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ELECTROCHEMISTRY IN NONAQUEOUS SOLVENTS: ELECTROREDUCTION OF CALCIUM*

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ABSTRACT

The electroreduction of calcium from aqueous solutions is prevented by solvent decomposition. The use of the aprotic solvents propylene carbonate (PC) and dimethylformamide (DMF) as possible solvent mediums for the electroreduction of calcium under ambient conditions is reported. The experimental program included testing various calcium salts, and combinations of calcium salts plus complexing agents as potential systems for electrodeposition of calcium. All systems studied proved to be unsatisfactory.

In addition, the results of electrochemical cell measurements for cells using calcium metal electrodes with PC or DMF as solvent are reported. The results indicate the cells show irreversible behavior in PC. The difficulties of electrodeposition of calcium from PC are discussed in relation to the stability of the univalent calcium ion.

Results of an initial study on the stability of $AlCl_3$(PC) solutions is also reported.

*This work was done under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION:

The electrodeposition and electrorefining of the alkali metals and alkaline earth metals, because of their reactivity, is presently confined to the use of molten salt baths operating at elevated temperatures. The advent of nonaqueous, aprotic solvents appears to offer a means of electroreduction of active metals at ambient temperature. One of the more successful nonaqueous, aprotic solvents in use is propylene carbonate (PC), originally proposed for electrochemical applications by Harris and Tobias[1]. The work of Jorné[2] and Tobias has established the feasiblity of electroreduction of the alkali metals from PC.

Calcium is presently produced by electroreduction from a molten salt bath. Based on the success of Jorné[2] and Tobias in electroreduction of the alkali metals from PC, a study into the possibility of electroreduction of calcium from nonaqueous solvent systems, notably propylene carbonate, under ambient conditions was undertaken. This report summarizes the results of a study on the feasibility of electroreduction of calcium from propylene carbonate.

EXPERIMENTAL:

I. Purification of Propylene Carbonate:

To realize the full benefits of nonaqueous solvents necessitates removal of electroactive impurities. For PC, the electroactive impurities include water, propylene oxide, 1,2 and 1,3 propylene glycol, allyl alcohol and various aldehydes. Table I lists the various impurities, their percent level, and chemical structure for commercially purchased PC. Table II lists the impurity levels after treatment by fractional distillation, and a method involving bubbling nitrogen gas through a sample of distilled PC followed by fractional distillation. One notes that the level of all impurities can be reduced below several ppm with the exception of propylene oxide which is evidently a byproduct of the distillation, being produced in the distillation column[3].

The method chosen for impurity removal was fractional vacuum distillation. The commercially purchased propylene carbonate (Jefferson Chemical Company, Houston, Texas) was vacuum distilled twice using a distillation column (Semi-CAL series 3650, Podbielniak, Franklin Park, Illinois) packed with stainless steel helices and equipped to provide for a variable reflux ratio (for other details see reference 2). The initial distillation was done at 0.5 torr at a

Table I [3]

Impurities in Commerical Propylene Carbonate as Recieved

Impurity	Level %	Structure
water	0.1	H_2O
1,2 and 1,3 propylene glycols	0.15	(1,2) $CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$ (1,3) $\underset{OH}{CH_2}-CH_2-\underset{OH}{CH_2}$
propylene oxide	0.05	$CH_3-CH\underset{O}{\diagdown\diagup}CH_2$
allyl alcohol propionaldehyde	up to 0.02	$H_2C=CH-CH_2-OH$ $CH_3-CH_2-\underset{H}{C}=O$
formaldehyde methonal acetone	below 0.01	$H-\overset{H}{C}=O$ CH_3-OH $CH_3-\underset{O}{\underset{\parallel}{C}}-CH_3$
carbon dioxide	various amounts	CO_2

Table II[3]

Impurities After Purification

Distillation

Impurity	Level ppm	Notes
water	<2	
propylene glycols	15-30	Propylene gycol can not be reduced below 11 ppm by distillation methods.
propylene oxide	9	
allyl alcohol	2	It is produced during distillation as a decomposition product in the distillation column.

Bubbling of $N_2(g)$ Through PC for Five Days

Impurity	Original Level ppm	Final Level ppm
water	5	<2
propylene gycols	20	20
propylene oxide	10	<0.4
allyl alcohol	5	<0.4

reflux ratio of 20:1, with a head temperature of 65°C. The first 20% and last 25% of the distillate was discarded. The middle portion was transferred to a stoppered flask containing activated molecular sieves (Linde 4A, 1/16" pellets, Union Carbine Corporation), 40 g. of sieves per 450 g. of solvent. The solvent was stored over the sieves for approximately seven days. The sieves were activated by prolonged heating (48 hrs.) at 350°C.

After the approximate seven day treatment with molecular sieves, the solvent was redistilled as follows: Activated molecular sieves were added to the distillation flask and the entire distillation assembly evacuated, flushed with dry argon, and evacuated. This procedure was repeated several times before a final vacuum was pulled on the assembly. The procedure is to degas the molecular sieves of oxygen and carbon dioxide.

The distillation flask, as supplied with the column by Podbielniak, was modified to accept a solvent holding flask fitted with a high-vac stopcock and mated to a ground glass joint on the distillation flask. Solvent was poured into the holding flask, and then injected into the evacuated distillation flask. This procedure helps in the initial degassing of the solvent and prevents the entry of oxygen into the distillation apparatus. The solvent was then pumped on for several hours with argon bubbling through it. The argon bubbling rate was then adjusted to allow vacuum distillation at 0.5 torr. The reflux ratio was 20:1 and the first 25% and last 25% of the distillate was discarded.

Upon completion of the distillation, the distillate collection flask was then isolated from the column by closing the appropriate valves and removed. It was then attached to the vacuum line using a ground-glass joint connection. The solvent was transferred to the vacuum line (see below) under vacuum thus preventing any contamination with water.

II. Vacuum Line:

To insure against contamination of water sensitive compounds and solvents, the experiments were carried out on a vacuum line shown in Figure 1.

The solvent distillate flask attaches to the line through the ground-glass joint A (Figure 1). The purified solvent is transferred into the evacuated storage flask F. After the transfer the storage flask is pressurized to one atmosphere with argon.

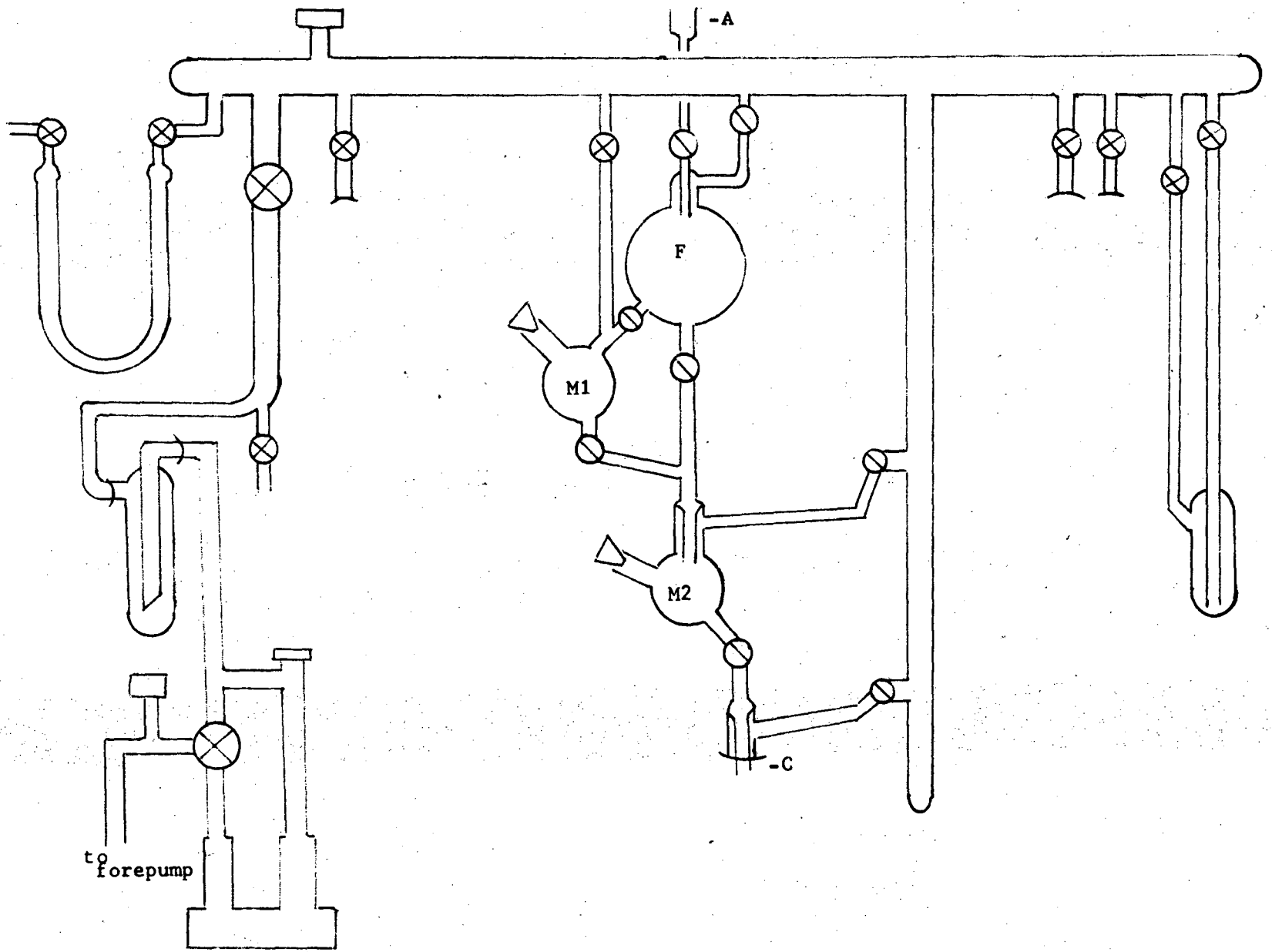


Figure 1.

