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On the Standard Potential of the Europium(II, III) Couple

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The standard emf of the cell $H_2|H^+||Eu^{3+}, Eu^{2+}|(Hg)$ has been determined in the ionic medium 1 M $((CH_3)_4N^+)Cl^-$ at 25°C and found to be -381 ± 1 mV. Europium(II) ions were prepared *in situ* by coulometry, and the unavoidable side reaction $Eu^{2+} + H^+ \rightarrow Eu^{3+} + \frac{1}{2}H_2$ has been taken into account by hydrogen ion concentration measurements. Evidence is given that the emf measured corresponds to the reversible reaction $Eu^{3+} + e^- \rightleftharpoons Eu^{2+}$.

The present work was undertaken with the intention of finding the experimental conditions for the use of the europium(II, III) half-cell in equilibrium analysis. In most reactions the equilibrium constants of Eu^{3+} and of Eu^{2+} differ greatly. Europium(II), which resembles Ba^{2+}, is a much weaker acid and has a much smaller tendency to form complex species with inorganic and organic ligands than europium(III). On the other hand Eu^{2+}, in contrast to Eu^{3+}, forms slightly soluble compounds with SO_4^{2-} and CO_3^{2-}; the solubility product of $Eu(OH)_3$ or EuOOH, however, is by many orders of magnitude lower than that of the $Eu(OH)_2$. Thus the experimental determination of $[Eu^{3+}][Eu^{2+}]^{-1}$ by emf measurements may serve for the calculation of the equilibrium concentration of one sort of europium ions as the concentration of the other can be set equal to its analytical concentration.

Moreover, we have hoped that, besides studying equilibria involving Eu^{3+}, measurement of the potential of the europium(II, III) half-cell might prove to be of value for the investigation of the complex formation equilibria of the lanthanide ions capable of existing only in the oxidation state three; in their presence Eu^{3+} can serve as an indicator ion. In addition experience on this system has been very useful for studies of other redox couples of high reducing power.

As a first step we attempted to determine the standard potential of the europium couple, e_R^0, over a wide range of acidities and europium concentrations. The constancy of e_R^0 may be regarded as the simplest criterion for the proper functioning of the half-cell.

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PREVIOUS WORK

The standard electrode potential of the Eu^{3+}—Eu^{2+} couple has earlier been studied by McCoy [1] and by Shul'gin and Koz'min.[2]

McCoy [1] used at 25°C the cell

$$Pt|Eu(HCO_2)_3,\ Eu(HCO_2)_2,\ HCO_2H,\ 1\ M\ KCl|\ 1\ M\ KCl|1\ M\ KCl|Hg_2Cl_2(s),\ Hg$$

Europium(II) formate solutions were prepared by cathodic reduction. The total europium concentration was maintained at about 0.1 M. The actual $[Eu^{2+}]$ was determined iodometrically in withdrawn samples.

Assuming the potential of the calomel half-cell to be 280.5 mV, McCoy calculated from two series of measurements the values −431.3 and −428.3 mV for $e^0(Eu^{3+}, Eu^{2+}, Pt)$ at 25°C.

Shul'gin and Koz'min [2] used a similar cell, redox electrode (Pt) *versus* calomel electrode. The redox half-cell initially contained "1 N" $EuCl_3$ solution, of pH = 1 (probably 0.1 M HCl), and to this was added a $EuCl_2$ solution containing "1 N" $EuCl_3$. They "recalculated their data to the hydrogen scale" (no details given), and concluded that at 25°C $e^0(Eu^{3+}, Eu^{2+}, Pt) = -428$ mV. They also obtained values for e^0 at temperatures from 23 to 58°C.

Thus, in both cases, the e^0 value was calculated on a "mixed scale" with unknown contributions from activity coefficients and liquid junction potentials.

