POLAROGRAPHIC STUDIES IN NON-AQUEOUS SOLUTIONS

by

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INTRODUCTION

During recent years an increasing number of polarographic studies have been carried out in non-aqueous solvents. Liquid ammonia as well as several organic and inorganic solutions have been used. The chief difficulty encountered in the use of organic solvents are the high resistance of the solutions and the necessity of finding a suitable supporting electrolyte. General application of the liquid ammonia systems is prevented by stringent temperature control. It would be desirable to find a non-aqueous solution that would eliminate these problems. A solvent formed by the condensation of ammonia with a salt offers certain desirable characteristics, such as low resistance, convenient temperature, and solvents for both inorganic and organic compounds.

Certain salts [$Hg(CN)_2$ (2,1), $Ca(NO_3)_2 \cdot 4H_2O$, $LiNO_3$, $UO_2(NO_3)_2 \cdot 6H_2O$ (4), $CaCl_2$ (3), $Ag_2Pt(SCN)_6$ (1), NH_4SCN (1,9), NH_4NO_3 (6)] are described in the literature as deliquescing with ammonia. Other salts that were found during this investigation were NH_4I, NaI, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and NaSCN. Of these NH_4NO_3, NaI, $LiNO_3$, NH_4SCN and NaSCN were tried and found to be satisfactory for polarographic studies. Ammonium nitrate and sodium iodide were chosen and studied more thoroughly.

Anhydrous ammonium nitrate condenses with dry ammonia, forming a solution which is commonly called Divers' (6) solution. The resulting solution has much the appearance of water. It boils at 26° C (7) and is an excellent electrolyte. According to Kuriloff (13) the composition of the solution is $NH_4NO_3 \cdot 3NH_3$. The solution is corrosive and dissolves mahy metal oxides and metals (6). Enrico Vecchi (15) studied the polarographic properties of cadmium and lead in Divers' solution. He found that these metals gave well defined waves and that the diffusion current had a linear relationship to the concentration of the metal ion.

Anhydrous sodium iodide condenses with dry ammonia gas to give a clear, aqueous appearing solution at room temperature. It freezes at -2° C, jells at 20° C and boils at 42° C. This solution is so stable that the odor of ammonia is scarcely detected. It, like Divers' solution, is also a good electrolyte. The simplest mole ratio of the solution was found to be approximately $NaI \cdot 3.6NH_3$.

The present investigation deals with a survey of polarographic reductions of various organic as well as some inorganic salts in both the ammonia-sodium iodide and ammonia-ammonium nitrate solutions. Maximums occur in each solution just as they do in aqueous solutions. Gelatine will suppress the maximums and produce well defined waves. A saturated lead-lead nitrate reference electrode was found to be satisfactory for the ammonia-ammonium nitrate system. The study of the ammonia-sodium iodide system was greatly simplified by the development of an internal silver reference electrode. This reference electrode, the first of it's nature to be tried, proved to be useful in this field of study. It gave no observable wave that could be attributed to the resulting reaction at the face of the electrode. Although the silver-electrode was used quite extensively, the electrode never lost its metallic luster.

EXPERIMENTAL

Chemicals

Reagent grade chemicals were used without further purification except for certain salts which were prepared in this laboratory. The anhydrous ammonia, which was dried by passing it thru a sodium drying tube, was purchased in fifty pound tanks from Armour & Co.

