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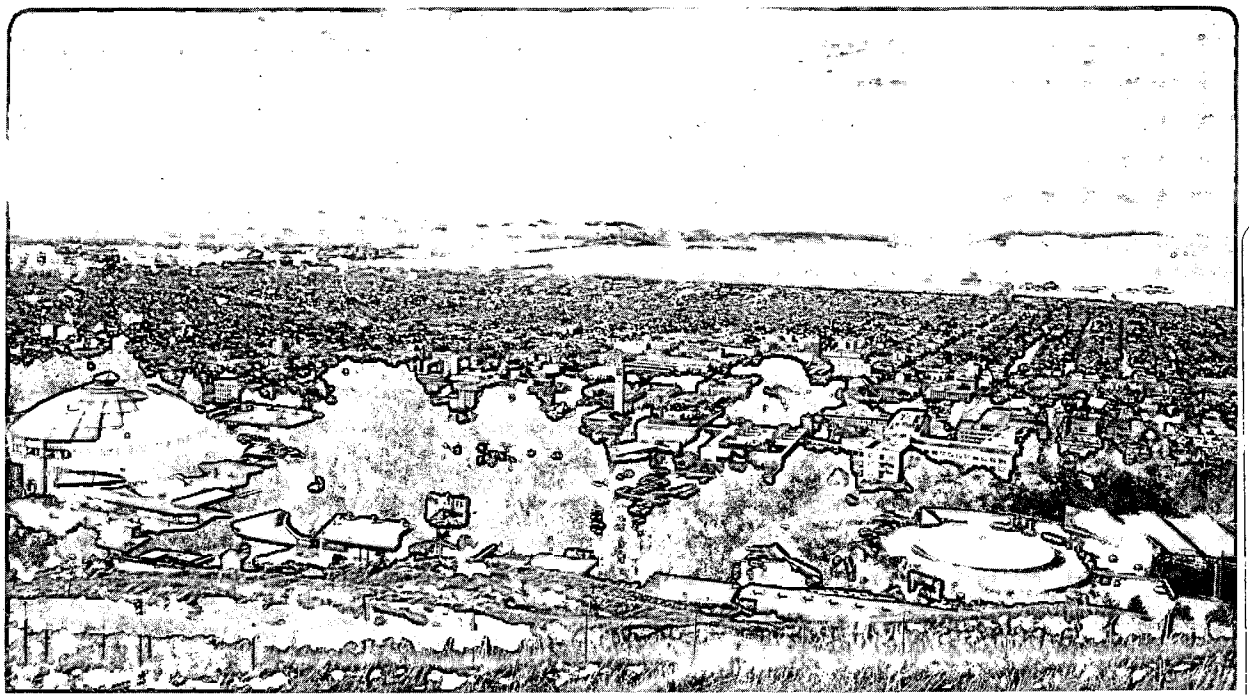

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ABSTRACT

Modeling calculations on the solubility of americium have indicated that basic americium carbonate, and not americium trihydroxide, is the solubility-controlling solid in the pH range from 6 to 10 under the influence of atmospheric CO_2. The solubility of crystalline $^{243}AmOHCO_3$ has been investigated in batch experiments in near-neutral and basic solutions as a function of dissolution time in 0.1 M $NaClO_4$ at room temperature under oxic conditions. After the solutions reached steady-state conditions, the influence of dissolved solids on the americium concentration in the supernatant solution was studied by utilizing several experimental methods to separate the solution phase from the solid. The solids were characterized by X-ray powder diffraction analysis.

INTRODUCTION

The intrusion of groundwater into an underground nuclear waste respository and the migration of potentially contaminated groundwater must be considered as one principal mechanism for the transport of radionuclides from a disposal site to the accessible environment. Major controls on the radioactive contamination of groundwater are the dissolution rate of the waste package, the formation of solubility-controlling solids, and the formation of soluble species. The formation of solids and solution species depends strongly on the radionuclide and its oxidation state, the ions present in the groundwater, the pH, Eh, and temperature of the groundwater, and the surrounding host rock.

