# Heavy metal interaction with Lead in the mercury drop

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## Abstract

*Voltammetry is a highly sensitive and selective technique, hence, used to determine heavy metal concentrations in natural water. Amalgam Voltammetry(aV) method has been used to study heavy metal interaction with lead in the mercury drop in model lake water at concentration levels of genuine lake water in $KNO_3$ at $23^0C$. Interaction of heavy metals Cu, Cd and Zn with Pb has been investigated in a hanging drop amalgam voltammetry in the Differential Polarography (DP) mode. Hanging drop amalgam electrode was prepared in situ prior to introducing solutions containing the metal ions. Deposition time for Pb was kept constant at 90 seconds while that for the other metal ions varied. Half-wave potentials at the metal ion concentrations were measured. The experimentally determined shifts in half-wave potentials are used to determine formulae of various complexes and their respective formation constants.*

*The Pb-Cu system forms a stable complex of formula $Pb_{14}Cu_1$ from the Pb curve while the complex, $Pb_{15}Cu_1$ identified from the Cu curve is highly destabilized. The Pb-Cd system forms a stable complex of formula $Pb_{12}Cd_1$ since the radii difference is only 12%. The Pb-Zn system forms a stable complex of formula $Pb_{14}Zn_1$, although radii difference is 21%. Introduction of $CO_3^{2-}$ stabilizes the Pb-Cu system without affecting the number of curves. However, the $CO_3^{2-}$ seems to favour an increase in the number of Cu atoms that interact with Pb while at the same time reduces the number of Pb atoms that react. From the Pb curve, $Pb_7Cu_{13}$ is identified while the Cu one gives $Pb_{13}Cu_2$.*

## Introduction

Most metals are toxic to living organisms and have a tendency to accumulate in food chains[1,2]. Increased public awareness on pollution can attributed to the potential health risks associated with various forms of water pollution, a significant increase in media coverage of environmental issues, recreation and leisure time spent at tourist sites and a great political concern for environmental issues[3]. For this reason, feasibility and design studies relating to water masses is of particular interest.

Lake Nakuru has inlets but no outlets and therefore, the concentrations of heavy metals are likely to continue rising to levels that may pose danger to aquatic life. In addition, increased use of automobiles in Nakuru town and agricultural practices, especially large scale farming for wheat and maize and livestock rearing in the catchment area[3-5] can lead to increased influx of heavy metals into the lake. Lead is one of the most toxic metals[6] and the free $Pb^{2+}$species, which is found to be in dissolved or hydrated ionic forms[7] is the most bioactive and most toxic[8]. There is evidence that when more than one pollutant is present, synergism occurs[9] .Voltammetric techniques can be used for metal analysis at low total metal concentrations. In differential pulse (DP) mode, and anodic stripping voltammetry (ASV), detection limits have to exceed values of about $10^{-7}$and $10^{-9}$ mol/l, respectively[10].

Whilst some metal alloy systems exhibit total or partial solubility and others are insoluble in the solid state, a number of metals combine together to form an intermediate phase or intermediate compounds. There are two types of intermetallic compounds which are often encountered in metallurgy. These compounds are of definite chemical crystal structure and arise if the two alloying metals are of different crystal structure, valency, and if one of these metals is electro- positive with the other being electro- negative. An example of this type of electron compound would be an alloy of the elements magnesium and tin which combine to form an intermetallic compound $Mg_2Sn$. The composition of the compound is fixed and consists of two atoms of magnesium combining with one atom of tin . Metallic compounds form a crystal lattice with the atoms of the alloying metals taking up specific positions within the lattice. These compounds are usually hard and brittle.

Interstitial compounds, as the name suggests form between metals, or metals and non-metallic elements, with atom sizes very similar to those that form interstitial solid solution. One set of atoms fit into the spaces, or interstices, between the larger atoms. Iron carbide ($Fe_3C$) or cementite which is important in the study of iron- carbon diagrams is an example of an interstitial compound. As the chemical symbol for cementite is $Fe_3C$ we know that cementite is an interstitial compound containing 3 iron atoms for every 1 atom of Carbon[11].

