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TOPICAL REPORT

SOME PHYSICAL PROPERTIES OF URANYL NITRATE SOLUTIONS

by

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SOME PHYSICAL PROPERTIES OF URANYL NITRATE SOLUTIONS

Boiling points, freezing points, and densities were measured in the concentration range between uranyl nitrate hexahydrate and uranyl nitrate dihydrate. The surface tension of molten uranyl nitrate hexahydrate was determined to be approximately 45 dynes per square centimeter at 90-100°C.

Introduction

Uranium is currently recovered from ore concentrates by solvent extraction of a nitric acid digest slurry and re-extraction into water. The resultant dilute solutions of uranyl nitrate are concentrated by boiling prior to thermal decomposition to uranium trioxide. Knowledge of the boiling points, freezing points, densities, and viscosities of highly concentrated uranyl nitrate solutions is necessary to determine engineering and design criteria for their handling.

A literature survey yielded much information on physical properties of the uranyl nitrate - water system for concentrations up to uranyl nitrate hexahydrate (47.4 weight per cent uranium), but only limited data were found for the range above this concentration. A representative bibliography appears at the end of this report.

The concentration range between uranyl nitrate hexahydrate and uranyl nitrate dihydrate (47-55 weight per cent uranium) is of special concern. It is known that beyond the hexahydrate concentration, both the boiling points and freezing points increase very rapidly, and, in fact, appear to converge at the composition corresponding to uranyl nitrate dihydrate. The magnitude of the temperature range between freezing and boiling points is a critical factor in maintaining solutions in the liquid state during transfer.

Experimental and Results

The material used in this investigation was Mallinckrodt Chemical Works Uranium Division's plant-purified uranyl nitrate hexahydrate. Uranyl nitrate dihydrate was prepared by drying the hexahydrate and storing under vacuum. Analysis of starting materials indicated hydrates corresponding to the hexahydrate and the dihydrate to within 0.5 to 1.0 per cent of the stoichiometric ratio. Uranium was determined gravimetrically by ignition to the oxide, U_3O_8 .

The freezing point was defined as the temperature at which a solution first produced crystals while cooling. For a series of low uranium concentrations (essentially all solutions at room temperature) the freezing points were determined in a glass flask (under reflux to maintain atmospheric pressure), the temperature of which was carefully varied by means of a Glass-Col heating mantle. For higher uranium concentrations a tube containing the material was immersed in an oil bath, employed as a heat transfer medium for slow and uniform temperature change. Additional freezing points were derived from samples removed at various boiling points during batch decomposition of uranyl nitrate hexahydrate. Freezing point data appear in Table I.

Table I
Physical Properties of Uranyl Nitrate Solutions

Uranium wt per cent	Density g/cc	Temperature of Measurement °C	U Concentration (calculated)		Freezing Point		Boiling Point	
			g/ml	lbs/gal	°C	°F	°C	°F
32.4	1.753	25	0.57	4.74	14	57	106.5	224
	1.746	40						
	1.714	81						
	1.702	98						
33.1	1.786	23	0.59	4.93	20.2-20.6	69	107.8	226
	1.768	46						
	1.751	80						
	1.729	108						
34.2	1.828	23.3	0.62	5.22	23.2	75	110	230
	1.827	28						
	1.815	42						
	1.791	76						
	1.778	96						
	1.762	110						
35.94	1.885	35.7	0.68	5.65	31.9	90	-	-
45.72	2.36	57	1.1	9.01	57	135	117	243
46.5	2.40	60	1.1	9.31	59	138	119	246
46.7	2.68	25	1.2	10.44	61	142	121	250
47.4	2.465 ^a	-	1.2	9.75	60	140	120	248
49.1	2.59 ^a	-	1.3	10.5	73	163	122	252
53.1	2.86 ^a	-	1.5	12.6	-	-	145-150	293-302
55.1	3.03 ^a	-	1.7	13.95	175-180	347-356	180-4	356-363
55.3	3.16	-	1.7	14.5	181-184	358-363	184-6	363-7
	3.04 ^a	-	1.7	14.05				

Data from UNH decomposition								
48.0	2.50 ^a	-	1.2	10.0			121	250
49.6	2.60 ^a	-	1.3	10.8			123	253
49.7	2.60 ^a	-	1.3	10.8	85	185	125	257
50.2	2.64 ^a	-	1.3	11.1	100	212	129	264
50.8	2.68 ^a	-	1.4	11.4			130	266
51.4	2.71 ^a	-	1.4	11.6			136-7	277-9
51.7	2.74 ^a	-	1.4	11.8	108	226	139	282
52.4	2.79 ^a	-	1.5	12.2	111	232	143	289
52.5	2.80 ^a	-	1.5	12.3			147	297
52.6	2.81 ^a	-	1.5	12.3			146	295
53.0	2.85 ^a	-	1.5	12.6			152	305
53.3	2.88 ^a	-	1.5	12.8	112	234	152	306
53.5	2.89 ^a	-	1.5	12.9			154	309
53.7	2.90 ^a	-	1.6	13.0			156	313
54.1	2.93 ^a	-	1.6	13.2	130	266	166	331
54.2	2.94 ^a	-	1.6	13.3			162	324
54.2	2.94 ^a	-	1.6	13.3	132	270	164	327
54.3	2.96 ^a	-	1.6	13.4			169	336
54.6	2.97 ^a	-	1.6	13.5			171	340
54.7	2.98 ^a	-	1.6	13.6	160	320	172	342
54.9	2.99 ^a	-	1.6	13.7			173	343

