The Effect of Acetone on Calomel Formation on a Mercury Film Electrode Surface in Chloride Medium

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In the presence of chloride ions, calomel formation takes place on the mercury thin film electrodes under open-circuit conditions, which leads to high base currents and erratic performance in ASV measurements. This study describes the effect of chloride concentration on the calomel formation on the surface by following the cathodic peak on the anodic scan. The effect of acetone on the surface reaction and baseline stability was studied. Application of the method with a sea water sample is also given.
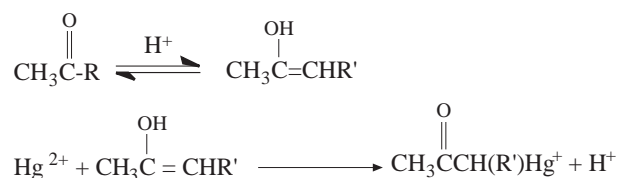
Introduction

Mercury thin film electrodes (MTFEs) are widely used for anodic stripping voltammetric (ASV) determination of mercury soluble trace elements[1]. The film is deposited on an inert substrate, typically on a glassy carbon electrode (GCE). MTFEs may be prepared in a pure mercury(II) solution (ex situ), in which case the electrode is then transferred into the sample solution, or they may be formed in situ by simply adding mercury(II) ions into the medium to be analyzed. The rate of mercury deposition is a function of the pH of the electrolyte, deposition potential, stirring rate and mercury ion concentration. Optic examinations of the mercury film electrodes revealed the formation of fewer and larger drops instead of a homogeneous film[2]. It has also been stated that the rupture of mercury droplets occurs at high rotation speeds. For a fully functioning film, an electrolysis time of 15 min is recommended. However, shorter electrolysis times are reported in recent studies dealing with the baseline stability of MTFEs[3,4].

Sea water and other natural water samples are usually acidified prior to voltammetric analysis[5]. However, the in situ film formation in an acidic medium may produce a less than optimum film coverage. The reduction of the hydrogen ion on the GCE results in buble formation, which contributes to the deformation of the film. With an application of an appropriate deposition potential at pH>2.3 this interference has been shown to be eliminated[6].

Although ASV with MTFE formed in situ provides high sensitivity and low detection limits, anomalous behaviour was observed in the presence of chloride ions. A chemical reaction between the mercury(II) ions in the solution and the elemental mercury on the electrode surface takes place under open-circuit conditions. This calomel formation leads a high baseline current and erratic performance. Although potentiostatic control has been proposed to eliminate this interference[2], the time intervals between the measurements may

not always be under control. In addition, the effect of chloride ion on calomel formation was noted but its effect in varying concentrations was not fully investigated.

On the other hand, CH_3COR ketones are known to react with mercury(II) ions in acidic media to form complexes. In a detailed study[7] polarographic and spectroscopic results revealed that the keto-enol tautomeric transformation determines the rate of the reaction and the product reacts with mercuric ion to give a complex and a hydrogen ion:

$$
\underset{\underset{\displaystyle CH_3C\text{-}R}{\overset{\displaystyle O}{\overset{\|}{}}}}{} \xrightleftharpoons{H^+} \underset{\underset{\displaystyle CH_3C=CHR'}{\overset{\displaystyle OH}{\overset{|}{}}}}{}
$$

$$
Hg^{2+} + \underset{\underset{\displaystyle CH_3C=CHR'}{\overset{\displaystyle OH}{\overset{|}{}}}}{} \longrightarrow \underset{\underset{\displaystyle CH_3CCH(R')Hg^+ + H^+}{\overset{\displaystyle O}{\overset{\|}{}}}}{}
$$

The reduction mechanism of the complex formed was elucidated polarographically as the ECE mechanism including the dimerization process[7].

It was also noted that in acidic mercury(I) solutions, ketone derivative complexes with mercury(II) ions form the equilibrium $(Hg_2^{2+} \rightleftharpoons Hg + Hg^{2+})$ and lead to the formation of elemental mercury. In fact, in the case of the mercury thin film electrode, the electrode reaction in Hg^{2+} solutions seems to be the reverse of the above disproportionation reaction. Therefore, in controlling the surface reaction of mercury(I) taking place on the MTFE surface, the effect of acetone, being the simplest ketone, on the disproportionation reaction was considered to be useful.