It has been found that if two metals are completely miscible with each other they can form a continuous range of solid solutions. Hume-Rothery[12] have shown that for complete miscibility, the two metals must be similar in size provided their metallic radii must not differ by more than 15%. Both metals must have the same crystal structure and the chemical properties must be similar and in particular the number of valency electrons should be the same. If one or two of the above is satisfied then random substitutional solid solutions will only occur over a very limited range at two extremes of composition. In between these extremes a number of intermetallic phases exist, each of which behaves as a compound of the constituent metals, though the exact stoichiometry may vary over a limited range. Hume-Rothery systematized the compositions of the phases formed and found that various phases occurred depending on the ratio of the sum of the valency electrons to the number of atoms irrespective of the particular metals involved. For example, copper compounds with zinc have been reported with formulae $CuZn$, $Cu_5Zn_8$ and $CuZn_3$[12] and in this paper a report on such compounds formed in a mercury drop using voltammetric technique is made.

## Materials and Methods

### Instrumentation

Voltammetric measurements were done using a Polarographic analyzer/stripping voltammeter (EG and G Princeton Applied Research, Model 364 A) connected to a stirrer (EG Model 305) and a static Mercury Drop Electrode (SMDE) Model 303A. This equipment was interposed to a personal computer (model Phoenix 80386 Bios Plus version 1.1030 COPAM) via an analog digital converter box to record data using a capture program Polre[6].The voltammeter was set at the differential pulse mode for all measurements. The toggle on the cell component was switched to the Hanging Mercury Drop Electrode (HMDE) position for the measurements. When a problem of mercury breaks arose, a soft plastic tubing syringe was attached to the tip of the capillary. Dispensing of a steady stream of mercury drops using the dispense function while slowly pulling on the syringe plunger effectively cleared the problem. Setting the right current range, the mode, scan rate and potential scan range necessitated the operation.

## Experimental Procedures

### Amalgam Voltammetry

The electrolytic preparation was done by putting 7.2ml of 2M $KNO_3$ into a 10ml measuring cylinder that was filled to the mark with distilled de-ionized water. The solution was then transferred to a 5ml polarographic cell cup. Using a micro pipette, $8.5 \times 10^{-6} M$ solution of $Pb^{2+}$ ions was injected into the cell cup. Nitrogen gas was then bubbled through the cell cup for 5 minutes to remove oxygen followed by Pb plating for 90 seconds to a hanging mercury drop (small size) at a constant potential. Stirring was done using a magnetic stirrer and the solution allowed to equilibrate for 30 seconds. After stripping, a polarograph was recorded to give the voltammogram for the free $Pb^{2+}$ ion from which the $E_{1/2}$ is determined.

To form the amalgam with another metal ion, the procedure for lead metal was repeated. However, instead of allowing stripping step to take place, the $Pb^{2+}$ ionic solution was removed and the electrode system carefully washed several times with distilled de-ionized water. If the amalgam drop fell during this procedure, the experiment had to be repeated. Finally, the solution containing another metal ion at a known concentration was inserted. Oxygen was again removed from the solution by bubbling pure $N_2$ through it for 5 minutes. Deposition or plating was then done for a varied period of time followed by stripping and recording of the anodic differential pulse voltammetric curve.

### Theoretical considerations

For a simple system in solution of metal M involving two electrons, the reaction can be represented as: $M(Hg) \longrightarrow M^{2+} + 2e^-$

This equation can be followed by the measurement of peak heights and determination of $E_p$ values. The Nernst equation relating the E value to the equilibrium constant for such a process is given by

$$E = -\frac{0.0592}{n} \log K \quad \dots\dots\dots\dots 1,$$

where n is number of electrons transferred and K the equilibrium constant. Assuming amalgam is a kind of solution, then equation 1 can be applied to the Hg drop. Therefore, the effect of another metal N will lead to the measurement of potential, $E'$. Thus, the reaction can have an equation in the Hg drop represented as:

$$xM(Hg) + yN(Hg) \longrightarrow M_x N_y (Hg)$$
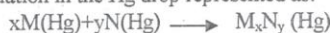
where x and y are of atoms of M and N respectively. The equilibrium constant for such a reaction is written as

$$K_{eq} = \frac{a_M^x \cdot a_N^y}{[M]^x \cdot [N]^y} \quad \dots\dots\dots\dots 2,$$

