Table VI

choline chloride, M	NaOD , M	% anhydrocholine calcd	obsd
0.82		0	
0.81	0.34	39	37
0.79	0.66	70	66
0.69	2.33	100	

where *L* is the conductance of the subscript compound or compounds at concentration *C*. The constant, *K*, was determined at a minimum of three concentrations, with *C* ranging from 10^{-4} to 10^{-2} mol/kg. The equilibrium constant, *K*, as defined by the above equations uses a value of unity for the concentration of H_2O in eq 1. Using the actual concentrations of H_2O yields *K* values that are somewhat different and ΔH and ΔS values that are slightly different from those in Table I. In the two ethanolic media, this calculation of *K* does not distinguish the relative contributions of OH^- and $C_2H_5O^-$ to the equilibrium but rather measures the *K* of the equilibrium $(CH_3)_3N^+CH_2CH_2OH + SO^- \rightarrow (CH_3)_3N^+CH_2CH_2O^- + SOH$ (SOH = solvent).

NMR Measurements. The proton NMR spectra of three solutions of choline chloride plus NaOH in D_2O and one of choline chloride alone in D_2O were recorded on a Varian T-60 spectrometer at 42.5 °C. The quaternary methyl peak was observed at δ 3.2 in all four samples, indicating no observable interaction between this group and hydroxide ion and no decomposition. The α-methylene resonances, at about δ 3.4, were found to shift steadily upfield on addition of NaOH. By use of this shift, the percent of anhydrocholine formed was calculated and compared with that calculated from our aqueous ΔH and ΔS values (Table VI).

Considering the very large concentrations that had to be used and the change from H_2O to D_2O, the agreement is quite reasonable. This experiment was repeated in H_2O solvent with similar results.

Calorimetry. Heats of solution were measured with an LKB-8700 reaction and solution calorimeter.

Acknowledgment. This work was supported in part by a grant from the City University of New York Faculty Research Award Program.

Registry No. $(CH_3)_3N^+CH_2CH_2OH$, 62-49-7; $(CH_3)_3N^+CH_2CH_2O^-$, 44519-34-8; $(CH_3)_3N^+CH_2CH_2OH\ Cl^-$, 67-48-1; $(C_4H_9)_4NCl$, 1112-67-0.

On the Use of Ion-Selective Electrodes for Monitoring Oscillating Reactions. 1. Potential Response of the Silver Halide Membrane Electrodes to Hypohalous Acids

Z. Noszticzius,[1] E. Noszticzius,[2] and Z. A. Schelly*

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019. *Received March 15, 1982*

Abstract: The potential response of halide ion selective (AgCl, AgBr, and AgI membrane) electrodes to hypohalous acids (HOCl, HOBr, and H_2OI^+) is investigated under experimental conditions prevailing in oscillating reactions, i.e., at H_2SO_4 concentrations of 0.15 and 1.5 M. Hypohalous acids are known intermediates in these reactions. The two current theories, the kinetic buffer theory (KBT) and the corrosion potential theory (CPT), of the potential response for halide ion concentrations $[X^-]$ below the solubility limit (i.e., where $[X^-] < K_s^{1/2}$) are compared. Experimental results are presented which clearly contradict KBT and confirm CPT. New methods of synthesis for silver-free HOBr and silver-free HOI, and a method of quantitative determination of H_2OI^+ beside IO_3^-, are described.

Introduction

Ion-selective electrodes play an important role in monitoring chemical oscillations. All the well-known and extensively studied oscillating reactions, the Bray–Liebhafsky (BL),[3,4] the Belousov–Zhabotinsky (BZ),[5-7] the Briggs–Rauscher (BR)[8,9] reactions, as well as their modifications,[10,11] and even a recently discovered new family of chemical oscillators,[12] have been followed by iodide- or bromide-sensitive electrodes. Possibly the apparent ease of their monitoring with specific electrodes has contributed to the fact that the iodide and bromide ions were assigned to be important, sometimes even essential, components in the complex mechanisms of these chemical oscillators.[7,10,13-16] Clearly, the understanding of the potential response of ion-selective electrodes under the conditions prevailing in oscillating systems is crucial. Nevertheless, the interpretation of the responses is not unanimous, especially when halide ion concentrations $[X^-]$ are believed to be measured below their solubility limits.[17,18]

In the present paper, we shall discuss the contradicting interpretations and present experimental results that support the de-

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[2] R. A. Welch Predoctoral Fellow. On leave of absence from the Technical University of Budapest.

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cision in favor of a model based on the corrosion potential theory.[19] We shall focus on the analysis of the potential response of halide-selective electrodes to hypohalous acids. In a subsequent paper, as a further step toward the description of the electrode behavior in the complex oscillating systems, the electrode responses to HXO_2 and HXO_3 acids will be investigated.

