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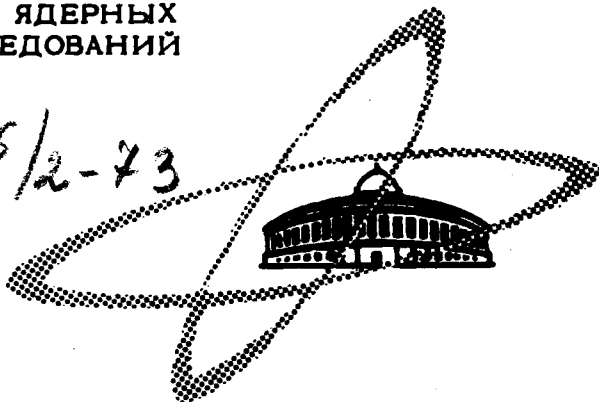
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M.H.Mihailov , V.Ts.Mihailova , V.A.Khalkin

ЛАБОРАТОРИЯ ЯДЕРНЫХ ПРОБЛЕМ

**A CORRELATION BETWEEN  
THE OVERALL STABILITY CONSTANTS  
OF METAL COMPLEXES II.  
APPLICATION TO DATA OBTAINED  
BY THE POLAROGRAPHIC METHOD  
FOR METAL-INORGANIC LIGAND SYSTEMS**

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**M.H.Mihailov\*, V.Ts.Mihailova\*, V.A.Khalkin**

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\*From the Bulgarian Academy  
of Sciences, Institute of Physics

## Introduction

In a previous paper <sup>/1/</sup> an equation relating the overall stability constants of the metal complexes for a given metal-ligand system was derived. On 9 metal halogenide systems it was demonstrated that the formation function  $\bar{n}$ , as defined by Bjerrum <sup>/2/</sup> for each system could be constructed by using a set of stability constants correlated according to Eq. (13) of Ref. <sup>/1/</sup>. This practically does not differ from the formation function  $\bar{n}$ , set up when using the values of the stability constants reported by the authors of the corresponding papers. In order to see if the same relation is applicable to experimental data from which the complexity function <sup>/3/</sup> is set up we directed our attention to data obtained by the polarographic method as one of the most extensively used for the determination of the consecutive stability constants of metal complexes.

In the present paper the validity of the relation connecting the overall stability constants is demonstrated on four metal-inorganic ligand systems: cadmium thiocyanate <sup>/4/</sup>, lead thiocyanate <sup>/5/</sup>, cadmium iodide <sup>/6/</sup> and rhodium chloride <sup>/7/</sup>. It was assumed that these systems satisfied the requirements encountered in Ref. <sup>/1/</sup>, e.g., i) the concentration of the complex forming metal  $M^{m+}$  is sufficiently low so the formation of polynuclear complexes could be neglected. ii) the metal  $M^{m+}$  does not participate in side reactions neither with the ligand  $L^-$  of the inert electrolyte nor with  $OH^-$  groups. iii) the ionic strength of the solution is sufficiently low, so the formation of ion-pairs (outer sphere complexes) between the negatively charged metal complexes and the  $C^+$ -ions coming from the dissociation of the  $CL$  and  $CL'$  electrolytes, could be neglected. iv) the activity coefficients of all species are considered constant, so

concentration terms could be used instead of activities in all equations expressing the equilibria in solution.

### Calculation of the Overall Stability Constants

According to the DeFord and Hume's method <sup>/8/</sup>

$$F = \text{antilog} \left\{ 0,435 \frac{nF}{RT} [(E_{1/2}^0)_S - (E_{1/2}^0)_C] + \log \frac{J_S}{J_C} \right\}. \quad (1)$$

Here the signs are the same as those in Ref. <sup>/8/</sup>, which became conventional. The right-hand side of Eq. (1) includes experimentally measurable quantities. On the other hand the complexity function  $F$  is defined as

$$F = 1 + \beta_1(L) + \beta_2(L)^2 + \dots + \beta_n(L)^n + \dots + \beta_N(L)^N, \quad (2)$$

where  $(L)$  is the ligand concentration,  $n$  is the number of ligands;  $0 \leq n \leq N$ ,  $N$  is the coordination number of the complex forming metal  $M$ ,  $\beta_n$  is the overall stability constant of the complex  $ML_n$ . From the experimental data the complexity function  $F$ , which is a polynomial in  $(L)$  is set up. The coefficients of the latter are the required  $\beta_n$ . Graphical extrapolation reduces the polynomial (2) to  $N$  equations from which the corresponding  $\beta_n$  are obtained.

