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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

COMPLEX FORMATION IN MOLTEN SALTS STUDIED BY DISTRIBUTION METHODS

II. Ca - CHLORO COMPLEXES IN K-Li-NO_3

by

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1964

Joint Nuclear Research Center
Ispra Establishment - Italy
Materials Department

Reprinted from
ZEITSCHRIFT FÜR NATURFORSCHUNG
Vol. 18 a, No. 7 - 1963

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Sonderabdruck aus der ZEITSCHRIFT FÜR NATURFORSCHUNG Band 18 a, Heft 7, 1963
Verlag der Zeitschrift für Naturforschung, Tübingen

Complex Formation in Molten Salts Studied by Distribution Methods

II. Cd—Chloro Complexes in K-Li-NO_3

By J. O. Liljenzin, H. Reinhardt, H. Wirries * and R. Lindner

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(Z. Naturforschg. 18 a, 840—842 [1963]; eingegangen am 22. April 1963)

With a distribution technique described earlier the stability constants of cadmium-chloro complexes were evaluated. The values obtained are practically identical with those obtained by other authors with polarographic methods with the exception of the first complex constant which was found to be considerably higher (832) than that described in the literature (200).

In an earlier paper [1] we have studied the distribution between grains of alumina and nitrate melts of cations more or less complexed by the addition of chloride ion. From the dependence of the distribution coefficient on chloride concentration various complex constants can be evaluated in a similar way as has been shown for aqueous solutions in many cases.

Compared with our first paper we introduce a change of the treatment of the information gained by the experiments inasmuch as the values for the complex constants are obtained purely analytically by a least square method.

Theory

We start from the equation

$$K_d = \frac{\lambda_0 + \sum_{n=1}^{\infty} \beta_n \lambda_n [A]_l^n}{1 + \sum_{n=1}^{\infty} \beta_n [A]_l^n} . \qquad (1)$$

$K_d = \sum_{n=0}^{\infty} [MA_n]_s / \sum_{n=0}^{\infty} [MA_n]_l$ is the distribution coefficient, λ_0 is the value of K_d in the absence of complex forming anions, $\lambda_n = [MA_n]_s/[MA_n]_l$ is the distribution coefficient for the n-th complex, $\beta_n = [MA_n]_l/[M]_l [A]_l^n$ is the complexity product for formation of the complex MA_n, and $[A]_l = C_{Al}$ is the concentration of the free complex forming anions in the liquid phase. Introducing the following simplifications and substitutions, $y = K_d$, $X = [A]_l$ and $\alpha_n = \beta_n \lambda_n$, eq. (1) is consequently transformed to

$$y = \sum_{n=0}^{\infty} \alpha_n x^n / \sum_{n=0}^{\infty} \beta_n x^n . \qquad (2)$$

The deviation u_i is defined as

$$u_i = \left(y_i \sum_{n=0}^{\infty} \beta_n x_i^n - \sum_{n=0}^{\infty} \alpha_n x_i^n \right) . \qquad (3)$$

A certain weight, w_i, can be assigned to each measured point, thus compensating for the different precisions. According to the wellknown X^2-method

$$w_i = \frac{1}{\Delta_{y_i}^2} \qquad (4)$$

where Δy_i stands for the standard deviation.

The sum, U, of the squared and weighted deviations is

$$U = \sum_{i=1}^{I} w_i u_i^2 . \qquad (5)$$

When U is minimized the following system of equations is obtained for the α's and β's

$$\sum_{i=1}^{I} w_i y_i x_i^{k_1} \left(y_i \sum_{n=0}^{N} \beta_n x_i^n - \sum_{n=0}^{N} \alpha_n x_i^n \right) = 0 ; \quad k_1 = 1, 2, \ldots, K_1 , \qquad (6\,a)$$

$$\sum_{i=1}^{I} w_i x_i^{k_2} \left(y_i \sum_{n=0}^{N} \beta_n x_i^n - \sum_{n=0}^{N} \alpha_n x_i^n \right) = 0 ; \quad k_2 = 1, 2, \ldots, K_2 \qquad (6\,b)$$

where $K_1 = N$ and K_2 has the same value as the highest index of α. The solution to this equation system gives the best values for the α's and β's.

