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The Measurement of the Diffusion Coefficients of Pu(VI) in Nitric Acid Solution with the Aid of the Analytical Ultracentrifuge

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As the transport processes of the actinides in solution are of special relevance for the field of spent fuel reprocessing, it was decided to investigate the concentration dependence of the diffusion coefficients of Pu(VI) in 1 M nitric acid solution over the concentration range 0.7 to 7.0×10^{-2} M as no data has been reported in the literature until now [1, 2]. A Beckman Instruments Ltd. Model E Analytical Ultracentrifuge was employed for the measurement with both the Schlieren and absorption optical systems (at 540 nm) being used to monitor the diffusion phenomena.

Experimental

The hexavalent plutonium solutions were prepared as follows. Plutonium peroxide was dissolved in 8 M nitric acid and purified by passage through an ion-exchanger (Dowex 1 × 4, 50–100 U. S. mesh), followed by reprecipitation by the addition of hydrogen peroxide. The freshly-precipitated peroxide was then redissolved in nitric acid and oxidized to the hexavalent state with silver oxide [3, 4]. Silver ions were subsequently removed by the addition of hydrochloric acid and precipitation as silver chloride and the nitric acid concentration was finally adjusted to 1 M. The total amount of plutonium and the fraction existing as Pu(VI) were determined by a potentiometric redox titration [5–7]. Stability tests showed that at least 95% of the total plutonium remained stable in the sixth valence state for a period of at least 30 days [8].

Diffusion measurements were carried out at 298 K using a capillary-type cell centerpiece consisting of two compartments which could be filled separately with test solution and solvent [9, 10]. The diffusion cell was fitted into a titanium rotor and accelerated in the Analytical Ultracentrifuge to the measurement velocity of 5,200 r.p.m., whereby an artificial boundary was created by overlaying the solution with solvent.

Results and Discussion

The results for Pu(VI) are given in Table I together with the diffusion coefficients of pure nitric acid for comparison purposes. As the diffusion of Pu(VI) across the boundary was measured simultaneously with both optical systems, it has proved possible to reduce the error limits to below 5%. It can be seen that the values of the diffusion coefficients of Pu(VI) show a maximum at a concentration of *ca.* 2×10^{-2} M although the effect is slight. Similar behaviour has been observed for other aqueous systems [11]. Work is currently in progress to elucidate the reasons for this behaviour although it is believed that a change in plutonium ionic species over this concentration range is not to be expected as nitric acid is present in a large excess. The diffusion coefficients of nitric acid increase slightly over the 0.05 to 1.30 M concentration range and are some 4.5 times larger than those of plutonium. During the investigation of the Pu solu-

TABLE I. The Diffusion Coefficients of Plutonium(VI) in 1 M Nitric Acid and of Pure Nitric Acid at 298 K.

Concentration of Plutonium(VI) Mol $dm^{-3} \times 10^{+2}$	Diffusion Coefficient $cm^2\ s^{-1} \times 10^{+5}$	Concentration of Nitric Acid Mol dm^{-3}	Diffusion Coefficient $cm^2\ x^{-1} \times 10^{+5}$
0.67	0.64	0.05	2.52
0.84	0.67	0.15	2.61
1.09	0.65	0.40	2.66
1.42	0.66	0.60	2.81
1.55	0.68	0.80	2.84
2.22	0.68	1.00	2.90
2.89	0.61	1.30	3.10
3.22	0.55		
4.02	0.54		
6.88	0.57		

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tions, a nitric acid concentration gradient was avoided by keeping the acid concentration in both compartments of the diffusion cell identical. Nevertheless, a coupling of the diffusion processes of nitric acid and Pu cannot be ruled out; this effect will also be the subject of further investigations.

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