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ЛАБОРАТОРИЯ ЯДЕРНЫХ ПРОБЛЕМ

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

Application to Data Obtained by the Polarographic Method for the Cadmium, Copper, Lead, and Zinc Formate Systems

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Introduction

As a part of a program involving the reevaluation of the data on the stability constants of metal complexes in order to check the validity of the relation connecting the overall stability constants of metal complexes derived in a previous paper of this series /1/ , the data on the formate complexes of cadmium, copper, lead, and zinc were analysed. These four systems had been studied by H.M. Hershenson, R.T.Brooks and M.E.Murphy /2/ using the polarographic technique as developed by DeFord and Hume /3/ at a constant temperature of 25.0 ± 0.2 °C and a constant ionic strength of 2 maintained by adding an appropriate amount of $NaClO_4$ in the solution as an inert electrolyte. The formate ions came in the solution from the dissociation of Na -formate.

Calculation of the Stability Constants

As far as the mathematical model of the complex formation process in aqueous solution is presented elsewhere /1/ , here only the main equations will be given. Here it have to be remembered that the above-mentioned mathematical model is concerned with a system of metal M^{m+} and univalent ligand L^- in an aqueous solution. It is based on the assumptions, (which are usually made for this kind of systems) that: i) the metal M and the ligand L form only mononuclear complexes. ii) the complex forming metal M does not participate in side reactions with the ligand L' coming from the dissociation of the electrolyte CL' used as an inert electrolyte as well as with OH^- ions. iii) no formation of ion-pairs (outer-sphere complexes) as a result of the interaction of the negatively charged metal complexes and the C^+ ions which come from the dissociation of the CL and CL' electrolyte of the solution occurs. iv) the activity coefficients of all species in the solution are constant formally equaled to unity.

It was found that for such system the overall stability constant β_n of the complex ML_n, formed as a product of the reaction: $M + n\,L \rightleftarrows ML_n$ (the coordinated water molecules and charges are dropped for clarity) should satisfy the following relation

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

where A and a are constants.
Then, the complexity function as defined by Froneus [4] will be transformed to

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

where (L) is the ligand concentration, N is the coordination number of the complex forming metal M. If the values of F as a function of the free ligand concentration of the solution are determined from experimentally measurable quantities as directed, for example, by the DeFord and Hume's method [3], taking two data points, let us say, F' at ligand concentration (L') and F'' at ligand concentration (L'') with a simple rearrangement of Eq. (2') the following two equations could be written

$$(F'-1) \sum_{1}^{n} a^{n-1} \frac{(L'')^n}{n!} - (F''-1) \sum_{1}^{n} a^{n-1} \frac{(L')^n}{n!} = 0 \qquad (3)$$

and

$$A = \frac{F'-1}{\sum_{1}^{n} \frac{a^n (L')^n}{n!}} . \qquad (4)$$

From Eqs. (3) and (4) the values of the constants A and a could be gotten by the conventional methods.

Results and Discussion

The values of F_{exp} as a function of the ligand concentration were taken from the corresponding Tables of Ref. /2/ for each system, where they are denoted as F_0 . Those functions were analysed as described above. As a result the values of the constants A and a were obtained. Inserting these values in Eq. (1) we get the whole set of stability constants for the given metal system. Then, the F_{exp} at each data point was compared with the values of the F_{calc} functions, the first one obtained when using the set of stability constants reported in Ref. /2/ and the second one calculated by using the set of stability constants obtained in this work. The quantity $\Delta F = 1/F_{exp}\,(F_{calc} - F_{exp})\,100$ was introduced as a measure of the fit at a given data point. As a measure of the overall goodness of the fit the quantity

$$S = const \cdot S_{min} = \{ \frac{1}{K} \Sigma W_i [(F_{calc})_i - (F_{exp})_i]^2 \} const \qquad (5)$$

was used throughout this paper/5/ , where K is the number of degree of freedom of the system, $(F_{exp})_i$ 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, $W_i = 1/(\sigma_F)^2_i$, $(\sigma_F)^2_i$, is the variance of F in the i^{th} data point.

Introducing the S-factor as defined in Eq. (5) we have made the assumptions as others did/6/ that the following relation is hold

$$(\sigma_F)^2_i = const\,(F_{exp})^2_i \qquad (6)$$

because no estimation of W_i from any experimental consideration was possible.

