

# STUDY OF THE CHARACTER OF COMPLEXES IN AQUEOUS PdCl<sub>2</sub> SOLUTION BY MEASURING MEAN MOLAR MASSES

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The mean molar mass of the components present in aqueous PdCl<sub>2</sub> solutions of different concentrations was measured cryoscopically. The palladium complexes under consideration are mostly mononuclear. The possible content of binuclear complexes becomes much smaller with a drop in the chloride concentration.

Most authors<sup>1-4</sup> studying solutions of palladium chloride came to the conclusion that this salt forms in aqueous solutions only mononuclear complexes of the type PdCl<sub>n</sub><sup>2-n</sup> ( $n = 1-4$ ). This is based mainly on the measurement of Pd electrode potentials in solutions<sup>1</sup> with different concentrations of PdCl<sub>4</sub><sup>2-</sup> and LiCl, determination of the formation functions<sup>2</sup> of Pd—Cl complexes in aqueous solution of PdCl<sub>2</sub>, and on the thesis of Weed<sup>3</sup>. On the other hand, evaluation of UV spectra of the studied solutions suggests that at low concentrations of PdCl<sub>2</sub> and low ratios of C<sub>Cl</sub> : C<sub>Pd</sub> (analytical concentrations of chloride and palladium) in aqueous solution also binuclear complexes may be present<sup>5</sup>.

To verify this result by another, independent method, we determined the mean molar mass of the components of aqueous PdCl<sub>2</sub> solutions at different concentrations and ratios of C<sub>Cl</sub> : C<sub>Pd</sub> and compared it with theoretically calculated values. After a critical evaluation of various methods for the determination of the mean molar mass of the components of PdCl<sub>2</sub> solutions we concluded that the cryoscopic method is best suited for this purpose.

Of the other methods, ebullioscopy is not suitable because of the volatility of HCl added to the PdCl<sub>2</sub> solutions to adjust the pH value and the ratio of C<sub>Cl</sub> : C<sub>Pd</sub> (at pH > 7, hydrolysis and precipitation of a hydrated oxide of palladium takes place). Osmometry and viscosimetry are subject to considerable errors in the case of low molecular masses as in our case.

## EXPERIMENTAL

Solutions of PdCl<sub>2</sub> were prepared from a 40% aqueous PdCl<sub>2</sub> solution (Safina, Prague) by diluting and adding HCl as desired. Their concentration was checked by potentiometric titration with KI and NaOH. Hydrogen chloride and other chemicals used were of reagent grade (Lachema, Brno). Cryoscopic measurements were done on a standard cryoscope<sup>6</sup> with the difference that the outer

vessel was replaced by a thermostated bath of a temperature by  $4 \pm 0.3$  K lower than the freezing point of the studied solution. The composition of the solutions is given in Table I. The ionic strength was not specially adjusted.

## RESULTS AND DISCUSSION

The mean molar masses,  $\bar{M}_{\text{exp}}$ , determined cryoscopically and summarized in Table I, were calculated from the concentrations of the solutes,  $a_i$  (g/kg H<sub>2</sub>O), and from the depression of the freezing point with respect to water,  $\Delta T_i$ , as

$$\bar{M}_{\text{exp}} = K_v a_i / \Delta T_i. \quad (1)$$

The cryoscopic constant of water is  $K_v = 1.86$  K mol<sup>-1</sup> kg.

For a theoretical calculation of the mean molar mass of the components of an aqueous solution, the knowledge of its exact composition is necessary; we therefore chose two mutually opposed models of the solution, first of which assuming the presence of only mononuclear, while the second one only binuclear Pd—Cl complexes. In the first case the mean molar mass  $\bar{M}$  can be calculated from the following equation (according to the definition of the mean molar mass):

$$\bar{M} = \frac{\sum_{n=0}^4 M_n [\text{PdCl}_n^{2-n}] + M_{\text{Cl}^-} [\text{Cl}^-] + M_{\text{H}} [\text{H}_3\text{O}^+]}{\sum_{n=0}^4 [\text{PdCl}_n^{2-n}] + [\text{Cl}^-] + [\text{H}_3\text{O}^+]}. \quad (2)$$

The brackets denote molal concentrations and these are multiplied by the corresponding molar masses  $M_n$ .

