OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL
CENTRAL FILES NUMBER

CF 52-3-253

DATE: March 10, 1952

SUBJECT: PHYSICAL PROPERTIES OF URANYL SULFATE
SOLUTIONS AT ATMOSPHERIC PRESSURE

TO: Listed Distribution

FROM: J. D. Roarty, S. I. Kaplan,
W. D. Powers and R. F. Redmond

Photostat Price \$ 3.30

Microfilm Price \$ 2.40

Available from the
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TABLE OF CONTENTS

	Page
ABSTRACT	3
INTRODUCTION	4
SURFACE TENSION	4
VISCOSITY	7
DENSITY	10
HEAT CAPACITY	13
HEAVY WATER SOLUTIONS VERSUS LIGHT WATER SOLUTIONS	15
CHEMICAL ANALYSIS OF SOLUTION	15
LITERATURE CITATIONS	16
TABLE OF GRAPHS AND FIGURES	
Figure 1 Surface Tension of Uranyl Sulfate Solutions	6
Figure 2 Viscosity of Uranyl Sulfate Solutions	9
Figure 3 Density of Uranyl Sulfate Solutions	10
Table 1 Surface Tension	5
Table 2 Viscosity	8
Table 3 Density	12
Table 4 Comparison of ORNL and Los Alamos values for Density	12
Table 5 Heat Capacity	14
Table 6 Analysis of UO_2SO_4	15

ABSTRACT

The surface tension, viscosity, density, and heat capacity of uranyl sulfate solutions were measured in a temperature range of approximately 0°C. to 100°C. at atmospheric pressure. Solutions of uranyl sulfate in concentrations of 100, 200, and 400 g. U/l. solution were investigated in both light and heavy water. The results of this investigation are shown in Figures 1, 2, 3, and tabulated in Tables 1, 2, 3, 4 and 5.

It is recommended that other studies be initiated to obtain physical property data for these solutions at temperatures above 100°C, and to improve on the accuracy of the data listed here.

The effect of concentration on the surface tension of uranyl sulfate solutions appears to be different than for any other salt solution. The possibility that these values may be in error due to impurities in the sulfate should be kept in mind.

INTRODUCTION

The physical properties of uranyl sulfate in solutions of ordinary water and heavy water are of interest as possible core fluids for homogeneous reactors. Unfortunately no reference could be found which listed the physical properties of uranyl sulfate in heavy water, and the only information in the literature on the properties of light water solutions of uranyl sulfate is limited to values for the density of the solution. (See Kennedy, Reference 1). NOTE: This work was performed before the current physical property program at the Mound Laboratory was underway.

The investigation described in this report was undertaken because of the urgent need for reliable information on the properties of both light and heavy water solutions of uranyl sulfate. Only equipment which was immediately at hand was used, and as a result, data above 100°C were not obtainable. With the possible exception of surface tension, values at higher temperatures can be obtained with reasonable assurance by extrapolation from the data presented in this report. It is estimated that the error in the measurements was at most $\pm 10\%$ of the measured value.

SURFACE TENSION

A Du Nouy Tensiometer was used to measure the surface tension directly in dynes/cm. Check runs were made periodically on distilled water to check the calibration of the tensiometer.

Measurements were taken at temperatures of 20°C., 40°C., 60°C. and 80°C. with concentrations in ordinary water of 25, 50, 100, 200 and 400 g. U/l. solution and concentrations of 100, 200, and 400 g. U/l. in heavy water.

680-4

The values of surface tension obtained are listed in Table 1, and are plotted in Figure 1.

TABLE 1
SURFACE TENSION
(dynes/cm.)

Temp. °C	H ₂ O - UO ₂ SO ₄ SOLUTIONS						D ₂ O - UO ₂ SO ₄ SOLUTIONS			
	0*	CONCENTRATION (g. U/l. Solution)					CONCENTRATION (g. U/l. Soln.)			
		25	50	100	200	400	0**	100	200	400
25	72.0						71.9			
30	71.2	68.0	66.0	60.0	52.0	51.0		63.0	53.5	49.5
40	69.6	62.5	60.0	54.0	48.0	50.0		62.0	52.0	48.0
60	66.2	60.0	56.0	50.0	45.0	48.0		58.0	49.0	46.0
80	62.6	56.0	52.2	46.0	43.0	46.0		55.0	46.0	44.0

* Reference 2

** Reference 3

For solutions of uranyl sulfate in distilled water the surface tension apparently passes through a minimum value as the concentration is increased. This fact is rather unusual, for most electrolytes tend to increase the surface tension of water when a solution is formed, whereas the uranyl sulfate in solution depressed the surface tension of water. A few electrolytes are known to depress the surface tension property of water, HCl and NH₄OH being examples; however, these electrolytes do not evidence a minimum-value surface tension relation with increasing concentration². The magnitude of the decrease in surface tension with concentration is much less for HCl and NH₄OH than was observed in the case of uranyl sulfate solutions.

Trends are much the same for the heavy water solutions of uranyl sulfate with a minimum point observed in the surface tension curves over the range of concentrations studied.