If the mathematical model of the complex formation process advanced in Ref. <sup>/8/</sup> is valid, for the stability constants of the metal complexes formed by the reaction:  $M + nL \rightleftharpoons ML_n$ , Eq. (13) of Ref. <sup>/1/</sup> will be true

$$\beta_n = A \cdot \frac{a^n}{n!}. \quad (3)$$

Then, the complexity function could be expressed by the following equation

$$F = 1 + A \sum_{n=1}^N \frac{a^n}{n!} (L)^n, \quad (4)$$

where  $A$  and  $a$  are constants. The values of the constants  $A$  and  $a$  could be obtained by solving the following two equations:

$$(F' - 1) \sum_1^n \frac{(L'')^n}{n!} \cdot a^{(n-1)} - (F'' - 1) \sum_1^n \frac{(L')^n}{n!} \cdot a^{(n-1)} = 0 \quad (5)$$

and

$$A = \frac{F' - 1}{\sum_1^n \frac{a^n (L')^n}{n!}}, \quad (6)$$

where  $F'$  and  $F''$  are the values of the experimental  $F$  function at ligand concentrations  $(L')$  and  $(L'')$ , respectively.

When  $n \leq 5$  the values of  $A$  and  $a$  are obtained as real roots of Eqs. (5) and (6) by conventional methods. When  $n > 5$  an approximate solution could be gotten.

The validity of the set of constants calculated by the authors of the corresponding papers and by the present method is tested by substitution of these values into Eq. (2). The values of  $F_{calc}$  corresponding to a given value of  $(L)$  are then calculated and compared with the appropriate value  $F_{exp}$ . The quantities  $\Delta F = |F_{calc} - F_{exp}| \cdot 100$  are also calculated for each data point. As a measure of the overall goodness of fit the quantity

$$S = \text{const} \cdot S_{\min} = \left\{ \frac{1}{K} \sum W_i [(F_{calc})_i - (F_{exp})_i]^2 \right\} \text{const} \quad (7)$$

is used [9], where  $(\bar{F}_{exp})_i$  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,  $W_i = 1/(\sigma_F)_i^2$ ,  $(\sigma_F)_i^2$  is the variance of  $F$  in the  $i$ th data point,  $K$  is the number of degree of freedom of the system. We could not estimate  $(\sigma_F)_i^2$  from experimental considerations, so we have applied Eq. (7) as an estimate for the overall goodness of fits, assuming as others did [10] that the following relation is hold

$$(\sigma_F)_i^2 = \text{const} \cdot (F_{exp})_i^2 \quad (8)$$

It is evident that smaller the value of the  $S$ -factor better the corresponding fit.

The  $F$  function expressed by Eq. (4) has an advantage in comparison to Eq. (2) and the extrapolation procedure that once

A and  $a$  constants are determined, all stability constants could be obtained simultaneously with higher accuracy for the higher complexes than it is done by the extrapolation procedure.

## Results and Discussion

Only systems for which the  $F$  function is a polynomial of higher order than 2 in  $(L)$  have been selected for analysis, because if  $n \leq 2$  in Eq. (2) always two constants  $A$  and  $a$  respectively could be found to satisfy this relation. But we do not consider this as a sufficient justification that the mathematical model advanced in the previous paper<sup>1/</sup> is valid for a given metal ligand system.