Solutions of the salts to be studied are prepared in either of the mixing flasks M1 or M2. The cell used for the electroreduction studies attaches to the line at point C.

III. Preparation and Handling of the Salts:

The salts to be studies were stored in a vacuum desiccator over anhydrous calcium sulfate. Prior to use, the salt was placed in the oven at 120°C for several days. The dired salt was then quickly weighed and transferred to one of the mixing flasks, M1 or M2, alone with a magnetic stirring bar. The bar was held out of the salt by an external magnet. The flask and its contents were then evacuated and the flask heated using a heat gun. Heating continued until a vacuum of 10^{-3} torr was obtained. The flask was then allowed to cool slowly to room temperature. The vapor pressure versus temperature, melting point, and decomposition temperature of each salt was obtained so that heating conditions could be adjusted to prevent decomposition or sublimation of the salt, but still allow for removal of water.

After cooling, the solvent was added to the mixing flask by opening the appropriate valve. The resulting mixture was stirred until a homogenous solution resulted. The solution was then transferred into the cell by opening the appropriate valves.

IV. Cell Design and Operation:

The cell used for the experimental work is shown in Figure 2. The cell consists of two chambers separated by a connecting tube with a glass frit. The chambers are fitted with standard taper joints, and to these attach mating caps containing the electrode holders. Electrodes employed were either the metal under study, graphite rods, of platinum metal sheets of approximately 1 cm^2 in size. The cell is also equipped for sampling of the gas for mass spectrometer analysis from above the solution in the anode and cathode compartments. The solution in each chamber is stirred by a magnetic stirring bar. Current for the experiments was supplied by a constant power supply (Model C 612 Electronic Measurements).

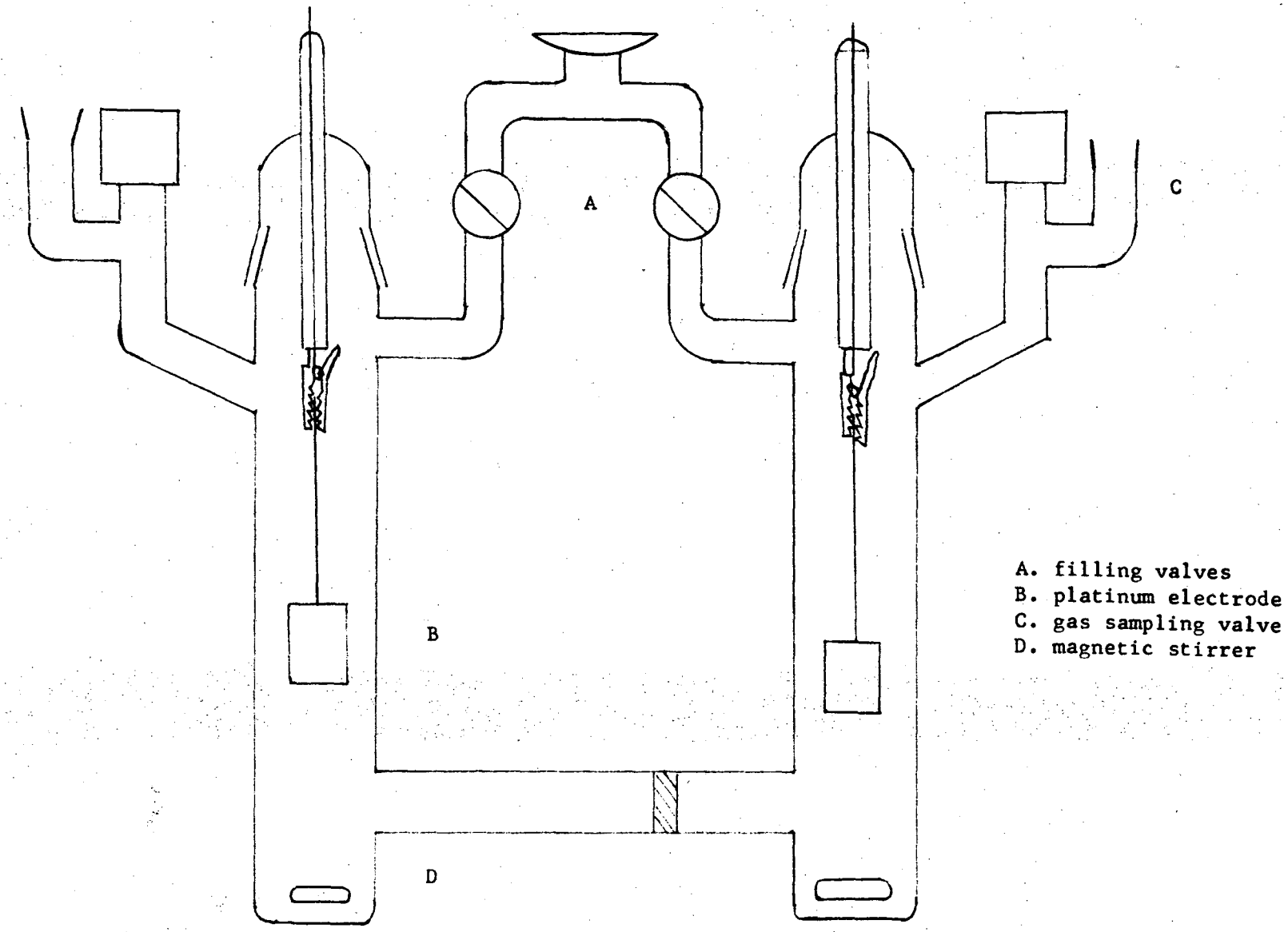


Fig. 2 Electrolysis cell

The cell operation is as follows: The cell is thoroughly washed in hot soapy water then soaked in running water over night. Afterwards it is dried in the oven and attached to the vacuum line. Gas sampling flasks (25 cm^3 capacity) are attached to the cell at point C (Figure 2). A magnetic stirring bar is placed in each compartment, and caps are attached in place of the electrode holders allowing the cell to be alternately evacuated and then flushed with argon.

The Pt electrodes (1 cm^2) were cleaned by dipping in 16M nitric acid, rinsing in distilled water, then evolving hydrogen off the surface for about $\frac{1}{2}$ hour using a 0.01 M aqueous sulfuric acid solution. The electrodes were given a final rinse in distilled water, initially air dried then placed in the cell and thoroughly dried under vacuum. The cell was then alternately evacuated to $< 10^{-3}$ torr, flushed with argon, then the solution under study added to the cell. The valves connecting the anode and cathode compartment were closed after filling with solution to prevent cross contamination of gas samples.

After the experiment, gas samples, when required, were taken by opening the appropriate valves. The cell is then pressurized with argon, and the electrodes removed for analysis.

V. Analysis of Deposits:

Deposits, when obtained in sufficient weight, were removed from the cell then washed by dipping the electrode in purified PC or cylcohexane. The washed sample was then transferred to a drying vessel connected to the vacuum line where the solvent was removed by evaporation under vacuum. The resulting dry deposits were then examined visually under a microscope, and finally analyzed for content by the standard methods of microquantitative analysis[4].

RESULTS:

I. Electroreduction of Calcium:

Table III lists the calcium salts studied in propylene carbonate. The measurements were qualitative in nature in order to be used as a screening method for the various electrolytes. The results for each salt system are listed below.

TABLE III

Calcium Salt Systems for Electroreduction from Propylene Carbonate.

