Some Liquid Phase Diffusion Coefficients
of Uranium and Plutonium

W. KNOCH

Laboratory of Nuclear and Radiochemistry, Technical University, Braunschweig, Germany

Diffusion coefficients of Pu(IV) and U(VI) in nitric acid solutions and some actual solvent extraction systems like tributylphosphate-kerosine and tri-iso-octylamine–xylene were determined. Activation energies for the U-diffusion are calculated.

DURING INVESTIGATIONS on the transfer of U and Pu compounds between water and organic solvents (5), determinations of the diffusion coefficients were carried out by means of an improved capillary cell method (3). The diffusion coefficients were calculated from the equation:

$$D = \frac{4\,l^2}{\pi^2 t} \ln \frac{8c_o}{\pi^2 \bar{c}}$$

where l is the capillary length, t the diffusion time, c_o the initial concentration, and $\bar{c}$ the mean concentration at time t. Correct results are obtained when $Dt/l^2 > 0{,}2$.

The diffusion of U(VI) and Pu(IV) in HNO_3-H_2O, 20% TBP-HNO_3-kerosine, and 10% and 20% tri-iso-octylamine (TIOA)-HNO_3-xylene was investigated using the nuclides U-233 and Pu-239 as tracers.

AQUEOUS NITRIC ACID SOLUTIONS

The HNO_3-H_2O solutions contain a mixture of complex ions like $[UO_2(NO_3)_n]^{2-n}$ with $n < 3$ and $[Pu(NO_3)_m]^{4-m}$ with $m < 6$. The composition is dependent on the HNO_3 concentration (3, 6).

A quantitative interpretation of the results is difficult because of the lack of any simple theory combining molecular weight and shape with diffusion factors. The Riecke-law seems to be invalid (2, 11). Moreover, the number of water molecules participating in the transport is quite uncertain.

Figure 1 illustrates the change in D_U with increasing HNO_3 concentration—i.e., changing composition of the ion mixture. The initial U-233 concentration of the capillary solution, (c_o), was in all cases $3 \times 10^{-5}M$. The sudden increase of D_U at $C_{HNO_3} > 7M$ is probably due to the formation of an undissociated complex like $[HUO_2(NO_3)_3]$ or the anionic complex $[UO_2(NO_3)_3]^{-1}$ in accordance with results obtained by extraction measurements and spectra (1, 3, 6). These complexes are formed at HNO_3 concentrations $> 6M$, their size being larger than that of the UO_2^{-2} ion.

The activation energy is 5.66 ± 0.10 kcal./mole and has been calculated from diffusion measurements at 25°, 40°, and 60° C. ($4M$ HNO_3, $3 \times 10^{-5}M$ U).

Hahn (5) related concentration to the uranium diffusion coefficient.

The diffusion coefficient of quadrivalent plutonium in HNO_3 solutions (Figure 2) depends strongly on the acidity. The D_{Pu} values are reproducible, but only if the Pu solutions are less than 24 hours old. This indicates that hydrolysis reactions occur even at high H^- concentrations. Hydrolysis increases rapidly at HNO_3 concentrations below $1M$; colloidal particles are formed and D decreases. Rising temperatures promote the hydrolysis and make it impossible to calculate activation energies.

These results are not, in all cases, consistent with other experiments (4, 9, 10). Different experimental methods may be a partial cause.
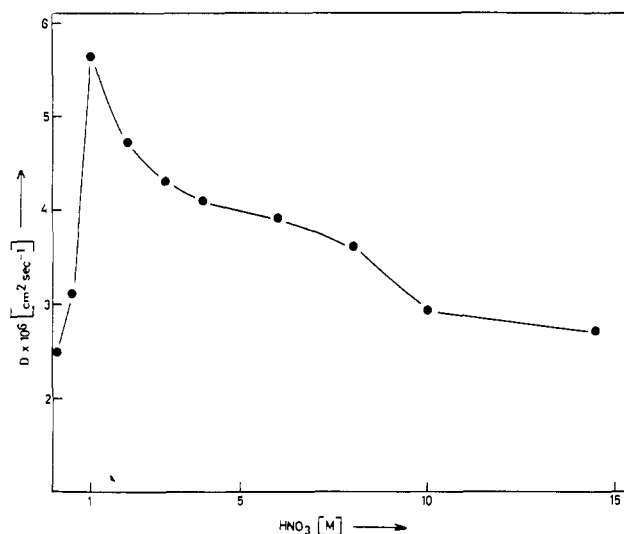

Figure 1. Diffusion coefficients of U(VI) tracer ($3 \times 10^{-5}M$) in HNO_3 solutions at 25° C.