CHOICE OF THE EXPERIMENTAL CONDITIONS AND METHODS

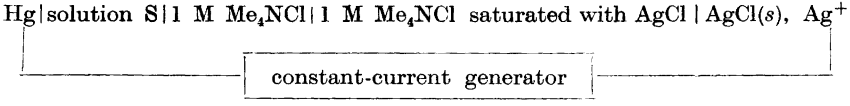
In the present work the europium redox half-cells were studied at 25°C with solutions where the chloride ion concentration was maintained at the 1 M level by the addition of tetramethylammonium chloride (Me_4NCl). This salt was chosen because the alkali metal cations might be reduced and form amalgams at the mercury cathodes which were employed to prepare Eu^{2+}; the Me_4N^+ cation does not seem to be reducible from water solutions.

All the test solutions, which will be denoted in the following discussion by S, were of the initial composition

$$B\ M\ Eu^{3+},\ H_0\ M\ H^+,\ (1-3B-H_0)\ M\ Me_4N^+,\ 1\ M\ Cl^-$$

In each experiment H_0 and B were chosen to have values of a few mM.

Oxygen-free solutions of Eu^{2+} and Eu^{3+} were prepared from S by constant current coulometry. This method is simple, highly accurate and avoids the addition of foreign substances. Electrolysis was performed in the circuit



The reduction was carried out in steps, and after each step of electrolysis the emfs of the cells

	−Hg|solution S|RE+	(R)
and	−glass electrode|solution S|RE+	(G)

were determined. The reference half-cell RE had the composition

$$RE = Ag,AgCl(s) \mid 1\ M\ Me_4NCl \mid \text{saturated with } AgCl \mid 1\ M\ Me_4NCl \mid$$

We shall assume, as it was confirmed by our experiments, that the electrode potential of the Hg electrode is determined solely by the reaction

$$Eu^{3+} + e^- \rightleftharpoons Eu^{2+} \tag{1}$$

With this assumption we can write for the emf of cell (R) at 25°C

$$E_R = E_{R0} - 59.16 \log [Eu^{3+}] + 59.16 \log [Eu^{2+}];\ E_{R0} = E_{ref} - e_R{}^0 = \text{constant} \tag{2}$$

where $e_R{}^0$ represents the standard potential of the redox couple, and E_{ref} the potential of the reference half-cell.

Since the $[Eu^{3+}]$, $[Eu^{2+}]$, and $[H^+](=h)$ never exceeded a few mM's in our experiments the variation of the activity factors of the reacting species and the liquid junction potential could be neglected. The reference state is defined so that the activities of the reacting species approach their concentrations as the composition of the solution tends to 1 M Me_4NCl. By similar arguments the emf of cell (G) can be expressed by the equation

$$E_G = E_{G0} - 59.16 \log h \tag{3}$$

where E_{G0} denotes a constant and h the concentration of hydrogen ions.

In our solutions the reaction

$$Eu^{2+} + H^+ \rightarrow Eu^{3+} + \tfrac{1}{2}H_2 \tag{4}$$

was far from equilibrium, and there was an unavoidable tendency for this reaction to proceed from left to right. Hence, both Eu^{2+} and H_2 will be formed by the coulometric reduction. The number of moles of electrons added per volume unit will then be

$$v/V = [Eu^{2+}] + \Delta h \tag{5}$$

where

$$\Delta h = H_0 - h \tag{6}$$

is the decrease of hydrogen ion concentration due to reaction (4), V is the volume of the test solution and v is the number of faradays passed through it.

Now, h can be determined from E_G, eqn. (3), and since H_0, v and V represent accurately known analytical data, one may calculate the $[Eu^{2+}]$ from eqn. (5). The concentration of Eu(III) is obtained as the difference

$$[Eu^{3+}] = B - [Eu^{2+}] \tag{7}$$

Finally the value of E_{R0} can be found by eqn. (2).