Cadmium Formate System

For this system the authors of Ref. /2/ reported the following set of stability constants: $\beta_1 = 3 \pm 1$; $\beta_2 = 13 \pm 1$; $\beta_3 = 22 \pm 7$ and $\beta_4 = 16 \pm 4$. As a result of the mathematical analysis performed as described above we have found the following values of the stability constants: $\beta_1 = 4.4$; $\beta_2 = 10.8$; $\beta_3 = 17.6$ and $\beta_4 = 21.6$. They are related according to Eq. (1), where $A = 0.90$ and $a = 4.90$. Table I compares the experimental complexity function (F_{exp}) with the theoretical ones (F_{calc}) obtained with the two sets of stability constants just described. The S-factors are $S_{Ref./2/} = 8.1\mathrm{x}10^{-3}$ and $S_{This\ work} = 4.1\mathrm{x}10^{-3}$. In Fig. 1 the mole fractions of the cadmium formate complexes vs. the formate concentration are plotted. The solid line presents the results obtained when the set of stability constants of this work is used and the dashed line presents the results with the set of stability constants reported in Ref. /2/.

Lead Formate System

For this system the following set of stability constants is reported in Ref. /2/: $\beta_1 = 6 \pm 1$; $\beta_2 = 23 \pm 4$; $\beta_3 = 27 \pm 10$ and $\beta_4 = 15 \pm 4$. We have found the following values of the constants A and a in Eq. (2): $A = 2.00$ and $a = 4.00$ respectively. Using Eq. (1) the following values of the consecutive stability constants of the lead formate complexes are obtained: $\beta_1 = 8.0$; $\beta_2 = 16.0$; $\beta_3 = 21.0$ and $\beta_4 = 21.0$. In Table II the comparison of the F_{exp} and F_{calc} functions is presented. The S-factors for this system are $S_{Ref./2/} = 2.0\mathrm{x}10^{-2}$ and $S_{This\ work} = 2.7\mathrm{x}10^{-2}$. In Fig. 2 the mole fractions of the lead complexes vs. the formate concentration in the solution are plotted. Solid line is used when the set of stability constants of this work is used and a dashed line - for the set of Ref./2/.

Zinc Formate System

In Ref. /2/ the following set of stability constants is reported: $\beta_1 = 4 + 1$; $\beta_2 = 9 \pm 2$; $\beta_3 = 3 \pm 1$ and $\beta_4 = 6 \pm 3$. Our results are: $\beta_1 = 3.15$; $\beta_2 = 5.5$; $\beta_3 = 6.4$ and $\beta_4 = 5.6$. These constants satisfy Eq. (1) where $A = 0.90$ and $a = 3.49$. The comparison of the F_{exp} and F_{calc} functions is presented in Table III. The S-factors are $S_{Ref./2/} = 5.0\mathrm{x}10^{-2}$ and $S_{This\ work} = 4.0\mathrm{x}10^{-2}$. On Fig. 3 the mole fractions of the zinc formate complexes in the solution calculated on the basis of both the sets of stability constants are plotted as a function of the ligand concentration.

Copper Formate System

For this system the following values of the stability constants are reported in Ref. /2/: $\beta_1 = 37 \pm 8$; $\beta_2 = 166 \pm 22$; $\beta_3 = 112 \pm 40$

and β_4 = 283 ± 23 respectively. The analysis of the F_{exp} function gives the following values of the constants: A = 6.55 and a = 5.80. For the stability constants Eq. (1) gives β_1 = 38; β_2 = 110; β_3 = 213 and β_4 = 309. The comparison of both fits is presented in Table IV. The S-factors calculated are $S_{Ref./2/}$ = 7×10^{-2} and $S_{This\ work}$ = = 5.5×10^{-2}. In Fig. 4 the mole fractions of the copper formate complexes calculated by using both sets of constants are plotted as a function of the ligand concentration in the solution.

The result of the analysis strongly confirm the validity of Eqs. (1) and (2) and the mathematical model developed in Ref. /1/ for the four formate systems studied. These results suggested a preference for this model since by two criteria this model interpreted the experimental data better than the classical one. These criteria are: First, that this model explains the complex formation process with less number of parameters than the classical one and from the mathematical point of view it is the preferable one and second, that the inspection of S-factor values indicated better fits in the cases when the sets of stability constants found in the present work are used. For the lead formate system both the fits could be practically considered as equal, that one of Ref. /2/ being better by a factor of about 1.4. But this difference is too small to need any explanation or discussion and some random error introduced in the course of the measurements could cause such effect.

