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The Stability of Metal Halide Complexes in Aqueous Solution

II. The Fluoride Complexes of Divalent Nickel, Copper, and Zinc

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The stabilities of the fluoride complexes of Ni^{2+}, Cu^{2+}, and Zn^{2+} have been determined. In the solutions studied ($[F^-] \leq 200$ mM; $C_M \leq 100$ mM; perchlorate medium of ionic strength 1 M at 20° C) only the first mononuclear complex exists in appreciable concentrations. The following values of the constant $\beta_1 = [MF^+] / [M^{2+}] [F^-]$ have been found:

Ni^{2+}: 4.6 ± 0.5 M^{-1}; Cu^{2+}: 9 ± 1 M^{-1}; Zn^{2+}: 5.9 ± 0.6 M^{-1}

The stability order of these complexes, as well as their strength relative to the complexes formed by the same metal ions with the other halide ions is in accordance with the views advanced in the first paper [1] of this series.

According to the views developed in part I of this series of papers [1], the fluoride complexes of Ni^{2+}, Cu^{2+}, and Zn^{2+} should be much stronger than the complexes formed by these ions with the other halides. However, even the fluoride complexes will be of moderate strength as the central ions are only divalent and do not have especially small ionic radii. The stability of the fluoride complexes will vary inversely with the ionic radii, *i. e.* in the order $Ni^{2+} < Cu^{2+} > Zn^{2+}$ (*cf.* Connick and Tsao [2]).

The aim of the present investigation was to test these views experimentally. The systems were studied in the same way as the uranyl fluoride [3] system. The ionic medium (perchlorate of ionic strength $I = 1$ M) and the temperature (20° C) were also the same as in the previous measurements.

From the emf E_H obtained experimentally * by means of the quinhydrone electrode the free ligand concentration [A] may be calculated using the equation

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* The same symbols are used as in the paper on uranyl fluoride [3].

$$\text{antilog}\ \frac{E_H}{RT/F} = \frac{C_H}{[\mathrm{H}^+]} = 1 + \delta_1\,[\mathrm{A}] + \delta_2\,[\mathrm{A}]^2 = X_H \tag{1}$$

where the constants δ_1 and δ_2 of the hydrogen fluoride system have been determined previously [3]. Then the ligand number $\bar{n}_M$ can be calculated from the relationship

$$\bar{n}_M = \frac{C_A - [\mathrm{A}] - \bar{n}_H \cdot C_H}{C_M} \tag{2}$$

where the value of $\bar{n}_H$ corresponding to the appropriate value of [A] is found from the known [3] complex formation function of the hydrogen fluoride system. Once the complex formation function $\bar{n}_M = \mathrm{f}([\mathrm{A}])$ has thus been found, the complexity constants can be calculated in the usual way [4].

The calculation of [A] and $\bar{n}_H$ described above presupposes however that neither the dimer H_2F_2 nor metal complexes with HF_2^- as ligand exist in the range of concentration used. It has previously [3] been shown that no H_2F_2 is formed and that HF_2^- does not compete appreciably with F^- in the formation of complexes with UO_2^{2+}. It was therefore assumed in the first instance that no complexes with HF_2 are formed by the present cations. This assumption may be tested experimentally in the same way as for UO_2^{2+}, *viz.* by determining the formation function for different values of total concentration of metal C_M. If this function is independent of C_M it may be concluded not only that no complexes of HF_2^- exist but also that the complex formation is entirely mononuclear [3].

It is well known that the present cations are not hydrolysed at low pH. This is also confirmed by the analysis performed (p. 729) in order to check if the preparations of perchlorates used contain any free perchloric acid. No buffering due to Cu^{2+} could be detected below a pH of 4 or 5; and the hydrolysis of Zn^{2+} and Ni^{2+} becomes perceptible only at still higher pH. Nevertheless series of measurement were performed at two different values of total concentration of acid, C_H, in order to ensure that complex formation is really independent of $[\mathrm{H}^+]$ (*cf.* Ref.[3]).

The calculation of the complex formation function from δ_1 and δ_2 also presupposes that the values of these constants do not change appreciably in the range of C_A used. To judge from previous measurements this is true for $C_A \lessapprox 200$ mM. For $C_A \gtrapprox 200$ mM a fairly tedious method of calculation must be used in order to find $\bar{n}_M = \mathrm{f}\ ([\mathrm{A}])$. For the present systems however no measurements are performed in this upper range, as they are not likely to give further information justifying the work involved. The systems are so unstable that only the first complex MF^+ can be shown to exist with certainty when $C_A \lessapprox 200$ mM. Even at the highest value of C_A, ≈ 400 mM, which can be reached by adding a fluoride solution almost saturated with respect to NaF, the concentration of the second complex must therefore be low. In view of the further uncertainty inherent in the change of the medium, a calculation of the stability constant of this complex is not really possible even if the measurements are extended to $C_A = 400$ mM.