Comparison of Models

In studies of oscillating reactions, the potential of the monitoring silver halide membrane electrode can go through values that correspond to halide ion concentrations $[X^-]$ typically between 10^{-7} and 10^{-9} M, which is below the so-called solubility limit; i.e.

$$[X^-] < K_s^{1/2} \tag{1}$$

where

$$K_s = [Ag^+][X^-] \tag{2}$$

the solubility product of the silver salt in question. In simple equilibrium systems, such a response could only be caused by excess silver ions, satisfying eq 2.

In oscillating systems, the interesting phenomenon was first observed by Woodson and Liebhafsky,[4] who reported for the BL reaction that "... the $[I^-]$ pulses oscillate undisturbed through the calculated solubility limit ... and lie entirely below the measured solubility limit." Similar observations were made for the $[Br^-]$ pulses in the BZ reaction by Field, Körös, and Noyes.[7] Two different explanations have been proposed for this unusual behavior. The first one will be termed the kinetic buffer theory, while the second explanation is based on the corrosion potential theory.

(1) The *kinetic buffer theory* (KBT) was proposed by Woodson and Liebhafsky.[4] According to their explanation, in the BL reaction "... some of the participating reactions remove iodide so rapidly—including iodide formed in Reaction 1—that the $[I^-]$ in the system is governed primarily by kinetic considerations: Reaction 1 may thus provide the $[Ag^+]$ required to establish Equilibrium 2 without raising the $[I^-]$ above its kinetically controlled value." (In their paper Reaction 1 is the dissolution of the AgI membrane of the electrode, AgI(c, membrane) = Ag^+(aq) + I^-(aq), and Equilibrium 2 is AgI(c) $\rightleftharpoons$ Ag^+(aq) + I^-(aq).) In other words, the production and consumption of I^- results in a very low-level steady-state concentration of iodide, and—assuming that the dissolution of the electrode membrane is not able to disturb the steady state significantly—the same kinetically buffered $[I^-]$ will be established on the surface of the electrode, as well as in the bulk solution. Hence, according to this model, the concentration of the Ag^+ ions at the surface of the electrode is determined by the kinetically enforced and uniform iodide level in the bulk solution. Field, Körös, and Noyes have adopted this interpretation for the potential response in the BZ reaction, although in their landmark paper[7] they write the following: "In static systems the electrode did not respond linearly to still lower bromide concentrations ..." (i.e., below the solubility limit), "... however, it did appear to behave ideally during short periods of depleted bromide ion."

(2) The *corrosion potential theory*[19] (CPT) offers an alternative explanation for the potential response of halide-sensitive electrodes in oscillating systems.[18] According to this model, oxidative agents, like hypohalous acids (which are intermediates of the BL, BZ, and BR oscillators) attack the electrode membrane and remove halide ions from the surface, as in the following reaction:

$$H^+ + X^- + XOH \rightarrow X_2 + H_2O \tag{3}$$

The relative excess of the Ag^+ ions produced this way at the surface of the silver halide membrane will determine the potential response.

According to these two models, the measured potential is explained by the excess of silver ions at the electrode surface which is produced by some rapid halide-removing processes in both cases. However, in KBT, the Ag^+ concentration at the surface is controlled by the halide ion concentration (supposedly uniform throughout the system) whereas in CPT the bulk concentration of the corrosive hypohalous acid is the controlling factor. Thus, while KBT states that the electrode potential refers to the bulk halide level of the oscillating system even below the solubility limit, CPT suggests that there is no functional relationship between those variables below the solubility limit, and only the concentration of the corrosive agent can be determined with the electrode.

In the following sections, we present the results of experiments that were carried out to test the two models. Special attention was paid to simulate conditions typical in oscillating systems.

Experimental Section

Materials and Methods of Analysis. *Chloride-free HOCl* was prepared according to a method by Chapin,[20] with the only difference that silver sulfate was substituted for mercuric sulfate. The concentration of HOCl was determined by potentiometric titration, where HOCl was added to a known amount of acidic KI solution ($[H_2SO_4]$ = 0.15 M) in the presence of an I^--sensitive end-point-indicator electrode. The reverse method of titration assured the presence of excess I^-, and thus the production of IO_3^- was avoided.

Bromide-free HOBr was prepared by two different methods: (a) from Br_2 and Ag_2SO_4 according to Chapin,[20] and (b) to avoid possible contamination by Ag^+ (which could affect the potential of the silver halide membrane electrodes to be tested), from $NaBrO_3$. In the latter method, 2 cm^3 of a 1 M aqueous $NaBrO_3$ was added dropwise to a continuously stirred mixture of 3 cm^3 of H_2O and 5 cm^3 of H_2SO_4 (96% w/w) at −10 °C. The mixture was warmed slowly to 40 °C, and, when the vigorous oxygen evolution ceased, the reaction mixture was diluted to 50 cm^3 with distilled water. The solution was freed from Br_2 by four successive extractions with CCl_4. In the strong acidic medium, the bromate decomposes to hypobromous acid