In order to obtain $e_R{}^0$, the standard potential of the redox couple referred to the hydrogen scale, we had to determine the emf of the cell

$$-H_2(Pt) \mid h\ M\ H^+,\ (1-h)\ M\ Me_4N^+,\ 1\ M\ Cl^- \mid RE + \qquad (h \ll 1\ M) \tag{H}$$

In the present work we have chosen 1 M Me_4NCl as the reference state and set the standard potential of the hydrogen half-cell equal to zero in this medium. Hence

$$E_H = E_{ref} - 59.16 \log h + 29.58 \log p(H_2) \quad (8)$$

The E_H measurements were carried out with solutions of $h \sim 1$ mM.

Determination of H_0. For this purpose a coulometric titration was carried out with another portion of solution S. In this case, oxygen was led in, and in the coulometric circuit the Hg cathode was replaced by a Pt cathode. There are several possible reaction paths at the cathode:

1) $Eu^{3+} + e^- \rightarrow Eu^{2+}$ followed by $Eu^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Eu^{3+} + \frac{1}{2}H_2O$ (9)

or, directly

2) $H^+ + e^- + \frac{1}{4}O_2 \rightarrow \frac{1}{2}H_2O$ (10)

3) $H^+ + e^- \rightarrow \frac{1}{2}H_2$ (11)

In any case, for each electron added, one H^+ disappears. The decrease of h with the addition of electrons was followed by measuring the emf of cell (G). The equivalence point was estimated by a Gran [3] diagram.

MATERIALS AND ANALYSES

Europium(III) chloride solutions were prepared from Eu_2O_3 of 99.99 % purity supplied by Typpi Oy, Oulu, Finland. This material was ignited at 900°C for several hours in a porcelain crucible to remove traces of carbonate, and the freshly ignited europium oxide was then dissolved in a slight excess of hot 6 M HCl. This solution was prepared from Merck's hydrochloric acid of *p.a.* quality, which after dilution to 6 M was purified by slow distillation in an all-glass apparatus. No trace of Fe^{3+} could be detected in the middle fraction.

The concentration of europium was determined by titration with a standardized solution of EDTA, using xylenol orange as indicator. The concentration of H^+ was determined by coulometric titration in the presence of oxygen, as described above.

Tetramethylammonium chloride, purum, was supplied by Fluka AG, Switzerland. It was not purified further, and the solutions were made up by weighing the dried substance.

Argon was taken from a cylinder and purified by letting it pass first through a column of activated copper kept at 180°C and then through wash-bottles containing, in order, 10 % NaOH, water, and finally 1 M Me_4NCl. The argon was finally filtered through a glass filter before the inlet to the titration vessel, to avoid dust that might act as a heterogeneous catalyst for the oxidation of Eu^{2+} by H^+. The system for gas purification and saturation was constructed entirely from glass parts. Thus contamination with stopcock grease and other oxidizing agents could be kept at a very low level.

Hydrogen was purified in the same way.

Oxygen was taken from a cylinder and passed through wash-bottles containing 0.1 M $KMnO_4$, water, and 1 M Me_4NCl.

Electrodes. The Ag,AgCl electrodes were prepared according to Brown.[4]

A Jena glass electrode of "Thalamid" type was employed. A separate study by one of us has shown that in the log h range -1 to -6 this type of glass electrode agrees with the hydrogen electrode to within ± 0.01 mV.

For the coulometric circuit, the anode was prepared from a silver foil, which was bent to a cylinder, about 10 mm in diameter and 30 mm long.

The cathode in the coulometric circuit for determining H_0 was a platinum mesh cylinder, about 10 mm in diameter and 30 mm long.

For the reduction of Eu^{3+}, the cathode was a mercury pool, placed in a recess at the bottom of the titration vessel. There was a large recess for the coulometric electrode, and two smaller recesses for the mercury pools which served as the redox electrodes. In each pool the electric contact was made by a Pt needle, sealed through a glass tube

which was dipped into the mercury. Freshly distilled and filtered mercury was used for each experiment. Without these precautions rapid oxidation of Eu^{2+} by H^+ has always been found to occur.