### Cadmium Thiocyanate System

This system had been studied by D.N.Hume, D.D.DeFord and G.C.B.Cave<sup>4/</sup>. The experimental data had been obtained at constant temperature of  $30 \pm 0.1^\circ\text{C}$  and a constant ionic strength of 2, kept by using potassium nitrate as an inert electrolyte. The authors of the above mentioned paper have reported the following values of the stability constants:  $\beta_1 = 11 \pm 0.5$ ;  $\beta_2 = 56 \pm 2$ ;  $\beta_3 = 6 \pm 5$  and  $\beta_4 = 30 \pm 10$ . We have applied to this system the mathematical analysis described in the previous part of this paper. The values of the experimental  $F$  function at each ligand concentration were taken from Table I of Ref.<sup>4/</sup> where they are denoted as  $F_0$ . Using Eqs. (5) and (6) the following values for the constants were obtained:  $A = 3.48$  and  $a = 4.2$  respectively. According to Eq. (3) the stability constants of the successive cadmium thiocyanate complexes are as follow:  $\beta_1 = 14.6$ ;  $\beta_2 = 30.7$ ;  $\beta_3 = 43.0$  and  $\beta_4 = 45.1$ . The fit of the calculated  $F$  function was compared with that of the  $F$  function calculated by using Eq. (2) with the values of  $\beta_n$  obtained by the authors of Ref.<sup>4/</sup> and the results are presented in Table I. The  $S$ -factor defined as a measure of the goodness of the fit was calculated for both  $F_{calc}$  functions using Eq. (7) and the following values are obtained:  $S_{Ref./4/} = 5.3 \times 10^{-2}$  and  $S_{This\ work} = 4.0 \times 10^{-2}$  respectively. In Fig. 1 the mole fractions of the cadmium thiocyanate complexes as a function of the ligand concentration of the solution are shown. Our results are presented as a solid line and those calculated on the basis of the  $\beta_n$  values taken from Ref.<sup>4/</sup> as a dashed line.

## Lead Thiocyanate System

This system had been studied by W.G. Leonard, E.G. Smith and D.N. Hume<sup>/5/</sup> at a constant temperature of  $25 \pm 0.1^\circ\text{C}$  and ionic strength of 2 maintained by using  $\text{NaClO}_4$  as an inert electrolyte. The authors of that paper have reported the following values for the stability constants:  $\beta_1 = 3.5$ ;  $\beta_2 = 7.5$ ;  $\beta_3 = 0$  and  $\beta_4 = 7$  respectively. These figures indicate that the complexity of the system is very weak. In this case, as it was pointed out by the authors of Ref. <sup>/5/</sup>, the experimental errors are high. The additional accumulation of errors in the course of the successive extrapolation procedure applied make the values of  $\beta_n$  obtained with smaller degree of confidence. Probably, this is the reason why the method is not sensitive to the presence of the intermediate complex  $\text{Pb}(\text{CNS})_3^-$ . Here again the  $F_{\text{exp}}$  taken from Table I of Ref. <sup>/5/</sup> was analyzed in the same manner as described above and the following values were obtained for the constants:  $A = 0.87$  and  $a = 3.447$ . The stability constants calculated by using Eq. (3) are:  $\beta_1 = 3.0$ ;  $\beta_2 = 5.2$ ;  $\beta_3 = 5.9$  and  $\beta_4 = 5.1$ . The fits done by the authors of Ref. <sup>/5/</sup> and by us are compared and the results are presented in Table II. The  $S$ -factors calculated by using Eq. (7) are:  $S_{\text{Ref.}/5/} = 2.1 \times 10^{-2}$  and  $S_{\text{This work}} = 1.5 \times 10^{-2}$  respectively. The mole fractions of lead thiocyanate complexes as a function of the ligand concentration in the solution are shown in Fig. 2, where the solid line is used for the mole fractions calculated by using the set of stability constants obtained by the present method and the dashed line is used for the mole fractions calculated by using the set of stability constants reported by the authors of Ref. <sup>/5/</sup>.

## Cadmium Iodide System

Cadmium iodide system had been studied by Y.I. Turyan and G.F. Serova<sup>/6/</sup> at temperature of  $25 \pm 0.3^\circ\text{C}$  and ionic strength of 0.1 kept by using potassium nitrate as an inert electrolyte. The values of the stability constants reported by the authors are:  $\beta_1 = 250$ ;  $\beta_2 = 4500$  and  $\beta_3 = 45000$ . As a result of the mathematical analysis applied to the  $F_{\text{exp}}$  function taken from Table II of Ref. <sup>/6/</sup> we have found that a better fit to the  $F_{\text{exp}}$  is achieved if a polynomial of four order in  $(L)$  is used with the following values of the constants:  $\beta_1 = 200$ ;  $\beta_2 = 2700$ ;  $\beta_3 = 24000$  and  $\beta_4 = 160000$ , which

