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Chemistry - Separation Processes
for Plutonium and Uranium
AEC Research and Development Report

A SURVEY OF ORGANIC SOLVENTS FOR THE ELECTRODEPOSITION OF PLUTONIUM

by

J. A. Porter
Separations Chemistry Division

July 1959

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina

Printed in USA. Price $0.50
Available from the Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

254869✓

DP - 389

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(TID-4500, 15th Ed.)

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John A. Porter

Work done by R. F. Sessions*

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E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed for
The United States Atomic Energy Commission
Contract AT(07-2)-1

Approved by
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ABSTRACT

The solubility and conductivity of cerium(III) salts (as stand-ins for plutonium(III) salts) in dimethylsulfoxide, acetonitrile, ethylenediamine, and dimethylformamide were investigated to evaluate these systems as possible electroplating baths. The system dimethylsulfoxide - cerium chloride is the most promising for electrodeposition of cerium at a mercury cathode.

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A SURVEY OF ORGANIC SOLVENTS FOR THE ELECTRODEPOSITION OF PLUTONIUM

INTRODUCTION

There is interest in the development of an electrolytic method for the production of pure plutonium metal. The electrodeposition of plutonium at a mercury cathode from an ethanol solution of plutonium trichloride was reported by White(1) and by Porter, et al.(2) In both instances very low current efficiencies were obtained and only trace amounts of plutonium were deposited as the amalgam. Alternate solvents that were investigated were less satisfactory than ethanol; however, the survey was limited in scope and it is reasonable to expect that a more suitable solvent can be found.

In the present investigation, additional nonaqueous solvents were evaluated as solvents for the electrodeposition of plutonium.

SUMMARY

The solubility and conductivity of cerium(III) salts in the nonaqueous solvents, dimethylsulfoxide, acetonitrile, ethylenediamine, and dimethylformamide were investigated in an attempt to find a promising electroplating bath for plutonium. Cerium was used as a stand-in for plutonium in these studies.

The dimethylsulfoxide - cerium chloride system was the most promising of those investigated. The solubility of cerium chloride in dimethylsulfoxide was 17.5 g/l (0.0713M). The saturated solution had a specific conductance of 2.90 x 10^{-3} mhos (equivalent conductance 13.55 mhos). The dimethylsulfoxide - cerium bromide system was less promising because of the lower solubility of the bromide. Both the solubility and the conductivity of cerium fluoride in dimethylsulfoxide were very low.

Cerium chloride was only slightly soluble in acetonitrile, ethylenediamine, and dimethylformamide, and the solutions had low conductivities. Therefore, these systems were not judged to be promising as plating baths.

Small additions of water to the solvents increased both the solubility of the cerium salts and the conductivity of the resulting solutions. However, the quantity of water necessary to cause large increases in solubility is probably greater than can be tolerated in the electrodeposition of a highly positive metal.

DISCUSSION

BACKGROUND

The electrodeposition of highly positive metals from aqueous solution is usually precluded by the preferential discharge of hydrogen and the reactivity of the metals. However, these difficulties are sometimes overcome by the use of mercury cathodes and/or nonaqueous baths. Nonaqueous baths include fused salts, fused organic compounds, and organic solvents; use of the last is sometimes preferred because of operational convenience.

A prime factor determining the success or failure of any attempted electrodeposition is the nature of the plating bath. Often, the most satisfactory bath is found by chance. However, there are several rules which may be formulated on the basis of previous experience to aid in selecting a plating bath: (1) the material to be electrodeposited must be in solution in a reducible, ionic form and should be present in significant concentration; (2) the solvent must be relatively stable under electrolysis and must not react with the material deposited; (3) solvents of low viscosity are to be preferred, since they permit high ionic diffusion rates.

Numerous electrodepositions of positive metals from organic solvent baths are reported in the literature. Of particular interest are depositions of rare earth metals, since certain of the rare earths resemble plutonium closely in chemical properties. Several investigators(3-6) have described the use of ethanol baths for the electrodeposition of lanthanum, cerium, neodymium, samarium, and yttrium at a mercury cathode. Amalgams with rare earth metal content as high as 3% have been prepared with a maximum current efficiency of about 12%.