EXPERIMENTAL

Chemicals. The preparations of *nickel perchlorate* and *copper perchlorate* were the same as used by Fronæus [5,6]. *Zinc perchlorate* was prepared by adding the equivalent amount of a solution of sodium hydroxide (EKA *puriss*) to a solution of zinc nitrate (Bakers analyzed), washing the precipitate free from nitrate ions and then dissolving it in a slight excess of perchloric acid (Bakers analyzed). When excess water was driven off nice crystals of the zinc perchlorate hexahydrate were obtained.

Stock solutions of the perchlorates, of an ionic strength $I = 1$ M, were prepared and their exact concentrations then determined by electroanalysis (according to the methods described by Vogel [7]).

The amounts of free perchloric acid possibly present in the stock solutions were determined by adding a known amount of acid to a sample which was then titrated potentiometrically with alkali. The metal ions present are all so weakly acidic that they do not interfere with the determination of the free acid. The stock solutions of Ni^{2+} and Zn^{2+} did not contain any free acid. For Cu^{2+} a small concentration of acid was found ($= 1.0$ % of the total perchlorate concentration) and taken into account when solutions were mixed for the fluoride titrations.

Table 1. Determination of the complex formation function of the nickel fluoride system.

A. $C_M = 50$ mM; $C_H = 10$ and 25 mM.

C_H mM →	10				25			
C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.8	59.3	10.46	10.78	0.054	31.6	3.49	2.91	0.036
43.6	82.7	26.4	27.5	0.116	66.9	14.13	14.78	0.093
62.5	95.0	43.0	43.6	0.160	84.3	28.2	29.3	0.142
79.9	103.2	59.5	58.2	0.208	95.2	43.3	43.9	0.172
95.9	109.3	75.7	72.1	0.242	102.6	58.1	57.1	0.210
110.5	114.3	92.3	85.2	0.27	108.4	73.1	69.8	0.234
137.0	121.6	123.2	108	0.33	116.8	101.9	92.6	0.28
160	127.0	152.6	128	0.38	122.7	128.7	112	0.34
189	132.9	192.8	153	0.45	129.1	165.9	137	0.40
213	137.1	227.7	174	0.51	133.8	199.8	158	0.45

B. $C_M = 100$ mM; $C_H = 10$ mM.

C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.6	55.6	9.04	9.20	0.042
42.8	78.7	22.6	23.6	0.090
60.9	90.9	36.6	37.5	0.127
77.3	98.9	50.2	50.2	0.160
92.1	104.7	63.1	61.6	0.187
112.0	111.3	82.0	77.1	0.231
137.3	118.3	108.2	97.2	0.28
159	123.4	132.4	114	0.32
189	129.5	168.5	138	0.38
213	133.7	199.0	157	0.42

Table 2. Determination of the complex formation function of the copper fluoride system.

A. C_M = 50 mM; C_H = 10 and 25 mM.

C_H mM →	10				25			
C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.8	56.7	9.44	9.64	0.079	31.0	3.41	2.81	0.044
43.6	79.8	23.6	24.7	0.174	64.5	12.85	13.38	0.126
62.5	92.2	38.5	39.3	0.248	81.6	25.3	26.4	0.206
79.9	100.5	53.5	53.1	0.31	92.3	38.6	39.5	0.27
95.9	106.5	67.8	65.4	0.38	99.7	51.8	51.5	0.33
110.5	111.4	82.3	77.4	0.43	105.2	64.4	62.7	0.38
137.0	118.8	110.3	98.6	0.52	113.6	89.8	83.3	0.48
160	124.4	137.7	118	0.58	119.6	113.9	101	0.55
189	130.4	174.6	142	0.68	126.1	147.3	125	0.66
213	134.8	207.8	163	0.74	130.8	177.4	144	0.73

B. C_M = 100 mM; C_H = 10 mM.

C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.6	51.9	7.81	7.83	0.058
42.8	74.3	18.95	19.8	0.130
60.9	86.3	30.5	31.6	0.190
77.3	94.3	41.8	42.5	0.239
92.1	100.1	52.6	52.3	0.28
112.0	106.5	67.8	65.4	0.35
137.3	113.5	89.4	83.1	0.42
159	118.6	109.4	98.1	0.48
189	124.7	139.3	119	0.57
213	129.1	165.9	137	0.63

The *sodium fluoride* was of the second preparation used for the uranyl fluoride measurements [3]. The *other chemicals* were also the same as used in this investigation.