$$H^+ + BrO_3^- \rightarrow HOBr + O_2 \tag{4}$$

which further decomposes to bromine

$$4HOBr \rightarrow 2Br_2 + 2H_2O + O_2 \tag{5}$$

About 50% of the bromate originally present was transformed into HOBr; the rest decomposed. Experiments with HOBr produced by methods a and b gave identical results. The HOBr solution was analyzed by potentiometric titration in acidic medium ($[H_2SO_4]$ = 1.5 M), using a 0.01 M KBr solution as titrant and a bromide-sensitive end-point-indicator electrode. The bromine contamination was determined by adding malonic acid to the HOBr solution and titrating the Br^- (produced from Br_2) with $AgNO_3$ in the presence of a bromide-sensitive end-point-indicator electrode. The bromine concentration of the freshly extracted solutions was less than 1% of the HOBr concentration.

There is some controversy concerning the synthesis of *iodide-free HOI*. Davis and Kibbey[21] have cast serious doubt on the accuracy of a method suggested in textbooks[22,23] (namely, mixing equimolar amounts of HgO and I_2 in distilled water). Probably, the HOI produced decomposes promptly to I_2 and IO_3^-. According to Chapin,[20] in contrast to HOCl and HOBr, no comparative stability of HOI could be demonstrated in acidic medium. Later on, Bell and Gelles[24] pointed out that, in strong acidic media (0.2 < $[H^+]$ < 1 M), the protonated hypoiodous acid in low concentrations ($[H_2OI^+] < 10^{-4}$ M) shows relative stability against disproportionation. They produced aqueous H_2OI^+ solution by adding silver salts to acidic I_2 solutions. Their method, however, cannot be used in our case because of contamination by Ag^+ ions. Thus, we developed a new procedure in which a strongly acidic solution containing iodine in the 1+ oxidation state is quickly diluted, where the possibility of disproportionation for H_2OI^+ is minimized. Masson's original prescription[25] was slightly modified for the preparation of the initial, dark brown "oxide" solution in concentrated sulfuric acid, where the fundamental process is the following:

$$4I_2 + 2HIO_3 \rightarrow 5I_2O + H_2O \tag{6}$$

H_2OI^+ is produced in the subsequent, sudden dilution in acidic media:

$$2H^+ + I_2O + H_2O \rightarrow 2H_2OI^+ \tag{7}$$

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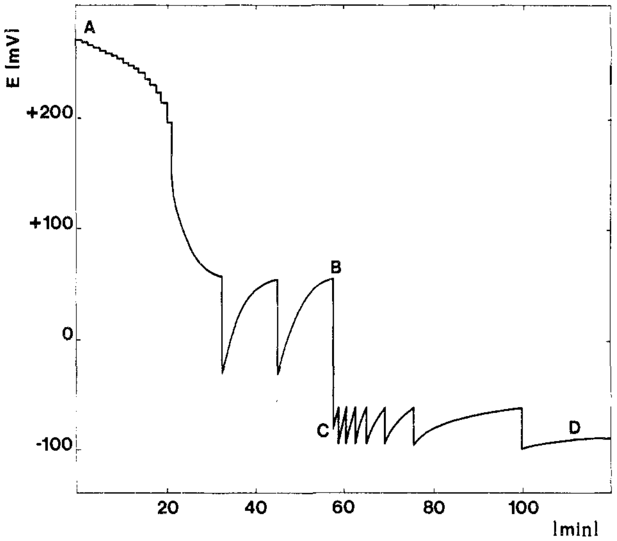

Figure 1. Potential of the iodide-selective electrode vs. standard calomel electrode (SCE) during the titration of H_2OI^+ and IO_3^- with 10^{-3} M KI. A 0.1-cm^3 sample was diluted to a total volume of 50 cm^3; $[H_2SO_4] = 0.15$ M. For the section A to B, each negative step corresponds to the addition of 0.1 cm^3 of the titrant (i.e., a total of 1.9 cm^3). The end point for H_2OI^+ is reached at 1.7 cm^3 of titrant added (corresponding to an initial $[H_2OI^+] = 3.4 \times 10^{-5}$ M). At B 1.1 cm^3, and from C to D 1.0 cm^3 of titrant was added at each negative step. The decreasing slope of the "relaxation" curves indicates the approach of the equivalence point for IO_3^-. The estimated $[IO_3^-]$ and $[I_2]$ initially present are 3.3×10^{-5} and 2.6×10^{-5} M, respectively.

For the preparation of the oxide solution, 127 mg of I_2 and 107 mg of KIO_3 were dissolved in 25 cm^3 of H_2SO_4 (96% w/w). An excess of KIO_3 is necessary to facilitate the dissolution of I_2, which otherwise is a slow process. (Some I(3+) intermediates produced this way decompose during dilution to HOI and HIO_3. The latter will be discussed in detail in a subsequent paper.[26]) The solution was allowed to stand overnight at 24 ± 1 °C, and a 0.1-cm^3 sample of it was quickly diluted to 50 cm^3 with 0.15 M H_2SO_4. The H_2OI^+ content of the resulting solution can be determined with a sharp end point, by titration with 10^{-3} M KI and recording the potential of an iodide-sensitive electrode (Figure 1).

