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The Measurement of the Diffusion Coefficients of Pu(III) in Hydrochloric Acid by Use of an Analytical Ultracentrifuge

V. FRIEHMELT*, A. HE**, Z. YANG** and G. MARX

Institut für Anorganische und Analytische Chemie, Forschungsgruppe Radiochemie, Freie Universität Berlin, Fabeckstrasse 34 - 36, 1000 Berlin 33, F.R.G.

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In the processing of spent nuclear fuel, plutonium is separated from uranium by selective reduction to the trivalent state followed by extraction. In order to attain optimal conditions for this process, the transport behaviour of the actinides in aqueous solutions must be known. As a consequence, the concentration dependence of the diffusion coefficients of plutonium in the trivalent state in a 1 M hydrochloric acid solution and over a concentration range from 0.8 to 4.0×10^{-2} M has been determined. The diffusion characteristics of Pu(III) were monitored by using a Beckman Instruments Ltd. 'Model E' analytical ultracentrifuge with the aid of both the Schlieren and absorption (at 550 nm) optical systems.

Experimental

Solutions of plutonium in the trivalent state were prepared as follows.

Plutonium peroxide was dissolved in 8 M nitric acid and purified by passage through an ion-exchanger (Dowex 1 X4, 50–100 U.S. mesh) followed by precipitation by the addition of hydrogen peroxide. The freshly precipitated peroxide was redissolved in hydrochloric acid and reduced to the trivalent state with mercury [1]. The mercury(I) chloride precipitate was removed by centrifugation and the concentration of hydrochloric acid adjusted to 1 M. The Pu(III) contents of these solutions were determined by carrying out potentiometric redox titrations using cerium(IV) sulphate. For the measurement of the total plutonium concentrations, the same procedure was used but first titanium(III) chloride was added as reductant. Stability tests showed that at least 95% of the total plutonium remained stable in the trivalent state for over 15 days [2].

Diffusion measurements were carried out with an analytical ultracentrifuge at 298 K using a capillary-type cell centerpiece consisting of two compartments which could be filled separately with test solution and solvent [3, 4]. The cell was fitted into a titanium rotor and accelerated to a final measurement velocity of 5.200 r.p.m., whereby an artificial boundary was created by overlaying the test solution with solvent.

Results and Discussion

Table I indicates the diffusion data measured for Pu(III) together with the plutonium complexes calculated to be present. During the diffusion measurements, the UV absorption of the solutions were also measured at 470 nm in order to confirm the absence of detectable quantities of Pu(IV) [1]. Furthermore, an acid concentration gradient was also avoided by keeping the hydrochloric acid concentration identical on both sides of the boundary. The diffusion behaviour of Pu(III) could be effectively observed by using the centrifuge's Schlieren and absorption optical systems. An error limit of below 5% can be ascribed to the values of the diffusion coefficients listed in Table I. These values compare well with those reported in the literature for Pu(III) in 0.5 M sulphuric acid, ($D = 4.7 \times 10^{-6}$ cm^2 s^{-1}) and in 1 M perchloric acid solution ($D = 4.8 \times 10^{-6}$ cm^2 s^{-1}) [5]. It can be seen that the values of Table I exhibit a maximum at a Pu(III) concentration of 2×10^{-2} M although this is not too significant. Similar behaviour has been observed for Pu(VI) in 1 M nitric acid [6] although in this case the values of the diffusion coefficients were higher. Unfortunately, it is not possible to measure the diffusion coefficients of Pu(III) in nitric acid solution without the presence of a valence stabilizer. Stability tests have shown that in the absence of a reducing agent to hold plutonium in its trivalent state, its oxidation to Pu(IV) occurs rapidly. Not only is it possible for such an agent to influence the diffusion process itself, but also it has not proved possible as yet to find a valence stabilizer which does not interfere with the optical measuring technique.

For the plutonium species believed to be present, it has been calculated that the concentrations of the hydroxocomplexes lie below 0.1% as a result of the large excess of hydrochloric acid present [7]. These species have therefore been neglected. The quantities of Pu^{3+}, $PuCl^{2+}$ and $PuCl_2^+$ have been calculated using values of the stepwise formation constants of $k_1 = 0.7$ M^{-1} and $k_2 = 0.5$ M^{-1} [8]. It can be seen that the ratio of these three species is only slightly affected by the change in total plutonium concentration. It is therefore likely that a coupling of the diffusion processes of Pu(III) complexes and hydrochloric acid could after all, be responsible for the observed diffusion behaviour, since the diffusion coefficient

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*Author to whom correspondence should be addressed.

**Visiting scientists from the Department of Nuclear Science, Fudan University, Shanghai, China.

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TABLE I. The Diffusion Coefficients of Plutonium(III) in 1 M Hydrochloric Acid and the Theoretical Ionic Species Composition.

Plutonium(III) Concentration (Mol dm^{-3} × 10^{+2})	%Pu^{3+}	%$PuCl^{2+}$	%$PuCl_2^+$	Diffusion Coefficient (cm^2 s^{-1} × 10^{+6})
0.82	48.2	34.3	17.5	5.14
1.42	47.7	34.5	17.8	5.20
1.63	47.6	34.5	17.9	5.43
2.40	47.0	34.7	18.3	4.84
2.88	46.7	34.8	18.5	4.62
3.76	46.0	35.0	19.0	4.74

of pure hydrochloric acid is some six times greater than that of Pu(III) [9]. More detailed investigations into both coupling effects and into the determination of stability constants of a higher accuracy than those currently to be found in the literature are urgently required in order to provide satisfactory explanation of the observed effects.

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