Electromigration Mobilities of Cadmium in Molten Cadmium Bromide, Pure and with Dissolved Cadmium Metal

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The mass effect of the cadmium ions for electromigration in pure molten cadmium bromide has been determined to -0.075 ± 0.004. An electromigration experiment with a solution of cadmium metal in molten cadmium bromide is discussed. It is concluded that the dissolved metal has a smaller mobility than the cadmium ions.

There are certain regularities in the mass effects of the cation for electromigration in molten metal halides [1]. This report covers a couple of experiments with cadmium bromide, made in order to determine the mass effect, and one analogous experiment with a solution of cadmium metal in cadmium bromide, made in order to see if it would give useful information about the nature of this solution [2].

Experimental

Data on the experiments are given in Table 1. In all the experiments cells of Supremax glass were used (Fig. 1). The separation columns had an inner diameter of about 4 mm and were packed with Supremax powder. A simple furnace of Supremax tubing was used for heating the cell and the temperature was measured with Chromel-Alumel thermocouples, placed in contact with the cell. For experiment no. 4 the temperature in the separation column was calculated using the results of HERZOG and KLEMM [3]. The enrichment of the light isotopes of cadmium was studied at the boundary $LiBr/CdBr_2$ (or Cd, $CdBr_2$) in the systems

I: cathode+$Br_2/LiBr/CdBr_2$/anode
II: cathode+$Br_2/LiBr/Cd, CdBr_2$/anode

(Cd, $CdBr_2$ denotes a solution of metal in the salt), and in system II also the change in concentration of

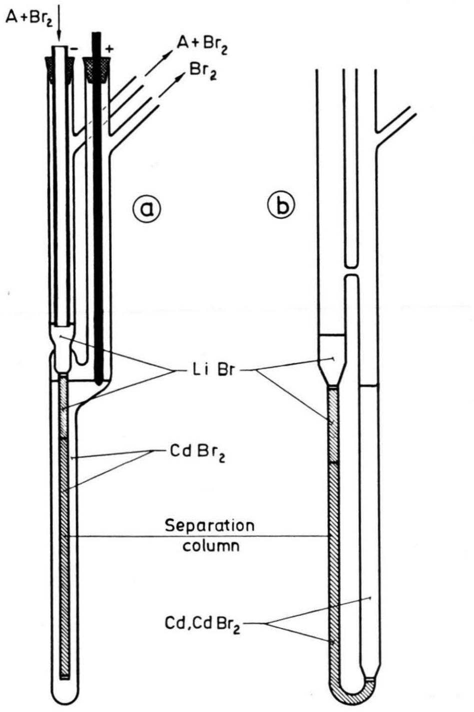

Fig. 1. Electrolysis cells. a) Experiments nos. 1—3. b) Experiment no. 4.

Experiment no.	1	2	3	4
System	I	I	I	II
Length of separation column, cm	24	24	24	28
Column packing, grain size, mm	0.15 — 0.20	0.15 — 0.20	0.12 — 0.15	0.10 — 0.12
Temperature in column, °C	610 ± 20	620 ± 20	620 ± 20	630 ± 30
Electrolysis time, hours	13	67	50	50
Transported charge (Q), Ah	3.29	15.06	16.03	10.05
Maximum current density, A/cm^2	4.1	4.4	5.8	3.6
Uncorrected mass effect ($-\mu$)	0.0560	0.0735	0.0697	0.0800

Table 1.

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[1] A. NEUBERT and A. KLEMM, Z. Naturforschg. **16 a,** 685 [1961].

[2] J. D. CORBETT, Fused Salts (Ed. B. R. SUNDHEIM), McGraw-Hill, New York 1964, p. 341.

[3] W. HERZOG and A. KLEMM, Z. Naturforschg. **13 a,** 7 [1958].

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the dissolved metal. As anode a carbon rod was used, as cathode a graphite pipe through which a mixture of bromine vapor and argon gas bubbled into the melt, thus preventing formation of lithium metal. The apparatus supplying the gas stream has been described earlier [4]; in experiments nos. 2–4 a back-flow arrangement was used for the bromine (Fig. 2). A copper coulometer measured the transported charge. Before the experiments, LiBr was dried by melting it under vacuum. $CdBr_2 \cdot 4\,H_2O$ was either treated in the same manner or dehydrated according to Hägg et al. [5]. The metal solution was made by melting a finely divided mixture of metal and bromide in the cell.

