

On the Standard Potential of the Eu^{3+} — Eu^{2+} Couple in 1 M LiClO_4 Medium

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On the basis of emf measurements with cells involving mercury redox electrodes the standard potential for $\text{Eu}^{3+} + e^- \rightleftharpoons \text{Eu}^{2+}$ has been determined at 25°C and in the medium 1 M LiClO_4 to have the value of -379 ± 1 mV. The main results are summarized in Table 2.

The coulometric approach employed for the determination of the standard potential has been found to be easily adaptable for equilibrium analysis.

In a previous report¹ of this laboratory a coulometric method was described for the study of redox couples of high reducing power, and the method was applied for the determination of the standard potential of the Eu^{3+} — Eu^{2+} half-cell in the ionic medium 1 M $(\text{CH}_3)_4\text{NCl}$. This solvent salt was chosen because of its inertness in redox reactions including cathodic reduction with a mercury electrode.

To work with tetramethylammonium chloride solutions entails, however, some disadvantages.

We have been unable to develop a practical method for the preparation of substantial amounts of $(\text{CH}_3)_4\text{NCl}$ of sufficiently high purity. As a consequence of the presence of traces of unidentified contaminants the life-time of europium(II) ions proved to be quite short. The rate of oxidation of Eu^{2+} by H^+ was found to be increased with the ratio $[\text{Eu}^{2+}][\text{Eu}^{3+}]^{-1}$ and this reaction hindered the study of tetramethylammonium solutions containing a high portion of europium ions in the oxidation state two. Moreover, the $(\text{CH}_3)_4\text{N}^+$ ion forms slightly soluble compounds with many ligands, and thus our main intention to introduce the Eu^{3+} — Eu^{2+} half-cell into equilibrium analysis may be realized to a limited extent only.

Finally, attention is called to the great need for creating a consistent set of standard potentials. This should replace the present data which have been

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evaluated partly from measurements with dilute solutions and partly on the basis of investigations carried out in various media of high ionic strengths. For many experimental and theoretical reasons lithium perchlorate seems to be particularly well suited to serve as the solvent salt when redox equilibria have to be studied, and to establish a reliable scale of standard potentials one would be inclined to choose a LiClO_4 concentration level, *e.g.* 1 M, as the ionic medium.

With these ideas in mind a series of preliminary coulometric experiments were made to test the reactivity of the Li^+ and ClO_4^- ions in the presence of Eu^{2+} . As we could not detect any evidence for the reduction of ClO_4^- and for the participation of Li^+ in the cathode reaction, we decided to undertake a precise determination of the $\text{Eu}^{3+} - \text{Eu}^{2+}$ standard potential in 1 M LiClO_4 medium. This forms the subject of the present publication.

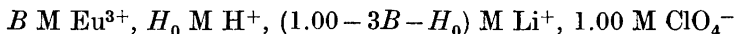
The method of investigation. In this work the europium redox couple was studied by starting with deoxygenated test solutions of precisely determined initial acidity and generating Eu^{2+} ions *in situ* by constant current coulometry. After each step of electrolytic reduction a local excess of Eu^{2+} is built up in the vicinity of the mercury cathode, and a certain period – 10 to 30 min – is needed until the solution attains a uniform $[\text{Eu}^{2+}]$. By placing several mercury redox electrodes into the test solution, and by measuring the emf among them and the cathode the disappearance of concentration differences could be readily followed.

Whatever precautions we have taken, as soon as an appreciable europium(II) concentration was produced a slow but steady decrease in the $[\text{Eu}^{2+}]$ occurred due to the reaction



which was recognized by measuring the potential change of the mercury redox electrodes as well as that of a glass electrode. The simultaneous determination of the instantaneous values of the prevailing hydrogen ion concentration and of the redox potential enabled us in combination with the stoichiometric and the electrolysis data to calculate the standard potential for each pair of emf measurements.

In detail, for each series of measurements a test solution of the initial composition

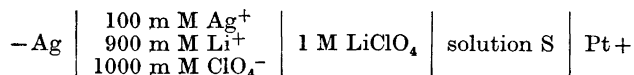


was taken which in the following discussion will be denoted by S_0 , while the solution arising from S_0 by electrolysis and reaction (1) will be represented by S .

B values ranging from 0.5 to 10 mM were studied; in more dilute solutions difficulties were encountered with the redox electrodes, higher europium concentrations would require current strengths not attainable with our equipment.