The IO_3^- content of the H_2OI^+ solution was estimated on the basis of the following kinetic considerations. When a known portion of the KI titrant is added to the solution, the electrode potential first drops suddenly and then rises (relaxes) slowly, due to the consumption of I^- by IO_3^- in the acidic medium (see Figure 1). This is the so-called Dushman reaction.[23] For low $[I^-]$, the rate of this reaction is given by[27]

$$d[I^-]/dt = -k[I^-][IO_3^-] \tag{8}$$

$$d \ln [I^-]/dt = -k[IO_3^-] \tag{9}$$

where k includes all other parameters that are essentially constant during the reaction. The rate of change of the electrode potential

$$d\epsilon/dt = -(RT/F)(d \ln [I^-]/dt) \tag{10}$$

can be expressed as

$$d\epsilon/dt = k'[IO_3^-] \tag{11}$$

by substituting eq 9 into eq 10, with $k' \equiv kRT/F$. Thus, the slope of the electrode potential curve is proportional to $[IO_3^-]$. Consequently, the slopes of the potential relaxations decrease on successive additions of KI to the solution, approaching zero at the equivalence point[27c] (see the lower sawtooth section of Figure 1).

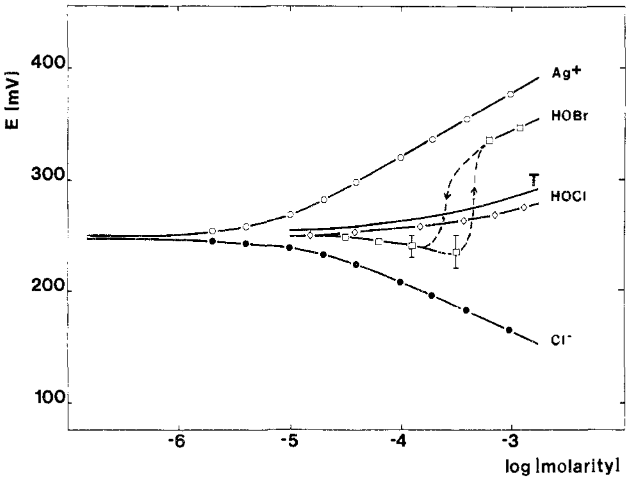

Figure 2. Response of the chloride-selective electrode vs. the concentration of the species determining the potential at $[H_2SO_4] = 1.5$ M. The theoretical curve (T) for HOCl was calculated with the use of CPT. The dashed section of the HOBr curve represents instability and memory effect in the response.

All the other chemicals were of reagent grade and were used without further purification.

Preparation of Electrodes. Commercial halide-sensitive membrane electrodes contain pellets made of a mixture of silver halide and silver sulfide.[28] In contact with hypohalous solutions, such electrodes show aging effects, due to the leaching-out of silver halide from the membrane, whereby a porous layer of silver sulfide remains on its surface. (Similar phenomena were reported for cyanide-sensitive electrodes.[29]) Consequently, the response of such electrodes changes gradually in oscillating reactions. To avoid this problem, we prepared our electrodes by using pressed pellets made of freshly precipitated and dried pure silver halide salts. The electrodes contain a silver wire inner reference electrode in a 0.1 M $AgNO_3$ solution, following the usual design.[30]

Experimental Setup. To simulate the strongly acidic medium of oscillating reactions, our experiments were carried out in 0.15–1.5 M H_2SO_4 solutions. A "salt" bridge (filled with H_2SO_4 of the same concentration as that of the system to be measured) was used to connect the solutions into which the ion-selective and reference calomel (with saturated KCl) electrodes immersed. The resulting galvanic cell used was the following:

ion-selective electrode|0.15–1.5 M H_2SO_4, containing the compounds
to be measured|sintered glass disk|0.15–1.5 M H_2SO_4|sintered glass
disk|10 M NH_4NO_3|saturated calomel electrode

The salt bridge filled with sulfuric acid is needed to avoid contamination by NH_4NO_3 of the solution to be measured. The use of the highly soluble NH_4NO_3 as part of the salt bridge chain is necessary for the suppression of the otherwise significant diffusion potential. The potential of the galvanic cell was measured with a Corning Model-10 pH meter and displayed on a Sargent Model-SR recorder. The solutions were stirred with a magnetic stirrer.

