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**ELECTROLYSIS AND EXTRACTION OF SOME LANTHANONS FROM AQUEOUS ELECTROLYTES
WITH LITHIUM AMALGAM***

By

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ABSTRACT

Phase transfer of Pr by electrolysis at a lithium amalgam cathode was found to be linear with time for fixed electrolysis conditions. The rate of electrolysis of Pr decreased with increasing lithium citrate concentration. Extraction of Pm from Pm-Gd mixtures with saturated lithium amalgam was found to vary with virtually any change in electrolyte composition. The Pm extraction was first order with respect to Pm concentration, but the extraction rate decreased with increasing excess citrate concentration. The presence of Gd did not affect the extraction of Pm very much at Gd concentrations less than 0.1M, but at higher concentrations of Gd the amount of Pm extracted was diminished. The results indicate that the exchange reactions are very fast and it may be possible to interpret rate data in terms of equilibria in the electrolyte phase.

INTRODUCTION

When steady-state transfer of a lanthanon takes place across the boundary of an electrolyte phase to a juxta-positioned liquid metal phase, supposedly all of the non-metallic species and solvent associated with the lanthanon ion are stripped from the lanthanon prior to entry into the metallic phase. If all exchange reactions in the electrolyte are sufficiently rapid, and if the lanthanon is electrolyzed or extracted sufficiently slowly, then the electrolyte composition should not vary enough even at the electrolyte-liquid metal phase boundary, to cause a significant change in the rate of electrolysis or extraction for short periods of time. Thus the condition of chemical equilibrium in the electrolyte can be approached experimentally, and steady-state electrolysis or extraction should have a specific dependence on the chemical potential of the electrolyte as defined by one or more equilibrium constants.

In contrast to homogeneous exchange reactions in the bulk of the electrolyte, the reactions to be considered here must be defined in terms of heterogeneity, since the stripping reactions and charge transfer reactions to produce metallic lanthanons take place very close to the metallic surface. The mathematics of the heterogeneous kinetics is expressible simply in two dimensional flow vectors or fluxes, and the functions become linear if the mass transfer is linear with time in all experiments. Interpretation of rate parameters is facilitated by log-log plotting.

Recently the linearity of steady-state electrolysis of Tm in methanol electrolytes was demonstrated (1), but interpretation of the rate data in terms of equilibrium thermodynamics was not possible because of multiple

electrode reactions and irreversible electrosolvolytic effects.

In this study some experiments on Pr electrolysis were done to verify linearity of rate data. Pm was chosen for amalgam extraction experiments because of the ease of following the mass transfer by radiochemical procedures and the ability to work at low concentrations.

Revived interest in amalgam extractions of lanthanons is shown by a series of recent papers by Barrett, Sweacey and Topp (2,3,4) in England. A review of prior work in this field is given in the first paper of this series (2).

EXPERIMENTAL

Details of apparatus, chemicals and procedures used in electrolysis experiments are given in previous papers (5,6,7).

Amalgam extractions of Pm were done with saturated Li amalgam which was prepared by electrolysis of a saturated solution of LiOH at a current density of about .08 amp/cm². Extractions were done on the laboratory bench with the air temperature controlled at 22 ± .2°C. Twenty-five ml of saturated Li amalgam were placed in a tall beaker with a cross sectional area of 14.5 cm². Fifty ml of electrolyte were added and the extraction was allowed to proceed for two minutes without stirring except by the gas generated by reaction of Li with the electrolyte. After quickly separating the phases the amalgam phase was washed with distilled water and the Pm was then extracted with HCl on a steam plate. Pm was determined by scintillation counting as described previously (7). During the extractions the temperature of the electrolyte was observed to increase one to two degrees from heat generated by reaction of the amalgam with the electrolyte.

RESULTS

Data on Pr electrolyses are plotted in Figure 1. For controlled electrolysis conditions the mass transport of Pr to the mercury phase was reasonably linear with time, even with high Joule heating in the electrolysis cell. At the highest current density of 0.06 amp/cm² the electrical power input to the cell was about forty watts.

The effect of excess citrate ion concentration on electrolysis rates is shown in Figure 2. Different symbols are used in the plot to show that some other parameters were not rigorously controlled and thus were not invariant in these experiments. There is considerable scatter of the data, but the mean slope of the plot is definitely negative.

Experiments on extraction of Pm were done with the Pm concentration kept very low; that is, within one or two orders of magnitude of one micromolar. An excess of citrate was used and Gd was added as the second lanthanon.

The dependence of Pm extraction on the concentration of Pm was investigated. Data in Table 1 show that the percentage of Pm extracted is independent of the Pm concentration in the particular concentration range of the experiments.

In Figure 3 are plotted data on the effect of excess citrate concentration on the extraction of Pm from electrolytes containing various concentrations of Pm. These data show the same trend as the data in Figure 2 for electrolysis of Pr, but there is less scatter.

The presence of Gd at concentrations of less than 0.1M does not affect the Pm extraction very much (Figure 4), but at higher concentrations of Gd a definite reciprocal relationship is demonstrated.