Where a is activity and [ ] concentration in the mercury drop. Rearrangement of equation 1 and taking log for equation 2 leads to

$$\log K = -\frac{nE}{0.0592} \quad \dots\dots\dots\dots 3, \text{ and}$$

$$\log K_{eq} = \log \frac{a_M^x \cdot a_N^y}{[M]^x \cdot [N]^y} \dots\dots\dots 4$$

Now equation 3 represents a free system for M with measurement of E while 4 is for the effect of N on M represented by $E'$. Since the value of x is represented by equation 3, the difference, $\triangle E = E' - E$ is the difference in logs and measures the effects of N on M, hence, y. Since $K_{eq}$ depends on number of atoms of M and N, the ratios of K's will give atomic ratios x and y.

## Chemicals

All chemicals used were analar grade purchased from Aldrich company.

## Sampling

Water samples were collected from lake Nakuru which is a salt water lake in plastic containers

## Results and Discussions

### Lead-Copper system
### Table 1 : Pb-Cu Complex

| Deposition time(sec.)Cu | $E_p$, mV Pb curve | $E_p$, mV Cu curve | Log K Pb curve | Log K Cu (Pb curve) | Log K Cu(Cu curve) |
|---|---|---|---|---|---|
| 0 | -0.400 | 0.060 | 13.514 | -0.338 | -2.027 |
| 60 | -0.390 | 0.055 | 13.176 | -0.405 | -1.858 |
| 120 | -0.388 | 0.053 | 13.108 | -0.507 | -1.791 |
| 180 | -0.385 | 0.050 | 13.007 | -0.574 | -1.689 |
| 240 | -0.383 | 0.052 | 12.939 | -0.608 | -1.757 |
| 300 | -0.382 | 0.053 | 12.905 | -0.642 | -1.757 |
| 360 | -0.381 | 0.055 | 12.872 | -0.642 | -1.858 |
| 420 | -0.381 | 0.056 | 12.872 | -0.676 | -1.892 |
| 480 | -0.380 | 0.060 | 12.838 | -0.743 | -2.027 |
| 540 | -0.378 | 0.070 | 12.770 | -0.743 | -2.365 |
| 600 | -0.360 | 0.080 | 12.162 | -0.743 | -2.703 |

Table 1 shows two curves and analysis of the lead curve identifies one Cu atom interacts with twenty one atoms of Pb to form a stable complex of formula $Pb_{21}Cu_1$ with a stability constant of 12.924. Here, the large Pb atoms may interact with one another without at the same time touching the small Cu atoms. Analysis of the Cu curve shows one Cu atom is surrounded by seven Pb atoms to give a destabilized complex of formula $Pb_7Cu_1$ with formation constant of -1.978. Metallic radii are 1.75 Å and 1.28 Å differing by 26.9%, hence, destabilized complexes with distorted structures. The ratios of the sum of the number of valency electrons to the number of atoms are 85:22 and 29:8.

### Lead-Cadmium system
### Table 2 : Pb-Cd Complex

| Deposition time(sec.) Cd | $E_p$ mV | Log K | Log K (Pb) |
|---|---|---|---|
| 0 | -0.390 | 13.176 | - |
| 60 | -0.400 | 13.514 | 0.338 |
| 120 | -0.410 | 13.851 | 0.675 |
| 180 | -0.430 | 14.527 | 1.351 |
| 240 | -0.440 | 14.865 | 1.689 |
| 300 | -0.430 | 14.527 | 1.351 |
| 360 | -0.420 | 14.189 | 1.013 |
| 420 | -0.410 | 13.851 | 0.675 |
| 480 | -0.4.00 | 13.514 | 0.338 |
| 540 | -0.405 | 13.682 | 0.506 |

The complex identified in this system is quite stable and a Cd atom seems to prefer thirteen Pb atoms to surround it giving the formula of the complex $Pb_{13}Cd_1$ with formation constant of 13.970. Metallic radii are 1.75 Å and 1.54 Å differing by 12%, and so a stabilized complex is formed. The ratio of the sum of the number of valency electrons to the number of atoms is 54:14.