Experimental Procedure. To establish the potential response of ion-selective electrodes to several different ions and molecules, we added relatively small volumes of dilute samples containing known amounts of Ag^+, halide ions, or hypohalous acids to 50 mL of a 0.15 M or 1.5 M H_2SO_4 solution. The increase of volume caused a maximum change in the sulfuric acid concentration of less than 5%. In the respective experiments, the H_2IO^+ concentration had to be determined directly in the experimental solutions by titration with I^-, and thus these solutions contained I_2 as well. The response of the electrodes to HOBr was examined mainly in 1.5 M H_2SO_4 (the usual medium of the BZ reaction), while to HOI in 0.15 M H_2SO_4 (typical for the BR reaction). The

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$$d[I^-]/dt = -f([I^-],[H^+])[IO_3^-] \tag{8'}$$

or

$$d \ln [I^-]/dt = -f([I^-],[H^+])[IO_3^-]/[I^-] \tag{9'}$$

At a given $[I^-]$, $d \ln [I^-]/dt$ and thus $d\epsilon/dt$ will be proportional to $[IO_3^-]$.

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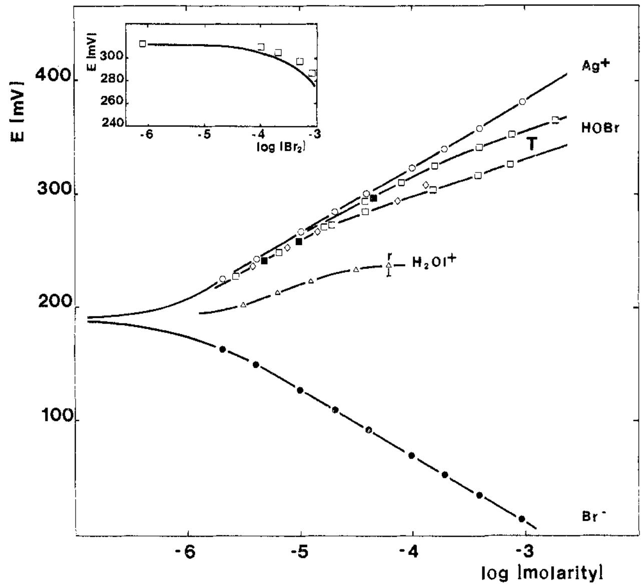

Figure 3. Response of the bromide-selective electrode vs. the concentration of the species determining the potential at $[H_2SO_4] = 1.5$ M (unless indicated otherwise). The potentials due to HOBr (□) were measured at two different concentrations of sulfuric acid: 1.5 (upper curve) and 0.15 (lower curve) M. The solid lines (T) going through the experimental points (□) were calculated with the use of CPT. In cases where bromine was added to the solution ([HOBr] = $[Br_2]$), the response is indicated by ■. The response due to HOCl is represented by ◇. Insert: Potential response as a function of the added $[Br_2]$ at a constant value of $[HOBr] = 7.8 \times 10^{-5}$ M. The solid line is the theoretical curve according to CPT.

bromide- and iodide-selective electrodes were studied more extensively than the chloride-selective one. All the experiments were performed at 24 ± 1 °C.

Results and Discussion

The potential response of the *chloride-selective electrode* is shown in Figure 2. The response to HOCl is small even at relatively high concentrations because the hydrolysis of Cl_2 is more favored thermodynamically than that of the other halogens[31] (cf. eq 3 and 29 and Table I). The theoretical response predicted by CPT agrees qualitatively with the measured one (see curve T in Figure 2). Above 10^{-4} M, HOBr produces a noisy signal followed by a sudden potential jump, showing hysteresis and poor reproducibility. It seems that, under such circumstances, the AgCl pellet is slowly transformed to a mixed phase of $AgCl_xBr_y$[32] (with $x + y = 1$) which is sensitive to hypobromous acid. No measurable response was observed to H_2OI^+.

The potential response of the *bromide-selective electrode* (Figure 3) to HOBr and (HOBr + Br_2) is in agreement with the CPT. The response to HOCl is very similar to that caused by HOBr in the low-concentration region. However, the electrode shows some "memory effects" that, again, can be explained by a partial conversion of the membrane surface.[32] H_2OI^+ causes a relatively small signal that decreases with time at higher concentrations.

The response of the *iodide-selective electrode* (Figure 4) to $H_2OI^+ + I_2$ can be explained by the CPT. The effect of the presence of I_2 becomes significant only at very large excess of I_2. In the concentration range of around 10^{-6} M and below for Ag^+ and I^-, the electrode potential is also affected by the oxygen dissolved in the 0.15 M H_2SO_4.[33a] Under ordinary circumstances, the dissolved oxygen determines the response (solid curve in Figure 4). However, to a certain extent, the electrode potential depends also on the conditioning of the membrane, as indicated by the dashed curve in Figure 4, which was obtained after immersing the electrode into a 10^{-3} M I_2 solution for a few minutes. (Such experimental conditions are common in the BR reaction.)

