

ELECTRODEPOSITION OF METALS FROM NON-AQUEOUS SOLVENTS

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INTRODUCTION

Electrochemists, particularly electroplaters, have paid comparatively little attention to the use of non-aqueous solvents. However, several researches in the past few years have indicated that developments will certainly include a study of the deposition of metals from solutions of their salts in solvents other than water. It may seem a bit premature to stress the application of non-aqueous solvents to the problem of electrodeposition of metals, particularly when the fundamental electrochemical reactions in aqueous solution are still so little understood and subject to so much dispute. The question may be asked whether it is of advantage to introduce another variable in the form of a new solvent when the effect of such factors as temperature, concentration of solute, current density, addition agents, etc., has been defined only in a qualitative way. However, our knowledge of electrodeposition from aqueous solution is limited to a comparatively small number of metals and non-metals, and attempts to discharge the remainder of the elements from aqueous solutions of their compounds, and under a variety of conditions, have thus far failed. Experience has shown that some metals, as such, will probably never be discharged from aqueous solution because of their reactivity with water. On the other hand, solvents are known which either do not attack these metals or which react with them only very slowly, and if such solvents give conducting solutions of compounds of these metals, their possible application as media for electrodeposition is worth investigation. De-

spite the comparatively small number of researches which have dealt with this subject, the success which has attended some of them should bring home to all electrochemists the applicability to their field of endeavor of a statement made by Conant (1) that, "Much important chemistry (particularly important to the organic chemist) has been obscured by our slavish devotion to water."

The experimental work thus far carried out brings to light several rather salient facts. A whole variety of solvents, *viz.*, sulfur dioxide, formamide, liquid ammonia, acetamide, pyridine, acetic acid, ethyl bromide, etc., differing widely in physical properties and chemical character, has been employed. Apparently no satisfactory basis for the choice of any one solvent has been given. It may safely be said that scientific curiosity has in most instances prompted these investigations, which have been for the greater part qualitative in nature. Even so, the results obtained have been rather surprising and quite encouraging.

Not only have many different solvents been employed, but the choice of a suitable electrolyte for solution in any specific medium has been hampered by a lack of information. Despite the immense amount of routine effort which has been expended in studying solubilities, we find that the data are limited largely to aqueous solutions. The literature contains few reliable references concerning solubilities in such solvents as pyridine, acetone, the various alcohols, acetonitrile, etc. In the case of liquid ammonia qualitative observations only are available.

Not only does the choice of the proper salt for any one solvent offer a serious obstacle, but the preparation of many anhydrous compounds, particularly the nitrates, bromides, iodides, thiocyanates and cyanides—these come nearest to being universal solutes—is fraught with difficulties. In some cases the presence of water, introduced as water of hydration, makes no difference so far as the final result is concerned, but in many instances the addition of water changes the solvent character in a rather surprising manner. Thus, water behaves as a weak acid in liquid ammonia, whereas it is basic towards acetic acid. In line with

the idea of using anhydrous salts, every effort should also be made to employ anhydrous solvents. The presence of a trace of water has been shown in some cases to prevent electrodeposition of certain metals, yet, on the other hand, to improve the character of the deposits obtained.

HISTORICAL

The first recorded instance where non-aqueous solvents were used for the electrodeposition of a metal involved the electrolysis of solutions of lithium chloride both in acetone (2) and in pyridine (3) as a means for preparing lithium metal. The same investigator, Laszynski, also succeeded in discharging potassium from a solution of the thiocyanate in pyridine and prepared the mercury amalgams of potassium, sodium and ammonium by electrolysis of soluble salts of these metals in acetone using a mercury cathode. Kahlenberg (4) continued the study of the deposition of lithium from solutions of lithium chloride in pyridine and obtained bright, shiny deposits. He subsequently extended his investigations to include other non-aqueous solvents such as aniline, benzonitrile, and quinoline in addition to acetone and pyridine (5). Bright, adherent deposits of silver were obtained from solutions of silver nitrate in all five solvents. Lead was deposited from lead nitrate in pyridine; antimony from a solution of antimony trichloride in methyl alcohol. Attempts to plate bismuth from solutions of bismuth trichloride in methyl alcohol yielded only black, spongy, non-adherent products.