Eq. (2) can be rewritten in a simpler form suitable for its practical use. The numerator contains the sum of masses of individual components, *i.e.*, the mass of the dissolved compound in 1 kg of water, which we denote as  $a_i$ . Analogously the denominator can be simplified by introducing the total concentration  $C_{\text{Pd}}$ :

$$\bar{M} = a_i / (C_{\text{Pd}} + [\text{Cl}^-] + [\text{H}_3\text{O}^+]). \quad (3)$$

The quantities  $a_i$ ,  $C_{\text{Pd}}$ , and  $[\text{H}_3\text{O}^+]$  can be easily determined experimentally. The values of  $[\text{Cl}^-]$  can be calculated from the known course of the formation function of Pd—Cl complexes and from the known values of  $C_{\text{Pd}}$  and  $C_{\text{Cl}}$ . The formation function has in the case of the first model solution the form<sup>2</sup>

$$\bar{n} = \frac{\beta_1 [\text{Cl}^-] + 2\beta_2 [\text{Cl}^-]^2 + 3\beta_3 [\text{Cl}^-]^3 + 4\beta_4 [\text{Cl}^-]^4}{1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4}, \quad (4)$$

where  $\bar{n}$  denotes average number of  $\text{Cl}^-$  ions bound to one Pd atom and  $\beta_n$  dissociation constant of the  $\text{PdCl}_n^{2-n}$  complex ( $n = 1-4$ ). In addition, we have the obvious relation

$$[\text{Cl}^-] = C_{\text{Cl}} - \bar{n}C_{\text{Pd}}. \quad (5)$$

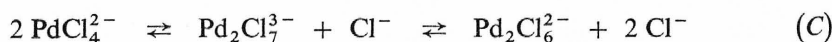
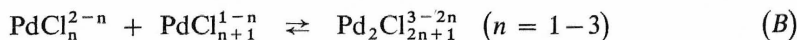
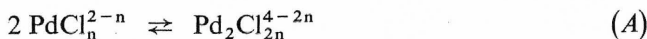
A survey of the hitherto measured values of the equilibrium constants among individual Pd—Cl complexes was given by Victori and coworkers<sup>4</sup> at various temperatures and ionic strengths; products give the values of  $\beta_n$ . The ionic strength of our solutions was between 0.1 and 0.9 mol/l. The equilibrium constants are known for  $\mu = 0$  and  $\mu = 1$ ; the ionic strength of the measured solutions lies within these limits. If we calculate the mean molar mass for  $\mu = 0$  and for  $\mu = 1$ , we obtain an interval within which the mean molar mass of the components of our  $\text{PdCl}_2$  solutions should lie.

According to Biryukov<sup>7</sup>, we have the following values at  $\mu = 0$ :  $\log \beta_1 = 6.0 \pm 0.2$ ,  $\log \beta_2 = 10.6 \pm 0.4$ ,  $\log \beta_3 = 13.1 \pm 0.6$ ,  $\log \beta_4 = 15.1 \pm 0.8$ . At  $\mu = 1$ , we found on the average five values for each equilibrium constant in the literature<sup>4</sup>. We used those of Burger<sup>8</sup> to calculate  $\beta_n$  since they are substantiated by several methods and differ only little from the averages of the published values if the smallest and largest ones are omitted. The results are:  $\log \beta_1 = 3.88 \pm 0.09$ ,  $\log \beta_2 = 6.9 \pm 0.1$ ,  $\log \beta_3 = 9.1 \pm 0.2$ ,  $\log \beta_4 = 10.4 \pm 0.2$  ( $\mu = 1$ ).

Thus, only two unknowns remained in Eqs (4) and (5),  $[\text{Cl}^-]$  and  $\bar{n}$ . They are best calculated by the graphical method, which is sufficiently accurate and rapid in this case.

To calculate the mean molar mass for the second model solution, where only binuclear complexes are present, we can proceed analogously; the total concentration of the Pd—Cl complexes is in this case equal to  $C_{\text{Pd}}/2$ . The values of  $\beta_n$  for the binuclear complexes are, however, unknown and cannot be calculated by our method. Therefore, the values of  $[\text{Cl}^-]$  cannot be calculated from the formation function of the binuclear complexes and must be estimated.

The following equilibria may be considered between mono- and binuclear complexes:



Hence, the equilibria are mostly independent of the  $\text{Cl}^-$  concentration and in solutions with  $\bar{n} < 3$  the value of  $[\text{Cl}^-]$  should be equal for both the model solutions at equal concentrations of palladium,  $C_{\text{Pd}}$ , chloride,  $C_{\text{Cl}}$ , and hydrogen ions. In solu-

tions with  $\bar{n} > 3$  the importance of the equilibrium (3) apparently increases resulting in a possible influence on the value of  $[\text{Cl}^-]$ .

The mean molar masses calculated on the above assumptions are given in Table I. Their relative error, due to errors in concentrations and in the values of  $\beta_n$ , is less than 3%. The relative error of the measured values varies according to the difference between the freezing points of water and the solutions from 0.5 to 3%.

It follows from the comparison of the measured and theoretically calculated mean molar masses that the Pd—Cl complexes are in aqueous solutions mostly mononuclear. The deviations between the measured and calculated  $\bar{M}$  values for the first model solution can be attributed to experimental errors. The method used does not prove unambiguously the absence of binuclear (or polynuclear) complexes,

TABLE I  
Mean Molar Masses of Components of Aqueous PdCl<sub>2</sub> Solutions

$C_{\text{Cl}} : C_{\text{Pd}}$	$C_{\text{Pd}}$ mol/kg	$C_{\text{Cl}}$ mol/kg	$[\text{H}_3\text{O}^+]$ mol/kg	$\bar{M}_{\text{exp}}$ g/mol	$\bar{M}_{\text{theor}}$		
					$\mu = 1^a$	$\mu = 0^a$	$\mu = 1^b$
4:41 : 1	0.278	1.226	0.670	66.2	65.7	68.1	67.6
4:41 : 1	0.149	0.659	0.361	67.2	63.8	67.2	66.8
4:41 : 1	0.123	0.542	0.296	67.7	63.6	67.0	66.4
4:41 : 1	0.071	0.311	0.170	65.1	61.9	65.8	65.4
3:72 : 1	0.148	0.552	0.255	78.4	78.9	83.5	87.1
3:72 : 1	0.126	0.470	0.217	77.2	78.2	83.2	86.6
3:72 : 1	0.100	0.372	0.172	77.7	77.3	82.7	85.5
3:72 : 1	0.080	0.299	0.138	76.4	76.0	82.0	84.6
3:72 : 1	0.049	0.138	0.084	71.9	73.2	80.1	81.2
2:92 : 1	0.453	1.323	0.417	100.8	108.5	—	140.0
2:92 : 1	0.182	0.530	0.167	105.0	106.8	108.5	136.2
2:92 : 1	0.140	0.409	0.129	108.9	106.0	108.0	134.0
2:92 : 1	0.108	0.316	0.099	109.1	104.5	107.0	132.5
2:92 : 1	0.047	0.137	0.043	105.2	101.1	105.1	128.1
2:60 : 1	0.133	0.345	0.079	118.5	121.5	123.1	174.9
2:60 : 1	0.087	0.226	0.053	117.0	119.2	121.6	170.1
2:60 : 1	0.062	0.162	0.038	118.9	118.1	121.1	167.9
2:19 : 1	0.207	0.453	0.039	150.8	153.3	154.4	262.7
2:19 : 1	0.118	0.259	0.022	150.4	152.5	154.1	259.9
2:19 : 1	0.098	0.214	0.018	152.8	151.8	153.9	258.3
2:19 : 1	0.054	0.117	0.010	153.3	149.7	153.2	252.3

<sup>a</sup> Model I, <sup>b</sup> model II; the values of  $\bar{M}_{\text{theor}}$  for model II at  $\mu = 0$  are not given since they are higher than  $\bar{M}_{\text{theor}}$  at  $\mu = 1$ .

but limits their possible content to the region of errors inherent in the method. With decreasing ratio of  $C_{Cl} : C_{Pd}$  the possible content of binuclear complexes drops considerably in contrast to the conclusions of Kravchik and coworkers<sup>5</sup>, which are therefore disputable.

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