DETERMINATION OF HYDROXIDE AND CARBONATE CONTENTS OF ALKALINE ELECTROLYTES CONTAINING ZINC

Dumas A. Otterson
Lewis Research Center
Cleveland, Ohio 44135
A method to prevent zinc interference with the titration of OH⁻ and CO₃²⁻ ions in alkaline electrolytes with standard acid is presented. It involves the use of the Ba-EDTA complex. Experimental evidence is presented which demonstrates the ability of this reagent to prevent zinc interference with acid-base titrations without introducing other types of interference. Theoretical considerations which are supported by the experimental evidence are discussed. They indicate that this method can be used to prevent interference by other metals.
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by Dumas A. Otterson

Lewis Research Center

SUMMARY

A means to avoid the interference due to zinc in the titrimetric determination of hydroxide (OH\textsuperscript{−}) and carbonate (CO\textsubscript{3}\textsuperscript{−2}) contents in alkaline electrolytes is presented. It involves the formation of the zinc-ethylenediaminetetraacetate (Zn-EDTA) complex. Theoretical considerations are presented which show the mechanism of zinc interference. Experiments have demonstrated that zinc interference can be prevented by the addition of EDTA. Thus, EDTA and its complexes of magnesium (Mg) and barium (Ba) were tested. Data are presented which show that the Ba-EDTA reagent at pH~8 with a sufficient excess of Ba\textsuperscript{+2} can be used to prevent zinc interference without any significant interference from uncomplexed EDTA. The possibility of using Ba-EDTA to eliminate the interference of other metals is also discussed.

INTRODUCTION

Advanced alkaline batteries, such as those composed of silver-zinc (Ag/Zn) and nickel-zinc (Ni/Zn) cells, are being investigated for possible use in electric power systems for both terrestrial and space applications. Improved reliability and increased life of these cells could lead to greater economy and hence to greater usage. Systematic improvements in the reliability and life of these new battery systems are possible if their failure mechanisms can be determined.

The investigation of the failure mode of alkaline batteries often requires a knowledge of the hydroxide (OH\textsuperscript{−}) and carbonate (CO\textsubscript{3}\textsuperscript{−2}) contents of the electrolyte. The concentrations of these components of the electrolyte are usually determined by titration with a standard acid. Both Ag/Zn and Ni/Zn batteries use alkaline electrolytes, which become saturated with Zn after a short period of time. This substance causes large errors in the results obtained by direct titration. Corrections based on the Zn content must be
applied. Such corrections are complicated by the fact that more than one Zn compound may interfere.

The interference could be eliminated if a sufficiently stable Zn compound were formed prior to titration with an acid. The use of such a stable Zn compound to prevent the interference of Zn with the determination of the OH\(^-\) and CO\(_3\)\(^{-2}\) in electrolytes has been investigated with synthetic samples. The procedure differs from the usual titrimetric method in that a metal chelate of EDTA is added to form the Zn-EDTA complex. Possible interferences due to EDTA are considered and ways to control them are developed. A procedure for the determination of OH\(^-\) and CO\(_3\)\(^{-2}\) in an alkaline battery electrolyte is described.

**THEORY**

The standard method for the determination of OH\(^-\) and CO\(_3\)\(^{-2}\) in an alkaline solution involves titration with a standard acid to two endpoints. The first is the phenolphthalein endpoint (pH~8), and the second is the methyl orange endpoint (pH~4). If no interfering materials are present, the OH\(^-\) is quantitatively neutralized and all the CO\(_3\)\(^{-2}\) is converted to bicarbonate ion (HCO\(_3\)\(^-\)) when the first endpoint is reached. This bicarbonate is then neutralized between the two endpoints. Specific details can be found in most textbooks of analytical chemistry.

