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Spectroscopic and theoretical analysis of Pd^{2+}–Cl^{-}–H_2O system

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ABSTRACT

Time dependent density functional theory (TD-DFT) and spectrophotometric methods were used for speciation analysis in Pd^{2+}–Cl^{-}–H_2O system. It was shown, that there is an excellent harmony between TD-DFT calculated UV-VIS spectra end those registered using spectrophotometric method. It was shown, that for simple electrolyte, a several different form of Pd(II) appears simultaneously. Thanks to TD-DFT method, it was possible to deconvolution experimental UV-VIS spectrum and determination which form of Pd(II) complexes are present in the solution.

1. Introduction

Palladium complexes are still the hot topic interesting of many scientist mainly due to its simple square-planar solvent exchange processes. It is difficult to distinguish which form of metal complex is dominated in the solution [1]. Moreover, the form of the complex consisting in the solution play a crucial role in the metal recovery process. Some of extractant are selective form the complex structure point of view. Therefore, knowledge in this area is fundamental [2–5]. Also, the forms of complexes existing in electrolytes as well as its concentration, has significant role for palladium and palladium base alloys electro deposition [6,7]. Equally important are applications of palladium complexes in medicine as antitumor compounds thanks to its significant biochemical activity [8–10]. For example a series of ternary palladium(II) complex type [Pd(L_{1-4})ox]·xH_2O (where L = formamidine ligands and ox = oxalate) have a good cytotoxicity against: breast cancer (MCF-7), colorectal carcinoma (HCT-116) or human prostate cancer (PC-3) cell lines [8]. Even simple palladium(II) chloride complex could be used for determination of antibiotics – Cephalosporins [11,12].

It is well known, that the palladium(II) chloride complex in effect of pH and/or chloride ions concentration changes, may change the structure. There is a several papers where Pd^{2+}–Cl^{-}–H_2O–OH^{-} system was described [13–18].

In general, palladium(II) aqua complex formation in chloride ions containing media can be described by the following reaction steps:

$$[PdCl_4]^{2-} + H_2O \overset{K_1}{\rightleftharpoons} [PdCl_3(H_2O)]^{-} + Cl^{-} \quad (1)$$

$$[PdCl_3(H_2O)]^{-} + H_2O \overset{K_2}{\rightleftharpoons} [PdCl_2(H_2O)_2]_{cis} + Cl^{-} \quad (2)$$

$$[PdCl_3(H_2O)]^{-} + H_2O \overset{K_2}{\rightleftharpoons} [PdCl_2(H_2O)_2]_{trans} + Cl^{-} \quad (3)$$

$$[PdCl_2(H_2O)_2]_{cis} + H_2O \overset{K_3}{\rightleftharpoons} [PdCl(H_2O)_3]^{+} + Cl^{-} \quad (4)$$

$$[PdCl_2(H_2O)_2]_{trans} + H_2O \overset{K_3'}{\rightleftharpoons} [PdCl(H_2O)_3]^{+} + Cl^{-} \quad (5)$$

$$[PdCl(H_2O)_3]^{+} + H_2O \overset{K_4}{\rightleftharpoons} [Pd(H_2O)_4]^{2+} + Cl^{-} \quad (6)$$

Chloride ion is substituted by water, in four steps. Boily et al. [13]

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suggest that *cis* and *trans* form of $[PdCl_2(H_2O)_2]$ complex can be formed.

To investigate the complex formation several different methods are often use. The one of the most popular method is UV-VIS spectrophotometry. This method is suitable to investigate complexes able to absorb light in UV-VIS range. Other often use method are: ion exchange, NMR/ESR, calorimetry, conductivity, voltammetry, kinetic etc. All those method have some advantage and disadvantage. First of all, all described above methods required significant numbers of reagents, experiments and time. It should be noted that the experimental methods are also very expensive one due to high price of chemical agents and sophisticated equipment.

The DFT methods are often applied for IR, Raman, UV-Vis spectra calculations as well as for molecule structure optimization [12,19–24].

The aim of the present work is to present very simply and quickly method which based on spectrophotometric measurements and TD-DFT calculations for determination which form of palladium(II) chloride complex is present in solution. Presented methodology is not expensive, required only a limited number of spectra measurements and PC computer with appropriate applications.

2. Experimental

2.1. Materials and measurements

The Pd(II) precursor was obtained in the following way: 10 g of $PdCl_2$ salt was dissolved in stoichiometric amount of concentrate hydrochloric acid (37%, POCH, A.R.). Then, obtained solution was complemented to 0.5 dm^3, using 0.1 M hydrochloric acid. The solution thus obtained was stored in the dark.