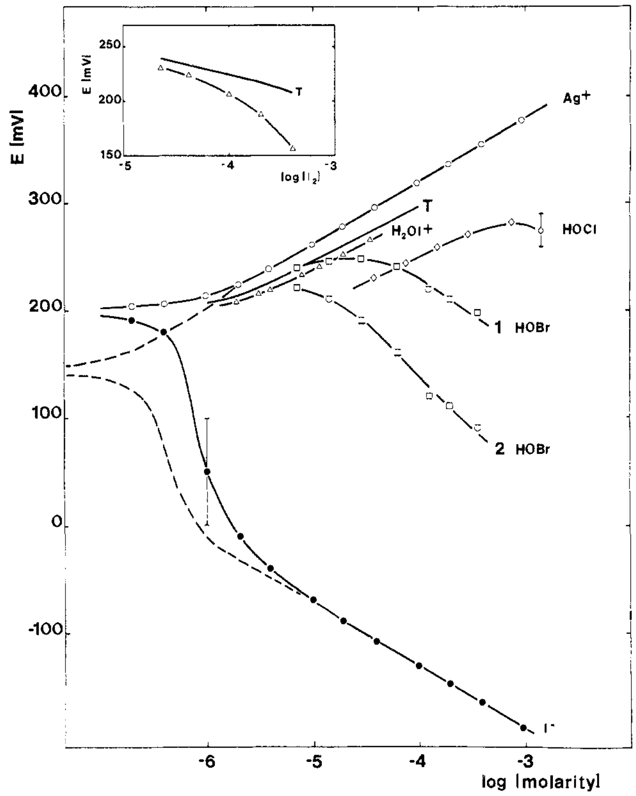

Figure 4. Response of the iodide-selective electrode vs. the concentration of the species determining the potential, at $[H_2SO_4] = 0.15$ M, except for HOBr (□) and HOCl (◇), where $[H_2SO_4] = 1.5$ M. For H_2OI^+, the solid line (T) is the theoretical curve obtained from CPT, and △ represent the experimental points. The rate of stirring strongly affects the response caused by HOBr as indicated by two extremes: (1) vigorously stirred and (2) unstirred solution. Insert: Potential response as a function of the added $[I_2]$ at a constant value of $[H_2OI^+] = 6.3 \times 10^{-6}$ M. The solid line (T) is the theoretical curve according to CPT.

Experimental Facts Contradicting the KBT. As was pointed out previously, according to the KBT the potential of a halide-sensitive electrode is determined by the halide in bulk concentration, even below the solubility limit. Let us examine the consequences of this assertion on the example of a bromide-selective electrode immersed in an acidic solution containing both Br_2 and HOBr. This is a relatively simple case compared to an oscillating system. The bromide concentration can be expressed from the hydrolysis equilibrium expression of bromine as[31]

$$[Br^-] = K_h[Br_2]/([H^+][HOBr]) \qquad (12)$$

where K_h is the hydrolysis constant, and concentrations are used instead of activities, as a first approximation. According to KBT the $[Br^-]$ is uniform throughout the solution (including the surface of the electrode) and the bromide level should control the $[Ag^+]$ at the surface of the membrane and consequently the potential of the electrode even below the solubility limit. With reference to Figure 3, the experimental facts are in clear disagreement with the predictions of KBT:

(i) The $[Br^-]$ and thus the electrode potential ought to be independent of the [HOBr] as long as the ratio $[Br_2]/[HOBr]$ is kept constant (see eq 12). Yet, as shown in Figure 3, the potential increases by 55 mV if the [HOBr] is increased by a factor of 10 at the constant ratio of $[Br_2]/[HOBr] = 1$ and at constant $[H^+]$.

(ii) Conversely, at constant [HOBr], increasing the ratio $[Br_2]/[HOBr]$ from less than 0.01 to 1 ought to decrease the electrode potential by more than 100 mV. Yet, no measurable change in potential takes place.

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Table I. Hydrolysis Constants K_h, Solubility Products K_s, and Diffusion Coefficients D_j Used in the Calculation of the Theoretical Responses at 25 °C

X	K_h	ref	K_s	ref	K_h/K_s	D_{Ag^+}/D_{XOH}	D_{Ag^+}/D_{X_2}
Cl	3.94×10^{-4}	38	1.56×10^{-10}	41	2.53×10^6	1 (0.90)	1 (0.99)
Br	5.8×10^{-9}	39	7.7×10^{-13}	41	7.53×10^3	1 (0.94)	1 (1.09)
I	5.4×10^{-13}	40	1.5×10^{-16}	41	3.60×10^3	1 (1.15)	1 (1.28)

All these results clearly indicate that, below the solubility limit, the electrode potential is a function of the corrosive HOBr concentration, and it is *independent* of the bulk concentration of the Br^-. In the following section we shall show how the CPT can be applied to interpret the results.

Application of the CPT. The classical example of a corrosive electrode is thallium metal immersed in an electrolyte saturated with air.[34] A nonclassical example of corrosion with membrane-type electrodes is the CN^--sensing AgI–Ag_2S membrane electrode.[35] Especially for the latter, a rather detailed theory has been presented.[33,35–37] Below, a similar theoretical model will be developed to describe the potential response of the silver halide ion-selective electrodes to hypohalous acids as corrosive agents.

