Potentiometric Determination of Alloy Like Combination of Cations Byusing Silver Amalgam ion Selective Electrode and its Analytical Applications

J. THAMARAISELVI

Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women Coimbatore- 641043, Tamilnadu, (India)
Corresponding Author Email: thamaramuthu1973@gmail.com
http://dx.doi.org/10.22147/juc/130104

Acceptance Date 7th December., 2016, Online Publication Date 2nd January, 2017

Abstract

A new efficient silver amalgam ion selective electrode has been prepared using silver wire & mercury. The sensor is used to determine binary, ternary & quaternary alloy like combination of mixture of metal ions in the acidic & basic medium using ethylene diamine tetra acetic acid as a titrating agent. The error of estimation is found to low. The proposed method is applied to simultaneous determination of metal ions in lactogen milk powder & anesthetic antacid gel.

Key words: Silver amalgam ion selective electrode, Ethylene diamine tetra acetic acid, alloys

1. Introduction

The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of various sensory elements according to the charge and size of the target ion in clinical and environmental assays. Potentiometric methods using ISEs for determining the metal ion have been studied extensively due to their importance in biological process, easy handling, nondestructive analysis and inexpensive sample preparation, applicability to coloured sample and turbid solution. Metal alloys are systems comprising two or several metals and those consisting of metals and non-metals and possessing metallic properties. Alloy components may form solid solutions i.e. Solid phases of variable composition and also chemical compounds.

An alloy typically consists of a base i.e. a metal (major constituent) and admixtures. Alloys are grouped into
i) iron-based ferrous alloys
ii) Light aluminium-based & magnesium-based alloys and
iii) Copper-based, tin based and lead-based non-ferrous alloys.

Taking into consideration of all the above facts that a new simple ionophore is used as an electro active material. In the present study the electrode show good selectivity and reproducibility over all the metatation and the results are presented in this paper.

2. Experimental Method
2.1 Chemicals used:
Reagent grade Ethylene diamine tetra acetic acid, Zinc sulphate, Copper sulphate, Magnesium sulphate, Cadmium sulphate, Manganese sulphate, Aluminium sulphate, Nickel sulphate, Copper chloride solution. All reagents were obtained from E. Merck and can be used without further purification. Throughout double distilled
ionized water was used for solution preparation.

2.2 Preparation of the silver amalgam electrode:
A pure silver wire (7 cm length, 0.5 mm diameter) was polished & cleaned and it was dipped in mercury. Stock solutions were prepared by dissolving reagent grade chemicals in double distilled water.

2.3 Potential measurements:
A digital Potentiometer (EQUIP-TRONICS EQ 602) which is used to measure the e.m.f is connected to silver amalgam electrode and saturated calomel electrode using KNO₃-agar salt bridge.

In the present study, the synthetic mixture of alloy like combination of the metal ion solution is taken in the beaker. The Ethylene diamine tetra acetic acid (EDTA) solution is taken in the burette. In the beaker solution necessary buffer solution $pH_5$ or $pH_{10}$ is added & the titration is continued. For each addition, the e.m.f is determined by using silver amalgam electrode. The representation of electrochemical cell for the EMF measurement is as follows.

```
Internal reference electrode   | Internal reference solution      | External electrode
(Silver amalgam electrode)  | (metal ion solution)             | (calomel electrode)
```

3. Results and Discussion
In Copper & Nickel ion mixtures Copper is estimated in the acidic pH 5 and after the first jump in the e.m.f pH is raised to 10 and the titration is continued. When the second jump in the e.m.f corresponds to Ni²⁺ ion. The error in the estimation is found to be low. (Table-1)

| S.No | Alloy            | % Composition |
|------|-----------------|---------------|
| 1    | Invar Steel     | Ni 36 + Fe 64 |
| 2    | Monel           | Ni 70 + Cu 30 |
| 3    | Coinage         | Ni 25 + Cu 75 |
| 4    | Magnalium       | Mg 10+ Al 90  |
| 5    | Aluminium Bronze| Cu 90 + Al 10 |

