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

**Copper-Methoxyacetate, Copper-Ethoxyacetate,
Copper-Thiodiacetate, Cadmium-Ethoxyacetate
and Cadmium-(Ethylthio)acetate Systems**

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Introduction

In an earlier paper [1] a mathematical model concerned with the complex formation in aqueous solution has been developed. As a result the following relation connecting the overall stability constants of the complexes in a given metal-ligand system has been derived

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

where β_n is the overall stability constant of the complex ML_n, A and a are constants.

Obviously, if Eq. (1) is valid for a given metal-ligand system in the conventional expressions for the complexity function or the formation function [2,3] only two unknown constants will enter instead of n (n is the number of ligands in a given complex). For example, the complexity function for such system will be given by:

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

where ( ) are concentrations, N is the coordination number of the complex forming metal M.

The validity of the relations (1) and (2) was demonstrated on a number of systems with inorganic ligands [1,4]. In the next paper [5] of this series an attempt was made to apply that model to systems with organic ligands. The very good results obtained for copper, zinc, lead and cadmium formate systems incourage us for looking for systems with another organic ligands, permitting a comparison of the complex formation tendency between metal central ion and ligands with different structure. Our attention was drawn to the

investigations of A.Sandell, which cover a great variety of metal-ligand systems all studied potentiometrically with high precision and great care for elimination of all possible sources of experimental errors. The results obtained for II systems investigated by A.Sandell are published in a series of five papers [6–10]. We have made an attempt to analyze all these systems, and the results obtained will appear in two successive papers.

In the present paper the results obtained for the copper-methoxyacetate, copper-ethoxyacetate, copper-thiodiacetate systems [6], cadmium-ethoxyacetate and cadmium(ethylthio)acetate systems [7] are presented. All these systems had been studied by the potentiometric method at a constant ionic strength of I and constant temperature of 20.0^{0}C for the copper-ligand systems and 25.0^{0}C for the cadmium-ligand systems respectively.

Calculation of the Stability Constants and Discussion

The details of the calculation procedure are given elsewhere [1,4] so here only the main points will be repeated: the problem to determine the constants A and a in Eq.(2) is reduced to a solution of the following equations:

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

and

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

where F' and F'' are the values of the experimental complexity function at ligand concentrations (L') and (L'') respectively. The complexity functions in Ref. [6] and [7] are denoted by X and their experimental values for some representative ligand concentrations could be taken for the copper-ligand systems from the corresponding Tables of Ref. [6]. For the cadmium-ligand systems they could be calculated by taking the values of E_M reported for a given free

ligand concentration from the data presented in the corresponding Tables and using the relation $E_M = 29.58 \log X$ [10].

Inserting now the A and a values so obtained in Eq. (2) the F_{calc} for each data point was calculated. To check the goodness of the fit at each point the quantity $\Delta F = 1/F_{exp} (F_{calc} - F_{exp}) 100$ was also calculated. The overall goodness of the fit was evaluated by the S-factor defined as

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

where $(F_{exp})_i$ is the experimental values of F in the ith data point, $(F_{calc})_i$ is the calculated value of F in the ith data point, K is the number of degree of freedom of the system. Smaller the value of the S-factor better the corresponding fit [4].

In Tables 1 - 5 the F_{exp} are compared with the complexity functions (F_{calc}) which are calculated by using the conventional expression with the values of the stability constants reported by Sandell and by using Eq. (2). The sets of the stability constants used for each system are as follows:

For the copper-methoxyacetate system:

	β_1	β_2	β_3	β_4	
A.Sandell [6]	66	640	1300	600	
This work	74	463	1927	-	$A = 5.92$ and $a = 12.50$

The S-factors are $S_{Ref./6/} = 2.2 \times 10^{-4}$ and $S_{This\ work} = 10.7 \times 10^{-4}$.

For the copper-ethoxyacetate system:

	β_1	β_2	β_3	β_4	
A.Sandell [6]	62	740	1600	600	
This work	76	513	2308	-	$A = 5.45$ and $a = 13.70$

The S-factors are $S_{Ref./6/} = 0.9 \times 10^{-4}$ and $S_{This\ work} = 16.5 \times 10^{-4}$.

