On the Problem of Bromide Control in a Tl^{3+}-perturbed Belousov-Zhabotinsky Oscillator

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It is shown that Tl^{3+} as a bromide removing perturbant of the BZ oscillators is superior to Ag^+ in several aspects. A most important advantage is that the upper limit of the actual Br^- concentration can be calculated from the potential of a bromide selective electrode in the presence of the corrosive Tl^{3+} ions. Experimental potentiometric traces of a bromide selective electrode in a Tl^{3+} perturbed BZ system show that the Br^- concentration stays much below its critical concentration during the oscillations. These observations suggest that free Br^- is not the critical intermediate formed during reduction of Ce^{4+} and responsible for the negative feedback associated with the oscillations.

Introduction

The main features of the mechanism of the classical Belousov-Zhabotinsky (BZ) reaction [1] – the oscillatory oxidation of malonic acid by acidic bromate catalyzed by the Ce^{4+}/Ce^{3+} redox couple – were clarified by Field, Kőrös, and Noyes (FKN) nearly two decades ago [2, 3]. According to their theory the oscillatory behavior is due to an interplay between a fast acting positive and a delayed negative feedback loop. The positive feedback forces the system to leave its unstable steady state and, after a certain delay, the negative loop pushes the system back again. The above interplay results in sustained oscillations. In the FKN theory the positive feedback is identified as the autocatalytic oxidation of Ce^{3+} to Ce^{4+} by acidic bromate where the autocatalytic species are bromous acid ($HBrO_2$) and bromine dioxide radicals ($BrO_2\cdot$). The negative feedback is accomplished by an inhibition of the autocatalytic reaction. The inhibitory species are bromide ions (Br^-) produced with a delay in a reaction of Ce^{4+} with bromomalonic acid. As bromide reacts with bromous acid controlling this way the autocatalytic cycle it is a so called control intermediate. According to the theory a "critical bromide concentration" can be defined. The autocatalytic reaction is "switched on" whenever the bromide concentration is below is critical value and it is "switched off" above that level.

While there is a general agreement in the literature regarding the positive feedback loop, opinions are more divided concerning the negative one. The first problems of the negative feedback loop came into light when Noszticzius [4] observed oscillations in the classical BZ system in the presence of a relatively high concentration (10^{-3} M) of silver ions. At first it was accepted [5, 6] that these oscillations are not controlled by bromide especially because the bromide level is much below its critical value in the silver perturbed system. Later on, however, a different interpretation was suggested by Ruoff and Schwitters [7, 8]. They pointed out correctly that bromide control is still possible even in the presence of silver ions provided that the precipitation reaction (R1)

$$Ag^+ + Br^- \rightarrow AgBr \qquad (R1)$$

is a relatively slow process. The above assumption stirred some debate in the literature and initiated new experiments, as well [9–14]. Recent calculations by Russo [15] based on the latest experimental data of Meisel and coworkers [16] show that there are still problems in the modeling of the silver ion perturbed BZ oscillator.

Another problem is the interpretation of the signal of the bromide selective electrode in the presence of silver ions. If (R1) is fast and, consequently, the solubility equilibrium holds, then there is no such a prob-

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lem. In equilibrium the electrode potential can be calculated either from the silver or the bromide ion concentration as the product of those ionic concentrations is known. On the other hand, if (R1) is a slow process then the solution becomes supersaturated and – at least in theory – the ionic product might be much higher than its equilibrium value. In that case the electrode potential would not be an exact measure of the bromide concentration of the solution. This would be so because the silver ion perturbant is able to affect the electrode potential directly not only via removing bromide ions from the solution. Thus a higher than equilibrium bromide concentration would not be detected by a bromide selective electrode in the presence of silver ions. (The membrane potential of the silver bromide membrane at the tip of the bromide selective electrode would be affected mostly by the silver ions which are in a much higher concentration compared to bromide ions in the silver perturbed system. It is important to emphasize again: such a far from equilibrium situation is possible only if (R1) is slow for some reasons.) In other words one cannot be absolutely sure that the bromide level is really under its critical value during the silver perturbed BZ oscillations.

Regarding the problems discussed above it seems highly desirable to find a perturbant which is able to remove bromide ions without precipitate formation and which does not affect the electrode potential directly. Tl^{3+} meets both conditions; it forms a strong but soluble complex with bromide ions and affects the electrode potential only by changing the bromide concentration of the solution and by reacting with bromide ions coming from the AgBr electrode (corrosion potential). Moreover the effect of Tl^{3+} on the BZ system is similar to the effect of Ag^+; Kőrös and coworkers [17] reported high frequency oscillations of the platinum electrode potential in Tl^{3+} perturbed BZ systems.