Apparatus and procedures. All emf measurements were carried out in a thermostated room kept at 25.0±0.3°C; the temperature fluctuation of the test solution was probably smaller.

In the redox measurements an eight-necked flask was employed, and the solution was agitated vigorously by a motor-driven glass stirrer.

The cell arrangement was similar to that previously used in this laboratory.[5,6] The reference half-cell, and the salt bridge were placed in a "Wilhelm" apparatus,[5] and a "Wilhelm" bridge formed also the anode compartment of the coulometric circuit. The emf values were measured with a Metrohm compensator (Herisau, Switzerland) of the type E 388. It could be read to within 0.1 mV.

The constant-current generator was a Metrohm coulometer of the type E 211. This apparatus was calibrated by passing the current through a standard resistance of 0.01 % accuracy and measuring the voltage drop with a recently calibrated digital voltmeter.

Before a series of E_R measurements was started, Ar was passed through the solution overnight to remove dissolved oxygen.

The redox emf, E_R, was measured between the reference electrode and each of the three mercury pools, as mentioned. When current was passed, the cathode pool differed at first by many mV's from the two others, but gradually all three attained the same value, usually within ±0.2 mV. This equilibration (which of course indicated that the solution had attained a uniform composition) was often rapid, but in some cases needed more than one hour. As a rule, it was faster in solutions where $[Eu^{3+}]$ was greater than $[Eu^{2+}]$.

There was a slow reaction of Eu^{2+} with H^+ in our solutions which resulted in a creeping of the E_R and E_G values. In dust-free solutions the rate of oxidation of Eu^{2+} by H^+ is governed by the acidity. At log h values below −4, E_R was found to decrease with a rate of about 1 mV/h. At millimolar hydrogen ion concentrations the rate of oxidation became much higher. For instance, in a solution with $B=1.941$ mM, and $H_0=4.745$ mM, E_R changed overnight (14 h) from 666.6 mV ($[Eu^{2+}]=1.528$ mM) to 601.6 mV ($[Eu^{2+}]=0.518$ mM) and E_G from 688.1 mV ($h=3.98$ mM) to 695.6 mV ($h=2.97$ mM).

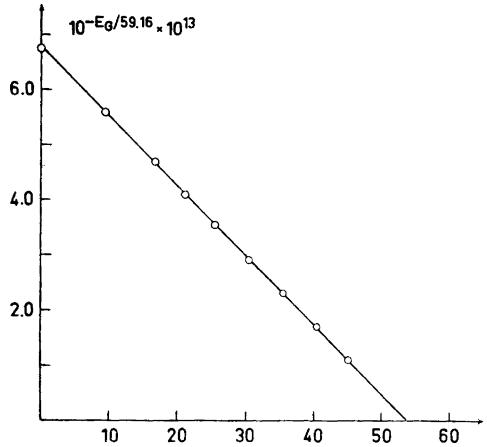


Fig. 1. The determination of H_0; $10^{-E_G/59.16}$ *versus* v. Circles: experimental data. The line represents the equation

$10^{-E_G/59.16} \times 10^{13} = 0.1254(53.9 - v)$.

$H_0 = 1.07_8 \pm 0.004$ mM, $E_{G0} = 721.9 \pm 0.1$ mV. $V = 50.00$ ml.

RESULTS

Titration for H_0. A typical coulometric titration for the hydrogen ion concentration of an europium(III) chloride solution containing Me_4NCl is graphically represented in Fig. 1, where the Gran function $10^{-E_G/59.16}$ is plotted as a function of v. For hydrogen ion concentrations exceeding 1 mM a precision of 0.2 % could easily be attained. The H_0 value was then employed to calculate E_{G0} the actual value of the standard potential of the glass electrode cell, see eqn. (3).

