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Complexometric Analysis of Magnesium and Manganese Examined by Exchange Extraction Separation Method

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ABSTRACT: Manganese(IV) oxide, MnO_2 (–60+230 mesh, 99+%) was purchased from Aldrich Chemical Company, Inc., USA. Magnesium chloride, ammonium acetate, and sodium chloride were purchased from Sigma Chemical Co., USA. Atomic Absorption Spectrophotometer was used to determine the magnesium ion concentration in the solution. The measurement of magnesium isotope ratio was carried out using Thermal Ionization Mass Spectrometer with a rhenium double filament. Amount of 1.0–2.0 μg magnesium with the MAT 262 was loaded on an evaporation filament. Ionization was then performed by passing a heating electric current through the ionization filament. After the ion beam intensities of $^{24}\text{Mg}^{2+}$, $^{25}\text{Mg}^{2+}$, and $^{26}\text{Mg}^{2+}$ became sufficiently high, the $^{24}\text{Mg}^{2+}$, $^{25}\text{Mg}^{2+}$, and $^{26}\text{Mg}^{2+}$ mass peaks were repeatedly recorded. The mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The mole fraction of $^{24}\text{Mg}^{2+}$, $^{25}\text{Mg}^{2+}$, and $^{26}\text{Mg}^{2+}$ of each feed solution was an average of three times in this measurement.

The manganese(IV) oxide ion exchanger was slurried in 1.0 M ammonium acetate solution ($K_d=32$). The slurried ion exchanger was packed in a water-jacketed glass column (0.2 cm I.D. $\times$ 35 cm height). The temperature was maintained at 20°C with a Water Circulator (HAAKE A-80). The volume of 0.1 ml of 0.01 M MgCl_2 solution was loaded on the top of the MnO_2 bed. Concentration of 1.0 M $\text{CH}_3\text{COONH}_4$ solution ($K_d=32$) was used as an eluent. The magnesium feed solution was then passed through the column under gravity flow. The flow rate was controlled by a fine stopcock to be 0.6 ml/h. The effluent was collected as a fraction of 0.1 ml each with an Automatic Fraction Collector.

KEYWORDS: magnesium, manganese, exchange extraction, separation, spectrometer, isotope, solution

I. INTRODUCTION

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.[1,2]

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.

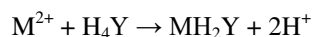
EDTA, ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a hexadentate ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations.[3,4]

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 ≤ 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, 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 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.[5,6]

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.

Extraction in chemistry is a separation process consisting of the separation of a substance from a matrix. Common examples include liquid-liquid extraction, and solid phase extraction. The distribution of a solute between two phases is an equilibrium condition described by partition theory. This is based on exactly how the analyte moves from the initial solvent into the extracting solvent. The term washing may also be used to refer to an extraction in which impurities are extracted from the solvent containing the desired compound. Liquid-liquid extractions in the laboratory usually make use of a separatory funnel, where two immiscible phases are combined to separate a solute from one phase into the other, according to the relative solubility in each of the phases. Typically, this will be to extract organic compounds out of an aqueous phase and into an organic phase, but may also include extracting water-soluble impurities from an organic phase into an aqueous phase. [7,8]

Common extractants may be arranged in increasing order of polarity according to the Hildebrand solubility parameter:

ethyl acetate < acetone < ethanol < methanol < acetone:water (7:3) < ethanol:water (8:2) < methanol:water (8:2) < water

Solid-liquid extractions at laboratory scales can use Soxhlet extractors. A solid sample containing the desired compound along with impurities is placed in the thimble. An extracting solvent is chosen in which the impurities are insoluble and the desired compound has at least limited solubility. The solvent is refluxed and condensed solvent falls into the thimble and dissolves the desired compound which then passes back through the filter into the flask. After extraction is complete the solvent can be removed and the desired product collected. Boiling tea leaves in water extracts the tannins, theobromine, and caffeine out of the leaves and into the water, as an example of a solid-liquid extraction.[9,10]

Decaffeination of tea and coffee is also an example of an extraction, where the caffeine molecules are removed from the tea leaves or coffee beans, often utilising supercritical fluid extraction with CO_2 or standard solid-liquid extraction techniques.

II. DISCUSSION

High adsorptive capacity of colloidal hydrous manganese dioxide for cations. They showed that the pH of the isoelectric point of MnO_2 is quite low, ranging from pH 2.8 to pH 4.5. At higher pH, colloidal manganese dioxide has a net negative charge. They demonstrated that the mechanism of adsorption by MnO_2 is primarily electrostatic by comparing the adsorption of cationic, anionic, and uncharged organic compounds. The removal of trace element cadmium by adsorption onto hydrous oxides of manganese, iron, and aluminum. Manganese dioxide is a much more effective adsorbent for cations. Takeuchi et al. 4) investigated the lithium isotope selectivity by use of sorbents prepared from lithium manganese oxides. They showed that the sorbents are ^6Li -specific and the values of the ^7Li -to- ^6Li isotopic separation factor are between 1.0040 and 1.0092 at 25°C . The separation of the pairs of the isotope ions, $^{63}\text{Cu}^{2+}$ – $^{65}\text{Cu}^{2+}$ and $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ was first attempted by Roberts et al. 5) and Martin et al. 6) Konstantinov et al. 7) investigated the separation of $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ and $^{63}\text{Cu}^{2+}$ – $^{65}\text{Cu}^{2+}$ isotope pairs in aqueous solutions of magnesium chloride and copper chloride using the method of countercurrent electromigration. [11,12] The concentration of the magnesium chloride and copper chloride solutions increased, the relative difference in the