In this work we study a Tl^{3+} perturbed BZ system using a bromide selective and a platinum electrode simultaneously. We point out that while the bromide concentration crosses its critical value in the normal oscillations of the unperturbed system, this is not the case with the Tl^{3+} perturbed system. The bromide concentration stays much below its critical value during the high frequency Tl^{3+} induced oscillations. To support the above conclusions we also calibrate the potential of a bromide selective electrode with respect to the Tl^{3+} concentration and compare our results with theoretical curves based on the corrosion potential theory [18, 19].

Experimental Section

Chemicals. All chemicals used in the experiments, H_2SO_4 (96% Merck), $KBrO_3$ (Merck), $Ce(SO_4)_2$ (Fluka), and malonic acid (Fluka), were of reagent grade and were used without further purification. A stock solution of Tl^{3+} was prepared following the instructions of Kőrös et al. [17b]. The solutions were prepared with distilled water.

Apparatus. The overall redox potential was measured by a bright platinum electrode. The home made molten AgBr type bromide selective electrode was produced following directions of Noszticzius et al. [20]. As a reference an $HgSO_4/K_2SO_4$ electrode was used. To decrease potential drifts due to diffusion potentials the reference electrode was placed into a cell filled with 10 M NH_4NO_3. That cell was connected to the reactor via a salt bridge (a tubing with diaphragm on both ends) containing 1 M sulfuric acid.

Measurements. Calibration of the bromide selective electrode for Tl^{3+} ions (Fig. 1) was carried out in magnetically stirred and in unstirred 1 molar sulfuric acid solution.

In the oscillatory experiments (Fig. 2) at first solutions of sulfuric acid, malonic acid, and bromate were mixed. After the electrode potentials reached a constant value (approximately 5 min.), the reaction was started by the addition of the catalyst. Tl^{3+} was added only at the second oscillation after the induction period as it was done in experiments of Kőrös et al. [17]. All experiments were performed at laboratory temperature ($22 \pm 1\,^\circ C$) in magnetically stirred solutions. Potentiometric traces were recorded on a two channel Kipp and Zonen BD 41 recorder.

Results and Discussion

Response of the Bromide Selective Electrode for Tl^{3+} Ions

The experimental calibration curve for Tl^{3+} ions – the electrode potential vs. the logarithm of Tl^{3+} concentration – is depicted in Figure 1. (The reference potential is the solubility limit potential. The latter was determined as the mean of two electrode poten-

