Technical Papers

Some Observations on the Electrolyses of Solutions of Rare-Earth Metal Salts in Basic Solvents*

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In an earlier discussion (*1*) of the general problem of electrodepositing the rare-earth metals from nonaqueous solvents, it was pointed out that successful depositions will most probably utilize highly basic solvents. Preliminary measurements using anhydrous ethylenediamine, monoethanolamine, and morpholine indicated that although anhydrous rare-earth metal acetates are comparatively soluble in these mediums, they behave as weak electrolytes. On the other hand, the nitrates, bromides, and iodides, although less soluble, are stronger electrolytes. Since both ethylenediamine and monoethanolamine gave excellent promise as electrolytic solvents for rare-earth metal salts, electrolyses studies in these mediums have been carried out. Anhydrous morpholine was not so investigated because of its poorer electrolytic solvent properties.

Anhydrous yttrium acetate, neodymium bromide, lanthanum nitrate, and impure neodymium iodide, prepared as previously described (*1*), were electrolyzed in anhydrous ethylenediamine and monoethanolamine in a 60-ml cell of the type described by Davidson and Jirik (*2*). Electrodes used were of bright platinum and were separated by a medium porosity glass disk. A potential difference of 110 v was employed, and the cell was maintained by external cooling at room temperature or no more than 25°C above room temperature. Gases generated were allowed to escape through tubes, the ends of which were immersed in paraffin oil. In a few instances, small quantities of water were added to increase conductivities. After each electrolysis, the cathode was immersed in dry, peroxide-free ether to remove the solvent. It was then transferred to a nitrogen-filled dry box, where the deposit was removed mechanically. Rare-earth metal contents were determined by weighing as oxides; reducing powers were measured with standard acidic permanganate solutions; and x-ray diffraction patterns were determined by using samples contained in sealed cellophane tubes.

Electrolyses of ethylenediamine solutions gave cathode deposits with all salts tested, but no deposits were obtained with monoethanolamine solutions. Because of reduced solubilities and conductivities, no deposit weighing more than 30 mg was obtained. Such deposits were shown by analysis to contain the respective rare-earth metals. All deposits possessed metallic characteristics and were smooth, the lanthanum and yttrium materials being silvery gray to black in color and the neodymium materials golden yellow. Comparable colors have been reported previously for the free metals (*3*). All deposits oxidized in air or in contact with water and evolved hydrogen from hydrochloric acid solution. Each was strongly reducing toward the permanganate ion. These are all properties of the free rare-earth metals. Results of typical electrolyses are summarized in Table 1.

The small quantities of cathode deposits available for study and their marked chemical reactivities precluded highly accurate analytic evaluations. Gravimetric data indicated average rare-earth metal contents of about 50 percent. Permanganate titrations showed the presence of reducing agents of relatively small equivalent weights—materials that might have been free metals, hydrides, or unipositive compounds. Since the deposits showed none of the properties of hydrides—for example, spontaneous flammability—and unipositive derivatives of these metals have not been described, the presence of free metals is logical. The reducing abilities of the various neodymium deposits averaged to 51 percent free metal—a figure remarkably close to that obtained by direct analysis. Microanalyses of cathode deposits showed the presence of substantial quantities of carbon, hydrogen, and nitrogen but in no consistent or logical atom ratios. It appears, therefore, that the free metals were deposited together with trapped or adsorbed organic materials. This is not uncommon when metals are deposited from organic mediums (*4*). Some reactions

Table 1. Data for typical electrolyses in ethylenediamine.

Solution	Current density (ma cm^{-2})	Time (hr)	Comment on deposit
0.185*N* $Y(C_2H_3O_2)_3$ + 6 drops H_2O in 60 ml	0.20	46	White, dendritic, forming after 18 hr
Saturated $Y(C_2H_3O_2)_3$	1.6 –0.32	96	Iron-gray, smooth, metallic
Saturated $Y(C_2H_3O_2)_3$	1.6 –0.32	48	Iron-gray, metallic
Saturated $Y(C_2H_3O_2)_3$ + 1 drop H_2O in 60 ml	0.29–0.04	96	Hard, smooth, crystalline, metallic, adhering strongly to platinum cathode
Saturated $NdBr_3$	5.4 –1.95	16	Golden yellow, lustrous, adherent
Saturated $NdBr_3$	1.95–0.36	72	Golden yellow, lustrous, metallic
Saturated $NdBr_3$	2.2 –0.075	48	Golden yellow, metallic plate
Saturated $La(NO_3)_3$	4.9 –0.33	18	Smooth, black, with some white incrustation near surface of solution

with oxygen, moisture, and carbon dioxide undoubtedly occurred during handling.