	Comments
CaF_2	Insoluble
$CaCl_2$	Oily Deposit
$CaCl_2$-PCl_3	Oily Deposit
$CaCl_2$-$SnCl_2$	Insoluble
$CaCl_2$-$SnCl_4$	Insoluble
$CaCl_2$-$AlCl_3$	Oily Deposit
$CaBr_2$	Oily Deposit
$CaBr_2$-$SnCl_4$	Tin Deposit
CaI_2	Oily Deposit
$Ca(BF_4)_2$	No Deposit
$Ca(PF_6)_2$	No Deposit

CaF_2: This salt is extremely insoluble in PC. Continued stirring of the CaF_2-PC mixture for up to one week showed no detectable calcium in solution upon analysis of the solution. The addition of complexing agents such as AlF_3 (ALF_3 is extremely insoluble in PC) or $AlCl_3$ produced no detectable increase in solubility.

$CaCl_2$: Calcium chloride is only moderately soluble in PC. Electroreduction of the colorless solutions gave an oily residue at the cathode.

$CaCl_2$-PCl_3: The use of PCl_3 (Baker and Adams Analytical Regent grade) as a complexing agent for the anion does not increase the solubility of $CaCl_2$ in PC; PCl_3 does dissolve readily in PC. The electroreduction of the resulting clear, colorless solution yielded no deposit of calcium. The cathode deposit was red in color with yellow striping. The solution in the anode compartment turned from colorless to green indicating the presence of chlorine in the solution.

$CaCl_2$-$SnCl_2$: The use of stannous chloride does not increase the solubility of $CaCl_2$, $SnCl_2$ itself being insoluble in PC.

$CaCl_2$-$SnCl_4$: The use of stannic chloride does not enhance the solubility of $CaCl_2$ in PC; SnCl4 is however very soluble in PC, giving clear, colorless solutions.

$CaCl_2$-$AlCl_3$: To purified PC, reagent grade $AlCl_3$ (Baker and Adams Reagent grade, $AlCl_3$-99.2%) was slowly added. The solution turned a light yellow in color shortly after addition of a small amount of $AlCl_3$. Further slow addition of the salt up to concentration of 1m $AlCl_3$-PC did not result in a further darkening of the solution. To the resulting solution was added enough $CaCl_2$ to make the final concentration of calcium ion 0.5m. The resulting mixture was stirred for over a day before the $CaCl_2$ dissolved. The above operations were carried out in the glovebox (see reference 2 for details of the glove-box).

The resulting solution was transferred to the mixing flask on the vacuum by use of specially designed flasks that allowed transfer without atmospheric contamination. The flask is shown in Figure 3. The solution was allowed to stand over activated molecular sieves for one day.

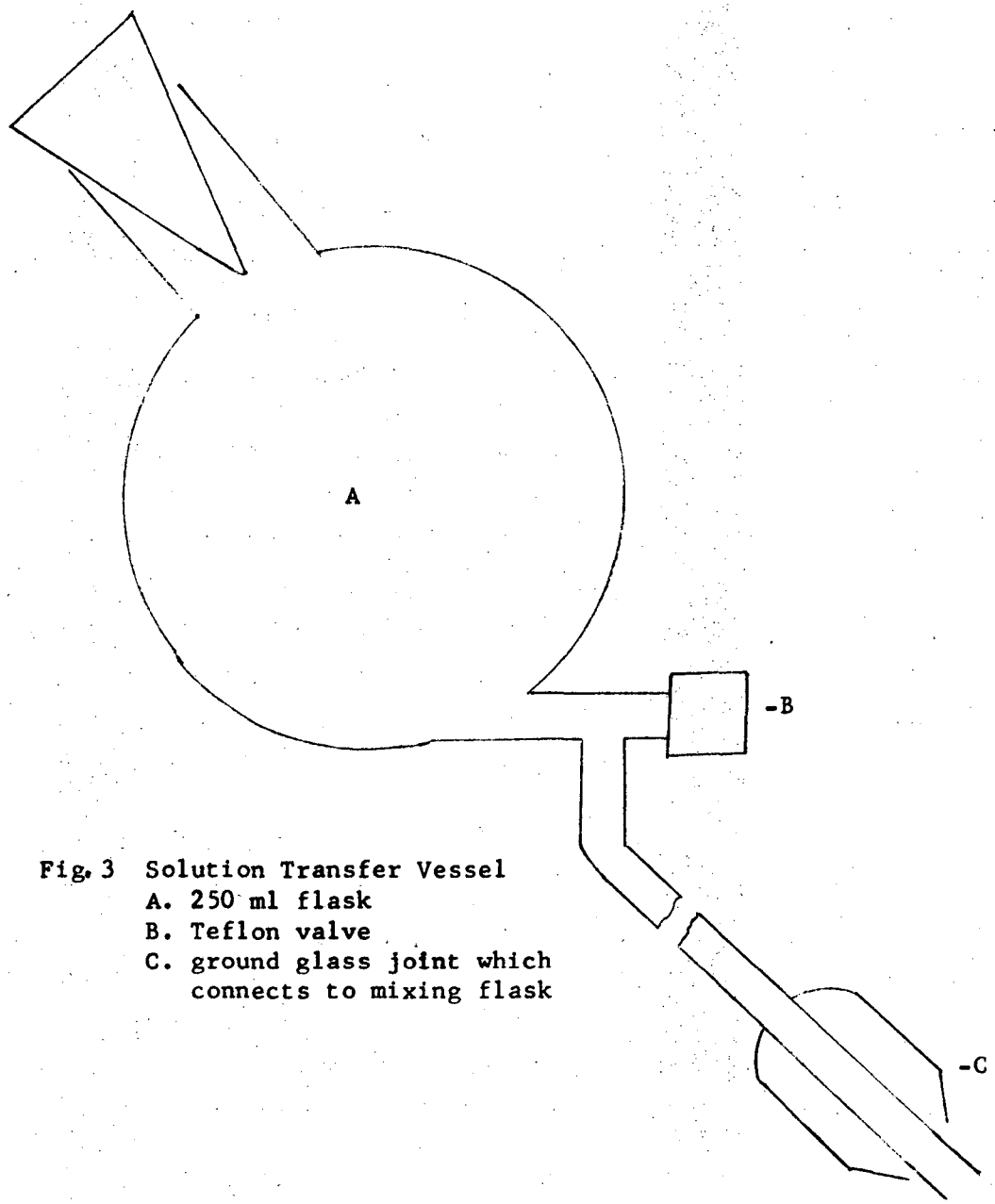


Fig. 3 Solution Transfer Vessel
A. 250 ml flask
B. Teflon valve
C. ground glass joint which connects to mixing flask

The solution was then run into the cell. The electrodes were Pt foil. The initial deposit on the cathode was purple in color then turned black in color. After this initial, very thin black deposit, a gelatinous precipitate formed at the cathode. The solution in the anode compartment turned green in color, indicating chlorine in solution.

The cathode was removed after the experiment, washed in dry cyclcohexane, dried under vacuum, then placed in water. The gelatinous precipitate readily dissolved, as did the thin deposit. Flame tests for Ca^{+2} indicated trace amounts. The flame test for Na^{+} was, however, very strong.

Repeated experiments with this system gave the same results.

<u>$CaBr_2$</u>: Calcium bromide (Research Inorganic Chemical, Sun Valley, Ca.) dissolves slowly in PC, usually requiring several hours of stirring for 0.5m solutions. The resulting solutions are clear and colorless.

Electroreduction of these solutions gave no deposits for several hours.

During the induction period, gassing at the cathode at irregular intervals was observed. The induction period was followed by deposition of a fine grain, very thin, dark coating, having no trees. The deposit proved in each case to be of insufficient amount for analysis. Further test work with $CaBr_2$-PC solutions employing Ca(s) metal cathode and anode also yielded no deposits, only an oily residue at the cathode. Visual examination under the microscope of the cathode and anode indicated no surface changes. The solution in the anode compartment turned the color of free bromine.

<u>$CaBr_2$-$SnCl_4$</u>: Stannic chloride was placed in a side arm attached in place of the ground-glass stopper on the mixing flask. The side arm was then immersed in liquid nitrogen and the $SnCl_4$ frozen. Propylene carbonate was then added to the dry $CaBr_2$ previously placed in the mixing flask and the salt was allowed to dissolve. The $SnCl_4$ was then allowed to melt and come slowly to room temperature. The gaseous $SnCl_4$ (vapor pressure of $SnCl_4$ (ℓ) at 25°C is 35 torr) readily dissolved in PC producing a very lightly yellow colored solution.

The deposition was carried out at 2 mA/cm^2 and produced a large gray, treed deposit. The cathode and anode were Pt foil.

The deposit was washed in dry cyclohexane, dried, and transferred to water. No visible reaction occurred after standing in water for several hours. Analysis of a sample of the solution tested negative for calcium. The mixture was then acidified with 6M HCl(aq), and only upon heating did the deposit dissolve. The resulting solution tested positive for tin and negative for calcium.

A sample of the original cell solution was removed from the mixing flask and a shinny calcium metal rod added. After several days, crystals of the same physical appearance as obtained by electroreduction of the solution appeared on the calcium metal surface. Analysis indicated these to be tin.

