Solubility of HI_3O_8 in Concentrated Nitric Acid

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The solubility of HI_3O_8 was determined in 12–20*M* HNO_3 over the temperature range 25–100°C. The results can be expressed by the following least-squares-developed equation: $\ln S$ (g HI_3O_8/l.) = 13.28 − 0.4515 C(HNO_3) (*M*) − 1170/*T* (K). The solid phase at equilibrium was identified as pure HI_3O_8 by X-ray diffraction.

Oak Ridge National Laboratory is currently engaged in the development of methods for reprocessing spent nuclear fuel. One of the major problems encountered in the development of suitable flow sheets for this purpose is the need to provide a means for retaining essentially all of the radioiodine released during the reprocessing. A promising technique (the Iodex Process) (*1, 2*) involves trapping the iodine in concentrated nitric acid, where it is ultimately oxidized to the pentavalent form.

Earlier work by Unger et al. (*4*) showed that the solubility of I^{5+} in nitric acid depended both on the temperature and the concentration of the acid, with the heat of solution being largely independent of the nitric acid concentration over the range 13–17*M*. Data scatter precluded accurate determination of the heat of solution, and the solid phase was not identified at that time. Later, however, it was determined to be HI_3O_8. Solubilities at 25°C in 12.5 and 14.3*M* HNO_3 can be found in the literature (*3*). In the studies reported in this paper, we measured the solubility of pentavalent iodine in 12–20*M* HNO_3 over the temperature range 25–100°C. The solid phase was isolated and identified.

Experimental

Materials used. The nitric acid solutions used in this study were prepared by dilution of reagent-grade fuming nitric acid. The pentavalent iodine was added as reagent-grade iodic acid (HIO_3).

Procedure. The various nitric acid solutions were placed in separate glass bottles along with an excess of HIO_3 and were sealed by caps with Teflon liners. The bottles to be examined at room temperature were held at 25° ± 1°C by the room thermostat. The others were placed in ovens maintained at 60° or 100° ± 2°C. Each bottle was shaken once a day and sparged briefly with air to remove oxides of nitrogen. At the end of seven days, a sample was withdrawn from each and immediately diluted with four volumes of water by rapidly mixing the acid solution into the water. This prevented loss of solute by precipitation.

The wet solids were removed from each equilibration bottle and were placed in a vacuum desiccator for about 48 hr to remove the adhering liquid preparatory to examination by X-ray diffraction. A portion of each solution was titrated to determine the acid content. Also, an extraction with carbon tetrachloride was performed to determine molecular iodine content to ensure that a significant portion of the dissolved iodine was not in a reduced form. The acid solution was then analyzed for pentavalent iodine by arsenite reduction followed by a potentiometric titration with silver nitrate.

Results

The experimentally determined values of HI_3O_8 solubility are given in Table I and are plotted as a function of temperature in Figure 1, where the curves are calculated from the correlation equation. The nitric acid concentrations given are those determined by titration at room temperature. The decrease in acid molarity with increased temperature was due to decomposition of the nitric acid. These data can be represented by the least-squares-determined equation:

$$\ln S = 13.28 - 0.4515C(HNO_3) - 1170/T$$

where *S* is the solubility of HI_3O_8 in g/l., C(HNO_3) is the molar concentration of HNO_3, and *T* is absolute temperature in K. The correlation coefficient of ln *S* is 0.998. The solid phase in each case was identified as HI_3O_8 by X-ray diffraction.

Discussion

The results obtained in this study are in general agreement with earlier approximate determinations by Unger et al. (*4*) but indicate a heat of solution about twice that found previously. The values given by Seidell and Linke (*3*) for the solubility at 25°C in 12.5 and 14.3*M* HNO_3 are

