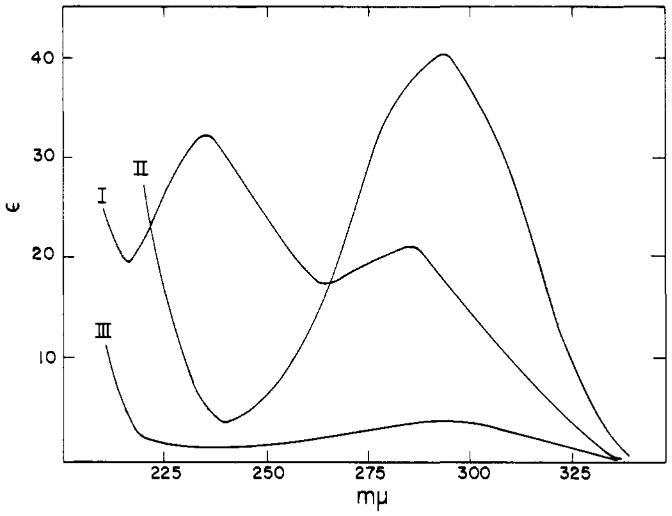

Figure 2. Ultraviolet spectra of chloroacetone (I), 1,1-dichloroacetone (II), and 1,3-dichloroacetone (III); 95% alcohol solvent

EXPERIMENTAL

Materials. Chloroacetone obtained from Eastman Organic Chemicals Department was analyzed by gas chromatography and ultraviolet spectrophotometry. As received, it contained about 2% water, 2% 1,1-dichloroacetone, and 1% of an impurity tentatively identified as mesityl oxide. Distillation of this material was carried out at 110 mm. of Hg pressure. After removal of the water and 1,1-dichloroacetone, a distillation cut boiling at 67° C. was obtained which was assayed at 99.5% purity based on chromatographic tests and chlorine analyses.

1,1-Dichloroacetone was obtained by distillation of a crude sample obtained by overchlorination of the commercial chloroacetone sample above. After a 40% molar excess of chlorine had been passed through the chloroacetone sample maintained at 25–30° C., the resulting crude dichloroacetone contained approximately 6% chloroacetone, 68% 1,1-dichloroacetone, 18% 1,3-dichloroacetone, 6% higher chlorinated acetones, and 2% water. After removal of the water, a fraction boiling at 59° C. at 110 mm. of Hg was obtained with a purity estimated at 99.2%.

1,3-Dichloroacetone was used as received from Eastman Organic Chemicals Department. It was a white crystalline material melting at 41–43° C. and was assayed at 99.5% purity.

Apparatus. The distillation column used was a Nester-Faust annular Teflon spinning band type. Tests with a *n*-heptane–methylcyclohexane mixture showed it to contain about 40 theoretical plates at total reflux. All characterization data were obtained with standard commercial instrumentation as follows: Matronics Model 500 gas chromatograph, Perkin-Elmer Model 21 infrared spectrophotometer, Bausch and Lomb Spectronic 600 ultraviolet and visible spectrophotometer, Sargent Model XXI polarograph.

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Solubility Isotherms for Calcium Fluoride in Nitric Acid Solution

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Solubility isotherms at 24°, 35°, 50°, and 70° C. were determined in the system CaF_2–HNO_3 in the range 0.1 to 10*M* HNO_3.

CALCIUM fluoride is one of several solid compounds produced during the calcination of fluoride containing highly radioactive wastes in the Waste Calcining Facility at the Idaho Chemical Processing Plant (*1*). This solid eventually must be dissolved in decontaminating solutions containing nitric acid during clean-up of the scrubbing system. Inasmuch as solubility values for calcium fluoride in nitric acid at various temperatures did not appear to be available in the literature, solubility values were obtained experimentally at four different temperatures and various concentrations of nitric acid.

EXPERIMENTAL

Reagent-grade anhydrous calcium fluoride (CaF_2), J. T. Baker analyzed reagent containing 0.025% SO_4, 0.01% Cl, 0.002% Fe, and 0.003% heavy metals as the main impurities, was used after heating 48 hours at 105° C. to obtain constant weight. Weighed samples (1 gram) of the dried CaF_2 were then contacted with 50 ml. of nitric acid in the range 0.1 to 10*M* HNO_3 and heated for 170 hours at 24°, 35°, 50°, and 70° C. The test samples, which were contained in polyethylene bottles, were agitated periodically. All samples were filtered through 0.45-micron-diameter pores before