The objectives of the present study are to investigate the effect of chloride ion concentration on the peak shapes, the interaction of the calomel with acetone added and the effect of acetone on baseline stability.

Experimental

Reagents : All the chemicals used were of analytical grade. Doubly distilled water supplied by the Maxima Ultra Pure Water system was used throughout the study.

Apparatus : Voltammetric studies were carried out with a Metrohm 693 VA Processor and 694 VA Stand. The working electrode was a glassy carbon electrode obtained from Metrohm with a 3 mm diameter. Potentials were measured against a Ag/AgCl reference electrode and a platinum wire was used as the auxiliary electrode. pH measurements were made with a Jenway Ionmeter. An LC 30 Ultrasonic bath was used for sonication. Optical investigations of the electrode surface were carried out with an ASA 72310 stereoscope.

Procedure : The GCE surface was polished with Al_2O_3 on a piece of wet velvet and rinsed with distilled water. Following the sonication step in water for 5 minutes, the electrode was placed in the voltammetric cell. Then the electrochemical cleaning procedure was initiated by cycling the potential 100 times at the potential range of -100 to -1200 mV. The mercury film was prepared by depositing the mercury from mercury(II) ions into the solution (1.0-5.0 x 10^{-4} M) by 3 successive electrolysis steps at -0.8 V for 200 s. A stirring rate of 1000 rpm was used in the deposition period. The conditioning step was repeated between deposition periods to remove any deposited metallic impurities. Following the film formation step, the stirrer was switched off for 20 s to allow the solution to become quiescent and then the potential was scanned anodically in direct current (dct) mode with a rate of 20 mV/s. Any formation that occurred on the electrode surface was

investigated by keeping the electrode under open-circuit conditions for certain time intervals and then the AS voltammogram was recorded. The same procedure was repeated by adding acetone to the cell.

The sea water sample was collected from a sea cage fishery around Çeşme, İzmir. The polyethylene bottles, previously shaken with nitric acid and rinsed with pure water, were used for sampling. Without further purification 10 mL of this sea water sample was placed in the voltammetric cell. The pH of the sample was brought to 2.20 by adding concentrated $HClO_4$ solution. Following the addition of 1 mL of standard mercury(II) solution (1 g/L), the same procedure was applied for obtaining MTFE. The lead ions in the sample were collected at -0.8 V for 30 s. At the end of the accumulation period, the potential was scanned anodically. The standard addition method was used for lead determination.

Results and Discussion

In this study, a rather low concentration of mercury(II) ions and a longer deposition time were considered to provide better film formation than in previous studies[3,4] carried out with higher mercury(II) concentrations and shorter electrolysis times. Since calomel formation occurs on the electrode surface by a chemical reaction, initial studies were conducted to investigate the influence of the open-circuit reaction time on the baseline stability of the MTFE in the presence of chloride ions. Subsequent to the formation of MTFE from a plating solution containing $1.0 - 5.0 \times 10^{-4}$ M mercury(II) ions, the electrode was held in the chloride solution for a certain time interval and then the potential was scanned in the anodic direction. The chloride content of the plating solutions varied in the range of 1.0 - 3.0% (w/V).

Figure 1 shows the effect of open-circuit reaction time on the baseline stability of the electrode prepared from the solution containing 1×10^{-4} M mercury(II) ions and held in the KCl solution containing 3.0% chloride ions similar to sea water for 0-60 min. The current-potential curves recorded in dct mode show a significant change in the baseline current in the cathodic region which may be attributed to the hydrogen evolution. It shifted to more positive potentials as time elapsed because of the changed surface characteristics of the electrode. Close visual examination showed that the texture of the mercury surface consisted of very finely distributed and densely populated mercury droplets rather than homogeneous film formation. This microscopic observation agrees well with previous studies[2,4]. These droplets assembled and grew larger as the time elapsed and a black glassy carbon base appeared. This deterioration of the surface is reflected in the baseline instability mainly due to the hydrogen evolution on the carbon base. In a previous study[2] the baseline changes in acidic and neutral media were said to be related with hydrogen evolution on the electrode surface.