Procedure. For each central ion three titrations were performed, the first two with C_M = 50 mM and C_H = 10 and 25 mM, the third with C_M = 100 mM and C_H = 10 mM. The values of C_M and C_H were kept constant throughout every titration. The titrations were all performed with the same reference electrode RE (with $[\mathrm{H}]_0$ = 10 mM) as was used before [3].

The quinhydrone electrode functioned well in the present solutions. Even at the highest concentrations of metal ions used, C_M = 100 mM, the potentials differed only slightly from the values calculated from known values of $[\mathrm{H}^+]$. Thus the emf $E^{(i)}$ measured initially which should be zero for the series of C_H = 10 mM is found to be 1—2 mV for C_M = 100 mM. This deviation may be caused by several factors which probably co-operate. The changes of the ionic medium may produce changes in the activity coefficients and the liquid junction potentials and some complex formation between the metal ion and the hydroquinone may occur. These slight deviations certainly have very little influence on the calculation of [A] (and $\bar{n}_M$) as E_H is the emf of a cell with the same value of C_M in both half-cells. The potentials measured reached equilibrium almost at once and as a rule they could be reproduced within 0.2 mV.

Table 3. Determination of the complex formation function of the zinc fluoride system.

A. C_M = 50 mM; C_H = 10 and 25 mM.

C_H mM	10				25			
C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$	E_H mM	X_H	[A] mM	$\bar{n}_M$
22.8	58.2	10.00	10.27	0.065	31.4	3.46	2.68	0.052
43.6	81.8	25.5	26.7	0.133	65.8	13.53	14.12	0.109
62.5	94.0	41.3	42.1	0.190	83.0	26.7	27.9	0.174
79.9	102.2	57.2	56.4	0.244	93.6	40.7	41.4	0.226
95.9	108.5	73.4	70.1	0.28	100.8	54.1	53.6	0.28
110.5	113.5	89.4	83.0	0.31	106.6	68.1	65.8	0.32
137.0	120.9	119.9	105.8	0.38	115.1	95.3	87.5	0.39
160	126.2	147.9	125	0.44	121.0	120.4	106	0.45
189	132.1	186.8	150	0.52	127.4	155.1	130	0.54
213	136.4	222	171	0.58	132.1	186.8	150	0.61

B. C_M = 100 mM; C_H = 10 mM.

C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.6	53.8	8.41	8.50	0.050
42.8	76.6	20.8	21.8	0.109
60.9	88.8	33.6	34.7	0.156
77.3	96.8	46.2	46.6	0.197
92.1	102.6	58.1	57.1	0.237
112.0	109.4	76.0	72.3	0.28
137.3	116.3	99.9	91.0	0.34
159	121.5	122.8	108	0.38
189	127.6	156.3	131	0.45
213	131.8	184.6	148	0.51

RESULTS

The complex formation functions are given in Tables 1—3 and plotted in Figs 1 and 2. For the three ions measured, this function is seen to be independent of both C_M and C_H within the experimental errors. It must be remembered that the errors are fairly large when weak complexes are determined by measurements of [A]. Thus no polynuclear complexes, no complexes containing HF_2^- and no hydroxo complexes exist in perceptible amounts in the solutions investigated. The mononuclear complex formation between metal ion and F^- is therefore the only process which need be considered.

The complexity constants are calculated from the complex formation functions in the same way as before [4]. When integrating the function $\bar{n}_M/[A]$ in order to find X_M it is suitable to choose [A] = 10 mM as the lower limit of integration. The results are in Table 4. As seen the function X_{1M} is virtually constant over the whole range of [A] for all the systems measured, with the

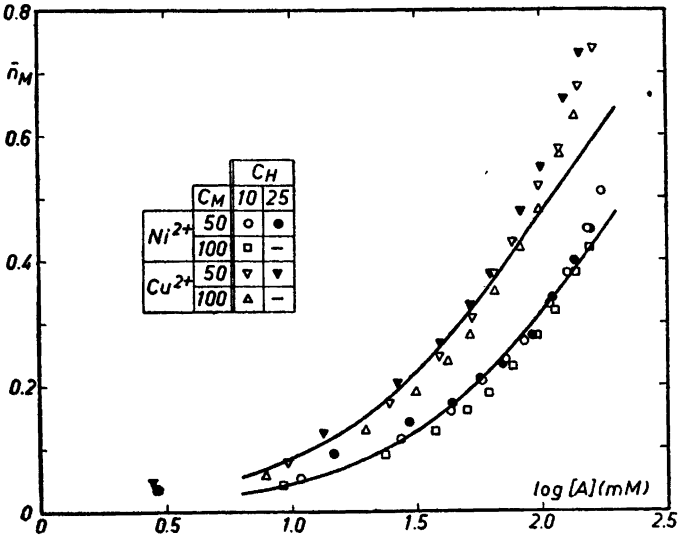

Fig. 1. The complex formation functions of the nickel and copper fluoride systems. The signs refer to different titrations as indicated by the scheme given in the fig. The curves are obtained from the values of β_1 found.