% Composition Observed In Binary Alloys(Table-2):

| Alloy         | $pH_5$  | $pH_{10}$ | % Composition Observed |
|---------------|---------|-----------|------------------------|
|               | M(2)    | M(1)      |                        |
| Invar Steel   | Fe²⁺    | Ni²⁺      | 35.8                   | 64.1 |
| Monel         | Cu²⁺    | Ni²⁺      | 69.9                   | 30.0 |
| Coinage       | Cu²⁺    | Ni²⁺      | 25.1                   | 74.8 |
| Magnalium     | Al³⁺    | Mg²⁺      | 9.9                    | 90.0 |
| Aluminium Bronze | Cu²⁺/Al³⁺ |           | 90.1                   | 9.7  |

This data reveals that when two metal ions are determined at different $pH$ level, when there is a large difference in the stability constants of M-EDTA, then the accuracy of estimation is found to be greater than, when the difference in the stability constants of M-EDTA is small.

In the estimation of Cu²⁺ & Al³⁺ the M-EDTA stability constants are not quite closer. (log k 18.8&16.3) and hence error is small.

The potentiometric complexometry of ternary mixture of ions is more interesting. The sequence of e.m.f jumps for the different metal ions in a mixture is presented in Table-2. From the data it is evident that the % errors of estimation are tolerable & the standard deviations are very low.
Table 2. % observed error of the ternary mixture of metal ions

| S.No | Sequence Of Metal Ions | $p_{H_5}$ | $p_{H_{EDTA}}$ |
|------|------------------------|-----------|---------------|
| 1    | Cu$^{2+}$ Cd$^{2+}$ Zn$^{2+}$ | Cu$^{2+}$ Cd$^{2+}$ | Zn$^{2+}$ |
|      | (18.8)$^a$ (16.6) (16.7) | (0.5)$^b$ 0.5 | 0.0 |
| 2    | Cu$^{2+}$ Ni$^{2+}$ Zn$^{2+}$ | Cu$^{2+}$ | Ni$^{2+}$ Zn$^{2+}$ |
|      | (18.8) (18.6) (16.7) | 0.5 | 0.0 |
| 3    | Cu$^{2+}$ Ni$^{2+}$ Fe$^{3+}$ | Cu$^{2+}$ Fe$^{2+}$ | Ni$^{2+}$ |
|      | (18.8) (18.6) (14.3) | 0.5 0.0 | 0.0 |
| 4    | Cu$^{2+}$ Ni$^{2+}$ Fe$^{3+}$ | Cu$^{2+}$ Fe$^{2+}$ | Ni$^{2+}$ |
|      | (18.8) (18.6) (25.1) | 0.5 0.5 | 0.0 |
| 5    | Cu$^{2+}$ Cd$^{2+}$ Zn$^{2+}$ | Cu$^{2+}$ Cd$^{2+}$ | Ni$^{2+}$ |
|      | (0.03) (7.5) (7.5) | 1.5 0.0 | 0.0 |

$log K_{M-EDTA}$

Even the 0.5% error raises due to the limitation in the addition of Ethylene diamine tetraacetic acid in 0.1 ml quantities in the vicinity of end point. Further it is reveals that the % of error is comparatively high for Cu$^{2+}$ in (S.NO-5) When the amount of Copper to be estimated is very low in comparison to other metal ions present in the mixture.

**Industrial Applications for this Method:**

1. When the Lactogen milk powder manufactured by Nestle India Ltd contains the metal ions such as Magnesium, Copper, Zinc & Manganese. The proposed method is applied to simultaneous determination of metal ions using silver amalgam electrode & titration with EDTA using suitable buffers. The error of estimation is negligible.

2. Anesthetic antacid gel:

Mucainegel, manufactured by Wyeth contains the metal ions such as Aluminium & Magnesium.

**Conclusion**

The Sequential estimation of metal ions are simple and can be applied to any number of metal ions in a mixture, provided their M-EDTA stability constants are different.

Since the sequential determination is done by potentiometry, use of different metal ion indicators is avoided.

The error involved in the estimation is less than 2% & in many cases no error is obtained when metal ion concentrations are not widely different. The results are very encouraging & the %errors are very minimum and the experiment is very simply to carry out.