The experiments were repeated with different concentrations of chloride solution to investigate the effect of the chloride ion on the open-circuit reaction. Figures 2 and 3 show the time-dependent voltammograms obtained with solutions containing 1.5 and 1.0% chloride ions. The anodic peaks on the voltammograms recorded subsequent to the deposition (0 min) resulted from the anodic dissolution of the lead and copper impurities, giving anodic peaks at -0.45 and around -0.25 V respectively. The change in background current at negative potentials was observed to shift to more positive potentials on the following scans. As can be seen from these figures, the change in baseline current becomes more apparent with increasing reaction time under open-circuit conditions.

Jagner et al.[3] observed a cathodic peak on the anodic scan, and they attributed this peak to the formation of calomel at the electrode surface. They also stated that the calomel deposited on the electrode

surface is reduced very slowly in the approximate potential range -0.90 to -1.20 V. The magnitude of this peak was reported to be independent of the chloride ions in the 0.001 to 3.5 M concentration range.
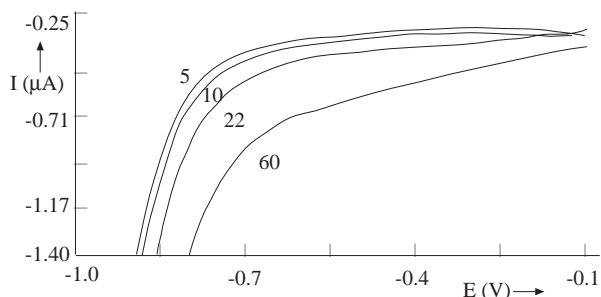

Figure 1. Time dependent anodic stripping voltammograms recorded in 3.0% Cl⁻ solution containing 1×10^{-4} M Hg^{2+} ions at a MTFE formed in situ (pH = 2.18). The open-circuit reaction times were given in minutes on the related curves.

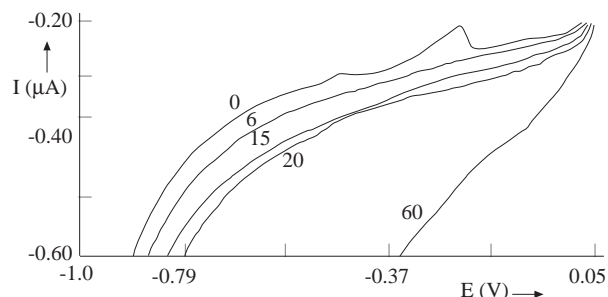**Figure 2.** Anodic stripping voltammograms recorded in 1.5% Cl⁻ solution containing 1×10^{-4} M Hg^{2+} ions at a MTFE (pH = 2.25). The open-circuit reaction times were given in minutes on the related curves.
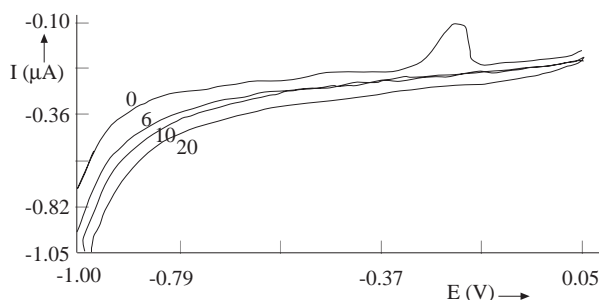

Figure 3. Anodic stripping voltammograms recorded in 1.0% Cl⁻ solution containing 1×10^{-4} M Hg^{2+} ions at a MTFE (pH = 2.08). The open-circuit reaction times were given in minutes on the related curves.

By taking into account the disturbing effect of calomel formation on the film, the chloride concentration was considered to have great influence on the baseline stability. However, no current changes related to calomel reduction were observed in this potential ragne. Therefore the open-circuit experiments were repeated with solutions containing a higher concentration mercury(II) (5×10^{-4} M) in the KCl solution containing 1.5% chloride ions. In Figure 4a, curve 0 shows the anodic stripping voltammogram recording initiated as soon as the film formation step was completed. The electrode was held in the same solution without applying any potential, an a few minutes later a broad cathodic peak appeared at -0.1 V during the anodic potential scanning. This peak corresponds to the reduction of calomel on the electrode surface and becomes more apparent on the following voltammograms recorded several minutes later. After 60 min under open-circuit conditions, the peak current had reached a magnitude of 8μA, while the noise in the background current had also increased.