Considering the variation of the measured distribution coefficient for a certain anion concentration

* In partial fulfilment of a planned thesis to be presented to the Faculty of Science of the Technical University of Brunswick (Germany).

[1] J. O. Liljenzin, H. Reinhardt, H. Wirries and R. Lindner, Complex Formation in Molten Salts; Co(II)-chloro-complex in K—Li—NO_3; Radiochimica Acta, in press.

with the cadmium concentration on the alumina it was necessary to recalculate K_d to a new constant K_d^* corresponding to a low and constant loading on the alumina [2, 3]. For comparison reference is made to similar methods which can be found in the literature [4–7].

To carry out the numerical calculations a FORTRAN-program was written and run on the computer IBM-7090.

Experiments

As described in our earlier paper [1] equilibrium of the distribution of the more or less complexed ions between γ-Al_2O_3 and an eutectic melt of $K-Li-NO_3$ was obtained in pyrex test tubes at 160 °C. By filtration the phases were separated and the radioactivity of the melt, containing Cd-115^m, was measured from which the distribution coefficient could be calculated.

The chloride concentration was determined by potentiometric titration with silver nitrate. The amount of alumina powder used in each experiment was determined after washing with water and drying.

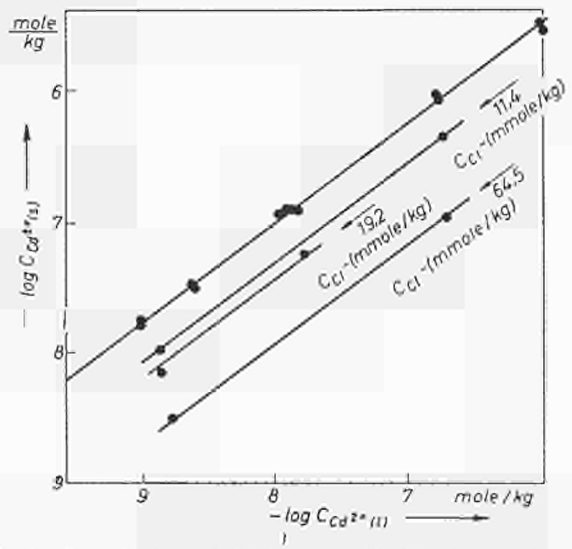

Fig. 1. Distribution of Cd between $K-Li-NO_3$ melt and alumina at 160 °C as function of Cd concentration at various chloride concentrations.

Results

First of all the distribution isotherm of pure cadmium and complexed cadmium between the solid and liquid phase had to be checked. The results are represented in Fig. 1.

It is evident from this figure that the slope of the curves is not one, but 0.7. This means that K_d is a function of the cadmium concentration on the alumina which could partly be explained by the formation of dimer molecules [8]. Nevertheless the slope seems to be independent of the chloride concentration.

The recalculated values, K_d^*, which were used for the calculation of the complex constants are assembled in Fig. 2. The experimental errors as discussed above are contained in Table 1.

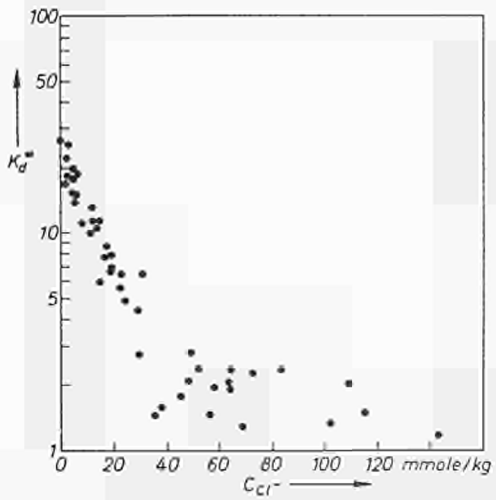

Fig. 2. Distribution of Cd between $K-Li-NO_3$ melt and Al_2O_3 as function of chloride concentration.

