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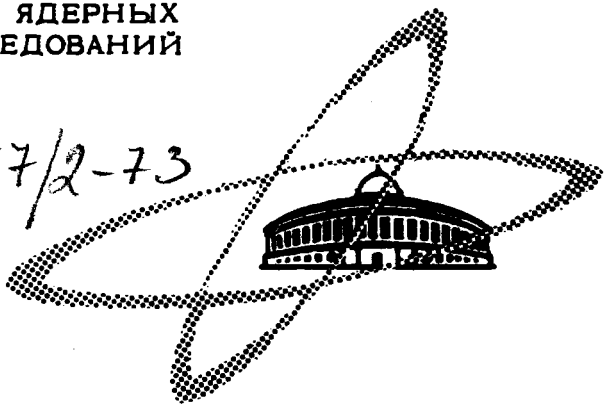
Дубна



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A CORRELATION BETWEEN THE OVERALL STABILITY CONSTANTS OF METAL COMPLEXES VI.

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Introduction

It was reported [1-5] that for 28 metal-ligand systems the experimental data allow the complexity function or the ligand number of the system under consideration to be constructed with a set of stability constants which vary in the following regular manner

$$\beta_n = A \cdot \frac{a^n}{n!} \qquad (1)$$

where β_n is the overall stability constant of the complex ML_n, n is the number of ligands $(1 \leq n \leq N)$, N is the coordination number of the complex forming metal M.
Hence, the complexity function of such a system could be expressed by

$$F = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!} (L)^n , \qquad (2)$$

where (L) is the free ligand concentration in the solution.

In the present paper it is demonstrated that the regularities expressed by Eqs. (1) and (2) are also valid for the zinc-pyrazole, copper-pyrazole and nickel-pyrazole systems. Those systems have been investigated polarographically with 0.1M potassium nitrate as a supporting electrolyte at temperature of 25 ± 0.1°C by D.R.Crow and J.V.Westwood [6].

Calculation of the Stability Constants

For all three systems the values of the experimental complexity function for each data point had been obtained by the authors of

the above paper using the conventional De Ford and Hume's method [7]. We have taken these values directly from the corresponding tables of the paper, where they are denoted as F_0 and analyzed them by the same method, which has previously applied to a number of metal-ligand systems [1-5]. That analysis consists mainly in solving Eq. (2) for two values of the experimental complexity function F_0 , e.g., F_0' and F_0'' at ligand concentrations (L') and (L'') respectively. In this way we could easily obtain the values of the constants A and a . These primary values have been usually refined by successive approximation in order to obtain better coincidence of the theoretical F -function calculated according to Eq. (2) and the experimental one. At each point the deviation has been estimated as $\Delta F = 1/F_{exp}\,(F_{calc} - F_{exp})\,100$. We have also calculated the F -function for each data point by using the conventional polynomial expression [8,9] with the set of the stability constants reported by the authors of Ref. [6]. So, for each experimental complexity function we have two theoretical F -functions calculated. To estimate which of them fits the experimental one better the S -factor, which was used throughout the present series [2-5], has been calculated

$$S = \frac{1}{K} \sum \left[\frac{(F_{exp})_i - (F_{calk})_i}{(F_{exp})_i} \right]^2 , \qquad (3)$$

where $(F_{exp})_i$ is the experimental value of F in the i^{th} data point, $(F_{calc})_i$ is the calculated value of F in the i^{th} data point, K is the number of degree of freedom of the system. For a given experimental function, this theoretical function for which the above factor has the smallest value will have the best fit.

Results and Discussion

The results obtained for the pyrazole complexes of zinc, copper and nickel are presented in Tables 1-3, respectively, where the values of the corresponding β_n , A and a constants as well as S - factors are also given. Inspection on the values of the S -factors calculated indicates that for all systems the F -functions calculated by using Eq. (2) of the present work fit the experimental

complexity function better than the F -functions calculated by using the polynomial expression /8/ with the stability constants of the corresponding complexes reported by Crow and Westwood. From the mathematical point of view the preference of the mathematical model developed in Ref. /1/ for these three systems is justified, on one hand, by the better fits obtained, and, on the other hand, by the fact that the application of that model makes possible the description of the complex formation process with a less number of parameters compared with the conventional expression /8/.