The points represent the mean of three determinations; the accuracy varies between 2 and 5%

Figure 2. Diffusion coefficients of Pu(IV) tracer ($2 \times 10^{-5}M$) in HNO_3 solutions at 25° C.

The points represent the mean of two determinations; the accuracy varies between 3 and 5%

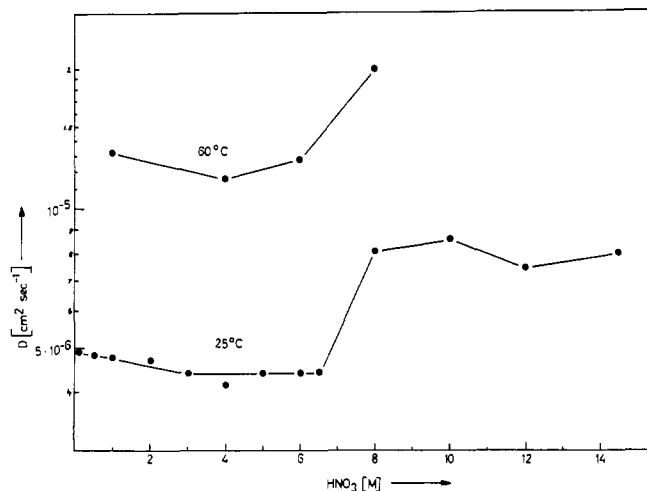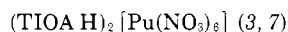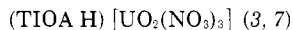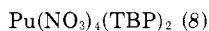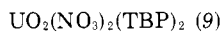## ORGANIC SOLVENTS

The diffusion coefficients of U and Pu in some organic solvent systems, previously equilibrated with aqueous HNO_3 solutions, are listed in Tables I and II. The HNO_3 equilibrium concentration of the organic phase is noted in the second column. The complexes formed in the organic phase are well defined:

$$UO_2(NO_3)_2(TBP)_2 \quad (9)$$

$$Pu(NO_3)_4(TBP)_2 \quad (8)$$

$$(TIOA\ H)\ [UO_2(NO_3)_3] \quad (3, 7)$$

$$(TIOA\ H)_2\ [Pu(NO_3)_6] \quad (3, 7)$$

They are undissociated and considerably larger than the ionic species in the aqueous phase and possess smaller diffusion coefficients at a given temperature.

The activation energy for the diffusion of the uranium-TIOA complex (total U concentration $1 \times 10^{-5}M$) in 10% and 20% TIOA/xylene is 2.35 ± 0.06 kcal./mole and 2.35 ± 0.02 kcal./mole, respectively.

Table I. Diffusion Coefficients of U in TBP and TIOA

Org. Phase	HNO_{3org} $[M]$	Uranium $[M]$, Total	Temp., °C	$D_U \times 10^{6a}$, $Cm.^2 Sec.^{-1}$
20% TBP-kerosine	0.002	1×10^{-5}	25	3.98 ± 0.07
	0.033	1×10^{-5}	25	4.17 ± 0.06
	0.290	1×10^{-5}	25	4.32 ± 0.06
	0.033	0.5	25	2.27 ± 0.05
	0.29	0.5	25	1.88 ± 0.05
10% TIOA-xylene	...	1×10^{-5}	25	3.88 ± 0.06
	...	1×10^{-5}	40	4.70 ± 0.06
	...	1×10^{-5}	60	5.90 ± 0.08
20% TIOA-xylene	...	1×10^{-5}	25	3.05 ± 0.08
	...	1×10^{-5}	40	3.71 ± 0.08
	...	1×10^{-5}	60	4.61 ± 0.09

^{a} Mean of three runs.

