Thermodynamic Studies of Solubility in Protium and Deuterium Oxides

III. Silver Iodate

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The solubility product (pK_{so}) of silver iodate, labeled with Ag-110, has been determined in H_2O and D_2O over the temperature range of 5–50°C using packed column equilibration followed by gamma scintillation counting. At 25°C, the results (molar basis) are as follows for H_2O and D_2O, respectively: pK_{so}, 7.515 and 7.711; $\Delta H°$, 13,520 and 13,635 cal; $\Delta S°$, 10.96 and 10.45 cal/deg.

The increasing use of deuterium oxide as solvent in diverse studies emphasizes the need for fundamental thermodynamic information on species and equilibria in heavy water. Previous work on silver bromate (*12*) includes references to all earlier D_2O solubility studies, and the results for copper(II) iodate (*11*) and silver chloride (*2*) have also been reported. Silver iodate was chosen for the present study because it has been well characterized in water (protium oxide) (*1, 5–8, 13, 14*), can be related to the silver bromate and copper(II) iodate work, and serves as a relatively simple model system for testing the experimental approaches to column equilibration and gamma well counting.

Attempts to equilibrate batches of silver iodate with water and with dilute potassium iodate solutions were successful and in agreement with the literature when the nonradioactive salt was used. When labeled with silver-110 using specific activities from 0.1 to 10 mCi/g, the solubility results were erratic and high in attempts to reach equilibrium from undersaturation by rotating the vessels at constant temperature, as previously reported (*10*). When equilibrium was reached by first heating the solutions and then allowing them to recrystallize at the desired constant temperature, results were in very good agreement with the literature. Spitsyn (*15*) has shown that the electron microscope picture of the surface of potassium sulfate crystals labeled with sulfur-35 is "loose, with projections and depressions resembling the corrosion picture," in contrast to the smooth appearance of nonradioactive material. Perhaps the continuous emission of beta particles leads to microaccumulations of charge, strain, and fissures. Prolonged tumbling in the rotation of the precipitate-solution mixtures may then cause abnormal abrasion and the formation of particles so small that they either escape the Millipore filters or actually lead to higher solubilities because of their greater surface energy.

Therefore, this report deals entirely with results obtained by passage of solutions through packed columns of finely divided silver iodate. This technique seems much more reliable, eliminates the problem of sampling, is much faster than batch methods, and greatly facilitates temperature control and the examination of samples over a wider range of temperature.

EXPERIMENTAL

Five millicuries of silver-110m,-110 was obtained from Oak Ridge National Laboratory as silver nitrate in nitric acid solution, with high specific activity. This was diluted with inert silver nitrate to prepare a sample having a specific activity of 0.3 mCi/g. The solution was scavenged by precipitation of ferric hydroxide with an excess of ammonia, and the filtrate was electrolyzed at controlled cathode potential of −0.25 V vs. SCE. The plated silver was dissolved with 3*M* nitric acid.

Crystalline silver iodate was prepared by precipitation from homogeneous solution as follows: To 25 ml of the silver stock solution were added 20 ml of 5*M* ammonia (prepared by bubbling tank gas into redistilled water), 20 ml of 0.12*M* potassium iodate, and 10 ml of distilled 2-hydroxyethylacetate. The mixture was allowed to stand in the dark for two weeks, over which time there was a quantitative yield of crystals ranging up to 1 mm in length. This coarse crystalline precipitate did not readily come to equilibrium with solutions passing through the column, presumably because the larger crystals provided open channels. The silver iodate was dissolved with excess ammonia and reprecipitated by slow addition of perchloric acid, and then was digested at near boiling for 2 hr. The resulting preparation was much more finely divided, and 4 grams was used to prepare a column 3 cm high in a 4-mm i.d. tube, drawn out at the bottom and having a borosilicate glass wool plug. The column was jacketed with a larger tube carrying circulating water from a constant temperature bath. Thermometers were checked using a National Bureau of Standards calibrated thermometer.

The procedure for sampling and counting was as follows: A weighed test tube was counted for the background correction in a location remote from the main radioactive area. A solution of $1 \cdot 10^{-4}M$ perchloric acid was forced through the column and the test tube was used to collect about 1 gram of solution, which was then precisely weighed and counted. Repeated determinations at each temperature gave assurance of reproducibility. Only the drawn tip of the column protruded from the constant temperature jacket, and evaporation was minimized by placement of the test tube and fairly rapid sample collection. In spite of thorough cleaning, the test tubes retained varying amounts of adsorbed radioactivity. Therefore, individual background counts with the empty tubes were performed for every determination.

Standards for gamma counting were taken by weight from stock solutions prepared by weighing dried samples of the radioactive precipitate followed by dissolving with sodium cyanide solution. Sodium hydroxide and inert silver nitrate were added, and the mixtures were diluted to known amounts and known solution weights.

