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KINETIC STUDIES ON EXTRACTION OF EUROPIUM BY LITHIUM AMALGAM
AND COMPARISON TO REMOVAL BY ELECTROLYSIS*

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ABSTRACT

Extraction of Eu by saturated lithium amalgam from aqueous lithium citrate electrolytes containing a preponderance of Gd proceeds linearly with time after an initial much more rapid extraction of a fraction of the Eu present in the electrolyte. When ammonium ion is substituted for lithium ion in the electrolyte, the initial rapid extraction of Eu is reduced by a factor of two to three, but subsequent steady-state extraction is virtually nil. The amount of Eu in the initial faster reaction depends on the method of contacting the phases. About twice as much Eu is extracted when the amalgam is dumped into the electrolyte compared to the reverse procedure of adding the electrolyte to the amalgam.

Removal of Eu by electrolysis from aqueous lithium citrate electrolytes containing a preponderance of Gd starting with pure mercury (lithium amalgam cathode method) is linear with time at constant current density for short electrolysis times. The rate of removal increases as the current density is increased. No initial very rapid removal of Eu by electrolysis is observed. When ammonium ion is substituted for lithium ion in electrolytes, the removal of Eu by electrolysis is a factor of about 1500 slower than with lithium ion present and ammonium ion absent.

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INTRODUCTION

In a previous paper we expressed the goal of combining thermodynamic and kinetic measurements to help elucidate reaction exchange mechanisms of rare earths on transfer from aqueous electrolytes to amalgam phases (1). In that paper we presented data showing that electrolysis of Pr proceeds linearly with time for fixed electrolysis conditions, and we naively assumed that extraction of rare earths by saturated lithium amalgam would likewise be linear with time. This assumption was in part correct, but later experiments demonstrated that the linearity is modified by a very rapid reaction at the outset on contact of the phases. This paper is concerned mainly with this reaction in relation to the kinetic behavior of Eu on extraction by saturated lithium amalgam, and comparison to the kinetic behavior of Eu on electrolysis with a lithium amalgam cathode.

Other recent work on extraction of Eu with lithium amalgam is that of Bubernak, Lew and Matlack (2).

EXPERIMENTAL

Eu 152-154 tracer, made by neutron irradiation of 99.9+% oxide in the Los Alamos reactor facilities, was used to follow the Eu. Scintillation counting of liquid samples was done with a Baird-Atomic 530 spectrometer.

Electrolyte composition was fixed except for adjustment of pH with LiOH or HCl. $GdCl_3$ was used in a preponderant concentration of 0.1M. The Eu was supplied mainly by the impurity in the 99.9% pure commercial Gd_2O_3 stock, specified to be 0.035%. Eu concentration was estimated to be one micromole per 25 ml of electrolyte. The total lithium citrate or ammonium citrate concentration was 0.7M, and the excess citrate ion concentration was computed by difference to be 0.5M. Lithium citrate was prepared from the carbonate and citric acid. Ammonium citrate was prepared from aqueous ammonia and citric acid.

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Saturated lithium amalgam was prepared by electrolysis of saturated LiOH at a current density of 0.08 amp/cm². One hundred ml of mercury were placed in a cylindrical vessel with a 5mm bore drain cock. An insulated platinum wire contacted the cathode, and carbon anodes were used. Electrolysis of about 200 ml of LiOH electrolyte containing surplus crystals of LiOH · H₂O was allowed to proceed for about an hour when a solid phase started to appear. The saturated amalgam was drained, sometimes through cotton gauze, and stored under mineral oil until used. Composition of the amalgam at the laboratory temperature of 22 ± 0.2 C was determined by first reacting the amalgam with a known amount of 1M HCl, then adding excess 0.1M NaOH, then titrating the excess NaOH with standardized 0.1M HCl. Results on six determinations were: 0.0445, 0.0439, 0.0438, 0.0438, 0.0443, 0.0434 % Li in mercury. In extraction experiments saturated liquid amalgam was used only after separation from solid amalgam by draining through a stopcock or cotton gauze.

The vessels used for extractions and electrolyses were polyethylene centrifuge tubes with a cross-sectional area of 5.47 cm². An extraction was done by placing 10 ml of amalgam in the vessel, then adding 25 ml electrolyte simultaneously with starting a timer. The reaction was quenched by pouring the contents of the reaction vessel through a layer of chloroform or carbon tetrachloride to separate the phases. (This operation should be done in a hood.) The amalgam was then washed with a large amount of distilled water to insure complete decontamination from adsorbed electrolyte. Eu was stripped from the amalgam with warm HCl then counted in polyethylene and/or glass test tubes (polyethylene is recommended because of probable residual radioactivity in glass). Some extractions also were done by dumping 10 ml of saturated lithium amalgam directly into 25 ml of electrolyte.

An electrolysis was done in much the same manner as an extraction except that 10 ml of purified mercury were used at the outset for the cathode and a 4 mm diameter spectrographic carbon electrode was used as the anode. The anode tip was placed 5 to 10 mm above the cathode surface. Twenty-five ml of electrolyte were used.

RESULTS

In previous work (1) the electrolyte composition was observed to have significant effects on the rate of extraction of rare earths by lithium amalgam. Consequently experiments on the effect of pH on the extraction of Eu were necessary to establish a safe working range for control of the pH parameter. Data for a number of experiments are given in Table I. These data show that the amount of Eu extracted is reasonably constant if the pH of the electrolyte is kept between 5.6 and 7.5 (and the concentration of no other major component is changed). Experiments reported in this paper were done with the pH of electrolytes kept as close as practical at 5.6 to 7.5.

