Method for Evaluation of Consecutive Formation Constants of Ternary Metal Complexes in Solution from Quasi-reversible and Irreversible Polarographic Data: Study of Pd (II) Complexes of L-2-Amino-3- (4-Hydroxy Phenyl) - Propanoic Acid, 2,2' Bipyrdyl and 1,10 Phenanthroline

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Polarographic method has been developed for the study of ternary metal complexes which are reduced quasi-reversibly and irreversibly by suitably modifying the well known Schaap and McMasters method for the reversible systems. This method has been applied to the determintion of successive formation constants of mixed complexes of palladium (II) with L-tyrosine, 2,2' - bipyridyl and 1,10 - phenanthroline. The binary step-wise formation constants have also been determined by modified DeFord and Hume's method. The formal rate constant and transfer coefficient are determined by Koutecky's method as extended by Meites and Isreal. The free energy, enthalpy and entropy changes of activation and those changes accompanying the complexation reaction have been calculated and discussed. The formation of ternary complexes have been favoured over binary complexes as has been shown on statistical consideration and disproportionation reaction.

Mixed ligand complex formation studies are increasing during the past thirty years. Polarographic technique has been extensively used in case of reversibly electro-reduced complex ions. Methods for the evaluation of stability constants are based on the changes in the reduction waves of cations in presence of the ligands. Among the methods applicable to ternary metal complexes are Souchay and Fauchare [1] and Schaap and McMasters [2]. The former method is based on the shift in the reduction potential of metal ion on complex formation and the method is applicable where single complex specie exists over the entire range of ligand concentration or atleast only one specie predominates in a particular interval of ligand concentration. The latter method is also based on similar principles, but takes into account the variation of the current when the ligand concentrtion is altered. It partly solves the problems of the Souchay and Fauchere method and permits simultaneous calculations of the stability constants of the consecutive complexes existing in the system.

The methods applicable to irreversible processes are limited owing to the need for an ***indicator ion*** fulfilling the stringent requirements. Some important treatments

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of this type are those of Ringboin and Erikson [3], Schwarzenbach [4] and Matsuda & Ayabe [5]. These methods are applicable to both reversible and irreversible processes and are based on the variation in diffusion coefficient of the electroreducible species when two ligand concentrations are altered. The method of Kacena and Matousek [6] is applicable when a single specie exists in a solution; this is also subject to high errors. The method due to Crow [7] starts from the Stokes Einstein equation but requires a series of approximations that reduce its applicability. More specialized methods have been developed by Tur'yan and coworkers [8] and are applicable to systems influenced by the kinetics of complex formation. The first attempt was made by Eyring [9], Neiman [10] Koutecky [11] Delahay [12], Tamamushi and Tanaka [13] Tachi [14], Randles [15], Stromberg [16], Satyanarayana [17] and Meites & Isreal [18]. The method of Schaap and McMasters [2] has been very widely used for the reversible systems. In the present study, the method is used for the irreversible systems for the first time - not in its original form but in the light of modification proposed by Heath and Hefter [19] for differential pulse polarography. This is a logical extention of the method due to Valcarcel, Gomez Nieto and Luque-de Castro [20] for the binary irreversible systems.

THEORETICAL

The situation considered is essentially the same as that discussed by Schaap and McMasters [2] i.e. the different possible forms of the metal species in solution are in equilibirum so that it is impossible to establish which of the species actually reacts at the electrode in electron-transfer process. This situation can be represented as:

$$M + iX + jY \rightleftharpoons MX_1Y_1 \rightleftharpoons MX_1Y_2 \rightleftharpoons MX_2Y_1 \rightleftharpoons MX_1Y_1 \quad ..(1)$$
$$\downarrow$$
$$M(Hg)$$

For simplicity and generality, charges and activity coefficients are not included in the equations.