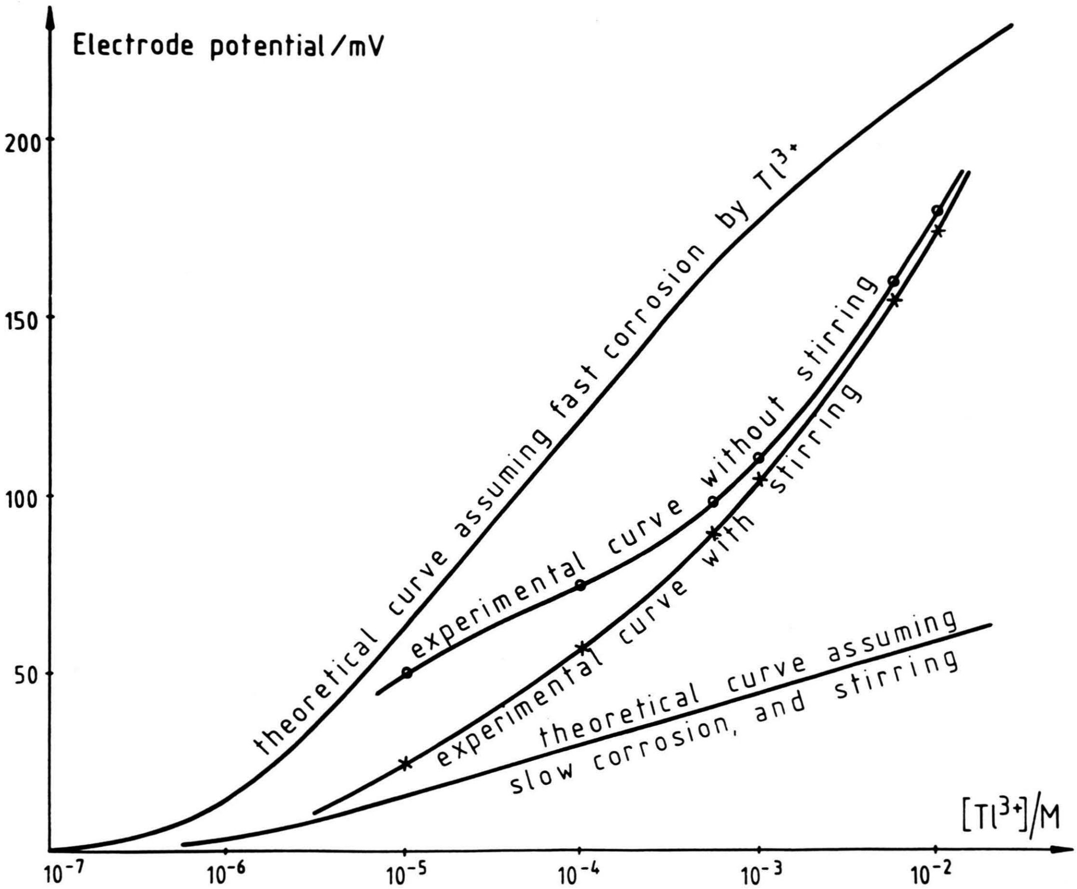

Fig. 1. Experimental and theoretical calibration curves of an AgBr electrode; the electrode potential as a function of the corrosive Tl^{3+} concentration. Theoretical calculations are given in the Appendix.

tials measured in 10^{-5} M Ag^+ and in 10^{-5} M Br^- solutions respectively.)

The potential response of the AgBr electrode can be explained by the corrosion potential theory. According to that theory Ag^+ or Br^- ions produced in a corrosion process of the electrode determine the potential of the electrode. In the present experiments Tl^{3+} ions react with the AgBr electrode and in this case there are silver ions among the reaction products. According to our measurements the coated wire type AgBr electrode gives a Nernstian response for silver ions in a 1 M sulfuric acid solution at 25 °C

$$\varepsilon = \varepsilon_0 + 59\,\mathrm{mV} \cdot \lg[Ag^+]_i . \qquad (1)$$

Thus, in fact, the electrode responds to the silver ion concentration $[Ag^+]_i$ at the electrode-electrolyte interface and not to the thallium ion concentration $[Tl^{3+}]_b$ in the bulk of the solution. While it is not the thallium but the silver ions which determine the electrode potential directly, there is a functional relationship between the silver ion concentration at the surface of the electrode and the bulk concentration of the corrosive thallium ions. The functional relationship is given by the corrosion potential theory [18, 19]. The theory assumes that concentration profiles near the electrode inside a thin-non-stirred boundary layer are determined by chemical reaction-diffusion equations. It was shown [19] that fast and slow corrosion processes behave differently. If the process is fast then most of the corrosion reaction takes place in the vicinity of the electrode surface, well within the boundary layer. As a result the potential is not affected by stirring and a theoretical calculation of the electrode potential is possible without knowing the hydrodynamic conditions. In Fig. 1 there is a theoretical calibration curve assuming a fast corrosion reaction (see Appendix I. for the details of the calculation). It should be stressed that the calculated curve does not depend either on the rate constant of the reaction or on the thickness of the boundary layer as long as the reaction is fast enough. On the other hand, if the corrosion reaction is relatively slow no exact calculation can be made without a precise knowledge on the rate constant of the corrosion reaction and the thickness of the boundary layer. As an example there is a theoretical calibration curve in Fig. 1 assuming a relatively slow corrosion reaction

$$Tl^{3+} + Br^{-} \rightarrow TlBr^{2+}. \qquad (R2)$$

As an approximation in the calculations $k_2 = 10^7\ M^{-1} \cdot s^{-1}$ and $\delta = 10\ \mu m$ was used. (The details of the calculations are given in Appendix II.) According to the calculations the electrode response is non-Nernstian, and the electrode potential is affected by the rate of stirring [19] because δ – the thickness of the boundary layer – is a function of stirring. This is just the case with the experimental calibration curve measured by us at low Tl^{3+} concentrations (10^{-5} M – 10^{-3} M). The electrode response is non-Nernstian and it depends on the rate of stirring in that concentration region. Above 10^{-3} M Tl^{3+}, however, the rate of stirring has little effect on the electrode potential which rises sharply with the increasing $[Tl^{3+}]$. Also the slope of the curve nears to the Nernstian 59 mV/decade. This can be explained partly by a faster corrosion reaction accompanied with a thinner reaction layer due to the higher concentration of the corrosive agent. This way the corrosion process speeds up and, as a result, the experimental calibration curve comes nearer to the theoretical one valid for fast corrosion processes. Moreover it is rather probable that at these higher concentrations a contribution from a heterogeneous reaction between Tl^{3+} ions and the solid electrode material becomes more significant. Similar effects were observed with an AgBr electrode when the corrosive agent was acidic bromate [19].

