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Summary

Portions of two samples of HRT fuel solutions were sealed in silica capillary tubes approximately three weeks after they were removed from the reactor and the temperature at which each solution separated into two liquid layers was determined. The values found, $325 \pm 1^\circ\text{C}$. for one sample and $326 \pm 1/2^\circ\text{C}$. for the other, are slightly lower than predicted from experiments with synthetic fuel solutions ($329-330^\circ\text{C}$.) but the discrepancies are small enough so that they could be accounted for by minor differences in composition between the synthetic and reactor fuel solutions. There appears to be little reason to believe that the high radiation level which the fuel solution is exposed to in the reactor has a significant effect on its phase behavior, at least after it has cooled to 2R per ml. Dilution of fuel solution with 8 volume per cent of 30% H_2O_2 (which decomposes to produce O_2 pressure) and with the same amount of H_2O increased the two-liquid phase formation temperature about 2°C . but increasing the free D_2SO_4 concentration from about 0.017 M to 0.04 M raised the immiscibility temperature 19° to 345°C .

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PHASE STABILITY OF HOMOGENEOUS REACTOR HOT FUEL SOLUTIONS

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Introduction

One of the fundamental assumptions involved in the operation of the homogeneous reactor is that the phase behavior of the fuel solution in an operating reactor is the same as that of a nonradioactive solution having the same composition. Since there is some doubt whether this assumption is completely valid, portions of two samples of radioactively hot fuel solution were observed at high temperature in sealed silica tubes approximately three weeks after their removal from the HRT during power operation. This report gives the results of these observations.

Experimental

Sample History and Analysis. Sample RFH20-168 was removed from the reactor on July 4, 1959, at 11:15 a.m. with the reactor operating at heat-loss power (250-300 kw). The reactor had been at this level for 8-1/2 hours before sampling. Before that, the reactor had operated at 1.7 Mw for 36 hours.

Sample RFH20-173 was removed from the reactor at 10:30 a.m. on July 5, with the reactor operating at 1.87 Mw. The reactor had been at that power level for 6 hours before sampling. Before that, it had been at 1.0 Mw for

2-1/2 hours and prior to that at heat-loss power for 24 hours. Table I contains analytical data as reported on these samples.

Table I
Analysis of HRT Solutions

Sample No.	Date Analyzed	Analysis - Ave. of Duplicate Detns.				Normality
		mg./ml.				
		U	Cu	Ni	SO ₄	Free H ⁺
RFH20-168	July 23	7.30	0.951	0.441	6.97	0.038
RFH20-168	July 4	6.95	0.904	0.424	6.63	0.041
RFH20-173	July 5	6.71	0.880	0.430	6.47	0.037

The increase in concentration of sample RFH20-168 between July 4 and July 23, is probably due to escape of D₂O vapor from the screw-capped sample container. The high radiation level of the solution when it was first obtained could have maintained the solution at a temperature appreciably above that of the room in which it stood. On July 23, the radiation level was down to about 2 roentgens per ml. on direct contact with the glass container. The sealed capillary tubes containing about 0.06 ml. of solution read approximately 200 mr. on direct contact. Sample RFH20-173 was not re-analyzed but since both samples were stored in the same type of container for approximately the same length of time, it is probable that it had increased in concentration to a similar degree.

A small amount of solid material was observed in the bottom of both sample containers. A portion of the clear, supernatant liquid was transferred from the RFH20-173 sample container to a small test tube to eliminate the possibility of getting solid material into the capillary tubes.

Experimental Technique. The operation of sealing portions of the hot fuel samples in silica capillary tubes, which was performed in a hood in the HR analytical laboratory of Building 3019, was carried out in the same manner as for nonradioactive solutions. Approximately 50% of the volume of the capillary tube was filled with liquid at room temperature. The sealed tubes were heated in a molten nitrate bath contained in a stainless steel box fitted with glass windows. The capillary tube containing the sample solution was suspended in the bath from a Vibra-tool used to agitate the tube which was illuminated by means of a microscope lamp and viewed with the help of a special telescope (Bausch and Lomb Baliscope). The rate of temperature increase of the bath was regulated by means of a Variac controlling the voltage applied to a Calrod heater in the bath and its temperature was measured with an iron-constantan thermocouple connected to a recorder having a sensitivity of .02 millivolts per scale division, equivalent to about $1/3^{\circ}\text{C}$. The bath temperature was slowly increased after the tube was inserted and the temperature at which the solution separated into two liquid layers was noted. The bath was then allowed to cool slowly and the temperature at which the heavy layer disappeared was also determined. This procedure was repeated for a number of samples. Only the temperature of appearance of the second

liquid phase is reported since this is considered to be the most sensitive indication of the true temperature of two-liquid phase formation. Actually, however, the spread between appearance and disappearance temperatures is usually less than 1°C . After this temperature had been determined, the tubes were cooled rapidly to room temperature by removing them from the hot bath and immersing them in water. They were then wiped dry and examined under a low-power microscope.

Results. The temperatures at which various portions of hot fuel solutions separated into two liquid phases are listed in Table II. Some observations on solid formation in these experiments are included in the following section.