The cornerstone of the CPT is the realization that the electrode potential is determined by the silver ions generated by the corrosion process

$$\epsilon = \epsilon_0 + (RT/F) \ln [Ag^+]_i \tag{13}$$

where the subscript i refers to concentration at the membrane–solution interface. Throughout the derivation, concentration will be used instead of activities as a first approximation. To calculate $[Ag^+]_i$ as a function of the bulk concentrations $[HOX]_b$ and $[X_2]_b$, besides the chemical processes, one must take into account the diffusion of the different components through the Nernst boundary layer. A schematic representation of the concentration profiles assumed in the vicinity of the electrode is shown in Figure 5. The corrosion reaction 3 takes place very near to the interface in the "reaction layer" (that is much thinner than the Nernst boundary layer), where, as a result of fast reactions,[31] equilibrium is reached. Thus, at the interface

$$K_h = [X^-]_i[XOH]_i[H^+]/[X_2]_i \tag{14}$$

Here, due to the high acidity prevailing in the solution, we used the approximation $[H^+]_i \approx [H^+]_b \equiv [H^+]$. Naturally, the solubility equilibrium holds also at the interface

$$K_s = [Ag^+]_i[X^-]_i \tag{15}$$

When Fick's first law for the transport of the different species through the boundary layer is applied, the diffusion fluxes are given by

$$J_{XOH} = (D_{XOH}/\delta)([XOH]_i - [XOH]_b) \tag{16}$$

$$J_{X_2} = (D_{X_2}/\delta)([X_2]_i - [X_2]_b) \tag{17}$$

$$J_{Ag^+} = (D_{Ag^+}/\delta)[Ag^+]_i \tag{18}$$

where the positive direction is pointing from the electrode toward the solution. It is reasonable to assume that outside the reaction layer the flux of the halide ions is negligible compared to the other currents, and the silver ion concentration in the bulk solution is negligibly small. The corrosive dissolution of the silver halide pellet can also be written as

$$AgX + H^+ + XOH \rightarrow Ag^+ + X_2 + H_2O \tag{19}$$

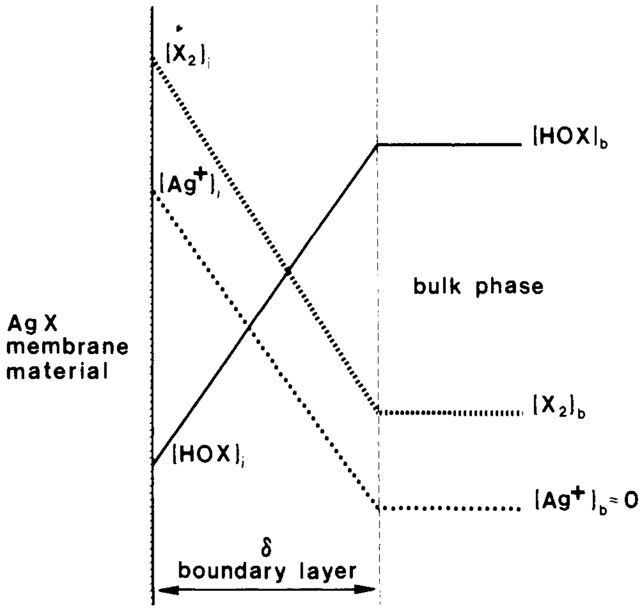

Figure 5. Schematic representation of the concentration profiles in the vicinity of the electrode surface. The subscripts indicate interfacial (i) and bulk (b) values of the concentrations. The diffusion processes take place in the Nernst boundary layer of thickness δ, whereas the concentrations in the bulk phase are considered to be uniform.

from which, under steady-state conditions, for the relevant species we have

$$-J_{XOH} = J_{Ag^+} = J_{X_2} \tag{20}$$

The H^+ and H_2O fluxes need not be considered, since their relative concentration changes due to reaction 19 are extremely small. Now, based on eq 14–20, $[Ag^+]_i$ can be expressed as

$$[Ag^+]_i = f(K_h, K_s, D_j, [XOH]_b, [X_2]_b, [H^+]) \tag{21}$$

with the result of (see Appendix for details)

$$[Ag^+]_i = \frac{K_{XH}}{2K_H}\{-1 + (1 + 4K_HK_{XH}^{-2}[XOH]_b)^{1/2}\} \tag{22}$$

where

$$K_H \equiv K_hD_{Ag^+}/(K_sD_{X_2}[H^+]) \tag{23}$$

$$K_{XH} \equiv K_h[X_2]_b/(K_s[H^+]) + D_{Ag^+}/D_{XOH} \tag{24}$$

With respect to eq 22, several limiting cases can be considered. If

$$4K_HK_{XH}^{-2}[XOH]_b \ll 1 \tag{25}$$

then

$$[Ag^+]_i \approx [XOH]_b/K_{XH} \tag{26}$$

Further, if the condition $[X_2]_b = 0$ holds, then eq 26 becomes

$$[Ag^+]_i \approx D_{XOH}[XOH]_b/D_{Ag^+} \tag{27}$$

Equation 27 was obtained previously[18] for X ≡ Br, with the assumption that $[HOBr]_i = [Br_2]_b = 0$.