DEPOSITION FROM PYRIDINE

The problem of electrodeposition from pyridine has in recent years been studied very carefully by Müller (6) and his coworkers in Graz. Müller took special pains to make his materials absolutely anhydrous and thus succeeded in discharging metals from solutions of their salts in pyridine where previous investigators had failed. The decomposition potentials of various metallic salts, as well as single potentials of the metals against solutions containing the respective ions in pyridine were determined.

Silver (6a, 6b), magnesium (6d), calcium (6d), zinc (6d), copper (6d), iron (6d), potassium (6c), sodium (6c), and lithium (6c) were discharged cathodically. No deposit of beryllium (6d) was obtained upon electrolysis of a solution of beryllium bromide in pyridine. Müller also investigated various other solvents (6c), but with less success. Neither lithium nor magnesium could be deposited from solutions of their respective nitrate and bromide

TABLE 1
Electrodeposition from pyridine

METAL	SOLUTE	CURRENT DENSITY PER SQUARE CENTIMETER	METAL BASE	REFERENCE
		<i>amperes</i>		
Li.....	LiCl	0.001-0.003	Pt or Fe	Laszynski
	LiNO ₃		Pt or Fe	Kahlenberg, Patten and Mott, Müller
Na.....	NaI, NaNO ₃ , NaSCN		Pt	Müller
K.....	KSCN		Pt	Müller
Ca.....	Ca(NO ₃) ₂	0.0007 at 18°	Pt	Müller
Ba.....	BaI ₂		Hg	Hevesy
Ag.....	AgNO ₃		Pt	Kahlenberg, Müller
Cu.....	Cu ₂ I ₂		Pt	Kahlenberg, Müller
Fe.....	FeCl ₂		Pt	Kahlenberg, Müller
Pb.....	Pb(NO ₃) ₂		Pt	Kahlenberg
Mg.....	MgBr ₂	0.0003	Pt	Müller
Zn.....	ZnI ₂		Pt	Müller
Mn.....	MnCl ₂	No deposits	Pt	Müller
Be.....	BeBr ₂	No deposits	Pt	Müller
U.....	UO ₂ Cl ₂	No deposits	Pt	Pierle
Ra.....	RaBr ₂	No deposits	Pt	Coehn

in acetonitrile. However, a deposit of silver from silver nitrate in this solvent was readily obtained. Calcium did not discharge from a solution of the nitrate in amyl alcohol.

Hevesy (7) found that the alkaline earth iodides were quite soluble in pyridine, but was unable to deposit these directly upon a platinum cathode. By using a mercury cathode he did succeed in obtaining a 30 per cent barium amalgam. Unsuccessful attempts have also been made to electrodeposit radium (8) and uranium (9) from solutions of their compounds in pyridine.

ACETONE AS AN ELECTROLYTIC SOLVENT

Acetone has also found some application in electrodeposition of metals. Deposits of strontium and sodium can be obtained from saturated solutions of the respective iodides when electrolyzed at high current densities. Electrolysis of solutions of the chlorides of cadmium, tin, antimony, bismuth, and arsenic at moderate current densities also yields the respective metals

