The Exchange Processes between Bismuth Chloride

Complexes and Liquid Bismuth Amalgam

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The kinetics of the exchange processes between bismuth amalgam and complex solutions of Bi^{3+}-Cl^- in an ionic medium of 2 M $HClO_4$ is studied by measurements of the impedance of the electrode-solution interface. The method with hanging amalgam drops of polarographical size is used.

The exchange current density i_0, which is a measure of the exchange rate, has been determined for a number of solutions of various compositions as regards to concentrations of bismuth(III) and chloride ions. Within the concentration intervals examined it is found that the complex $BiCl_2^+$ predominates in the exchange, irrespective of the fact that in some of the solutions this complex is present in a minute amount only, compared with other bismuth(III) chloride complexes.

Investigations of exchange processes between bismuth in liquid amalgam and solutions containing tervalent bismuth either in perchloric acid merely or in acid medium containing complexing agents such as chloride or bromide ions have been reported by Randles and Somerton [1] and Moussa and Samour.[2] These authors have determined specific rate constants in different media and they have reported relative rates in solutions containing different anions. The aim of the present investigation is to determine more quantitatively the alterations in exchange rate with the composition of the solutions in order to get an answer to the question which of the complexes present in the solution predominates in the exchange.

The investigations have been carried out by using electrode impedance measurements with alternating current, the experimental procedure described and used before by Vetter [3] and Fronæus [4] among other. In the case of bismuth it is not possible to study exchange reactions by means of radioactive bismuth isotope because there is no such isotope with a suitable half-life. Thus it has not been possible to check the results by comparing independent methods as is the case with cadmium cyanide complexes and cadmium amalgam investigated in two ways: radioactive tracer method by Fronæus and Östman [5] and impedance measurements on the amalgam electrode by Gerischer.[6]

THE KINETICS OF THE EXCHANGE

In the actual case we have bismuth metal solved in mercury to an amalgam which is in contact with a solution containing bismuth(III). The bismuth ions form complexes with chloride ions present in the solution. It might be thought that each bismuth chloride complex present can take part in the exchange of bismuth between the solution and the amalgam. According to an investigation by Ahrland and Grenthe [7] the $Bi^{3+}-Cl^-$-system consists of mononuclear complexes of which the sixth $BiCl_6{}^{3-}$ is the highest one. Thus, for the reversible electrode processes we can write

$$BiCl_j{}^{3-j} + 3 \ e^- \rightleftharpoons Bi(am) + j \ Cl^- \qquad (1)$$
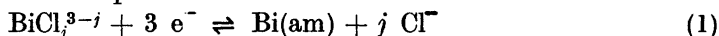
where $j = 0,1,...6$. In order to get the expression as short and simple as possible the water ligands in the lower complexes have been omitted. At equilibrium between the amalgam and solution there is a certain electrode potential. At this state the rates of the processes in (1) from left to right are the same as the corresponding ones from right to left and the sum of the rates of the different steps is equal to the total exchange rate of bismuth.

The discharge process. It is supposed (*cf.* Glasstone, Laidler and Eyring [8]) that the discharge process of a certain complex takes place in two stages. In the first stage the bismuth ion is set free from ligands including water and at the same time the "naked" bismuth ion is taken up to the amalgam surface. In the second stage the bismuth ion is discharged and taken up in the amalgam, and we can say that this is an electron transfer stage.

The principle of the following deduction of the expression for the exchange current density at the investigated electrode processes is found in a paper by Fronæus and Östman.[9]

For electrode processes of this kind there is a change in the free energy of activation when the electrode potential is altered. At first, let us assume that the electrode potential has a certain value e'. If the electrode potential is then altered to $e<e'$, the activation energy of the reaction from left to right diminishes with the amount of $(1-\alpha)(e'-e)3F$, where α is, as usual, the transfer coefficient and F is the faraday. The corresponding increase in the reaction from right to left will be $\alpha(e'-e)3F$. For the transfer coefficient α we have $0<\alpha<1$ and α can be considered as constant if e does not differ too much from e'.

The current density of the forward reaction of (1) is denoted $\overrightarrow{i_j}$ for the discharge of the complex $BiCl_j{}^{3-j}$ at the electrode potential e. Then we have:

$$\overrightarrow{i_j} = k_j{}'[BiCl^{3-j}] \ exp \ \{(1-\alpha)(e'-e)\}3F/RT \qquad (2)$$

and for the reverse reaction for the same complex we get

$$\overleftarrow{i_j} = k_j{}''\cdot \ q\cdot[Cl^-]^j \ exp \ \{-\alpha(e'-e)\}3F/RT \qquad (3)$$

where q is equal to the bismuth concentration in the amalgam.