mobilities of the isotope $^{24}\text{Mg}^{2+}$ and $^{26}\text{Mg}^{2+}$ ions, and the mobilities of the $^{63}\text{Cu}^{2+}$ and $^{65}\text{Cu}^{2+}$ ions also risen, and at the high concentrations employed, magnesium chloride and copper chloride may not be completely dissociated. Neubert et al. 8) also reported the isotope enrichment of magnesium, calcium, strontium, and barium through the migration of ions in molten halides. Aaltonen⁹) reported the separations of magnesium and calcium isotopes using a recycle ion exchange technique. He found that the separation factors of magnesium, $^{25}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ and calcium, $^{40}\text{Ca}^{2+}$ – $^{48}\text{Ca}^{2+}$ were 1.00016 and 1.00087, respectively. Nishizawa et al. 10) obtained a separation factor of 1.0112 as a maximum value for the $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ isotope pair by a liquid-liquid extraction system using DC18C6. The production of isotopically pure ^{24}Mg is important because magnesium isotope, ^{24}Mg is a precursor of ^{22}Na through the nuclear reaction of $^{24}\text{Mg}(\text{d}, \alpha) ^{22}\text{Na}$. The reaction product, ^{22}Na is one of the rare β^+ emitters and this isotope is used in various scientific fields as a source of annihilation radiation. Scientists carried out an elution chromatographic separation of magnesium isotopes with N_3O_2 azacrown ion exchanger, and obtained the large separation factors. They also found that the heavier isotopes were enriched into the resin phase, while the lighter isotopes were enriched into the solution phase. In this work, magnesium isotope separation was examined using manganese (IV) oxide by the ion exchange elution chromatography [13,14]

III. RESULTS

The ion exchange capacity of MnO_2 ion exchanger was 0.5 meq/g. Distribution coefficient of magnesium ion on the MnO_2 exchanger was measured with changing the concentration of $\text{CH}_3\text{COONH}_4$ solution from 1.0×10^{-3} M to 2.0 M using batch method. The distribution coefficients were calculated. Separation of magnesium isotopes was investigated by chemical ion exchange with MnO_2 ion exchanger using an elution chromatography. The capacity of MnO_2 ion exchanger was 0.5 meq/g. The heavier isotopes of magnesium were concentrated in the MnO_2 ion exchanger phase, while the lighter isotopes were enriched in the solution phase. The single stage separation factor was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factors of $^{24}\text{Mg}^{2+}$ – $^{25}\text{Mg}^{2+}$, $^{24}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$, and $^{25}\text{Mg}^{2+}$ – $^{26}\text{Mg}^{2+}$ were 1.008, 1.014, and 1.006, respectively. Magnesium ions, with concentration as low as 10^{-4} M have been quantitatively separated from $\text{Mn}(\text{II})$ and $\text{Zn}(\text{II})$ ions by precipitations with some halogen substituted of diphenylthiocarbazon in a buffered solution of about 50% V/V aqueous – dioxan. [15,16]

As a precipitant the di-p-iodophenylthiocarbazon in dioxan solution was employed. The use of this ligand is promising for both qualitative test and quantitative determination of traced of magnesium. Preliminary work with the di-p-fluoro, di-p-chloro, di-p-bromo, and di-m-trifluoromethylphenylthiocarbazon indicated the formation precipitates analogous to the magnesium di-p-iodo- compound. [17,18]

IV. CONCLUSIONS

Solvent extraction (SX) is one such proven technique in the hydrometallurgical processing for selective extraction and separation of metals due to the ease of applicability, versatility and ability to produce high value products. It is used on commercial scale for the recovery of different metals from different solutions viz. copper, nickel, cobalt, zinc, tungsten molybdenum, uranium, rare earths etc. The effluents from waste streams are also processed to recover metals using organic extractants. With the development of improved design of SX equipment and material of construction and newer organic extractants, it is possible to recover metals as value added products even from the complex solutions containing various ionic species. The process has been used first time in USA for nuclear application for extraction of uranium from nitrate solution using ether. Subsequently, developments were made for efficient extraction of uranium from other complex solutions. [19,20] In the solvent extraction process, the extraction of metal ions, or uncharged species in the aqueous phase takes place by ion pair transfer, ion exchange with the extractant. In the case of ion-pair transfer, electrically neutral molecules interact with the extractant to form an addition compound. The most suitable extractants for such interaction are those having an oxygen atom with a lone pair of electrons viz. ether, alcohols, and the neutral phosphoric acid esters. For example, tri-butyl phosphate extracts uranium from nitric acid solutions as follows: $\text{UO}_2(\text{aq}) + 2\text{NO}_3(\text{aq}) + 2 [\text{TBP}] \rightarrow [\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2] + 2\text{H}_2\text{O}$. Similarly, the metal is transferred from the aqueous phase as simple ion, and at the same time an ion from the extractant is transferred stoichiometrically to the aqueous phase in the ion exchange process. The ion present in the aqueous phase may be either cationic or anionic form. [20]



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