Apparatus

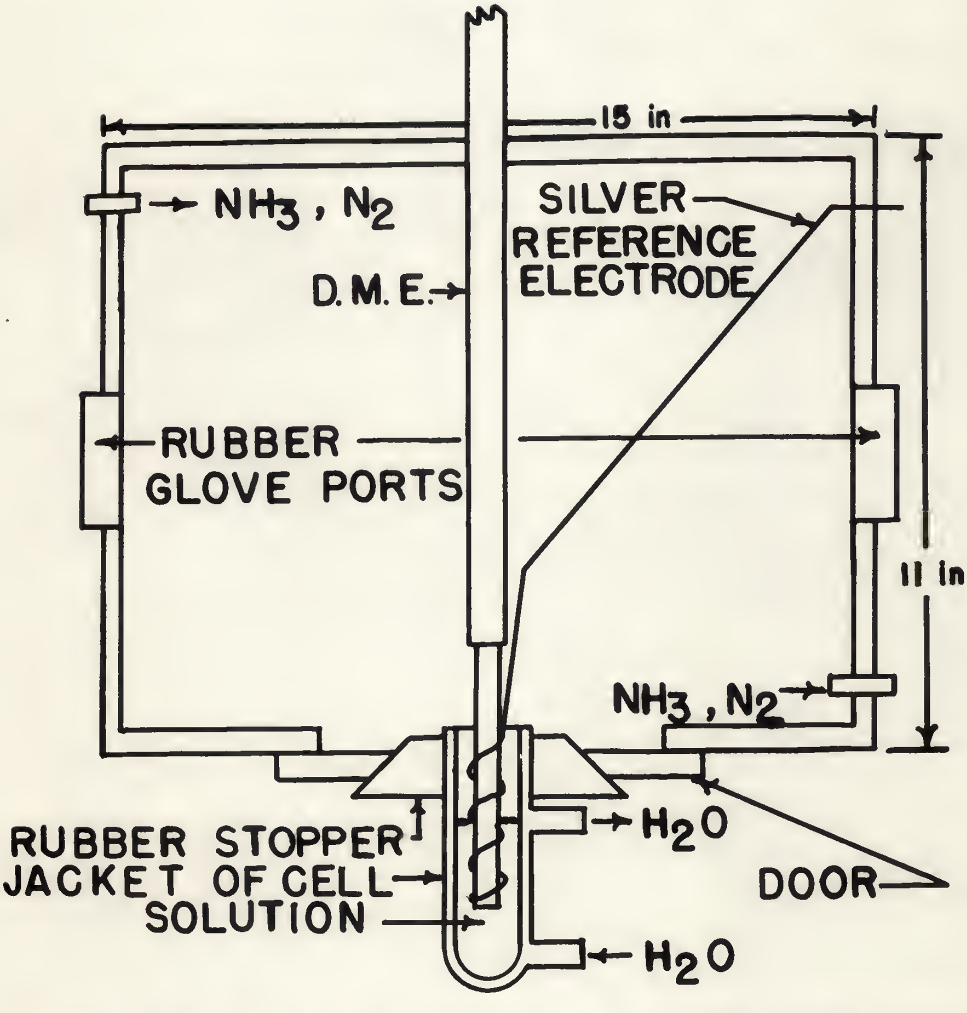
A Sargent-Heyrovsky Polarograph Model XII with a wave spreader was used Hume and Gilbert (11). A Rubicon Portable Potentiometer was used to measure the applied potential at the beginning and at the end of the polarogram. Calibration points were marked on the photographic record by adjusting the galvanometer to 20 and opening the shutter at each point.

A saturated lead-lead nitrate electrode was used as the reference electrode for use in Divers' solution. The electrolysis cell of the H type proved to be satisfactory when used with this solution. When Divers' solution was used, the cell circuit had a resistance as measured by an Industrial Conductivity Bridge Model RC, of 31 ohms.

The silver metal reference electrode proved satisfactory when used in the sodium iodide solution. The apparatus used in the sodium iodide-ammonia investigation is described in Fig. 1. The resistance in the cell circuit with the sodium iodide was 28 ohms.

Procedure Used With Divers' Solution

A weighed amount of previously dried ammonium nitrate was placed in one arm of the H cell and an approximately equal amount was placed in the other half of the cell. The cell was then placed in a constant temperature bath maintained at 0° C by melting ice. Anhydrous ammonia was simultaneously passed through each cell until the system reached vapor pressure equilibrium with 1 atm. ammonia at 0° C. The condition of equilibrium was indicated by



BUBBLER CONNECTED TO INLET WHEN USED

Fig. 1. Apparatus used in the ammonia-sodium iodide investigation.

the total solution of the ammonium nitrate and contained approximately three moles of ammonia per mole of ammonium nitrate. After equilibrium was established the reference cell was saturated with lead nitrate, the lead electrode was placed in the solution, and a weighed amount of sample placed in the sample compartment. Ammonia was again bubbled through both cells for about ten minutes to insure thorough mixing. The polarograms were then taken with a span of 0.2 volts. When gelatine was used, a few grains of gelatine were added with the sample to be studied. When equilibrium had been established the solution was saturated with gelatine.