Obviously, for systems for which the mathematical model developed in Ref. /1/ is valid, the β_n values could be determined directly from Eq. (1) after A and a constants are obtained from the experimental complexity function. This is less time consuming and much more accurate procedure than the conventional method of the successive graphical extrapolation /7/ usually applied for the determination of the polynomial coefficients β_n.

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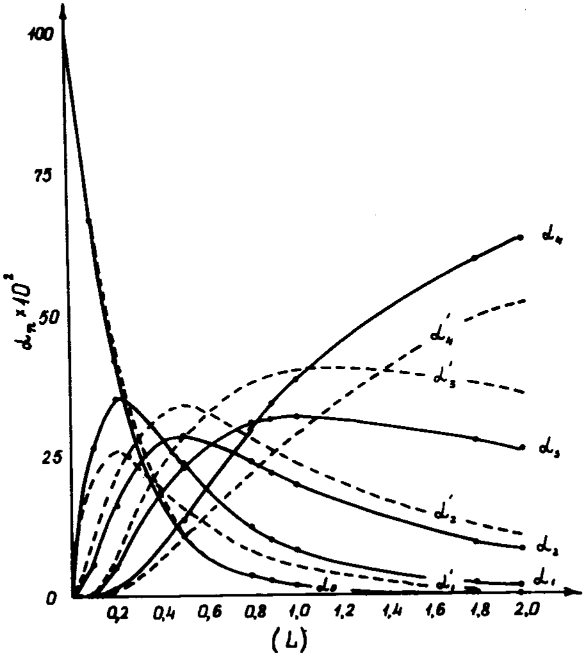

Fig. 1. Distribution of complex species in the cadmium formate system.

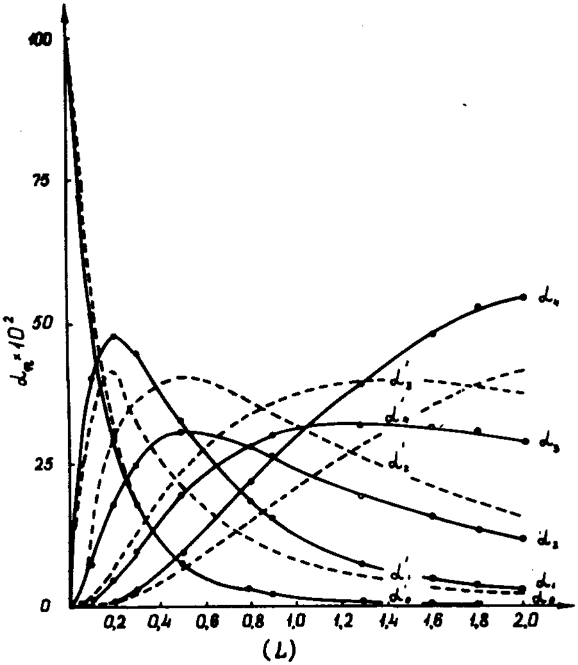

Fig. 2. Distribution of complex species in the lead formate system.

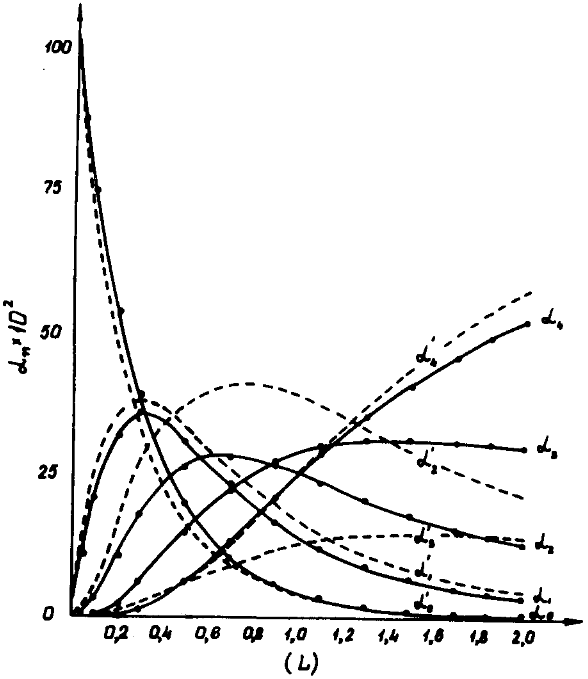

Fig. 3. Distribution of complex species in the zinc formate system.