Potential Oscillations of Platinum and Bromide Selective Electrodes in Unperturbed and in Tl^{3+} Perturbed BZ Systems

Experimental results with unperturbed and perturbed systems are shown in Figure 2.

In the beginning of the experiment no Tl^{3+} was present and normal oscillations started after an induction period. These normal oscillations cross both the solubility limit potential and a critical potential which can be calculated from the critical bromide concentration. The critical bromide concentration is given by the well known formula [2, 21]

$$[Br^{-}]_{crit} = 18 \cdot 10^{-6} \cdot [BrO_3^{-}]. \qquad (2)$$

In this case the critical bromide concentration is $0.9 \cdot 10^{-6}$ M, which value is rather near to the solubility limit value. Really there is a break point in the potentiometric trace of the bromide selective electrode which point lies near the solubility limit potential and its position is compatible with the calculated critical bromide concentration. The electrode potential sinks below that critical value periodically, which means that during these periods the bromide concentration rises above its critical value in the course of the normal oscillations. This is not the case with the perturbed system. In the presence of the corrosive Tl^{3+} the electrode potential stays permanently above the potential compatible with the critical bromide concentration. This observation suggests that most probably the bromide concentration stays permanently below its critical value during the Tl^{3+} perturbed oscillations provided that the electrode potential gives a correct information about the bromide level of the solution. But is it possible to calculate, or at least to estimate, the bromide level of the solution from the signal of an electrode whose potential is above the solubility limit due to a corrosion process? This is a major problem to be addressed before making any theoretical conclusions based on the signal of a bromide selective electrode recorded in the course of an oscillating reaction.

Estimation of the Bromide Ion Concentration from the Electrode Potential Above the Solubility Limit Potential

As we pointed out previously the electrode potential is determined by the silver ion concentration $[Ag^{+}]_i$ at the electrode-electrolyte interface and these silver ions are coming from the electrode itself as a result of the corrosion process. From the electrode potential we can calculate $[Ag^{+}]_i$, and from $[Ag^{+}]_i$ an estimated bromide concentration $[Br^{-}]_e$ can be calculated based on the solubility product L:

$$[Br^{-}]_e = \frac{L}{[Ag^{+}]_i}. \qquad (3)$$

Formula (3) assumes a solubility equilibrium at the surface of the electrode. Two questions arise at this