The interference due to Zn results from the formation of Zn compounds or complex ions that contain OH\(^-\) or CO\(_3\)\(^{-2}\). Such entities may be so stable above pH~8 that some of the OH\(^-\) or CO\(_3\)\(^{-2}\) is neutralized along with the HCO\(_3\)\(^-\) when the endpoint at pH~4 is attained. The Zn species that may be present in alkaline solutions during titration with acid include the soluble zincate ion and insoluble ZnCO\(_3\) and zinc oxide. Data based on the solubility of the zincate ion are consistent with this ion being either ZnO\(_2\)\(^{-2}\) or Zn(OH)\(_4\)\(^{-2}\). Raman spectroscopy supports the view that Zn(OH)\(_4\)\(^{-2}\) predominates in strongly alkaline solutions (ref. 1). The reactions which have occurred as each endpoint is reached can be readily ascertained. One need only substitute the values of [H\(^+\)] or [OH\(^-\)] that correspond to pH = 8 or pH = 4 into the equation for the appropriate constants. Thus, we find that at pH = 8 virtually no Zn(OH)\(_4\)\(^{-2}\) (instability constant, 2.8x10\(^{15}\) (ref. 2)) is present but that Zn(OH)\(_2\) (solubility product, 4.5x10\(^{-17}\) (ref. 2)) remains undissolved. Hence, at pH = 8 it will not neutralize any acid. But it will do so before the second endpoint (pH~4) is reached. Similar calculations are based on the solubility product for ZnCO\(_3\) (2x10\(^{-10}\) (ref. 2)) and the ionization constants for carbonic acid (H\(_2\)CO\(_3\)) (K\(_1\) = 4.2x10\(^{-7}\) and K\(_2\) = 4.8x10\(^{-11}\) (ref. 2)). These calculations reveal that virtually all of the ZnCO\(_3\) reacts with the acid between these two endpoints. Thus, erroneously high results would be obtained for CO\(_3\)\(^{-2}\), as well as correspondingly low results.
for OH\(^-\), if the assumption were made that only HCO\(_3^-\) is neutralized between the two endpoints when Zn is present. Moreover, these considerations indicate that the total alkalinity (OH\(^-\) + CO\(_3^{2-}\)) can be determined by titration to pH~4 without interference from Zn.

Correct results for the OH\(^-\) and CO\(_3^{2-}\) contents could be obtained in the presence of Zn either by eliminating interference through the formation of a stable Zn compound or by applying a correction based on the Zn content. The latter course requires the determination of the Zn content and can be complicated by the possibility that two Zn compounds can be involved. Therefore, a method to eliminate the interference due to Zn was considered.

The ethylenediaminetetraacetate (EDTA) ion is a well-known chelating agent for many metal ions (ref. 3). Its use for the elimination of interferences in acid-base titrations is complicated by the fact that the acidic form of EDTA is a weak tetra basic acid (H\(_4\)Y (ref. 3, p. 17)). Hence, either it or its salts would interfere with acid-base titrations. This type of interference can be avoided by using an EDTA reagent with the same pH as that at the endpoint; namely, pH~8. The predominate form of EDTA at this pH is HY\(^-\)\(_3\) (ref. 3, p. 23).

Another type of interference would occur if HY\(^-\)\(_3\) were used to form the Zn-EDTA complex. The reaction (ref. 4, p. 5) is

\[
\text{Zn}^{2+} + \text{HY}^{-3} \rightarrow \text{ZnY}^{-2} + \text{H}^+
\]

The H\(^+\) liberated when the Zn-EDTA complex is formed by this reaction would neutralize some of the alkali and thus cause the results to be low.

No H\(^+\) would be introduced if a metal (Me\(^+2\)) complex of EDTA were used as the source of the complexing agent. The reaction (ref. 4, p. 11) to form the Zn complex is

\[
\text{Zn}^{2+} + \text{MeY}^{-2} \rightarrow \text{Me}^{+2} + \text{ZnY}^{-2}
\]

Alkaline earth metals form much weaker complexes with EDTA than does Zn\(^{2+}\) or many other metal ions (ref. 3, p. 23). The solubilities of the alkaline earth carbonates and hydroxides at pH~8 (ref. 4, pp. 6 to 9) are such that both Mg\(^{2+}\) and Ba\(^{2+}\) would be suitable metal ions in MeY\(^-\)\(_2\) to control the Zn\(^{2+}\) interference with the titration of OH\(^-\) and CO\(_3^{2-}\) with an acid.