Now if the electrode potential e is put equal to the equilibrium potential we have $\overrightarrow{i_j} = \overleftarrow{i_j} = i_{0j}$ where i_{0j} is the exchange current density of the electrode process (1). Eliminating $e'-e$ from eqns. (2) and (3) and putting $k_j{}'^{\alpha} \cdot k''^{1-\alpha} = k_j$ we get

$$i_{0j} = k_j \ q^{1-\alpha} \ [BiCl_j{}^{3-j}]^{\alpha}\cdot[Cl^-]^{j(1-\alpha)} \qquad (4)$$

where k_j is a measure of the ability of the complex $BiCl_j^{3-j}$ to exchange. For the total exchange current density we can write

$$i_0 = \sum_{j=0}^{6} i_{0j} \qquad (5)$$

Here we must emphasize that α could have different values for different complexes. However, if we use a concentration range of the free chloride ion not too wide, it can be presumed that only one of the complexes present has such a favourable activation energy for the exchange, that the total exchange current density is determined practically solely by this single complex. Investigations reported in literature show that it is by no means certain that the complex present in the highest concentration is responsible for the magnitude of the exchange rate. An example is the investigation by Fronæus and Östman [5] mentioned above: In a cadmium cyanide solution containing cyanide ions in so great an excess that the complex $Cd(CN)_4^{2-}$ predominates, it was found that the total rate of cadmium exchange between this solution and cadmium amalgam occurs *via* $Cd(CN)_2$. Another example is the investigation of Zn(II) complex by Gerischer [10] who showed that the exchange occurs via $Zn(OH)_2$ in a solution with high cyanide concentration where the complex $Zn(CN)_4^{2-}$ predominates.

Thus we can presuppose that in the right member of eqn. (5) there is only one term which must be taken into account. This presumption is necessary, otherwise there is little chance of elucidating the mechanism of the exchange from the experimental results. But it must be emphasized that this presumption is only valid for a certain limited concentration range. Then it is natural to set us the aim to find out which of the bismuth complexes that predominates in the exchange. It is clear from eqn. (4) that it is the quantities α and j that must be determined.

We consider the complex system in a solution containing bismuth(III) and chloride ions. According to Ahrland and Grenthe [7] we have a set of reactions

$$Bi^{3+} + j\ Cl^- \rightleftharpoons BiCl^{3-j};\ j = 0,\ 1,..6 \qquad (6)$$

and only mononuclear complexes are formed in the strong acid medium (2 M $HClO_4$ in the present work). Further we use the usual system of notation

β_j = complexity constant
C_{Bi} = total concentration of bismuth(III) in solution
C_{Cl} = » » » chloride » »
$\bar{n}$ = ligand number

Then we have with conventional notations

$$\beta_j = \frac{[BiCl_j^{3-j}]}{[Bi^{3+}][Cl^-]^j}\ ;\quad j = 0,\ 1,...6. \qquad (7)$$

$$X = X([Cl^-]) = 1 + \sum_{j=1}^{6} \beta_j[Cl^-]^j \qquad (8)$$

$$\bar{n} = \frac{C_{Cl} - [Cl^-]}{C_{Bi}} \qquad (9)$$

$$C_{Bi} = [Bi^{3+}] \cdot X \qquad (10)$$

Now, by raising to α in eqn. (7) we get:

$$[BiCl_j^{3-j}]^\alpha = \beta_j^\alpha \cdot [Bi^{3+}]^\alpha \cdot [Cl^-]^{j\alpha} \qquad (11)$$

If the concentration of bismuth in the amalgam (q in eqn. (4)) is kept constant, the combination of the eqns. (4), (10), and (11) gives

$$i_{0j} = \text{constant} \cdot \frac{C_{Bi}^\alpha}{X^\alpha} \cdot [Cl^-]^j \qquad (12)$$

If $[Cl^-]$ and consequently $\bar{n}$ are kept constant but C_{Bi} is varied, the transfer coefficient α can be determined. Eqn. (12) then turns into

$$i_{0j} = \text{constant} \cdot C_{Bi}^\alpha \qquad (13)$$

By determining i_0 ($\approx i_{0j}$) at various C_{Bi} one can calculate the value of α.

The method to determine j is best seen from the calculations done below, because there are slight differences in the various cases. However, as a main principle the equations are rearranged in such a way that one should obtain a straight line when plotting experimental results, and from the graph the value of j can be calculated.

Theory of the impedance measurements. The theories of electrode impedance measurements used in the present investigation have been carefully outlined by Randles.[11] In the present paper the same symbols are used as in the paper of Fronæus.[4] Therefore only a short summary of the most important relations and the meaning of symbols is given below.

The small electrode consisted of a bismuth amalgam droplet placed on a very small gilt platinum tip. The other electrode in the cell was a large pool of amalgam with the same bismuth concentration. A sinusoidal alternating voltage of small amplitude (5 mV) is applied to the cell. It is necessary to keep this voltage small, otherwise eqn. (14) below will not be valid with an accuracy good enough. An equivalent circuit of the electrochemical cell can be drawn, see Fig. 1.

