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SUMMARY

The program for the measurement of the physical properties of aqueous uranyl sulfate solutions is well under way. The preparation and analysis of pure uranyl sulfate solutions is under close investigation since small errors can make big differences in the physical properties. Good check results are being obtained on the analysis of both uranyl ion and the sulfate ion.

Equipment has been designed and ordered for the surface tension, vapor pressure, viscosity, and density determinations at elevated temperatures and pressures. Some delays in construction by suppliers are anticipated because of shortages of critical materials and large backlogs of orders.

Measurements of viscosity, density, and refractive indices have been made at 20° and 30°C and work is continuing at higher temperatures.

Surface tension work is incomplete at 20°C but some of the results are reported.

Work is under way on the preliminary measurements of the vapor pressure of uranyl sulfate solutions at temperatures below 100°C.

INTRODUCTION

The physical properties of aqueous uranyl sulfate solutions have not been studied extensively to this date. With the increased interest in uranyl sulfate, a program has been undertaken to measure all the physical properties possible from room temperatures to 300°C and from atmospheric pressure to 2,500 pounds per square inch. This program has been divided into two parts, with one phase being that up to 90°C at atmospheric pressure, and the others being carried out at elevated temperatures and pressures. The first is well under way while the latter is lagging because of delays in the delivery of specially constructed equipment for the pressure work.

DETAILED REPORT

Preparation of Uranyl Sulfate Solutions - L. V. Jones

The uranium trioxide, obtained from the Mallinckrodt Chemical Company, contains a small amount of undecomposed uranyl nitrate. The nitrate and any other impurities that may have crept into the oxide are removed by the following procedure: the trioxide, as received, is screened through a No. 60 sieve. The oxide appears to contain an appreciable amount of black foreign matter, probably uranium oxide, U_3O_8 , which has a larger particle size and is retained on the screen. The screened oxide is thoroughly washed at a temperature of 80° to 90°C for three days with the wash water being changed each morning by decantation. It is screened again through the No. 60 sieve after being dried for 24 hours at 103° to 105°C.

The formula, uranium trioxide monohydrate, was used to determine the amount required to react stoichiometrically with sulfuric acid. Thus, a batch of uranyl sulfate was prepared by adding 5 moles of purified uranium trioxide to 5 moles of 3 molar sulfuric acid while it is vigorously stirred and heated. When the oxide is completely dissolved, the solution is filtered through a fritted-glass filter, cooled, and analyzed in triplicate for uranium and sulfate. The uranium is determined by evaporating a weighed portion of the solution to dryness followed by ignition to U_3O_8 . The sulfate is determined gravimetrically

as barium sulfate. A calculated amount of uranium trioxide or sulfuric acid is added so that the uranium-to-sulfate ratio of the final solution is 1.000 ± 0.002 .

In an attempt to check the reliability of the classical method for sulfate, five solutions of uranyl sulfate were prepared by the reaction of sulfuric acid of a known concentration with uranium trioxide. Each solution prepared contained the same molar concentration of sulfate ion. A sixth solution of sulfuric acid of the same molar concentration as the other five solutions was also prepared. Each of the solutions was analyzed for sulfate content according to the procedure outlined by Kolthoff and Sandell.¹ The quantity of uranyl sulfate taken for analyses was weighed instead of being measured volumetrically. The barium sulfate was digested on a steam bath overnight before filtration. The results obtained are shown in Table I. The agreement between the calculated and analyzed results is excellent. However, experiments will be continued to study the effects of standing and the effects of increased uranyl concentration.

The density of each solution was measured by a Mohr-Westphal balance. Figure 1 is a plot of the density versus the ratio of the uranyl ion to the sulfate ion concentrations. From the slope of the curve, it has been calculated that, at 1.53 molar uranyl sulfate concentration, a change of 0.001 in the ratio of uranyl to sulfate ion makes a difference of 0.0004 in the density. This points out the importance of good analytical methods for the determination of uranyl and sulfate ion as well as the need for precisely preparing the solutions for physical investigation.

