

# Potentiometric Study on the Complexes and Stability of Zinc Complexes of Thioglycolic Acid in Aqueous--Non Aqueous Media

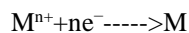
Nitin Gupta<sup>1</sup>, S.M. Nafees<sup>2</sup>, Seema Agarwal<sup>3</sup>

<sup>1</sup>Assistant Professor, Dept. of Chemistry, Government College, Kota, India

<sup>2,3</sup>Associate Professor, Dept. of Chemistry, Government College, Kota, India

**ABSTRACT:** Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution. To do this, two electrodes are used, an indicator electrode (the glass electrode and metal ion indicator electrode) and a reference electrode. Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half cell with the interested ions in the test solution. The reference electrode forms the other half cell.

The overall electric potential is calculated as  $E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_{\text{sol}}$   $E_{\text{sol}}$  is the potential drop over the test solution between the two electrodes.  $E_{\text{cell}}$  is recorded at intervals as the titrant is added. A graph of potential against volume added can be drawn and the end point of the reaction is halfway between the jump in voltage.  $E_{\text{cell}}$  depends on the concentration of the interested ions with which the indicator electrode is in contact. For example, the electrode reaction may be



As the concentration of  $M^{n+}$  changes, the  $E_{\text{cell}}$  changes correspondingly. Thus the potentiometric titration involve measurement of  $E_{\text{cell}}$  with the addition of titrant. Types of potentiometric titration: acid–base titration (total alkalinity and total acidity), redox titration (HI/HY and cerate), precipitation titration (halides), and complexometric titration . Compounds of zinc are chemical compounds containing the element zinc which is a member of the group 12 of the periodic table. The oxidation state of zinc in most compounds is the group oxidation state of +2. Zinc may be classified as a post-transition main group element with zinc(II). Zinc compounds are noteworthy for their nondescript behavior, they are generally colorless (unlike other elements with the oxidation number +2, which are usually white), do not readily engage in redox reactions, and generally adopt symmetrical structures. Thioglycolic acid (TGA) is the organic compound  $\text{HSCH}_2\text{CO}_2\text{H}$ . TGA is often called mercaptoacetic acid (MAA). It contains both a thiol (mercaptan) and carboxylic acid functional groups. It is a colorless liquid with a strongly unpleasant odor. TGA is miscible with polar organic solvents.

**KEYWORDS:** potentiometric, zinc complexes, thioglycolic acid, redox, aqueous, media, electrode

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## I. INTRODUCTION

An aqueous solution is a solution in which the solvent is water. It is mostly shown in chemical equations by appending (aq) to the relevant chemical formula. For example, a solution of table salt, or sodium chloride (NaCl), in water would be represented as  $\text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ . The word aqueous (which comes from aqua) means pertaining to [1,2], related to, similar to, or dissolved in, water. As water is an excellent solvent and is also naturally abundant, it is a ubiquitous solvent in chemistry. Since water is frequently used as the solvent in experiments, the word solution refers to an aqueous solution, unless the solvent is specified.

A non-aqueous solution is a solution in which the solvent is a liquid, but is not water [3,4].

The first potentiometric titration was carried out in 1893 by Robert Behrend at Ostwald's Institute in Leipzig. He titrated mercurous solution with potassium chloride, potassium bromide, and potassium iodide. He used a mercury electrode along with a mercury/mercurous nitrate reference electrode. He found that in a cell composed of mercurous nitrate and mercurous nitrate/mercury, the initial voltage is 0. If potassium chloride is added to mercurous nitrate on one side, mercury (I) chloride is precipitated. [5,6] This decreased the osmotic pressure of mercury (I) ions on the side and creates a potential difference. This potential difference increases slowly as additional potassium chloride is added, but then increases more rapidly. He found the greatest potential difference is achieved once all of the mercurous nitrate has been precipitated. This was used to discern end points of titrations. [7,8]

Wilhelm Bottger then developed the tool of potentiometric titration while working at Ostwald's Institute. He used potentiometric titration to observe the differences in titration between strong and weak acids, as well as the behavior of polybasic acids. He introduced the idea of using potentiometric titrations for acids and bases that could not be titrated in conjunction with a colorimetric indicator. [9,10]

Potentiometric titrations were first used for redox titrations by Crotono. He titrated halide ions using potassium permanganate using a shiny platinum electrode and a calomel electrode. He says that if an oxidizing agent is added to a reducing solution then the equilibrium between the reducing substance and reaction product will shift towards the reaction product. The changes the potential very slowly until the amount of reducing substance becomes very small. A large change in potential will occur then once a small addition of the titrating solution is added, as the final amounts of reducing agent are removed and the potential corresponds solely to the oxidizing agent. This large increase in potential difference signifies the endpoint of the reaction. [11,12]

The first indicator electrode is also presumed to be used in 1893 since potentiometric titration cannot be carried out without it unless ofcourse Robert Behrend used something he did not reveal.