Putnam and Kobe(7) studied the properties of anhydrous ethylenediamine and concluded that it is an ionizing solvent comparable to liquid ammonia. They found that ethylenediamine is more inert than liquid ammonia toward certain highly positive metals and should be a suitable medium for performing reductions requiring high negative electrode potentials.

Moeller and co-workers(8-10) reported that they also favor ethylenediamine as an ionizing solvent. These investigators studied the solubility and conductivity of various rare earth metal salts in anhydrous ethylenediamine and also anhydrous monoethanolamine. They obtained metallic deposits of yttrium, lanthanum, and neodymium on platinum cathodes from ethylenediamine baths, but no deposits were obtained from monoethanolamine. Thorium, unlike the rare earths, was not deposited from ethylenediamine baths. It was observed that "traces" (0.3 - 0.5% by weight) of water in the plating baths facilitated the electrodeposition of the rare earths, but larger amounts caused hydrous oxide formation.

Considering the previous experience in the electrodeposition of highly positive metals, it would seem that plating baths for such metals should consist of an ionic solute dissolved in a highly basic nonaqueous solvent which has a high dielectric constant and low viscosity. Brenner and co-workers(11-15), however, are not in complete accord with this conclusion. They have emphasized the fact that metals are not necessarily deposited from a solvent even though the solvent forms a conductive bath with the solute. These investigators studied the electrodeposition of aluminum, beryllium, magnesium, titanium, and zirconium and made a general survey to determine the most suitable types of plating baths. They found that, for these metals, the best solutes were halides, hydrides, boro-hydrides, and organo-metallic compounds of low molecular weight. Mixed halide-hydride solutes were found to be the most satisfactory. It was concluded that the best solvents are those that form a loose coordination compound with the metallic ion. With the above solutes, ethyl ether, which has a very low dielectric constant, was found to be the best solvent.

There are other instances(16) in which Grignard-, hydride-, or pyridinium-type baths have been employed with success for specific metals or families of metals. However, there seem to be few generalizations to be formulated about the behavior of such systems.

Hughes and Hartley(17) studied the effect of small concentrations of water upon the conductivity of electrolytes in nonaqueous solvents. They observed that small amounts of water slightly decreased the conductivity of strong electrolytes and greatly increased the conductivity of weak electrolytes. They concluded that a small amount of water (0.5% or less) probably does not alter significantly any physical property of a nonaqueous solvent except viscosity.

MATERIALS AND EQUIPMENT

The solvents used in this investigation were the best available commercial products and were used without further purification or dehydration. The physical properties of the solvents are summarized in Table I where the corresponding properties of water are included for comparison.

TABLE I

Physical Constants of Selected Solvents

Solvent	M.P., °C	B.P., °C	ΔH_V T(B.P.)	Specific Gravity	Dielectric Constant	Viscosity, cps
Dimethylsulfoxide	18.45	189	29.6	$1.100 \frac{20^\circ}{20^\circ}$	45.0	1.1^{27°
Acetonitrile	-41.0	81.6	20.2	$0.783 \frac{20^\circ}{4^\circ}$	38.8^{20°	0.345^{25°
Ethylenediamine	8.5	117.2	28.8	$0.8994 \frac{20^\circ}{4^\circ}$	16.0^{18°	1.54^{25°
Dimethylformamide	-61	153		$0.9445 \frac{25^\circ}{4^\circ}$		0.802^{25°
Water	0	100	26.1	$0.998 \frac{20^\circ}{4^\circ}$	80^{20°	1.005^{20°