For the copper-thiodiacetate system:

	β_1	β_2	β_3	β_4
A.Sandell[6]	1.5×10^4	1.2×10^7	$4. \times 10^8$	$8. \times 10^{11}$
This work	1.60×10^4	7.68×10^6	2.46×10^9	5.90×10^{11}

$A = 16.66$ and $a = 960$

The S-factors are $S_{Ref./6/} = 8.6 \times 10^{-4}$ and $S_{This\ work} = 6.0 \times 10^{-4}$.

For the cadmium-ethoxyacetate system:

	β_1	β_2	β_3	β_4	
A.Sandell[7]	11.7	49	35	98	
This work	12.8	35.2	64.6	88.8	$A = 2.33$ and $a = 5.50$

The S-factors are $S_{Ref./7/} = 0.1 \times 10^{-4}$ and $S_{This\ work} = 2.7 \times 10^{-4}$.

For the cadmium-(ethylthio)acetate system:

	β_1	β_2	β_3	β_4	
A.Sandell[7]	18.7	133	320	520	
This work	20.9	98	304	713	$A = 2.23$ and $a = 9.38$

The S-factors are $S_{Ref./7/} = 0.3 \times 10^{-4}$ and $S_{This\ work} = 5.8 \times 10^{-4}$.

As it is seen from the data presented in Tables 1-5 the complexity functions calculated according to Eq. (2) fit F_{exp} reasonably well. The calculated S-factors show that for all system except for the copper-thiodiacetate system Sandell's fits are better than ours. But we consider the accuracy we have achieved to be reasonably good for the confirmation of the mathematical model developed in Ref. /1/. A further refinement of the values of A and a constants by successive approximation could give an improvement in the fits but in the given case it is not necessary. Our aim was to show that the relations (1) and (2) are hold for the above analyzed systems and this was confirmed with sufficient confidence.

In all cases but two Eq. (2) was a polynomial of the same order in (L) as that used by Sandell for the corresponding system. For copper-methoxyacetate and for copper-ethoxyacetate systems Sandell has found that the F_{calc}, which fits the experimental data is a forth order polynomial in (L) and for the same systems we found that a third order polynomial in (L) with appropriate coefficients gives a satisfactory fit to the experimental complexity function for both the systems. So the existence of the fourth complex becomes

questionable. Moreover, Sandell reported [6] 2.5 as a maximum value of the ligand number $\bar{n}$ reached by both systems for the ligand range studied. This fact could also serve as an indication that even if the fourth complex exists, its concentration in the ligand concentration range studied is comparatively low.

Irrespective of the fact that there is a difference between the values of the particular constant reported by Sandell and by us, the results in Tables 1-5 demonstrate that both sets fit the F_{exp} reasonably well.

In Fig. 1-5 the mole fractions of the complexes $vs.$ the free ligand concentration in the solution are given. The solid line is used to present the results obtained by using the β_n obtained by the present method, and the dashed line is used for the results obtained when the β_n values reported by Sandell [6,7] are used.

Only the system copper-(ethylthio)acetate which had been studied by Sandell [6] could not be analyzed with good accuracy and for this reason the results are not presented here. We could not advance any explanation for this fact but one of the reasons may be that only for this system as Sandell pointed out the direct measurements of the central metal ion concentration by using the metal amalgam electrode had been prevented by some side reactions and a precipitate formation.

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Table 1
Comparison of the experimental and calculated complexity
functions for the copper-methoxyacetate system

(L) mM	F_{exp}	A. Sandell		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
15.8	2.21	2.20	− 0.45	2.28	3.17
17.8	2.39	2.38	− 0.42	2.47	3.35
22.2	2.80	2.79	− 0.36	2.89	3.21
27.0	3.28	3.27	− 0.30	3.37	2.74
35.2	4.16	4.17	0.24	4.26	2.40
41.3	4.87	4.91	0.82	4.98	2.26
77.5	10.77	10.58	− 1.76	10.41	− 3.34
102	16.00	15.83	− 1.06	15.41	− 3.69
130	23.77	23.42	− 1.47	22.68	− 4.58
163	35.2	34.8	− 1.14	33.7	− 4.26
245	77.8	76.9	− 1.16	75.3	− 3.21
356	171.8	173.9	1.22	173.0	0.70
423	255.3	261.0	2.23	261.0	2.23
495	379	384	1.32	385	1.58
580	564	576	2.13	576	2.13
671	838	848	1.19	841	c.:6