Table II

Temperatures of Formation of Two-Liquid Phases
in HRT Hot Fuel Solutions

<u>Sample No.</u>	<u>Tube No.</u>	<u>Two-Liquid Phase Temp. °C.</u>	<u>Remarks</u>
RFH20-168	1	320.5 - 321 - 321	Small amt. colorless ppt.
RFH20-168	2	324.5 - 325 - 325	Small amt. colorless ppt.
RFH20-168	3	326 - 326	Small amt. colorless ppt.
RFH20-168	4	314 - 314	
RFH20-168	5	325	
RFH20-168	6	324	
RFH20-173	I	-	11 parts fuel:1 H ₂ O ₂ *
RFH20-173	II	328.5 - 328.5	12.5 parts fuel:1 H ₂ O ₂ *
RFH20-173	III	345.5	14 parts fuel:1.3 D ₂ SO ₄ **
RFH20-173	IV	345.5	18 parts fuel:1.5 D ₂ SO ₄ **
RFH20-173	V	329.5 - 328.5	18 parts fuel:1.5 H ₂ O
RFH20-173	I'	327 - 326.5	Undiluted fuel from transferred sample.
RFH20-173	II'	327 - 328.5 - 327	Undiluted fuel from transferred sample.
RFH20-173	III'	326 - 326	Undiluted fuel from original sample.
RFH20-173	IV'	326	Undiluted fuel from original sample.

*30% H₂O₂

**0.2925 M D₂SO₄

Discussion

There appears to be no unambiguous explanation for the large variation in two-liquid layer temperatures observed with sample RFH20-168. The four-degree spread between the first two tubes is much larger than the spread between results shown in Table II for individual tubes. The sample solution was stirred just before the second pair of tubes (3 and 4) were prepared and it is possible that the very low result obtained with Tube No. 4 resulted from the inclusion of a solid particle in the solution in the capillary tube (approximately 0.06 ml volume) which subsequently dissolved in the high temperature liquid. A rough calculation indicated that the solution contains only about 0.9 mg of solid material ($\text{UO}_2\text{SO}_4 + \text{CuSO}_4 + \text{NiSO}_4$) so that a comparatively small particle would produce a substantial increase in solute concentration. The last two tubes prepared from this sample solution, which were prepared after the solution had stood for several hours without further stirring, gave more consistent results. Since four of the six tubes gave results in the range 324 to 326°, 325 ± 1° is believed to be the best value for the two-liquid phase temperature for this solution. A very small amount of solid material was observed at high temperature in all of the tubes prepared from this solution. The quenched samples contained some colorless precipitate when they were quenched to temperatures substantially below the two-liquid phase temperature.

A binocular microscope was used to observe the tubes which were placed on a blue background. After observing at room temperature a tube containing clear liquid (but including the few colorless particles) for a few seconds,

finely divided red particles would suddenly appear in the solution and on the tube surfaces. These red particles were very small and would not settle easily. They appeared as a reddish haze to the naked eye. After 16 to 24 hours at 25°C. the red particles redissolved. Apparently, the red haze is not present at elevated temperature nor is it stable at 25°C. but is perhaps due to some metastable phenomenon related to the quick quenching.

An attempt to prepare larger amounts of red solid by heating 3 ml. of a synthetic solution in an 8 mm. I.D. silica tube to 329° for 17 hours, and then dropping the tube in ice water failed to produce any solid. In this experiment there is a very large liquid volume to tube surface area ratio compared to all previous experiments in 1 mm. I.D. silica tubes. If corrosion of silica is a factor in the precipitation of solid then the lower volume-area ratio would minimize this effect. Also, the cooling rate by quenching is very much slower than a similar rate for 1 mm. I.D. tubes. If, indeed, rapid cooling is an important factor in the production of red haze then this slower rate might explain the failure to find solid..

It has been previously reported (W. L. Marshall, et al., HRP Quarterly Progress Report, ORNL 2696, p. 208, January 31, 1959) that the appearance of this reddish haze, identical in mode of formation, and believed to be a metastable phenomenon, is prevented by an oxygen overpressure. To test this report, a small amount (about 7 or 8% by volume) of 30% H_2O_2 was added to two portions of RFH20-173 (Tubes I and II). An equal amount of water was

added to a third portion of this sample (Tube V) as a check on the dilution effect of the water added with the H_2O_2 . A precipitate, presumably UO_4 hydrate, was noted in the tubes containing H_2O_2 at room temperature, but this precipitate decomposed and dissolved before the two-liquid phase separation temperature was reached. However, as a result of the precipitation and redissolving of the uranium, a concentration gradient existed within the length of the sample solution so that the two liquid phase temperature was much lower at the bottom of the tube than at the top. The tube was allowed to stand in the bath at a minimum temperature of 276°C . overnight in an effort to eliminate the concentration gradient but it was found to contain an appreciable amount of colorless solid material which could be due to reaction with the SiO_2 tube; consequently no effort was made to determine the two-liquid phase temperature with this tube. The second tube with added H_2O_2 showed behavior on heating similar to that of the first tube but it was allowed to stand inverted overnight at 25°C . rather than 276°C . which seemed to eliminate the concentration gradient and no precipitate was observed. When this tube was quenched from about 327°C , no red haze was observed in the tube but a small amount of the unidentified colorless precipitate was found in the tip of the tube. No difference was found in the two-liquid phase temperature for the solution diluted with H_2O_2 and that diluted with water.

Increasing the free acid content of the solution from about .017 molal to approximately .04 molal resulted in a 19°C . increase to 344°C . in the two-liquid phase separation temperature (Tube III and IV). The reddish haze or

precipitate was absent in the tubes quenched from about 344°C. and only a trace of the colorless precipitate was present. It is thus seen that, in addition to considerably raising the two liquid phase boundary temperature, the excess free acid in solution lends a greater degree of overall stability to the homogeneous reactor fuel.

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