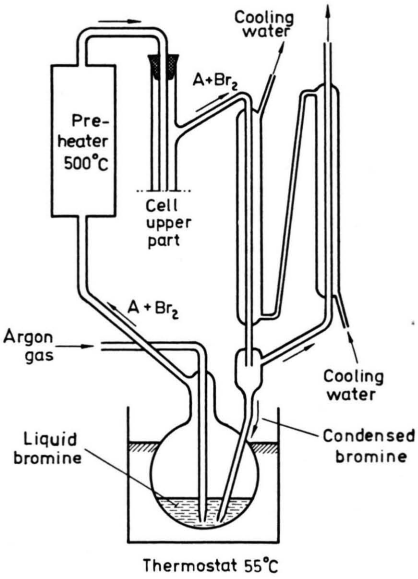

Fig. 2. Principle of the bromine back-flow apparatus, used in experiments nos. 2–4.

After the electrolysis was finished, the cell was cooled and the separation column divided into samples. The cadmium bromide was dissolved by boiling the samples in water. For experiment no. 4, the residues of the samples were treated with nitric acid to dissolve the cadmium metal. It should be remarked here, that this cell was cooled rather slowly, since rapid quenching might give finely divided metal partly reacting with water [6]. The amounts of cadmium in the solutions were determined by titration with EDTA, using Erio-T as an indicator [7]. For some of the samples, cadmium was separated as sulphide, which was dissolved in hydrochloric acid [8], and this solution was used for the titration. For other samples, the titration was made in the original solution, masking with ammonium fluoride [9]. In a few cases both methods were used for the same samples, and the results were in good agreement. For a few samples the filtrate from the precipitation of cadmium sulphide was analysed in a flame spectrophotometer (Beckman DU) for lithium, sodium, potassium and calcium. From the solutions cadmium metal was deposited electrolytically on copper-wire cathodes. These samples were used for the isotope abundance analyses, which were made in a mass spectrometer [10], equipped with an electron-impact ion source and a small furnace for the heating of the sample. An electrometer tube and a DC-amplifier were used for the measurement of the ion currents. To diminish memory effects, the ion source and the furnace were heated for several hours between analyses, and the samples were taken in order of increasing (or decreasing) enrichment during each series of analyses.

Results

The results of the analyses are summarized in Table 2 and Fig. 3. The abundance of the isotope with mass number A relative to isotope 116 in sample no. r is called V_{Ar}, and the same quantity in the samples of original composition is called V_{A0}. It appears that for each sample $\log(V_{Ar}/V_{A0})$ is very nearly proportional to $(116-A)$; similar relation-

Experiment no.	Sample no.	Amount of cadmium, millimoles	$k_r \cdot 10^2$	W_r
1	1	0.171	0.469	13.88
	2	0.542	0.792	14.24
	3	1.02	0.616	14.05
	4	1.07	0.152	13.54
2	1	0.182	4.26	19.29
	2	0.349	3.91	18.58
	3	1.20	2.52	16.49
	4	1.76	1.01	14.55
	5	1.91	0.238	13.69
3	1	0.036	2.60	16.58
	2	0.278	3.99	18.78
	3	0.813	3.26	17.54
	4	2.03	1.49	15.12
	5	2.00	0.281	13.69
4	1	1.45	2.04	15.84
	2	2.02	1.03	14.55
	3	2.43	0.199	13.60

Table 2. Results of the analyses of the enriched samples. The numbering of the samples starts at the boundary $LiBr/CdBr_2$ (or Cd, $CdBr_2$). $W_0 = 13.37$ for all the experiments.

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[4] A. Lundén, S. Christofferson, and A. Lodding, Chalmers Tekn. Högskolas Handl. No. 221, Göteborg 1959.

[5] G. Hägg, R. Kiessling, and E. Lindén, Arkiv Kemi, Mineral, Geol. **16 B**, No. 4, 1 [1943].

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[7] G. Schwarzenbach, Die chemische Analyse, Band 45, Stuttgart 1955, p. 69.

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[10] I. Holmlid, A. Lodding, and M. Lövenby, to be published.

