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A total experimental study of electrolysis based on precise observation and analysis of products (color, solubility)

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ABSTRACT

Electrolysis of salts is mainly used for electroplating and electro refining. For this acidic solutions are used (chiefly dilute H2SO4). Alkaline solutions are hardly used because metal hydroxides are formed which are mostly insoluble. But precise experiment shows that alkaline solutions can significantly help in metal deposition at cathode as seen case of SnCl2.2H2O and (CH3COO)2Pb.3H2O and help in the formation of salts like (CH3COO)2Cu which can not be synthesized generally. Organic compounds like alcohols can form salts by this process salts containing RO- (R being an alkyl group primary or secondary). If acidic alcohols are electrolyzed, aldehydes and carboxylic acids are formed. So the difference can be easily noticed. Highly covalent aromatic compounds like benzene, toluene e.t.c. can accelerate some3 reactions, retard some and some times change the products .In this Paper it has been discussed about the electrolysis of Ca(NO3)2.4H2O, SnCl2.2H2O, (CH3COO)2Pb.3H2O in alkaline medium and how organic compounds like benzene can affect the products.

Keywords: Ca(NO3)2.4H2O;SnCl2.2H2O;(CH3COO)2Pb.3H2O;C6H6;2 Butanol; NaOH.

INTRODUCTION

The primary idea of electrolysis comes from the electrolysis of acidulated water with dilute H2SO4 and inert electrodes like Platinum, graphite (carbon) which gives O2 at anode and H2 at cathode. The reaction can be given as:- $H2O \rightarrow H++OH-$ (Ionization of H2O) $H2SO4 \rightarrow 2H++SO42-$ On passing current:- $2H++2e- \rightarrow H2$ (At cathode) 4OH- - 4e- \rightarrow 2H2O + O2 (At anode) Bubbles are formed at both electrodes due to the liberation of gases. But as d[H2]/dt = 2d[O2]/dt, bubbles of O2 are formed at a slower rate. Principle applications of electrolysis include electro refining and electroplating in which cathode and anode are both metals. For instance for electroplating of copper, CuSO4 solution is taken as electrolyte. Sometimes dilute H2SO4 is added to increase conductivity When salt solutions having cations of high reduction potential like Ca2+ are electrolyzed using inert electrodes like graphite, H2 is liberated at cathode (because the other cation has more negative reduction potential than H2 which is 0V). At anode O2 is released but it corrodes graphite into tiny particles. The cathode reaction remains same in all cases. But if metallic electrodes are used, two cases arise:

If anode is inert like platinum, O2 is released. But anode does not corrode. Only a thin coating of oxide develops.

If anode is reactive like copper, O2 is not obtained. Cu ionizes into Cu2+ and combines with OH- to form pale blue Cu(OH)2. Consequently no bubble is observed.

So if pure salt solution is used, anode ionizes if it is not inert in to hydroxides and H2 is liberated at cathode. Even if a salt containing a cation having low negative reduction potential like Sn, Pb is used the respective metals can not be deposited at cathode. H2 is formed which causes formation of bubbles at cathode. If Sn has to be deposited, SnCl2 solution must be acidified using a suitable acid like HCl.

Experiment reveals that alkalis like NaOH, Ba(OH)2.8H2O can change the cathode reaction resulting in more than one product at cathode (like H2 and Sn as will be discussed in this paper).

MATERIALS AND METHODS

Symbols used: Black colored plus (+) indicates addition while sea green (+) ones represent charges on the respective ions.

*** In this paper the research has been done with anode and cathode made of Cu (copper).

Salts studied:

Ca(NO3)2.4H2O, SnCl2.2H2O and (CH3COO)2Pb.3H2O, Ba(NO3)2.

Standard reduction potentials of various ions studied:

 $Pb2++2e- \rightarrow Pb (-0.13V)$

 $\text{Sn2+} \rightarrow \text{Sn}(-0.14\text{V})$

 $2\mathrm{H}++2\mathrm{e}-\rightarrow\mathrm{H2}\ (0.00\mathrm{V})$

 $Cu2++2e \rightarrow Cu (0.34V)$

SnCl2.2H2O

- 1. A mixture of the salt and 4-5 pellets of NaOH were diluted with H2O.
- 2. It was electrolyzed using Cu electrodes.
- 3. Slowly black mass was formed at cathode
- 4. Cu gradually corrodes.
- Ba(OH)2.8H2O if used instead of NaOH, it only slows down the reaction and substantial black mass at cathode is not formed. Ca(NO3)2.4H2O
- 1. A mixture of Ca(NO3)2.4H2O and NaOH was diluted with H2O and boiled.
- 2. The boiling solution was diluted to about 100m.l. and electrolyzed.
- 3. Bright blue mass forms at anode and H2 is liberated at cathode.
- 4. After some time bubbles start forming at anode while formation of the bright blue mass almost stops.