Whenever different ion species or the effect of the concentration on the diffusion current was studied, new sample and reference solutions were prepared. The face of the lead electrode was cleaned each time to insure a fresh lead surface with each solution studied.

Procedure Used With Sodium Iodide Solution

Sodium iodide was placed in a weighing bottle and dried at 110° C for twenty-four hours or more. After the sodium iodide had been removed from the oven, cooled, and weighed, it was placed in the dry box (Fig. 1). The sample to be studied was weighed, placed into the electrolysis cell and the cell then fitted into position in the bottom of the dry box. If gelatine was used, approximately 50 mg was placed also into the cell along with the sample to be studied. This amount of gelatine insured saturation of the solution. By placing the rubber gloves in position, the dry box was closed. Dry nitrogen was used to sweep out any moisture. After passing the nitrogen thru the box for ten minutes, a sufficient quantity of sodium iodide was taken from the weighing bottle and placed into the cell to yield approximately four milliliters of solution. The cooling water, maintained at 24° C ±0.2° C by means of a water bath, was started thru the jacketed cell. The NH_3, which had been previously passed thru a drying tube of sodium, was then passed through the sodium iodide crystals in the cell by means of a glass tube that served as a bubbler. The condition of equilibrium was obtained as described above for Divers' solution. After equilibrium had been reached, the dropping mercury and the reference electrodes were inserted into the cell and the polarogram taken with a span of 0.2 volts. The remainder of the sodium iodide in the weighing bottle was then removed from the dry box, heated to expell any adsorbed NH_3 and weighed. If different concentrations were to be studied, the solutions were diluted by adding more sodium iodide from a different weighed weighing bottle. Again ammonia was bubbled through the solution until equilibrium had been reached. When different substances were to be studied at the same time, all of the constituents that had not been added, as described above, were placed inside the dry box and added when needed.

RESULTS AND DISCUSSION

A preliminary investigation of Divers' solution using a mercury pool as the reference electrode revealed that the potential of the reference electrode was dependent upon the length of time the mercury had been in contact with the solutions. Since equilibrium conditions could not be readily obtained, and since reproducible measurements of half-wave potentials could not be obtained, the mercury pool was replaced with the saturated lead-lead nitrate reference cell. A lead-0.1M lead nitrate reference electrode has been described in the literature Pleskov and Monosson (14) but because of the difficulty of preparing such an electrode, a saturated lead-lead nitrate reference electrode was developed for use in Divers' solution. The saturated lead-lead nitrate reference cell gave results which could be reproduced within ±0.003 volts. The polarographic investigation of a sample could be completed before detectable amounts of lead diffused from the reference cell into the working cell.

The influence of moisture contamination upon the half-wave potential in Divers' solution are shown in Fig. 2 and Table 1. The half-wave potential of $Pb^{++} + 2e^{-} = Pb$ couple was shifted toward more positive potentials as the amount of water contamination was increased in the working cell. No water was added to the reference cell. A similar dependency upon moisture content was found for the half-wave potentials of diphenylthiocarbazone (curve 2, Fig. 1). However, the shift in the half-wave potentials was much less than that for the lead couple. Although, as is shown in Fig. 2, there is a change in the half-wave potential accompanying a change in the water content, reproducible results for the half-wave potentials could be obtained.

Table 2 shows the typical compounds that were found to be soluble in Divers' solution. Table 3 shows those that were found to be insoluble. Not all of the compounds shown in Table 1 gave polarographic waves falling within the useable voltage span, +0.4 to -0.8 volts, of the ammonia-ammonium nitrate electrolyte against the saturated lead-lead nitrate reference cell. Table 4 lists the compounds that gave well defined polarographic waves. The copper, cobalt and cadmium compounds were prepared and purified according to recommended procedures (12, 8, 5). A plot of $\log i/(i_d - i)$ against E gave straight lines with very little scatter of points. The slopes of the plots for lead, cadmium, and cobalt were respectively 0.0289, 0.031, 0.105 indicating that lead and