satisfy the relation (3) where  $A = 7.41$  and  $a = 27.0$ . The comparison of the fit  $F_{calc.}$  so obtained and that when using the values of the stability constants reported by the authors of Ref. <sup>16/</sup> is presented in Table III. The  $S$  -factors calculated on the basis of Eq. (7) are:  $S_{Ref./6/} = 3.2 \times 10^{-1}$  and  $S_{This work} = 3.4 \times 10^{-2}$  respectively. The mole fractions of the corresponding complexes as a function of the ligand concentration in the solution are given in Fig. 3, where the solid line is used for our results and the dashed line for the mole fractions calculated using the values of the stability constants reported by the authors of Ref. <sup>16/</sup>. As is seen in Fig. 3 irrespective of the fact that a high value for the stability constant of  $CdI_3^-$  is obtained by us, its concentration is practically negligible to ligand concentration of  $5.36 \times 10^{-2} M$  i.e. to the data point before the last one. In the last data point this complex is about 18% of the total concentration of cadmium (central group) in the solution.

### Rhodium (III) - Chloride System

This system had been studied by D. Cozzi and F. Pantani <sup>17/</sup>. Hydrochloric acid had been used as an electrolyte supplying the solution with  $Cl^-$  ions. The concentration of  $H^+$  ions had been kept constant equal to unity by adding  $HClO_4$  to the solution as an inert electrolyte. The authors of the above-mentioned paper reported the following values of the stability constants of the rhodium chloride complexes:  $\beta_1 = 2.8 \times 10^2$ ;  $\beta_2 = 3.5 \times 10^4$ ;  $\beta_3 = 8.3 \times 10^5$ ;  $\beta_4 = 1.2 \times 10^7$ ;  $\beta_5 = 5.6 \times 10^8$  and  $\beta_6 = 2.7 \times 10^8$  respectively. The mathematical analysis as described above was applied on the  $F_{exp}$  function taken from Table V of Ref. <sup>17/</sup>. It revealed that a polynomial of the fifth order in  $(L)$  with the following constants:  $\beta_1 = 4.20 \times 10^2$ ;  $\beta_2 = 2.4 \times 10^4$ ;  $\beta_3 = 9.26 \times 10^5$ ;  $\beta_4 = 2.66 \times 10^7$  and  $\beta_5 = 6.12 \times 10^8$ , which satisfy Eq. (3), where  $A = 3.65$  and  $a = 115$ , fits the data better than the polynomial of sixth order in  $(L)$  with the constants reported by the authors of Ref. <sup>17/</sup>. The comparison of the calculated  $F$  functions is presented in Table IV. The estimate of the goodness of both fits is done by calculating the  $S$  -factors using Eq. (7). They are found to be as follows:  $S_{Ref./17/} = 6.5 \times 10^{-2}$  and  $S_{This work} = 9.7 \times 10^{-3}$  respectively. The mole fractions of the rhodium chloride complexes as a function of the ligand concentration in the solution are shown in Fig. 4, where our results are presented as a solid line and those obtained when using the values of the stability constants reported by Cozzi and Pantani <sup>17/</sup> as a dashed line.



In a conclusion it may be said, that the proposed mathematical model '1' could be consider as a sufficiently good approximation of the complex formation process taking place in all for metal-ligand systems analyzed. This conclusion is supported first by the fact that an inspection on the  $S$ -factors indicates better fits in all cases when the  $\beta_n$  values obtained in this work are used and second by the fact that the number of constants is fewer. From the mathematical point of view, when some fenomenon is equally well described, let us say, by two mathematical models, that one which explains the experimental data with the fewest number of parameters is the best model.

