

Kinetics of the Exchange of Cadmium between Amalgam and Cadmium Salt Solutions at Equilibrium Potential.

II. The Influence of Complex Formation

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In a previous paper by the present author¹ it was mentioned that the cadmium exchange reaction could be divided into different partial processes, *e. g.*, the electron exchange including the loosening and coordinating of ligands, and the transport of cadmium in both phases up to the interface. For the analogous zinc exchange Randles and Somerton² have shown by their impedance measurements that the rate of the electron exchange is influenced by halogenide ions, and for that reason it is to be expected that these ions influence the electron exchange for cadmium also, especially as the halogenide complexes of cadmium are much stronger than those of zinc (*cf.* Leden³, Sillén and Liljeqvist⁴).

On the other hand it was proved in the previous investigation by the use of a radioactive isotope that in cadmium perchlorate solutions under the concentration conditions chosen the over-all exchange reaction at equilibrium potential difference between amalgam and solution was controlled by the diffusion of cadmium ions through the Nernst diffusion layer of the solution. Thus, as long as the same rate law is valid, the effect of complex formation upon the whole exchange reaction is determined by the difference in diffusibility of various complexes, and it is the aim of the present investigation to study this effect for some ligands that give complexes of medium strength with the cadmium ion.

THEORETICAL

In the previous investigation it was proved that the rate h of the cadmium exchange is proportional to the total cadmium concentration C of the perchlorate solutions and independent of the concentration q in the amalgam, that is:

$$h = k_0 \cdot C \quad (1)$$

where k_0 is called the rate constant of the process. An equation of the same form was derived on the basis of a diffusion-controlled exchange, and then the relation: $k_0 = \text{constant} \cdot \frac{D}{\delta}$ was obtained. Here D is the diffusion coefficient of the cadmium ion and δ the thickness of the Nernst diffusion layer of the solution. In our measurements k_0 has the dimension $\text{cm}^2 \cdot \text{g}^{-1}$, and the proportionality factor, simply called "constant", is equal to $\frac{s_0}{m_0} \lim_{x \rightarrow 0} \frac{dt}{dx}$ where s_0 and m_0 are the surface area and weight of an amalgam droplet and t the time of contact for the passage of the droplet through a solution layer of the thickness x . For the measurements below it will be shown that $\delta^{-1} \cdot \lim_{x \rightarrow 0} \frac{dt}{dx}$ no doubt has a constant value in the different measurement series. Then, if the the same rate law still holds, variations in the value of the rate constant obtained for different solutions can be referred to variations in the diffusion coefficient.

Now, if the cadmium solution contains a ligand A giving a system of mononuclear complexes of the type MA_j ($j = 1, 2, \dots, N$), each of these complexes takes part in the exchange process with an individual rate constant k_j and diffusion coefficient D_j . Furthermore, if we denote by α_j the fraction of the total cadmium concentration that is present as the complex MA_j , the expression for the rate of exchange becomes:

$$h = C \cdot \sum_{j=0}^N \alpha_j k_j \quad (2)$$

Then for the average rate constant k we have:

$$k = \sum_{j=0}^N \alpha_j k_j \quad (3)$$

and for the ligand number (Fronæus⁵) in the complex solution:

$$n = \sum_{j=1}^N j \alpha_j \quad (4)$$

When the solution contains some radioactive cadmium, Cd^* , the average constant k is, of course, also valid for the (Cd^*, Cd) and (Cd, Cd^*) processes (cf. Fronæus¹). Thus the differential equation, derived in the previous paper¹, for the radioactive exchange takes the form

$$\frac{d\bar{q}_a}{dx} = k \frac{C_a q_i - C_i q_a}{q_a + q_i} \quad (5)$$

for a complex solution. The subscripts a and i refer to radioactive and inactive cadmium respectively, and \bar{q}_a is an average concentration in the amalgam droplet, while q_a is the one close to the interface at the end of the contact time. From eq. (5) it is evident that $\frac{d}{dx} \left(\frac{\bar{q}_a}{C_a} \right)$ for $x = 0$ (i. e., $q_a = 0$) gives

the value of k . The determination can be performed graphically from a plot of \bar{q}_a/C_a against x . If the values of the quantities α_j are known for varying ligand concentrations and the corresponding k -values are obtained from the experiments, it is possible to calculate according to eq.(3) the rate constant k_j for the different complexes.