(CH3COO)2Pb.3H2O (4 separate experiments were performed with this salt)

Experiment a:

- 1. A solution of lead acetate and NaOH was electrolyzed.
- 2. Black mass is deposited at cathode which reduces the conductivity of Cu.
- 3. Slowly a clear blue solution forms.
- 4. Anode corrodes and no bubbles are observed.

Experiment b:

- 1. Ba(OH)2.8H2O was used instead of NaOH in experiment (a).
- 2. No blue solution was formed.
- 3. Pale blue Cu(OH)2 was formed which is insoluble .
- 4. No Black mass was obtained at cathode. Formation of bubbles indicated the production of H2 at a slow rate.

Experiment c:

- 1. About 20 m.l. alkaline solution of (CH3COO)2Pb.3H2O (alkali used was NaOH) was boiled with 2 butanol for 5 minutes.
- 2. The hot solution was diluted to about 100 m.l. and electrolyzed.
- 3. Bright green mass forms at anode which slowly dissolves to form a green solution.

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4. This color strictly varies from the one obtained in experiment (a).

Experiment d:

- 1. (CH3COO)2Pb.3H2O and C6H6 were boiled.
- 2. Two layers of liquids are formed.
- 3. The hot liquid is poured in a beaker.
- 4. In the same test tube an equal volume (10m.l.) of NaOH is added and boiled.
- 5. A brick red mass is formed
- 6. It is poured in the beaker, diluted to about 60m.l. and electrolyzed.
- 7. Very quick deposition of black mass at cathode occurs.
- 8. Anode corrodes very slowly and need not be replaced for a long time. Bubbles are formed at anode.
- A. Ca(NO3)2.4H2O
- 1. The salt in its pure state is heated till it melts and starts to boil.
- 2. To the boiling mass SnCl2.2H2O is added and heated.
- 3. The mixture swells and foams and turns yellow.
- 4. Little NaOH is added and allowed to react.
- 5. After 5 minutes the mass is diluted to 100m.l. and electrolyzed.
- 6. Light green mass forms at anode.
- 7. It is allowed to stand for about 12 hours. The entire green mass changes to brick red.
- 8. Bubbles are formed at cathode.
- B. Ba(NO3)2
- 1. Alkaline solution of the salt was electrolyzed.
- 2. The solution shows very poor conductivity.
- 3. A little blue mass at anode is formed. H2 bubbles at cathode.
- C. Ca(NO3)2.4H2O
- 1. Calcium nitrate is heated till it melts and starts boiling.
- 2. C6H6 of an equal volume as the molten salt was mixed with it and boiled.
- 3. The boiling mass was diluted and with H2O electrolyzed.
- 4. The reaction was slower than the electrolysis of pure calcium nitrate solution.
- 5. Though bubbles were seen forming at cathode, the anode reaction could hardly be detected. This is very different from pure calcium nitrate solution where a pale blue mass of Cu(OH)2 can be detected within about 10 minutes of switching ON the current.

Contrast noticed when pure salts are used: SnCl2.2H2O in its neutral solution state gives H2 at cathode and the anode corrodes to give insoluble mass of pale blue Cu(OH)2. Also the reaction is very slow.

 $SnCl2 + H2O \rightarrow Sn2+ + 2Cl$ - (Ionization in water)

 $Cu - 2e \rightarrow Cu2 + (At anode)$

 $2H+ + 2e- \rightarrow H2$ (At cathode)

Every other salt mentioned in this paper shows the same reaction. The only difference lies in their conductivities i.e. calcium nitrate has very high conductivity while lead acetate and stannous chloride show very poor conductivity.

RESULTS AND DISCUSSION

Experiment A

SnCl2.2H2O is fairly soluble in water at S.T.P. Its ionization occurs as:

 $SnCl2 + H2O \rightarrow Sn2+ + 2Cl$. As aqueous solution is used, H+ is also present. Sn2+ has more negative reduction potential than H+. So cathode reaction is self explanatory, i.e. H+ is reduced in preference to Sn2+.

Cu has lower oxidation potential than OH-. So Cu2+ and combines with OH- to give pale blue Cu(OH)2.

When NaOH is added Na+ and OH- increase the conductivity. Cl- and OH- migrate to anode. But they have higher oxidation potential than Cu. So anode reaction does not change. But at cathode the reaction gets altered. The ionization of SnCl2 increases in presence of NaOH as the salt gets hydrolyzed to form

Sn(OH)2. In the solution Sn2+ gets oxidized to Sn4+ which has a positive reduction potential of 0.15V. So it is easily reduced to Sn2+ at first and finally to Sn.