At pH~8, both Mg(OH)\(_2\) and MgCO\(_3\) would dissolve and be neutralized in the same manner as the alkali hydroxide and carbonate. Hence, Mg\(^{2+}\) would not interfere. At this pH, all of the Ba(OH)\(_2\), but virtually none of the BaCO\(_3\), would be neutralized. The BaCO\(_3\) dissolves completely between the two endpoints. This fact has led to a procedure for the determination of OH\(^-\) and CO\(_3^{2-}\) in alkaline solutions in which excess Ba\(^{2+}\) is added (ref. 5, p. 558). In this procedure, only OH\(^-\) is neutralized at the first endpoint,
and the CO$_3^{--2}$ is completely neutralized between the two endpoints. Hence, the use of the Ba-EDTA reagent should prevent interference due to Zn and would permit the direct determination of OH$^-$ with titration to only one endpoint. Herein a procedure for the determination of OH$^-$ is described that makes the determination of CO$_3^{--2}$ and Zn$^{+2}$ unnecessary (see section PROCEDURE). Of course, if the CO$_3^{--2}$ determination is needed, the total alkalinity must also be determined.

The use of EDTA to overcome metal interference in the determination of the acidity of aqueous solutions has been reported previously (refs. 6 and 7). In one method, sufficient EDTA is added to complex all of the Zn and iron (Fe) ions present. The titer obtained in the determination of the acidity of this solution must then be corrected for the acid liberated during the formation of the Fe-EDTA and Zn-EDTA complexes (ref. 6). In the other method, calcium (Ca)-EDTA supplies the EDTA to complex interfering metals in titration to pH~4 (ref. 7). The use of this reagent for titrations to pH~8 may lead to error because calcium carbonate (CaCO$_3$) is more apt to be only partially neutralized.

**MATERIAL PREPARATION**

**Reagents**

The reagents used in this work are 0.2500 N hydrochloric acid, 0.2500 N potassium hydroxide, 0.2500 N sodium carbonate, and 0.1 M zinc chloride.

The Ba-EDTA reagent was formed by dissolving 9.3 grams of disodium salt of EDTA (Na$_2$C$_{10}$H$_{14}$N$_2$O$_8$·2H$_2$O) in 200 cm$^3$ of H$_2$O. (Potassium hydroxide (KOH) may be added to hasten solution if the alkalinity is not allowed to exceed pH = 8. The EDTA must be completely dissolved before proceeding.) Then the solution was mixed with 150 cm$^3$ of saturated BaCl$_2$ solution and diluted almost to 500 cm$^3$. The pH of the solution was adjusted to that of the phenolphthalein endpoint by adding KOH until a persistent faint pink appeared. One drop of 0.2500 N hydrochloric acid (HCl) was added to remove color. Only the amount that would be used within a few hours was neutralized. (A precipitate tends to form at this pH.) The final solution was approximately 0.05 M EDTA and 0.5 M BaCl$_2$.

The excess Ba$^{+2}$ is needed to minimize the HY$^{-3}$ content of the Ba-EDTA reagent at pH~8. If there were no excess Ba$^{+2}$, a detectable amount of alkali would be neutralized by the HY$^{-3}$.

The amount of time before precipitation starts in the Ba-EDTA reagent is influenced by several factors. If the EDTA is not completely dissolved prior to mixing with the BaCl$_2$ solution, copious amounts of precipitate will form in about an hour after neutralizing. If the EDTA is completely dissolved, precipitation may not occur for a day or
more. This precipitate can be dissolved by adding acid. However, the pH of the reagent must again be adjusted to pH~8 prior to its use.