The Viscosity of Uranyl Sulfate Solutions at High Temperatures and Pressures - *J. R. Heiks*

The viscosity determinations of aqueous uranyl sulfate solutions at elevated temperatures and pressures will be determined using the Lawaezeck type² (falling plummet) viscometer described in the last quarterly report.³

It was thought advisable to design a second method for the determination of viscosity to be used in case of some unforeseen difficulty with the Lawaezeck viscometer or as a check method. An investigation of the literature revealed that the rolling-ball viscometer provides the most satisfactory alternate method. This is true because the present Lawaezeck viscometer could be converted into a rolling-ball viscometer with very few changes. In addition, the latter is simple to operate, and provides an absolute measure of viscosity by a well established method which has been used by numerous investigators. An undesirable feature is that the rolling-ball viscometer is considerably more difficult to calibrate than the falling-plummet type. The rolling-ball viscometer was first used by Flowers,⁴ but, more recently, theoretical work has been done by Hubbard and Brown⁵ and others.^{6, 7, 8, 9}

The following are the modifications that would be necessary to convert our present viscometer into a rolling-ball viscometer:

1. Arrangements must be made to lock the viscometer at a desired angle (approximately 15° from horizontal).
2. The timing unit must be remounted to correspond to angle of viscometer.
3. A stainless steel ball of appropriate size plugged with a 10-millicurie cobalt-60 source must be obtained.

These minor modifications can be made in the present viscometer in a relatively short period of time. Thus, it is feasible to make check runs by two independent methods at high temperatures and pressures with a minimum of effort.

The Density of Uranyl Sulfate Solutions at High Temperatures and Pressures -

L. V. Jones and J. R. Heiks

As a result of a literature search, the measurement of the densities of uranyl sulfate solutions at elevated temperatures and pressures appears to be best accomplished by a displacement method since the determination of the weight of a known volume of the solution at a pressure of 2,000 pounds per square inch and a temperature of 250°C becomes impractical. In addition, the requirement that the solution must be saturated with oxygen under these conditions eliminates all but the displacement method.

In the application of this method, a quartz bob is attached to an elastic quartz helix and mounted in a long thermostated tube which contains the fluid under investigation. The density of the medium can be found from the change in length of the helix which has been calibrated with a standard solution.

The accuracy of this method is limited by the precision of the temperature and pressure control as well as by the precision of measurement of the extension of the helix. However, Wagner, Bailey, and Eversole¹⁰ employed this method to determine the density of water. They reported the density to within ± 0.00003 over the temperature range from 10° to 35°C. This high accuracy will not be obtained under the conditions of high temperature and pressure which is required by our work because the temperature control will be $\pm 0.5^\circ\text{C}$, pressure measurement will be $\frac{1}{2}$ to 1 per cent, and extension of the helix will be measured to ± 0.02 millimeter.

A diagram of the apparatus to be used is shown in Figure 2. The solutions will be saturated with oxygen in the mixing chamber in the upper right hand corner of the oven while the measurements will be made in the measuring chamber.

A glass mock-up of the tube to contain the quartz spiral and sinker will be constructed for preliminary runs. The Mound Laboratory Quartz Fiber Group will construct quartz spirals of varying size to cover the range of densities anticipated. They will be calibrated by measuring the extension with known weights over the entire temperature range of this investigation.

The Viscosity, Density, and Refractive Index of Uranyl Sulfate Solutions at Low Temperatures and Atmospheric Pressures - J. Jegart and J. R. Heiks

DENSITY

The preliminary work was done with a modified Sprengel-Ostwald pycnometer calibrated with doubly distilled water. Some difficulty was found in filling these at the higher concentrations. Hence, for the more accurate measurements, a new design, which is easier to fill is being used. The difficulties experienced with the pycnometer at high concentrations and temperatures have led to a change to the Mohr-Westphal balance with a quartz bob for determination of densities. An analytical balance is being altered for this purpose, but, in the meantime, less precise data are being taken with the usual classroom-type balance. The data taken at 20° and 30°C with this balance is listed in Table II.

Check results with a pycnometer are shown in the fourth column with the average deviation obtained. A graph of these results is shown in Figure 3. A determination of the slopes of 20° and 30°C density curves were found to be 0.3166 and 0.3146, respectively.

VISCOSITY

The absolute viscosity data for several uranyl sulfate-water solutions at 20° and 30°C ± 0.05°C are listed in Table III and are shown graphically in Figure 4. These data were obtained using a 5-milliliter Ostwald viscometer, double-distilled water being used for calibration. The time of flow was measured with a stop watch. The average of three determinations was chosen as the flow time for both the calibration and the solutions under investigation.