<u>CaI_2</u>: The hydrated salt was placed in a glass tube, evacuated, and heated to 300°C. The resulting salt was white in color and readily dissolved in PC. Electroreduction of the solution yielded an iodine colored solution at the anode and an oily deposit at the cathode. Both electrodes were Pt foil.

To the solution in the mixing flask a small amount of ethylenediamine ($H_2N-CH_2-CH_2-NH_2$), which acts as a complexing agent for many cations, was added. Electroreduction of the resulting solution gave the same results, no calcium, only an oily coating of the cathode.

<u>$Ca(BF_4)_2$</u>: Calcium tetrafluoroborate was the most interesting of the calcium salts tested as Jorné[2] reports obtaining a gray deposit with this salt that gave an X-ray analysis of $CaF_2(s)$.

The salt was dried on the vacuum line, then solvent added. The salt dissolves readily (0.5m) in PC giving a clear, colorless solution. However, contrary to the results obtained by Jorné, no deposit was obtained at either the anode or cathode for experiments lasting up to three days employing various current densities.

Treatment of the solution (0.5m $Ca(BF_4)_2$) in the mixing flask for three days with activated molecular seives (Linde 4A) and subsequent electroreduction of the solution gave an initial deposit, purple in color, at the cathode which turned light brown with green-yellow streamers from the electrode into the solution. The deposit, very thin in coating, eventually fell from the electrode.

Subsequent experiments under various conditions of concentrations (0.01 m to 0.5m) of $Ca(BF_4)_2$ run under widely differing current densities (.001 mA/cm^2 to 1mA/cm^2) produced no calcium deposits.

Treatment of solutions with molecular sieves gave consistently the same result: a light purple, very thin deposit, followed by eventual solvent decomposition.

Tests of the solutions indicated that calcium was present in solution ruling out the possibility of the salt not being a calcium salt.

<u>$Ca(PF_6)_2$</u>: Since this salt was not available commercially, it was synthesized from the reaction of $KPF_6(aq)$ with $Ca(ClO_4)_2(aq)$. The supernate was evaporated to dryness and the salt recrystalized several times. The dried salt readily dissolved in PC (0.1m) to give a clear, colorless solution. The solution was treated with molecular sieves. Electroreduction of the solution gave an initial purple deposit which disappeared immediately, to be replaced by a light brown deposit which also disappeared, and finally an oily deposit at the cathode.

Electroreduction of the solution without treatment by molecular sieves, yielded similar results.

II: <u>Electrochemical Stability Study of Propylene Carbonate</u>:

Because of the interest in PC for battery research and electroreduction application, a series of experiments on the stability of PC toward electroreduction were performed.

The solvent was purified and transferred to the vacuum line as described earlier. Without further treatment, the solvent was run into the cell and electrolysis preformed using Pt. foil electrodes. The electrolysis was carried out for several days and a gas sample then taken from the anode and cathode compartments. The samples were analyzed by mass spectrometer for molecular weights of the various components. After subtracting out the background by comparison with gas samples taken over purified PC, not subjected to electroreduction, the major constituents were identified as CO_2, ethylene, oxygen, and CO, plus lesser amounts of higher molecular weight components. Because the gas samples from each compartment gave very similar, and at times conflicting results, the conclusion is that either the electrode reactions proceed by several different mechanisms that result in the same gases product, or more likely that this method of analysis is unsatisfactory. However, the products obtain clearly indicate

ring opening and degradation to simpler compounds. One must remember that analysis of gas samples, is good only for those products that have an appreciable vapor pressure over the solvent.

The solvent was, however, clear, and colorless at the termination of the experiment, with no deposits of any type present on the anode or cathode.

A study on the electrochemical decomposition of propylene carbonate on graphite electrodes by Dey and Sullivan[5] indicated the decomposition products to be propylene (95%) and CO_2, H_2 and ethylene (< 1%). Their experiments were run with 1M $LiClO_4$ as a supporting electrolyte. For futher work on the decomposition of pure PC, analysis should be done by vapor phase chromotography on both gas phase and liquid phase samples taken separately from the anode and cathode compartments.

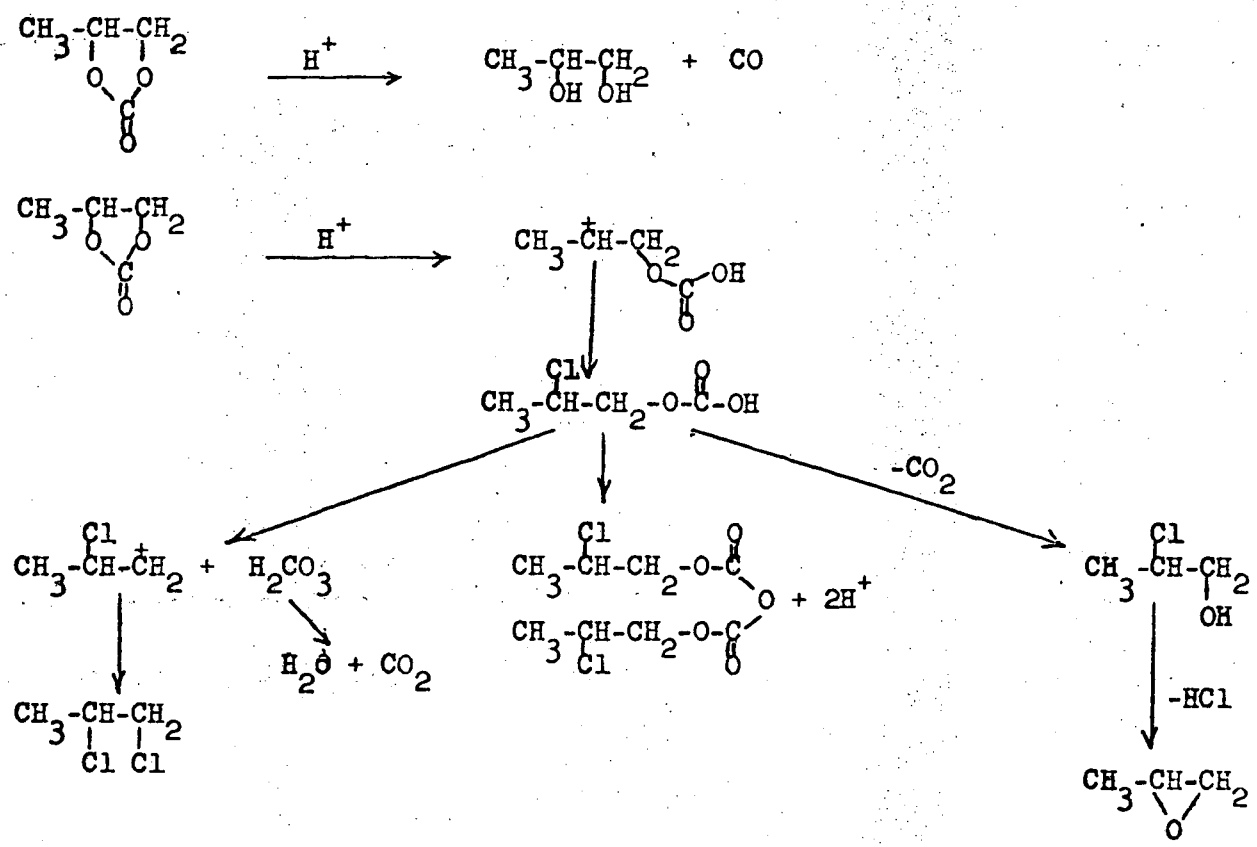
<u>$AlCl_3$-PC</u>: Because the success of the electroreduction of the alkali metals from their chloride salts rested on the use of $AlCl_3$ as a complexing agent with chloride to increase the solubility of the alkali metal chloride salt, the stability of the $AlCl_3$-PC solutions was investigated.

If reagent grade $AlCl_3$ was added to commercially available PC that had not been distilled in the laboratory, a gelationous precipitate of $Al(OH)_3$ formed immediately. The same result was found for PC containing more than 50 ppm of water. The hydrolysis of $AlCl_3$ in PC produces insoluble $Al(OH)_3$ and soluble HCl The latter in the presence of water act as a catalysis for the hydrolysis of the solvent. The possible reactions are outlined in Table IV. If the water is removed by reaction with $AlCl_3$, then the decomposition of the solvent by HCl under "anhydrous" conditions can still occur. The possible reactions are also outlined in Table IV. The rate of decomposition of the solvent via the reactions listed in Table IV is not known but is probably slow because of the low concentration of reactant. The important point is, however, that the products of decomposition are themselves electroactive and could act as an initiators for more rapid solvent decomposition during electrochemical processes being carried out in the solvent, e.g., electroreduction of some metal. All the products listed are capable of attacking PC and forming polymeric chains which could yield gelatinous or oily ppt. at the anode or cathode.