Samples

Two types of samples were used in this work: alkaline battery electrolytes consisting of 45-percent KOH which had become contaminated with CO\textsubscript{3}\textsuperscript{2-} and Zn; and synthetic samples of known composition, which were used to test the method of analysis.

Synthetic samples were made by pipetting aliquots of standard sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) (5.00±0.01 cm\textsuperscript{3}) and standardized KOH (25.00±0.03 cm\textsuperscript{3}) into a flask. A graduated cylinder (5 cm\textsuperscript{3}) was used for the Zn solution. Each sample contained the equivalent of 0.0902±0.0003 gram of K\textsubscript{2}CO\textsubscript{3} and 0.3551±0.0006 gram of KOH. Tests were made with 0.013±0.002 to 0.065±0.003 gram of Zn\textsuperscript{2+}.

Samples of battery electrolyte were weighed and not pipetted because the viscosity of the electrolyte could cause pipetted samples to be measured inaccurately. The use of pipetted aliquots is not recommended. If a larger sample were to be diluted enough to permit accurate pipetting, ZnCO\textsubscript{3} or Zn(OH)\textsubscript{2} could precipitate. If this occurred, the composition of the aliquot would not be representative of the electrolyte.

Two samples were required for the determination of both OH\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-}. The determination of OH\textsuperscript{-} was carried out by titration of a sample (sample B) containing Ba-EDTA to pH~8. The determination of total alkalinity (OH\textsuperscript{-} + CO\textsubscript{3}\textsuperscript{2-}) must be carried out on another sample (sample A) with no Ba-EDTA present. The EDTA would react with the standard acid to produce erroneously high results.

The titration of synthetic samples and samples of battery electrolyte was carried out in exactly the same manner after the latter type had been diluted. Hence, only one procedure need be described in detail. The procedure for battery electrolytes is somewhat more complicated and hence is given in the following section.

PROCEDURE

In order to determine total alkalinity, an analytical balance was used to accurately weigh 0.5 to 0.6 gram of battery electrolyte (sample A) into a 250-cm\textsuperscript{3} Erlenmeyer flask. The electrolyte was then diluted to about 50 cm\textsuperscript{3} with water. A rough estimate of the CO\textsubscript{3}\textsuperscript{2-} content can be made by titration to pH = 8.35 (the phenolphthalein endpoint) with standard normal HCl. An acid with a normality of about 0.2 N is suggested for these electrolyte samples. The volume was recorded as \( V_1 \) (cm\textsuperscript{3}). The solution was then titrated to pH = 4 (the methyl orange endpoint). The volume was recorded as \( V_2 \) (cm\textsuperscript{3}),
which includes the volume $V_1$.

In order to determine $\text{OH}^-$ content accurately, a 0.5- to 0.6-gram sample (sample B) was weighed into a 250-cm$^3$ Erlenmeyer flask. The amount of Ba required for this sample was estimated by using the following formula:

$$
(V_2 - V_1) \frac{N}{1000} \times \frac{S_A}{S_B} = \text{mole Ba required}
$$

If 25 cm$^3$ of the Ba-EDTA reagent (0.05 M EDTA and 0.5 M BaCl$_2$) did not supply more than the required amount of Ba$^{+2}$, more was added as BaCl$_2$. Twenty-five cm$^3$ of the Ba-EDTA reagent (and BaCl$_2$ if needed) were added, and the solution was diluted to about 50 cm$^3$. After titration to pH = 8.35, 5 cm$^3$ of Ba-EDTA reagent were added. If the pH of the solution increased, titration was continued to the same endpoint (pH = 8.35).

The addition and titration sequence was repeated until the addition of Ba-EDTA did not alter the pH of the solution. The total volume was recorded as $V_3$ (cm$^3$).