The effect of acetone on this chemical reaction was investigated by adding acetone at 1.0 M to the plating solution prior to the film formation. The current noted for the deposition step was found to be very low, at nanoampere levels, compared to the current at microampere levels observed in the absence of acetone. This can be attributed to the surface active characteristics of acetone, which may prevent film formation. Therefore, the acetone solution was added as soon as the film formation step was completed. Figure 4b shows the voltammograms recorded after the addition of acetone to be 0.75 M in the final solution. It can

be clearly seen that the oscillations in the background current are reduced to a great extent in the presence of acetone. However, the cathodic peaks were observed to be bigger and after 15 min elapsed the peak grew larger. This unexpected behaviour encountered in the voltammogram indicates a complex formation between acetone and mercury(II) and chloride ions, which reduces at potentials around -0.1 V. On the addition of mercury(II) ions to the solution at 20-fold the initial concentration, the peak was observed to grow larger, and on addition of acetone to this solution a shoulder was observed on the anodic scan (Figure 5). This can be interpreted as the reduction of more than 1 complex on the electrode surface.

Close visual investigation of the electrode surface reveals the nature of mercury coatings under various conditions. The electrode prepared with a plating solution containing 3% chloride ions gave an almost homogeneous film formation consisting of finely distributed droplets. These droplets assemled and grew larger as the water layer on the surface evaporated and a black carbon base appeared. This finding agrees well with the findings in which the film was examined microscopically[4].

On allowing the water layer to evaporate completely, cubic KCl crystals were spotted around the electrode circle. The electrode prepared with mercury(II) solution (1×10^{-4} M) containing 1.0% chloride ions was held in the same solution for 90 min in open-circuit condition and then the electrode was examined microscopically. Besides the cubic KCl crystals around the electrode edges, needle-like crystals at the centre were noticed. The stability of the electrode was found to be longer after the addition of acetone to the solution.
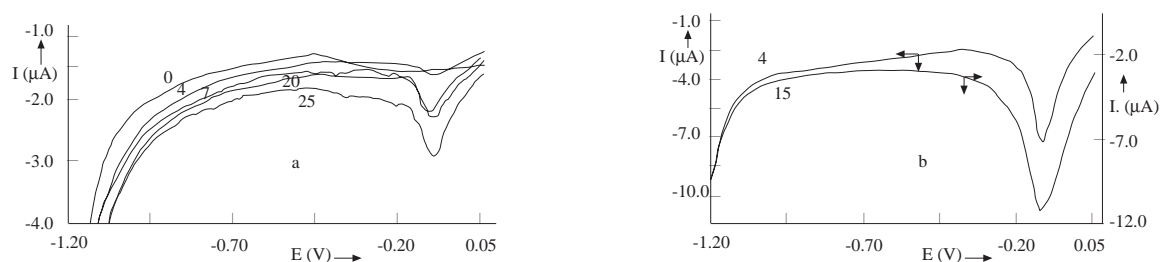

Figure 4. Anodic stripping voltammograms recorded in (a) 1.5% Cl^- solution containing 5×10^{-4} M Hg^{2+} ions (b) after addition of 0.5 mL (0.7 M) acetone at a MTFE (pH = 2.08). The open-circuit reaction times were given in minutes on the related curves.
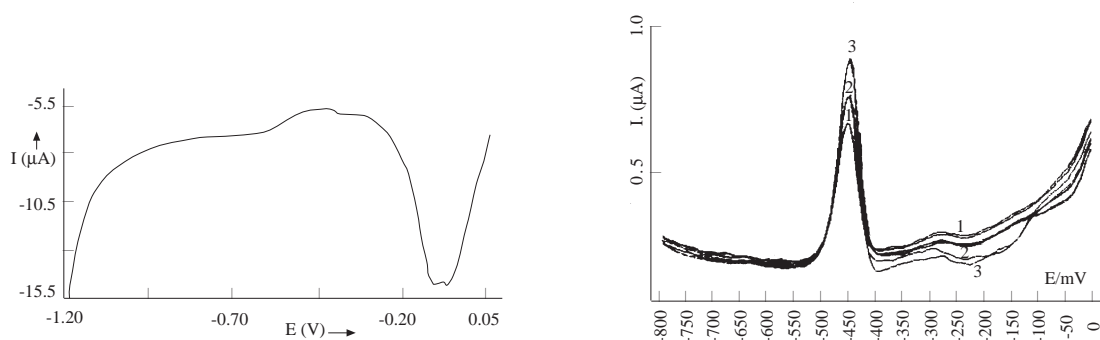

Figure 5. Anodic stripping voltammograms obtained with a 1.5% Cl^- solution containing 5×10^{-4} M Hg^{2+} ions 40 min after addition of 0.5 mL (0.7 M) acetone Details are given in the text.