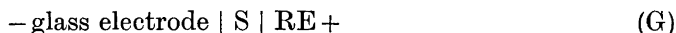
Since all our subsequent conclusions are based on the value of the *initial hydrogen ion concentration*, H_0 , prior to the redox potential measurements a coulometric titration was carried out with S_0 to obtain this master variable as accurately as possible. For this purpose a platinum foil was immersed into

S_0 and it served as the anode in the electrolysis circuit (constant current supply)

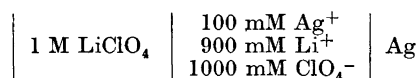


which was employed to generate exact amounts of hydrogen ions in S by the oxidation of water.

After each step of electrolysis the emf of the cell



where RE denotes the reference half-cell



was determined. The emf of cell (G) can be written at 25°C

$$E_G = E_{G,0} - 59.16 \log h \quad (2)$$

In eqn. (2) $E_{G,0}$ represents a constant, which includes the potential of the reference half-cell, and h is the symbol for the hydrogen ion concentration. As the sum of B and h was chosen never to exceed 2 % of the $[\text{ClO}_4^-]$, the activity factor of hydrogen ions [as well as those of the europium(III) and europium(II) ions] could be regarded as constants. The standard state is chosen so that the activity factors of all the reacting species tend to unity as their concentrations in the solvent 1 M LiClO_4 approach zero. Moreover we ascribe the value of zero to the standard potential of the hydrogen half-cell in the solvent 1 M LiClO_4 , thus for the potential of a half-cell consisting of hydrogen of p atmosphere and a 1 M ClO_4^- solution containing h M H^+ and $(1.00 - h)$ M Li^+ with $h \ll 1$ we may write $e = 59.16 \log (hp^{-\frac{1}{2}})$.

On the basis of the corresponding data pairs (E_G, μ_A) where μ_A is employed to represent the number of faradays passed through solution S for acidification, a Gran-type plot was constructed which served for the evaluation of the initial hydrogen ion concentration, H_0 , and of the constant $E_{G,0}$. The H_0 value so obtained differed sometimes as much as 2 % from the value calculated from the hydrogen ion concentrations of the stock solutions.

We first attempted to find H_0 and $E_{G,0}$ by alkalification which would be expected to yield more accurate results and which could be performed in chloride solutions.¹ In the presence of ClO_4^- , however, alkalification resulted inevitably, even at such a low current level as 0.1 mA, in the formation of some europium hydroxide which redissolved but slowly in our slightly acidic solutions.

After having completed the titration for H_0 the platinum foil anode was immersed in a mercury pool, and the polarity of the constant current supply was reversed. Next oxygen was expelled by passing through S nitrogen overnight and then the *main experiment*, the reduction of the europium(III) ions, was started.

In each series of measurements a glass electrode and three mercury pools were employed, one having a great surface served as the cathode and the two

others for the measurements of the redox potential. No redox potential value was accepted as significant unless all the pools, including that one which was used as the cathode but after electrolysis was disconnected from the current supply, were found to agree to within 0.2–0.3 mV.

To obtain the standard potential for the europium couple the instantaneous value of the emf of the cell



was determined. By recalling the arguments brought out in connection with cell (G) the emf of cell (R) may be expressed by the equation

$$E_{\text{R}} = e_{\text{ref}} - e_{\text{R}}^{\circ} - 59.16 \log[\text{Eu}^{3+}]/[\text{Eu}^{2+}] \quad (3)$$

where e_{ref} denotes the potential of the reference half-cell and e_{R}° is the symbol for the standard potential of the europium couple. In every experiment a set of corresponding data triplets ($E_{\text{R}}, E_{\text{G}}, \mu$) was obtained where the symbol μ is introduced for the number of faradays employed for reduction.

On the basis of each data triplet a value could be obtained for ($e_{\text{ref}} - e_{\text{R}}^{\circ}$) by combining equations (3) and (2) with the stoichiometric relationships

$$\begin{aligned} \mu &= \text{number of faradays employed for the reduction of } \text{Eu}^{3+} = \\ &= V([\text{Eu}^{2+}] + \Delta h) \end{aligned} \quad (4)$$

$$\Delta h = h_0 - h \quad (5)$$

$$[\text{Eu}^{3+}] = B - [\text{Eu}^{2+}] \quad (6)$$

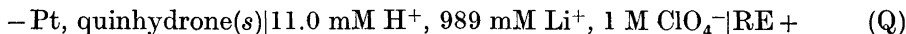
where V denotes the volume of the test solution, h_0 is the hydrogen ion concentration attained at the end of the preliminary acidification and h is the instantaneous value of the hydrogen ion concentration. A part of a typical series is shown for illustration in Table 1.

Table 1. Some data selected from series 7.