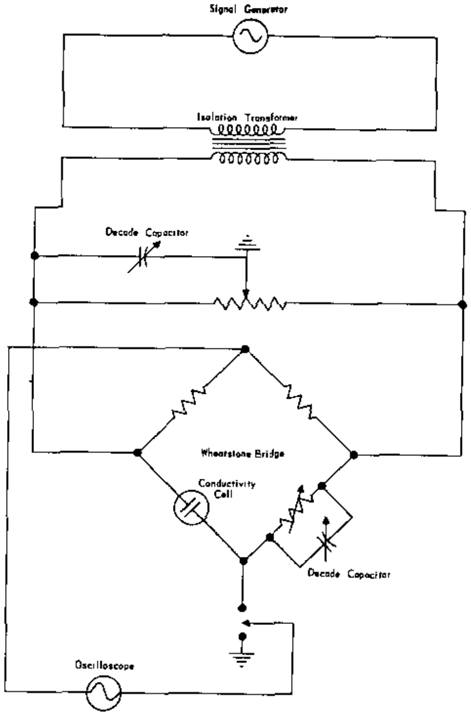

FIGURE 1 - CONDUCTIVITY BRIDGE

Anhydrous cerium chloride and cerium bromide were prepared by the methods previously described(2). Anhydrous cerium fluoride was prepared by precipitation from aqueous solution and vacuum drying. These salts were not completely anhydrous, but the water content was low (0.5 - 3.0%).

Conductivity measurements were made with conventional instruments. A Waveforms 510-B signal generator, the Wheatstone bridge portion of a General Radio Company impedance bridge, a DuMont 304A oscilloscope null indicator, and supporting equipment as shown in Figure 1 allowed reasonably precise measurements.

A dipping-type conductivity cell with heavily platinized platinum electrodes and a cell constant of 0.100 was employed. The cell was held at 25° ±2°C in an atmosphere of dry purified nitrogen in a plastic gloved box.

EXPERIMENTAL PROCEDURES

SOLUBILITY MEASUREMENTS

Saturated solutions of the cerium salts in the solvents were prepared by agitating an excess of salt with solvent for a period of several days. A tightly stoppered glass cell held at 25° ±2°C and equipped with a magnetic stirrer was used for this purpose. The equilibrations were performed in the dry box.

In some instances, the resulting saturated solutions contained suspended matter which could not be removed by filtration. However, clear supernatants could be decanted after several days. The cerium content of these solutions was determined spectrophotometrically after oxidation to cerium(IV). Water content was determined by the Karl Fischer method.

CONDUCTIVITY MEASUREMENTS

After a solvent was saturated with cerium salt, the solution was transferred to the conductivity cell and the conductivity was measured. The solution was then removed from the cell and diluted with pure solvent to give cerium concentrations 1/2, 1/20, 1/200, and 1/2000 that of the saturated solution. The conductivity of each solution was measured at frequencies of 1,000, 2,000, 4,000, and 10,000 cps to allow corrections for polarization errors. It was often necessary to wait for several hours before constant values for the conductivity were obtained. This effect was due to the adsorption of the cerium salt on the heavily platinized electrodes. Therefore, to obtain the exact concentration of cerium, each solution was analyzed for cerium and water after the solution was removed from the cell.

EXPERIMENTAL RESULTS

DIMETHYLSULFOXIDE

The solubility of anhydrous cerium chloride in dimethylsulfoxide that contained about 0.7% water was 17.5 g/l (0.0713M). The saturated solution had a specific conductance, of 2.90×10^{-3} mhos (equivalent conductance, 13.55 mhos). These data and conductivity data for less concentrated solutions are presented in Table II.

TABLE II

Solubility and Conductivity of Cerium Chloride in Dimethylsulfoxide

Solution	Cerium Concentration, M	Water Content, Weight %	Specific Conductance, mhos cm^{-1}	Equivalent Conductance *, mhos cm^2 eq^{-1}
Dimethylsulfoxide	-	0.73	4.02×10^{-6}	
Saturated Ce Cl_3	7.13×10^{-2}	0.76	2.90×10^{-3}	13.53
1:2 Dilution	3.14×10^{-2}	0.86	1.77×10^{-3}	18.78
1:20 Dilution	4.60×10^{-3}	0.85	3.64×10^{-4}	25.79
1:200 Dilution	9.99×10^{-4}	0.86	9.42×10^{-5}	29.43
1:2000 Dilution	3.07×10^{-4}	0.92	3.27×10^{-5}	31.14
		1.6% Water Added		
Dimethylsulfoxide	-	2.33	2.34×10^{-6}	
Saturated Ce Cl_3	1.94×10^{-1}	2.32	5.49×10^{-3}	9.43
1:2 Dilution	8.92×10^{-2}	1.94	3.77×10^{-3}	13.57
1:20 Dilution	9.42×10^{-3}	2.38	6.25×10^{-4}	22.05
1:200 Dilution	1.06×10^{-3}	1.98	9.62×10^{-5}	29.53
1:2000 Dilution Solution	1.78×10^{-4}	2.25	1.69×10^{-5}	27.34
		10% Water Added		
Dimethysulfoxide		10.73	2.06×10^{-6}	
Saturated Ce Cl_3	1.42×10^{-1}	9.06	5.40×10^{-3}	12.61
1:2 Dilution	7.32×10^{-2}	8.90	3.45×10^{-3}	15.71
1:20 Dilution	7.46×10^{-3}	12.30	5.52×10^{-4}	24.58
1:200 Dilution	7.56×10^{-4}	8.69	7.58×10^{-5}	32.50
1:2000 Dilution	1.00×10^{-4}	8.66	1.17×10^{-5}	32.13