8

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

(L) mM	F_{exp}	A. Sandell		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
16.2	2.208	2.205	- 0.13	2.352	6.52
20.4	2.587	2.585	- 0.04	2.753	6.46
29.8	3.55	3.55	0.00	3.74	5.35
41.1	4.87	4.91	0.87	5.09	4.52
54.2	6.69	6.80	1.64	6.92	3.44
99	16.00	16.00	0.00	15.66	- 2.12
125	23.77	23.58	- 0.80	22.87	- 3.79
156	35.2	35.1	- 0.28	33.9	- 3.69
193	52.4	52.9	0.95	51.2	- 2.29
234	77.8	78.3	0.64	76.4	- 1.80
280	115.6	115.2	- 0.35	113.2	- 2.08
333	171.8	170.2	- 0.93	168.8	- 1.75
396	255.3	255.7	0.16	255.7	0.16
468	379	385	1.58	387	2.11
543	564	561	- 0.53	566	0.35

Table 3
Comparison of the experimental and calculated complexity
functions for the copper-thiodiacetate system

(L) mM	F_{exp}	A. Sandell		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
0.138	3.279	3.299	0.61	3.361	2.50
0.22	4.873	4.887	0.08	4.919	0.94
0.33	7.239	7.280	0.57	7.212	− 0.37
0.48	10.77	11.04	2.51	10.75	− 0.18
0.66	16.00	16.39	2.44	15.72	− 1.75
0.89	23.77	24.64	·3.62	23.43	− 1.43
1.15	35.24	36.13	2.52	34.33	− 2.58
3.14	255.3	256.6	0.51	260.5	2.04
3.67	379	382	0.79	392	3.43
4.24	564	569	0.89	584	3.55
5.56	1245	1289	3.53	1314	5.54
7.00	2748	2752	0.11	2750	0.07

Table 4
Comparison of the experimental and calculated complexity
functions for the cadmium-ethoxyacetate system

(L) mM	F_{exp}	A. Sandell		This work	
		F_{calc}	ΔF in %	F_{calc}	ΔF in %
20.7	1.262	1.263	0.08	1.281	1.50
43.2	1.595	1.600	0.31	1.624	1.82
67.0	2.015	2.016	0.05	2.037	1.09
93.4	2.544	2.556	0.47	2.562	0.71
121.5	3.215	3.229	0.43	3.210	0.15
151.6	4.060	4.073	0.32	4.021	- 0.96
183.6	5.128	5.128	0.00	5.038	- 1.75
218.2	6.476	6.472	- 0.06	6.342	- 2.07
255	8.181	8.165	- 0.19	7.999	- 2.22
295.5	10.33	10.38	0.48	10.20	- 1.26
337	13.05	13.11	0.46	12.93	- 0.92
380	16.49	16.49	0.00	16.35	- 0.85
426	20.82	20.81	- 0.05	20.76	- 0.29
474	26.30	26.23	- 0.27	26.34	0.15
526	33.21	33.31	0.30	33.66	1.35
578	41.95	41.83	- 0.29	42.54	1.41
634	52.98	52.87	- 0.21	54.07	2.06
692	66.91	66.63	- 0.42	68.48	2.35
751	84.53	83.42	- 1.31	86.07	1.82

Table 5
Comparison of the experimental and calculated complexity
functions for the cadmium-(ethylthio)acetate system