In Figs. 1-3 the distribution of the complex forming metal (central group) in the given system is presented. The solid line presents the results obtained with the set of stability constants which were calculated in the present work. The dashed line presents the results obtained with the set of the stability constants reported by Crow and Westwood.

For the zinc and nickel pyrazole systems our analysis reveals as many complex species in the solution as found by Crow and Westwood, while for the copper pyrazole system we have found three consecutive complexes, whereas Crow and Westwood had found four of them. In this way our analysis makes the presence of the fourth complex species questionable. If we consider the values of the S -factors calculated and the number of the parameters, our results can be regarded as more reliable than that of the authors of Ref. /6/.

It should be pointed out that in the earlier papers of this series /1-5/ metal-ligand systems in which the ligand was a monovalent anion (inorganic or organic) have been analyzed and this strictly corresponds to the mathematical model developed in Ref. /1/. The results for the above metal-ligand systems in the present paper clearly show that the same model can be adopted for the systems in which the ligand is a neutral molecule, and that the relations derived on the basis of that model are strictly followed here. At the same time Crow and Westwood found that the stability constants obtained by them for all these metal pyrazole systems do not vary in a regular manner with the increasing coordinated ligand number and they commented on the possible factors which could cause such a behaviour.

In Ref. /6/ the sets of stability constants for the pyrazole complexes of Mn^{2+}, Fe^{2+} and Co^{2+} are also reported but the experimental data for these systems are given only in the form of a graphical plot $\bar{n}$ vs pyrazole concentration, which does not permit a reasonably accurate analysis to be performed.

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Table I
Comparison of the experimental and calculated complexity functions for the zinc-pyrazole system

(L) M	$\bar{P}_{exp}$	Crow and Westwood		This work	
		$\bar{P}^{*}_{calc}$	$\Delta \bar{P}^{*}$ in %	$\bar{P}^{**}_{calc}$	$\Delta \bar{P}^{**}$ in %
0.1	2.67	2.23	- 16.47	2.38	- 10.86
0.2	4.40	4.25	-3.40	4.49	2.04
0.3	7.48	7.28	- 2.67	7.53	0.67
0.5	17.84	17.25	- 3.31	17.31	- 3.00
0.7	33.75	33.86	0.32	33.53	- 0.65
1.0	74.11	75.00	1.20	73.80	- 0.42
1.5	183.3	201.3	6.90	198.3	5.31
2.0	441.7	423.0	- 4.23	418.6	- 5.23

* - obtained by using the following values of β_n reported in Ref. 6: $\beta_4 = 9$; $\beta_2 = 29$; $\beta_1 = 36$.
** - obtained by using the following values of β_n: $\beta_3 = 11$; $\beta_2 = 24.7$; $\beta_1 = 37.1$, which are correlated according to Eq. (1), where $\bar{q} = 2.44$ and $a = 4.50$.
$s_{Ref.\ 6} = 8.9 \times 10^{-3}$ and $s_{This\ work} = 3.7 \times 10^{-3}$

Table 2
Comparison of the experimental and calculated complexity functions for the copper-pyrazole system

(L) M	F_{exp} x 10^6	Crow and Westwood		This work	
		F^{M}_{calc} x 10^6	ΔF^{M} in %	F^{MM}_{calc} x 10^6	ΔF^{MM} in %
0.1	0.146	0.163	11.64	0.144	- 1.37
0.2	0.644	0.639	- 0.78	0.591	- 8.23
0.4	3.11	3.16	1.61	3.24	4.18
0.6	8.83	9.13	3.40	9.34	5.77
0.8	21.63	20.55	- 4.99	20.64	- 4.58
1.0	39.54	39.90	0.91	38.65	- 2.25
1.2	58.86	70.12	19.13	64.94	10.33
1.5	134.9	143.4	6.30	123.3	- 8.60

* - obtained by using the following values of β_n reported in Ref. /6/: $\beta_1 = 0.5 \times 10^6$; $\beta_2 = 9.4 \times 10^6$; $\beta_3 = 18 \times 10^6$; $\beta_4 = 12 \times 10^6$; $\beta_5 = 5.34 \times 10^6$; $\beta_6 = 32.73 \times 10^6$, which are correlated according to Eq. (1), where $A = 3.15 \times 10^4$ and $a = 18.4$.