**CALCULATIONS**

For synthetic samples with no Ba-EDTA added,

$$
\text{gram KOH} = \frac{56.10}{1000} (2V_1 - V_2)N
$$

and

$$
\text{gram K}_2\text{CO}_3 = \frac{138.2}{1000} (V_2 - V_1)N
$$

For synthetic samples with excess Ba-EDTA present,

$$
\text{gram KOH} = \frac{56.10}{1000} V_3N
$$

and

$$
\text{gram K}_2\text{CO}_3 = \frac{138.2}{2000} (V_2 - V_3)N
$$

For alkaline battery electrolytes, the moles of Ba$^{+2}$ that should be added are equal to
\[
\left( V_2 - V_1 \right) \left( \frac{N}{1000} \right) \left( \frac{S_B}{S_A} \right) \\
\text{percent KOH} = V_3N \frac{56.10}{1000} \left( \frac{100}{S_B} \right)
\]

and

\[
\text{percent } K_2CO_3 = \frac{138.2}{2000} \left( \frac{V_2}{S_A} - \frac{V_3}{S_B} \right) 100N
\]

where

- \( V_1, V_2 \) volumes of standard acid required to reach endpoints at pH~8 and pH~4, respectively, with no Ba-EDTA reagent added, cm\(^3\)
- \( V_3 \) volume of standard acid required to reach endpoint at pH~8 in presence of excess Ba-EDTA, cm\(^3\)
- \( N \) normality of standard acid
- \( S_A, S_B \) weights of battery electrolyte used for determination of total alkalinity and OH\(^-\), respectively, g

**RESULTS AND DISCUSSION**

The results obtained for the OH\(^-\) and CO\(_3\)\(^{-2}\) contents of synthetic samples containing between 0.011 and 0.015 gram of Zn are given in table I. Some of the samples were titrated with standard acid, with no additives to control interference. In the other samples, Ba-EDTA reagent was added. All calculations were based on the assumption that Zn did not interfere.

The calculations used to evaluate the \( K_2CO_3 \) content of samples with added Ba\(^{+2}\) in the titrations to pH~8 differ from those without added Ba\(^{+2}\). The reason is that BaCO\(_3\) dissolves below pH~8. Hence, all of the CO\(_3\)\(^{-2}\) is neutralized between the two endpoints. In the absence of Ba\(^{+2}\) the dissolved CO\(_3\)\(^{-2}\) is converted to HCO\(_3\)^\(-\) before the endpoint at pH~8 is reached. Therefore, the titer between the two endpoints for a specific amount of CO\(_3\)\(^{-2}\) is only half as great as when Ba\(^{+2}\) is present in excess.

The extent of the interference caused by approximately 0.013 gram of Zn in these samples is readily noted by comparing the results obtained for KOH and \( K_2CO_3 \) with no Ba-EDTA (first two columns of table) with those present in each sample. Even though each sample contained 0.3551±0.0006 gram of KOH, no result obtained for KOH was greater than 0.316 gram when EDTA was not used to chelate the Zn. On the other hand,
no result for $K_2CO_3$ was less than 0.139 gram even though only the equivalent of 0.0902 ± 0.0003 gram was present. Clearly, the presence of Zn causes the KOH results to be low and those for $K_2CO_3$ to be high if no correction is applied.

The data in the last two columns of table I demonstrate the beneficial effect of adding sufficient Ba-EDTA reagent. The mean amount of KOH found was 0.3559 gram, with a standard deviation of 0.0006 gram; and the mean $K_2CO_3$ content was found to be 0.0897 gram, with a standard deviation of 0.0007 gram. Clearly, Zn caused virtually no interference when sufficient Ba-EDTA reagent was added in the titration to pH~8. The good agreement also supports the view that Zn does not interfere with the determination of total alkalinity, which was done by titration to pH~4 without any Ba-EDTA being present.