In its compounds,  $\text{Zn}^{2+}$  ions have an electronic configuration  $[\text{Ar}] 3d^{10}$ . As such,  $\text{Zn}^{2+}$  tends to have a symmetrical coordination geometry in both its complexes and compounds. In both ZnO and ZnS, (zincblende) zinc is bound tetrahedrally bound to four ligands (oxide and sulfide, respectively). Many complexes, such as  $\text{ZnCl}_4^{2-}$ , are tetrahedral. Tetrahedrally coordinated zinc is found in metallo-enzymes such as carbonic anhydrase. Six-coordinate octahedral complexes are also common, such as the aquo complex  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ , which is present when a zinc salts are dissolved in water. Five- and seven-coordination numbers can be imposed by special organic ligands. [13,14]

Many zinc(II) salts are isomorphous (have the same type of crystal structure) with the corresponding salts of magnesium(II). This parallel results from the fact that  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  have almost identical ionic radii as well as filled electron shells. That two elements so different in atomic number have the same radius is a consequence of the d-block contraction. Whilst calcium is somewhat larger than magnesium, there is a steady decrease in size as atomic number increases from calcium to zinc.

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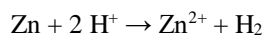
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Zn(II) complexes are kinetically labile, i.e. the Zn-ligand bonds exchange with other ligands rapidly. For this reason, zinc ions are at the catalytic centers in many enzymes.

Zinc compounds, like those of main group elements, are mostly colourless. Exceptions occur when the compound contains a coloured anion or ligand. However, zinc selenide and zinc telluride are both coloured due to charge-transfer processes. Zinc oxide turns yellow when heated due to the loss of some oxygen atoms and formation of a defect structure. Compounds containing zinc are typically diamagnetic, except in cases where the ligand is a radical.[15,16]

Zinc is a strong reducing agent with a standard redox potential of  $-0.76$  V. Pure zinc tarnishes rapidly in air, rapidly forming a passive layer. The composition of this layer can be complex, but one constituent is probably basic zinc carbonate,  $Zn_5(OH)_6CO_3$ .<sup>[8]</sup> The reaction of zinc with water is slowed by this passive layer. When this layer is corroded by acids such as hydrochloric acid and sulfuric acid, the reaction proceeds with the evolution of hydrogen gas.<sup>[1][9]</sup>



Zinc reacts with alkalis as with acids.

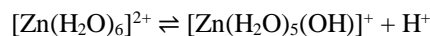
With oxidants such as chalcogens and halogens, Zn forms binary compounds such as ZnS and ZnCl<sub>2</sub>.

Zinc oxide, ZnO, is the most important manufactured compound of zinc, with a wide variety of uses. It crystallizes with the Wurtzite structure. It is amphoteric, dissolving in acids to give the aqueous Zn<sup>2+</sup> ion and in alkali to give the zincate (a.k.a. tetrahydrozincate) ion,  $[Zn(OH)_4]^{2-}$ . Zinc hydroxide, Zn(OH)<sub>2</sub> is also amphoteric.[17,18]

Zinc sulfide, ZnS, crystallizes in two closely related structures, the zincblende crystal structure and the Wurtzite crystal structure, which are common structures of compounds with the formula MA. Both Zn and S are tetrahedrally coordinated by the other ion. A useful property of ZnS is its phosphorescence. The other chalcogenides, ZnSe and ZnTe, have applications in electronics and optics.

The most common structure of zinc complexes is tetrahedral which is clearly connected with the fact that the octet rule is obeyed in these cases. Nevertheless, octahedral complexes comparable to those of the transition elements are not rare. Zn<sup>2+</sup> is a class A acceptor in the classification of Ahrland, Chatt and Davies, and so forms stronger complexes with the first-row donor atoms oxygen or nitrogen than with second-row sulfur or phosphorus. In terms of HSAB theory Zn<sup>2+</sup> is a hard acid.[19,20]

In aqueous solution an octahedral complex,  $[Zn(H_2O)_6]^{2+}$  is the predominant species. Aqueous solutions of zinc salts are mildly acidic because the aqua-ion is subject to hydrolysis with a pK<sub>a</sub> of around 9, depending on conditions.