TABLE 2
Electrodeposition from acetone

METAL	SOLUTE	CURRENT DENSITY PER SQUARE CENTIMETER	METAL BASE	REFERENCE
		<i>amperes</i>		
Li.....	LiCl	High	Cu	Laszynski
	LiCl	0.001	Pt	Patten and Mott
Na.....	NaSCN	0.2	Hg	Laszynski
	NaI		Pt	Patten and Mott
K.....	KSCN	0.001	Hg	Laszynski
NH ₄ ⁺	NH ₄ SCN		Hg	Laszynski
Ca.....	CaCl ₂	0.001	Pt	Siemens
Sr.....	Sr(NO ₃) ₂	0.001	Pt	Siemens
	SrI ₂	0.2	Pt	Patten and Mott
Cu.....	CuCl ₂	0.1	Pt	Patten and Mott
Ag.....	AgNO ₃	0.001	Pt	Kahlenberg
Zn.....	ZnCl ₂		Pt	Patten and Mott
Cd.....	CdCl ₂	0.001	Pt	Patten and Mott
Fe.....	FeCl ₃	0.2	Pt	Patten and Mott
Sn.....	SnCl ₂	0.001	Pt	Patten and Mott
As.....	AsCl ₃	0.136	Pt	Patten and Mott
Sb.....	SbCl ₃	0.0007	Pt	Patten and Mott
Bi.....	BiCl ₃	0.028	Pt	Patten and Mott

(10). Patten and Mott found that zinc (11) and lithium (12) could be deposited from solutions of their chlorides in this solvent. Siemens (13) also studied the deposition of lithium, sodium, potassium and calcium from acetone in an effort to utilize such a process commercially.

FORMAMIDE AS A SOLVENT

On the basis of a study of the conductivity of various inorganic salts in formamide, Walden (14) suggested that this solvent

might be employed very advantageously for the electrodeposition of metals. A preliminary study was subsequently made by Röhler (15), who employed the following compounds as electrolytes for the deposition of the respective cations: $\text{Pb}(\text{NO}_3)_2$, PbCl_2 , CuSO_4 , Cu_2Cl_2 , ZnO , ZnCl_2 , SnCl_2 . Metallic anodes composed of the metals to be deposited were used. A quantitative study of the electrolytic reactions showed that the anodic losses were invariably found to be greater than the weight of metal deposited. These differences were ascribed to the solvoly-

TABLE 3
Electrodeposition of metals from formamide at 100°

COMPOUND	SOLUTE PER 15 CC. SOLVENT	CURRENT DENSITY PER SQUARE CENTIMETER	TYPE OF DEPOSIT
	<i>grams</i>	<i>amperes</i>	
$\text{Zn}(\text{CN})_2$	0.5	0.03	Adherent. Continued electrolysis yielded spongy material
$\text{Cd}(\text{CN})_2$	1.4	0.02	Smooth and adherent
$\text{Pb}(\text{NO}_3)_2$	3.0	0.03	Non-adherent
		0.06	Crystalline. Deposit is not uniform, but adheres only in spots
SnI_4	1.0	0.04	Smooth and adherent
$(\text{NH}_4)_2\text{SnCl}_6$	2.0	0.04	Excellent deposition
$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	2.0	0.02	Poor
		0.05	Better deposition; adherent
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$	Saturated	0.018	Fair and adherent
$\text{Ni}(\text{NH}_3)_6\text{Br}_2$	2.0	0.025	Good and adherent

sis of the respective electrolytes with the resultant formation of the metallic formamide derivative and the free acid. Chemical action of the acid, so formed, upon the metallic anodes was postulated to account for these discrepancies. It was found that dissolved oxygen, as well as exposure of the solution to air, influenced the character of the deposit very decidedly. These observations have recently been checked and confirmed by the investigations of Yntema and Audrieth (16). In addition to the metals which Röhler was able to plate from formamide these investigators succeeded in depositing cadmium, nickel and co-

balt. Magnesium, aluminum, iron, and some of the more active metals could not be discharged.

ACETAMIDE AS A SOLVENT

Another solvent which resembles formamide closely is acetamide. Although a solid at ordinary temperature, it is liquid at 100°C., and has been found to be an excellent solvent for a great many inorganic salts. The compounds $\text{Zn}(\text{CN})_2$, $\text{Cd}(\text{CN})_2$,