In the irreversible case, some equilibrium reactions at the electrode are too slow for overall process to be completely reversible. To take this into consideration two asumptions are made:

i) The equation for the half wave potential is modified to include the term that accounts for the irreversibility of the process;

ii) The half wave potential, $E_{1/2}$, is replaced by the peak potential, E_p, by means of the equation of Parry and Osteryoung [21].

It is only a pragmatic assersion and justified as the results obtained are reasonable. Then, the following experssions are obtained [20]:

$$E_{pM} = E_o - 1/2\ \Delta E_{1/2} - \frac{RT}{(n\alpha)_o F} \ln \frac{I_M}{I_A} + IRE_1 \quad \ldots (2)$$

$$E_{pC} = E_o - 1/2\ \Delta E_{1/2} - \frac{RT}{(n\alpha)_{ij} F} \ln \frac{I_M X_i Y_j}{I_A} \sum_{\substack{i=0 \\ j=0}}^{N} \beta MX_iY_j [X]^i [Y]^j + IRE_2 \quad .. (3)$$

where E_{pM} and E_{pC} are the peak potentials for the free and complexed metal ion

respectively. IRE terms are defined [7,22] as

$$IRE_1 = \frac{RT}{(n\alpha)_o F} \ln \frac{0.886\, k_o\, t^{1/2}}{D_o^{1/2}} \quad \ldots. (4)$$

$$IRE_2 = \frac{RT}{(n\alpha)_{ij} F} \ln \frac{0.886\, k_{ij}\, t^{1/2}}{D_{ij}^{1/2}} \quad \ldots. (5)$$

The terms $(n\alpha)_o$ and $(n\alpha)_{ij}$ are the number of electrons involved in the reaction at the electrode multiplied by the transfer coefficient for the metal reduction in the absence and presence of the ligands respectively; k_o and k_{ij} are the rate constants for the electrode reactions. The other terms have their usual significance. The change in the peak potential of the cation when the ligand concentration is altered, is given in ref. [20]

$$\Delta E_p = E_{pM} - E_{pC}$$

$$\Delta E_p = \frac{RT}{F} \ln \frac{I_M X_i Y_j^{[1/(n\alpha)ij]}}{I_M^{[1/(n\alpha)o]}}$$

$$+ \frac{RT}{F} \ln \frac{I_A[(n\alpha)_{ij} - (n\alpha)_o]}{(n\alpha)_{ij}\,(n\alpha)_o}$$

$$+ \frac{RT}{(n\alpha)_{ij}F} \ln \sum_{i=0,\, j=0}^{N} \beta\, MX_iY_j\, [X]^i\, [Y]^j + IRE_1 - IRE_2$$

In pulse polarography, when the applied pulse is sufficiently small, the peak intensity is given [23] as

$$I_p = \left(\frac{(n\alpha)^2F^2}{4RT}\right) AC\, \Delta E \left(\frac{D}{\pi t_M}\right)^{1/2} = KIC \quad \ldots(6)$$

where ΔE is the pulse amplitude, t_M is the integration time of the apparatus, I is the diffusion current constant and K is the conversion constant, i.e. the ratio between the current constants in d.c. and d.p. polarography.

$$K = \frac{k'(n\alpha)\, F\, \Delta E}{4.609\, RT} \quad \ldots (7)$$

where k' is a constant that takes into account the ratio between the characteristics of the capillary in the d.c. and d.p. techniques.