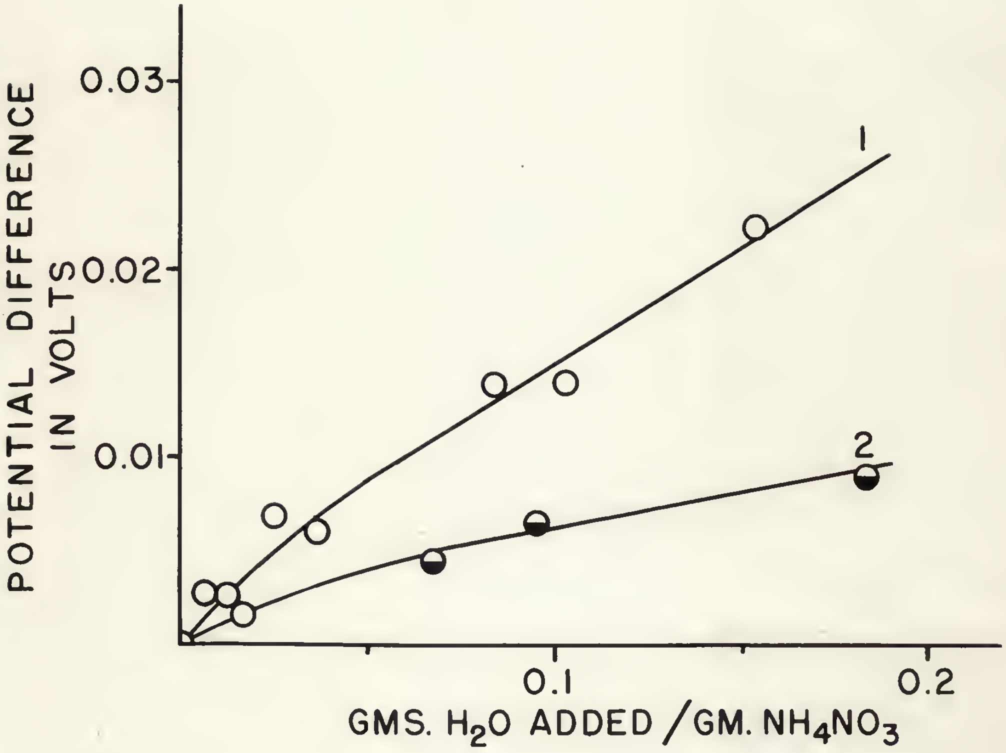


Fig. 2. Effect of moisture content upon half-wave potentials in Divers' solution at 0° C.

1. Change of half-wave potential for the lead system.

2. Change of half-wave potential for the diphenyl thiocarbazone system.

Potential difference = $E\frac{1}{2}$ without added water -

$E\frac{1}{2}$ with given amount of water added

Table 1. Effect of moisture upon the half-wave potential in Divers' solution at 0° C.

Lead System

gms H_2O added/gm NH_4NO_3	Potential Difference*
0	0
0.0063	0.003
0.0123	0.003
0.0173	0.002
0.0256	0.007
0.0372	0.006
0.0837	0.014
0.103	0.014
0.153	0.022

Diphenylthiocarbazone System

gms H_2O added/gm NH_4NO_3	Potential Difference*
0	0
0.0675	0.005
0.0944	0.007
0.183	0.009

*Potential Difference = $E_{\frac{1}{2}}$ without added water - $E_{\frac{1}{2}}$ with given amount of water added.

Table 2. Inorganic and organic compounds which are soluble in Divers' solution at 0° C.

As_2O_3

BaO

HgO

PbO

$PbBr_2$

PbI_2

$Pb(NO_3)_2$

$AgSCN$

$Hg(SCN)_2$

$CdSO_4$

$Cu(NH_3)_4(SCN)_2$

$Co(NH_3)_6(NO_3)_2$

m-Nitroaniline

Diphenyl thiocarbazone

Benzoic acid

Nicotinic acid

Aspartic acid

Thiourea

Maleic anhdride

Benzil

Azobenzene

1-Naphthol-5-sulfonic acid

Table 3. Inorganic and organic compounds which are insoluble in Divers' solution at 0° C.

Al_2O_3

CuO

Fe_2O_3

MgO

Sb_2O_5

SeO_2

TeO_2

TiO_2

$Co(CN)_2$

$Ni(NH_3)_6Br_2$

Benzophenone

$Ni(CN)_2$

p-Hydroxybenzophenone

Phenyl-α-chloroisobutyrate

Benzoyl peroxide

Phthalic anhydride

Table 4. Half-wave potentials and diffusion current constants for various inorganic and organic compounds in Divers' solution at 0° C.