Hydrolysis explains why basic salts such as basic zinc acetate and basic zinc carbonate,  $Zn_3(OH)_4(CO_3) \cdot H_2O$  are easy to obtain. The reason for the hydrolysis is the high electrical charge density on the zinc ion, which pulls electrons away from an OH bond of a coordinated water molecule and releases a hydrogen ion. The polarizing effect of Zn<sup>2+</sup> is part of the reason why zinc is found in enzymes such as carbonic anhydrase.

No fluoro complexes are known, but complexes with the other halides and with pseudohalides,  $[ZnX_3]^-$  and  $[ZnX_4]^{2-}$  can be prepared. The case of the thiocyanate complex illustrates the class A character of the zinc ion as it is the N-bonded isomer,  $[Zn(NCS)_4]^{2-}$  in contrast to  $[Cd(SCN)_4]^{2-}$  which is S-bonded. Being a class-A acceptor does not preclude the formation of complexes with sulfur donors, as is shown by zinc dithiophosphate and the zinc finger complex [21,22]

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The zinc acetylacetonate complex,  $Zn(acac)_2$  is interesting. As the ligand is bidentate a tetrahedral structure might be expected. However, the compound is in fact a trimer,  $Zn_3(acac)_6$  in which each Zn ion is coordinated by five oxygen atoms in a distorted trigonal bipyramidal structure. Other 5-coordinate structures can be designed by choosing ligands which have specific stereochemical requirements. For example, terpyridine, which is a tridentate ligand forms the complex  $[Zn(terpy)Cl_2]$ . Another example would involve a tripodal ligand such as Tris(2-aminoethyl)amine. Square pyramidal 5-coordinate Zinc is found in Tetra(4-pyridyl)porphinatomonopyridinezinc(II) Solution studies of other 5-coordinate Zinc porphyrins have been reported. The compound zinc cyanide,  $Zn(CN)_2$ , is not 2-coordinate. It adopts a polymeric structure consisting of tetrahedral zinc centres linked by bridging cyanide ligands. The cyanide group shows head to tail disorder with any zinc atom having between 1 and 4 carbon atom neighbours and the remaining being nitrogen atoms. These two examples illustrate the difficulty of sometimes relating structure to stoichiometry.

A coordination number of 2 occurs in zinc amide  $Zn(NR^1R^2)_2$  ( $R^1=CMe_3$ ,  $R^2=SiMe_3$ ); the ligand is so bulky that there is not enough space for more than two of them.

Thioglycolic acid is about 100 times stronger acid than acetic acid, with a pKa of 3.83.

Thioglycolic acid is a reducing agent, especially at higher pH.

Thioglycolic acid, usually as its dianion, forms complexes with metal ions. Such complexes have been used for the detection of iron, molybdenum, silver and tin.[23]

## II. DISCUSSION

Zinc is a chemical element with the symbol Zn and atomic number 30. Zinc is a slightly brittle metal at room temperature and has a shiny-greyish appearance when oxidation is removed. It is the first element in group 12 (IIB) of the periodic table. In some respects, zinc is chemically similar to magnesium: both elements exhibit only one normal oxidation state (+2), and the  $Zn^{2+}$  and  $Mg^{2+}$  ions are of similar size. Zinc is the 24th most abundant element in Earth's crust and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. The largest workable lodes are in Australia, Asia, and the United States. Zinc is refined by froth flotation of the ore, roasting, and final extraction using electricity (electrowinning).

Zinc is an essential trace element for humans and other animals for plants and for microorganisms and is necessary for prenatal and postnatal development. It is the second most abundant trace metal in humans after iron and it is the only metal which appears in all enzyme classes. Zinc deficiency affects about two billion people in the developing world and is associated with many diseases. In children, deficiency causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea. Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans. Consumption of excess zinc may cause ataxia, lethargy, and copper deficiency.

Brass, an alloy of copper and zinc in various proportions, was used as early as the third millennium BC in the Aegean area and the region which currently includes Iraq, the United Arab Emirates, Kalmykia, Turkmenistan and Georgia. In the second millennium BC it was used in the regions currently including West India, Uzbekistan, Iran, Syria, Iraq, and Israel. Zinc metal was not produced on a large scale until the 12th century in India, though it was known to the ancient Romans and Greeks. The mines of Rajasthan have given definite evidence of zinc production going back to the 6th century BC. To date, the oldest evidence of pure zinc comes from Zawar, in Rajasthan, as early as the 9th century AD when a distillation process was employed to make pure zinc. Alchemists burned zinc in air to form what they called "philosopher's wool" or "white snow".