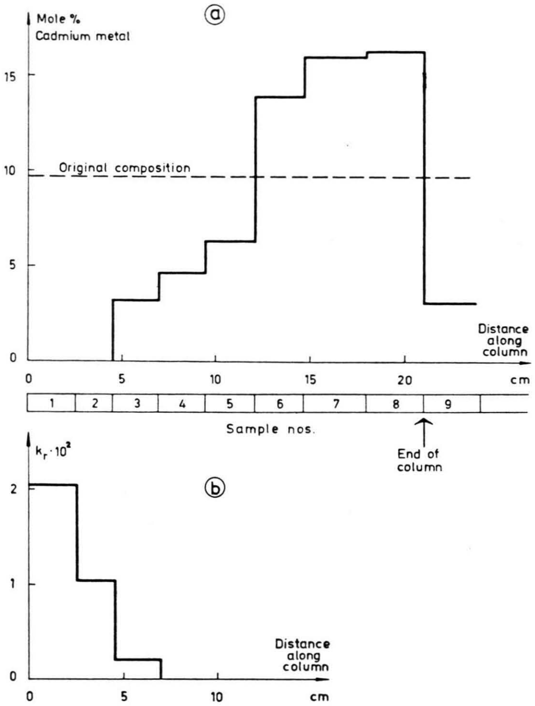

Fig. 3. Results of the analyses for experiment no. 4. a) Proportion of metal. b) Isotope enrichment (k_r; see text).

ships have been used earlier, see e. g. [11]. For each sample the quantity k_r has been calculated as the weighted mean of $[\log(V_{Ar}/V_{A0})]/(116-A)$. A calculation of the variance of this later quantity [12] from the variances of the V_{A0}:s shows that as weights [13] could be used $(116-A)^2$ for $A=110$ to 114, and $\frac{1}{3}(116-A)^2$ for $A=106$, 108.

The usual principle was used for calculating the mass effect [14]. Expressed in quantities for any pair of isotopes (mass numbers A and B) the mass effect is

$$\mu = \frac{b_{AB}}{b_\mathrm{m}} \cdot \frac{A_\mathrm{m}}{A-B} = \frac{F\,Z\,A_\mathrm{m}}{Q} \cdot \frac{N_A/x_A - N_B/x_B}{A-B} \,. \tag{1}$$

Here b_{AB} is the mobility of isotope A relative to isotope B, b_m the mean mobility of the cations relative to the anions and x_A the molar fraction of isotope A. These quantities refer to the original composition of the melt. N_A is the total amount of isotope A in the enriched region at the end of the experiment, A_m the mean mass number, F FARADAY's constant, Z the charge number of the cations and Q the transported charge. Eq. (1) can obviously be generalized to

$$\mu = \frac{F\,Z\,A_\mathrm{m}}{Q} \cdot \frac{\mathrm{d}(N_A/x_A)}{\mathrm{d}A}$$

where A is considered as a continuous variable. Using the expressions for N and x and the relation

$$\log(V_{Ar}/V_{A0}) = k_r(116-A)$$

the result is

$$\frac{\mathrm{d}(N_A/x_A)}{\mathrm{d}A} = -2.303\; W_0 \sum_r \frac{n_r\, k_r}{W_r} \cdot 10^{k_r(116-A)} \,. \tag{2}$$

n_r is the amount of cadmium in sample no. r and $W = \sum V_A$, the sum taken over all the isotopes. Eq. (2) gives a slight dependence of μ on A. Here A was taken as 111, i. e. the midpoint of the mass number interval.

Q should be the charge transported by the cadmium ions. The chemical analyses show, however, that the samples contain small amounts of impurities, probably coming from the glass cell, and of lithium, that contribute to the charge transport. The mass effects thus come out too small. An estimation, based on the determined amounts of impurities and on the mobilities of these in the corresponding pure molten bromides, gives an upper limit of the correction to the mass effect of about 10 percent for experiments nos. 2 – 4. The result of experiment no. 1 is less reliable from several causes: The enrichments are smaller, and disturbances during the experiment have probably caused larger amounts of lithium and impurities to reach far down into the separation column. An indication of the unusual conditions is given by the effective coefficient of diffusion [14], which was about 3 times larger than in experiments 2 – 4.

The mass effects given in Table 1 are uncorrected. The value quoted for the bromide in Table 3 is the mean of the results from experiments nos. 2 and 3, increased by 5 percent. The error covers the scatter in the results and the 0 – 10 percent correction interval. Table 3 shows also the mass effects found for cadmium in some other of its halides. ROMANOS and KLEMM showed [15] that cadmium iodide does not fit with the previously observed regularities [1]. The present result for the bromide may be said to confirm

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[11] A. KLEMM, H. HINTENBERGER, and W. SEELMANN-EGGEBERT, Z. Naturforschg. **3 a**, 172 [1948].