680.5

SURFACE TENSION OF
URANYL SULFATE SOLUTIONS

FIG. I

Dwg.-18063

There is a possibility that some impurity in the UO_2SO_4 salt is responsible for the unusual surface tension behavior of uranyl sulfate solutions. Chemical analysis of the solution, as reported in the section, "Chemical Analysis of the Solutions Used" did not indicate impurities which could have caused so low a value of surface tension. It is possible, though unlikely, that small quantities of detergent were picked up by the salt during its preparation in glass equipment.

VISCOSITY

The viscosity of the uranyl sulfate solutions was measured with an Ostwald pipette, No. 100, which was calibrated with distilled water and benzene at room temperature. The viscometer was immersed in a constant temperature oil bath with a stirrer to provide the various temperatures at which readings were recorded.

Measurements were made at concentrations of 100, 200 and 400 g. U/l. in light and heavy water and at temperatures ranging from room temperature to approximately 100°C .

The viscosity changes of uranyl sulfate solution for changes in temperature and concentration as indicated in Table 2 and Figure 2 are consistent with the behavior of electrolytes in general, i.e., the viscosity increases with an increase of concentration and with a decrease of temperature.

TABLE 2
VISCOSITY

H ₂ O - UO ₂ SO ₄ SOLUTIONS			D ₂ O - UO ₂ SO ₄ SOLUTIONS		
CONCENTRATION (g. U/l. SOLN.)	TEMPERATURE °C	VISCOSITY (POISES)	CONCENTRATION (g. U/l. SOLN.)	TEMPERATURE °C	VISCOSITY (POISES)
100	25.0	0.01220	100	28.0	0.01544
100	52.0	0.00789	100	71.0	0.00590
100	74.0	0.00462	100	95.5	0.00344
100	86.0	0.00339			
100	100.0	0.00247			
200	25.0	0.01710	200	28.0	0.02118
200	46.0	0.01184	200	51.0	0.01296
200	78.0	0.00595	200	73.0	0.00826
200	100.0	0.00396	200	101.0	0.00452
400	25.0	0.04160	400	28.0	0.04248
400	48.0	0.02658	400	77.5	0.01420
400	81.0	0.01456	400	102.0	0.00946
400	100.0	0.01050			
0	0	0.0180*	0	10	0.0169**
0	20	0.0101*	0	20	0.0126**
0	40	0.0065*	0	25	0.0110**
0	60	0.0047*	0	30	0.0097**
0	80	0.0036*	0	35	0.0086**
0	100	0.0028*	0		

* Reference 2

** Reference 3

VISCOSITY OF URANYL SULFATE SOLUTIONS

FIG. 2

Dwg.-18065

DENSITY

The buoyancy method was employed to determine the density of the solutions. A metal plummet, suspended from a balance by a fine wire, was first weighed in air, and then weighed in the liquid. The density of the liquid was calculated from the computed volume of the plummet at the temperature in question and the difference between the weight of the plummet in the liquid and its weight in air.

The density measurements were made on both ordinary water and heavy water solutions of uranyl sulfate. Concentrations for both of these types of solutions were 100, 200, and 400 g. U/l. solution. The experiments were conducted in the temperature range from approximately room temperature to 100°C., and at atmospheric pressure. The results are plotted in Figure 3 and are tabulated in Table 3.

The effect of temperature on the density of uranyl sulfate solution was small as seen in Figure 3. A density change of -0.05 g./cc. was observed for a temperature increase of 80°C. which compares closely to the density change that occurs for pure water under the same temperature increase. It was observed that the density of uranyl sulfate solutions increased with increasing concentration, an effect which is similar to that which occurs in most salt solutions.

Of the physical properties contained in this report, only the density of uranyl sulfate solutions has been reported previously in the literature¹. Some approximate comparisons are given in Table 4.

DENSITY OF URANYL SULFATE SOLUTIONS

FIG. 3

Dwg.-18064

TABLE 3

DENSITY

H ₂ O - UO ₂ SO ₄ SOLUTIONS			D ₂ O - UO ₂ SO ₄ SOLUTIONS		
CONCENTRATION (g. U/l. SOLN)	TEMPERATURE °C	DENSITY (g./cc.)	CONCENTRATION (g. U/l. SOLN)	TEMPERATURE °C	DENSITY (g./cc.)
100	27.1	1.110	100	28.2	1.203
100	52.0	1.100	100	58.0	1.190
100	56.0	1.090	100	75.0	1.180
100	74.9	1.080	100	88.5	1.171
100	82.2	1.080	100	92.8	1.168
100	93.0	1.080	100	100.0	1.163
100	94.8	1.070	-	-	-
200	32.0	1.222	200	28.0	1.364
200	50.8	1.210	200	39.1	1.349
200	55.9	1.210	200	50.0	1.343
200	62.5	1.200	200	61.0	1.334
200	78.0	1.192	200	67.0	1.315
200	92.0	1.191	200	88.0	1.323
200	98.5	1.182	200	95.5	1.299
400	34.1	1.464	400	28.5	1.558
400	59.0	1.448	400	48.8	1.547
400	64.5	1.445	400	66.2	1.535
400	75.2	1.441	400	82.0	1.523
400	81.0	1.433	400	99.0	1.510
400	86.2	1.429	-	-	-
400	93.2	1.424	-	-	-
400	99.0	1.421	-	-	-
0	4.0	1.000	0	4.0	1.106**

**Reference 3

TABLE 4

Concentration (g. U/l. soln.)	LOS ALAMOS Density (30°C.) (g./cc.)	ORNL Density (30°C.) (g./cc.)
400	1.52	1.46
200	1.26	1.23

Agreement is within the 10% error which is believed to be the maximum error in the ORNL measurements.