The absolute viscosity of these solutions were obtained using the following equation:

$$N = N_o \frac{\rho t}{\rho_o t_o}$$

where:

N = absolute viscosity of solution.

N_o = absolute viscosity of water.

ρ = density of solution.

ρ_o = density of water.

t = flow time of solution.

t_o = flow time of water

REFRACTIVE INDEX

The refractive indices of 10 uranyl sulfate water solutions were obtained at 20° and 30°C ± 0.05°C using an Abbe' refractometer. These data are listed in Table IV and are represented graphically in Figure 5.

The Surface Tension of Uranyl Sulfate Solutions Saturated with Oxygen at Elevated Temperatures and Pressures - *M. K. Barnett*

The surface tension of aqueous uranyl sulfate solutions saturated with oxygen at elevated temperatures and pressures is to be measured by the capillary-rise method.³ The original plan called for saturating the solution and making the measurement in a single vessel, but this has been abandoned in favor of a two-vessel system illustrated in Figure 6. The system to be used will be similar to that employed by Swartz¹¹ in his study of the influence of dissolved gases on the surface tension of petroleum. The measuring vessel is represented in detail in Figure 7.

In the two-vessel system, the necessity for rocking the measuring vessel, incurring troublesome drainage problems, and possibly disturbing the capillary tube position will be avoided. A further advantage of the two-vessel design is the possibility which it provides of controlling the quantity of solution in the measuring vessel and thus bringing the capillary meniscus to the same point in the tube each time. A knowledge of the radius at this point only will then be required.

Because of the sensitivity of surface tension to temperature fluctuations, electrical heating jackets have been abandoned as a means of temperature control in favor of a large oven of the forced-convection type in which the entire apparatus will be placed. These ovens can be controlled to $\pm 0.5^\circ\text{C}$ at 260°C .

In making a run, the solution will first be introduced into the mixing vessel and saturated with oxygen at the desired temperature and pressure. It will then be drained by gravity into the measuring vessel where the capillary tube will be thoroughly flushed with solution. The menisci will be observed through the windows with a cathetometer from time to time until equilibrium is reached. The final equilibrium value for the capillary rise may be obtained from an enlarged photograph of the menisci. After completion of the measurement, the solution will be returned to the mixing vessel by gas pressure. Oxygen will then be introduced until the next higher pressure is attained and the solution resaturated at the new pressure, whereupon the measurement will be repeated as before.

Surface Tension of Aqueous Uranyl Sulfate Solutions at Low Temperatures and Atmospheric Pressure - M. K. Burnett

The surface tension of aqueous uranyl sulfate solutions in contact with air at 20°C has been determined by the capillary-rise method. The rises were measured with a cathetometer relative to an uninterrupted surface approximately five centimeters in diameter. The capillary tube was calibrated by introducing varying quantities of pure benzene into the apparatus and observing the capillary rise.

The surface tension, γ , was calculated from the equation

$$\gamma = \frac{1}{2} (h + r/3) dgr$$

where h is the capillary rise, r the radius of the capillary, d the density of the solution and g the acceleration due to gravity. Enlarged photographs of the solution meniscus have indicated a zero angle of contact between solution and glass.

The results are given in Table V and formulated graphically in Figure 8. The curve intersects the ordinate of zero concentration approximately at the accepted value of the surface tension of water.

The Vapor Pressure of Uranyl Sulfate Solutions - W. C. McCluggage

The vapor pressures of uranyl sulfate solutions are quite an important property on which measurements must be made since no data exists at elevated temperatures and pressures.

A study of the vapor-pressure lowering of an aqueous solution of a bivalent salt, such as magnesium sulfate,¹² has shown that for a 3-molar solution at 100°C we might expect a vapor-pressure lowering of 45-millimeters of mercury. No information is at hand for uranyl sulfate solutions at elevated pressure, but if we assume that the vapor pressure is the same order of magnitude, it would be necessary to measure it with an accuracy of 0.05 per cent at a total pressure of 1,500 pounds per square inch to detect any lowering. For this reason, a differential-pressure measurement apparatus has been chosen since a pressure difference of 0.5 millimeter can be measured. It is planned to use a differential manometer system, as described by Weissberger,¹³ in which the difference in levels of mercury or some other heavy liquid in the two arms of the manometer can be observed. Thus, the uranyl sulfate solution can be compared directly with the reference liquid. For preliminary measurements on pressures up to atmospheric, an all-glass system will be used (Figure 9). The two liquids will be placed in the bulbs attached to the manometer arms. A liquid column extending from each bulb to the mercury surface will permit the manometer to be maintained at room temperature while the temperature of the bulbs may be varied. A correction for the temperature variation along each arm of the manometer and for the differences in densities of the solution and standard must be made.