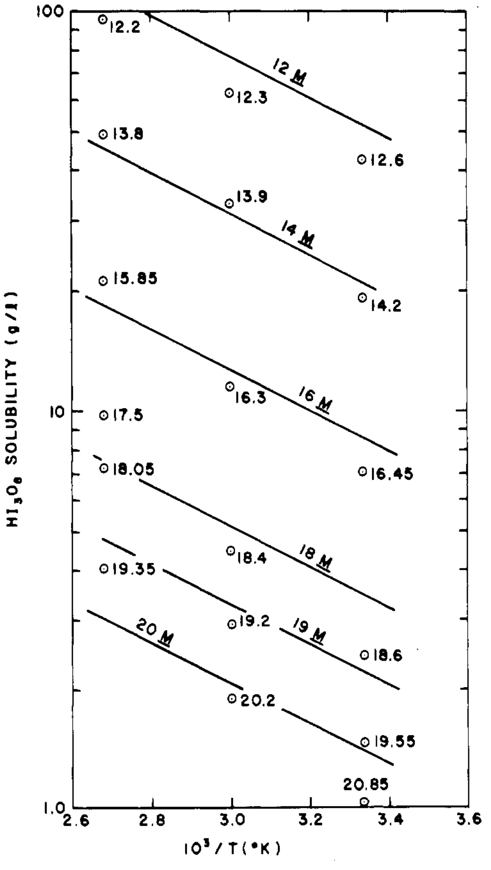

Figure 1. Solubility of HI_3O_8 in nitric acid. Numbers adjacent to experimental points denote HNO_3 molarity. Lines are calculated from correlation equation

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Table I. Solubility of HI_3O_8 in Nitric Acid

Temp, °C	HNO_3, *M*	HI_3O_8 solubility, g/l.
25	12.6	42.4
25	14.2	19.3
25	16.45	7.03
25	18.6	2.42
25	19.55	1.46
25	20.85	1.03
60	12.3	62.8
60	13.9	33.1
60	16.3	11.4
60	18.4	4.48
60	19.2	2.92
60	20.2	1.89
100	12.2	95.7
100	13.8	49.0
100	15.85	21.2
100	17.5	9.77
100	18.05	7.23
100	19.35	4.06

within 5% of our values. An average heat of solution of 2320 cal/g-mol is determined from the slope of the correlation equation.

That the correlation coefficient is so close to unity demonstrates that no appreciable deviation from a constant heat of solution exists over the 12-20*M* range of nitric acid concentrations. The log of the solubility of HI_3O_8 varied linearly with the nitric acid molarity, showing no apparent perturbation at the azeotrope of HNO_3 and water. Molecular iodine was not present in the solutions except at 100°C where trace quantities (up to 33 ppm) were detected.

Acknowledgment

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Optical Constants for Sulfuric and Nitric Acids

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Attenuated total reflection (ATR) spectroscopy is applied to aqueous sulfuric acid solutions (75 and 90%) and to 68% nitric acid. Reflectivity data are reduced to the optical constants, *n* and *k*, for the particular solution. These data are given over the range 6-13 μ for H_2SO_4 and 8-12 μ for nitric acid.

The optical constants, refractive index (*n*) and absorption index (*k*), are useful for predicting the optical behavior and for deducing information about the molecular dynamics of the liquid state. In the course of an investigation by one of us (*4*) of the light-scattering properties of atmospheric aerosols, the optical constants of aqueous sulfuric acid, nitric acid, and ammonium sulfate were determined. This paper reports optical constants of aqueous sulfuric and nitric acids calculated from attenuated total reflection (ATR) measurements. Similar data for H_2O, and D_2O and aqueous ammonium sulfate, will be reported elsewhere, as will the predicted behavior of atmospheric aerosols (*5*).

Experimental

Sample preparation. Two solutions of aqueous sulfuric acid were prepared from reagent concentrated acid. Analyses of the samples by titration against N/2 NaOH solution yielded acid concentrations of 90 and 75% by weight according to the same technique. Nitric acid was similarly prepared and analyzed; our sample was 68 wt %.

Instrumental. Reflectivities were measured with a Perkin-Elmer 112C monochromator coupled with a Wilks Model 44 infrared goniometer. Internal reflection elements were hemicylinders of germanium for the H_2SO_4 measurements and silver chloride for the HNO_3 measurements. All other parts of the cell in contact with the sample were teflon or were silver plated. All measurements were made at 23°C.

Data presentation. The calculation of optical constants from reflectivity data by nonlinear least-squares fitting of Fresnel's equations has been described (*2*). Some of these data are tabulated in Tables I and II along with standard errors and correlation coefficients. More complete data are given in Tables A-1 through A-3 (deposited with the ACS Microfilm Depository Service). Data were taken over the ranges shown in the figures at 870 frequencies for 75% H_2SO_4, 866 frequencies for 90% H_2SO_4, and 339 frequencies for 68% HNO_3. Tables A-1

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