

were used in the experiments. The sedimentation coefficients were calculated from the sedimentation rate, and the $s_{20,w}$ values were corrected in the usual way for the temperature, viscosity and density of the medium. The absorption spectra of the leghemoglobin solutions were recorded before and after each run.

The pH measurements were performed with a Radiometer Titrator type TTT 1c. The pH of 0.05 M potassium hydrogen phthalate was taken to be 4.01 at 23°C.

Results and discussion. The sedimentation coefficients of Lba, as complexes with different ligands, and of a mixture of equal concentrations of Lba and Lbc, are presented in Table 1. The coefficients differ only slightly from one another, showing that leghemoglobin exists only in a monomeric form under the experimental conditions chosen for this study, and that there is no hybrid formation between the two main components. Thus leghemoglobin differs in this respect from lamprey (*Petromyzon marinus*) hemoglobin, the components of which have been found to form hybrids,¹⁰ and shows some resemblance to the myoglobins in forming no associated forms.^{6,7}

The function of leghemoglobin in root nodules is still obscure. However, the similarity between leghemoglobin and myoglobin shown by this study justifies the theory that leghemoglobin facilitates the diffusion of oxygen into the root nodule tissue¹¹ in a similar way to that in which myoglobin is assumed to function in animal tissue (cf. Wittenberg).¹² This is further supported by the fact that leghemoglobin *in situ* has been found to exist in the form of an oxygen complex.¹³

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On the Hydrolysis of Plutonyl Ion in Sodium Perchlorate Medium

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Very few data¹⁻⁴ are available on the hydrolysis of the plutonyl ions so it may be of some interest to publish preliminary data on this system, especially as the main complex found here (2,2) is not mentioned in any of the above papers.

Method. The investigations were performed as EMF-titrations at 25°C. The following cell was used:

glass electrode | plutonyl solution | RE

where RE = Ag, AgCl | 2.99 M Na⁺, 0.01 M Ag⁺, 3 M ClO₄⁻.

A solution of the general composition $H M H^+, (3-H) M Na^+, 3 M ClO_4^-$ was added to a solution with the composition $B M PuO_2^{2+}, H M H^+, C M Ag^+, (3-2B-H-C) M Na^+, 3 M ClO_4^-$.

Thus the value of *B* was decreasing during the titration.

Preparation of plutonyl solutions. The plutonyl solutions were prepared from plutonium metal, which was dissolved in a known

amount of 5 M HClO_4 . This solution was oxidized to PuO_2^{2+} by adding a known amount of solid AgO . At the same time the excess of acid was neutralized. The excess of Ag^{2+} was destroyed by warming the solution. Finally NaClO_4 was added.

Radiolysis. As the radiolysis of plutonium solutions causes a continuous reduction of PuO_2^{2+} to lower valence states, only freshly prepared solutions were used. The plutonium solutions were never more than one day "old", when titrated. Analysis of the total amount of Pu and the amount of PuO_2^{2+} was always made the same day. The difference was never more than 1 %.

Due to the radiolysis the H^+ -content of the plutonium solutions was increasing with time and had to be taken into account. $[\text{H}^+]$ was usually determined before and after each titration with a Gran plot. It was found that the order of this H^+ -increase was 0.0004–0.0016 M H^+ /M PuO_2^{2+} per hour, or a correction in Z of at most 0.010 during a titration, which usually took one day.

Data. To be certain that the solutions were in equilibrium forward and back titrations were performed. In this system it could be done at rather low Z ($Z < 0.2 - 0.3$). At higher Z it was rather easy to reach stable potentials when increasing Z , but during the back titration the EMF was creeping.

In these preliminary calculations only the true equilibrium data at low Z have been treated. B was varied from about 15 mM to about 130 mM. In Fig. 1 the experimental data are given as points and the curves are calculated with the species (2,2) and the best value of β_{22} .

Calculations. The computer program LETAGROP⁵⁻⁹ was used to evaluate the composition (p, q) of the complexes and their equilibrium constants β_{pq} for the general reaction



In Table 1 species and their β_{pq} found by other authors are collected. As some resemblance between the uranyl and plutonyl systems might be expected, the species found in the uranyl system^{10,11} (1,1), (2,2), (5,3), (4,3), (1,2), (6,4), (7,4), (8,5), and (6,7) were tried together with these in Table 1. A fairly good fit to the experimental data was achieved when considering only (2,2). It was slightly improved by adding some higher complex, e.g. (5,3). By calculations with the computer program HALTAFALL¹² assuming (1,1), (2,2), and (5,3) it was found, that in the region investigated the dominating species was (2,2). The higher complex (5,3) starts to form at the upper limit of the Z -values used. The amount of (1,1) was small (Fig. 2). Assuming only (2,2) the following values were reached:

$$\log \beta_{22} = -8.21 \pm 0.02 \text{ with } \sigma(Z) = 0.010$$

Discussion. It is interesting to notice that the complex (2,2), which seems to be fairly well established in this investigation, is not mentioned by any of the authors in Table 1. (2,2) is also found to be the main complex in analogous uranyl solutions. Furthermore the dimer is found as discrete groups in a solid uranyl-hydroxy salt investigated by X-ray analysis at this Institute.¹³

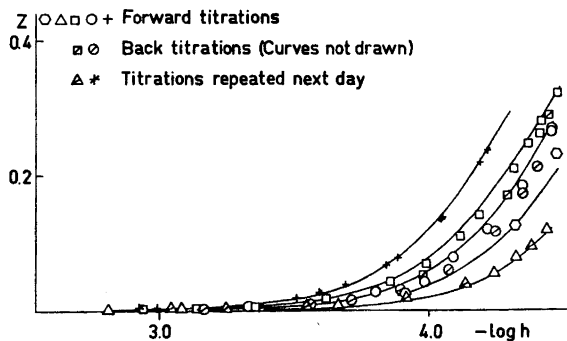


Fig. 1. Hydrolysis of plutonyl ion in 3 M $(\text{Na})\text{ClO}_4$. Points are experimental data $Z(\log h)$ and curves are calculated with $\log \beta_{22} = -8.21$.

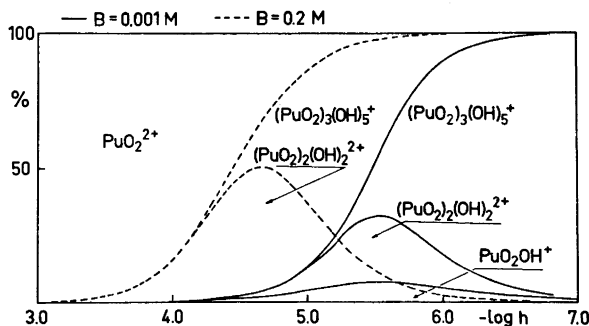


Fig. 2. Percentages of total amount plutonium present in the three species (1,1), (2,2), and (5,3) as a function of $-\log h$ calculated by HALTAFALL with $\log \beta_{11} = -6.31$, $\log \beta_{22} = -8.27$, and $\log \beta_{53} = -21.72$.

Table 1.

$-\log \beta_{11}$	$-\log \beta_{21}$	$-\log \beta_{32}$	$-\log \beta_{52}$	$-\log \beta_{22}$	(Ref. No.) Author (year)
5.30					(1) O'Connor (1944)
5.71	11.42				(2) Kraus <i>et al.</i> (1949)
3.33	7.38				(3) Krevinskaya <i>et al.</i> (1959)
3.39	8.64	17.77	31.50		(4) Moskvina <i>et al.</i> (1962)
				8.21	The present paper

Further investigations at higher Z are now under way and might give information about possible higher complexes.

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