Such a calculation is, of course, quite formal, if the k_j -values obtained are not specific to the complexes in question but depend upon various factors. For instance, it cannot be excluded *a priori* that close to the amalgam the diffusion coefficient of a charged complex could be influenced by the magnitude of the potential difference between amalgam and solution. In the previous paper¹ it was proved that k_0 in perchlorate solutions was a constant and thus independent of the potential variations accompanying the changes of C . For a rather strong complex system, on the other hand, we have the possibility of keeping the concentration of the saturated complex MA_N constant but still being able to vary the potential by changing the excess of ligand. Then we can see whether k_N is dependent on the amalgam potential or not, and at the same time it should be evident whether a partial exchange of perchlorate ions of the neutral salt medium for the ligand could affect appreciably the k_N -values.

EXPERIMENTAL

Chemicals used. Stock solutions of sodium bromide, sodium iodide, and ammonium perchlorate of analytical grade were prepared and their concentrations were checked by the use of a cation exchanger in the hydrogen form. From carbon dioxide-free ammonia and ammonium perchlorate a buffer was obtained. The other chemicals used were prepared as before¹.

The radioactive exchange measurements were carried out with the apparatus of the previous investigation¹ and under the same experimental conditions. Thus the rate constants obtained in this investigation can be compared with the k_0 -value determined before. For a description of the calculation of the average concentration \bar{q}_a from the experimental data the reader

Table 1. Determination of the ligand number \bar{n} for some values of the bromide, iodide, and ammonia concentrations. The concentration of cadmium perchlorate is 5.00 mC.

C _{Br} - mC	<i>E</i> mV	\bar{n}	C _I - mC	<i>E</i> mV	\bar{n}	C _{NH₃} mC	<i>E</i> mV	\bar{n}
100	23.3	1.1	100	52.6	3.5	100	100.5	3.4
200	35.0	1.6	200	86.1	3.9	200	135.2	3.8
300	44.6	2.2	300	107.5	4.0	300	155.2	3.9
400	52.6	2.4	400	121.5	4.1	400	169.8	4.0
500	60.3	2.7	500	133.7	3.9			
600	66.7	3.0	600	142.2	4.2			
700	72.7	3.1	700	150.5	4.2			
800	77.0	3.1	800	155.5	3.8			
900	81.7	3.2	900	161.5	3.8			

Table 2. Measurements of the exchange of radioactive cadmium between amalgam and solution in the presence of different complex forming ligands.

Conc. of ligand mC	q_i % by weight	C_i mC	$C_a \cdot 10^{-1}$ cpm	x cm	C'_a cpm	m g	$\frac{\bar{q}_a}{C_a} \cdot 10^2$ $\text{cm}^2 \cdot \text{g}^{-1}$
$\text{C}_{\text{Br}^-} = 900$	1.00	2.23	1 140	3.0	32.0	1.002	4.2
	1.00	2.23	1 140	4.9	58.5	1.107	7.0
	1.00	2.23	1 140	8.1	95.0	1.080	11.6
	1.00	2.23	1 140	12.1	174	1.280	17.9
	1.00	13.4	5 870	3.1	203	1.249	4.2
	1.00	13.4	5 870	6.4	406	1.255	8.3
	1.00	13.4	5 870	10.0	743	1.570	12.0
	1.00	13.4	5 870	12.5	377	0.715	13.5
$\text{C}_{\text{Br}^-} = 450$	1.00	2.23	1 000	2.8	27.0	1.152	3.5
	1.00	2.23	1 000	5.7	42.0	0.908	6.9
	1.00	2.23	1 000	9.4	63.0	0.815	11.6
	1.00	2.23	1 000	11.8	129	1.366	14.2
$\text{C}_{\text{I}^-} = 900$	1.00	2.23	1 150	3.1	28.5	0.850	4.4
	1.00	2.23	1 150	5.0	54.0	1 142	6.2
	1.00	2.23	1 150	8.5	100	1.180	11.1
	1.00	2.23	1 150	11.2	122	1.093	14.5
$\text{C}_{\text{I}^-} = 450$	1.00	2.23	1 080	2.5	33.0	1.224	3.7
	1.00	2.23	1 080	5.3	35.5	0.740	6.7
	1.00	2.23	1 080	9.0	120	1.459	11.4
	1.00	2.23	1 080	11.6	134	1.252	14.9
$\text{C}_{\text{NH}_3} = 300$	2.00	2.23	672	3.8	24.5	1.253	4.4
	2.00	2.23	672	5.3	42.0	1.423	6.6
	2.00	2.23	672	8.1	44.0	1.040	9.5
	2.00	2.23	672	13.0	127	1.738	16.3