TABLE 4
Electrodeposition of metals from acetamide at 100°

COMPOUND	SOLUTE PER 10 GRAMS OF SOLVENT	CURRENT DENSITY PER SQUARE CENTIMETER	TYPE OF DEPOSIT
	<i>grams</i>	<i>amperes</i>	
$\text{Zn}(\text{CN})_2$	0.177	0.05	Deposit localized
$\text{Cd}(\text{CN})_2$	0.164	0.03	Smooth and adherent
SnI_4	0.624	0.05	Smooth and bright
$(\text{NH}_4)_2\text{SnCl}_6$	0.368	0.04	Smooth, bright, deposit; "treeing" after two minutes
	(Not completely soluble)		
PbCl_2	0.278	0.037	Spongy and non-adherent
$\text{Ni}(\text{NH}_3)_6\text{Br}_2$	0.320	0.03	Good, adherent deposit; higher current densities give a black powdery deposit
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	0.250		No deposit
$\text{K}_3\text{Co}(\text{CN})_6$	0.332		No deposit
CoCl_2		0.02	Smooth deposit; higher current densities give a black powdery deposit
$\text{TlC}_2\text{H}_3\text{O}_2$	0.263	0.025	Some adherent deposit, with marked "treeing"

SnI_4 , $(\text{NH}_4)_2\text{SnCl}_6$, PbCl_2 , $\text{Ni}(\text{NH}_3)_6\text{Br}_2$, CoCl_2 , $\text{TlC}_2\text{H}_3\text{O}_2$ were used for the deposition of the respective metals(16). Here, again, metals higher than zinc in the electromotive series could not be discharged directly from solutions of their salts in acetamide.

The effect of water upon the character of a deposit is strikingly shown in the case of the electrolysis of a solution of zinc cyanide in acetamide. Very poor deposits were obtained using a solution

of zinc cyanide in pure acetamide. The addition of a drop of water to the electrolytic bath caused the formation of bright, adherent deposits, considerably superior to those obtained where pure acetamide solutions had been used.

ELECTRODEPOSITION FROM LIQUID AMMONIA

Perhaps no non-aqueous solvent has attracted so much attention in recent years as liquid ammonia. To quote Franklin (17): "Indeed in all these properties which give water its unique position among solvents liquid ammonia shows a most striking similarity to water. Excepting water itself, it is, so to speak, by far the most water-like substance known. Approaching water as it does in general properties, one might expect to find many resemblances between derivatives of ammonia and the analogous water compounds." Reactions in liquid ammonia have been the subject of considerable study and have led to the adoption by progressive laboratories of methods of synthesis involving liquid ammonia as a solvent.

The study of the electrochemical behavior of solutions of salts in liquid ammonia dates back to the time when interest was first manifested in the nitrogen prototype of water and involves the determination of conductivities (18) of various substances in it. The most important discovery in the course of these investigations was the fact that many organic amides, imides, and nitro compounds yielded conducting solutions. These substances had been regarded as non-electrolytes in aqueous solution, yet in liquid ammonia they were found to behave in many instances as strong electrolytes. In other respects conductivity phenomena were found to be similar to those observed in aqueous solution.

Attempts were made at an early date to prepare free ammonium (19) by the electrolysis of solutions of ammonium salts in liquid ammonia, but none of these experimental efforts have ever yielded any conclusive results. More success attended the electrolysis of solutions of quaternary ammonium salts. The remarkable solubility of the alkali and the alkaline earth metals to give the characteristic blue solutions undoubtedly caused Palmer (20) to investigate the behavior of tetramethylammonium

and tetraethylammonium chlorides upon electrolysis. He noted the appearance of the blue color in the neighborhood of the cathode and concluded that the free quaternary radicals were discharged. Kraus (21) subsequently confirmed these results and in addition prepared several free mercury alkyl radicals, *viz.*, HgCH_3 , HgC_2H_5 , HgC_3H_7 , by electrolysis of the corresponding iodides or chlorides at temperatures as low as -60° . In the case of these substances Kraus says, "Ammonia not only makes it possible to carry out electrolyses at temperatures favorable to stability, but it also provides a solvent which, even with the most electropositive metals, reacts at a very slow rate."