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Table I  
Comparison of the experimental and calculated complexity  
functions for the cadmium thiocyanate system

| (L)<br>M | $F_{\text{exp}}$ | Hume et al.       |                    | This work         |                    |
|----------|------------------|-------------------|--------------------|-------------------|--------------------|
|          |                  | $F_{\text{calc}}$ | $\Delta F$<br>in % | $F_{\text{calc}}$ | $\Delta F$<br>in % |
| 0.1      | 2.65             | 2.67              | 0.75               | 2.81              | 6.04               |
| 0.2      | 5.57             | 5.58              | 0.18               | 5.56              | - 0.18             |
| 0.3      | 9.44             | 9.99              | 5.83               | 9.67              | 2.44               |
| 0.4      | 15.00            | 16.28             | 8.53               | 15.66             | 4.40               |
| 0.5      | 26.4             | 25.0              | - 5.30             | 24.17             | - 8.33             |
| 0.7      | 53.8             | 52.6              | - 2.23             | 51.81             | - 2.72             |
| 1.0      | 123.6            | 134.0             | 8.41               | 134.4             | 8.74               |
| 1.5      | 467              | 468               | 0.21               | 465               | - 0.43             |
| 2.0      | 1274             | 1255              | - 1.49             | 1219              | - 4.32             |

Table II  
Comparison of the experimental and calculated complexity  
functions for the lead thiocyanate system

| (L)<br>M | $F_{exp}$ | Leonard et al. |             | This work  |             |
|----------|-----------|----------------|-------------|------------|-------------|
|          |           | $F_{calc}$     | $F$<br>in % | $F_{calc}$ | $F$<br>in % |
| 0.1      | 1.38      | 1.42           | 2.90        | 1.36       | - 1.45      |
| 0.2      | 1.41      | 2.01           | 42.55       | 1.86       | 31.91       |
| 0.3      | 2.81      | 2.78           | - 1.07      | 2.57       | - 8.54      |
| 0.4      | 3.52      | 3.78           | 7.39        | 3.54       | 0.57        |
| 0.5      | 4.60      | 5.06           | 10.00       | 4.86       | 5.65        |
| 0.6      | 7.00      | 6.71           | - 4.14      | 6.61       | - 5.57      |
| 0.8      | 12.2      | 11.5           | - 5.74      | 11.8       | - 3.28      |
| 0.9      | 15.6      | 14.8           | - 5.13      | 15.6       | 0.00        |
| 1.0      | 19.0      | 19.0           | 0.00        | 20.2       | 6.31        |
| 1.1      | 22.6      | 24.2           | 7.08        | 25.9       | 14.60       |
| 1.3      | 36.9      | 38.2           | 3.52        | 41.2       | 11.65       |
| 1.4      | 49.9      | 47.5           | - 4.81      | 51.2       | 2.60        |
| 1.7      | 92        | 87             | - 5.43      | 93         | 1.09        |
| 1.8      | 108       | 105            | - 2.78      | 111        | 2.78        |
| 1.9      | 141       | 126            | - 10.64     | 132        | - 6.39      |
| 2.0      | 165       | 150            | - 9.09      | 157        | - 4.84      |

Table III  
Comparison of the experimental and calculated complexity  
functions for the cadmium iodide system

| (L)<br>M              | $P_{\text{exp}}$ | Turyan & Serova   |                    | This work         |                    |
|-----------------------|------------------|-------------------|--------------------|-------------------|--------------------|
|                       |                  | $P_{\text{calc}}$ | $\Delta P$<br>in % | $P_{\text{calc}}$ | $\Delta P$<br>in % |
| $1.24 \times 10^{-3}$ | 1.50             | 1.32              | - 12.00            | 1.25              | - 16.67            |
| $4.77 \times 10^{-3}$ | 2.19             | 2.30              | 5.02               | 2.02              | - 7.76             |
| $1.00 \times 10^{-2}$ | 3.54             | 3.99              | 12.71              | 3.30              | - 6.78             |
| $1.29 \times 10^{-2}$ | 4.55             | 5.06              | 11.21              | 4.09              | - 10.11            |
| $2.75 \times 10^{-2}$ | 7.35             | 12.22             | 66.26              | 9.13              | 24.22              |
| $5.36 \times 10^{-2}$ | 21.0             | 34.3              | 63.33              | 24.4              | 16.19              |
| $1.00 \times 10^{-1}$ | 91.2             | 116.0             | 27.19              | 88.0              | - 3.51             |