$S_{Ref./6/} = 19.4 \times 10^{-3}$ and $S_{This\ work} = 6.4 \times 10^{-3}$

Table 3
Comparison of the experimental and calculated complexity functions for the nickel-pyrazole system

(L) M	F_{exp}	Crow and Westwood		This work	
		F^{*}_{calc}	ΔF^{*} in %	F^{**}_{calc}	ΔF^{**} in %
0.05	4.3I	4.70	9.05	4.34	0.70
0.I	I2.4	I2.9	4.03	I2.6	I.69
0.2	82.8	82.8	0.00	78.0	- 5.80
0.3	395	385	- 2.53	365	- 7.59
0.4	I266	I288	I.74	I335	5.45
0.5	3900	3962	I.59	3989	2.28
0.6	9680	9965	2.94	I0204	5.4I
0.7	24700	22400	- 9.3I	23I40	- 6.32
0.8	45700	46063	0.79	47743	4.47
0.9	87I00	88086	I.I3	9I3I4	4.84
I.0	I72000	I5866I	- 7.75	I64I77	- 4.55
I.2	459000	446299	- 2.77	458677	- 0.07

* - obtained by using the following values of β_n reported in Ref. /6/: $\beta_1 = 80$; $\beta_2 = 100$; $\beta_3 = 2500$; $\beta_4 = 22000$; $\beta_5 = 8000$; $\beta_6 = 126000$.

** - obtained by using the following values of β_n: $\beta_1 = 41$; $\beta_2 = 373$; $\beta_3 = 2263$; $\beta_4 = 10300$; $\beta_5 = 37487$; $\beta_6 = 113712$, which are correlated according to Eq. (I), where $A = 2.25$ and $a = 18.2$.

$S_{Ref\ /6/} = 5.5 \times 10^{-3}$ and $S_{This\ work} = 2.7 \times 10^{-3}$.

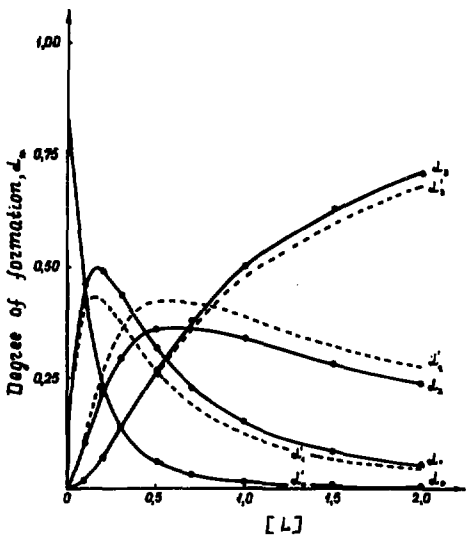

Fig. 1. Distribution of complex species in the zinc-pyrazole system.

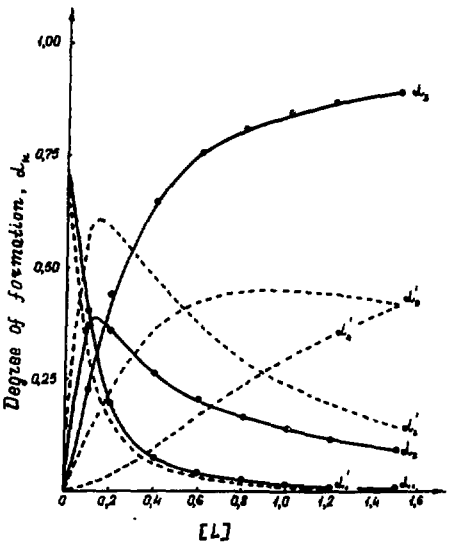

Fig. 2. Distribution of complex species in the copper-pyrazole system.

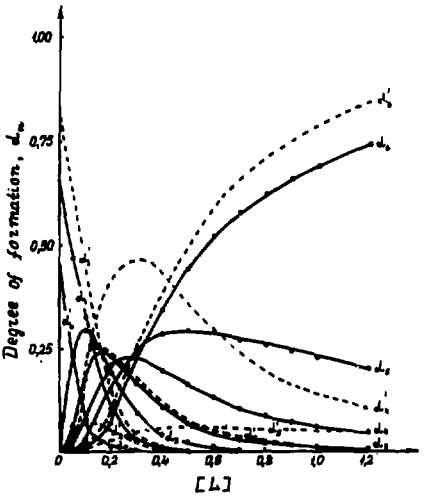

Fig. 3. Distribution of complex species in the nickel-pyrazole system.