The Nuclear-Chicago Corp. equipment used in this work was as follows: A DS-202 shielded detector with a well-type sodium iodide crystal and DS-5 basic probe was connected to the Model 1820A gamma-ray spectrometer. The output of the radiation analyzer section was also taken to a Model 186P scaler with a 1-μsec first decade. Consideration of the gamma spectrum of silver-110 led to an arbitrary choice of a low energy cutoff of 0.10 MeV, and since a single radionuclide was being used, it was desirable to use integral counting for higher sensitivity. The background count was about 200 cpm, and samples for analysis gave 10^4 cpm or higher. To ensure statistical accuracy, total count accumulations ranged from 10^5–10^6. Counting times were measured with a Standard Electric Time Co. timer Model SM-60-3H-30, with an accuracy of ±0.1 sec.

All chemicals were of analytical reagent grade, and all volumetric ware was calibrated. Protium oxide solutions were prepared with redistilled water stored in a borosilicate glass jug long used for this purpose. Deuterium oxide was used as supplied by Liquid Carbonic Division of General Dynamics Corp., with their specification of greater than 99.5% purity.

RESULTS

With the assumption that silver iodate is completely dissociated in the solutions it follows that

$$K_{so} = [Ag^+][IO_3^-]f^2 = S^2f^2$$

where K_{so} is the thermodynamic value of the solubility product constant, the brackets indicate molarities, and f is the molar activity coefficient of a singly charged ion. Values of f were calculated using the Davies equation (*4*), $\log f = -A\cdot\mu^{1/2}/(1 + \mu^{1/2}) + 0.1\ \mu$, with appropriate values (*9*) of the Debye-Huckel constant, A. The analyses were all performed on a weight basis, and the densities of protium oxide and deuterium oxide (*3*) were used to make the change to molarity. The results are shown in Table I.

By the method of least squares the protium oxide results follow the relationship,

$$\log K_{so} = 8.9270 - 0.010953\cdot T - 3298.4/T \qquad (1)$$

where T is the absolute temperature. The equation gives −7.515 as the value of $\log K_{so}$ as 25°C, in excellent agreement with the literature values.

The results in deuterium oxide are described by the equation

$$\log K_{so} = 8.8255 - 0.010970\cdot T - 3955.2/T \qquad (2)$$

The thermodynamic calculations shown in Table II were based on the hypothetical ideal 1*M* solution as the standard state. On a molal basis the results would differ as follows for deuterium oxide (density = 1.1) at 25°C: $\Delta G°$ would be 120 cal higher, $\Delta H°$ would not be significantly different, and $\Delta S°$ would be 0.6 cal/deg higher. For protium oxide there would be little difference between the molar and molal basis.

DISCUSSION

The literature contains no other results for silver iodate solubility in deuterium oxide, seen to be about 79% of that in protium oxide compared to 84% in the case of silver bromate, 73% for copper iodate, and 87% for silver chloride.

The results of Li and Lo (*8*) cover the range from 10–35°C and are described by the equation

$$\log K_{so} = 0.9869 + 0.002353\cdot T - 2743.4/T \qquad (3)$$

In the 15–35°C range, this equation gives values rather close to those of the present work (Equation 1 above), but it is noted that the coefficient for the T term is positive in Equation 3, but negative in Equation 1. This is equivalent to saying that a plot of $\log K_{so}$ vs. $1/T$ is curved in opposite directions for the two sets of data, or, in other words, that the value of ΔC_p is positive according to Li and Lo, negative according to the present work. Support for the present results is afforded by Baxter's result (*1*) at 75°C, $\log K_{so} = -6.207$. Equation 1 "predicts" a value of −6.17, while Equation 3 predicts −6.07.

The observed entropy change for silver iodate solubility in protium oxide, 11.0 cal/deg may be compared with that calculated from tabulated (*16*) values of entropies. Taking 17.37 for Ag^+, 28.3 for IO_3^-, and 35.7 for $AgIO_3$(c), the calculated value is 10.0.

As was found for silver bromate, the enthalpy change in deuterium oxide is more positive than in protium oxide. However, for silver iodate, the entropy change is found to be less positive in deuterium oxide, contrary to the finding for silver bromate.

Table I. Solubility Results for Silver Iodate in H_2O and D_2O

t, °C	Molar solubility·10^4	pK_{so}
	H_2O	
2	0.667	8.364
11	1.005	8.010
20	1.457	7.689
25	1.793	7.510
30	2.148	7.354
40.2	3.090	7.041
49.1	4.121	6.794
	D_2O	
5	0.608	8.45
15	0.953	8.05
25	1.411	7.72
35	2.06	7.39
50.3	3.45	6.95

Table II. Thermodynamic Results for Silver Iodate in H_2O and D_2O

t, °C	$\Delta G°$, cal	$\Delta H°$, cal	$\Delta S°$, cal/deg	$\Delta C_p°$, cal/deg
		H_2O		
0	10,557	14,236	13.47	−27
25	10,252	13,520	10.96	−30
50	10,009	12,741	8.45	−32
		D_2O		
0	10,812	14,352	12.96	−27
25	10,520	13,635	10.45	−30
50	10,290	12,856	7.94	−32

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