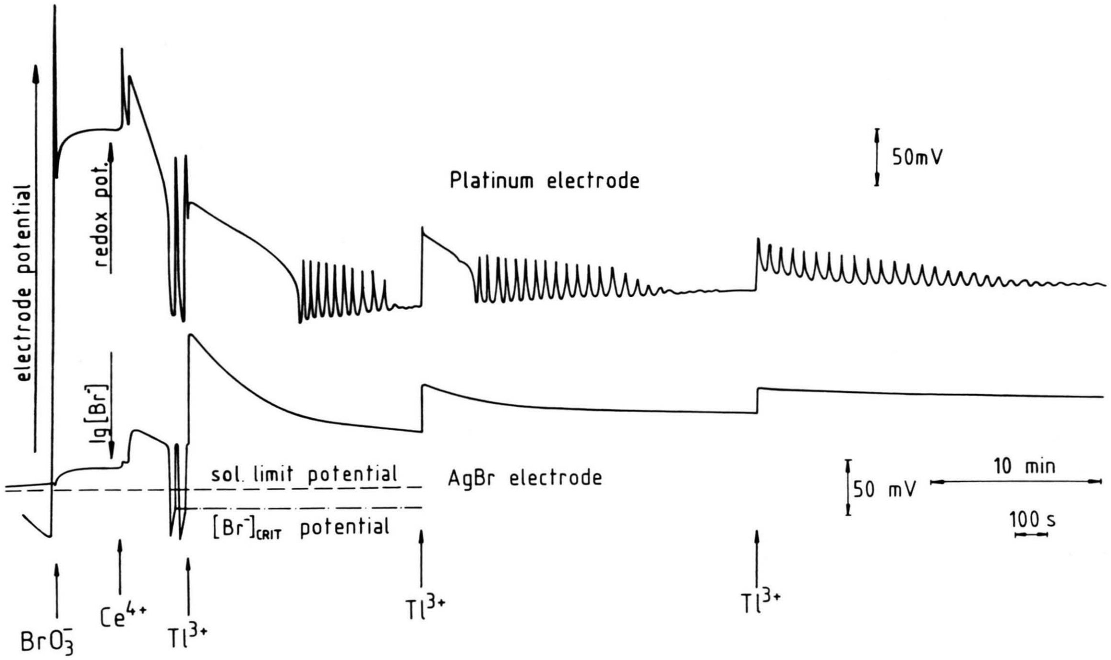

Fig. 2. Potentiometric traces of a platinum and an AgBr electrode in a Tl^{3+} perturbed BZ system of the following composition: 0.05 M $KBrO_3$, 0.1 M malonic acid, 0.002 M Ce(4+), and 1 M H_2SO_4. Arrows denote the times when the different components were added to the system. After two bromide controlled oscillations, 1.5×10^{-2} M Tl^{3+} was injected and this was repeated two more times.

point immediately:

i) What is the relationship between the above estimated value and the real bromide concentration at the surface of the electrode, and

ii) in the bulk of the solution?

i) Estimation of the Non-Equilibrium Bromide Concentration at the Surface of the Electrode

The problem of a possible non-equilibrium bromide and silver ion concentration was first discussed in the case of silver ion perturbed BZ systems [7, 8, 15]. In that case AgBr precipitate is forming during the oscillations and a supersaturation of the solution for AgBr is possible, at least in theory. Whenever the concentration of the dissolved AgBr is above its final equilibrium value, the real (non-equilibrium) bromide concentration can be proportionally higher. This argument is based on the fact that there is a very fast equilibrium among $[Ag^+]$, $[Br^-]$, and [AgBr], where [AgBr] is the concentration of the "monomeric" AgBr molecules [16].

$$[Br^-] = \frac{k_1^- \cdot [AgBr]}{k_1^+ \cdot [Ag^+]}, \text{ where } \begin{array}{l} k_1^- = 4.6 \times 10^5\ s^{-1}, \\ k_1^+ = 1.3 \times 10^{10}\ M^{-1}\,s^{-1}. \end{array} \tag{4}$$

When Tl^{3+} ions are added to a BZ system the situation is different. Now the AgBr coating of the electrode is dissolving and the solution should be less than saturated for AgBr during this process. If the solution is undersaturated for AgBr, then the real (non-equilibrium) bromide concentration is also proportionally lower. Moreover, if we assume that any step leading to the solubility equilibrium is slow then the corresponding real bromide concentration should be even lower. Thus, as we can see, the bromide concentration estimated according to (1) is an **upper limit** of the real one at the surface of the electrode.

ii) Estimation of the Real Bromide Concentration in the Bulk of the Electrolyte

Whenever an electrode is placed into a chemical system, concentrations are disturbed in the neighbourhood of the electrode provided the electrode reacts with some components of the chemical system (corrosion). As a result, surface and bulk concentrations can be different. In the case of an AgBr electrode Ag^+ and Br^- ions are leaving the electrode and reacting with any corrosive agents like Tl^{3+} or HOBr. This way the electrode is a bromide source and the local bromide concentration at the electrode should be somewhat higher than the bromide concentration in the bulk.

In summary, regarding both arguments i) and ii), we can conclude that the bromide concentration calculated from the solubility product using (1) and (3) is an **upper estimate** of the real bromide concentration in the bulk. The same conclusion holds for the case of other corrosive agents different from Tl^{3+}, e.g. for hypobromous acid.

iii) Response Time of the Electrode

Finally errors due to the fast changing oscillatory concentrations should be estimated. These errors can be estimated if the response time of the electrode is known. It was shown [22] that in the case of a solid state ion selective electrode the response time for a concentration jump is determined by hydrodynamic conditions. The time constant τ can be calculated from the thickness of the boundary layer δ and the diffusion coefficient D according to the expression

$$\tau = 4\delta^2/\pi^2 D. \tag{5}$$

In the present experiments the time constant can be estimated with the same expression because the corrosive agents reach the surface of the electrode and the products of the corrosion reaction leave the surface of the electrode through the boundary layer in a diffusion controlled process. Assuming $D = 2 \times 10^{-5}$ cm^2/s and $\delta = 10^{-3}$ cm τ is 0.02 s. Thus, after a sudden concentration jump, the electrode potential can relax to its new value well within 0.1 s. (More precisely 0.1 s after the concentration jump the difference between the measured and final concentrations decreases to less than 1% of the original value.) As the time period of the thallium perturbed oscillations is two or three orders of magnitude greater than the time constant of the electrode we can conclude that any error due to the time delay in the response of the electrode should be negligible.