| (L) mM	P_{exp}	A. Sandell		This work	
		F_{calc}	ΔP in %	F_{calc}	ΔP in %
12.8	1.262	1.262	0.00	1.284	1.74
26.3	1.595	1.590	-0.31	1.623	1.75
41.1	2.015	2.017	0.10	2.048	1.64
56.8	2.544	2.554	0.39	2.566	0.86
73.2	3.215	3.222	0.22	3.195	- 0.62
90.6	4.060	4.059	- 0.02	3.972	- 2.17
109.0	5.128	5.104	- 0.47	4.937	- 3.72
129.0	6.476	6.492	0.25	6.177	- 4.62
150.8	8.181	8.212	0.38	7.791	- 4.77
173.2	10.33	10.36	0.29	9.78	- 5.32
197.1	13.05	13.09	0.31	12.33	- 5.52
222.2	16.49	16.50	0.06	15.56	-.5.64
249.5	20.82	20.93	0.53	19.80	- 4.90
278.5	26.30	26.56	0.99	25.30	- 3.80
308	33.21	33.41	0.60	32.03	- 3.55
339	41.95	41.96	0.02	40.61	- 3.19
374	52.98	53.53	1.04	52.38	- 1.13
409	66.91	67.35	0.66	66.69	- 0.33
445	84.53	84.23	- 0.35	84.45	- 0.09
485	106.8	106.6	- 0.19	108.3	- 1.40
526	134.8	134.0	- 0.59	137.9	2.30
569	170.3	168.1	- 1.29	175.4	3.00
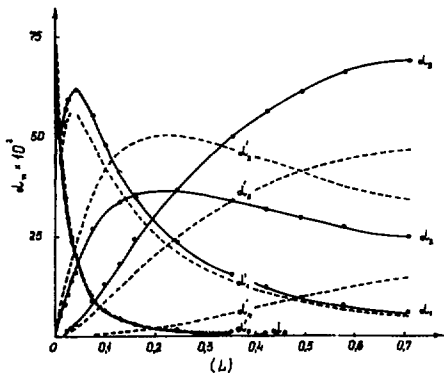
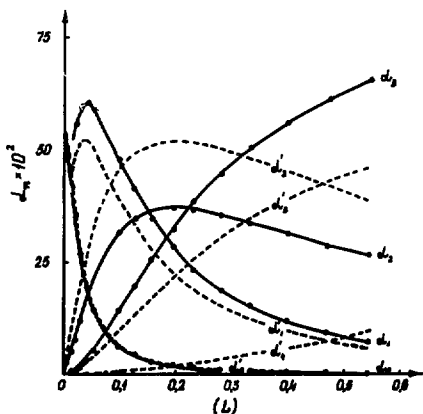Fig. 1. Distribution of complex species in the copper-methoxyacetate system.

Fig. 2. Distribution of complex species in the copper-ethoxyacetate system.
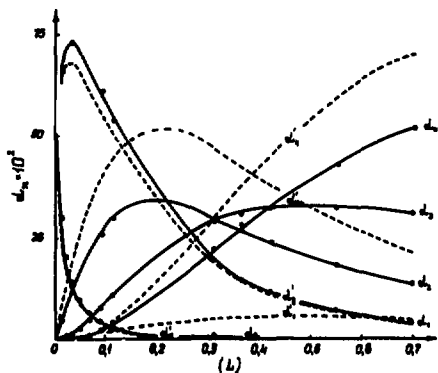
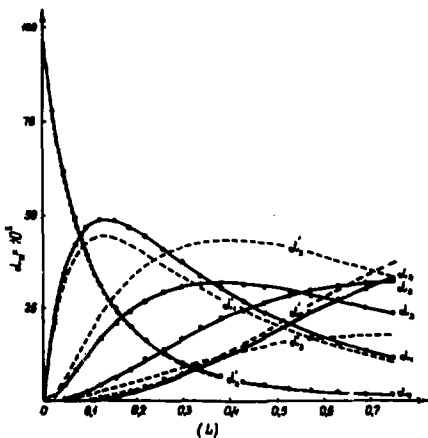Fig. 3. Distribution of complex species in the copper-thiodiacetate system.

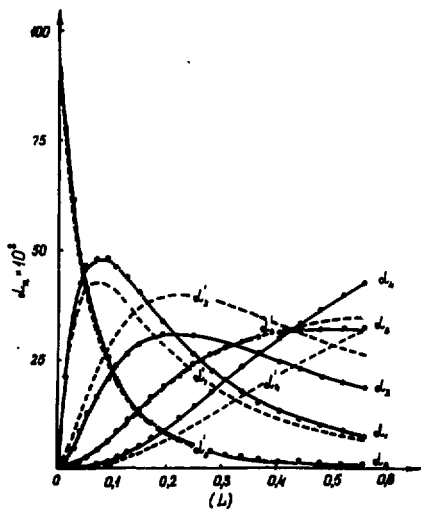Fig. 4. Distribution of complex species in the cadmium-ethoxyacetate system.

Fig. 5. Distribution of complex species in the cadmium-(ethylthio) acetate system.