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The element was probably named by the alchemist Paracelsus after the German word Zinke (prong, tooth). German chemist Andreas Sigismund Marggraf is credited with discovering pure metallic zinc in 1746. Work by Luigi Galvani and Alessandro Volta uncovered the electrochemical properties of zinc by 1800. Corrosion-resistant zinc plating of iron (hot-dip galvanizing) is the major application for zinc. Other applications are in electrical batteries, small non-structural castings, and alloys such as brass. A variety of zinc compounds are commonly used, such as zinc carbonate and zinc gluconate (as dietary supplements), zinc chloride (in deodorants), zinc pyrithione (anti-dandruff shampoos), zinc sulfide (in luminescent paints), and dimethylzinc or diethylzinc in the organic laboratory.[24]

## III. RESULTS

It is the procedure through which the quantity of the given test substance is determined by the measured addition of titrant until the entire test substance undergoes reaction. After the titration process, the potential difference between the two electrodes (namely the reference and indicator electrode) is measured in conditions where a thermodynamic equilibrium is maintained and the current passing through the electrodes does not disturb this equilibrium.

### Potentiometric Titration Principle

Potentiometric titration is a laboratory method to determine the concentration of a given analyte. It is used in the characterization of acids. In this method, there is no use of a chemical indicator. Instead, the electric potential across the substance is measured.

### Potentiometric Titration Method

Potentiometric Titration is done via the usage of two electrodes – an indicator electrode and a reference electrode (generally a hydrogen electrode or a silver chloride electrode). One half-cell is formed with the indicator electrode and the ions of the analyte, which is generally an electrolyte solution. The other half-cell is formed by the reference electrode.

### Types of Potentiometric Titration

There are four types of titration that fall under the category of potentiometric titration, namely acid-base titration, redox titration, complexometric titration, and precipitation titration. A brief description of each of these types of titration is given below.

**Acid-Base Titration:** This type of potentiometric titration is used to determine the concentration of a given acid/base by neutralizing it exactly using a standard solution of base/acid whose concentration is known.

**Redox Titration:** This type of potentiometric titration involves an analyte and titrant that undergo a redox reaction. An example of this type of titration would be the treatment of an iodine solution with a reducing agent which produces iodide ion (a starch indicator is used to get the endpoint).

**Complexometric Titration:** This type of titration can also be referred to as chelatometry. In this method, a coloured complex is formed, indicating the end point of the titration. This method is used to determine a mixture of metal ions in a given solution.

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Precipitation Titration: This type of titration involves a reaction between the given analyte and the titrant wherein an insoluble precipitate is formed. The end-point of this titration is noted when the addition of the titrant no longer forms a precipitate.[25]

## IV. CONCLUSIONS

Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration. Complexometric titration are those reactions where a simple ion is transformed into a complex ion and the equivalence point is determined by using metal indicators or electrometrically. In theory, any complexation reaction can be used as a volumetric technique provided that:

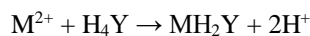
1. The reaction reaches equilibrium rapidly after each portion of titrant is added.
2. Interfering situations do not arise. For instance, the stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process.
3. A complexometric indicator capable of locating equivalence point with fair accuracy is available.

In practice, the use of EDTA as a titrant is well established.

EDTA, ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a hexadentate ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations.

Disodium EDTA is commonly used to standardize aqueous solutions of transition metal cations. Disodium EDTA (often written as  $\text{Na}_2\text{H}_2\text{Y}$ ) only forms four coordinate covalent bonds to metal cations at pH values  $\leq 12$ . In this pH range, the amine groups remain protonated and thus unable to donate electrons to the formation of coordinate covalent bonds. Note that the shorthand form  $\text{Na}_{4-x}\text{H}_x\text{Y}$  can be used to represent any species of EDTA, with  $x$  designating the number of acidic protons bonded to the EDTA molecule.

EDTA forms an octahedral complex with most  $2+$  metal cations,  $\text{M}^{2+}$ , in aqueous solution. The main reason that EDTA is used so extensively in the standardization of metal cation solutions is that the formation constant for most metal cation-EDTA complexes is very high, meaning that the equilibrium for the reaction:



lies far to the right. Carrying out the reaction in a basic buffer solution removes  $\text{H}^+$  as it is formed, which also favors the formation of the EDTA-metal cation complex reaction product. For most purposes it can be considered that the formation of the metal cation-EDTA complex goes to completion, and this is chiefly why EDTA is used in titrations and standardizations of this type.

To carry out metal cation titrations using EDTA, it is almost always necessary to use a complexometric indicator to determine when the end point has been reached. Common indicators are organic dyes such as Fast Sulphon Black, Eriochrome Black T, Eriochrome Red B, Patton Reeder, or Murexide. Color change shows that the indicator has been displaced (usually by EDTA) from the metal cations in solution when the end point has been reached. Thus, the free indicator (rather than the metal complex) serves as the endpoint indicator.[25]

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