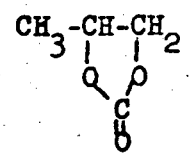
Table IV

Decomposition of PC in Presence of Acid or Base (H^+ or OH^-)

A) H^+ (HCl) under anhydrous conditions

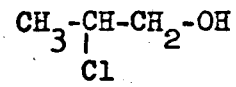


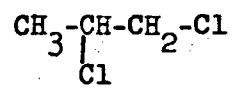
B) H^+ in presence of H_2O

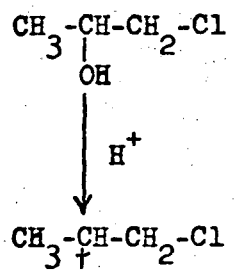


$\xrightarrow[H^+]{H_2O}$ propylene gycol + propylene + propylene oxide + CO_2

also some chloride such as



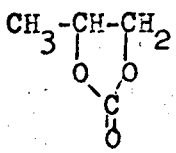




$\xrightarrow{\text{loss of } H^+ \text{ or } Cl^-}$

propylene or CH_3-CH=CHCl

C) OH^- in the presence of H_2O)



$\xrightarrow{OH^-}$ propylene gycol (1,2) + propylene + propylene oxide + CO_2

As mentioned earlier, when analytical reagent grade $AlCl_3$ was added to purified PC, ($H_2O<2$ ppm), no precipitate of $Al(OH)_3$ was visible, albeit the solution turned light yellow in color. The discoloring of the solvent could be the result of some reaction of $AlCl_3$ with the solvent, or the reaction of solvent impurities with $AlCl_3$, or from some impurity in the $AlCl_3$. The latter was thought to be the case since reagent grade $AlCl_3$ contains up to 0.1% $FeCl_3$ which produces yellow colored solutions upon dissolving in PC. All attempts at cooling the solutions ($\Delta\overline{H}_{soln} \simeq 40$ kcal for $AlCl_3$(PC)) or slow addition of $AlCl_3$ to PC produced light yellow colored solutions.

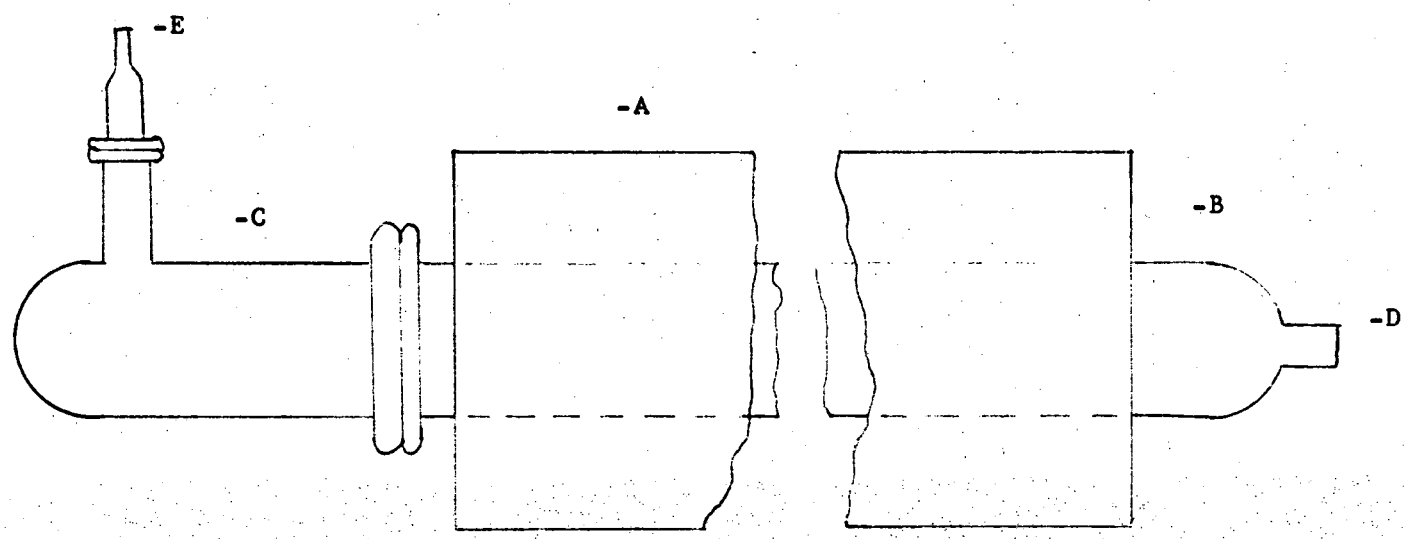
Consequently, some very pure $AlCl_3$ was synthesized as follows[6]: About 500 g. of reagent grade $AlCl_3$ was placed in a glass tube (50 mm × 460 mm) along with 50 g. of Al metal pellets. The tube was placed in a tube furnace lying in a horizontal position. To one end of the tube was attached a receiver (see figure 4) and to other end a tube connected to an argon gas supply. Argon gas was slowly bleed through the tube while it was heated to 300°C for eight hours. The $AlCl_3$ sublimates at these temperatures and condenses out on the cool end of the receiver as a free flowing white powder. The $FeCl_3$ also sublimated under these conditions but reacts with the Al metal, or condenses out in the hotter end of the receiver as long, yellow, needle-like crystals.

Sublimated $AlCl_3$ was then placed in a glass tube, evacuated to 10^{-3} torr, sealed off with a torch, and placed in the furnace. The tube furnace for this operation is placed in a vertical position so that the tube containing the $AlCl_3$ maybe totally immersed inside the furnace. The tube was then slowly with drawn over a 4-6 hour period after it reached the operating temperature (300°C) of the furnace. The tube was withdrawn by attaching it to a harness fashioned from wire which in turn attached to a string on a spool driven by a gear reduction electric motor. The aluminium chloride thus produced condenses out at the cool end of the tube as clear, colorless crystals, hexagonal in the plane, which separate like sheets of mica. Any impurities are left in the bottom of the tube as an oily residue or an ash.

The tube was then transferred to the glove-box, broken open, and the proper amount of $AlCl_3$ added slowly to PC. The $AlCl_3$ in this form dissolves much more slowly in PC and generally gave clear solutions. However, on several occasions light yellow solutions were obtained. The source of the problem

Fig. 4 Sublimator

A. furnace
B. generator
C. collector
D. Argon inlet
E. Argon outlet



could have been in the $AlCl_3$, the PC, or a contaminated atmosphere in the glove-box. Solutions prepared with the sublimated $AlCl_3$ showed no visible deterioration (i.e. color changes from colorless) for up to one month (length of the experiment).

Electrolysis of the $AlCl_3$-PC solution gave $Cl_2(g)$ at the anode and an oily deposit at the cathode.

III. Electrochemical Thermodynamic Studies Involving Calcium:

In order to determine whether or not calcium exhibits electrochemical reversible behavior in PC, cells of the following type were run:

$$Ca(s) \mid CaBr_2(PC) \mid TlBr(s) \mid Tl(Hg)$$

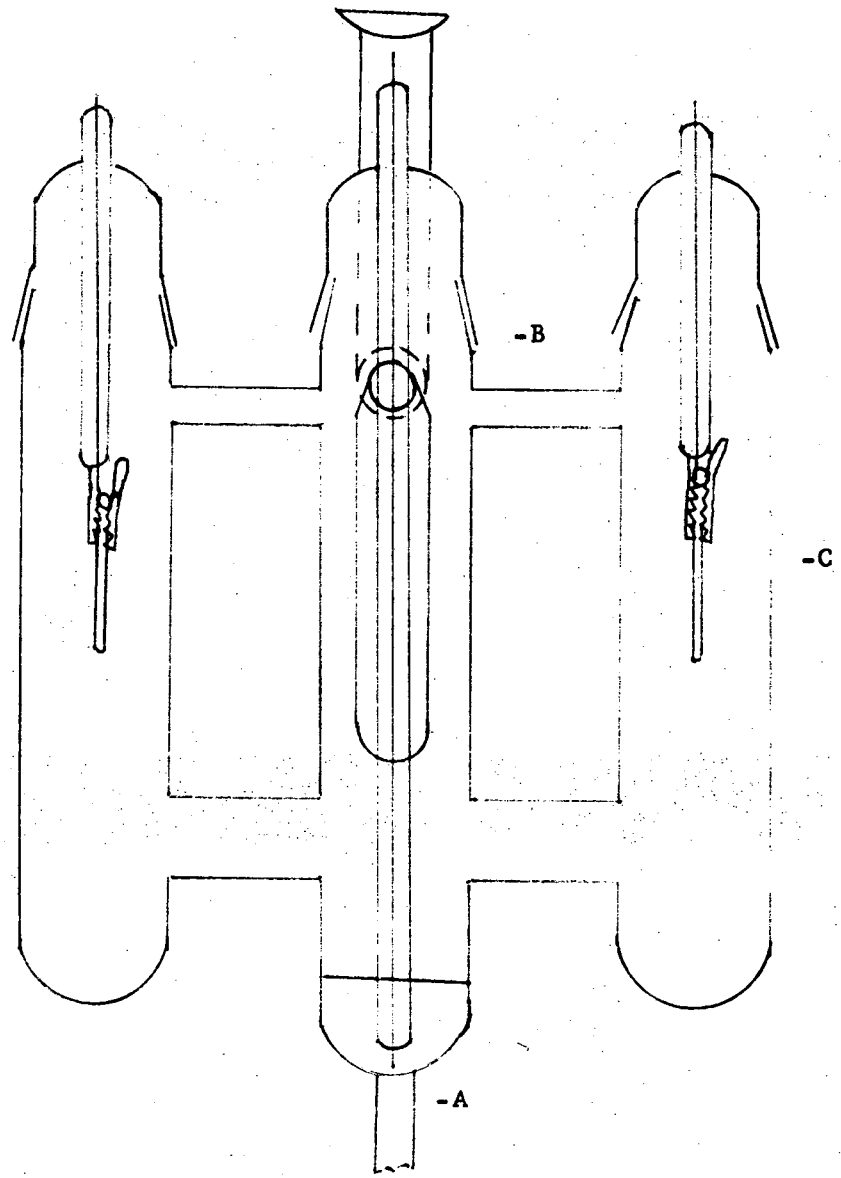
The cell construction is shown in Figure 5. The thallium amalgam was prepared by cleaning thallium wire in distilled water until a shiny surface appeared, then rinsing several times in water before transferring the metal to a drying tube where the water was removed by evaporation under vacuum. The resulting metal was very shiny in appearance. A known weight of the metal was then added to a known weight of mercury (Ballard Tripley Distilled, San Francisco, Calif.). The resulting amalgam was then stored in a reservoir attached to the vacuum line. From the outlet valve of the reservoir a glass tube was attached to the cell at point A (Figure 5). The TlBr(s) (Alfa Inorganics, ultra high purity) was dried in the oven at 120°C before transfer to a small holding cup that inserts into a mating joint located over the amalgam electrode, part B (Figure 5). By turning the cup over, the TlBr(s) could be distributed over the surface of the amalgam.

Two calcium electrodes were used in each cell. They were prepared by machining on a lathe a block of the metal approximately 1/4" × 1/4" × 2" into rods of 3/16" to 1/8" diameter and of the appropriate length.

The cell was setup and operated as follows:

The cell was attached to the vacuum line with a ball and socket joint. A filling tube was attached between the amalgam electrode compartment and the amalgam reservoir. The amalgam electrode contact was inserted, and false caps placed over the calcium electrode compartments. The dried TlBr(s) was placed in

Fig. 5 Calcium Cell



A. amalgam inlet
B. TlBr(s) dropper
C. Calcium electrode

the dropper. The cell was then evacuated and flushed several times with argon. The solution of $CaBr_2$ in PC (0.05m) was prepared as described earlier.

The metal electrodes were cleaned by dipping them in a solution composed of 45 ml of 2-propanol (MC/B Spectro-quality grade) plus 5 ml of 12M HCl(aq) (Baker and Adams) for several seconds until a bright surface appeard. The metal was then rinsed in a beaker of 2-propanol, then in dry cyclcohexane. The electrode, now attached to the electrode holder, was transferred through the air into the cell. After inserting the electrode, the protective coating of cylcohexane was removed by evacuating the cell. The result was a bright shiny electrode that retained this appearance throughout the experiment. The second electrode was treated in the same manner.

After assembly of the cell, the Tl(Hg) (4.13% Tl)[2,9] was run into the cell under vacuum and the connecting tube to the analgam reservoir sealed off with a torch. The TlBr(s) was then dumped onto the surface of the amalgam, then the solution run into the cell. Measurements using a Fulk Digital Voltmeter were then begun.

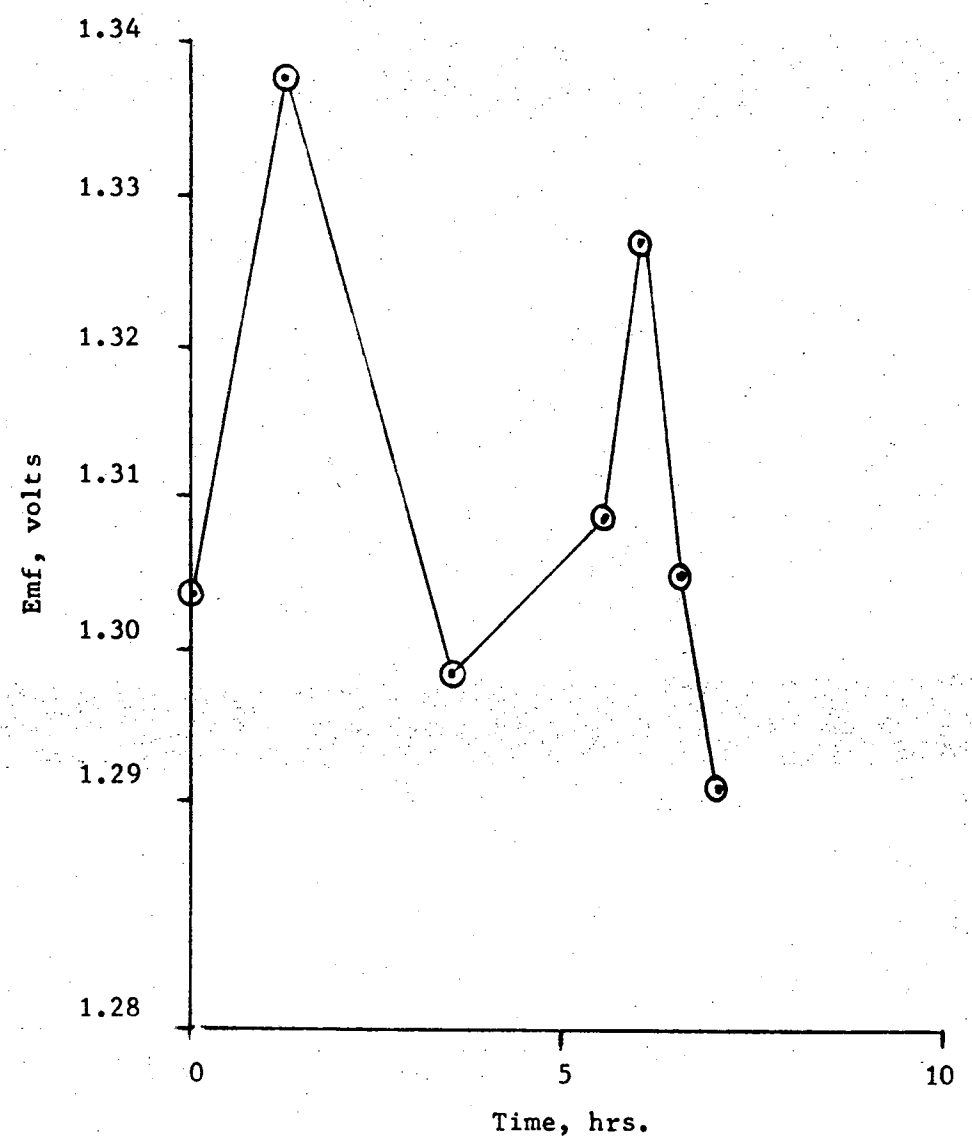
I. Cells in PC:

Four cells of the above type using PC as a solvent were run employing various concentrations of $CaBr_2$ (0.05m to 0.01m). All cells gave erratic behavior. For the first cell, the initial bias potential between the two calcium electrodes was 58 mV and continued to increase with time in a highly irregular manner. In the latter cells the calcium electrodes were annealed by placing them in a quartz tube and heating the metal for several hours under an argon atmosphere to a temperature where they glowed cherry-red ($\simeq$ 700°C). They were then allowed to cool slowly to room temperature over a period of several hours. The electrodes were then chemically cleaned and placed in the cell. This method of electrode treatment gave initial bias potentials of 3 mV. However, in each case the bias potential increased erratically over several days to a much higher value (60 mV).

The $\mathcal{E}$mf measurements for each cell also exhibited erratic behavior. Figure 6 is a plot of the $\mathcal{E}$mf for cell #2 versus time. The potential values for all cells fluctuated around 1.30 ± 0.15 volts. During cell readings, the

Fig. 6 Emf versus Time for the Cell

Ca(s) $CaBr_2$ (PC) TlBr(s) Tl(Hg)



cell $\mathcal{E}$mf would consistently increase going from some initial value to one 50 to 100 mV higher. Such behavior is shown in Figure 7.