There is also a strong possibility that this method will be applicable to measuring the vapor pressure of uranyl sulfate solutions under elevated oxygen pressures.

After the apparatus and contents are completely degassed, the bulbs will be evacuated and sealed off. The upper part of the apparatus, including the bulbs will be placed in an air bath and the vapor-pressure difference read at the desired temperatures.

The same design will be used for measurement at temperatures between 125° and 250°C except that the apparatus will be constructed entirely of Type 347 stainless steel. The level of the mercury in the steel manometer will be detected possibly by a cobalt-60 source which will be floated on the surface of the mercury or by the change in intensity of a beam of gamma rays as it moves down the steel column and passes the mercury solution interface.¹⁴

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TABLE I
THE EFFECT OF THE RATIO OF $U:SO_4$ ON
THE DENSITY AND SULFATE ANALYSES

CONCENTRATION OF URANIUM (moles/liter)	CONCENTRATION OF SULFATE (moles/liter)	DENSITY (grams/liter)	CALCULATED SULFATE (per cent)	ANALYZED SULFATE (per cent)
0	1.53	1.0900	13.48	13.48
1.27	1.53	1.4037	10.47	10.47
1.39	1.53	1.4300	10.28	10.26
1.53	1.53	1.4642	10.04	10.02
1.68	1.53	1.4993	9.80	9.77
1.84	1.53	1.5377	9.56	9.57

TABLE II
DENSITY OF URANYL SULFATE SOLUTIONS
NEW SOLUTIONS RATIO 1:1.0011

CONC. (moles/liter)	WESTPHAL BALANCE DENSITY		PYCNOMETERS DENSITY (20°C)
	(20°C)	(30°C)	
0.174	1.0543	1.0521	
0.436	1.1381	1.1341	
0.644	1.2028	1.1986	
0.827	1.2614	1.2567	
0.986	1.3127	1.3068	1.3144
1.233	1.3911	1.3839	
1.406	1.4440	1.4383	
1.604	1.5072	1.5026	
1.792	1.5658	1.5610	
2.473	1.7789	1.7727	1.7789

TABLE III
ABSOLUTE VISCOSITY OF URANYL SULFATE -
WATER SOLUTIONS AT 20° AND 30°C

CONC. (moles/liter)	VISCOSITY IN CENTIPOISES	
	(20°C)	(30°C)
0.174	1.128	0.8901
0.436	1.359	1.063
0.644	1.573	1.231
0.827	1.809	1.403
0.986	2.047	1.572
1.233	2.509	1.921
1.406	2.912	2.218
1.604	3.501	2.641
1.792	4.178	3.145
2.473	8.541	6.256

TABLE IV
REFRACTIVE INDICES OF URANYL SULFATE
SOLUTIONS AT 20°C AND 30°C

CONC. (moles/liter)	REFRACTIVE INDEX	
	(20°C)	(30°C)
0.174	1.3388	1.3378
0.436	1.3469	1.3459
0.644	1.3533	1.3522
0.827	1.3595	1.3580
0.986	1.3640	1.3630
1.233	1.3718	1.3708
1.406	1.3770	1.3755
1.604	1.3829	1.3818
1.792	1.3885	1.3878
2.473	1.4092	1.4088

TABLE V
SURFACE TENSION OF AQUEOUS URANYL SULFATE SOLUTIONS AT 20°C

CONCENTRATION (moles/liter)	SURFACE TENSION (dynes/centimeter)
0.174	72.90
0.436	73.03
0.644	73.46
0.827	73.88
0.986	74.26
1.233	74.88
1.406	75.49
1.604	75.89

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fig 1

FIGURE 1

MLM-663

APPARATUS FOR MEASURING THE DENSITY OF SOLUTIONS AT ELEVATED TEMPERATURES AND PRESSURES.

fig 4

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FIGURE 4

MLM-663

HIGH PRESSURE VESSEL WITH WINDOW FOR MEASURING SURFACE TENSION.

EFFECT OF CONCENTRATION ON SURFACE TENSION OF
URANYL SULFATE SOLUTION AT 20°C.