Contribution from the Oak Ridge National Laboratory Chemistry Division

DENSITY AND REFRACTIVE INDEX OF URANYL FLUORIDE SOLUTIONS[1]

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

In the course of an ultracentrifugal investigation of uranyl fluoride solutions, their densities and refractive indices were measured as a function of concentration.

The measurements were carried out near 25 and 30°C and if necessary extrapolated to 25.0 and 30.0°C from the observed temperature coefficients. Most density data were obtained pycnometrically (25 cc samples) and a few with gradient tubes[2]. The refractive index measurements were carried out with a Bausch and Lomb dipping refractometer (calibrated with "known" solutions) using sodium-D light (reproducibility ± .00004).

(2) a. K. Linderstrom-Lang, and H. Lanz. Compt. Rend. trav. lab. Carlsburg 21, 315, (1938).
b. C. Anfinsen, Preparation and Measurement of Isotopic Tracers. J. Edwards, Ann Arbor, Michigan, (1947) p. 61.

The materials used and the analytical procedures were described earlier[3]. Although the accuracy of the density measurements was approximately one part in 10,000, the accuracy of the determinations at high UO_2F_2 concentration is considerably less, in view of the uncertainty in the uranium analyses (± 0.2% in the uranium concentration).

(3) J. S. Johnson and K. A. Kraus. J. Am. Chem. Soc. 74. 4436 (1952).

1. Density. The density data which are listed in Table 1, could be fitted to the quadratic equation

$$1/d = 1/d_0 + aF_2 + bF_2^2 \qquad (1)$$

where d is the density of the solution, d_0 the density of the pure solvent, and F_2 the weight fraction of UO_2F_2. The empirical constants a and b were obtained from the intercept and slope of a plot of $(1/d - 1/d_0) / F_2$ vs. F_2. At 25°C. a = -.9120 and b = .0567, and at 30°C. a = -.9126 and b = .0569 give satisfactory fit as shown in Table 1 and Figure 1. For comparison, the earlier data of Dean[4] have been included

(4) O. R. Dean. Report CC 2092. September 1944.

in Figure 1. Since Dean reported his densities only to 0.1%, his values are in excellent agreement with the ones determined here and thus indicate that there is no systematic error in the uranium analyses.

Assuming that the density of uranyl fluoride solutions follows Equation (1), the apparent molal volume ϕ_v at 25°C was computed by the equation

$$\phi_v = \underline{M}_2 (1/\underline{d}_o + \underline{a} + \underline{b}\underline{F}_2) = 308.07 (0.0909 + 0.0567\underline{F}_2) = 28.0 + 17.5\,\underline{F}_2 \qquad (2)$$

where $\underline{M}_2 = 308.07$ is the molecular weight of uranyl fluoride.

Since it had been shown earlier[3][5] that uranyl fluoride in the concentration range studied does not appreciably dissociate into ions (i.e. essentially is a non-electrolyte under these conditions), the large variation of ϕ_v with concentration is surprising. For non-electrolytes ϕ_v would have been expected to change little with concentration[6]. It is of interest that extrapolation of ϕ_v to $\underline{F}_2 = 1$ yields $\phi_v = 45.5$ cc which may be compared with the molal volume $\underline{V} = 48.3$ cc of solid UO_2F_2 which was calculated from the crystallographic value of the density ($\rho = 6.38$)[7].

(5) J. S. Johnson and K. A. Kraus, J. Am. Chem. Soc. (in print).

(6) See for example, H. S. Harned and B. B. Owen, Electrolytic Solutions, Reinhold Publishing Co., New York, 1950 (Second Edition) p. 260.

(7) W. H. Zachariasen, Acta Cryst. 1, 277 (1948).