Compound	E ½ in volts versus the lead-lead nitrate reference electrode	$\frac{i_d}{cm\ 2/3\ t\ 1/6}$
PbO	+0.019	10.9
$Cu(NH_3)_4(SCN)_2$*	+0.185	4.04
$Cu(NH_3)_4(SCN)_2$*	-0.026	4.04
$Co(NH_3)_6(NO_3)_2$	+0.191	**
$CoSO_4$	-0.387	14.9
m-Nitroaniline*	-0.034	48.8
Diphenyl thiocarbazone	+0.173	0.536
Benzil*	+0.088	**
Azobenzone	+0.196	**

* Gelatin added to suppress the maximum

** Low solubility

m 2/3 t 1/6 equaled 1.97 at a potential of 0.4769 versus the lead-lead nitrate electrode. c is expressed in mg/gm of NH_4NO_3.

cadmium gave reversible reactions, corresponding to a two electron change, whereas the cobalt reduction was irreversible. The copper compound formed two reversible waves each representing a one electron change. This corresponds to the reduction of cupric to cuprous and then cuprous to copper as indicated by a slop of 0.0562 and 0.068. Some of the compounds formed a maximum in the polarogram but the maximum was easily suppressed by the addition of gelatine. Since gelatine is just slightly soluble in Divers' solution, a saturated solution was prepared by adding a few grains of gelatine to the solution and bubbling ammonia through it for five minutes to assure thorough mixing. The diffusion current was found to be proportional to the concentration of reducible material, and the half-wave potential was found to be dependent upon the species present.

Preliminary investigation of the sodium iodide solution involved the use of the mercury pool reference electrode. Like Divers' solution, reproducible results could not be obtained within a reasonable deviation. When a metallic cadmium reference electrode was used, Galvanic action occurred and rendered this electrode useless for compounds with a lower oxidation potential than that of cadmium. The silver metal reference electrode proved satisfactory in this solution and gave reproducible results of ± 0.003 volts.

Table 5 shows that typical compounds that were found to be soluble in the sodium iodide solution. Table 6 shows the ones that were found to be insoluble. Not all of the compounds that were soluble gave well defined waves within the useable range of +0.2 to - 0.11 volts versus the silver metal electrode. This corresponds to observations with Divers' solution. Table 7 lists the compounds that give well defined curves. A plot of $i/(i_d-i)$ versus E gave straight lines with very little scattering of the points. The

Table 5. Inorganic and organic compounds which are soluble in ammonia-sodium iodide solution at 24° C.

PbI_2
HgI_2
$KMnO_4$
Dithiozone
$Cu(NH_3)_4(CNS)_2$
p-Hydrozybenzophenone
Dimethyglyoxime
m-Nitroaniline
o-Nitroaniline
Glycine
$Ce(HSO_4)_4$
Benzil
As_2O_3
CdI_2
Azobenzene
Benzoin
o-Chlorobenzoic acid
p-Aminosalcylic acid
p-Dimethylaminobenzaldeyde
o-Nitrophenol
p-Chloronitrobenzene
Cupric mandelate

Table 6. Inorganic and organic compounds which are insoluble in ammonia-sodium iodide solution at 24° C.

$Ni(NH_3)_6Br_2$

Nicotinic acid

Phthalic anhydride

Maleic anhydride

Thiourea

$MnCl_2$

$FeCl_2$

Gallic acid

Ferric oxalate

$FeSO_4$

$CdSO_4$

2,4-Dichlorobenzoic acid

β-alanine

Benzoic acid

Table 7. Half-wave potentials and diffusion current constants for various inorganic and organic compounds in the ammonia-sodium iodide solution at 24° C.

