CORRECTION OF THE PARAMETERS OF THE Pd(II) COMPLEXES WITH 2-(2-THIAZOLYLAZO)-4-METHOXYPHENOL (TAMP). COMMENTS ON THE USE OF THE GENERAL MINIMIZATION PROGRAM SPEKTFOT FOR CALCULATIONS FROM SPECTROPHOTOMETRIC CURVES*

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Using more suitable estimates of the constants and selecting another minimization strategy, the real parameters for PdL$^+$, PdL$_2$ and PdL(OH) complexes with 2-(2-thiazolylazo)-4-methoxy-phenol have been determined; they differ substantially from some data given in our previous work. Simultaneously, some possible shortcomings of the use of the SPEKTFOT minimization program are pointed out.

In a previous paper[1], intensely coloured PdL$^+$, PdL(OH) and PdL$_2$ complexes were found and described in palladium(II) solutions containing 30% (v/v) dimethyl-formamide, perchlorate and excess 2-(2-thiazolylazo)-4-methoxyphenol (TAMP, HL), formed in dependence on pH. The complexation equilibria in the solution were studied using graphical and graphical logarithmic analysis of the absorbance dependences[1]; the stability constants of the complexes were computed on a TESLA 200 computer by means of a minimization procedure with the SPEKTFOT program[2]. For estimation of the initial data for the SPEKTFOT program, the incorrect conditional stability constant, $\log \beta'_{110} = [PdL]/[Pd]'[L]' = 6·60$, obtained in a 1M--HClO$_4$ medium from the continuous variation curves at 600 nm was employed in ref.[1]; the actual stability constant is almost nine orders of magnitude higher ($\log \beta_{110} = 15·35$). This fact unfavourably affected the initial data for the stability constants of the remaining complexes, PdL(OH) and PdL$_2$, which were calculated from the former value and the experimental values of equilibrium constants $\log K$ $(PdL + H_2O \rightleftharpoons PdL(OH) + H^+)$ and $\log K(PdL + HL \rightleftharpoons PdL_2 + H^+)$ (*cf.* Eqs (*1*), (*2*), (*3*) in Table I in the present work and Tables VII and VIII in ref.[1]). A considerable difference between the estimated value of a constant and the correct value is mostly quite unimportant. The SPEKTFOT program, similar to the LETAGROP SPEFO program[3,4], permits computation of complex constants even

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TABLE I

The Final Calculation of the Parameters for Complexes of Pd(II) with 2-(2-Thiazolylazo)-4-methoxyphenol (TAMP) Using the SPEKTFOT Program

The values of the differential absorbance, $\Delta A = A - A_L$, were employed for the calculation; constant $\beta_{11(OH)}$ (Pd + L + OH$^-$ ⇌ PdL(OH)); log $\beta_{11(OH)}$ = 23·8 was calculated from the relationship, log $\beta_{11(OH)}$ = log β_{110} + log K_{nk} − log K_{H_2O}, for comparison with the other complexes. The values of constant K_{nk}(log K_{nk}) − 5·64 (graphical analysis, ref.[1]); −5·80 (calculated back from the minimized value of constant log β_{11-1}, ref.[1]); −5·86 (calculated back from the minimized value of constant log β_{11-1} obtained in this work); see equilibrium (A) in the rext. The values of constant k_2(log k_2): −2·76 (graphical analysis, ref.[1]); −3·86 (calculated back from the minimized value of log β_{120}, ref.[1]); −3·61 (calculated back from the minimized value of log β_{120} obtained in this work); see equilibrium (B) in the text.
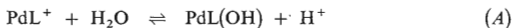
Complex constant	Initial data from graphical analysis (ref.[1])		Calculated parameters			
	log K	ε, 600 nm	log $(K \pm 3s_K)^d$	log $(K \pm 3s_K)^e$	$\varepsilon \pm 3s\varepsilon$, 600 nm^d	$\varepsilon \pm 3s_2$, 600 nm^e
β_{110}(Pd + L ⇌ PdL)	15·35^a	2 535	15·41 ± 0·02	15·37 ± 0·11	2 802 ± 57	2 630 ± 160
β_{11-1}(Pd + L + H$_2$O ⇌ PdL(OH) + H$^+$)	9·71^b	6 500	9·39 ± 0·03	9·51 ± 0·02	7 880 ± 125	8 224 ± 1 367
β_{120}(Pd + 2 L ⇌ PdL$_2$)	20·98^c	8 250	20·19 ± 0·03	20·52 ± 0·02	8 530 ± 12	8 690 ± 3 287