Not until the past year has the problem of electrodeposition from ammonia been studied intensively. Although investigations involving electrolytic corrosion, specifically nitridation (22) of metallic anodes in liquid ammonia, have been carried out, it was not until Groening and Cady (23) determined decomposition potentials of salts and metal overvoltages in liquid ammonia, that any interest was manifested in the electrodeposition of metals. The decomposition potentials were found, in general, to be of the same order of magnitude as those in water, but the metal overvoltages were found to be somewhat higher. They did not concern themselves with the type of deposit obtained. Taft and Barham (24) took up this problem in some detail to determine the effect of such factors as current density, concentration, acidity, nature of anion, temperature, addition agents and metal base, upon the type of deposit obtained in the electrolysis of solutions of various lead, cadmium, silver, nickel and zinc salts [$\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ni}(\text{NH}_3)_6(\text{NO}_3)_2$, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$, AgNO_3 , $\text{Zn}(\text{NO}_3)_2$]. The current densities necessary for the best deposits were found to be lower in liquid ammonia than in aqueous solutions, except in the cases of zinc and silver. Taft and Barham advocate particularly the possible practical application of liquid ammonia solutions in the deposition of cadmium and lead. (See table 5.)

This same problem has also been studied in a qualitative fashion in the author's laboratory (25). An effort was made here to cover as wide a range of metals as possible by judicious choice of

compounds. (See table 6.) In addition to the metals mentioned by Taft and Barham, mercury, thallium, tin and cobalt plates were also obtained. Cyanides were found to be especially soluble in liquid ammonia and were used in the deposition of zinc and cadmium. The hydrated nitrates of zinc and cobalt were found to give deposits of the respective cations from liquid ammonia. As was expected, electrolysis of soluble alkali metal salts¹ brought about discharge of the free metals with formation of the characteristic blue solution. The persistence of the blue cathodic

TABLE 5
Electrodeposition from liquid ammonia

Conditions for the formation of "best" deposits (TAFT AND BARHAM: J. Phys. Chem. 34, 952 (1930)): temperature, boiling point of solution; anion, nitrate.

METAL	METAL BASE	CURRENT DENSITY PER SQUARE DECIMETER	NORMALITY	ACIDITY PER 100 CC. OF SOLVENT
		<i>amperes</i>		<i>grams</i>
Pb.....	Fe	0.61	1.0	1.0
Ni.....	Ni	0.15	0.14	0
Cd.....	Fe	1.21	0.5	10
Cu.....	Fe	3.3	0.5	5
Ag.....	Fe	0.92	0.23	0
Zn.....	Fe	1.9	0.53	2

solution is dependent upon the activity of the alkali metal. Blue sodium solutions are quite stable, whereas the similar solution formed as the result of the discharge of cesium disappears shortly after electrolysis is discontinued. The conclusion was reached from these experiments that "the phenomena of electrodeposition of metals from liquid ammonia solutions of their salts closely parallel the behavior of the corresponding aqueous solutions."

Perhaps the most striking advance in recent months was the announcement by Booth (26) and his coworkers that they had

¹ In the case of sodium nitrate and sodium nitrite the alkali metal primarily discharged reacts with the solute to give a yellow precipitate. Analysis of this substance indicates that its composition agrees with the formula Na_2NO_2 , sodium hydronitrite. See MAXTED: J. Chem. Soc. 111, 1016 (1917); also ZINTL AND KOHN: Ber. 61B, 189 (1928).