Compound	$E_{\frac{1}{2}}$ in volts versus the silver metal electrode	$\frac{i_d}{cm^{2/3}t^{1/6}}$
PbI_2*	-0.072	3.49^o
$Cu(NH_3)_4(SCN)_2$	-0.102	3.78^o
CdI_2	-0.466	**
Azobenzene*	-0.233	**
o-Nitrophenol*	-0.281	**
m-Nitroaniline*	-0.175	14.2^o
m-Nitroaniline*	-0.507	18.8^o
o-Nitroaniline*	-0.260	8.52^o
o-Nitroaniline*	-0.506	12.6^o
p-Chloronitrobenzene*	-0.109	9.50^o
p-Chloronitrobenzene*	-0.498	10.4^o
Benzil*	-0.243	2.02^o

* Gelatine added to suppress the maximum

o These values are only approximate because of the non-linearity of concentration vs. i_d plot.

** Low solubility

$m^{2/3}t^{1/6}$ equaled 1.69 at zero potential. c is expressed in mg/gm NaI.

slope of the plot for cadmium was 0,029 indicating that a reversible two electron reaction had occurred. Copper gave more than one wave, of which only one was in the useable range. This wave gave a E versus $i/(i_d-i)$ plot whose slope was 0.059. This indicates copper gave a reversible one electron reaction, which probably corresponds to the cuprous to copper reduction. The plot of lead gave a slope of 0.041 which would indicate that something other than a direct one or two electron reaction had occurred.

Most of the compounds formed a maximum in the sodium iodide solution. Gelatine, as in Divers' solution, suppressed the maximums and gave well defined polarograms. The gelatine is only slightly soluble in this solution and so a saturated solution was always used. This was obtained by adding approximately 50 mg of gelatine to the sample of sodium iodide and the unknown. A saturated gelatine solution was obtained by passing ammonia through the sample and sodium iodide mixture until equilibrium had been reached. The diffusion current was found to be proportional to the concentration of the reducible material. However, it was observed that this proportionality was not a linear relationship. The half-wave potential was found to be dependent upon the species which were reduced. The resulting waves from the nitrobenzene compounds indicate that the half-wave potential is not only dependent upon the nitro group that is being reduced, but also upon other groups that are present and their position on the ring with respect to the nitro group.

The composition of the sodium iodide solution was determined in the following manner. A weighing bottle was fitted with a rubber stopper that contained an inlet and an exit for ammonia. Both had valves to keep the moisture out during the weighing. A weighed amount of sodium iodide was placed in the flask. Dry ammonia gas was passed thru until an equilibrium had been reached. The valves were closed and the flask weighed. This gave the amount of ammonia needed to condense a known amount of sodium iodide. The mole ratios were calculated and found to be approximately $NaI \cdot 3.6NH_3$.

CONCLUSION

Ammonium nitrate and sodium iodide condense with anhydrous ammonia to produce non-aqueous solutions that are suitable for polarographic studies. These solutions are stable at convient temperatures, are good electrolytes, and need no supporting electrolyte. Two different types of reference electrodes were tried and both proved satisfactory in their respective solutions. Reversible electrode reactions were obtained in both solutions. Maximums occurred in both solutions. However, gelatine was found to suppress these reactions and give well defined waves. It was observed, in the case of the substituted nitrobenzenes in the sodium iodide solution, that not only the group that was reduced but also other groups present and their position with respect to the nitro group had a pronounced effect upon the half-wave potential.

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Precision polarography was used to study organic and inorganic compounds in solvents which result from the condensation of anhydrous ammonia and certain inorganic salts.

The ammonia-ammonium nitrate, Divers' solution, and the ammonia-sodium iodide solutions were the particular ones studied. The lead-lead nitrate cell served satisfactorily in Divers' solution as a reference electrode. Although the measured half-wave potentials were shown to be shifted in Divers's solution by the addition of water to the solvent, values for the half-wave potential, reproducible within ≠0.003 volts, were obtained. The metallic silver electrode was used in the sodium iodide solution and gave the same reproducibility results as the lead-lead nitrate electrode in Divers' solution. Well formed waves were obtained in both solutions. The diffusion current was found to be proportional to the concentration and the half-wave potential was found to be dependent upon the species present. Maximums occur in both solutions. However, gelatine suppresses the maximums and produces well defined waves. Substituted nitrobenzenes were studied in the ammonia-sodium iodide solution. The resulting half-wave potential was found to depend not only upon the nitro group that was reduced but also upon the other groups that were present. Similarly the position of the groups with respect to the nitro group show some influence upon the reduction.