Here

R_t = transfer resistance
R_d = diffusion resistance
C_d = diffusion capacitance
C_1 = double layer capacitance
R_c = cell resistance

Further we denote $R_t + R_d = R_s$
The transfer resistance R_t is caused by the charge transfer step and one can deduce

$$R_t = \frac{RT}{3F} \cdot \frac{1}{i_0} \qquad (14)$$

where i_0 is the exchange current density.

The quantities R_t and C_1 are independent, R_d and C_d are dependent of the frequency of the alternating voltage. The total impedance of the cell was measured in an alternating current Wheatstone bridge circuit described by
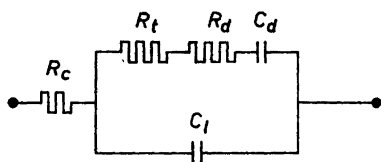
Fig. 1. Equivalent circuit of the electrochemical cell. R_t = transfer resistance; R_d and C_d = diffusion resistance and diffusion capacitance; C_1 = double layer capacitance; R_c = cell resistance.
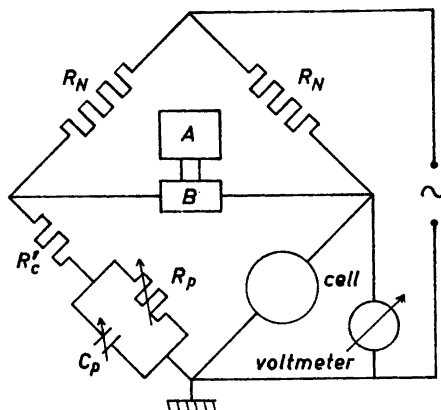
Fig. 2. Alternating current Wheatstone bridge circuit. R_N, R_p, and R_c' are decade resistors; C_p is a decade capacitor; A is a cathode-ray oscilloscope; B is a preamplifier.

Fronæus.[4] The building up of the bridge is shown by Fig. 2. In two branches there are equal standard resistors R_N (which could be varied if necessary with regard to the sensitivity of balancing the bridge). The balance indicator consisted of a cathode-ray oscilloscope A combined with a preamplifier B. Parallel to the cell there is connected a voltmeter which makes it possible to check that the applied voltage is not too high. All the bridge components were shielded and the circuit connections were made short and as straight as possible in order to avoid scattered inductance.

The cell resistance R_c was compensated in the following way: When the frequency is put to a high value, the cell circuit (Fig. 1) is simplified to C_1 and R_c in series. Then R_p in the bridge is disconnected and the bridge is now balanced with the aid of R_c' and C_p. Then R_c' is fixed during the measurements. After this elimination of R_c, the total impedance of the interphase, Fig. 3a, is represented by R_p and C_p in parallel, Fig. 3b. The bridge is balanced for a range of values of the frequency ν with the aid of the decade resistor R_p and the decade capacitor C_p. Then R_t can be calculated in the following way: It can be shown that for high frequencies
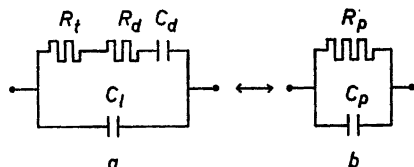

Fig. 3. a, b. Equivalent circuits of the total impedance of the interphase. The same notations as in Figs. 1 and 2.
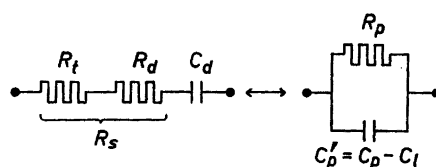
Fig. 4. The equivalent circuits in Fig. 3 after elimination of the double layer capacitance C_1.

$$C_p \approx C_1 + \frac{K'}{\omega \sqrt{\omega}} \qquad (15)$$

where K' is independent of the frequency and $\omega = 2\pi\nu$.

Thus, C_1 can be determined graphically by plotting C_p *versus* $(\omega \sqrt{\omega})^{-1}$ or $(\nu \sqrt{\nu})^{-1}$. This makes it possible to represent the equivalent circuits as in Fig. 4. Now we can apply the usual method to convert the R_p- and C_p-values to the corresponding R_s- and C_s-values. Then we get:

$$R_s = \frac{R_p}{1 + \omega^2 C_p'^2 R_p^2} \qquad (16)$$

$$C_s = C_p'\left(1 + \frac{1}{\omega^2 C_p'^2 R_p^2}\right) \qquad 17)$$

It can be shown that

$$R_d = K/\sqrt{\omega} \qquad (18)$$

where K is independent of the frequency. Thus we have

$$R_s = R_t + (K/\sqrt{\omega}) \qquad (19)$$

Now, if R_s for a range of values of ν is calculated and plotted aginst $\omega^{-\frac{1}{2}}$ or $\nu^{-\frac{1}{2}}$, a straight line should be obtained and we get R_t from