HEAT CAPACITY

The mean heat capacity of a substance is defined by the equation

$$\bar{c}_p = \frac{H_2 - H_1}{T_2 - T_1} \bigg|_{p = \text{constant}}$$

where $\bar{c}_p$ is the mean heat capacity, $H_2 - H_1$ is the difference in heat contents of the substance at temperatures T_2 and T_1 , and p is the pressure.

The heat capacity of the uranyl sulfate solutions was determined by dropping a sealed steel capsule containing the solution from a tube furnace at a known temperature into a modified Bunsen calorimeter which contained ice and water. Any heat absorbed by the calorimeter resulted in a volume reduction in the ice-water mixture because of the isothermal melting of some of the ice. The change in heat content of the capsule and sample, as it cooled in the calorimeter, was measured by observing the volume change in a burette assembly connected to the calorimeter. The change in heat content of the sample was obtained by subtracting the change in heat content of the empty capsule from the total observed change in heat content.

Because the temperature range studied in this investigation was small, no attempt was made to find the effect of temperature on the heat capacity of the uranyl sulfate solutions. The values given are mean heat capacities in that they represent the average quantity of heat required to raise one gram of the solution one degree centigrade in temperature over the temperature range indicated in Table 5. The variation of the mean heat capacity with concentration was similar to the variation evidenced by most electrolytes in that the mean heat capacity decreased with concentration.

680-13

TABLE 5
HEAT CAPACITY

H ₂ O - UO ₂ SO ₄ SOLUTIONS				D ₂ O - UO ₂ SO ₄ SOLUTIONS			
CONCENTRATION (g. U/l.SOLN.)	TEMPERATURE °C	ΔH_f° (cal/g.°C)	C _p (cal/g.°C)	TEMPERATURE °C	ΔH_f° (cal/g.°C)	C _p (cal/g.°C)	
100	28	25.2	0.90	26	23.5	0.90	
100	28	28.6	1.02	47	39.5	0.84	
100	-	-	-	103	79.4	0.77	
100		Cp (Average)	0.96		CP (Average)	0.84	
200	28	20.9	0.75	26	20.2	0.78	
200	31	21.0	0.68	85	75.0	0.88	
200	55	42.2	0.77	87	71.9	0.82	
200	56	40.1	0.72	-	-	-	
200		Cp (Average)	0.73		Cp Average)	0.83	
400	28	15.6	0.55	46	34.4	0.75	
400	28	18.0	0.64	67	47.4	0.71	
400	57	36.6	0.64	79	58.9	0.74	
400	58	36.4	0.63	-	-	-	
400		Cp (Average)	0.61		Cp (Average)	0.73	

HEAVY WATER SOLUTIONS OF URANYL SULFATE VS LIGHT WATER SOLUTIONS

The density and viscosity of the heavy water solutions of uranyl sulfate compare with the corresponding properties of the ordinary water solutions in the same manner as the properties of the pure liquids compare, e.g., the density of the heavy water solution is greater than the density of the ordinary water solution for the same temperature and concentration. For the surface tension and heat capacity values, the above generalization is apparently not true. For example, the surface tension of D₂O relative to H₂O at 25°C is 0.99946 (see Reference 3). The relative heat capacity, $\frac{D_2O}{H_2O}$, at 280° K. is 1.115 and at 295° K. 1.100 (see Reference 3).

CHEMICAL ANALYSIS OF THE SOLUTIONS USED

A chemical analysis of the UO₂SO₄ used in preparing solutions for this investigation gave the results listed in Table 6.

TABLE 6

July 26, 1951

Sample: Batch 42055-1
 UO₂SO₄ (Mall. oxide)
 No acetone ppt.
 Duplicate samples (50 ml. each)

Total Uranium	<u>T-66</u>	<u>T-67</u>
	567.3 mg./ml.	565.1 mg/ml.
NO ₃	0.70	1.12
SO ₄	223.9	222.6
NH ₄	0.03	0.03
ph(0.1M)	2.52	2.52
Density	1.757	1.756
SO ₄ /U	0.98	0.98
U(IV)	< 0.1	< 0.1

LITERATURE CITATIONS

1. Kennedy, J., "Chemistry of Uranium and Plutonium," Los Alamos Scientific Laboratory, Report No. LA-1017 (Chapter 7) (1947)
2. Lange, N. A., "Handbook of Chemistry," 3rd Edition, p. 1346-7, Handbook Publishers, Inc. Sandusky, Ohio (1939)
3. "Project Handbook," Chapter II, Vol. I, k.p. 1.