From the above, one can reduce

$$\Delta E_p = E_{pM} - E_{pC}$$

$$= \frac{RT}{F} \ln \frac{I_{pC}^{[1/(n\alpha)i,j]}}{I_{pM}^{[1/(n\alpha)o]}}$$

$$+ \frac{RT}{(n\alpha)_{ij}F} \ln \sum_{i=0,\, j=0}^{N} \beta\, MX_iY_j\, [X]^i\, [Y]^j + \delta_{(i,j)} \quad ..(8)$$

where $\delta_{(i,j)}$ is given by

$$\frac{RT}{F} \ln (KCI_A\, 0.886\, t^{1/2})^{[(n\alpha)ij\, -\, (n\alpha)o/\, (n\alpha)ij\, (n\alpha)o]}$$

$$+ \frac{RT}{F} \ln \frac{[D_{ij}^{1/2}]^{[1/(n\alpha)ij]}}{[D_o^{1/2}]^{[1/(n\alpha)o]}}$$

$$+ \frac{RT}{F} \ln \frac{k_o^{[1/(n\alpha)o]}}{k_{ij}^{[1/(n\alpha)ij]}} \quad \ldots (9)$$

For the systems in which an increase in the ligand concentration does not cause an appreciable change in $n\alpha$, D and k paremeters, regardless of the reversibility of the process, the $\delta_{(i,j)}$ term and experimental errors are of similar order. If this term is not considered, then equation 8 on manipulation leads to

$$F_{10}[X,Y] = \frac{I_{pM}^{[(n\alpha)_{i,j}/(n\alpha)_0]}}{I_{pC}} \quad \exp \frac{\Delta E_p[(n\alpha)_{i,j}]\, F}{RT} \quad \ldots(10)$$

$$= \sum_{i=0}^{N} \sum_{j=0} \beta\, MX_iY_j\, [X]^i\, [Y]^j \quad \ldots(11)$$

For metals forming a maximum of 1:3 complex, this can be expanded to take the form

$$= \beta_0 + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3 + \beta_{10}[X] + \beta_{11}[X][Y] + \beta_{12}[X][Y]^2 + \beta_{20}[X]^2 + \beta_{21}[X]^2[Y] + \beta_{30}[X]^3 \quad \ldots. \quad (12)$$

This can be written in the form

$$F_{10}[X.Y] = A + B[X] + C[X]^2 + D[X]^3 \quad \ldots (13)$$

This equation is similar to Schaap and McMaster equation, but instead of the theoretical number of electrons involved (n), the product of the number of electrons by the transfer coefficient (nα) is considered. When $(n\alpha)_{ij} = (n\alpha)_0 = n$, the equation reduces to Schaap and McMaster equation for differential pulse polarography [19].

Data Management

Polarographic measurements are made by keeping the concentration of one ligand constant while that of other is varied. The $F_{ij}(X,Y)$ functions can readily be analysed by a Laden type approach. The value of the constant 'A' for a given concentration of 'Y' can be calculated if the consecutive formation constants for metal - Y binary system are known. This value of 'A' may be compared with the value obtained by plotting F_{10} *vs* [X] at the same value of [Y]. The plot represents a cubic equation whose intercept at [X] = O is 'A' and limiting slope at [X] —> O is 'B'. Subtracting the value of 'A' from F_{10} and dividing by [X] gives F_{20}. This can be calculated at each value of [X].

$$F_{20} = \frac{F_{10} - A}{[X]} = B + C[X] + D[X]^2 \quad \ldots (14)$$

A plot of F_{20} function *vs* [X] represents a quadratic equation whose intercept is 'B' and limiting slope is 'C'. Continuing this procedure, F_{30} function is to be seen linear with slope 'D'. For a system forming a maximum of 1:2 complex, F_{30} *vs* [X] plot is horizontal to the [X] axis (D=0).

Equations 13 and 14 show that 'D' is equal to β_{30}, the overall complexity constant of the binary system containing the metal ion with X alone. The value of 'C' is equal to $\beta_{20} + \beta_{21}[Y]$ and allows the value of β_{21} to be calculated directly if β_{20} is known for the simple system. The expression for B contains two unknown constants, β_{11} and β_{12} (in addition to β_{10}, which can be known from the simple system), thus B must be measured at a minimum of two different values of [Y] to evaluate the constants. The concentrations should be chosen in a region where appreciable amounts of corresponding complexes are present in solution. At concentration far from these regions, the F_{ij} values may vary widely and become meaningless.