$$R_t = \lim_{\nu^{-\frac{1}{2}} \to 0} R_s \qquad (20)$$

In those cases where $C_p' = C_p - C_1 \ll C_p$ the value of C_p' cannot be determined with an accuracy great enough for calculating R_s from eqn. (16). Then we can solve the equations as follows:

$$R_p = R_s \left(1 + \frac{1}{\omega^2 C_s^2 R_s^2}\right) \qquad (21)$$

$$C_p - C_1 = \frac{C_s}{1 + \omega^2 C_s^2 R_s^2} \qquad (22)$$

Here we insert

$$R_s = R_t + (K/\sqrt{\omega}) \qquad (23)$$

$$C_s = K/1\sqrt{\omega} \qquad (24)$$

and we get (for high frequencies)

$$\frac{1}{R_p} \approx \frac{1}{R_t} - \frac{const}{\sqrt{\nu}} \qquad (25)$$

Thus, the plot of R_p^{-1} *versus* $\nu^{-\frac{1}{2}}$ should give the value of R_t:

$$R_t^{-1} = \lim_{\nu^{-\frac{1}{2}} \to 0} R_p^{-1} \qquad (26)$$

EXPERIMENTAL

Chemicals. The stock solutions used were prepared from chemicals of analytical grade. The bismuth perchlorate solution was prepared by dissolving Bi_2O_3 in 3 M $HClO_4$, and then this stock solution was analysed for Bi(III) by gravimetric determination as $BiPO_4$ according to the procedure described by Wagner, Hull and Markle.[12] The water was redistilled and boiled, and the hydrochloric acid was redistilled twice. Liquid bismuth amalgam was prepared by dissolving metallic bismuth in mercury under water at about 80°C. The concentration of bismuth was taken as 0.1 % of weight. The amalgam was cautiously washed with very diluted perchloric acid and distilled water. Then it was carefully dried with filter paper and immediately brought over to the store bottle (filled with nitrogen) in a polarographic stand. In this way the amalgam could not come in contact with the air during the measurements. By bubbling nitrogen through the solutions, these were freed from oxygen.

Measurements. The cell was similar to that used by Gerischer.[10] In order to avoid the difficulties caused by the inconstant droplet face every measurement was carried out on a fresh droplet of bismuth amalgam. For this purpose the droplets were taken from a polarographic capillary and were brought over to a minute gilt platinum tip with the aid of a little glass spoon. In this way one could get the readings of C_p and R_p on the bridge fairly good reproducible when the bridge was just balanced at a certain time after the droplet had fallen from the capillary. In the measurements this time interval was fixed to exactly 2 min.

All measurements were made in an air thermostat at (25.0 ± 0.2)°C for practical reasons and 2.0 M $HClO_4$ was used as medium. The concentration q of bismuth in the amalgam was kept constant throughout. Data of the bismuth chloride complex system are taken from Ahrland and Grenthe.[7] Their measurements were carried out at 20°C and in a medium containing sodium perchlorate, but these divergences in the experimental performances hardly could have any essential influence upon the mutual distribution of the various complexes.

The exchange rate is throughout fairly high which means that the R_t-values will be small. Therefore, for higher values of C_{Cl} (> 10 mM) it was necessary to add a substance, in this case gelatin, in order to lower the rate. Randles[11] has described this rate lowering effect caused by certain substances. It is very likely that this addition of a "foreign" substance only lowers the exchange rate (presumably by some adsorption phenomenon) but does not in other respects affect the exchange mechanism.

CALCULATIONS

The transfer resistance R_t is inversely proportional to i_0 according to eqn. (14). The R_t-values are determined by extrapolation according to eqn. (20).

Table 1. The exchange current density i_0 for different values of bismuth(III) concentrations. No chloride ions and no gelatin in the solutions.

C_{Bi} mM	R_t Ω	i_0 mA·cm^{-2}
2.0	1330	0.161
4.0	1080	0.198
8.0	840	0.255
17.7	610	0.351
38.4	470	0.455

Table 2. The exchange current density i_0 for low values of $\bar{n}$. Two different concentrations of chloride ions but the same bismuth(III) concentration. No gelatin in the solutions.

C_{Bi} mM	C_{Cl^-} mM	$[Bi^{3+}]$ mM	$[Cl^-]$ mM	$[BiCl^{2+}]$ mM	$\bar{n}$	R_t Ω	i_0 mA·cm^{-2}
4.0	2.0	3.2	1.2	0.8	0.2	9.3	23
4.0	4.0	2.5	2.5	1.5	0.4	2.4	89

Earlier investigations by Randles and Somerton [1] show that the exchange current density is much greater in solutions containing chloride ions than in those of pure perchloric acid. In the present investigation measurements were also carried out in 2 M HClO$_4$ without addition of chloride ions. Here, the R_p-values read off from the bridge were fairly constant for low frequencies and for a certain value of C_{Bi}. Therefore the extrapolated R_t-values were obtained by plotting R_p *versus* $1/\sqrt{v}$ (*cf.* Gerischer [10]). The results are listed in Table 1. The i_0-values are calculated from eqn. (14), taking the area of the amalgam droplet as 0.040 cm^2. Plotting log i_0 *versus* log C_{Bi} (Fig. 5) we get the value $\alpha = 0.4$.