^{a} log β_{110} = log β'_{110} + log $\alpha_{L(O)}$; $\alpha = [H]^2/K_{a1} . K_{a2} + [H]/K_{a1} + [H]/K_{a2} + 1$; p$K_{a1}$ = 0·1; pK_{a2} = 8·39 (I); ^{b} log β_{11-1} = log β_{110} + log K_{nk} (2); K_{nk}(PdL + H$_2$O ⇌ PdL(OH) + H$^+$) (ref.[1]); ^{c} log β_{120} = log k_2 + log β_{110} + pK_{a2} (3); k_2(PdL + HL ⇌ PdL$_2$ + H$^+$); K_{a2}/K_{a1} = 10$^{8·75}$; K_{nk}(PdL + L + H$_2$O ⇌ PdL(OH) + H$^+$) (4) (ref.[1]); ^{d} c_L = 8·0 . 10^{-4} M. ^{e} c_L = 1·2 . 10^{-3} M.

from quite erroneous estimates (with a difference of up to ± 10 orders of magnitude). However, in the given case even multiple iteration did not lead to the correct values of the complex constants, β_{11-1} (Pd + L + H$_2$O $\rightleftharpoons$ PdL(OH) + H$^+$) and β_{120} (Pd + 2 L $\rightleftharpoons$ PdL$_2$). Nonetheless, very good agreement was obtained between the experimental absorbances curve and that calculated from the minimized incorrect parameter values (*cf.* Table IX in ref.[1]). The new final calculation given in this paper using the SPEKTFOT program, which is based on constant estimates considering the initial value of the true stability constant β_{110} (Eq. (*1*) in Table I), leads to the values of the constants and parameters given in Table I after seven iterations attaining the lowest value of U (*5*)

$$ U = \sum_{i=1}^{Np} \left(A_{calc} - A_{exp} \right)^2 . \tag{5} $$

The optimum strategy of simultaneous minimization was initially based on a six-cycle gradual variation of the parameters for complexes PdL(OH) and PdL$_2$ at constant values of log β_{110} and ε(PdL$^+$). On attainment of the lowest value, $U = 5\cdot1484 . 10^{-4}$, the values of log β_{110} and ε(PdL) were varied in a further cycle, attaining a further decrease in U to a value of $U = 3\cdot568 . 10^{-4}$. Thus a very good match of the calculated and measured absorbance pH-curves within thousandths of an absorbance unit was achieved, which is even better than the result obtained in the previous communication (Table IX)[1]. The very good agreement of the calculated and experimental absorbance pH-curves obtained in the previous paper[1] in spite of the completely incorrect minimized values of constants $\beta_{110}, \beta_{11-1}$ and β_{120} indicates unambiguously that a change in the values of β_{110} and of the derived constants virtually does not affect the transitions in the minimization region, where equilibria (*A*) and (*B*) overlap:

$$ \text{PdL}^+ + \text{H}_2\text{O} \;\rightleftharpoons\; \text{PdL(OH)} + \text{H}^+ \tag{A} $$

$$ \text{PdL}^+ + \text{HL} \;\rightleftharpoons\; \text{PdL}_2 + \text{H}^+ \tag{B} $$

Complex PdL$^+$ is formed practically quantitatively even in the acidic region at pH $\leqq 0$ and the formation region for this complex (*C*)

$$ \text{Pd}^{2+} + \text{H}_2\text{L}^+ \;\rightleftharpoons\; \text{PdL}^+ + 2\,\text{H}^+ \tag{C} $$

is sufficiently separated from the regions of transitions (*A*) and (*B*). It follows clearly from Fig. 1 that various values of constant β_{110} exert no influence on equilibria (*A*) and (*B*) within the pH region of the experimental points employed for minimization. For the selected initial value of β_{110}(PdL$^+$), constants β_{11-1}[PdL(OH)] and β_{120} . . [PdL$_2$] will vary so that the minimization criterion (*5*), $U = $ min, is satisfied; however, the constants for equilibria (*A*) and (*B*) will not change.

It is *e.g.* valid for the constants of coupled equilibria, β_{110} and β_{120}, that

$$\beta_{120}/\beta_{110} = K_2 \,, \qquad (6)$$

where $K_2 = [\text{PdL}_2]/[\text{Pd}^{2+}][\text{L}]$. Hence relationship (7),

$$\log \beta_{120} = \log K_2 + \log \beta_{110} \qquad (7)$$

is also valid. Therefore, on a change in the estimate of $\log \beta_{110}$, or on substituting an incorrect $\log \beta_{110}$ value, the calculated $\log \beta_{120}$ value will also change, but the difference, $\log \beta_{120} - \log \beta_{110}$, will still equal $\log K_2$, whose most probable value will correspond to the minimum of function U and will be constant for a series of pairs of $\log \beta_{110}$ and $\log \beta_{120}$. Dependence (7) is the equation of a straight line with a slope of unity and with an intercept on the $\log \beta_{120}$ axis equal to $\log K_2$. A quite analogous situation is encountered during minimization in the PdL and PdL(OH) system. The values of the equilibrium constants for (A) and (B), calculated for various sets of minimized constants for PdL, PdL(OH) and PdL$_2$, are given in Table I.