^a Indicates densities assumed

The boiling point was defined as the temperature at which either the first bubbles appeared during heating or the last bubbles appeared during cooling of a solution or melt. During batch decomposition of the hexahydrate, samples were removed at various boiling points and analyzed for uranium content. Five separate batches of material were subjected to decomposition. Again, an oil bath was used as a controllable heat source. Other boiling points were measured for solutions maintained under reflux. Boiling point data also appear in Table I.

All freezing points and boiling points which were determined are plotted as a function of uranium concentration in Figure 1. The measured values have been combined with values derived from the literature. Selection of data from conflicting sources was made by choosing those points which best fit a smoothed curve.

The measurement of densities of uranyl nitrate solutions as a function of temperature was accomplished by weighing the contents of a calibrated pipet. Densities of uranyl nitrate compositions which are solids at room temperature were determined by volume displacement in pycnometers. All data for densities agree with those found in the literature and are ~~xxx~~ tabulated in this report.

Viscosities in the range hexahydrate-dihydrate were determined. A Brookfield Synchro-lectric viscometer which was standardized against distilled water was used. The values measured were in the lowest available, that is, least sensitive, range of the instrument. Nevertheless, the values obtained for viscosity and temperature variation of viscosity compared favorably with literature values. A viscosity of about 19 centipoises was indicated for the hexahydrate at 85°C and about 31 centipoises for a solution of approximately the trihydrate composition at 159°C. A No. 1 spindle at 20 rpm on the 100 scale was used for these measurements.

In addition, the surface tension of uranyl nitrate hexahydrate was measured. Using a Du Nöuy tensiometer, a value of approximately 45 dynes per square centimeter was found for the molten hexahydrate at 90-100°C. The instrument was standardized against water and acetone.

Discussion

Uranyl nitrate solutions exhibit a very marked tendency to superheat and to supercool. For this reason it is somewhat difficult to determine accurately a precise temperature of physical change. Concentrations above the hexahydrate are especially difficult to examine experimentally. The molten salts exhibit no sharp freezing point breaks as would be evidenced in normal cooling curves. Differences of several degrees may be observed in successive measurements of the temperature of first crystallization of the same solution. The best freezing point values were obtained by repeated determinations at close to equilibrium conditions. The estimated precision of the experimental results varied from $+1^{\circ}\text{C}$ for systems having concentrations less than 48 wt percent uranium to about $+5^{\circ}\text{C}$ for systems having concentrations above 48 wt percent uranium.

Another difficulty is encountered in maintaining equilibrium conditions with respect to hydrate water during determinations. During heating the crystals lose water before a definite phase change occurs. Water vapor pressure becomes appreciable, as is evidenced by the formation of condensate on the walls of the container. Thus, even keeping a system under reflux does not always insure constant composition throughout a measurement.

Examination of the boiling point curve in Figure 1 will indicate another difficulty. When a boiling point of 155-160°C is reached (note the greater slope above the inflection corresponding to the trihydrate of 53.1 weight per cent uranium), the dehydration becomes more rapid due to the very fast rise of the boiling point and change in composition with temperature. In this region the solution changes in color from yellow to deep orange; the temperature range between the melting and boiling points narrows; and the material becomes difficult to handle or to sample. Apparent recrystallization is sometimes observed, and homogeneity is probably not maintained.

No evidence of NO_2 fumes is observed below the dihydrate composition. Upon heating the dihydrate to approximately 180°C, evolution of $\text{H}_2\text{O}_{(g)}$ and $\text{NO}_{2(g)}$ are seen during boiling and immediately after the first indication of melting. At this composition there is no longer a significant difference between the boiling and melting temperatures, allowing no finite temperature range for the existence of a solution. Decomposition readily occurs in this range.

The investigations presented in this report were undertaken for the purpose of providing working data for plant engineering and design. Hence, the data are not intended to be of a higher degree of accuracy than such usage warrants or necessitates.

For plant use, all data were converted to units commonly used by plant engineers. Literature values for densities were assumed and extrapolated in order to convert weight per cent to pounds of uranium per gallon. Curves were drawn to fit freezing point, boiling point, and density data, particularly in the region between the hexahydrate and the dihydrate.

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