I. Addition of small amounts of chloride ions raises the i_0-values to a great extent. For the lowest values of $\bar{n}$, where measurements have been carried out, the i_0-values were found to be greater than 20 mA · cm^{-2}; results in Table 2. Here and in the subsequent tables, $[Bi^{3+}]$ and $[Cl^-]$ have been calculated with the aid of complexity constants and ($\bar{n}$—log $[Cl^-]$)-graph of the Bi^{3+}—Cl^--system (Ref.[7]).

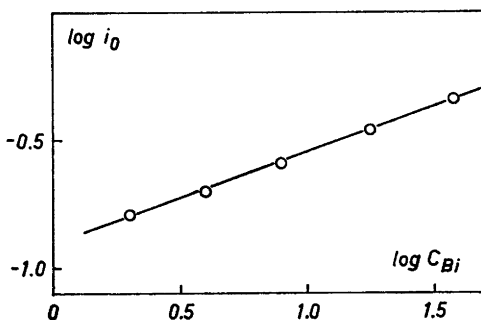*Fig. 5.* log i_0 (i_0 in mA·cm^{-2}) as a function of log C_{Bi} (C_{Bi} in mM). No chloride ions in the solutions.

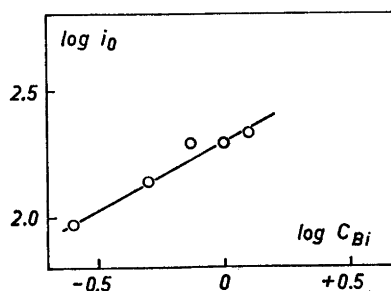*Fig. 6.* log i_0 (i_0 in mA·cm^{-2}) as a function of log C_{Bi} (C_{Bi} in mM). $[Cl^-] = 4.1$ mM ($\bar{n} = 0.5$). No gelatin in the solutions.

II. $\bar{n}$ varies about 0.5. Taking logarithms in eqn. (13) we get

$$\log i_{0j} = \text{const.} + \alpha \log C_{Bi} \tag{27}$$

From Table 3 and Fig. 6 one gets $\alpha = 0.5$ at $\bar{n} = 0.5$.

Table 3. The exchange current density i_0 at constant $[\text{Cl}^-] = 4.1$ mM ($\bar{n} = 0.5$) but different C_{Bi}. No gelatin in the solutions. The R_t-values listed are mean values obtained from R_s and $1/R_p$ plotted *versus* $1/\sqrt{v}$.

C_{Cl} mM	C_{Bi} mM	R_t Ω	i_0 mA·cm^{-2}
4.2	0.25	2.3	93
4.4	0.50	1.6	134
4.5	0.75	1.1	195
4.6	1.00	1.1	195
4.7	1.25	1.0	214

Determination of j: Combination of eqns. (4) and (11) gives

$$i_{0j} = \text{const.} \cdot [\text{Bi}^{3+}]^{\alpha} \cdot [\text{Cl}^-]^j \tag{28}$$

and

$$\log i_{0j} = \text{const.} + \alpha \log [\text{Bi}^{3+}] + j \log [\text{Cl}^-] \tag{29}$$

or

$$\log i_{0j} - \alpha \log [\text{Bi}^{3+}] = \text{const.} + j \log [\text{Cl}^-] \tag{30}$$

A plot of the left member *versus* $\log [\text{Cl}^-]$, see Table 4 and Fig. 7, gives $j = 2.0$ from the slope of the line. This means according to the theory that it is the second complex BiCl_2^+ that determines the exchange rate.

Table 4. $C_{\text{Bi}} = 1.00$ mM constant; $\bar{n}$ varies $0.2 - 0.9$. Calculations of $\log i_0 - \alpha \log [\text{Bi}^{3+}]$ for various $[\text{Cl}^-]$ in order to determine the value of j in eqn. (30). No gelatin in the solutions.