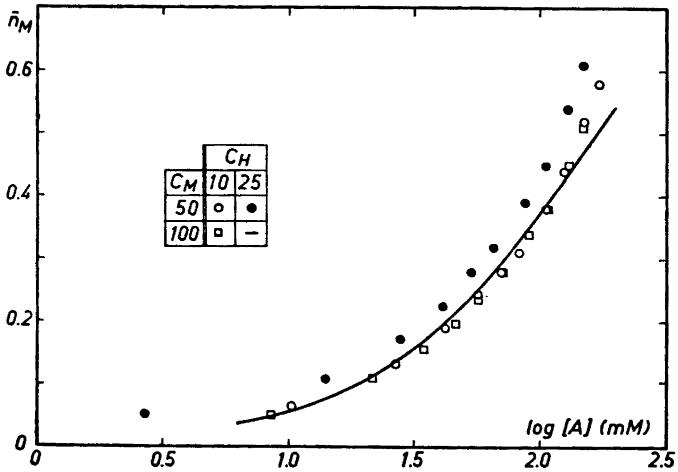

Fig. 2. The complex formation function of the zinc fluoride system. The signs refer to different titrations as indicated by the scheme. The curve is obtained from the value of β_1 found.

Table 4. Computation of the first complexity constant β_1 for the three systems measured.

M →	Ni^{2+}		Cu^{2+}		Zn^{2+}	
[A] mM	$\frac{X_M([A])}{X_M(0.01)}$	X_{1M} M^{-1}	$\frac{X_M([A])}{X_M(0.01)}$	X_{1M} M^{-1}	$\frac{X_M([A])}{X_M(0.01)}$	X_{1M} M^{-1}
0	0.956		0.920		0.945	
10	1.000	4.6	1.000	8.7	1.000	5.8
25	1.071	4.8	1.120	8.3	1.087	6.0
40	1.136	4.7	1.238	8.7	1.168	5.9
60	1.219	4.6	1.396	8.6	1.275	5.8
80	1.301	4.5	1.561	8.7	1.383	5.8
100	1.383	4.5	1.736	8.9	1.493	5.8
120	1.467	4.5	1.921	9.1	1.608	5.8
140	1.555	4.5	2.116	9.3	1.727	5.9
160	1.645	4.5	2.324	9.6	1.853	6.0
180	1.739	4.5	2.545	9.8	1.985	6.1
200	1.837	4.6	2.782	10.2	2.124	6.2
β_1 M^{-1} →	4.6 ± 0.5		9 ± 1		5.9 ± 0.6	

exception of the highest values of Cu^{2+}, where a slight upward trend is found. Thus the first complex MF^+ is the only one existing in measurable amounts in the present solutions. Therefore the value of β_1 is taken for each ion as the mean of the values of X_{1M} over the whole range of [A] (with the highest values for Cu^{2+} left out). The values of β_1 thus found are given in Table 4, with the random errors indicated.

As could be foreseen from their charge and ionic radii, Ni^{2+}, Cu^{2+}, and Zn^{2+} form only weak fluoride complexes with the stability order $Ni^{2+} < Cu^{2+} > Zn^{2+}$. Nevertheless the fluoride complexes are all, as expected, much stronger than the complexes formed by the other halides. Thus in the case of Cu^{2+} and Zn^{2+}, β_1 of the fluoride system is 10 times greater than β_1 of the next strongest system, the chloride [8,9]. In the case of Ni^{2+}, there are no quantitative data about the other halides, but they are typical strong electrolytes (*cf.*[1] and references therein). From the sequence of ionic radii one would rather expect them to be less stable than the corresponding complexes of Cu^{2+}.

The results of this investigation thus agree in all respects with the predictions made on the basis of the views put forward in I. Moreover the ions Ni^{2+}, Cu^{2+}, and Zn^{2+}, which were previously considered as only probable members of the first group of central ions (as defined in I), are now shown as certainly belonging to this group.

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