2. Refractive Index. The results of the refractive index measurements are also listed in Table 1. The refractive indices were fitted to the equation

$$\underline{n}_D^t = \underline{n}_D^{ot} + \alpha\,\underline{c} + \beta\,\underline{c}^{3/2} \qquad (3)$$

where $\underline{c}$ is the concentration (molarity), α and β are constants, and where $\underline{n}_D^t$ and $\underline{n}_D^{ot}$ are the measured refractive indices of the solutions and of water at temperature $\underline{t}$ respectively. Satisfactory fit of the data to Equation (3) was obtained at 25°C using $\alpha = 0.02055$ and $\beta = -0.00185$, and at 30° using $\alpha = 0.02049$ and $\beta = -0.00183$. The deviations between experimental and calculated values are shown in Table 1. It is believed that the scatter is due, to a large extent, to the inaccuracies in the analyses of the uranium solutions.

Values of the mole refraction ($\underline{R}$) of UO_2F_2 were calculated according to the equation[8]

$$\underline{R} = \frac{\underline{n}^2 - 1}{\underline{n}^2 + 2} \frac{1}{\underline{d}} \left(\frac{1000}{\underline{m}} + \underline{M}_2 \right) - \frac{(\underline{n}^o)^2 - 1}{(\underline{n}^o)^2 + 2} \frac{1}{\underline{d}_o} \frac{1000}{\underline{m}} \qquad (4)$$

(8) W. Geffcken, Z. Phys. Chem., B5, 81 (1929).

where $\underline{m}$ is the molality of the solution. The results of the calculations are also listed in Table 1. Within the accuracy of the data, $\underline{R}$ appears to be constant ($\underline{R} = 17.1 \pm 0.1$ cc) and hence does not reflect the considerable change in the degree of dimerization of uranyl fluoride which occurs in this concentration range.

Table 1

Density and Refractive Index of Uranyl Fluoride Solutions

Wt % UO_2F_2	DENSITY				REFRACTIVE INDEX				Mole Refraction (cc) (25°C)
	25°		30°		25°		30°		
	$\underline{d}$	$\Delta\underline{d}^{(a)}$ x 10^4	$\underline{d}$	$\Delta\underline{d}^{(a)}$ x 10^4	n_D^{25}	$\Delta\underline{n}^{(a)}$ x 10^5	n_D^{30}	$\Delta\underline{n}^{(a)}$ x 10^5	
1.002					1.33319	-1	1.33266	-4	17.
2.495	1.0202[b]	+0			1.33417	0	1.33366	-5	17.0
4.985	1.0443	0	1.0429	0	1.33586	0	1.33531	-2	17.0
5.025	1.0448	-1			1.33597	-8			17.1
7.481					1.33764	-2	1.33705	-2	17.1
9.607					1.33925	-10	1.33864	-7	17.2
10.20	1.0983	0	1.0967	0	1.33963	-5	1.33907	-7	17.1
15.01					1.34333	-6	1.34275	-7	17.04
20.09	1.2164	+2	1.2146	0	1.34756	-5	1.34692	-2	17.09
20.48	1.2219[b]	-2			1.34788	-2	1.34721	+3	17.01
24.89					1.35188	-1	1.35114	+9	17.06
30.10	1.3632	+0			1.35705	0			17.09
30.18	1.3632	+13	1.3607	+15	1.35705	+6	1.35636	+11	17.21
33.39					1.36059	+1	1.35988	+5	17.09
40.30	1.5509	+4	1.5481	+6					
40.27					1.36888	-5	1.36825	-9	17.14
46.36					1.37726	-1	1.37647	+6	17.15
50.27	1.7893	+2	1.7859	+1	1.38316	+14	1.38239	+18	17.13
50.90					1.38439	-5	1.38370	-11	17.15
56.90					1.39503	+1	1.39418	+10	17.13
57.10					1.39542	0	1.39457	+9	17.13
61.12					1.40392	-26	1.40303	-15	17.14
61.63	2.1627	-1	2.1589	-15	1.40475	+2	1.40407	-9	17.11

(a) $\Delta\underline{d}$ and $\Delta\underline{n}$ are the differences: calculated values minus experimental values.

(b) Measured by gradient tube method.