Another limiting case arises if

$$4K_HK_{XH}^{-2}[XOH]_b \gg 1 \tag{28}$$

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In this case

$$[Ag^+]_i \approx ([XOH]_b/K_H)^{1/2} \qquad (29)$$

Comparison of the Theoretical (CPT) and Experimental Results. The theoretical curves in Figures 2–4 were obtained in the following way: First eq 22 was used to calculate $[Ag^+]_i$, and then the theoretical electrode potential was determined from ϵ vs. $[Ag^+]$ calibration curves. (The calibration curves were established in systems with no chemical reactions taking place; hence, $[Ag^+]_i = [Ag^+]_b$ was valid.) The other parameters that we used in eq 22 are summarized in Table I. Although the diffusion coefficients of the hypohalous acids are not known, they can be estimated by using a textbook method.[42] The diffusion coefficient of Ag^+ can be obtained from its limiting mobility.[43] The actual ratios of the diffusion coefficients are listed in parentheses in Table I. Nevertheless, following Morf et al.,[33b] the approximate value of unity was used for all ratios in our calculations, which does not cause a deviation larger than the experimental error in most cases.

For the Cl^--selective electrode, the theoretical and measured results agree qualitatively (Figure 2). A small amount of chlorine (2–3% of the [HOCl]) contaminating the hypochlorous acid can explain the difference observed. Another possibility for the deviation is that reaction 3, which is relatively slow for chlorine,[31] may not be fast enough to establish equilibrium at the surface of the electrode.

For the Br^--selective electrode, the agreement between the experimental and theoretical curves is good at both $[H^+] = 1.5$ M and $[H^+] = 0.15$ M. The effect of excess Br_2 added is somewhat smaller than expected.

Since the HOI synthesized always contained a considerable amount of iodine, its presence was taken into account in the computation of the theoretical curve for the I^--selective electrode. The effect of additional I_2 added was much larger than what could be explained by the CPT alone. It is rather likely that the presence of iodine inhibits the slow corrosive process involving the dissolved oxygen and at least part of the measured potential change is due to such effects.

We made no special effort to explain in detail the sometimes unusual potential responses observed when the silver halide membrane and the hypohalous acid contained different halogens. Obviously the responses are influenced by some chemical and structural conversions of the membrane surface. Nevertheless, the finding alone is significant that silver halide electrodes, besides halide ions, also respond to a variety of corrosive species.

Conclusion

In the presence of corrosive hypohalous acids the potential response of silver halide based ion-selective electrodes can be explained by the corrosion potential theory. Below the solubility limit of the halide ions, the kinetic buffer theory fails because, in this concentration range, the electrode potential is independent of the halide ion concentration in the bulk of the solution and it depends on the concentration of the corrosive agent only. Since in oscillating systems monitored with silver halide electrodes potentials referring to halide levels below the solubility limit are common, and the hypohalous acids are well-known intermediates of these systems, we conclude that previous estimates of halide levels below the solubility limits in the BL, BZ, and BR reactions are not valid. The hypohalous acids, however, are not the only corrosive components in these systems. Results of our investigation of halous and halic acids in this respect will be reported in a subsequent paper.

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Appendix

Derivation of Eq 22. First, all interfacial concentrations $[X^-]_i$, $[XOH]_i$, and $[X_2]_i$ are expressed as a function of bulk concentrations and $[Ag^+]_i$. Thus, eq 17 and 18 substituted into eq 20 yield

$$[X_2]_i = (D_{Ag^+}/D_{X_2})[Ag^+]_i + [X_2]_b \qquad (A1)$$

and eq 16 and 18 substituted into the left part of eq 20 give

$$[XOH]_i = [XOH]_b - (D_{Ag^+}/D_{XOH})[Ag^+]_i \qquad (A2)$$

Then, the expression for $[X^-]_i$ (obtained from eq 15) and eq A1 and A2 are substituted into eq 14 which results in a quadratic equation in $[Ag^+]_i$. With the symbols introduced in eq 23 and 24, the quadratic equation becomes

$$K_H[Ag^+]_i^2 + K_{XH}[Ag^+]_i - [XOH]_b = 0 \qquad (A3)$$

whose solution is eq 22.

In the derivation of result 26 for the limiting case specified in eq 25, the approximation $(1 + x)^{1/2} \approx 1 + x/2$ was applied.

Registry No. ClO^-, 14380-61-1; BrO^-, 14380-62-2; IO^-, 15065-653; HOBr, 13517-11-8; HOI, 14332-21-9; $NaBrO_3$, 7789-38-0; KIO_3, 7758-05-6; I_2, 7553-56-2; I_2O, 39319-71-6.

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