### Lead-Zinc system
### Table 3 : Pb-Zn Complex

| Deposition time(sec.) Zn | $_pmV$ | Log K | Log K (Cd) |
|---|---|---|---|
| 0 | -0.390 | 13.176 | - |
| 60 | -0.380 | 12.838 | -0.338 |
| 120 | -0.360 | 12.162 | -1.014 |
| 180 | -0.380 | 12.838 | -0.338 |
| 240 | -0.380 | 12.838 | -0.338 |
| 300 | -0.375 | 12.669 | -0.507 |
| 360 | -0.380 | 12.838 | -0.338 |
| 420 | -0.375 | 12.669 | -0.507 |
| 480 | -0.380 | 12.838 | -0.338 |
| 540 | -0.375 | 12.669 | -0.507 |
| 690 | -0.380 | 12.838 | -0.338 |

A stable complex of formula $Pb_{29}Zn_1$ with stability 12.761 is reported for this system. Stabilization is achieved by interaction of one atom of Zn with twenty nine atoms of Pb. Metallic radii are 1.75 Å and 1.38 Å and the difference of 21.1% is substantial, yet the complex formed is fairly stable. The ratio of sum of the number of valency electrons to the number of atoms is 118:30.

### Lead-Copper-Carbonate system
### Table 4 : Pb-Cu-$CO_3^{2-}$ Complex

| $[CO_3^{2-}]$ M | $E_p$ mV | $E_p$ mV Pb curve | Log K Cu curve | Log K Pb curve) | Log K Cu (Cu curve) |
|---|---|---|---|---|---|
| 0 | -0.390 | - | 13.176 | - | |
| 0 | -0.420 | -0.040 | 14.189 | 1.013 | - |
| I. | -0.430 | -0.120 | 14.527 | 1.351 | 4.054 |
| 0.2 | -0.440 | -0.170 | 14.865 | 1.689 | 5.743 |
| 0.3 | -0.460 | -0.166 | 15.541 | 2.365 | 5.574 |
| 0.4 | -0.465 | -0.168 | 15.709 | 2.533 | 5.676 |
| 0.5 | -0.470 | -0.180 | 15.878 | 2.702 | 6.081 |
| 0.6 | -0.472 | -0.183 | 15.946 | 2.770 | 6.182 |
| 0.7 | -0.475 | -0.185 | 16.047 | 2.871 | 6.250 |

Two curves are observed in presence of $CO_3^{2-}$ ligand just like in the Pb-Cu system. The Pb curve identifies the presence of seven Pb atoms surrounded by the less bulky thirteen Cu atoms, of formula $Pb_7Cu_{13}$ with a stability constant of 15.098. The Cu curve, on the other hand, shows a less stable complex formation of formula $Pb_{13}Cu_2$ with a stability constant of 5.651. In this system, the $CO_3^{2-}$ ligand stabilizes complex formation by generally favouring increase in number of Cu atoms that interact with Pb and at the same time reduction of Pb atoms. Ratios of sum of valency electrons to number of atoms are 41:20 and 54:15.

## Conclusions

A number of stable complexes between Pb and heavy metals namely, Cd, Cu and Zn have been identified in the amalgam. Pb-Cd system forms most stable complexes. Introduction of $CO_3^{2-}$ as a ligand in $Pb-Cu-CO_3^{2-}$ alters the number of reacting atoms and enhances stability of the complex by about 1.2 times.

## Acknowledgment

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