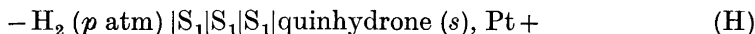
μ μF	Time	$B = 10.86 \text{ mM}$ $h_0 = 1.846 \text{ mM}$		$E_{\text{G},0} = 12.7 \text{ mV}$ $V = 50.00 \text{ ml}$		$e_{\text{ref}} = 676.0 \text{ mV}$		
		E_{G} mV	$E_{\text{R},1}$ mV	$E_{\text{R},2}$ mV	E_{cathode} mV	h mM	$[\text{Eu}^{2+}]$ mM	$-e_{\text{R}}^{\circ}$ mV
167.84	12:40	177.3	1030.5	1030.5	1030.9	1.65 ₁	3.16 ₂	377.5
	12:58	177.7	1030.8	1030.7	1030.7	1.62 ₅	3.13 ₇	378.0
	13:07	177.8	1031.0	1030.7	1031.1	1.62 ₀	3.13 ₁	378.1
195.81	14:22	178.5	1034.5	1034.3	1034.9	1.57 ₆	3.64 ₇	376.1
	14:40	178.6	1034.6	1034.4	1034.8	1.57 ₀	3.64 ₁	376.2
251.75	17:20	181.8	1045.3	1045.1	1045.6	1.38 ₆	4.57 ₆	377.4
	17:40	182.1	1045.8	1045.6	1045.8	1.37 ₀	4.55 ₉	378.0
336.59	21:50	187.2	1059.7	1059.7	1060.3	1.12 ₃	6.00 ₉	378.4
	21:55	187.2	1059.4	1059.4	1059.9	1.12 ₃	6.00 ₉	378.1
	22:10	187.4	1058.9	1058.8	1059.2	1.11 ₄	6.00 ₁	377.6
	22:15	187.9	1058.8	1058.7	1059.0	1.09 ₃	5.97 ₉	377.6

In order to calculate the standard potential itself, e_{R}° , the value of the reference half-cell potential, e_{ref} , is required. This has shown a slow trend in the course of this work which comprised several months. The drift can be ascribed to the contamination of the solutions kept in the half-cell vessel with stopcock grease and with substances dissolved from glass, and to the disappearance of lattice imperfections in the silver electrode.

The actual value of e_{ref} was determined by measuring immediately after the completion of a reduction experiment the emf of the cell



By taking into account the liquid junction potential which was calculated on the basis of an unpublished work in this laboratory to amount to $0.066 \times 11.0 = 0.73 \text{ mV}$, the emf of cell (Q) provided the value $e_{\text{Q}}^{\circ} - e_{\text{ref}}$ where e_{Q}° denotes the standard potential of the quinhydrone half-cell. This in turn was obtained by the emf of the cell



where S_1 denotes the test solution of cell (Q) and $p = p_{\text{atm}} - p_{\text{H}_2\text{O}}$. The vapor pressure of a 1 M LiClO_4 solution was estimated from the data of Rush and Johnson² to amount to 22.8 torr, and thus we could calculate from the average value of several E_{H} determinations that in 1 M LiClO_4 medium $e_{\text{Q}}^{\circ} = 686.1 \pm 0.1 \text{ mV}$.

Substitution of the quinhydrone for the hydrogen half-cell in the daily routine saved us much time and effort, and it influenced the precision of the standard potential values but little if at all.

EXPERIMENTAL

Reagents and analyses

The life-time of the Eu^{2+} ions was found to depend primarily on the purity of the water employed to make up the test solutions. To keep this source of contamination at a minimum some potassium permanganate and sodium hydroxide were first added to water purified by ion exchanger treatment (which was available from a large scale central unit), and the resulting alkaline solution was then slowly distilled while nitrogen was passed through it. The distillate was next acidified with some sulfuric acid and was redistilled in a nitrogen atmosphere. Care was taken to protect the distillates from atmospheric contamination, especially dust, by maintaining above them a slight overpressure of nitrogen throughout these and the subsequent manipulations.

Europium(III) perchlorate stock solutions were prepared from a europium oxide preparation of 99.99% purity supplied by Typpi Oy, Oulu, Finland. After overnight ignition at 900°C which was needed to transform the small amounts of carbonate ions always present to oxide ions, the sample was dissolved in a slight excess of a standardized perchloric acid solution. The $[\text{Eu}^{3+}]$ of this stock solution was checked gravimetrically by precipitating europium(III) oxalate; this was transformed after washing and drying by ignition to Eu_2O_3 .