INTERPRETATION OF RESULTS

Scatter of the data in Figure 2 cannot be attributed to chronological changes in electrolysis conditions or lack of temperature control during any

one experiment, since the plots in Figure 1 are reasonably linear. The most likely reason for the variation in rates is a variation in the electrolyte composition apart from the excess citrate concentration. The data in Figure 3 are better than those in Figure 2, but still are not precise enough to define the slopes properly. Two or more types of behavior may be shown by the results in Figure 3. These results indicate the need for data from experiments in which the ionic strength is kept constant.

The negative slopes shown by Figure 2 and Figure 3 are expected since an increase in excess citrate ion concentration should diminish the free lanthanum ion concentrations and thus make the extractions more difficult and less rapid. If one citrate group affects the equilibrium, then the slope should be minus one; if two citrate groups take part, then the slope should be minus two.

Data in Table 1 show that the amount of Pm extracted is simply proportional to that present in the electrolyte. Thus the reaction is first order with respect to Pm concentration.

At high concentrations of Gd the extraction of Pm is diminished by an amount proportional to the increase in Gd concentration. The minus one slope of the lines in Figure 4 is indicative that Gd interferes with the Pm extraction in an inverse first order mode. This effect of Gd is not unexpected since previous results on separation of some juxtalanthanons showed that the separation factors changed as the concentration of one lanthanum of the mixtures was made large (5,6,7).

In Figure 5 are plotted data which depict changes in the extraction of Pm as the average separation of Gd ions in the electrolyte is decreased. We guess that the distance of about 25 Å is significant and that the reactions that immediately precede phase transfer may take place predominantly in an electrolyte layer of this approximate thickness at the amalgam surface.

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Table 1

Extraction of Pm from electrolytes containing
0.1M Gd and 0.1M excess citrate

<u>Approx. Pm conc. -</u> <u>μ-molarity</u>	<u>Pm extracted</u> <u>in 2 min. - %</u>
0.2	1.26
2.0	1.25
4.0	1.22
20	1.32

FIGURE CAPTIONS

- Figure 1 - ELECTROLYSIS OF 0.5M PrCl_3 IN 1.25M TRILITHIUM CITRATE AT $\text{pH } 5.6 \pm 0.2$; TEMP. $25 \pm 2^\circ\text{C}$.
- Figure 2 - ELECTROLYSIS OF Pr AT 0.05 AMP/ CM^2 AND AT $25 \pm 1^\circ\text{C}$. WITH VARIATION IN EXCESS CITRATE CONCENTRATION PLUS VARIATION IN SOME OTHER PARAMETERS. THE LINE IS DRAWN WITH A SLOPE OF MINUS ONE.
- Figure 3 - EXTRACTION OF Pr AS A FUNCTION OF EXCESS CITRATE CONCENTRATION WITH CONTROLLED Gd CONCENTRATION. THE UPPER LINE IS DRAWN WITH A SLOPE OF MINUS TWO AND THE LOWER LINE IS DRAWN WITH A SLOPE OF MINUS ONE.
- Figure 4 - EXTRACTION OF Pr AS A FUNCTION OF Gd CONCENTRATION WITH CONTROLLED EXCESS CITRATE. THE HORIZONTAL LINES ARE DRAWN WITH A SLOPE OF ZERO AND THE SLANTED LINES ARE DRAWN WITH A SLOPE OF MINUS ONE.
- Figure 5 - PLOT OF COMPUTED Gd ION SPACING IN THE ELECTROLYTE VERSUS Pr EXTRACTION RATE CONSTANT.

FIG. 1. ELECTROLYSIS OF 0.5M PrCl₃ IN 1.25M TRILITHIUM CITRATE
AT pH 5.6±0.2; TEMP. 25±2°C.

FIG. 2. ELECTROLYSIS OF Pr AT 0.05 AMP/CM² AND AT 25 ± 1°C. WITH VARIATION IN EXCESS CITRATE CONCENTRATION PLUS VARIATION IN SOME OTHER PARAMETERS. THE LINE IS DRAWN WITH A SLOPE OF MINUS ONE.

FIG. 3 EXTRACTION OF Pm AS A FUNCTION OF EXCESS CITRATE CONCENTRATION WITH CONTROLLED Gd CONCENTRATION. THE UPPER LINE IS DRAWN WITH A SLOPE OF MINUS TWO AND THE LOWER LINE IS DRAWN WITH A SLOPE OF MINUS ONE.

FIG. 4. EXTRACTION OF Pm AS A FUNCTION OF Gd CONCENTRATION WITH CONTROLLED EXCESS CITRATE. THE HORIZONTAL LINES ARE DRAWN WITH A SLOPE OF ZERO AND THE SLANTED LINES ARE DRAWN WITH A SLOPE OF MINUS ONE.

FIG. 5. PLOT OF COMPUTED Gd ION SPACING IN THE ELECTROLYTE
VERSUS Pm EXTRACTION RATE CONSTANT.