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* Corrected for conductivity of solvent

A plot of equivalent conductance versus the square root of the cerium concentration is shown in Figure 2. This curve indicates that cerium chloride behaves as a strong electrolyte in dimethylsulfoxide.

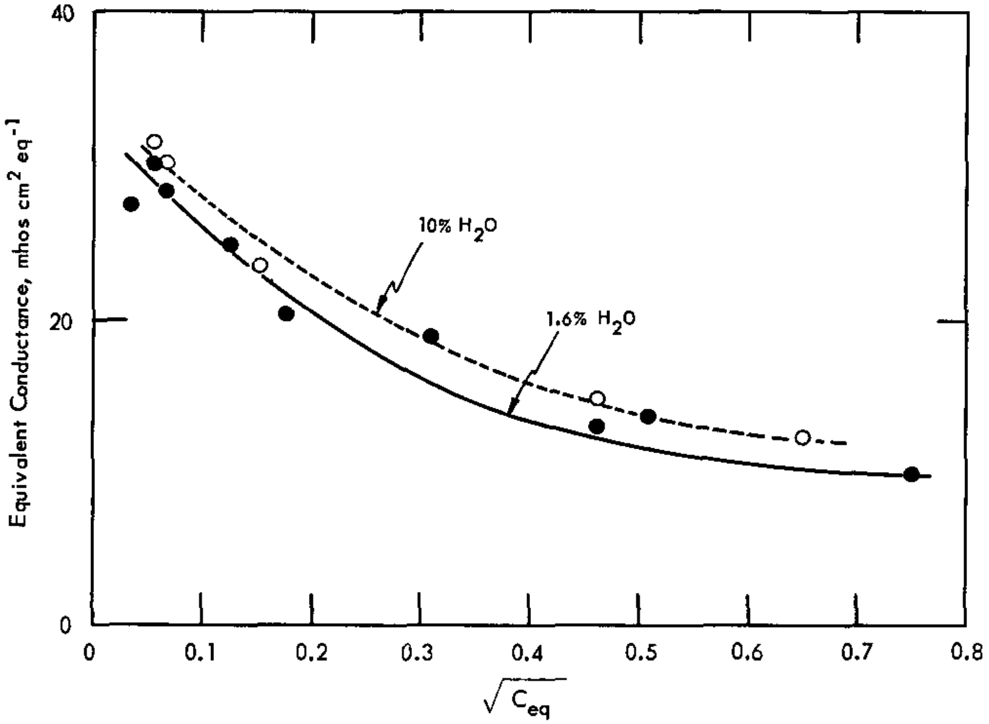

FIGURE 2 - CONDUCTIVITY CURVES FOR CERIUM CHLORIDE IN DIMETHYLSULFOXIDE

The solubility and conductivity of anhydrous cerium chloride in dimethylsulfoxide were increased by a small increase in the concentration of water in the solution. When the concentration of water was increased to 10%, there was a slight decrease in both solubility and conductivity. This effect is shown by the data in Table II.

Anhydrous cerium bromide was less soluble than the chloride in dimethylsulfoxide, while anhydrous cerium fluoride was much less soluble than the chloride. Solubility and conductivity data for these salts are presented in Table III.