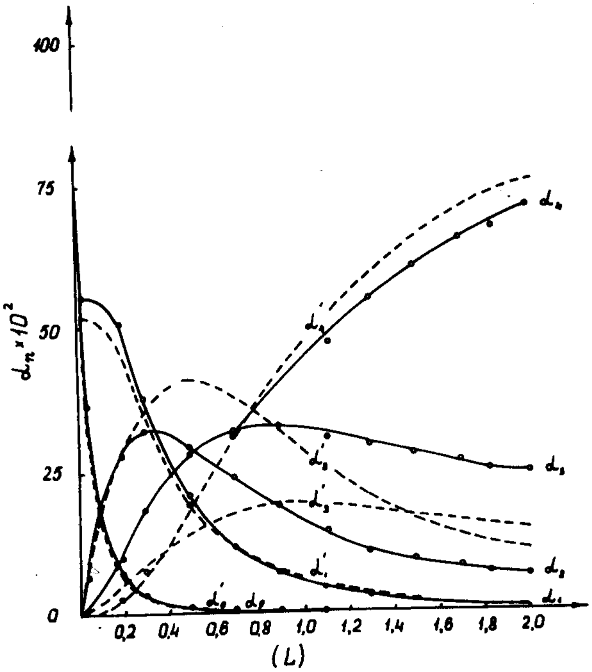

Fig. 4. Distribution of complex species in the copper formate system.

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

(L) M	F_{exp}	Hershenson et al.		This work	
		F_{calc}	ΔF_{calc} in %	F	ΔF in %
0.09	1.40	1.39	- 0.71	1.50	7.14
0.19	2.28	2.21	- 3.07	2.37	3.95
0.49	9.53	9.10	- 4.51	9.06	- 4.93
0.79	26.6	28.6	7.52	28.3	6.39
0.89	37.0	39.5	6.76	39.4	6.49
0.99	55.2	53.4	- 3.26	53.8	- 2.54
1.79	349	338	- 3.15	366	4.87
1.98	525	475	- 9.52	521	- 0.76

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

(L) M	F_{exp}	Hershenson et al.		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
0.04	I.30	I.28	- I.54	I.34	3.85
0.09	I.32	I.75	32.57	I.87	4I.67
0.I9	3.I8	3.I7	-0.3I	3.27	2.83
0.29	5.48	5.44	- 0.73	5.33	- 2.73
0.49	I4.5	I3.5	- 6.90	I2.4	- I4.48
0.79	40.5	39.2	- 3.2I	35.8	- II.60
0.89	5I.7	53.0	2.5I	48.8	- 5.65
I.29	I46	I46	0.00	I4I	- 3.42
I.59	256	273	6.64	273	6.64
I.79	4II	394	- 4.I4	403	- I.95
I.98	570	543	- 4.74	565	- 0.88

Table III

Comparison of the experimental and calculated complexity functions for zinc formate system

(L) M	F_{exp}	Hershenson et al.		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in%
0.04	1.34	1.17	- 12.69	1.13	- 15.67
0.09	1.8	1.4	- 22.22	1.3	- 27.78
0.19	1.8	2.1	16.67	1.8	0.00
0.29	2.8	3.0	7.14	2.6	- 7.14
0.49	5.4	5.8	7.41	4.9	- 9.26
0.69	12.8	10.4	- 18.75	9.2	- 28.13
0.89	16.0	17.6	10.00	16.2	1.25
1.09	23.3	28.4	21.89	27.2	16.74
1.29	37.9	44.2	16.62	43.5	14.78
1.49	68.8	66.4	- 3.49	66.7	- 3.05
1.69	88.7	96.9	9.24	98.6	11.16
1.84	145	126	- 13.10	130	- 10.34
1.98	259	160	- 38.22	164	- 36.68

Table IV
Comparison of the experimental and calculated complexity functions for the copper formate system

(L) M	F_{exp}	Hershenson et al.		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
0.04	2.96	2.76	- 6.75	2.72	- 8.II
0.I9	I0.3	I5.2	47.57	I4.I	36.89
0.29	34	30	- II.76	29	- I4.70
0.49	87	88	- I.I5	89	2.30
0.69	226	206	- 8.85	220	- 2.65
0.89	42I	422	0.24	466	I0.69
I.09	799	783	- 2.00	884	I0.64
I.29	2I97	I349	- 38.60	I546	- 29.63
I.49	I807	2I90	2I.I9	2529	39.95
I.69	4550	3387	- 25.56	3928	- I3.67
I.84	4630	4573	- I.23	53I2	I4.73
I.98	7725	5944	- 23.05	69I0	- I0.55