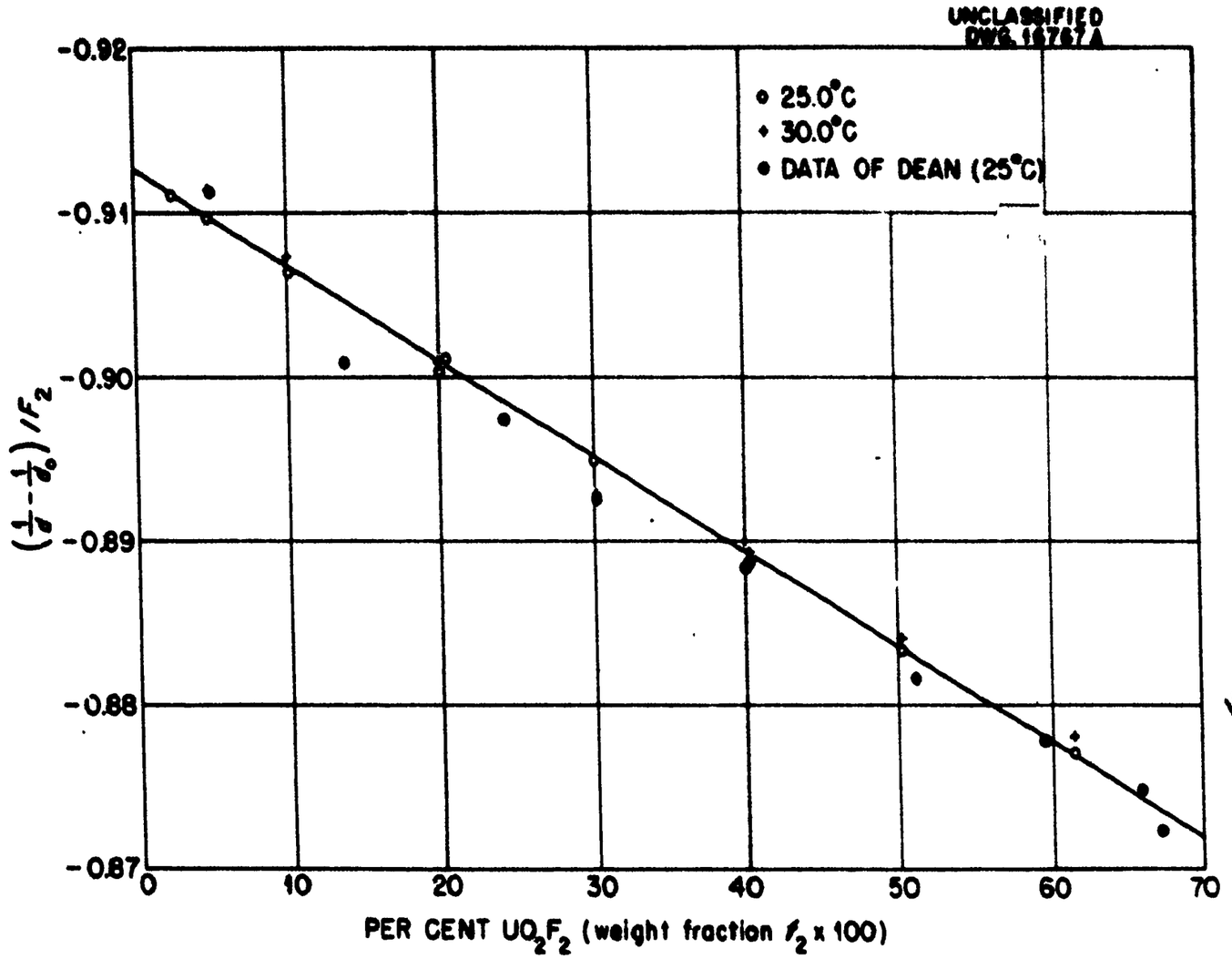

FIGURE 1
CHANGE OF DENSITY OF AQUEOUS SOLUTIONS WITH CONCENTRATION