TABLE III

Solubility and Conductivity of Cerium Bromide and Cerium Fluoride in Dimethylsulfoxide

Solution	Cerium Concentration, M	Water Content, Weight %	Specific Conductance, mhos cm^{-1}	Equivalent Conductance*, mhos cm^2 eq^{-1}
Dimethylsulfoxide	-	0.73	4.02×10^{-6}	
Saturated Ce Br_3	4.20×10^{-2}	0.81	2.26×10^{-3}	17.92
1:2 Dilution	2.06×10^{-2}	0.66	1.93×10^{-3}	31.17
Saturated Ce F_3	3.57×10^{-3}	0.82	1.26×10^{-5}	0.80
1:2 Dilution	8.71×10^{-4}	0.68	1.00×10^{-5}	2.31

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* Corrected for conductivity of solvent

ACETONITRILE

The solubility and conductivity of anhydrous cerium chloride in acetonitrile (0.12% water) were low. The saturated solution was 1×10^{-3}M in cerium and had a specific conductance of 3.20×10^{-5} mhos (equivalent conductance, 10.67 mhos). Addition of water to the solvent increased the solubility and conductivity only slightly. The solubility and conductivity data are given in Table IV.

TABLE IV

Solubility and Conductivity of Cerium Chloride in Acetonitrile

Solution	Cerium Concentration, M	Water Content, Weight %	Specific Conductance, mhos cm^{-1}	Equivalent Conductance*, mhos cm^2 eq^{-1}
Acetonitrile	-	0.12	1.12×10^{-5}	
Saturated Ce Cl_3	9.99×10^{-4}	0.24	3.20×10^{-5}	6.94
1:2 Dilution	1.20×10^{-4}	0.09	2.52×10^{-5}	38.89
		(0.1% Water Added)		
Acetonitrile		0.16	1.03×10^{-5}	
Saturated Ce Cl_3	1.71×10^{-4}	0.16	3.44×10^{-5}	46.98
1:2 Dilution	1.07×10^{-4}	0.16	2.08×10^{-5}	32.71
		(0.5% Water Added)		
Acetonitrile		0.50	8.57×10^{-6}	
Saturated Ce Cl_3	6.87×10^{-5}	0.50	3.69×10^{-5}	139.13
1:2 Dilution	5.71×10^{-5}	0.51	2.82×10^{-5}	113.54
		(1% Water Added)		
Acetonitrile		1.16	1.11×10^{-5}	
Saturated Ce Cl_3	3.60×10^{-5}	0.96	4.12×10^{-5}	278.70
1:2 Dilution	2.14×10^{-6}	1.02	3.25×10^{-5}	333.30
		(10% Water Added)**		
Acetonitrile		10.1	1.29×10^{-5}	
Saturated Ce Cl_3	7.85×10^{-4}	4.24	2.63×10^{-4}	106.20
1:2 Dilution	1.32×10^{-5}	6.21	1.77×10^{-4}	414.40

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* Corrected for conductivity of solvent.

** These data are for the organic phase of the two-phase system that was formed.

A saturated solution of cerium chloride in 90% acetonitrile - 10% water was not obtained, for some of the water was salted out of the solvent to form a second phase. The data in Table IV are for the organic phase of this system.

ETHYLENEDIAMINE

Ethylenediamine containing about 4% water was a poor solvent for anhydrous cerium chloride. The saturated solution was less than 10^{-5}M in cerium and had a specific conductance of 4.26×10^{-3} mhos. The saturated solution was not stable since a precipitate formed after the solution stood for several hours. Data for this solvent are presented in Table V.

DIMETHYLFORMAMIDE

The experimental data obtained for dimethylformamide containing about 0.15% water show that it is a poor solvent for anhydrous cerium chloride. The saturated solution was less than 10^{-5}M in cerium and had a specific conductance of 1.43×10^{-4} mhos. As was the case with ethylenediamine, a cerium-containing precipitate formed after the solution was allowed to stand. Table V contains the experimental data for this solvent.

TABLE V

Solubility and Conductivity of Cerium Chloride in Ethylenediamine and Dimethylformamide

Solution	Cerium Concentration, M	Water Content, Weight %	Specific Conductance mhos cm^{-1}
Ethylenediamine		~ 4	not determined
Saturated Ce Cl_3	$<10^{-5}$	4.13	4.26×10^{-3}
Dimethylformamide		0.15	
Saturated Ce Cl_3	<10.5	0.14	1.43×10^{-4}

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