Literature survey reveals no method on record for the study of mixed ligand complexes which are reduced quasi reversibly or irreversibly at d.m.e. The

method developed above is therefore, of interest. This is then applied for the evaluation of successive formation constants of irreversibly reduced Pd(II) complexes with L-tyrosine, 2,2' bipyridyl and 1,10 phenanthroline.

EXPERIMENTAL

Palladium chloride (Johnson Mathey) and L-tyrosine were supplied by B.D.H. chemicals Ltd., Poole, England. 2, 2'-bipyridyl and 1,10-phenanthroline were supplied by E. Merck (India) Pvt. Ltd., Bombay. All other chemicals used are of AnalaR grade. Polarograms were recorded on a manual polarograph using a H cell and S.C.E. reference electrode. KNO_3 was used as supporting electrolyte to maintain ionic strength constant (0.1M) and 0.02% triton X-100 as maximum suppressor. Purified nitrogen was used for deaerating the solution.

RESULTS AND DISCUSSIONS

It is observed that Pd(II) binary and ternary complexes with L-tyrosine, 2,2' bipyridyl and 1,10- phenanthroline yield a single, well defined cathodic wave at pH = 9.0 and 8.0 respectively and hence all subsequent studies were made at these pH values. The plot of i_d *vs* $h^{1/2}_{eff}$ was found to be linear indicating the diffusion controlled nature of the electrode process. The number of electrons 'n' involved in electrode process was found by millicoulometric method [24] as 2.

The plot of log $[i/(i_d-i)]$ *vs* - E_{dme} [25] was found to be linear but slope value was found to be much larger than the theoretical value expected for reversible process. This indicates that the electrode process is irreversible both in simple and mixed ligand complexes. A perusal of polarographic data

Table 1

Formation Constants and Thermodynamic parameters of Binary Complexes

Metal ion Pd(II): Ligand Tyrosine / Bipyridyl / Phenanthroline
Log K values Calculated by the method of Valcarcel [20]
ΔG° & ΔH° in k.cal/mole; ΔS° in cal/ deg. mol

Complexes	log K			Thermodynamic Parameters		
	25°C	35°C	45°C	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°
[Pd(Tyr)]	5.18	5.04	4.91	7.10	5.86	4.04
$[Pd(Tyr)_2]^{-2}$	7.40	7.21	7.03	10.16	8.03	6.92
$[Pd(Tyr)_3]^{-4}$	11.40	11.16	10.98	15.75	10.97	15.40
$[Pd(Bipy)]^{+2}$	4.70	4.56	4.42	6.43	6.08	1.13
$[Pd(Bipy)_2]^{+2}$	6.60	6.41	6.22	8.96	8.25	2.55
$[Pd(Bipy)_3]^{+2}$	9.45	9.20	8.97	12.96	10.85	6.84
$[Pd(phen)]^{+2}$	5.15	5.00	4.86	7.04	6.29	2.44
$[Pd(phen)_2]^{+2}$	6.30	6.12	5.95	8.63	7.58	3.36
$[Pd(phen)_3]^{+2}$	9.79	9.60	9.23	13.39	12.14	4.05

and various criteria [26,27,28,29] of ascertaining the irreversibility also show that the electrode process is irrversible. The values of kinetic parameters [the transfer coefficient (αn) and formal rate constant ($k^{\circ}_{f,h}$)] for the electrode reaction of simple and mixed ligand complexes have been determined earlier [30] by Koutecky's method as extended by Isreal [11, 18] and used here.

Binary Complexes

Binary complexes were studied in Pd(II) - L-Tyrosine, Pd(II) - 2,2' - bipyridyl and Pd(II) - 1,10-phenanthroline systems separately in order to obtain data under conditions similar to those used in mixed ligand complex studies. Valcarcel and coworkers method [20] was used for determining the successive formation constants of these complexes and reported in Table 1.