TABLE 6

Electrodeposition of metals from liquid ammonia

Temperature, boiling point of solution; metal base, copper

SALT USED	CONCENTRATION PER 50 CC.	SOLUBILITY	CURRENT DENSITY PER SQUARE CENTI-METER	CHARACTER OF DEPOSIT
	<i>grams</i>		<i>amperes</i>	
Cu ₂ Cl ₂	Saturated	Slightly soluble	0.025	Fair
CuBr ₂	Saturated	Moderately soluble	0.1	Smooth and adherent
AgNO ₃	5	Very soluble	{ 0.015 0.09	Mottled Smooth and adherent
Zn(NO ₃) ₂ ·6H ₂ O.....	5	Very soluble	{ 0.06 0.55	Smooth and adherent Crystalline; formation of tree-like growths
Zn(CN) ₂	3	Very soluble	{ 0.02 0.11	Uneven Smooth
CdI ₂	Saturated	Slightly soluble	{ 0.04 0.14	Uneven Smooth and adherent
Cd(CN) ₂	Saturated	Moderately soluble	0.04	Smooth deposition. Continued electrolysis caused formation of Cd crystals
HgI ₂	Saturated	Moderately soluble	0.04	Hg is discharged. Cu displaces Hg directly from solution
TlI.....	Saturated	Moderately soluble	{ 0.04 0.14	Crystalline and tree-like, mossy
TlNO ₃	2	Very soluble	{ 0.04 0.14	Dendritic and crystalline
SnCl ₄	Saturated	Slightly soluble	{ 0.025 0.14	Excellent deposition
SnI ₄	Saturated	Slightly soluble	0.14	Excellent deposit. Continued electrolysis causes the deposit to scale off
Pb(NO ₃) ₂	5	Very soluble	{ 0.03 0.2	Crystalline and uneven Smooth; continued electrolysis results in the appearance of crystalline growths
Co(NO ₃) ₂ ·6H ₂ O.....	Saturated	Very soluble	{ 0.016 0.045	Smooth and adherent Gives a metallic deposit which on contact with air turns black. (Possible formation of an active form of cobalt)

succeeded in depositing beryllium from liquid ammonia and related solvents. Their success attended the preparation of anhydrous beryllium nitrate by dehydration of the hydrated salt in fused ammonium nitrate. By the addition of ammonium nitrate to the solvent they were able not only to decrease the vapor pressure of the solution to such an extent as to make possible electrolysis at room temperatures, but to increase the solubility of the solute as well. Their investigations covered the electrolysis of many different salts in liquid ammonia and publication of these data is awaited with a great deal of interest.

With the manufacture of liquid ammonia in huge quantities and at reasonable prices, its use as a solvent is bound to find practical application. Certainly it has demonstrated its value as an electrolytic medium and its further application along this line awaits only a more extended investigation of its possibilities. Not only the electrodeposition of metals, but cathodic reduction of organic compounds, should be studied in more detail. In consideration of the solubility and conductivity of many organic compounds in liquid ammonia, a study of electro-organic syntheses in this solvent should be particularly fascinating.

DEPOSITION FROM MISCELLANEOUS SOLVENTS

A great many attempts have been made to deposit aluminum electrolytically, but not one of the proposed methods has thus far proven to be of any commercial value. As early as 1902 Plotnikov (27) succeeded in depositing aluminum from a solution of the bromide in ethyl bromide. He also found aluminum bromide to dissolve in toluene, benzene, nitrobenzene, and carbon disulfide to give conducting solutions, but was not successful in depositing the metal from any of these. His experiments were subsequently confirmed by Patten and Mott (28) and other investigators.

A British patent covers the use of acetonitrile (29) as a solvent for the electrodeposition of aluminum. The specifications call for 10 per cent solution of aluminum chloride in this solvent and suggest the use of potassium acid fluoride or phosphorus trifluoride to the extent of about 1 per cent to increase the conductance.

Electrolysis is permitted to take place at temperatures anywhere from 0–100° and the most favorable current density is given as 2–3 amperes per square decimeter.

A U. S. patent issued to G. L. Williams (30) covers the use of aluminum sulfate dissolved in oleum. This suggestion is interesting, even if not practical, from a consideration of 100 per cent sulfuric acid as an acidic solvent of the same type as acetic and formic acids. Sulfuric acid should, therefore, constitute the parent substance of a solvent system in the same sense as we now speak of ammonio, aquo and thio compounds. There is only one slightly disturbing feature connected with the patent specifications, since Davidson (31) reports anhydrous aluminum sulfate as absolutely insoluble in 100 per cent sulfuric acid.