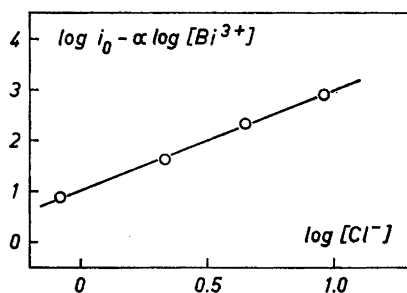| C_{Cl} mM	$[\text{Cl}^-]$ mM	$[\text{Bi}^{3+}]$ mM	$\bar{n}$	R_t Ω	i_0 mA·cm^{-2}	$\log i_0 - \alpha\log[\text{Bi}^{3+}]$
1.00	0.84	0.82	0.2	32	6.7	0.88
2.50	2.14	0.66	0.4	6.2	34.5	1.63
5.00	4.44	0.48	0.6	1.5	143	2.32
10.00	9.12	0.29	0.9	0.5	428	2.90

Fig. 7. Plot of ($\log i_0 - \alpha\log [\text{Bi}^{3+}]$), eqn. (30), *versus* $\log [\text{Cl}^-]$. The slope of the line gives $j = 2.0$.
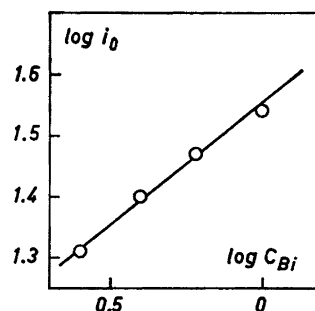

Fig. 8. $\log i_0$ (i_0 in mA·cm^{-2}) as a function of $\log C_{\text{Bi}}$ (C_{Bi} in mM). $[\text{Cl}^-] = 11.0$ mM ($\bar{n} = 1.0$). Conc. of gelatin $= 0.02$ % by weight.
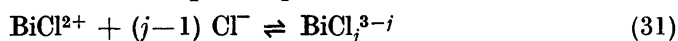
Table 5. i_0-values at constant $[Cl^-] = 11.0$ mM ($\bar{n} = 1.0$) but different C_{Bi}. Conc. of gelatin $= 0.02$ % by weight.

C_{Cl} mM	C_{Bi} mM	R_t Ω	i_0 mA·cm^{-2}
11.3	0.25	10.5	20.4
11.4	0.40	8.5	25.2
11.6	0.60	7.2	29.7
12.0	1.00	6.2	34.5

III. $\bar{n}$ varies about 1. The value of α is determined in the same way as in point II above with the aid of eqn. (27). From Table 5 and Fig. 8 one finds

$$\alpha = 0.40 \pm 0.04 \text{ at } \bar{n} = 1.0$$

Determination of j: From the complex equilibrium

$$BiCl^{2+} + (j-1)\ Cl^- \rightleftharpoons BiCl_j^{3-i} \tag{31}$$

we have

$$[BiCl_j^{3-i}] = \text{const.} \cdot [BiCl^{2+}]\ [Cl^-]^{i-1} \tag{32}$$

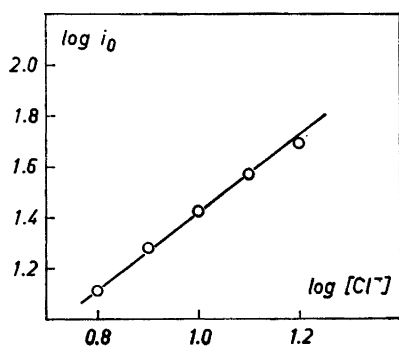*Fig. 9.* log i_0 (i_0 in mA.cm^{-2}) as a function of log $[Cl^-]$ ($[Cl^-]$ in mM). The slope of the straight line gives the value of $(j-a)$ in eqn. (35).
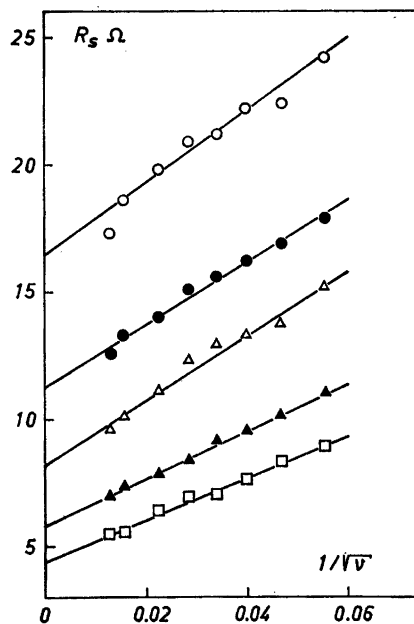
Fig. 10. R_s as a function of $1/\sqrt{v}$. The composition of the solutions will be evident from Table 6. $[Cl^-] = 6.3$ (O), 7.9 (●) 10.0 (△), 12.6 (▲), and 15.9 mM (□).