The standard free energy (ΔG°) and enthalpy (ΔH°) and entropy (ΔS°) changes for complex reaction have been calculated with the help of standard equation [32] and are summarised in Table 1. The negaive values of the standard free energy changes show that the complex reaction proceeds spontaneously. The standard enthalpy and free energe changes (ΔH° & ΔG°) are negative indicating exothermic nature and spontaneity of the complex reaction. The positive value of entropy changes (ΔS°) show that the complex reaction is favoured by both enthalpy and entropy factors [33].

Table 2

Polarographic Results & F_{ij} [X] functions By Schaap & McMaster's Method

System: Pd(II) - Bipyridyl - Tyrosine
Capillary characterisatics in 0.1M KNO_3 at -0.5 volts vs SCE at h_{Hg} = 85 cm were
m = 2.74 mg/sec ; t = 2.63 sec./drop ($m^{2/3} t^{1/6}$ = 2.297 mg $^{2/3}$ sec. $^{1/2}$)
[Pd(II)] = 0.015 M; KNO_3 = 0.1 M; Triton - X = 0.002%; pH = 8.0; Temp 25°C; [Bipy] = 0.3 mM Fixed

[Tyr] mM	$-E_{1/2}$ V	i_d μA	$F_{00}[X]$ X10⁴	$F_{10}[X]$ X10⁸	$F_{20}[X]$ X10¹¹	F_{30} X10¹⁵
0.00	0.838	3.8	-	-	-	-
0.149	0.97	3.55	3.1	2.0	7.25	1.5
0.297	0.995	3.35	21.0	7.3	21.30	5.49
0.446	1.025	3.15	253.0	56.8	125.0	26.90
0.594	1 050	2.95	1900.0	319.0	535.0	89.2
0.748	1.075	2.80	14000.0	1880.0	2530.0	340.0
0.892	1.090	2.65	47400.0	5320.0	5690.0	668.0
1.04	1.100	2.55	108000.0	10300.0	9900.0	951.0

A_{grap} = 5 X 10³; B = 10 X10⁸; C = 5 X 10¹¹; D not Possible ; A_{cal} = 16.43

Table 3

Polarographic Results & F_{ij} [X] functions By Modified Method

System: Pd(II) - Bipyridyl - Tyrosine
Capillary characterisatics in 0.1M KNO_3 at -0.5 volts *vs* SCE at h_{Hg} = 85 cm were
m = 2.74 mg/sec ; t = 2.63 sec./drop ($m^{2/3} t^{1/6}$ = 2.297 $mg^{2/3} sec.^{-1/2}$)
[Pd(II)] = 0.015 M; KNO_3 = 0.1 M; Triton - X = 0.002%; pH = 8.0; Temp 25°C; [Bipy] = 0.3 mM Fixed

[Tyr] mm	$-E_p$ V	i_p μA	$F_{10}[X]$ X10²	$F_{20}[X]$ X10⁵	$F_{30}[X]$ X10⁹	F_{40} X10¹¹
0.00	1.02	4.55	-	-	-	-
0.149	1.10	4.25	1.64	9.91	1.43	2.51
0.297	1.112	4.04	3.76	12.10	1.47	2.50
0.446	1.120	3.90	6.62	14.50	1.50	2.47
0.594	1.127	3.65	10.23	16.90	1.54	2.54
0.748	1.133	3.55	14.65	19.50	1.58	2.48
0.892	1.137	3.40	19.96	22.20	1.66	2.50
1.04	1.142	3.35	26.17	25.00	1.66	2.53

A_{grap} = 16.50; B = 7.78 X10⁵; C =1.39 X 10⁹; D 2.51 X 10¹¹ A_{cal} = 16.43

Ternary Complexes

From the polarographic data, $F_{ij}[X,Y]$ functions are calculated

i) By original Schaap and McMaster's method [2] and
ii) By the method developed here for use with quasireversible and irreversible ternary complex systems and reported in Table 2 and 3.