is referred to the earlier paper. The ligands selected were the bromide and iodide ions and ammonia. The complex solutions had the compositions:

$$\left\{ \begin{array}{l} (C_i + C_a) \\ 20 \\ C_A \\ (900 - C_A) \end{array} \right. \begin{array}{l} \text{mC Cd}(\text{ClO}_4)_2 \\ \text{mC HClO}_4 \\ \text{mC NaBr or NaI} \\ \text{mC NaClO}_4 \end{array} \quad \left\{ \begin{array}{l} (C_i + C_a) \\ 300 \\ 900 \end{array} \right. \begin{array}{l} \text{mC Cd}(\text{ClO}_4)_2 \\ \text{mC NH}_3 \\ \text{mC NH}_4\text{ClO}_4 \end{array}$$

The complexity has been investigated by Leden³ but at another ionic strength, and for that reason an approximate determination of the ligand number \bar{n} was performed potentiometrically. These measurements are reported in Table 1. E denotes the potential difference between the amalgam in a solution without the ligand and in the complex solution at the same cadmium concentration. For the calculation of \bar{n} the Bodländer equation (cf. Fronæus⁵) was used.

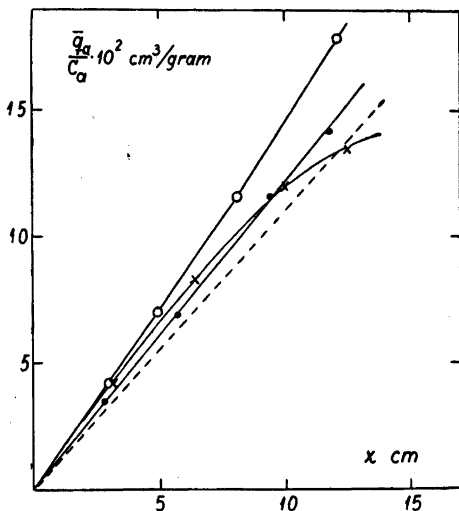


Fig. 1. $\frac{\bar{q}_a}{C_a}$ as a function of x for $q_i = 1.00$ per cent and with different complex bromide solutions. 1. $C_i = 2.23$ mC, $C_{\text{Br}^-} = 900$ mC (\circ); 2. $C_i = 13.4$ mC, $C_{\text{Br}^-} = 900$ mC (\times); 3. $C_i = 2.23$ mC, $C_{\text{Br}^-} = 450$ mC (\bullet). The slope of the dashed line indicates the value of k_0 .

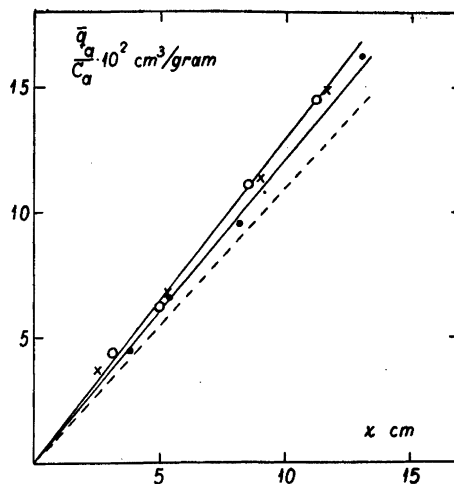


Fig. 2. $\frac{\bar{q}_a}{C_a}$ as a function of x for different complex iodide and ammonia solutions. 1. $q_i = 1.00$ per cent, $C_i = 2.23$ mC, $C_{\text{I}^-} = 900$ mC (\circ) or 450 mC (\times); 2. $q_i = 2.00$ per cent, $C_i = 2.23$ mC, $C_{\text{NH}_3} = 300$ mC (\bullet). The slope of the dashed line indicates the value of k_0 .