The most recent method for the deposition of aluminum makes use of solutions of aluminum alkyl derivatives such as diethyl aluminum iodide and ethyl aluminum diiodide in dry ether (32). The stringent conditions under which this process must be carried out make its practical application of questionable value. However, from a purely scientific point of view this method offers a new line of attack for many other elements which have not yet been obtained even in the metallic form.

Evans (33) has reported the formation of a cathodic deposit of magnesium upon electrolysis of various Grignard solutions. Similar results have also been obtained by Drane and French (34) who used solutions of isoamyl magnesium chloride in ether.

Various alcohols have been tried as electrolytic media. In fact, a process (35) for obtaining metallic lithium by electrolysis of solutions of lithium chloride in ethyl, propyl, butyl and amyl alcohols has been patented. In this connection it is interesting to note that Carrara (36) studied the decomposition potential of sodium ethylate in ethyl alcohol.

In a series of researches being carried out in the author's laboratory at the present time, a whole variety of solvents has been investigated in an attempt to electrodeposit the rare earth metals. Of the fifteen elements which are included in this group only five have ever been prepared in the metallic form and of these only two, cerium and lanthanum, have been obtained in the

pure state. The very fact that the rare earths resemble aluminum, beryllium and barium in their chemical properties makes the problem one which combines the objectionable features of all of these.

Not only have these metals never been deposited from solution, but attempts to prepare amalgams of the rare earths electrolytically have failed (37). Although no marked success has, as yet, been attained in the actual deposition of the rare earth metals from various non-aqueous solvents, no difficulty was encountered in the preparation of rare earth amalgams. Thus, electrolysis of a saturated solution of anhydrous neodymium chloride in absolute ethanol at a current density of 0.06 amperes per square centimeter using a mercury cathode yielded after 10 hours a 2.1 per cent neodymium amalgam (38). Electrolysis of saturated aqueous solutions at higher current densities (0.4-0.6 amperes per square centimeter) also results in the formation of amalgams, but of lesser concentration. Lanthanum amalgams (39) have been prepared in this way, but the preparation of amalgams from aqueous solutions is always accompanied by formation of a heavy precipitate of the basic chloride, when the chloride is employed as solute. It would seem, therefore, that the preparation of amalgams by electrolysis of solutions in non-aqueous solvents possesses certain advantages, especially when a more concentrated product is desired and side reactions are to be avoided.

An interesting solvent which has been found to behave in a rather curious manner is phosphorus oxychloride. Metallic potassium has been discharged cathodically from a solution of potassium iodate in this solvent (40).

Increased interest in non-aqueous solvents has naturally brought about an attempt to classify these on the basis of some common variable. For instance, the suitability of a solvent as an ionizing medium was once believed to be dependent upon its dielectric constant. This idea has long been discarded, for it has been found that given the proper solute practically any substance may act as an ionizing medium. One of the most satisfactory means of differentiating solvents has recently been

given renewed prominence by Hall and Conant (41) and depends upon the affinity of a substance for the proton or hydrogen ion. From this point of view ammonia, because of its pronounced affinity for the hydrogen ion in the formation of the ammonium ion, is regarded as a basic solvent. Water has a lesser affinity for the proton and exhibits a smaller tendency to form the hy-

TABLE 7
Electrodeposition from miscellaneous solvents

METAL	SOLUTE	SOLVENT	REFERENCE
Li.....	LiCl	Methyl, ethyl, propyl, butyl, amyl alcohol	Patten and Mott
Ag.....	AgNO ₃	Acetonitrile Aniline Benzonitrile Quinoline	Müller Kahlenberg Kahlenberg Kahlenberg
Sb.....	SbCl ₃	Methyl alcohol	Kahlenberg
Bi.....	BiCl ₃	Methyl alcohol	Kahlenberg
Al.....	AlBr ₃	Ethyl bromide	Plotnikov
	AlCl ₃	Acetonitrile	Lalbin
	Al ₂ (SO ₄) ₃	Sulfuric acid	Williams
	(C ₂ H ₅) ₂ AlI C ₂ H ₅ AlI ₂	Ether	Keyes, Swann, Kla- bunde and Schick- tanz
Mg.....	Magnesium in ether	Grignard solutions	Evans Drane and French
K.....	KIO ₃	Phosphorus oxy- chloride	Cady and Taft
Sb.....	SbCl ₃	Glacial acetic acid	Nelson, Smith and Audrieth
Bi.....	BiCl ₃		
Sn.....	SnCl ₄		
As.....	AsCl ₃	C ₂ H ₅ OH	Jukkola and Audrieth
Nd amalgam.....	NdCl ₃		