This reveals that the $F_{00}[X,Y]$ values from Schaap and McMaster's method are higher than the $F_{10}[X,Y]$ values from modified method. The theoretical value of the number of electrons (n=2) (considered in $F_{00}[X,Y]$ is never attained by the product αn; on the other hand, the variation of $F_{00}[X,Y]$ with ligand concentration is higher than that for $F_{10}[X,Y]$ which, in practice, means that the coefficient of the [X] polynomial are smaller than those calculated when the theoretical number of electrons involved are considered. The values of $F_{ij}[X,Y]$ functions obtained by employing Schaap and McMasters method are higher.

The value of A can be calculated using the values of binary constants β_{01}, β_{02} and β_{03}. This value also is included in Tables 2 & 3. The value of A can be derived from $F_{00}[X,Y]$ function on extrapolation of the graph between $F_{00}[X,Y]$ *vs* [X]. This value from McMasters method (see Table 2) is much higher than the calculated value. Hence the values of other constants B, C and D obtained are unreliable. It is therefore, concluded that the original form of Schaap and McMaster's method is not suitable for the study of ternary complexes which

reduce quasi-reversibly and irreversibly at the d.m.e.

However the values of the constant A on extrapolation of the graph $F_{10}[X,Y]$ vs [X] to [X] —> 0 obtained employing the developed method is nearly equal to the theoretical value calculated (Table 3). Hence the values of other constants B, C and D appear to be more reliable. It may further be noted that the value of D obtained be equal to β_{03}. D value can be obtained by the modified method, but D is not obtained from Schaap and McMaster's method because of non-linear nature of the last $F_{ij}[X]$ function.

From these studies, it is amply clear that the modified method developed in the present work can be applied without any reservation for the study of the quasi-reversible and irreversible mixed ligand complexes in solution.

The polarograms are recorded for deaerated solutions containing Pd(II) with two values of fixed concentrations of 2,2' bypridyl / 1:10 phenanthroline with L-tyrosine concentrations varying. Above described method is used for evaluation of the successive formation constants of Pd(II) ternary complexes are reported in Table 4. Thermodynamic parameters are also included in the Table.

Thermodynamic Parameters of Activation

The free enrgy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) changes for activation of the electrode process have been calculated with the help of usual method and shown in Table 5. The positive values of free energy changes (ΔG^*) show that the electrode reaction is endergonic [31]. The positive values of enthalpy changes (ΔH^*) also supports the endergonic nature of the

Table 4

Formation Constants and Thermodynamic parameters of Ternary Complexes
Metal ion - Pd(II); Ligands - Tyrosine / Bipyridyl / Phenanthroline
Log K values Calculated by the modified method developed
ΔG° & ΔH° in k.cal/mole; ΔS° in cal/ deg. mol

Complexes	log K			Thermodynamic Parameters		
	25°C	35°C	45°C	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°
[Pd(bipy)(Tyr)]	9.32	9.05	8.78	12.76	11.50	4.09
$[Pd(bipy)(Tyr)_2]^{-2}$	11.83	11.50	11.16	16.21	14.55	5.39
$[Pd(bipy)_2(Tyr)$	12.66	12.30	11.95	17.34	15.41	6.28
[Pd(phen)(tyr)]	9.28	9.55	9.26	13.46	12.80	2.14
$[Pd(phen)(tyr)_2]^{-2}$	11.97	11.63	11.30	16.39	14.54	6.02
$[Pd(phen)_2(tyr)]$	12.81	12.45	12.10	17.55	15.40	6.96