Table IV  
Comparison of the experimental and calculated complexity  
functions for the rhodium (III) chloride system

| (L)<br>M | $F_{exp}$          | Cossi & Pantani    |                    | This work          |                    |
|----------|--------------------|--------------------|--------------------|--------------------|--------------------|
|          |                    | $F_{calc}$         | $\Delta F$<br>in % | $F_{calc}$         | $\Delta F$<br>in % |
| 0.01     | 9.25               | 8.31               | - 10.16            | 8.87               | - 4.11             |
| 0.02     | $3.81 \times 10^1$ | $3.10 \times 10^1$ | - 18.64            | $3.27 \times 10^1$ | - 14.17            |
| 0.04     | $2.46 \times 10^2$ | $2.10 \times 10^2$ | - 14.63            | $2.46 \times 10^2$ | 0.00               |
| 0.06     | $1.00 \times 10^3$ | $9.27 \times 10^2$ | - 7.30             | $1.13 \times 10^3$ | 13.00              |
| 0.08     | $3.24 \times 10^3$ | $3.07 \times 10^3$ | - 5.25             | $3.76 \times 10^3$ | 16.05              |
| 0.1      | $9.35 \times 10^3$ | $8.28 \times 10^3$ | - 11.44            | $9.99 \times 10^3$ | 6.84               |
| 0.2      | $2.52 \times 10^5$ | $2.24 \times 10^5$ | - 11.11            | $2.47 \times 10^5$ | - 1.98             |
| 0.4      | $6.62 \times 10^6$ | $7.21 \times 10^6$ | 8.91               | $7.01 \times 10^6$ | 5.89               |
| 0.6      | $4.90 \times 10^7$ | $5.79 \times 10^7$ | 18.16              | $5.12 \times 10^7$ | 4.49               |
| 0.8      | $2.24 \times 10^8$ | $2.60 \times 10^8$ | 16.07              | $2.12 \times 10^8$ | - 5.36             |
| 1.0      | $6.45 \times 10^8$ | $8.43 \times 10^8$ | 30.70              | $6.40 \times 10^8$ | - 0.78             |

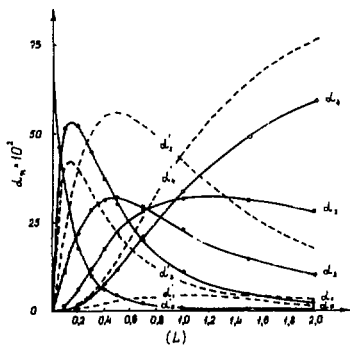


Fig. 1. Distribution of complex species in the cadmium thiocyanate system.

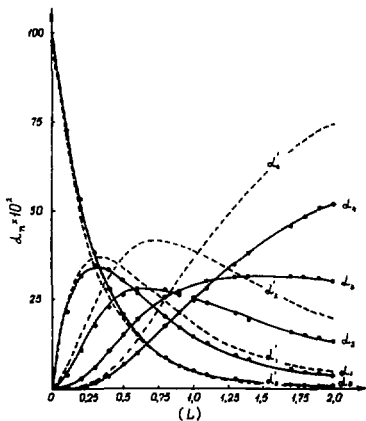


Fig. 2. Distribution of complex species in the lead thiocyanate system.

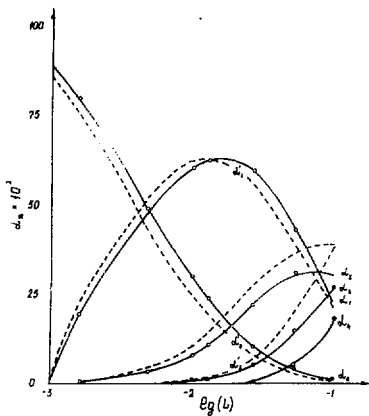


Fig. 3. Distribution of complex species in cadmium iodide system.

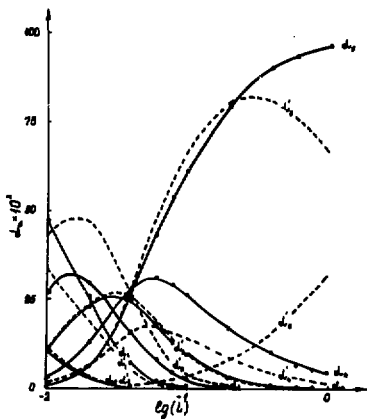


Fig. 4. Distribution of complex species in the rhodium chloride system.