**Reference**

1. M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, and A. R. Massah, “Urananyl selective PVC membrane electrodes based on some recently synthesized benzo-substituted macrocyclic diamides,” Talanta, vol. 58, no. 2, pp. 237–246, (2002).
2. Z.R. Zhang and R.Q. Yu, “The synthesis and membrane transport characteristics of macrocyclic polyether ligands composed of 1,10-phenanthroline as carriers for primary amine species,” Talanta, vol. 41, no. 2, pp. 327–333, (1994).
3. A. K. Singh, P. Saxena, S. Mehtab, and B. Gupta, “Strontium(II)- selective electrode based on a
1. Analytical chemistry in metallurgy by V.I. Posypaiko and N.A. Vasina Book No. 3
2. S. Yamada, “Advancement in stereochemical aspects of Schiff base metal complexes,” Coordination Chemistry Reviews, vol. 190, pp. 537–555, (1999).
3. Boumann, E.W. Anal. Chem. 1975, 47, 959.
4. Akami, N.; Zimmer, H.; Mark, H.B. Anal. Lett., 24, 1431–1443 (1991).
5. Mojtaba Shamsipur, Sayed Yahya Kazemi and Hashem Sharghi, “design of a selective and sensitive PVC-membranepotentiometric sensor for strontium ion based on 1,10-Diaza-5,6-Benzo 4,7 Dioxacyclohexadecane-2,9-Dione as a neutral ionophore”, sensor, 7(4), 438–447 (2007).
6. Khun. K., Ibupoto. Z.H., Chey. C.O., Jun. Lu, Nur. O., Willander. M., “Comparative study of Zn Onanorods and thin films for chemical and biosensing applications and the development of ZnO nanorods based potentiometric strontium ion sensor”, Applied Surface Science, 268, 37–43 (2013).
7. Mohammad hossein arbab-zavar, gholam hossein rounagh and elhamfahmideh-rad "Strontium Ion-Selective Electrode Based on 18-Crown-6 in PVC Matrix" Asian Journal of Chemistry 21(3), 2224-2232 (2009).
8. Kia. M., A. Islamnezhad. A. and  Shariati. Sh “Construction of Sr2+-Selective Electrode and Thermodynamic Study of the Ternary Aqueous Mixed Electrolyte System (SrCl2, KCl, H2O) Using Potentiometric Method” Journal of Physical and Theoretical Chemistry, 8 (2), 79-83 (2011).

4. A. K. Singh, P. Saxena, and A. Panwar, “Manganese (II)-selective PVC membrane electrode based on a pentaazamacrocyclic manganese complex,” Sensors and Actuators B, vol. 110, no. 2, pp. 377–381, (2005).
5. M. R. Ganjali, T. Razavi, R. Dimarvand, S. Riahi, and P. Norouzi, “New diltiazem potentiometric membrane sensor stands on theoretical calculations as a useful device for diltiazem hydrochloride analysis in pharmaceutical formulation and urine,” International Journal of Electrochemical Science, vol. 3, pp. 1543–1558, (2008).
6. M. R. Ganjali, Z. Memari, F. Faridbod, and P. Norouzi, “Samarium microsensor: an asymmetric potentiometric membrane sensor,” International Journal of Electrochemical Science, vol. 3, pp. 1169–1179, (2008).
7. S. S. Beheshiti and M. K. Amini, “A simple and selective flowinjection potentiometric method for determination of iodide based on a coated glassy carbon electrode sensor,” International Journal of Electrochemical Science, vol. 2, pp. 778–787, (2007).
8. H. Zhang, Z. Zhang, J. Li, and Sh. Cai, “Effects of Mg2+ on supported bilayer lipid membrane on a glassy carbon electrode during membrane formation,” International Journal of Electrochemical Science, vol. 2, pp. 788–796, (2007).
9. P. Paker, McGraw-Hill Concise Encyclopaedia of Science and Technology, McGraw-Hill, New York, NY, USA, (1994).
10. S. F. D’Souza, “Microbial biosensors,” Biosensors and Bioelectronics, vol. 16, no. 6, pp. 337–353, (2001).