Table II. Diffusion of Pu(IV) tracer ($10^{-4}M$) in TBP and TIOA

Org. Phase	HNO_{3org}, M	Temp., °C	$D_{Pu} \times 10^6$ $Cm.^2 Sec.^{-1a}$
20% TBP-kerosine	0.002	25	1.86 ± 0.05
	0.033	25	1.79 ± 0.05
	0.29	25	1.95 ± 0.05
10% TIOA-xylene	0.4	25	0.76 ± 0.03
	0.4	35	1.56 ± 0.05
	0.4	45	2.96 ± 0.08
20% TIOA-xylene	0.8	25	0.40 ± 0.03
	0.8	35	0.79 ± 0.04
	0.8	45	1.50 ± 0.05

^{a} Mean of two runs.

LITERATURE CITED

(1) Banerjea, D., Tripath, K.K., *J. Inorg. Nucl. Chem.* **18**, 199 (1961).
(2) Baker, L.C.W., Pope, M.T., *J. Am. Chem. Soc.* **82**, 4176 (1959).
(3) Baroncelli, F., Scibona, G., Zifferero, M., *J. Inorg. Nucl. Chem.* **24**, 541, 547 (1962).
(4) Berne, E., Weill, M.J., *J. Phys. Chem.* **64**, 258, 272 (1960).
(5) Hahn, H.T., *J. Am. Chem. Soc.* **79**, 82 (1957).
(6) Knoch, W., Thesis, Technical University, Brunswick, Germany, 1961.
(7) Knoch, W., *Z. Naturforschg.* **16a**, 525 (1961).
(8) McKay, H.A.C., *Proc. Intern. Conf. Peaceful Uses At Energy, Geneva, 1955*, Vol. 7, 314 (1956).
(9) Moore, R.L., AECD-**3196**, 1951.
(10) Ockenden, D.W., Welch, G.A., *J. Chem. Soc.* **1956**, p. 3358.
(11) Ondrejcin, R.S., AEC-DP **653**, 1961.
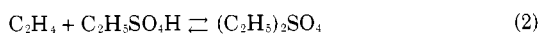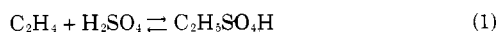(12) Ottar, B., "Self-Diffusion and Fluidity in Liquids," University Press, Oslo, 1958.

Kinetics of the Reaction of Ethylene with Sulfuric Acid

H. G. HARRIS and D. M. HIMMELBLAU
Department of Chemical Engineering, University of Texas, Austin, 12, Tex.

AMONG THE EXAMPLES of complex chemical reactions that have widespread application are the reactions of olefins with sulfuric acid. The ethylene reactions with concentrated sulfuric acid actually involve a family of reactions of which the following are well known:

$$C_2H_4 + H_2SO_4 \rightleftarrows C_2H_5SO_4H \quad (1)$$

$$C_2H_4 + C_2H_5SO_4H \rightleftarrows (C_2H_5)_2SO_4 \quad (2)$$

$$2C_2H_5SO_4H \rightleftarrows (C_2H_5)_2SO_4 + H_2SO_4 \quad (3)$$

If ethylene is reacted with dilute sulfuric acid, reactions other than 1, 2, and 3 occur to some degree and the following equilibria are set up:

$$
\begin{array}{ccc}
(C_2H_5)_2O + H_2SO_4 & & C_2H_5HSO_4 + C_2H_5OH \\
\uparrow \downarrow & & \uparrow \downarrow \\
C_2H_5OH & & H_2O \\
+ & & + \\
H_2SO_4 + C_2H_4 \rightleftarrows C_2H_5HSO_4 & C_2H_5HSO_4 + C_2H_4 \rightleftarrows (C_2H_5)_2SO_4 \\
+ & & + \\
H_2O & & H_2SO_4 \\
\uparrow \downarrow & & \uparrow \downarrow \\
C_2H_5OH + H_2SO_4 & & 2C_2H_5HSO_4 \quad (4)
\end{array}
$$