Lithium perchlorate solutions were prepared as usual in this laboratory.³ In an attempt to remove dust and other suspended material, such as filter paper fibre, the final product was twice recrystallized from purified water. The perchlorate concentration of the stock solution was determined by passing a sample through a column of a cation exchanger in the hydrogen form and titrating the eluate with a standardized NaOH solution. The hydrogen ion concentration of the stock was determined potentiometrically by coulometric alkalification.

The *silver perchlorate* solutions used in the reference half-cells were prepared from silver carbonate. This was made by adding portionwise 0.1 M Na_2CO_3 to a 0.2 M AgNO_3 solution. The coarse Ag_2CO_3 so formed was washed free by decantation from Na^+ and NO_3^- ions, and then it was dissolved in dilute HClO_4 . The silver content of the stock solution was determined by potentiometric titration with a solution of sodium chloride prepared from a sample of NaCl which serves as a primary standard in this laboratory.

Impurities which gather at the surface must be absent from *mercury* to be employed as a redox electrodes. We started from Hg of commercial quality, this was then distilled twice in vacuum. For each series freshly purified mercury was used which was in addition let to pass through a sintered glass filter immediately before its introduction into the cell.

Apparatus

All the emf measurements were carried out in a thermostated room kept at $25.0 \pm 0.5^\circ\text{C}$.

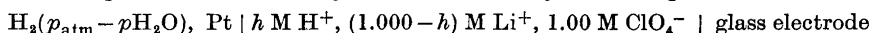
The *cell arrangement* was similar to that described in the previous communication dealing with europium.¹ The vessel for the test solution was somewhat modified for greater convenience. It is provided with eight ground glass inlets so that a reagent can be added and a sample can be withdrawn without admitting air. The nitrogen inlet and outlet are made to form parts of the vessel itself, the inlet tube terminates close to the central receptacle which is designed to contain the cathode pool. This is kept in a constant motion by the nitrogen current, and thereby the local excess of Eu^{2+} in the vicinity of the cathode can be prevented to attain a high value.

The *nitrogen* employed for deoxygenation and for the maintenance of an indifferent atmosphere was taken from a cylinder and it was led first through a column containing finely divided copper and then in succession 1 M LiOH , 1 M HClO_4 , water, and 1 M LiClO_4 . A sintered glass filter was inserted between the last solution and the inlet tube to remove dust and droplets carried by the gas stream.

The emfs of the glass and redox cells were measured with valve potentiometers of the type E 388 of the Metrohm AG, Herizau, Switzerland. The uncertainty of the emf measurements never exceeded 0.2 mV.

A Metrohm type E 211 coulometer was applied as the constant current source. The current levels were calibrated by inserting into the circuit standard resistances, supplied by the Leeds and Northrup Co., and measuring the average value of the resulting potential drop with a recently certified digital voltmeter.

Beckman general purpose glass electrodes of the types 40498 and 41263 were employed throughout this work. They were calibrated by measuring the emf of the cell



as a function of h in the range 0.1 to 1 mM. In each experiment the emf was found to remain constant to within ± 0.1 mV. The other electrodes were prepared and treated as usual in this laboratory.

RESULTS

The standard potential values obtained in the seven final series of measurements as well as the main experimental conditions are concisely summarized in Table 2.

As the most important result we may infer on the basis of the data of this table, which cover the $\log B$ range -3.4 to -2 and the $\log h$ range -5 to -3 , that the e_{R}° values do not show any appreciable trend either with the europium or with the hydrogen ion concentration. Thus our two fundamental assumptions expressed by eqns. (3) and (4) may be regarded as close approximations.

This conclusion is further corroborated by the examination of the in-

Table 2. Summary of the results.

Series	B mM	h_0 mM	e_{ref} mV	Range of $[\text{Eu}^{3+}][\text{Eu}^{2+}]^{-1}$	Range of h mM	Number of reduction steps	Average $-e_{\text{R}}^\circ$ value of the series, mV
1	0.424	0.500	678.0	1.00–0.594	0.220–0.114	8	378.9 ± 0.9
2	0.511	0.344	677.8	2.66–2.11	0.0566–0.0051	4	378.6 ± 0.8
3	0.996	0.820	677.1	4.59–0.20	0.733–0.338	35	380.0 ± 1.2
4	1.55	0.507	677.8	1.96–0.80	0.208–0.0130	14	379.3 ± 0.9
5	1.97	0.686	677.4	1.02–0.24	0.571–0.371	21	379.7 ± 0.8
6	10.24	1.605	676.2	3.84–0.46	1.474–1.062	17	377.7 ± 1.1
7	10.86	1.846	676.0	2.47–0.81	1.65–1.09	14	377.9 ± 0.7