The values obtained in the exchange measurements are collected in Table 2. The first two series are carried out at the same bromide concentration (900 mC) but at different values of $C_i \approx C_i + C_a$. In Fig. 1 it is seen that the curves 1 and 2 have the same slope $k = 1.42 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$ for $x = 0$, and this shows that the rate constant is independent of the potential change of about 23 mV accompanying the variation of C_i . At this bromide concentration \bar{n} has the value 3.2, and then we can put approximately $\alpha_3 \approx 1$ and obtain $k_3 = 1.4 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$. For $C_{\text{Br}^-} = 450$ mC the corresponding curve 3 in Fig. 1 gives a somewhat lower value $k = 1.23 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$. Since in this case $\bar{n} = 2.5$, we put $\alpha_2 \approx \alpha_3 \approx 0.5$, and from eq. (3) we get: $k_2 + k_3 = 2.45 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$ and $k_2 = 1.1 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$, which is about the same as the k_0 -value determined in the previous paper.

The measurements on the iodide system were carried out at $C_{\text{I}^-} = 900$ mC and 450 mC. In both cases we had $\bar{n} = 4$, $\alpha_4 = 1$ and $C_i = 2.23$ mC. Thus the concentration of the exchanging saturated complex CdI_4^{2-} was constant, but the potential difference E changed about 35 mV. In Fig. 2 it is seen that the same curve 1 was obtained for the two iodide concentrations. From this result we conclude that either the expression $\delta^{-1} \lim_{x \rightarrow 0} \frac{dt}{dx}$ was constant and thus D specific for the complex and not appreciably dependent upon E and the change of the salt medium, or else both $\delta^{-1} \lim_{x \rightarrow 0} \frac{dt}{dx}$ and D depend upon the factors

mentioned, but the variations compensate each other, so that k remains constant. The first-mentioned alternative seems most probable and it will be shown in the following section that it must be valid, and then we have $k_4 = 1.30 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$. As the conditions must be similar in bromide solutions, it is likely that the rate constants k_2 and k_3 obtained above also have a physical meaning.

Finally a measurement series with ammonia as the ligand was performed. In this case the salt medium was 900 mC ammonium perchlorate and C_{NH_3} was 300 mC. From Table 1 we get $\bar{n} = 4$ and $\alpha_4 = 1$. Curve 2 in Fig. 2 gives us $k_4 = 1.20 \cdot 10^{-2} \text{ cm}^2 \cdot \text{g}^{-1}$.

DETERMINATION OF ABSOLUTE VALUES OF THE RATE CONSTANTS

As mentioned before the values of the reaction rate constants, hitherto determined in this paper and in the previous one, are relative, that is, they include the factor $\frac{s_0}{m_0} \lim_{x \rightarrow 0} \frac{dt}{dx}$, which depends upon the apparatus used. Though the aim of the present investigation has been attained very well by the determination of these relative values, it is for several reasons of great interest to know also the absolute values of the rate constants, and this necessitates a determination of the factor mentioned. In the following the performance of that part of the investigation will be described, and in connection with this the reader is referred to Fig. 1 of the previous paper¹, where the apparatus used is drawn.

When leaving the mouthpiece of the funnel A the liquid amalgam at first formed a thin, well-defined squirt which then divided into a row of small droplets. While the amalgam squirted out it was photographed against a luminous background, after which the radius r of the squirt was measured on the photographic plate by means of a microscope with an ocular scale. The graduation on the burette of the apparatus was photographed on the same plate and gave us a calibration of the ocular scale.

In addition, the weight w of the amalgam that was collected per unit time was determined by separate measurements. Then, if ρ is the density of the amalgam and v_0 the velocity of the squirt, the following is valid:

$$\rho \cdot \pi \cdot r^2 \cdot v_0 = w \quad (6)$$

and from this relation the value of v_0 was computed.

After this a determination of the average radius of the amalgam droplets formed was undertaken. For this purpose a lower part of the burette, where the squirt had divided into the row of droplets which were still present in the gas phase, was photographed in the same way. Then a time of exposure as short as 10^{-4} sec. (electronic light-flash) was chosen, so that a clear marking of the fast droplets was obtained on the plate. It was, however, impossible to measure directly on the plate the droplet radius, but this had to be determined indirectly. The velocity v of a droplet at a point at a known distance from the end of the coherent squirt was computed from the law of the free fall. The number of droplets per unit length was put equal to the average number n_1 per unit length within an interval, symmetrically surrounding the point. Then the average radius R was obtained from the relation:

$$\rho \cdot \frac{4\pi}{3} \cdot R^3 \cdot n_1 \cdot v = w \quad (7)$$

Finally the part of the burette that contained the solution was photographed during the passage of the droplets, and the average number n_2 of droplets per unit length in this phase was measured. Because of the turbulence in the solution during the experiments it was necessary to use a great number of plates to obtain a reliable value of n_2 . Furthermore, owing to the retardation of the droplets in the solution n_2 was a function of the layer thickness, and the measurements had to be repeated for different x -values. Then the time t of contact between amalgam and solution could be calculated from the relation:

$$\rho \cdot \frac{4\pi}{3} \cdot R^3 \cdot n_2 \cdot x = w \cdot t \quad (8)$$

With the apparatus used R had the value $(3.5 \pm 0.1) \cdot 10^{-2}$ cm and ρ was approximately $= 13.6$ g \cdot cm $^{-3}$. In a series of measurements, when the salt medium had the composition: 20 mC HClO $_4$ + 900 mC NaClO $_4$ the following values of t/x were obtained:

x cm	t/x sec \cdot cm $^{-1}$
5.0	0.016 ± 0.002
7.0	0.017 ± 0.003
10.0	0.024 ± 0.003

The value 0.016 ± 0.002 sec \cdot cm $^{-1}$ can be accepted as $\lim_{x \rightarrow 0} \frac{dt}{dx}$ for $x \rightarrow 0$, and then we get:

$$\frac{s_0}{m_0} \lim_{x \rightarrow 0} \frac{dt}{dx} = 0.10 \pm 0.01 \text{ sec} \cdot \text{cm} \cdot \text{g}^{-1}$$

In order to decide whether this value is applicable also to the complex solutions measurements of the density and relative determinations of the viscosity of the different liquids were performed at a constant temperature. It was found that when all sodium perchlorate was exchanged for sodium bromide or iodide the variations in density were within 4 % and the variations in viscosity within 2 %. Only with the solution containing the ammonia buffer did the value of the viscosity differ as much as 7 % from that of the perchlorate solution. Thus if the experimental random errors in the photographic measurements are taken into consideration, the use of the same values of t/x for all the solutions is justified. This was checked experimentally on the bromide solutions. Then for the absolute values of the rate constants the following is valid: $K = 10 \cdot k$ cm \cdot sec $^{-1}$. Especially for the perchlorate solutions we have $K_0 = 0.11$ cm \cdot sec $^{-1}$, which is a considerable specific exchange rate. The absolute values of the other rate constants are collected in Table 3.

Table 3. Absolute values of the rate constants obtained for the different complexes.

Ligand	K_1 cm \cdot sec $^{-1}$	K_2 cm \cdot sec $^{-1}$	K_4 cm \cdot sec $^{-1}$
Br $^-$	0.11	0.14	
I $^-$			0.13
NH $_3$			0.12

As the variations in viscosity and density were so slight, the thickness δ of the diffusion layer must be nearly constant in the different solutions. For a calculation of δ the relation: $K = D / \delta$ can be applied to the perchlorate solutions. An accurate value of D for the cadmium ion in the salt medium used is not known, but if we presuppose that it is of the order of magnitude 10^{-5} $\text{cm}^2 \cdot \text{sec}^{-1}$, we find $\delta \approx 10^{-4}$ cm at a linear velocity of about 60 $\text{cm} \cdot \text{sec}^{-1}$ of the amalgam droplets.

Of course the diffusion layer will not maintain a spherical shape around the droplet, and thus the calculated value of δ will be the average layer depth.

DISCUSSION

The results of this investigation make it clear that the rate of the cadmium exchange is only slightly affected by the formation of complexes of moderate strength, and this is what could be expected for a diffusion-controlled process, where the rate constant is proportional to the diffusion coefficient. When the water ligands are displaced by bromide or iodide ions or by ammonia, the diffusion coefficient D increases somewhat. As the magnitude of the potential difference between amalgam and solution and small changes of the salt medium have no influence on the D -value of a certain complex, the differences between the diffusion coefficients of the complexes investigated probably must be ascribed to differences in the sizes of the ions or molecules.

SUMMARY

The influence of complex formation on the exchange of cadmium between amalgam and solution is studied by a radioassay procedure developed in a previous work¹. The bromide and iodide ions and ammonia are selected as ligands, and the concentrations of the different complexes in the solutions are known.

The rate constant is not very greatly influenced by the formation of these complexes of moderate strength, as the exchange is still diffusion-controlled. For the different complexes the rate constants are proportional to the corresponding diffusion coefficients.

It is shown that the differences in the values obtained of the rate constants are probably ascribable entirely to different size of the complexes.

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