Finally according to equations (6a) and (6b) the constants for stepwise complex formation are calculated and the values are given in Table 2, first line. The same table contains the respective values obtained by Christie and Osteryoung [9] and Inman [8].

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[9] J. H. Christie and R. A. Osteryoung, J. Amer. Chem. Soc. **82**, 1841 [1960].

Nr.	C_{Cl} (m mole/kg)	K_d^*	error %	w_i
0	—	26.2	—	—
1	2.15	22.0	6.3	0.521
2	4.49	17.5	8.2	0.486
3	13.0	10.5	10.6	0.860
4	19.3	7.94	12.6	1.00
5	29.7	4.41	21.8	1.08
6	49.0	2.73	31.8	1.33
7	73.1	2.29	31.6	1.91
8	103	1.36	44.7	2.71
9	144	1.19	47.3	3.16
10	2.82	18.1	12.6	0.192
11	5.19	15.2	12.2	0.291
12	7.47	11.8	13.8	0.377
13	11.2	9.68	18.1	0.309
14	15.0	11.7	17.9	0.228
15	19.3	6.75	19.0	0.610
16	24.8	4.89	26.3	0.606
17	30.9	6.46	21.7	0.505
18	46.4	1.76	66.4	0.730
19	64.2	2.08	52.8	0.830
20	110	2.01	54.3	0.840
21	3.00	25.1	5.2	0.588
22	5.70	19.5	5.1	1.01
23	6.40	18.5	5.3	1.04
24	11.4	11.1	7.5	1.44
25	16.8	7.67	10.0	1.70
26	19.2	6.61	9.8	2.38
27	22.8	6.37	9.4	2.79
28	30.4	2.75	15.9	5.24
29	39.7	1.59	24.6	6.54
30	48.8	2.08	23.1	4.31
31	57.0	1.47	27.4	6.14
32	64.8	1.91	24.9	1.61
33	69.3	1.29	24.7	1.64
34	84.3	2.66	21.9	2.94
35	116	1.48	29.3	5.28
36	2.27	16.39	5.3	1.325
37	5.12	13.87	5.4	1.783
38	6.48	14.77	6.4	1.119
39	11.2	13.03	7.1	1.168
40	15.2	5.87	9.6	3.150
41	17.6	8.77	8.8	1.679
42	22.9	5.60	12.1	2.178
43	30.5	2.76	18.4	3.877
44	36.2	1.48	31.1	4.660
45	52.3	2.403	23.1	3.246
46	58.3	1.95	24.8	4.275
47	65.4	2.37	23.5	3.224

Table 1. Experimental Error of Determination.

Two things can be seen clearly:

As observed in a number of cases the substitution of sodium by lithium in nitrate melts does not lower the complex formation constants of metal halogen complexes. On the contrary, these constants are increased.

Secondly, cadmium shows a very high constant of the formation of the first chloro complex which is already evident from Fig. 2. The value stated by us

	$n=1$	$n=2$	$n=3$	$n=4$
Our values	832	2.300	120.000	600.000
Values according to CRISTIE and OSTERYOUNG[9] (Li-K-NO_3 Eut.)	200	3.000	120.000	600.000
Values according to INMAN[8] (Na-KNO_3 Eut.)	40	200	11.800	—

Table 2. $CdCl_n$ Complex Formation Constants (β_n).

is even higher than that found by CHRISTIE and OSTEROUNG, but our method should give better results in the low chloride concentration range than the polarographic method used by those authors.

The mathematical method used in this paper seems to us of a more universal use than that in our previous paper [1]. We intend to investigate similar systems, especially those of uranium and fission products in nitrate melts or other molten salts.

Acknowledgement

The support by teams of the Ispra Computer Centre CETIS and the reactor Ispra 1 is gratefully acknowledged.