Conclusions

The question of the control intermediate is a central problem in the mechanism of the BZ reaction [23, 24]. Study of BZ oscillators in the presence of bromide removing perturbants is a potentially important method to test whether bromide ion is the only control intermediate in the system. Silver ion perturbed oscillators were studied extensively but there is no general agreement among different authors regarding the interpretation of the experimental results. As a bromide removing perturbant Tl^{3+} has distinct advantages over Ag^+.

i) Tl^{3+} does not form a precipitate with Br^-. (In the case of silver perturbed systems the mechanism of the precipitate formation is a controversial point.)
ii) Tl^{3+} is a not potential determining ion for a silver bromide ion selective electrode; it affects the electrode potential only indirectly by reacting with bromide ions.
iii) Tl^{3+} is a corrosive agent for the silver bromide based ion selective electrode. Thus, instead of a continuous AgBr precipitation, there is a continuous dissolution of AgBr and the solution is not supersaturated but less than saturated for AgBr.

On the basis of i)–iii) it was shown that electrode potentials measured in the presence of Tl^{3+} (or other corrosive agents like HOBr) give an upper estimate of the real bromide concentration only. That is calculating bromide concentrations from the Nernst equation when the electrode potential is above the solubility limit gives a result above the real value. This is in agreement with Ganapathisubramanian and Noyes' conclusions [25]. They compared experimentally measured bromide levels with theoretical ones calculated from the Oregonator model.

The present experiments with a Tl^{3+} perturbed BZ system show that in this case potential oscillations of a platinum electrode can be detected while the potential of a bromide selective electrode is nonoscillatory and stays high above its solubility limit potential (see Figure 2). According to the theoretical considerations presented here this also means that bromide levels stay below the critical bromide concentration continuously. Consequently the Tl^{3+} perturbed oscillations studied here are not controlled by free bromide. Our present experiments do not answer the question what is the real control intermediate here. In our opinion there are two possibilities:

i) Bromide complexed with Tl^{3+} (like $TlBr^{2+}$ for example) can play the role of the control intermediate. In this case the control reaction would be a direct reaction between $TlBr^{2+}$ and $HBrO_2$, and the mechanism would be somewhat similar to the one proposed by Kshirsagar et al. [11] for Ag^+ perturbed system.

ii) Organic free radicals can also play the role of control intermediates as it was shown by Försterling et al. [23, 24]. The control reaction in their mechanism is a reaction between BrO_2 radicals and malonyl or other organic free radicals.

Analogous experiments with Bi^{3+}, another bromocomplex forming metal ion, are in progress in our laboratories.

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Appendix

I. Theoretical Calibration Curve of an AgBr Electrode for Tl^{3+} Ions Assuming a Fast Corrosion Process

In the case of fast corrosion the reaction takes place near the electrode surface well within the unstirred boundary layer. The thickness δ of that layer is determined by the hydrodynamic conditions [26]. Tl^{3+} ions diffuse through the boundary layer toward the electrode-electrolyte interface in the vicinity of which they react with the bromide ions. The reaction products – Ag^+ and $TlBr^{2+}$ ions – leave the site of the reaction diffusing through the boundary layer again, now in the reverse direction toward the bulk of the solution. In steady state an interfacial silver ion concentration $[Ag^+]_i$ is established depending on the corrosive thallium ion concentration in the bulk $[Tl^{3+}]_b$. Knowing $[Ag^+]_i$ the electrode potential can be calculated according to the Nernst equation:

$$\varepsilon = 59\,\text{mV} \cdot \lg\{[Ag^+]_i/[Ag^+]_{sl}\}, \qquad \text{(A1)}$$

where $[Ag^+]_{sl}$ is the solubility limit silver ion concentration, which is the square root of the solubility product L

$$[Ag^+]_{sl} = \sqrt{L}. \qquad \text{(A2)}$$

As our reference zero potential is the solubility limit potential, ε is zero if the interfacial silver ion concentration is equal to the solubility limit value. This is the case when no Tl^{3+} is present. The theoretical calibration curve is obtained by calculating $[Ag^+]_i$ as a function of $[Tl^{3+}]_b$ and then plotting ε against $[Tl^{3+}]_b$. To this end, relationships given by chemical equilibria, balance equations, and Fick's law for steady state diffusion are used. As an estimation it is assumed that all ions have the same mobility or diffusion coefficient D. If the positive direction points from the interface toward the bulk then the steady state current densities can be given by the following constitutive equations:

$$J_{Ag} = D\,[Ag^+]_i/\delta, \quad J_{Br} = D\,[Br^-]_i/\delta, \qquad \text{(A3)}$$

$$J_{TlBr} = D\,[TlBr^{2+}]_i/\delta, \quad J_{Tl} = -D\,\{[Tl^{3+}]_b - [Tl^{3+}]_i\}/\delta,$$

where the indices i and b refer to interfacial and bulk concentrations, respectively. The bulk concentrations are zero for the different ions except Tl^{3+}. In steady state the following balance equations are valid:

$$J_{Ag} = J_{Br} + J_{TlBr}, \quad J_{TlBr} = -J_{Tl}. \qquad \text{(A4)}$$

Substituting the constitutive equations for the current densities into the balance equations two relationships can be obtained:

$$[TlBr^{2+}]_i = [Ag^+]_i - [Br^-]_i, \qquad \text{(A5)}$$

$$[Tl^{3+}]_i = [Tl^{3+}]_b + [Br^-]_i - [Ag^+]_i. \qquad \text{(A6)}$$

In addition two more relationships are provided by assuming fast chemical equilibria at the solid liquid interface:

$$\frac{[Tl^{3+}]_i\,[Br^-]_i}{[TlBr^{2+}]_i} = K, \qquad \text{(A7)}$$

$$[Ag^+]_i\,[Br^-]_i = L. \qquad \text{(A8)}$$

Using the above four relationships (A5)–(A8) between the different steady state interfacial concentrations the desired final equation connecting $[Tl^{3+}]_b \equiv t$ and $[Ag^+]_i \equiv a$ can be derived:

$$K \cdot L^{-1} a^3 + a^2 + (K+t)\,a - L = 0. \qquad \text{(A9)}$$

This cubic equation cannot be made explicite for a, thus the potential determining silver ion concentration cannot be given as an explicite function of the bulk concentration of the corrosive thallium ion. Nevertheless t can be expressed explicitly as a function of a, thus the inverse function of the theoretical calibration curve $t = t(\varepsilon)$ instead of $\varepsilon = \varepsilon(t)$ can be calculated directly. The theoretical calibration curve calculated this way is depicted in Figure 1. In the calculations we used the following data: $L = 7.7 \times 10^{-13}\,\mathrm{M}^2$ [27] and $K = 4.17 \times 10^{-10}\,\mathrm{M}$ [17].

II. Theoretical Calibration Curve of an AgBr Electrode for Tl^{3+} Ions Assuming a Slow Corrosion Process

If the reaction between thallium and bromide ions is relatively slow then the concentration of the corrosive Tl^{3+} is roughly constant and equal to its bulk concentration $[\mathrm{Tl}^{3+}]_b$ throughout the boundary layer. Again, the aim of the following derivation is to find a relationship between the interfacial silver ion concentration $[\mathrm{Ag}^+]_i$ and the thallium concentration in the bulk $[\mathrm{Tl}^{3+}]_b$. In steady state the current density of the silver ions is independent of the space coordinate x within the boundary layer or thickness δ. According to Fick's law

$$J_{\mathrm{Ag}} = D\,[\mathrm{Ag}^+]_i/\delta. \qquad (\mathrm{A10})$$

On the other hand the current density of bromide ions does depend on the distance x measured from the solid liquid interface. The current density decreases due to the reaction between bromide and thallium ions:

$$\frac{\mathrm{d}(J_{\mathrm{Br}})}{\mathrm{d}x} = -k\,[\mathrm{Tl}^{3+}]\,[\mathrm{Br}^-], \qquad (\mathrm{A11})$$

where k is the rate constant of the reaction. The above equation can be written in a dimensionless form by introducing the so called Thiele modulus [28] h_{T} defined as

$$h_{\mathrm{T}}^2 \equiv -\frac{k\,[\mathrm{Tl}^{3+}]_b\,\delta^2}{D}. \qquad (\mathrm{A12})$$

The dimensionless form is

$$\frac{\mathrm{d}^2[\mathrm{Br}^-]}{\mathrm{d}(x/\delta)^2} = h_{\mathrm{T}}^2\,[\mathrm{Br}^-]. \qquad (\mathrm{A13})$$