Cathodic evolution of hydrogen in small quantities decreased current efficiencies but did not preclude deposition of the metals. In ethylenediamine, hydrogen reduction is generally insignificant. Simultaneous hydrogen and metal deposition have been noted in many cases—for example from chromium and iron salts in liquid ammonia (*5*) and from rare-earth salts in absolute ethanol (*6*). Addition of up to 4 drops of water per 60 ml of solution facilitated formation of black, lustrous deposits from yttrium acetate solutions, but larger quantities gave hydrous yttrium oxide. The accelerating effects of water have been noted in other systems. Thus, copper is plated from moist copper (II) nitrate solutions in liquid ammonia but not from anhydrous solutions, presumably because of greater ease of reduction of the $[Cu(H_2O)_x]^{++}$ ion (*7*). Also, poor deposits of zinc are obtained from anhydrous acetamide solutions, but bright plates result in the presence of traces of moisture (*8*). Perhaps water converts $[Y(en)_x]^{+3}$ species to more readily reducible $[Y(H_2O)_y]^{+3}$ species.

X-ray diffraction established the fact that the deposits were not rare-earth metal compounds. Very high "d" spacings in the lattices of the yttrium deposits were noted. The neodymium deposits appeared to be on the borderline between crystallinity and the amorphous state, and the lanthanum deposits were amorphous. Initial deposition in amphorous forms have been reported in other cases (*9*).

References and Notes

* Paper LXIV in a series on the rare-earth elements.

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Energy Transfer in Irradiated Solutions of Mixed Phosphors

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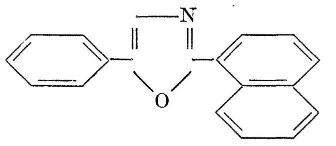
The field of scintillation counting for the determination of radioactivity is rapidly expanding. One of its most interesting developments has been the replacement of organic and inorganic crystals by solutions of selected organic phosphors. The high efficiencies obtained by Hayes (*1–3*) and his coworkers and by Arnold (*4*) in counting radiations from tritium and C^{14} with a toluene solution of diphenyloxazole (DPO) and alphanaphthylphenyloxazole (ANPO) indicate that mixtures of solutes are more efficient than single solutes. Mixtures of p-terphenyl

and ANPO



have been found to be highly efficient.

In the afore-mentioned studies, solutions containing 3 to 4 g of a primary phosphor such as p-terphenyl and about 0.05 g of a secondary phospher such as ANPO in 1 lit of toluene or xylene were used. The addition of this small amount of ANPO markedly increased the efficiency of the scintillation counter. This enhancement has been ascribed to an energy transfer from the primary to the secondary phosphor. Kallmann and Furst (*5*) proposed such a transfer. Bowen and his coworkers (*6*) have reported that at concentrations in the afore-stated range the shift of energy from the primary phosphor to the secondary phosphor is almost complete and the emission of light from the primary is almost completely eliminated.

Several explanations of the course of this energy transfer have been suggested (*5–8*). They generally are based on a process of successive energy transfer from a radioactive source to a solvent, to a primary phosphor, to a secondary phosphor, and to emitted light that is directed onto the photocathode of a photomultiplier tube. It seemed that an understanding of the energy-transfer process might be facilitated by a more straightforward experimental procedure.

Harrison (*9*) has reported that fluorescence under ultraviolet excitation and scintillation under radioactive excitation are identical phenomena. Therefore it was decided to investigate these energy transfers by normal ultraviolet spectrographic procedures (*10*). Accordingly a cylindrical quartz cell 2 cm in diameter was supported so that its flat end faced the slit of a Hilger quartz spectrograph. A UA-2 mercury lamp was placed so that light from it was incident at 45° on this flat surface. The rest of the cell was effectively shielded. By this means light that fails to penetrate the cell is reflected away from the slit of the spectrograph. Only a small amount of direct light from the mercury lamp enters the spectrograph. This light causes the narrow pips on the tracing in Fig. 1. These are characteristic lines of the mercury spectrum and serve as reference points.

The fluorescence spectra were recorded on Type 103-0 Kodak Spectrographic plates. Examination of the spectral images with a recording densitometer produced tracings, three of which are reproduced in Fig. 1. The number of grid spaces under a tracing appears to be an approximate factor for the comparison of the