Table 5

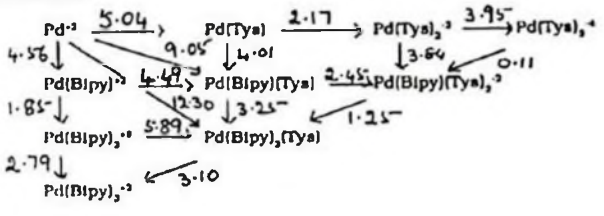
Thermodynamic Parameters for Activation of Electrode Process

Complex System	ΔG°	ΔH°	-ΔS°
Pd(II) - Tyrosine	17.78	8.17	31.20
Pd(II) - 2,2' bipyridine	16.69	10.40	20.42
Pd(II) -1,10 phenanthroline	16.88	8.80	26.23
Pd(II) - 2,2' bipyridine - tyrosine	18.55	10.90	24.86
Pd(II) -1,10 phenanthroline -Tyrosine	18.36	9.95	27.31

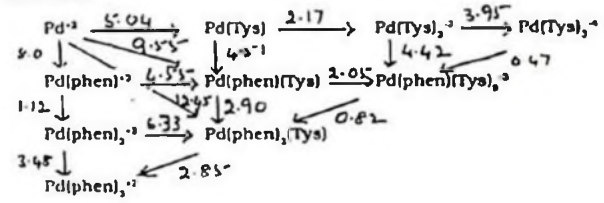
electrode process. The negative values of entropy changes (ΔS°) lends support to the irreversible nature of the electrode process. The values of the thermodynamic parameters of activation and thermodynamic quantities relating to the complexation are approximately equal in magnitude with opposite sign. This can however, be explained on the basis that the forward reaction involving the formation of the complex goes for completion and the backward reaction involving the reduction of the complex at d.m.e. does not take place which confirms the irreversible nature of the process as a whole. These observations are supported by the negative values of standard free energy changs (ΔG°) suggesting the spontaneity of the process, whereas positive values of free energy changes for activation (ΔG°) indicating the non-labile nature of the complex formed in solution.

It should be emphasized that the values of the thermodynamic function of activation are approximate. Such approximate values can nevertheless be very useful in the interpretation of the mechanism of reaction [26,34].

Scheme I



Scheme II



Guiding Parameters for Ternary Complex Formation

The result of the present study are conveniently summarized in the diagrams, where the nummerical values shown are the logarithm of the equilibrium constant for the reaction indicated.

The tendency for a tyrosine ion to add as the second ligand to [Pd(Tyr)] and to [Pd(Bipy)]$^{+2}$ and to [Pd (Phen)]$^{+2}$ can be

compared; log K values are 2.17, 4.49 and 4.55, indicating favour of mixed complex. The large difference in log K values in both the systems must be due to neutralization of charge accompanying the latter reactions and positive entropy changes are due to decreased orientation of the solvent molecules would be expected. In case of addition of uncharged bipyridyl and phenanthroline molecules, a strong charge neutralization effect would not be expected. The log K values 4.01 and 4.99 (System I) and 4.51 and 4.55 (System II) show that the mixed complexes are slightly favoured by an amount corresponding closely to that predicated by the statistical factor [35].

The constant for the disporportionation (-Δlog K) for system I is 4.48 and that of system II is 5.77 favouring the mixed complex formation and the effect of charge neutralization including the entropy change are again apparent.

The values of mixing constants (K_M) and stabilization constants (K_S) obtained from the standard equations [36,37] are found to be positive.

$K_{M11} = 2.24$; $K_{S11} = 2.06$

$K_{M12} = 2.12$; $K_{S12} = 1.82$

$K_{M21} = 1.32$; $K_{S21} = 1.02$

Which again suggest that the mixed complexes are more stable than the simple complexes.

Statistical probability of forming either of the mixed complexes is three times that of either of simple complexes [38]. Gross statistical effect is absent in the complexity constant of the saturated complex. On the basis of these considerations, the complexity constant could be predicated to be 7.55, 10.31 and 10.97 which are in close agreement to the values already calculated form experimental data.

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