INVESTIGATIONS IN NON-AQUEOUS SOLVENTS

Part II. Solubility and Conductances of Some Rare Earth Metal and Thorium Acetates in Ethylenediamine

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ABSTRACT

In investigations preliminary to the study of the electrolysis of certain rare earth metal and thorium salts in anhydrous basic solvents, it was found that anhydrous acetates of La³⁺, Ce³⁺ and Th⁴⁺ are moderately soluble in anhydrous ethylenediamine. The resulting solutions show the conductance behaviour of weak electrolytes. Cerium (III) acetate solution in ethylenediamine undergoes oxidation in air to cerium (IV).

INTRODUCTION

The electrodeposition of the rare earth metals and thorium is usually accomplished by the use of their molten halide mixtures; but the possibilities of lower temperature depositions from electrolytic solutions are interesting from the theoretical and practical aspects. Inasmuch as the highly electropositive nature of these metals preclude their electrodeposition from aqueous solutions of its salts owing to the preferential hydrogen discharge, such procedures must of necessity involve basic non-aqueous solvents. Such solvents, because of their strong donor characters, provide media in which solvated electrons can readily exist and in which lower oxidation states are strongly stabilised. The stabilities of alkali and alkaline earth metals in liquid ammonia are well known. The formation of solvolysis products of limited solubility with anhydrous rare earth metal and thorium compounds preclude the use of liquid ammonia. The favourable electrolytic properties of anhydrous ethylenediamine,² the success which has been achieved in the electrodeposition of certain alkali³ and rare earth metals from this medium⁴⁻⁶ and the failure to electrodeposit thorium from thorium (IV) chloride in this solvent¹ prompted investigation of electrolytic behaviour of anhydrous acetates of some rare earth metals and thorium in anhydrous ethylenediamine. The present investigation reports data on solubilities and conductances of acetates of lanthanum (III), cerium (III) and thorium (IV) in anhydrous ethylenediamine. In a
subsequent communication, results of electrolysis experiments will be described.

**EXPERIMENTAL**

1. *Purification of solvent.*—Commercial ethylenediamine monohydrate (B.D.H.) was dehydrated and purified as previously outlined. The anhydrous product had a specific conductance of $1.35 \times 10^{-6}$ mho cm$^{-1}$ at 30°C. It was stored in glass-stoppered flasks sealed with Dow-Corning silicone high vacuum grease which has been found to have very little effect on electrical conductance in this solvent. These flasks were kept in desiccators containing soda lime, magnesium perchlorate and phosphorus (V) oxide and were opened only in a dry box since ethylenediamine absorbs both moisture and carbon dioxide from the atmosphere.

2. *Preparation of metal acetates.*—The usual method of obtaining anhydrous metal acetates was by the high temperature reaction of the respective oxides with excess quantities of ammonium acetate, followed by the removal of the unreacted ammonium salt by heating first in a current of dry nitrogen and then in vacuo. Anhydrous acetates of lanthanum (III), cerium (III) and thorium (IV) were obtained by the reaction of the respective analytically pure nitrates with acetic anhydride. It is found that this method adopted by Panda and Patnaik is easy and results in purer products than that obtained by Moeller and Zimmermann through the above high temperature reaction. The composition of these anhydrous acetates were established by ignition to oxides in tared platinum crucibles over a Meker burner.

3. *Apparatus and manipulation.*—All anhydrous materials were handled in moisture- and carbon dioxide-free air in a “Gloved Box, Berkeley Type,” Model—R1104 supplied by Scientific Service Inc., California. All the solutions were prepared in this dry box and all apparatus containing such solutions was sealed by Dow-Corning silicone high vacuum grease before removal to the atmosphere.

4. *Solubility determinations.*—The respective powdered metal acetate was added in small amounts slowly and with brisk shaking to 20 ml. of anhydrous ethylenediamine in a big test-tube fitted with ground glass stopper until some sizable amount remained undissolved. Portions of this suspension kept in this stoppered test-tube were thermostated for five days at $30 \pm 0.05$° C. with frequent agitation. Then the tubes were centrifuged for twenty minutes and opened inside the dry box. The rare earth and thorium contents of these solutions were determined by precipitating the hydrous hydroxides from measured volumes with excess water and weighing as ignited oxides in a platinum crucible.