The solution of the above differential equation is

$$[\mathrm{Br}^-] = [\mathrm{Br}^-]_i\,\mathrm{sh}\{h_{\mathrm{T}}(1 - x/\delta)\}/\mathrm{sh}(h_{\mathrm{T}}), \qquad (\mathrm{A14})$$

which solution satisfies the boundary conditions as well:

$$[\mathrm{Br}^-] = [\mathrm{Br}^-]_i \text{ at } x = 0 \quad \text{and} \quad [\mathrm{Br}^-] = 0 \text{ at } x = \delta. \qquad (\mathrm{A15})$$

As the bromide and silver ion currents are generated by the dissolution of the AgBr electrode, these current densities should be equal to each other at the solid liquid interface:

$$J_{\mathrm{Br}} = J_{\mathrm{Ag}} \quad \text{at} \quad x = 0. \qquad (\mathrm{A16})$$

The interfacial current density of bromide is

$$(J_{\mathrm{Br}})_{x=0} = -D\left\{\frac{\mathrm{d}[\mathrm{Br}^-]}{\mathrm{d}x}\right\}_{x=0} = -D\,\frac{h_{\mathrm{T}}[\mathrm{Br}^-]_i}{\delta\,\mathrm{th}(h_{\mathrm{T}})}. \qquad (\mathrm{A17})$$

Regarding the above relationships between the currents and the expression for the silver ion current density (A10) the interfacial silver ion concentration can be given as:

$$[\mathrm{Ag}^+]_i = \sqrt{h_{\mathrm{T}}\,L/\mathrm{th}(h_{\mathrm{T}})}. \qquad (\mathrm{A18})$$

The derivation also assumes a solubility equilibrium at the interface – see (A8) – L being the solubility product. Now the electrode potential can be expressed as a function of the Thiele modulus

$$\varepsilon = 59\,\mathrm{mV}\cdot\lg\{[\mathrm{Ag}^+]_i/\sqrt{L}\} = 28.5\,\mathrm{mV}\cdot\lg\{h_{\mathrm{T}}/\mathrm{th}(h_{\mathrm{T}})\}. \qquad (\mathrm{A19})$$

Thus the theoretical calibration curve can be calculated provided that k, D, and δ are given. For the diffusion coefficient $D = 2 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and for the hydrodynamic boundary layer $\delta = 10^{-3}$ cm are usual approximations. To estimate k, Eigen's theory [29] can be applied. According to this theoretical considerations and experimental findings most metal ions show well defined characteristic substitution rates almost independent of the nature of the substituting ligand. (In our case a water molecule in the coordination sphere of Tl^{3+} is substituted by a bromide ion.) The characteristic rate depends on the charge, the ionic radius, and the electronic configuration of the outer shell of the metal ion. While no direct data for Tl^{3+} are known, the second order rate constant for In^{3+} was found to be $2 \times 10^6\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ by Geier [30]. In^{3+} has the same charge (+3) and the same outer shell electronic configuration ($s^2p^6d^{10}$) like Tl^{3+}, but Tl^{3+} has a larger ionic radius (0.81 and 1.05 Å, respectively [31]). As the rate of substitution increases considerably with the increasing ionic radius it can be expected that k is around $10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for Tl^{3+}. In the one molar sulfuric acid medium, however, a $\mathrm{Tl(HSO_4)_2(H_2O)_4^+}$ complex formation might slow down the rate of the reaction according to Varga et al. [32]. They suggest that k is around $10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. In this respect it is interesting to remark that while the hydrogensulfato complex formation should really diminish the stability of the outer sphere ion pair complex $\mathrm{Tl(HSO_4)_2(H_2O)_4^+Br^-}$ compared to $\mathrm{Tl(H_2O)_6^{3+}Br^-}$ and slow down this way the overall rate of the reaction, the presence of HSO_4^- ions in the inner coordination sphere, however, make the coordinated H_2O molecules more labile in the first complex than in the second. This would accelerate the transition of the bromide ion from the outer sphere into the inner one and would cause an opposite effect by accelerating the overall rate of the reaction. Anyway, if k is two orders of magnitude smaller than $10^7\ M^{-1}\ s^{-1}$ then the corrosive Tl^{3+} concentration should be increased by two orders of magnitude to produce the same Thiele modulus. In other words a theoretical calibration curve assuming $k = 10^5\ M^{-1}\ s^{-1}$ would be similar to the one depicted in Fig. 1 except it would be shifted to the right along the concentration axis by two orders of magnitude.

The first estimate for k based on direct ^{205}Tl NMR measurements was reported just recently by Bányai and Glaser [33]. Their estimate is $k < 10^{10}\ M^{-1}\ s^{-1}$.

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