The UV-Vis spectra were registered using spectrophotometer Shimadzu model U-2501PC.

2.2. Computational details

Theoretical modeling was performed with Gaussian 09 Rev. D.01 (Gaussian, Inc.) [25]. The final geometry was obtained by using DFT with the B3LYP (the Becke three-parameter-Lee–Yang–Parr) functional [26] and the LanL2DZ basis set [27]. Molecular orbitals and surfaces were plotted from GausView5 software. Electronic transitions were calculated by using time-dependent TD-DFT with the B3LYP functional and the LanL2DZ basis set. In addition the electronic spectra were calculated in water solution using the IEFPCM method [25]. UV-Vis spectra were deconvoluted using Origin 8.5 software.

3. Results and discussion

The experimental UV-VIS spectra of Pd(II) in Pd^{2+}–Cl^-–H_2O system exhibit 3 peaks. The first one located at 223 nm, second one at 279 nm and the third one at 445 nm [28]. Those to first are strong, that's means, that the light at this regions is strongly adsorbed. The third one exhibit low intensity, however is located in visible spectrum of the light. Thanks to that, the solution has intensive brown color for high concentration of Pd(II).

In our work we present the influence of different conditions for measured spectra, such as concentration and temperature. At the beginning we measured the UV-VIS spectra of Pd(II) for different initial concentration of Pd^{2+}. The result are showed in Fig. 1 A.

Vertical back lines were added, to shown that those peak are asymmetrical. This in turn suggest that observed peaks are composed. It should be noted, that the UV-VIS spectra's were registered with 1 nm resolution, therefore λ_{max} has accuracy ±1 nm.

In Fig. 1 B graphical determination of molar absorption coefficient using Lambert-Beer dependency (see eq. (7)) is shown.

$$Abs = \varepsilon_1 \cdot [Pd(II)] \cdot L \tag{7}$$

where:Abs – absorbanceL – optic path lengthε_1 – molar absorption coefficient for λ_1

As it can be seen, the absorbance v.s. Pd(II) concentration plot is linear. Obtained R square is at high level. However, obtained values of ε can be only use for total concentration of palladium determination, under restriction, that all other parameters are constant.

In the next step of our analysis of Pd^{2+}–Cl^-–H_2O system, the influence of temperature on UV-VIS spectra was investigated. The influence of temperature was investigated for two different initial concentration of Pd(II). Obtained results are shown in Fig. 2 and Fig. 3.

As it can be seen, increase of temperature effect in decrease of absorbance level at the wavelength 279 nm. The absorbance level of the pick located at 445 nm, slightly increase. Similar experiment was performed for the sample containing lower amount of Pd(II). Thanks to that it was possible to observe peak at the wavelength 223 nm.

Obtained results are unexpected. In general, absorbance level of the solution containing absorbing light species is decreasing with decreases of temperature [29]. Moreover, the absorbance level should have an limit equal to 0 at the temperature of absolute zero. Here, however the situation is opposite. It is due to superposition of two phenomena. The first one is directly physical one and related to electron structure changes with changes of temperature and the second one is purely chemical one.

Absorption of light in UV-VIS range is mainly related to electron structure of absorbing light species. Those species may contains valence electrons of low excitation energy. The spectrum of light absorbed by those species especially in aqueous solutions is complex. This is related to superposition of rotational and vibrational transitions of the electronic transitions. Moreover, in the solution atoms are dense packed, and also interact. The species exert influences on each other's. Those effects are observed as continuous absorption band, where in case of vapours sharp peaks are observed. Those exert influences of each species might to be reduced by decrease of temperature [30]. In such a case an increase of absorbance can be observed as well as peak maximum shift.

From the chemical point of view, it is well known, that increase of temperature effect in increase of reaction rate according to Arrhenius as well as to Eyrin-Polanyi dependence.

In case of equilibrium of two species the following relation can be given:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{8}$$

Now, let's take a look at the Arrhenius dependence:

$$k_1 = A_1 \cdot e^{-\frac{E_{a,1}}{RT}} \tag{9}$$

where:A1 – pre exponential constantR – gas constantT – temperature in Kelvin scaleEa1 – activation energy of reaction 1

At the equilibrium, the rate of the forward and reverse reactions are equal, therefore the following equation is valid:

$$k_1 \cdot [A] = k_2 [B] \tag{10}$$

After rearranging of equation (10) the following form can be obtained: