STUDY OF THE NATURE OF THE COMPLEXES PRESENT IN PdCl$_2$ AQUEOUS SOLUTION

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The existence of complexes of palladium chlorides in aqueous solutions was examined for different chloride-to-palladium molar ratios. Spectral and potentiometric methods were employed in conjunction with the cryoscopic technique, and the complexes of palladium with chlorides were found to be only mononuclear; the existence of binuclear complexes can be practically ruled out.

In most papers dealing with the study of PdCl$_2$ solutions, the existence of mononuclear Pd–Cl complexes of the general formula PdCl$_n^{2-n}$ ($n = 1$ to 4) only has been assumed in aqueous solutions[1-4]. On the other hand, Kravchik and coworkers[5] and Volchenskova and Yatsimirskii[6] have suggested that in some concentration circumstances, binuclear Pd–Cl complexes are found in aqueous solutions. This discrepancy has led us to re-examine the works cited as to the methodics used.

The assumption[5,6] of the binuclear Pd–Cl complex relies on the occurrence of the corresponding peaks in the absorption spectra in the ultraviolet region of PdCl$_2$ aqueous solutions. The conclusions drawn by these authors[5,6] may be incorrect if the same absorption maxima belong to mononuclear Pd–Cl complexes as well, particularly if their theoretical calculations were erroneous and mononuclear complexes were in fact present in those solutions from which the absorption maxima of the binuclear complexes have been determined[7,8].

There are three arguments against the existence of the binuclear complexes: Levanda and coworkers[2] have obtained for constant temperature, ionic strength, and constant concentration of the Cl$^-$ ions nonbonded in the complexes (henceforth free chlorides) a linear dependence of the potential of a palladium electrode (E_{Pd}) on the logarithm of the PdCl$_4^{2-}$ concentration calculated assuming that the palladium in the solution occurs only in the forms PdCl$_4^{2-}$ and PdCl$_3^-$, or Pd^{2+}. It can be argued that in the conditions applied in[2] a predominant portion of the palladium occurs in the PdCl$_4^{2-}$ form and only a small proportion (3 to 15% (m/m)) can be present in the form of PdCl$_3^-$ and of binuclear complexes. The function $E_{Pd} = f(\ln . [PdCl_4^{2-}])$ should be therefore sensitive even to small deviations of the actual composition from the calculated. On the other hand, the authors used an incorrect value of the equilibrium constant[4,9] for the calculation of [PdCl$_4^{2-}$], the error did not, however, show up in the dependence examined. This indicates that the method in question is insufficiently sensitive with respect to the possible content of the binuclear complexes, which makes it necessary to repeat the measurements with lower concentration of free chlorides, where the proportion of the PdCl$_4^{2-}$ complex is lower.

Biryukov and Shlenskaya[1] have inferred the absence of binuclear complexes from the fact that the generating function of the Pd–Cl complexes measured at different wavelengths were equal. However, for the function to be different it is necessary that the mono- and binuclear complexes also absorb differently at the wavelengths used. Thus this argument can be verified by comparing the spectrum of an aqueous solution only containing mononuclear complexes with the spectra obtained by Kravchik[5] and Volchenskova[6] for binuclear complexes.

A number of works[4] have been concerned with the determination of the equilibrium constants of the mononuclear Pd–Cl complexes; in all cases the binuclear complexes have been assumed to be absent from the aqueous solution, mostly with reference to the paper by Levanda[2]. The equilibrium constants obtained by different authors and by means of different method were, however, often very different. One of the conceivable reasons may be also the presence of binuclear complexes in different concentrations. This possibility can be eliminated by increasing the precision of the equilibrium constant determination; otherwise it is necessary to give evidence of the absence of the binuclear complexes by means of some other method.

In our previous work[10] we were able to demonstrate by means of molecular weight measurements that in the concentration conditions applied by Kravchik and co-workers[5], in contrast to their conclusions, the Pd–Cl complexes are predominantly mononuclear. In this work we present the UV spectra of our solutions in comparison with those given by Kravchik[5] and Volchenskova[6], supplementing the measurements to the Levanda's method, as well as another method suitable for the establishing of the presence of the binuclear Pd–Cl complexes in aqueous solutions.

EXPERIMENTAL

Chemicals and Apparatus

The $PdCl_2$ solutions were prepared from a 40% aqueous solution of $PdCl_2$ (Safina, Vestec). The concentrations of $PdCl_2$ and HCl were determined by potentiometric titratons with titrant solutions of KI and NaOH, respectively. The other chemicals used were reagent grade purity.

The spectrophotometric measurements were conducted on an instrument Spekord UV VIS (Zeiss, Jena) in quartz cells, thickness 0·1 to 0·5 cm. The blanks contained NaOH, $HClO_4$, and $NaClO_4$ in concentrations identical with those in the samples. The measurements were performed for the concentration ranges $1 . 10^{-5}$ and $7 . 10^{-2} M \cdot PdCl_2$ and $4 . 10^{-5}$ to $1 M \cdot Cl^-$, ionic strength 2 and temperature 25°C. The ionic strength was adjusted with $NaClO_4$. The potentiometric measurements were carried out on a potentiometer OP-401/2 (Radelkis, Budapest) using a cell Pd | $PdCl_2$, HCl, $HClO_4$, $NaClO_4$ $(\mu = 1)$| s.c.e. The palladium electrode employed was of the size 1×1 cm. The palladium concentrations were 0·005 to 0·1 mol l^{-1}, temperature 25°C, ionic strength $\mu = 1$, $[Cl^-] = 0·055$ mol l^{-1}, for which the average ligand number of palladium is $n \approx 3·5$. The total chloride concentration (C_{Cl}) requisite to maintain a constant concentration of Cl^- was calculated from the relation $C_{Cl} = 0·055 + 3·5 C_{Pd}$ (where C_{Pd} is the total concentration of palladium), which follows from the generating function of the Pd–Cl complexes.

RESULTS AND DISCUSSION

Fig. 1 shows the ultraviolet spectra of the Pd–Cl complexes as measured by Kravchik and coworkers[5] and Volchenskova and coworkers[6], which according to those

authors are typical for aqueous solutions of binuclear complexes (curve *1* and *3*), along with the spectrum of an aqueous solution of PdCl₂ and HCl in which only mononuclear Pd–Cl complexes are present according to the mean molecular weight measurements[10] (curve *2*). As can be seen, it is not possible to attribute the absorption maximum at $48 . 10^3 \text{ cm}^{-1}$ unambiguously only to the terminal chlorides of the binuclear Pd–Cl complexes and that at $42 . 10^3 \text{ cm}^{-2}$ only to the bridge chlorides of these complexes (as has been done by Volchenskova[6] and by Mason[8], or reversely, as done by Baranovskii[7] and by Kravchik[5]), because the same absorption maxima appear in the spectrum of the aqueous solution of mononuclear complexes, in which a single ligand chloride occurs. This implies that the presence of binuclear Pd–Cl complexes cannot be proved based solely on the occurrence of the absorption maxima at $48 . 10^3$ and $42 . 10^3 \text{ cm}^{-1}$ in the ultraviolet spectra of PdCl₂ solutions.

On the other hand, however, it follows from Fig. 1 also that the argument advanced by Shlenskaya and Biryukov[1] favouring the absence of binuclear complexes is not rigorous either, since the provable binuclear Pd–Cl complexes[6,7,11] possess analogous spectra as the mononuclear ones, and thus it is not possible to uniquely establish the wavelength region in which the different absorptions by the mono- and binuclear Pd—Cl complexes should reflect in the generating function of these complexes.
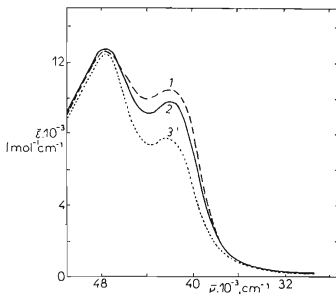
A thorough analysis of the relation between the solution composition and the generating function, constructed based on the spectra in the ultraviolet and visible region, indicates that some properties of the generating function can be used to establish the presence of bi- and polynuclear Pd–Cl complexes in the solution or their absence from it. The generating function can be derived from the relation

$$\bar{n} = C_{Pd}^{-1} \sum_{n=1}^{4} n[\text{PdCl}_n^{2-n}] + C_{Pd}^{-1} \sum_{m=1}^{7} m[\text{Pd}_2\text{Cl}_m^{4-m}], \qquad (1)$$

FIG. 1

Electronic Absorption Spectra of Aqueous Solutions of PdCl₂ and HCl

1 Spectrum obtained by Kravchik and coworkers[5] for $C_{Cl} : C_{Pd} = 3\cdot7$, *2* spectrum obtained by the authors of this work for solution containing only mononuclear Pd–Cl complexes, $C_{Cl} : C_{Pd} = 2\cdot92$, *3* spectrum obtained by Volchenskova and Yatsimirskii[6] for aqueous solution of Pd₂Cl₄(H₂O)ₙ, $C_{Cl} : C_{Pd} = 2$.

where $C_{Pd} = \sum\limits_{n=0}^{4} [PdCl_n^{2-n}] + 2\sum\limits_{m=1}^{7} [Pd_2Cl_m^{4-m}]$ is the total palladium concentration, n and m are the numbers of the chloride ligands in the mono- and binuclear complexes, respectively, $[PdCl_n^{2-n}] = \beta_n[Pd^{2+}][Cl^-]^n$ is the concentration of the mononuclear complexes and $[Pd_2Cl_m^{4-m}] = \beta_m[Pd^{2+}][Cl^-]^m$ the concentration of the binuclear complexes, and β_n, β_m are the stability constants of the mononuclear and binuclear Pd–Cl complexes, respectively, and Pd^{2+} is the concentration of the free palladium(II) ions.

On rearrangement we obtain the generating function for the Pd–Cl complexes in the form

$$\bar{n} = \frac{\sum\limits_{n=1}^{4} n\beta_n[Cl^-]^n + [Pd^{2+}]\sum\limits_{m=1}^{7} m\beta_m[Cl^-]^m}{1 + \sum\limits_{n=1}^{4}\beta_n[Cl^-]^n + 2[Pd^{2+}]\sum\limits_{m=1}^{7}\beta_m[Cl^-]^m}. \qquad (2)$$

If the Pd–Cl complexes present in the solution are only mononuclear, the generating function reduces considerably and will be independent of the concentration of the free palladium(II) ions. This applies also to binuclear complexes, except solutions in which $[Pd^{2+}]$ cannot be neglected with respect to C_{Pd} (where $C_{Cl} \leqq C_{Pd}$, or where $[Cl^-]$ is very low).

If mono- and binuclear complexes are simultaneously present in the solution, the $\bar{n}$ value will vary not only with the $[Cl^-]$, but also with the $[Pd^{2+}]$ values.

The total chloride concentration (C_{Cl}) is obviously

$$C_{Cl} = [Cl^-] + \bar{n}\, C_{Pd}. \qquad (3)$$

Thus the function $C_{Cl} = f(C_{Pd})$ for constant temperature and ionic strength (hence $\beta = const$) will be linear for solutions with the same $\bar{n}$ only in case that the Pd–Cl complexes occurring in the solution are mononuclear solely or binuclear solely and at the same time $[Pd^{2+}]$ can be neglected against C_{Pd}; really, only if these conditions are met, an increase of $[Pd^{2+}]$, induced by an increase of C_{Pd}, does not bring about a change of $[Cl^-]$. If polynuclear Pd—Cl complexes are present in the solution besides the mononuclear ones, a growth of $[Pd^{2+}]$ with a constant $\bar{n}$ results in a decrease of $[Cl^-]$, the function $C_{Cl} = f(C_{Pd})$ thus will not be linear — it will bend towards lower C_{Cl} values with increasing C_{Pd} and with a decreasing C_{Pd} it will approach asymptotically a straight line with the slope $\bar{n}$, with the intercept of the $[Cl^-]$ concentration pertaining to the mononuclear complexes.

The plotting of the $C_{Cl} = f(C_{Pd})$ straight line is a necessary intermediate step to the construction of the generating function by means of the Bjerrum's spectrophotometric method. Thus it is not the finding that the generating functions con-

structed at different wavelengths are equal, but the fact itself that several authors[1,4,9] were able to construct the generating function of the Pd—Cl complexes by means of the Bjerrum's method and the generating functions obtained were identical (except for the region of $3 < \bar{n} < 4$), that gives evidence that in aqueous solutions are formed either mononuclear Pd–Cl complexes or binuclear ones and $PdCl_4^{2-}$ whose presence at high $[Cl^-]$ values has been unambiguously proved[4,12]. A simultaneous existence of the binuclear complexes and the $PdCl_4^{2-}$ complex would require in the region of $3 \ll \bar{n} \ll 4$ the conversion of the mononuclear $PdCl_4^{2-}$ to the binuclear complexes on decreasing the $[Cl^-]$ value, or on increasing the C_{Pd} value at a constant $[Cl^-]$. Since it is in this region of $\bar{n}$ values that the highest deviations occur between the generating functions constructed by different authors, we tested this region for the linearity of the $C_{Cl} = f(C_{Pd})$ function.

Fig. 2 shows the above dependences of the molar absorptivities on the total chloride concentration for various C_{Pd} values, and Fig. 3 presents the $C_{Cl} = f(C_{Pd})$ dependences derived from Fig. 2. As can be seen, in the critical region the $PdCl_4^{2-}$ convert to mononuclear complexes rather than to binuclear ones; the content of the bi-
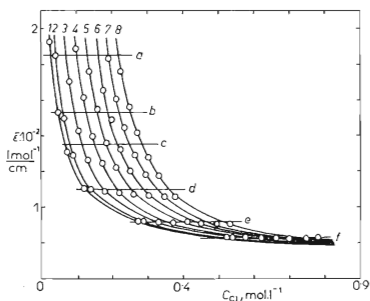

Fig. 2

Dependence of the Absorptivity of Aqueous Solution of $PdCl_2$ and HCl on the Total Chloride Concentration (C_{Cl}) at $\lambda = 435$ nm and $t = 25°C$

Palladium concentration (mol l⁻¹): *1* 0·006, *2* 0·01, *3* 0·02, *4* 0·03, *5* 0·04, *6* 0·05, *7* 0·06, *8* 0·07; *a—f* some ε values for which the dependences $C_{Cl} = f(C_{Pd})$ were constructed.

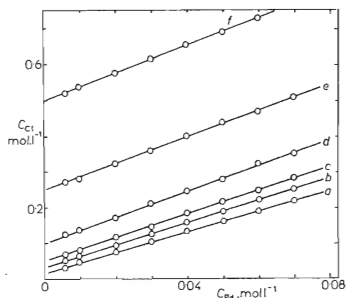Fig. 3

Functions $C_{Cl} = f(C_{Pd})$ for Aqueous Solutions of $PdCl_2$ and HCl Obtained at $\lambda = = 435$ nm, for Various Values of the Molar Absorptivity ε (*a* to *f*)

nuclear complexes is negligible, as the dependence $C_{Cl} = f(C_{Pd})$ does not depart appreciably from a straight line plot.

The dependence of the generating function of the Pd–Cl complexes on their nature appears also in the dependence of the palladium electrode potential (E_{Pd}) on the palladium concentration (C_{Pd}), The E_{Pd} value is given by the Nernst equation as $E_{Pd} = E^0_{Pd^{2+}} + (RT/2F) \ln a_{Pd^{2+}}$. For constant $\bar{n}$, $[Cl^-]$, and β_n and for the case that only mononuclear Pd–Cl complexes occur in the solution, $a_{Pd^{2+}}/C_{Pd} = k$ is a constant according to the generating function, and thus we have

$$E_{Pd} = E^0_{Pd^{2+}} + (RT/2F) \ln k + (RT/2F) \ln C_{Pd} . \qquad (4)$$

If under otherwise identical conditions the Pd–Cl complexes present in the solution are exclusively binuclear, it can be derived from their generating function that in concentration conditions where $[Pd^{2+}]$ can be neglected against C_{Pd}, $a_{Pd^{2+}} = k' C_{Pd}^{0.5}$, and from this

$$E_{Pd} = E^0_{Pd^{2+}} + (RT/2F) \ln k' + (RT/4F) \ln C_{Pd} , \qquad (5)$$

where k' is constant for constant $\bar{n}$, $[Cl^-]$, and ionic strength.

Thus E_{Pd} will be a linear function of $\ln C_{Pd}$ for both types of complexes, but in the case of the binuclear complexes the slope of the straight line will be half of that for the mononuclear complexes.

If both mono- and binuclear complexes are present simultaneously in the solution, then — for constant temperature, ionic strength and the $[Cl^-]$ value — an increase of C_{Pd} must result in a change of the $\bar{n}$ value and thereby also of the k or k' value; thus E_{Pd} will not be a linear function of $\ln C_{Pd}$. With increasing C_{Pd} value, when the concentration of the binuclear complexes should grow too, the slope of the function $E_{Pd} = f(\ln C_{Pd})$ will vary within the region of $RT/2F$ to $RT/4F$.

It can be seen that in order to prove the nature of the Pd–Cl complexes it is not necessary to calculate the concentration of $PdCl_4^{2-}$ and to examine the dependence $E_{Pd} = f(\ln [PdCl_4^{2-}])$, as has been done by Levanda and coworkers[2]; it is sufficient merely to examine the dependence $E_{Pd} = f(\ln C_{Pd})$, in conditions applied by Levanda and coworkers[2]. As mentioned above, these authors investigated the dependence $E_{Pd} = f(\ln [PdCl_4^{2-}])$ at too high $PdCl_4^{2-}$ concentrations, and so the possible content of the binuclear complexes in the solutions was too low. We tested therefore the linearity of the dependence $E = f(\ln C_{Pd})$ at $[Cl^-] = 0.055$ mol l^{-1} (Fig. 4), a concentration that, on the one hand, can be maintained constant with sufficient accuracy and at which, on the other hand, only 50% of the palladium occurs in the form of the $PdCl_4^{2-}$ complex, according to the calculations involving the known value of the stability constants of the mononuclear Pd–Cl complexes[4,10]. The obtained

straight line (Fig. 4) with the slope of $RT/2F$ gives evidence that under the conditions applied in the aqueous solutions, the binuclear complexes are absent.

Comparing the concentration regions in which the various methods prove the absence of the binuclear Pd–Cl complexes from the aqueous solutions (Table I), we find the methods employed to complement one another suitably and to cover the whole palladium concentration region used for the study of the mechanism of olefin oxidation by palladium dichloride ($1 . 10^{-5}$ to 0.2M-PdCl$_2$, $1 . 10^{-5}$ to 1M-Cl$^-$).

TABLE I

Concentration Regions in Which the Methods Employed Prove the Absence of Binuclear and Polynuclear Pd–Cl Complexes from Aqueous Solution of PdCl$_2$ and HCl

Method[a]	C_{Pd} mol l^{-1}	[Cl$^-$] mol l^{-1}	$\bar{n}$
1	0.05 to 0.3	$1 . 10^{-3}$ to 0.03	2 to 3.5
2	$1 . 10^{-5}$ to 0.07	$1 . 10^{-8}$ to 0.5	0 to 3.8
3	$1 . 10^{-3}$ to 0.2	0.05 to 1.1	3.5 to 3.97

[a] 1 Measurements of the mean molecular weight, 2 construction of the function $C_{Cl} = f(C_{Pd})$ for [Cl$^-$] = const, t = const, μ = const; 3 construction of the function $E_{Pd} = f(\ln C_{Pd})$ for [Cl$^-$] = = const, t = const, μ = const.
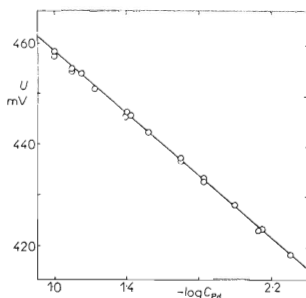

FIG. 4

Dependence of the Voltage of the Cell Pd | PdCl$_2$, HCl, HClO$_4$, NaClO$_4$ | S.C.E. on log C_{Pd} at 25°C

[Cl$^-$] = 0.055 mol l^{-1}, [H$_3$O$^+$] = 0.5 mol l^{-1}, $\mu = 1$, $C_{Pd} = 0.005$ to 0.1 mol l^{-1}.

In conclusion it can be stated that the three methods applied to the identification of the palladium complexes types, although mutually independent, all indicate the presence of only mononuclear types of chloropalladium(II) complexes in aqueous solutions.

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Translated by P. Adámek.