Since the specific conductance of $CaBr_2$ in PC for the concentrations used in these experiments is about 5×10^{-4} ohm^{-1} cm-1, which indicates reasonable concentration of free ions ($LiAlCl_4$, strong electrolyte in PC has specific conductance of 1×10^{-3} $ohms^{-1}cm^{-1}$), and since the thallious bromide-thallium amalgam electrode is known to exhibit reverible behavior in PC[7], one must conclude the difficulty lies with the electrode reaction at the calcium metal electrode.

II. Cells in N,N dimethylformamide (DMF):

Anodic dissolution of calcium in DMF is known to occur,[8] consequently the possibility of using this solvent in revisible electrochemical cells involving calcium metal electrodes was investigated.

To check for revisible behavior of calcium in DMF, cells of the following type were run:

$$Ca(s) \mid CaBr_2(DMF) \mid TlBr(s) \mid Tl(Hg)$$

The set up and cleaning of the electrodes was done as described above. The solvent was purified by the standard method.[9]

Only two cells were run in DMF. Both cells gave good stability for a concentration of $CaBr_2$ in DMF of 0.0517m, and the measured $\mathcal{E}$mf was 1.5838 ± 0.0025 volts. The bias potential was in each case about 3 mV, and steady with time. The cells gave stable readings within about 1/2 hour after filling with cell solution. The stable period continued for about four days, after which the potential became erratic because of small trees that started to grow on the calcium electrodes.

Analysis of the deposit indicated it to be thallium metal. In effect, the cell died from internal short-circuiting.

When solutions of $CaBr_2$ and $CaCl_2$ in DMF were separately teated for electroreduction of calcium at Pt foil electrodes, no metal deposits were

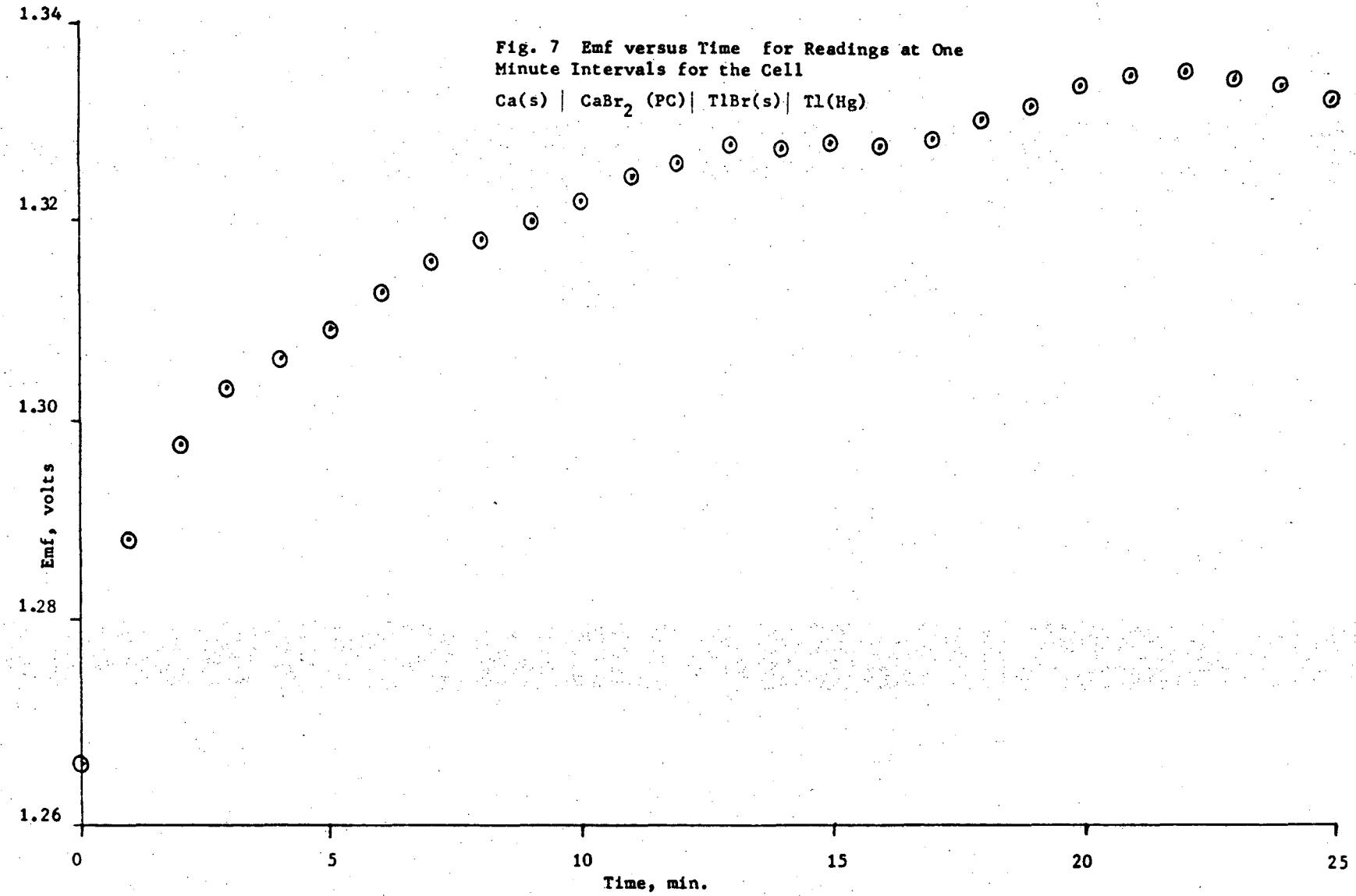


Fig. 7 Emf versus Time for Readings at One Minute Intervals for the Cell

Ca(s) | $CaBr_2$ (PC)| TlBr(s)| Tl(Hg)

obtained. No visible reaction occurred at the anode, while a black deposit on the cathode proved to be insoluble in water or acidic aqueous solutions.

Discussion:

The fact that for all of the salts studied, no calcium metal deposit was obtained can be traced to several possibilities.

One, in several of the salts, the only metals deposited were very light coatings, and the initial deposit was purple in color. From Jorné's[2] work on the electroreduction of the alkali metals from PC, a purple colored deposit is characteristic of potassium and/or sodium metal. Flame tests of the deposit obtained from $CaCl_2$-$AlCl_3$(PC) and $Ca(BF_4)_2$(PC) indicated the presence of sodium.

One source of the alkali metal impurity could be the calcium salts. Obtaining calcium salts of purity greater than 98 - 99% (analytical reagent grade purity for calcium salts) is difficult (ultra pure grade, < 5 ppm per impurity, for many calcium salts is available). The specific impurities vary with the particular salt, but usually contain 0.5 - 1% alkali metal impurities in the form of sulfates. Even though calcium sulfate is insoluble in PC, as are the alkali metal sulfates, the fact that the soluble calcium salts dissolve without any visible residue indicates that whatever the form of the alkali metal impurities, they dissolve.

The disturbing fact, however, is that the initial depoits of the alkali metals occurred only in those solutions treated for more than one day with activated molecular sieves. The possibility of anion exchange with the zeolite is presumably minimal as the use of molecular sieves for drying nonaqueous solvents and salt solutions, containing the same anions used in this study, is a well established procedure.[10] The only exception is fluoride-containing solutions. Solutions of tetraethylammonium fluoride in PC show ion exchange[11] with Linde 4A molecular sieves, the soluble species replacing the fluoride ion were thought to be aluminum fluoride or fluorosilicate complexes.

Since calcium ion is known to exchange with many zeolites, the source of the sodium contamination is most likely the slow exchange of calcium with the sodium present in the molecular sieves (the unit cell formula for activated

Linde 4A sieves is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$).

The fact, however, that the alkali metals deposit in prefence to calcium suggests that the deposition of calcium from PC has a much higher activation energy for electroreduction than the alkali metals.

This point suggests a second possible explanation of the experiments which is based on some thermodynamic considerations. Unfortunately, the followig must be based on aqueous solution values as the necessary data in PC for calcium does not exist.