[12] A. HALD, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 118.

[13] l. c. [12], p. 244.

[14] A. KLEMM, Z. Naturforschg. **1**, 252 [1946].

[15] J. ROMANOS and A. KLEMM, Z. Naturforschg. **19 a**, 1000 [1964].

that the mass effect for cadmium in its halides is less dependent on the mass of the anion than for other metal ions in their halides. Another possibility is, although unlikely, that the mass effect found in the chloride is too large, and that the mass effects of the cadmium halides all lie about the same amount below the curve for the $1-1$ salts [1]. It should be remarked that the mass effects in Table 3 are not measured at corresponding temperatures (relative to the melting point), and that a temperature dependence is possible [16].

The results of the analyses of experiment no. 4 are given in Fig. 3. In the metal part of sample no. 3 no isotope enrichment was found; k_3 in Fig. 3 refers to the bromide part, which had a small enrichment. This difference between the two parts of the sample indicates that the dissolved metal was concentrated at the anode side of the sample and the enriched material at the cathode side. The distribution of metal concentration is partly unexpected (cf. [17]). The small concentration in the anode compartment (sample no. 9) is caused by convection currents bringing down nearly metal-free salt from the vicinity of the anode, where the dissolved metal is oxidized to ions, whereas the high concentration in samples nos. $6-8$ is not easily explained. It is evident that the unknown variation with time in the metal concentration precludes calculations of mobilities. Some conclusions can be drawn from the available information, however:

1. The small metal concentration in samples nos. $1-5$ was expected, as the melt in this region changed in colour during the electrolysis and finally became transparent in the vicinity of the boundary LiBr/Cd, $CdBr_2$. This means that the dissolved metal has a smaller mobility than the cadmium ions, as is the case for Cd, $CdCl_2$ [17].

2. From an experiment of this kind, where the original metal concentration remained throughout the experiment in part of the separation column, it would be possible to calculate

$$\beta_{AB}=\frac{b'_{AB}}{b^+_{\mathrm{m}}}=\frac{b^+_{AB}+[x^0/(1-x^0)]\,b^0_{AB}}{b^+_{\mathrm{m}}}=\frac{F\,Z}{Q}\left(\frac{N_A}{x_A}-\frac{N_B}{x_B}\right) \tag{3}$$

where superscript + means cadmium ions and 0 means dissolved metal. x^0 is the mole fraction of dissolved metal, and N_A is the total amount of isotope A, i.e. cadmium both as bromide and as metal. (The expressions "dissolved metal" and "cadmium ions" used here does not mean a choice of a particular model for the metal solution, but refers only to the two parts of the samples after solidification.) Measurements of b^+_{m} and β_{AB} at different metal concentrations would give b'_{AB} as a function of x^0, and this might be useful for testing models for the solution. In experiment no. 4, x^0 changed during the electrolysis. As the mass effect probably depends on x^0, the quantity

$$\beta_{AB}\cdot A_{\mathrm{m}}/(A-B)$$

for this experiment is an average mass effect. The calculation gives -0.084 ± 0.004 for this quantity, if the correction of 5 percent is applied. The numerical value seems significantly larger than the mass effect in the pure bromide. If b^+_{m} is independent of x^0 (this holds for Cd, $CdCl_2$ [18]), then the experiments indicate that b'_{AB} is larger than b_{AB} in the pure salt.

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A preliminary report on this work was read at the Conference of the Swedish National Committee for Physics in June, 1963. A summary of this has been published in Arkiv för Fysik [19].

Anion	Mass effect of the cation ($-\mu$)	Temp. (T) °K	Reference	Melting point (T_{m}) °K	$\dfrac{T}{T_{\mathrm{m}}}$
Cl^-	0.067	970	11	841	1.15
Br^-	0.075 ± 0.004	890	this work	840	1.06
J^-	0.0764 ± 0.003	850	15	660	1.29

Table 3. Mass effects of the cations in cadmium halides.

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[16] W. Fischer, K. Heinzinger, W. Herzog, and A. Klemm, Z. Naturforschg. **17 a**, 799 [1962].

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