Experiment B

Both Ca(NO3)2.4H2O and NaOH are strong electrolytes. When boiled with water NaNO3 and Ca(OH)2 are formed which are also strong. In case of a pure NaOH solution concentration of OH- is very high. So Cu can not be oxidized. OH- is oxidized in preference to Cu owing to its high concentration.

For Pure Ca(NO3)2.4H2O concentration of OH- is not increased. NO3- has high oxidation potential and so Cu ionizes to Cu2+.

When a mixture of both is used, the solution contains H_+ , Ca_{2+} and Na_+ . The reduction potential of Na_+ and Ca_{2+} is very high as compared to H_+ . So H2 is liberated at cathode and bubbles are observed.

At anode initially Cu ionizes to form bright blue Cu(OH)2. Though the said hydroxide is slightly soluble, it increases the concentration of OH- such that OH- is oxidized at anode and O2 is formed. $4OH- - 4e- \rightarrow 2H2O + O2$. Now bubbles are seen forming at anode.

Experiment C

Exp a : (CH3COO)2Pb.3H2O in an alkaline medium (NaOH solution) gets hydrolyzed to form CH3COOH (a weak organic acid) and Pb(OH)2.

The valency of Pb is 2+ and that of Cu is also 2+. At anode Cu usually forms Cu(OH)2. Cu(OH)2 is a base. So it reacts with CH3COOH to form Blue solution of (CH3COO)2Cu. At cathode Pb2+ is deposited as a black mass. The solution contains Cu2+ coming from (CH3COO)2Cu and Pb2+ (Pb(OH)2 is amphoteric, so it reacts with NaOH to form Na2PbO2). But concentration of Cu2+ is negligible as compared to Pb2+. So Pb2+ gets reduced in preference to Cu2+.

If neutral lead acetate is use, hydrolysis is not possible. So at anode Cu(OH)2 is obtained and H2 is liberated at cathode. The H+ (for H2) and the OH- for Cu(OH)2 comes from H2O. The charges are balanced which need not be explained.

Exp b : Ba(OH)2.8H2O is a weak alkali as compared to NaOH. So hydrolysis of (CH3COO)2Pb.3H2O can not take place. Consequently Pb2+ can not be deposited and blue solution of (CH3COO)2Cu is not formed. (In reality it is formed but to such a nominal amount that it can be ignored).

Exp c :- (CH3COO)2Pb.3H2O + NaOH + CH3-CH.OH-CH2-CH3 makes the solution both alkaline as well as alcoholic. The following reactions are expected:-

OH-

 $(CH3COO)2Pb + 2H2O \rightarrow 2CH3COOH + Pb(OH)2$

 $Pb(OH)2 + 2NaOH \rightarrow Na2PbO2 + 2H2O$

CH3COOH + 2 butanol + OH- (catalyst) \rightarrow CH3-CH(COOCH3)-CH2-CH3 (an ester)

Also on boiling with strong alkali like NaOH 2butanol gets partly ionized to form 2butoxide ion i.e. H+ gets separated from OH to give negative charge on O (it is not possible to draw a very neat structure in MS Word). So Cu2+ combines with the said ion to form (CH3.CHO.CH2.CH3)2Cu . CHO is not aldehydic group. Here oxygen and carbon are linked by single bond and Oxygen bears a negative charge. This Oxygen links with Cu. An equilibrium is established between the alcohol and the Cu salt.

Exp d :- (CH3COO)2Pb on heating with C6H6 melts and gets denatured. Now when a little amount of concentrated NaOH is added and the mixture is boiled, as usual hydrolysis occurs to give CH3COOH and Pb(OH)2. Now due to the presence of C6H6 which acts as catalyst Pb2+ gets farther oxidized to Pb4+ to give brick red PbO2. Pb4+ has a strong tendency to get reduced (much greater than H+, Na+ which are also present in the solution. So it migrates to cathode readily and gets reduced to Pb2+. As the concentration of Pb2+ becomes high around the cathode, it is reduced to neutral Pb.

C6H6 being a dielectric increases the concentration of OH- at the anode which consequently gets oxidized to O2. This O2 tends to convert C6H6 into C6H5OH. Thus anode corrodes at a very slow rate. Hence it is seen that suitable treatment of alkaline lead acetate with highly covalent compound like C6H6 not only

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speeds up the cathode reaction but alters the anode reaction too. But if compounds containing oxygen is present, it ionizes and therefore can not act as dielectric. So this reaction does not occur for alcohols.