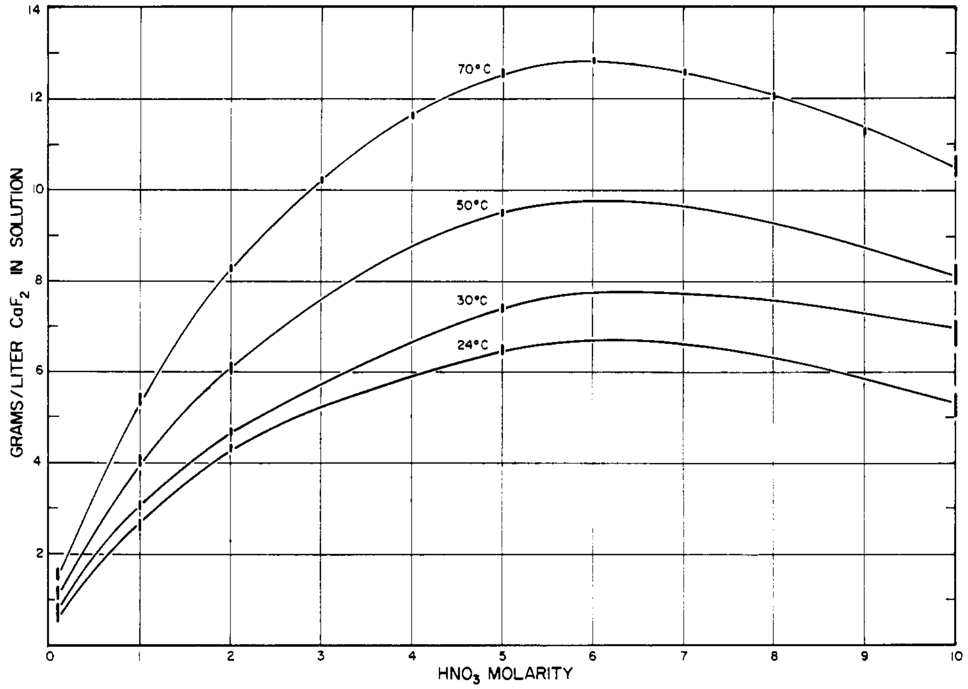

Figure 1. Solubility of CaF_2 in HNO_3 solution

cooling. The residues (undissolved solids) were oven-dried at 105° C. for 48 hours and weighed. The amount in solution was then determined by weight difference. Samples of the supernatant solutions were diluted tenfold to prevent reprecipitation of the dissolved solids, and were then analyzed for calcium by atomic absorption spectrometry.

RESULTS

The solubility isotherms for CaF_2 as a function of nitric acid concentration with temperature as a parameter are shown in Figure 1. These curves were drawn using average values obtained from triplicate samples. The deviations in the measurements are shown graphically in Figure 1. Additional results obtained by determining the concentration of calcium in solution agreed with the values obtained by weighing within ±5%.

Tests were also run at 70° C., using 3, 4, 6, 7, 8, and 9*M* HNO_3 to better define the maximum in the curve. The apparent maximum occurs at 6*M* HNO_3. The reason for the decreasing solubility with increasing acid concentration above 6*M* HNO_3 was not investigated, but was presumed to be due to a "salting-out effect," which is somewhat usual for solubilities involving concentrated electrolyte media.

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Stability Constants of Mn(II) and Zn(II) Acetylacetonates in 1-Propanol–Water Mixtures

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STABILITY constants of Ni(II) and Co(II) acetylacetonates have been determined in mixed solvent systems (*2*, *4*). The purpose of this work is to investigate in a similar manner the solvent effect on the stepwise formation of Mn(II) and Zn(II) acetylacetonates in 1-propanol–water solvent systems.

MATERIALS

Acetylacetone (Eastman Kodak Co., white label) was standardized by the method of Smith and Mitchell (*7*) and found to be 98.7% pure. An infrared spectrum was taken and the peaks corresponded to those reported in the literature (*6*). A gas chromatograph analysis resulted in two peaks, the smaller being 1.3% of the total area of both peaks, indicating one impurity, which was found to be water. Attempts to distill the acetylacetone for further purification were not successful, and since minor impurities were not considered to be significant sources of error (*2*), the acetylacetone was used without further purification. Solutions of acetylacetone were made up in recognition of the fact that it was 98.7% pure.

Manganese perchlorate and zinc perchlorate (G. Frederick Smith Chemical Co.) were standardized according to the standard methods. The specifications of the other chemicals

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