Variations in the Zn content of the synthetic samples used in this work explain quite satisfactorily why the variation in data was much greater in the first two columns than in the last two columns, in which the Zn interference was virtually eliminated. Noninterference was not the case for the data of the first two columns. Some of the larger errors reported in table I were obtained on samples that were known to contain slightly more Zn than some of the samples that had smaller errors. Another sample, which contained about 0.019 gram of Zn, showed even larger values for $K_2CO_3$ and smaller values for KOH than those reported in the table. These observations are in accord with the view that Zn interference increases with increasing Zn content. In connection with this, it should be stated that the large variations in the unprocessed data were observed in the absence of EDTA only in the titrations to pH~8 and not in those to pH~4. This result supports the contention that Zn interferes only with those titrations to pH~8 and does not do so with those to pH~4.

Finally, tests were made concerning the ability of Ba-EDTA to control interference as Zn content was increased. As much as 0.066 gram of Zn did not adversely affect the accuracy of the results. However, the endpoint was reached slowly in the samples with the highest Zn content. Similar results were obtained with the Mg-EDTA reagent. In this case, the endpoint could be reached only very slowly in the presence of as little as 0.013 gram of Zn. Calculations based on the solubility products suggest that Mg(OH)$_2$ is more insoluble than Ba(OH)$_2$ at the pH of the endpoint. Therefore, the Ba-EDTA mixture is the preferred reagent.

When Ba-EDTA reagent is used, enough $Ba^{+2}$ must be added to precipitate all of the $CO_3^{-2}$ present prior to the addition of any acid. The $CO_3^{-2}$ that is allowed to remain in solution (not precipitated as $BaCO_3$) will react with the acid to form $HCO_3^-$ in the titration to the endpoint at pH~8. This reaction will cause the results for KOH to be high and those for $K_2CO_3$ to be low when it is assumed that only $OH^-$ is neutralized as is done when the Ba-EDTA reagent is used.
CONCLUDING REMARKS

In closing, the data show that the barium-ethylenediaminetetraacetate (Ba-EDTA) reagent can be used to prevent the interference of zinc in acid-base titrations. It is expected that tests would show that the same method can be used to prevent the interference of other metals in this type of analysis. The interference of any metal whose EDTA complex is significantly more stable than BaY\(^{-2}\) may well be controlled. The other requirement is that the EDTA-metal complex be more stable at the pH of the appropriate endpoint than is the hydroxide of that metal. If CO\(_3\)^{-2} and OH\(^{-}\) are being determined by the method of this report, the metal carbonate does not need to be soluble in EDTA at pH = 8. It would have the same effect as the Ba\(^{+2}\); that is, only the OH\(^{-}\) would be involved in the titration to the endpoint at pH~8. Thus, Ba-EDTA can be used to eliminate the interference of those metals whose CO\(_3\)^{-2} is very insoluble. Magnesium-EDTA cannot do this.

The elimination of zinc interference with the determination of KOH leads to more accurate analyses of alkaline battery electrolytes and to more positive identification of battery failure modes. This information is helpful in systematic research to lengthen the life of alkaline batteries.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 14, 1975,
506-23.

REFERENCES


TABLE I. - ELIMINATION OF ZINC INTERFERENCE WITH DETERMINATION OF OH\(^-\) AND CO\(_3\)^{2-} IONS

<table>
<thead>
<tr>
<th>No Ba-EDTA present</th>
<th>Excess Ba-EDTA present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of KOH found, g</td>
<td>Amount of K(_2)CO(_3) found, g</td>
</tr>
<tr>
<td>0.3122</td>
<td>0.1430</td>
</tr>
<tr>
<td>0.3158</td>
<td>0.1392</td>
</tr>
<tr>
<td>0.3158</td>
<td>0.1392</td>
</tr>
<tr>
<td>0.3144</td>
<td>0.1412</td>
</tr>
<tr>
<td>0.3097</td>
<td>0.1460</td>
</tr>
<tr>
<td>(\bar{x} = 0.3117)</td>
<td>(\bar{x} = 0.1441)</td>
</tr>
<tr>
<td>(s = 0.005)</td>
<td>(s = 0.005)</td>
</tr>
</tbody>
</table>

\(\bar{x}\) is the mean value of the set.

\(s\) is the standard deviation.

\[s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}\]
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