droxonium ion, and consequently is regarded as less basic. Glacial acetic acid from this point of view is regarded as a very acidic solvent. Both Hantzsch and Walden (42) have also pointed out that 100 per cent nitric acid, as well as pure sulfuric acid, may be considered an acidic solvent. The investigations of Hammett (43) and his students seem to indicate that anhydrous formic acid is also a very acidic solvent.

On the basis of this classification of solvents and from a previous study of the electrodeposition of metals from liquid ammonia, an investigation of the behavior upon electrolysis of solutions of salts in glacial acetic acid (44) was undertaken in the author's laboratory. Ammonia and substituted amines are rather distinctive, since they permit electrolytic discharge of the alkali and alkaline earth metals. These elements cannot ordinarily be discharged from more acidic solvents. Compounds of such metals as antimony, bismuth, arsenic and tin undergo considerable solvolysis in more basic media, consequently the use of an acidic solvent such as glacial acetic acid suggested itself for the deposition of those elements which in their chemical properties lie on the borderline between metals and non-metals.

The chlorides of tetravalent tin and of antimony, arsenic, titanium, germanium, and bismuth were found to be appreciably soluble in glacial acetic acid. However, only in the cases of arsenic, antimony, tin, and bismuth was it possible to obtain deposits of the respective metals.

Particularly gratifying were the deposits obtained in the case of antimony and arsenic. Fairly concentrated solutions had to be employed to make them appreciably conducting. Due to the high resistivity of the electrolytic bath some difficulty was encountered in controlling the temperature.

Solutions of antimony trichloride (40–50 grams SbCl_3 per 100 cc. of $\text{HC}_2\text{H}_3\text{O}_2$) when electrolyzed at low current densities (0.001–0.003 amperes per square centimeter) gave bright deposits upon copper and brass. The addition of water was found to increase the conductivity of the solutions up to the point where more water caused formation of a precipitate. Although the antimony plates obtained were fairly adherent, bending and vigorous treatment caused the metal deposit to peel and dust off.

Good deposits of arsenic were obtained upon electrolysis of a solution of arsenic trichloride (60 grams of AsCl_3 per 100 cc. of glacial acetic acid) at a current density of 0.005–0.006 amperes per square centimeter. The use of higher temperatures did not cause the formation of burnt plates as in the case of antimony.

CONCLUSION

It is a rather striking fact that the subject of electrodeposition from non-aqueous solvents has not been given more prominence until comparatively recent times. The experimental work which has been noted in the literature would warrant, it seems, a more extended investigation. There is no doubt that the publications of Franklin and Kraus dealing with liquid ammonia, those of Walden dealing with such solvents as liquid sulfur dioxide, acetonitrile, etc., those of Maass concerning hydrogen peroxide, those of Davidson, Conant and Hall concerning acetic acid, and many others also have opened up a prolific field of experimental endeavor and have spurred investigations in all phases of non-aqueous solvent chemistry.

Many factors must be considered in undertaking investigations which deal with the electrodeposition of metals from non-aqueous solvents. Unfortunately, no satisfactory criteria are at hand to enable the ready choice of solute and solvent for the discharge of any one particular ion. However, it is to be hoped that some generalization may still be applied to the isolated and fragmentary information at our disposal, so that we may be able to predict what solvent and solute to employ to bring about discharge of any element in the periodic table. The possible realization of such an aim should be sufficient incentive for a more thorough and extended study of electrodeposition from non-aqueous solvents.

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