Eqns. (4) and (32) give

$$i_{0j} = \text{const.} \cdot [\text{BiCl}^{2+}]^{\alpha} \cdot [\text{Cl}^-]^{j-\alpha} \tag{33}$$

and accordingly

$$\log i_{0j} - \alpha \log [\text{BiCl}^{2+}] = \text{const.} + (j-\alpha) \log [\text{Cl}^-] \tag{34}$$

A plot of the left member *versus* log [Cl⁻] would vive a straight line with the slope $(j-\alpha)$. However, here a simplification is possible. From the distribution curves of the complexes (Ref.[7]) it can be seen that within the examined interval $(0.80 \leqslant \log [\text{Cl}^-] \leqslant 1.20)$, the concentration of the complex BiCl^{2+} is approximately constant (55—58 % of C_{Bi}). Therefore, the second term in the left member of eqn. (34) can be considered constant and the equation can be written

$$\log i_{0j} = \text{const.} + (j-\alpha) \log [\text{Cl}^-] \tag{35}$$

A plot of log i_0 *versus* log [Cl⁻], see Table 6 and Fig. 9, gives $(j-\alpha) = 1.45 \pm 0.05$ and accordingly $j = 1.9 \pm 0.1$. That is to say, even for this $\bar{n}$-interval the exchanging complex would be $\text{BiCl}_2{}^+$.

Fig. 10 shows an example of extrapolation of $(R_s - 1/\sqrt{\nu})$-graphs. The R_t-values obtained are listed in Table 6. The diagram will give a conception of the accuracy in the measurements.

IV. $\bar{n}$ varies about 2. In this n-interval, the R_t-values are found to be fairly small, and there is a greater uncertainty in the extrapolation of R_t than for lower values of $\bar{n}$. This fact can be a reason for putting $\alpha = 0.4 \pm 0.1$ (without any special measurement) for calculating j. Whithin the examined interval $(1.20 \leqslant \log [\text{Cl}^-] \leqslant 1.60)$ the concentration of the second complex $\text{BiCl}_2{}^+$ is constant (15 % of C_{Bi}).

The complex equilibrium

$$\text{BiCl}_2{}^+ + (j-2) \text{ Cl}^- \rightleftharpoons \text{BiCl}_j{}^{3-j} \tag{36}$$

gives

$$[\text{BiCl}_j{}^{3-j}] = \text{const.} \cdot [\text{BiCl}_2{}^+] [\text{Cl}^-]^{j-2} \tag{37}$$

Combination of eqns. (4) and (37) and putting $[\text{BiCl}_2{}^+] = \text{const.}$ will give

$$i_{0j} = \text{const.} \cdot [\text{Cl}^-]^{j-2\alpha} \tag{38}$$

Thus

$$\log i_{0j} = \text{const.} + (j-2\alpha) \log [\text{Cl}^-] \tag{39}$$

Table 6. $C_{\text{Bi}} = 0.50$ mM constant; $\bar{n}$ varies $0.7-1.3$. Calculations of log i_0 for various [Cl⁻] for determining the j-value in eqn. (35). Conc. of gelatin = 0.02 % by weight.

C_{Cl} mM	$\bar{n}$	[Cl⁻] mM	R_t Ω	i_0 mA·cm⁻²
6.65	0.7	6.3	16.5	13.0
8.30	0.8	7.9	11.3	18.9
10.47	0.9	10.0	8.2	26.1
13.15	1.1	12.6	5.8	36.9
16.55	1.3	15.9	4.4	48.6
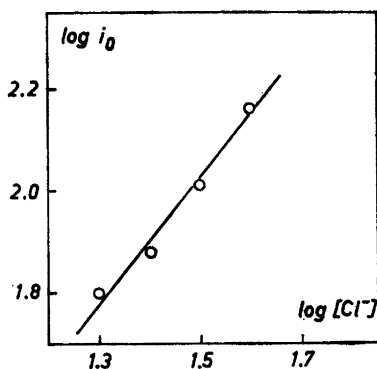
Fig. 11. $\log i_0$ (i_0 in mA.cm^{-2}) as a function of $\log$ [Cl$^-$] ([Cl$^-$] in mM). The slope of the line gives the value of $(j-2a)$ in eqn. (39).

Table 7. $C_{Bi} = 0.50$ mM constant. $\bar{n}$ varies 1.5—2.3 Calculations of $\log i_0$ for various [Cl$^-$] for determining the value of $(j-2a)$ in eqn. (39). Conc. of gelatin $= 0.02$ % by weight.

C_{Cl} mM	$\bar{n}$	[Cl$^-$] mM	R_t Ω	i_0 mA·cm^{-2}
20.8	1.5	20.0	3.4	63
26.0	1.8	25.1	2.8	76
32.7	2.1	31.6	2.1	102
41.0	2.3	39.8	1.5	143

From Table 7 and Fig. 11 it will be found that $j-2a = 1.3 \pm 0.1$. Inserting the value of a one gets $j = 2.1 \pm 0.3$, *i.e.* even in this $\bar{n}$-interval the exchanging complex is found, though with somewhat greater uncertainty, to be the same as for lower values of $\bar{n}$.