Fig. 2 depicts the values of the sum of the squares of deviations U for minimization of the values of the $\log \beta_{110}$ and $\log \beta_{120}$ pair.
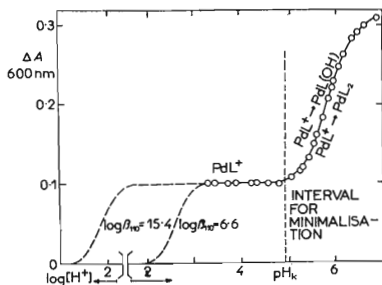

Fig. 1

Schematic Dependence of the Differential Absorbance on the Solution Acidity in the Pd(II)-2--(2-thiazolylazo)-4-methoxyphenol-30% (v/v) Dimethylformamide System ($c_M = 4 \cdot 10^{-5}$M, $c_L = 8 \cdot 0 \cdot 10^{-4}$M)

Various values of β_{110}(Pd + L $\rightleftarrows$ PdL) used as the initial values for the minimization of the values of constants β_{11-1}(PdL(OH) and β_{120}(PdL$_2$) exert practically no effect on the shape of the experimental branch of transitions PdL $\rightarrow$ PdL(OH) (A) and PdL $\rightarrow$ PdL$_2$ (B).

For any value of the constant for complex $PdL^+(\beta_{110})$ a well-developed minimum is obtained, but the value of constant β_{120} for complex PdL_2 is always different. Dependence $U(\log \beta_{110}, \log \beta_{120})$ represents a parabolic plane with a minimum "trough", almost parallel with the base plane, $\log \beta_{110} \times \log \beta_{120}$. The course of the minimization indicates a slight bend of this "trough", so that it is suitable to calculate the constants for PdL_2 and $PdL(OH)$ using an initial value of the constant for $PdL^+(\beta_{110})$ that is very close to the true value.

The above considerations concerning the independence of the values of the equilibrium constants of (A) and (B) of the absolute values of the minimized set of constants β_{110}, β_{120} and β_{11-1}, however, do not hold for the molar absorption coefficient of complex PdL^+ that will in any case affect the shape of the calculated absorbance curve, $A = f(pH)$.

The apparent failure of the SPEKTFOT program in the previous communication[1] is caused by the fact that complex PdL^+ is formed quantitatively before the region of minimized experimental data (Fig. 1) and that its stability constant is very different from the constants of the equilibria that actually take place. When using a minimization program, it is necessary that the minimized data should be located in a region within which the shape of the absorbance curve is affected by the value of the constants to be determined by means of the minimization procedure. From this point of view it is more suitable to employ the constants in the program for real equilibria taking place in the solution within the experimental region and not the stability constants of the individual complexes, or to use the above minimization strategy. If the complex stability constants are used as the initial data, there is a real
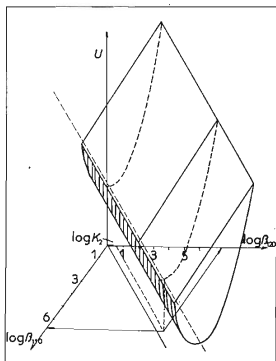

Fig. 2

Graphical Representation of Function $U = \sum_{i=1}^{N_p} (A_{calc} - A_{exp})$ in Minimization in the $PdL(\beta_{110})$–$PdL_2(\beta_{120})$ System

The line connecting the points in the minimum of the "trough" is parallel with the straight line passing through the origin at an angle of $45°$ in plane $\log \beta_{110} \cdot \log \beta_{120}$.

danger of attempting to minimize or calculate the constant for a complex that has already been formed "quantitatively". Moreover, with polybasic reagents it might not be clear which of the protons is dissociated during the complex formation; possibly qualitatively different protons are dissociated in the acid–base and the complexation equilibria. Consequently, the recalculation of the experimental equilibrium constants to the true complex stability constants is rendered quite uncertain.

It is also suitable to subject the results of the minimization computation to a reasonable chemical consideration and apply the principles of scientific logic in their evaluation. When using simpler minimization programs it is always desirable that the initial parameter values should be close to the true values.

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