Redox potential measurements. Table 1 gives the data from four coulometric redox titrations; the data are arranged in the order of decreasing $h=[H^+]$. The table shows the measured h (from E_G and E_{G0} using eqn. (3)), the redox emf E_R, $[Eu^{2+}]$ and $[Eu^{3+}]$ calculated by eqns. (5) and (7); the Nernst term 59.16 log $[Eu^{3+}]$—59.16 log $[Eu^{2+}]$, and finally the value of E_{R0} calculated

Table 1. Survey of experimental data.

h mM	E_R mV	$[Eu^{2+}]$ mM	$[Eu^{3+}]$ mM	$59.16 \log \frac{[Eu^{3+}]}{[Eu^{2+}]}$ mV	E_{R0} mV
4.673	597.8	0.484	1.457	28.3	626.1
4.492	619.9	0.869	1.072	5.4	625.3
1.923	591.2	0.773	3.109	35.8	627.0
1.841	586.9	0.691	3.191	39.3	626.2
1.799	583.9	0.631	3.251	42.1	626.0
1.663	576.5	0.513	3.369	48.4	624.9
1.552	596.4	0.961	2.921	28.6	625.0
1.109	601.7	1.114	2.768	23.4	625.1
0.836	607.0	1.288	2.594	18.0	625.0
0.693	603.8	0.601	1.340	20.6	624.4
0.466	612.4	1.477	2.405	12.5	624.9
0.201	609.2	0.687	1.254	15.5	624.7
0.096	623.0	1.852	2.030	2.4	625.4
0.019	607.5	0.641	1.300	18.2	625.7

Probable value $625._4 \pm 1.0$ mV

with eqn. (2). From the data in the last column we may conclude that the E_{R0} values do not show any appreciable systematic trend either with h or with $\log([Eu^{3+}]/[Eu^{2+}])$. This result furnishes evidence for the validity of the assumption that (1) is the potential-determining reaction. Points with $[Eu^{2+}]>[Eu^{3+}]$ were omitted from this table, because in such solutions the concentration differences disappeared rather slowly after the passage of current, and we often did not care to wait sufficiently long.

The emf of cell (H) was measured with solutions of $h=0.776$ mM, this value was established by coulometric titrations. At this low level of hydrogen ion concentration the activity factor of hydrogen ions certainly can be set equal to unity and the liquid junction potential is negligible. To estimate $p(H_2)=P_{atm}-p(H_2O)$ we used the data of Lindenbaum and Boyd.[7] By density measurements a 1 M Me_4NCl solution was found to be 1.124 molal, interpolation from the results of Ref. 7 gave that $p(H_2O)=23.0$ torr.

We have obtained in this way by using eqn. (8)
$E_{ref} = 244.4 \pm 0.1$ mV and hence
$e_R^0 = E_{ref} - E_{R0} = 244.4 - 625.4 = -381.0 \pm 1.0$ mV
at 25°C and in the medium 1 M $(CH_3)_4NCl$.

This value is considerably more positive than those given by the previous investigators.[1,2]

The different ionic media may be partly responsible for this disagreement. McCoy studied 1 M KCl solutions, while Shul'gin and Koz'min made their experiments in $\frac{1}{3}$ M $EuCl_3$ solutions where $[Eu^{2+}][Eu^{3+}]^{-1}$ was kept below 0.01.

Moreover, in McCoy's solutions containing formic acid an appreciable part of the europium(III) may have been present as a formate complex. This assumption appears to be plausible because the tervalent lanthanides have been shown [8] to form a series of complex ions with ligands containing carboxylate groups, *e.g.* with acetic acid.

In addition these previous investigators used a different and not well-defined ("mixed") activity scale. The conclusions in Ref. 2 may have been also seriously influenced by the neglect of the liquid junction potential between $\frac{1}{3}$ M $EuCl_3$ and 1 M KCl solutions.

Finally to employ platinum as the redox electrode is objectionable in this case. According to our experience platinum catalyses reaction (4), and consequently in the vicinity of the electrode the concentrations are uncertain and different from the bulk concentrations. Under such conditions there is also a risk that mixed potentials are measured.

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