V. $\bar{n}$ varies about 3. For these great values of $\bar{n}$ the R_t-values were found to be very small (about 0.5 ohm) and the extrapolations very uncertain. Accordingly, at these ligand concentrations it is impossible to get information about the exchanging complex from this kind of measurements.

Now, since we have obtained the value $j = 2$, we can get a check on the values in section I, Table 2. We combine eqns. (4) and (32) and get

$$i_{0j} = K[\text{BiCl}^{2+}]^\alpha \, [\text{Cl}^-]^{j-\alpha} \qquad (40)$$

where K is a constant. Inserting $\alpha = 0.5$, $j = 2$ and the connected values from Table 2 we get the quotient

$$\frac{i_{0j}}{[\text{BiCl}^{2+}]^\alpha \cdot [\text{Cl}^-]^{j-\alpha}} = 20 \text{ and } 18, \text{ respectively}$$

and thus we can say that the values in Table 2 too, are a ratification of the importance of the second complex $\text{BiCl}_2{}^+$ for the exchange rate.

DISCUSSION

Combination of eqns. (4), (10), and (11) gives

$$i_{0j} = k_j \cdot q^{1-\alpha} \, \beta_j^{\alpha} \cdot (C_{Bi}^{\alpha}/X^{\alpha}) \, [Cl^-]^j \tag{41}$$

and taking the sum we can write

$$i_0 = q^{1-\alpha} \cdot C_{Bi}^{\alpha} \cdot \sum_{j=0}^{6} k_j \, \frac{\beta_j^{\alpha} \cdot [Cl^-]^j}{X^{\alpha}} \tag{42}$$

Here we put

$$\frac{\beta_j^{\alpha} \cdot [Cl^-]^j}{X^{\alpha}} = f_j \tag{43}$$

and we have

$$i_0 = q^{1-\alpha} \cdot C_{Bi}^{\alpha} \sum_{j=0}^{6} k_j \cdot f_j \tag{44}$$

Now, we will study f_j as a function of $\bar{n}$ for various values of j. It can easily be shown that the function f_j has a maximum in the point $\bar{n} = j/\alpha$, and in our concrete case, the (Bi^{3+}—Cl^-)-system, this would have a real meaning for $j = 0$, 1, and 2 only if we put α approximately 0.5. We can calculate the function f_j for $j = 0$, 1, 2... taking $\alpha = 0.5$. The functions f_j plotted *versus* $\bar{n}$ are shown in Fig. 12. The functions f_1 and f_2 have their maxima at $\bar{n} = 2$ and $\bar{n} = 4$, respectively, but f_3 and f_4 will not reach any maxima ($\bar{n}$ cannot be so high in practice, Ref.[7])
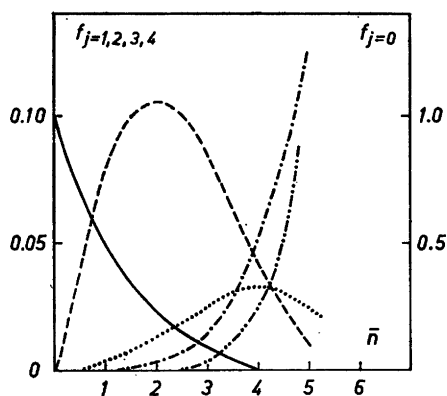

Fig. 12. The function f_j (eqn. (43)) plotted *versus* $\bar{n}$ for various values of j. The vertical scale to the right is for $f_{j=0}$ and the scale to the left is for the other f_j-values. $j = 0$ (————); $j = 1$ (— — — —); $j = 2$ (·····); $j = 3$ (— · — ·); $j = 4$ (·· — ··).

Considering the values of i_0 found, it will be seen that i_0 will be much greater after adding only a little amount of chloride. According to the present investigation the second complex $BiCl_2^+$ predominates in the exchange, and from Fig. 12 it will be seen that $f_1 > f_2$ within the $\bar{n}$-interval examined. Accordingly, the constant $k_2 \gg k_1$. Since $f_0 \gg f_2$ for the same values of $\bar{n}$, the constant $k_2 \gg k_0$. However, we cannot draw any conclusion about the mutual relation between k_0 and k_1.

As has been mentioned it was not possible to measure i_0 for $\bar{n}$ higher than 2.3 because R_t will be too low. From Fig. 12 we can understand that for $\bar{n} = 2$ the value of f_2 is greater than f_3 approximately by a factor 4. This leads to the conclusion that the constant k_3 at the most can be of the same order of magnitude as k_2. If $k_2 \approx k_3$ this would mean that the complex $BiCl_3$ could have a share of the total exchange current density amounting to 25 % roughly. However, this will not be inconsistent with the results of the measurements, because a 25 % contribution to i_0 by the complex $BiCl_3$ can hardly be discovered at the determination of the j-value. Only if it were possible to measure i_0 at higher $\bar{n}$-values, we could get information about the contribution to i_0 by the higher complexes.

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