Experiment D

Both Ca(NO3)2.4H2O and SnCl2.2H2O contain water of crystallization. When heated H2O becomes free. SnCl2 produces HCl which reacts with NO3- from Ca(NO3)2 to liberate NO2 (yellow). The reaction is similar to synthesis of HNO3 by laboratory method using H2SO4 and KNO3. Here some of the HNO3 decomposes to give NO2 which remains soluble imparting yellow color.

On addition of NaOH the solution starts to neutralize. Thus the yellow color disappears. When it is diluted the solution contains Na+, Ca2+, H+ and Sn2+. Here H2 is liberated at cathode just as electrolysis of neutral salt solution. Now in case of alkaline SnCl2 solution (without Ca2+ and NO3-) Sn was deposited as was seen in Experiment A. So the presence of these two ions stops the reduction of Sn2+ at the cathode.

Anode corrodes into Cu(OH)2 for sometime. After that OH- due to excessive concentration starts to get oxidized at anode liberating O2. But corrosion of anode doesn't totally stop. Since OH- is getting oxidized, Cu is no longer able to hold 2 hydroxide ions. So it decomposes to form unstable CuOH which changes to brick red Cu2O and settles at the bottom. It is insoluble and after about 5 days gets oxidized to black CuO.

Experiment E

Pure solution of Ba(NO3)2 has very poor conductivity. On mixing NaOH, NaNO3 and Ba(OH)2 is formed to some extent. Hence conductivity increases slightly. OH- can not be oxidized because Ba has great affinity for it. Ba(OH)2 is more soluble than Ca(OH)2. All these factors do not let OH- be oxidized at anode. So anode corrodes slowly to pale blue Cu(OH)2 and H2 liberates at cathode. This OH- and H2 come from water.

Experiment F

Ca(NO3)2 is a very good oxidizing agent as it contains NO3- ion. Boiling it with benzene does not produce any considerable reaction. Conductivity of Ca(NO3)2.4H2O is very high. But Presence of viscous C6H6 slows down the movement of ions. It does not allow Cu(OH)2 settle down and so products are not noticeable for a substantial amount of time.

Reduction potential of Cu2+ is .34V and that of H+ is 0.00V. So it is evident that Cu can not displace H2 from acids. When neutral solutions of salts of alkali metals, alkaline earth, or transition metals like Zn are electrolyzed using Cu electrodes, in each and every case anode corrodes into pale blue insoluble Cu(OH)2 and H2 is produced at cathode. The salts used as electrolyte i.e. Ca(NO3)2, Ba(NO3)2 SnCl2, (CH3COO)2Pb remain unchanged in mass and composition. If acidic solutions containing HCl, H2SO4 are used Cu(OH)2 gets dissolved to give CuCl2 or CuSO4.

But electrolysis of alkaline solutions using strong alkalis like NaOH can affect the products to a great extent. The principle effects include:-

Deposition of metal at cathode as in case of alkaline SnCl2 and (CH3COO)2Pb which does not occur if neutral solutions are used.

Synthesis of compounds like (CH3COO)2Cu and (CH3.CHO.CH2.CH3)2Cu which can not be obtained normally.

Farther the reaction can be accelerated, retarded, and anode products can be altered by addition of covalent organic compounds like C6H6 e.g. alkaline (CH3COO)2Pb gives blue solution of (CH3COO)2Cu but suitable treatment with benzene gives O2 at anode.

Though electrolysis of CH3COOH and alcohols can be done, to obtain salts but the reaction is very slow. It results in the evaporation of alcohols because they are highly volatile.

APPLICATION

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The Paper has discussed about the electrolysis of Ca(NO3)2.4H2O, SnCl2.2H2O, (CH3COO)2Pb.3H2O in alkaline medium and is useful for knowing how organic compounds like benzene can affect the products.

CONCLUSION

If electrolysis of salt solutions is carried out using metallic electrodes (like Cu as discussed in this paper) give metal hydroxides at anode which are mostly insoluble. On the other hand if inert non metal graphite is used, O2 is liberated at anode but it breaks the graphite anode into tiny carbon particles. Hence it has to be periodically replaced. If acidic salt solution along with Cu electrodes is used, Cu(OH)2 dissolves to give salt of Cu. Electrolysis of alkaline solution of weakly electropositive metals like Pb, Sn, can cause deposition of the metal at cathode (explanation already given). Not only this, proper treatment with covalent compounds like C6H6 can improvise the reaction to a great extent by altering speed and anode products. The color of precipitated mass is different for each neutral solution due to absorption of different wavelengths which is beyond the scope of this paper. The effect of alkalis on solutions is best noticed for metals having negative reduction potential close to zero e.g. Pb, Sn.