Experiments were designed to measure the mass transport of Eu as a function of time with a number of parameters individually varied, but with the solution composition kept as invariant as practical. Parameters studied were: methods of contacting the phases, effect of substituting ammonium for lithium in the amalgam, effect of electrolysis in removing Eu from the electrolyte with simultaneous lithium amalgam formation or ammonium amalgam formation.

Data on lithium amalgam extractions are plotted in Fig. 1. In Fig. 2 are plotted kinetic data for comparison of extractions and electrolyses.

TABLE I

Effect of pH on Extraction of Eu by Saturated Lithium Amalgam

Twenty-five ml of Electrolyte were added to
10 ml of amalgam for a period of two minutes.

<u>Initial pH</u>	<u>Final pH</u>	<u>Eu Extracted*</u> <u>%</u>
5.60	5.98	12.2
5.70	6.17	11.3
6.65	7.17	11.3
6.98	7.25	12.0
7.50	7.52	10.0

<u>Initial pH</u>	<u>Final pH</u>	<u>Eu Extracted*</u> %
7.80	7.82	8.94
8.58	8.70	5.54
9.40	10.60	4.55
10.28	10.90	4.18
11.30	11.49	4.05

*Each 25 ml of electrolyte initially contained one micromole of Eu including tracer and carrier.

INTERPRETATION OF RESULTS

Two distinctly different reactions are shown by the data in Fig. 1. The extrapolated intercepts on the ordinate represent the faster reaction and the slower reaction is represented by the straight line. The shortest time which the phases were in contact (limited by the manual manipulations) was about 3 seconds. This period represents the upper limit of time required to remove about 5% of the Eu on adding the lithium citrate electrolyte to the amalgam. The time required to remove an additional 5% of Eu, as computed from the slope of the straight line was 90 seconds. Thus the initial extraction is at least 30 times faster than the steady-state extraction.

The method of contacting the phases has a significant effect on the amount of Eu extracted in the initial reaction. When the amalgam is dumped into the electrolyte the amount of Eu extracted is about twice as much as when the electrolyte is added to the amalgam. Apparently a larger surface exposure is provided when the amalgam falls through the electrolyte.

When ammonium is substituted for lithium in the electrolyte the amount of Eu extracted initially is 2 to 3 times less, but the steady-state extraction is almost nil. Evidently ammonium is preferentially extracted to Eu. In experiments with ammonium present in the electrolyte the amount of ammonium extracted was sufficient to cause frothing of the amalgam after one or two minutes contact time.

The effect of current density on removal of Eu by electrolysis is shown in Fig. 2. The rate of removal compared to extraction by lithium amalgam with duplicate geometry is also shown. For short electrolysis times the higher current density electrolysis data are linear and extrapolate through the origin. For longer electrolysis times at high current densities there is departure from linearity, which is attributed to depletion of Eu in the electrolyte. These data could be better represented by a first order rate plot in which the rate is proportional to Eu electrolyte concentration rather than by the simple plot which is provided to show the linearity and of the lithium amalgam extraction data.

The effect of ammonium in the electrolyte on electrolysis of Eu is shown markedly by two experiments which were done. In one experiment the amount of Eu electrolyzed in 2 minutes at a current density of 0.02 amp/cm² was 0.00006 micromoles, and in 2 minutes at 0.05 amp/cm² the amount electrolyzed was 0.00014 micromoles, representing an amount about 1500 less than when lithium ion is present in the electrolyte and ammonium ion is absent. This effect can be attributed to preferential electrolysis of ammonium compared to Eu. An ammonium amalgam cathode obviously is not much good for removal of Eu.

Our results indicate that the very rapid extraction of Eu at the outset of the contact of the phases is due to the presence of lithium in the amalgam initially, and the steady-state extraction of Eu by lithium amalgam probably is rate limited by replenishment of lithium from the interior of the amalgam rather than by replenishment of Eu from the bulk of the electrolyte. The latter conclusion is substantiated by the departure from linearity of the electrolysis data for long electrolysis times as high current density compared to amalgam extraction data which are linear with time.

REFERENCES

- (1) Proceedings of the Fourth Rare Earth Research Conference, Phoenix, Arizona, April, 1964; LeRoy Eyring, Editor, Gordon and Breach

Science Publishers, Inc., New York, in press.

- (2) Joseph Bubernak, Marion S. Lew and George M. Matlock, paper submitted to Anal. Chem.

- Lithium citrate electrolyte, pH range 5.60 - 6.12, electrolyte was added to amalgam.
- △ Same as ○, except pH range was 6.65 - 7.30.
- ▲ Same as △, except amalgam was dumped into electrolyte.
- Ammonium citrate electrolyte, pH range 7.30 - 7.70, electrolyte was added to amalgam.
- Ammonium citrate electrolyte, pH range 7.12 - 7.57, amalgam was dumped into electrolyte.

Fig. 1. Comparison of extractions with Li^+ or NH_4^+ in electrolyte, and comparison of differences in the method of contacting the phases. One micromole of Eu was initially present in the electrolyte.

- △ Extraction with 25 ml of electrolyte added to 10 ml of lithium amalgam, pH range 6.65 - 7.30.
- Electrolysis with 25 ml of lithium citrate electrolyte and 10 ml of mercury, pH range 6.88 - 7.48, 0.10 amp/cm².
- Same as ■, except current density 0.05 amp/cm².
- ◼ Same as ■, except current density 0.02 amp/cm².
- ▲ Same as ■, except current density 0.005 amp/cm².

Fig. 2. Comparison of extraction of Eu by lithium amalgam to removal by electrolysis. One micromole of Eu was initially present in the electrolyte.