Looking at the reaction:

$$Ca^+(aq) + H^+(aq) = Ca^{2+}(aq) + \tfrac{1}{2}H_2(g) \qquad (1)$$

the Gibbs energy maybe calculated for reaction (1) by considering the following reactions.

$$Ca^+(aq) = Ca^+(g) \qquad (2) \quad \Delta G^o(2) = 70 \text{ kcal}$$

$$Ca^+(g) = Ca^{2+}(g) + 1e^- \qquad (3) \quad \Delta G^o(3) = 274 \text{ kcal}$$

$$Ca^{2+}(g) = Ca^{2+}(aq) \qquad (4) \quad \Delta G^o(4) = -362 \text{ kcal}$$

$$e^- + H^+(aq) = \tfrac{1}{2}H_2(g) \qquad (5) \quad \Delta G^o(5) = -115 \text{ kcal}$$

Adding reactions (2) through (5) yields

$$\Delta G^o(1) = 70 + 274 - 362 - 115 = -133 \text{ kcal}$$

or subtracting out the $\mathcal{E}^o$ for the hydrogen half reaction we obtain,

$$Ca^+(aq) = Ca^{2+}(aq) + 1e^- \qquad (6) \quad \mathcal{E}^o(6) = +5.8 \text{ volts}$$

By similar reasoning, one can compute

$$Ca(s) = Ca^+(aq) + 1e^- \qquad (7) \quad \mathcal{E}^o(7) = +0.2 \text{ volts}$$

The calculation indicates that Ca^+ is unstable in aqueous solution. Looking at the analogs to reaction (6) and (7) in the gas phase one finds,

$$Ca(g) = Ca^+(g) + 1e^-(g) \qquad (8) \quad \Delta G^o = 140 \text{ kcal}$$

$$Ca^+(g) = Ca^{2+}(g) + 1e^-(g) \qquad (3) \quad \Delta G^o = 274 \text{ kcal}$$

Adding the reverse of reaction (3) to reaction (8) yields

$$Ca(g) + Ca^{2+}(g) = 2Ca^{+}(g) \qquad (9) \quad \Delta G^{o} = -134 \text{ kcal}$$

in other words, in the absence of solvating effects, $Ca^{+}(g)$ is stable. Referring reaction (9) to solid calcium we have

$$Ca(s) = Ca(g) \qquad (10) \quad \Delta G^{o} = 38 \text{ kcal}$$

$$Ca(g) + Ca^{2+}(g) = 2Ca^{+}(g) \qquad (9) \quad \Delta G^{o} = -134 \text{ kcal}$$

adding yields

$$Ca(s) + Ca^{2+}(g) = 2Ca^{+}(g) \qquad (11) \quad \Delta G^{o} = -96 \text{ kcal.}$$

The analogous reaction in water is

$$Ca(s) + Ca^{2+}(aq) = 2Ca^{+}(aq) \qquad (12) \quad \Delta G^{o} = 133 \text{ kcal}$$

Comparison of reactions (11) and (12) indicates that solvation of Ca^{2+} by water effectly stabilizes this species with respect to $Ca^{+}(aq)$, causing auto oxidization-reduction of $Ca^{+}(aq)$. The Gibbs energy of reaction (12) converts to -5.6 V.

The implications of reactions (11) and (12) is that when solvation is not highly important electroreduction would be more favored. Propylene carbonate is known to have weak acidic and basic properties,[12] and consequently does not normally exhibit highly specific coordination phenomena such as found in solvents like dimethylformamide or dimethylsulfoxide. The solvation in PC of calcium is presumably weaker than in water and consequently should favor electroreduction of calcium. In fact, electroreduction may take place but only to Ca^{+} which in turn reacts with the solvent and is oxidized to Ca^{2+}. The reaction of Ca^{+} with PC could conceivably be via a radical reduction mechanism similar to that proposed[2] for the reduction of PC in the presence of magnesium salts. Data supporting the existence of Ca^{+} exists for DMF[8] and molten salt mixtures[13].

The evidence is based on proposed kinetic mechanisms that are consistant with observed electrochemical kinetic data. The isolation of an univalent calcium salt has not been reported.

The idea of $Ca^{+}(PC)$ as the initial product in the electroreduction of calcium from PC may be the key to rationalizing the results obtained by Jorné[2] using solutions of $Ca(BF_4)_2$ in PC.

Using $Ca(BF_4)_2(PC)$ solutions, Jorné obtained a deposit whose X-ray analysis indicated $CaF_2(s)$. A highly spectulative explanation of Jorné's results is the following: A study of lithium-isotope-exchange reactions[14] using cells of the type

$$^{7}Li(s)|^{7}LiF(s)|KBF_4(PC)|^{6}LiF(s)|^{6}Li(s)$$

indicated that the $Li(s)|LiF(s)$ couple is reversible in solutions of KBF_4 in PC. The reaction for the couple is

$$Li(s) + BF_4^{-}(PC) \rightarrow LiF(s) + BF_3(PC) + 1e^{-} \qquad (13)$$

Boron trifluoride, through a gas at room temperature, is highly soluble in PC.

The cell works by taking advantage of the equilibrium

$$BF_4^{-} \rightleftarrows BF_3 + F^{-} \qquad (14)$$

Quite possibly, Jorné's experimental conditions were exactly right for the following reactions to occur.

$$Ca^{2+} + 1e^{-} \rightarrow Ca^{+} \qquad (15)$$

$$Ca^{+} + BF_4^{-} \rightarrow CaF + BF_3 \qquad (16)$$

$$CaF + Ca^{2+} \rightarrow CaF^{+} + Ca^{+} \qquad (17)$$

$$CaF^{+} + BF_4^{-} \rightarrow CaF_2(s) + BF_3 \qquad (18)$$

The net reaction may be written as the sum of the two reactions

$$Ca^{2+} + 1e^{-} \rightarrow Ca^{+} \qquad (19)$$

and

$$Ca^{2+} + 2BF_4^{-} \rightarrow CaF_2(s) + 2BF_3 \qquad (20)$$

The last reaction is not an oxidation-reduction reaction and could be prevented from happening spontaneously by a high activation energy or lack of a suitable site for crystal nucleuation. The presence of Ca^+ species, however, may have proved an alternate route for reaction (20). The results obtained by Jorné could not be reproduced in this study. The reasons are not known.

From Table III, one notes that all calcium salts tried were 2:1 electrolytes. The anions were all halides, or some anion involving halides. These particular salts were chosen since they are relatively inexpensive and readily available. Electrodeposition experiments on solution involving these salts do not indicate what role, if any, the anion played in the reactions at the cathode.

With 2:1 electrolytes of calcium the possibility of ion association exists. The following equilibria would be important.

$$CaX_2 \rightleftarrows CaX^+ + X^- \qquad (21)$$

$$CaX^- \rightleftarrows Ca^{2+} + X^- \qquad (22)$$

If reaction (21) is significant in PC, then the anion might have some effect on the electroreduction of calcium since the species near the cathode would be CaX^+. To check the possibility of anion interference, calcium 2:2 salts should be tested. This would make the ion associated pair neutral and thus presumably a nonparticipant in the electrode reactions. Also, if the initial reaction of calcium in PC produces univalent calcium, the anion could be critical towards stabilizing these species. The idea is that reduction would proceed through the reduction sequence

$$Ca^{2+} + 1e^- \rightarrow Ca^+$$

$$Ca^+ + X^- \rightarrow CaX$$

$$2CaX \rightarrow Ca^{2+} + Ca(s) + 2X^-$$

and/or the sequence

$$Ca^{2+} + 1e^- \rightarrow Ca^+$$

$$Ca^+ + X^- \rightarrow CaX$$

$$CaX + 1e^- \rightarrow Ca(s) + X^-$$

In either scheme the anion is not consumed but functions as a strong "solvating" medium for the intermediate.

Such a stabilizing effect on the proposed univalent calcium could also be provided by the use of chelating agents or macrocyclic esthers. The complexing agents might be neutral ligands in a solution of the calcium salt under study, or a small quantity of a second calcium salt capable of forming ion pairs.[15] A possible second salt might be the calcium salt of didecylphosphoric acid,[16] and a neutral carrier might be a synthetic lipophilic ligand[17,18] or binding agent such as ethylene dinitrilotetracetic acid[19,20]. Such complexing agents would in principle not be consumed in the electrochemical reduction of calcium. Alternatively rather large quantities of some chelating agent might be necessary. The chelating agent would maintain the concentration of free Ca^{2+} ion at some fixed level, but below some critical level that allows electroreduction to proceed.

The calcium cells run in PC were all erratic and unstable, suggesting irreversible behavior. Surface impurities from the cleaning procedure may have rendered the calcium metal electrode passive, or the clean metal may have been passivated by reaction with solvent impurities. Freshly cleaned calcium is known to be highly reactive.[20]

Work done by Butler and Hunter[21] using cells of the type

$$Ca(s)|CaCl_2(0.01m,\ PC)|Ca(Hg)$$

suggest irreversible behavior. Though the Ca(Hg) electrode is known to operate reversibly[22] if the proper precautions are taken, the investigators did not employ an external reference electrode (e.g., TlCl(s) Tl(Hg)) and consequently were unable to localize the source of the irrevisibility.

The combined evidence of electroreduction and electrochemical thermodynamic experiments strongly suggest that for the systems studied calcium behaves irreversibly in propylene carbonate. This conclusion does not rule out the use of PC as a solvent for other calcium systems, but certainly suggests that calcium systems involving mainly free, uncomplexed, calcium ions in PC will not work. A good possibility exists that the use of cation complexing agents such as macrocyclic ethers, or saturated nitrogen chelates, could be used with PC as a solvent to give electroreduction of calcium. Therefore, before PC is entirely ruled out as a solvent, experiments involving cation complexing agents should be performed.

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