Figure 6. (1) Anodic stripping voltammograms of acidified sea water samples (pH = 2.2) at a MTFE formed in situ (2) and (3) show the voltammograms recorded after subsequent addition of 5 ng/mL lead ions to the cell. Accumulation was performed at -0.8 V for 30 s.

By taking into account the stabilizing effect of the acetone on the background current, determination of lead ions in sea water samples was carried out. The lead content of the acidified sea water sample was collected on the MTFE formed in situ in the presence of 5×10^{-4} M mercury(II) ions at -0.8 V for 30 s deposition time. The dp anodic stripping voltammograms recorded gave a peak at -0.45 V which can be utilized for lead determination. The standard addition of 5 ng/L lead ions into the solution gave a linear response for the peak currents against the concentration (Figure 6). The experiment was repeated with the addition of acetone to the medium to be analyzed at 1.0 M soon after the film formation was completed. On comparison of the peak heights with those obtained in the absence of acetone, it was shown that the acetone had no suppression effect on the peak heights. Furthermore, the standard deviation calculated for the experiment with acetone was found to be less than 0.01 nA, in comparison to that obtained in the absence of acetone, which was in the range of 1-10 nA for the same set of standard addition. This result indicates the stabilizing effect of the acetone on the baseline current. On the other hand, the standard addition graphs obtained with and without acetone revealed that the slopes of the curve were 25 and 19 mAL/g respectively. This result shows the increase in the sensitivity of the analysis in the presence of acetone. The main focus of the study was to investigate the effect of acetone on the baseline current obtained in the voltammogram in a real life sample. Therefore, the actual lead concentration was beyond the theoretical concentration.

Conclusion

In this study, the calomel formation on MTFEs, which limits the electrode performance in trace metal analysis was investigated in the presence of chloride-containing solutions. Since the calomel formation takes place on the electrode surface in the absence of electrochemical potential, the waiting time of the electrode held in the chloride solutions under open-circuit conditions was considered to be very important for understanding the electrode failure encountered. This study shows that the chloride concentration has a significant effect on baseline changes and calomel formation. This effect can be clearly observed in particular using diluted chloride solution of 1.5% and more containing 5×10^{-4} M mercury(II). Chloride ions interact with metallic mercury and mercury(II) ions adjacent to the electrode surface according to the equation given below, and the resultant calomel undergoes reduction in the potential range studied.

$$\mathrm{Hg^{2+} + Hg - MTFE + 2Cl^- \rightleftharpoons Hg_2Cl_2 - MTFE}$$
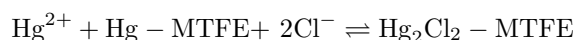
The related cathodic peak at -0.1 V on the anodic scan was expected to diminish in the presence of acetone. In fact, the mixed complex formation among acetone, mercury(II) and chloride ions take place and reduce at the potentials close to the potentials at which calomel reduction occurs. Therefore, the experimental conditions which provide the shift in the reduction potential of this complex should be considered in future studies. A detailed investigation of the chloro complexes of the acetone-mercury(II) in acidic solutions revealed that these mixed complexes are very stable[7]. This interaction with acetone in the solution phase is quite probable on the electrode surface as well. This interaction was also supported by needle-like crystal formation in the presence of acetone.

The stabilizing effect of the acetone on the background current in the potential range studied and electrode performance is very promising. The time-dependent effect of the changed electrode characteristics on hydrogen evolution in chloride solutions results in a narrower study range due to the lower reduction potential of hydrogen. This effect was not seen in the presence of 1.0 M acetone, which may be attributed

to the surface active properties of acetone.

The addition of acetone was found to be useful in ASV determination of lead ions in terms of reproducibility without any suppression effect on the peak current. This is also true for the determination of metal ions, namely copper, thalium, cadmium and zinc, which undergo reduction in the potential range available. Furthermore, acetone can be obtained in very pure form and therefore no impurity is introduced into the solution to be analyzed. The investigations of the mixed complex formation and the elimination of the interference by the use of the other ketone derivatives which dissolve in water are under study.

References

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