fluence of the $[\text{Eu}^{3+}][\text{Eu}^{2+}]^{-1}$ ratio on the e_{R}° values of the individual series; in no case could any systematic variation be detected. Fig. 1, which shows data pertaining to the B level 1.97 mM, illustrates a typical random spread in e_{R}° . We would therefore propose as the most probable value the mean of the individual averages

$$e_{\text{R}}^\circ = -379 \pm 1 \text{ mV}$$

Thus the magnitude of the europium standard potential in 1 M LiClO_4 medium differs by 2 mV only from that valid in 1 M $(\text{CH}_3)_4\text{NCl}$ where e_{R}° was found to equal -381 mV .¹ The proximity of the two results is somewhat unexpected since both the cations and the anions of the solvent salts were chosen different. The little effect of the replacement of the large $(\text{CH}_3)_4\text{N}^+$ ion by the small and strongly hydrated Li^+ ion is especially remarkable.

Before turning to a discussion of some additional experiments the question should be raised how could the precision of the redox potential measurements, which in the present work was about 1 mV, be improved. As the hydrolysis of the Eu^{3+} ions is certainly negligible for $\log h > -5$, we could always choose a $h B^{-1}$ ratio less than unity in our experiments. As a consequence the rate of oxidation of Eu^{2+} by H^+ could be kept low, and therefore—as a straightforward error calculation applied to eqn. (3) shows—the effect of the uncertainty of the instantaneous hydrogen ion concentration determination on the evaluation of e_{R}° is less than that of the difference usually found among simultaneously employed redox electrodes.

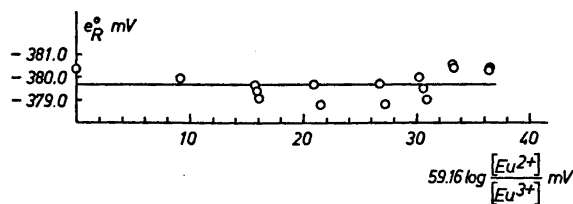


Fig. 1. The standard potential e_{R}° as a function of $59.16 \log[\text{Eu}^{2+}]/[\text{Eu}^{3+}]$. The data were taken from series 5 pertaining to the B level 1.97 mM, cf. Table 2. The horizontal line represents the average value of the standard potential, -379.7 mV .

The main source of the uncertainty is probably the presence of traces of impurities in our test solutions. The contaminants which may react at the mercury cathode and (or) protolyze at the low acidities studied, arise from the lithium perchlorate and the nitrogen employed. A cell design recently developed in this laboratory which makes it possible to work under a slight overpressure would eliminate the contamination from the protecting gas; however, we have not been able to find a method for the removal of the remaining, mainly organic, impurities from our lithium perchlorate preparations, which for safety reasons cannot be brought to a high temperature.

Additional experiments. At the conclusion of the experiments serving for the evaluation of the standard potential some pioneering work was made to determine the solubility products of europium(III) hydroxide and europium(II) sulfate.

To precipitate europium(III) hydroxide such a high $[\text{Eu}^{2+}][\text{Eu}^{3+}]^{-1}$ ratio was achieved by cathodic reduction of a test solution S that the Eu^{2+} ions became rapidly oxidized by hydrogen ions. Thereby h diminished so far that colloidal europium(III) hydroxide started to form. The continuous rapid decrease of the $[\text{Eu}^{3+}]$ and the increase of h was followed for several days but, as no evidence was found for the approachment of a steady state, the experiment was discontinued.

We were somewhat more successful with europium(II) sulfate. Its solubility product was studied by adding an oxygen-free lithium sulfate solution of $[\text{Li}^+] = 1 \text{ M}$ to an S solution made by cathodic reduction to contain 8 mM Eu^{2+} , 3.1 mM Eu^{3+} and 0.1 mM H^+ . In the first three days the redox electrode has shown the $[\text{Eu}^{2+}]$ to decrease with a diminishing rate while the glass electrode indicated h to remain constant to within a few percent.

After about 96 h the europium(II) concentration seemed to attain a steady level as no further systematic change in E_R could be detected for additional 24 h. On the basis of this final E_R value $\text{p}K_s$ for $\text{EuSO}_4(s) \rightleftharpoons \text{Eu}^{2+} + \text{SO}_4^{2-}$ was calculated to equal 6.3. This result, which we cannot claim to correspond to equilibrium, is not far from the value of Koz'min *et al.*⁴ who reported $\text{p}K_s = 6.6$ in 1 M KCl medium.

By employing a cell technique not requiring a steady stream of protecting gas and which allows contact between the test and the bridge solutions to be made only when it is needed, we hope to find reliable data for these important heterogeneous equilibria attainable but slowly.

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