2 distances ranging from 2.04 to 2.11 Å. These distances, which were chiefly independent of temperature, were reproduced with MP2 and B3LYP calculations using various basis sets. The nature of Pd-Cl and Pd-O bonds was also investigated by topological analyses of the electron density and of the Electron Localisation Function.

3.6.15

A spectrophotometric study of Palladium (II) complexation in chloride solutions

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The formation constants of Palladium (II) complexes in chloride solutions have been determined spectrophotometrically at a temperature of 25 °C and at 25 °C intervals from 100 to 250 °C, and a pressure of 64 bars using a high-temperature flow-through UV-visible spectroscopic system. Spectrophotometric measurements were made at 0.2 nm intervals over the range 190 to 400 nm using a Cary 100 double-beam spectrophotometer. Absorption spectra were collected for 19 solutions with total Pd concentrations ranging from $1.15 \cdot 10^{-4}$ to $6.35 \cdot 10^{-4}$ mol/kg, total chloride concentrations from $5.86 \cdot 10^{-4}$ to $3.26 \cdot 10^{-1}$/kg and $pH^{25°C}$ varying from 1.92 to 3.22.

It was found that under the conditions investigasted simple chlorides of Pd(II) dominate in the solution ($PdCl^+$, $PdCl_2°$, $PdCl_3^-$, $PdCl_4^{2-}$), whereas $PdCl_3(OH)^{2-}$ and $Pd(OH)_2°$ were only detected at temperatures below 125° C in trace concentrations. Cummulative formation constants were calculated for the following reactions: $Pd^{2+}+Cl^- = PdCl^+$ ($\beta_{1,0}$); $Pd^{2+}+2Cl^- = PdCl_2°$($\beta_{2,0}$); $Pd^{2+}+3Cl^- = PdCl_3^-$ ($\beta_{3,0}$); $Pd^{2+}+4Cl^- = PdCl_4^{2-}$ ($\beta_{4,0}$); $Pd^{2+}+3Cl^-+OH^- = PdCl_3(OH)^{2-}$ ($\beta_{3,1}$); $Pd^{2+}+2OH^- = Pd(OH)_2°$ ($\beta_{0,2}$) and are summarized in the Table below. The question marks refer to the values characterized by high uncertainty of derivation caused by insignificant concentrations of the corresponding species.

T °C	logarithm of formation constant					
	$\beta_{1,0}$	$\beta_{2,0}$	$\beta_{3,0}$	$\beta_{4,0}$	$\beta_{3,1}$	$\beta_{0,2}$
25	5.33	8.80	10.85	12.83	17.9(?)	22.8(?)
100	5.06	7.86	10.06	11.15	15.7 (?)	
125	5.04	7.80	9.75	10.64		
150	5.05	7.92	9.80	10.35		
175	5.10	8.22	10.13	10.26		
200	5.26	8.49	10.35	10.40		
225	5.44	8.75	10.70	10.69		
250	5.67	9.08	11.04	11.07		

It was found that the values of formation constants obtained in the study are similar to these published in the literature. However, the observed trends suggest higher stability of $PdCl_3^-$ and $PdCl_4^{2-}$ at elevated temperatures than that supposed before.