The trivalent actinide americium forms rather strong carbonate complexes [1, 2, 3]. Therefore, the presence of carbonate, a common constituent of groundwaters, can have a substantial influence on the nature of solids and solution species formed by americium in groundwaters. Silva has published modeling calculations on the solubility of americium using the computer code MINEQL [4, 5]. As input, a thermodynamic data base was generated from available literature data, which included the solubility products of $Am(OH)_3$ and $AmOHCO_3$, the hydrolysis constants, and the carbonate complexation constants for Am^{3+}. From this simplified model, which considered only hydroxide and carbonate complexation, $AmOHCO_3$—and not $Am(OH)_3$—was found to be the solubility-controlling solid in the pH range between 6 and 10 under atmospheric CO_2 pressure. The ionic strength was held at 0.1 M and a temperature of 25°C was assumed.

The purpose of this study was to verify experimentally the calculations that indicate $AmOHCO_3$ is less soluble than $Am(OH)_3$ under atmospheric CO_2 conditions. The measurements were made in batch experiments from undersaturation by contacting crystalline $^{243}AmOHCO_3$ in 0.1 M noncomplexing $NaClO_4$ solution with air. The pH values were maintained constant at pH values near 6, 8, and 10, and the solution concentration of americium was determined as a function of equilibration time. At the end of each experiment, the solids were investigated by X-ray powder diffraction analysis.

EXPERIMENTAL METHODS

The ^{243}Am used in these experiments was obtained through the U.S. Department of Energy's Heavy Element Production Program at Oak Ridge National Laboratory. Since americium was in solution from a previous experiment, it was purified of soluble salts and silica by two $NaClO_4$ precipation-dissolution cycles. The resulting tan $Am(OH)_3$ was

dissolved in 0.05 M $NaClO_4$, and pure Am^{3+} was obtained by cation-exchange chromatography using Biorad AG 50 X 8 resin [6]. The eluate was taken to incipient dryness and redissolved in 0.1 M HCl. Alpha- and gamma-ray energy analysis of samples from this solution indicated the isotopic composition to be 99.83% ^{243}Am, 0.14% ^{241}Am, and 0.025% ^{244}Cm by weight. A 50 μg sample underwent analysis by spark emission spectroscopy and showed no metal contaminants above the detection limit of the method [7]. The americium was precipitated with NaOH and the precipitate centrifuged and washed twice with H_2O. Approximately 9 mg of $Am(OH)_3$ was converted to the trichloroacetate complex, $Am(C_2Cl_3O_2)_3$, by dissolution in 25% trichloracetic acid. The subsequent slow hydrolysis of the americium trichloroacetate complex produced the light brown $AmOHCO_3$ [4, 8, 9]. The precipitate was centrifuged, washed with H_2O and alcohol, and dried in air. A few micrograms of the precipitate was subjected to X-ray powder diffraction measurement (11.46 cm Debye-Scherrer camera, Philips Electronics, Inc., Norelco III X-ray generator, Cu-K_α radiation). The d-spacings and intensities agreed very well with published X-ray data on $AmOHCO_3$.

Solubility measurements were made in 100 ml preleached low-density polyethylene cells. Approximately 3 mg of crystalline $AmOHCO_3$ was placed in each of several separate cells with 50 ml of 0.1 M $NaClO_4$ at 23 ± 1°C. The $NaClO_4$ (reagent grade, G.F. Smith Chemical Company) was recrystallized twice from H_2O before it was used to make the 0.1 M $NaClO_4$ noncomplexing supporting electrolyte solution. Prior to its use, the $NaClO_4$ solution was filtered through a 0.05 μm polycarbonate membrane filter (Nuclepore Corp.) to avoid the possibility of forming americium pseudocolloids with suspended particulate material.

The pH of the individual test solutions was adjusted to target values of 6.2, 7.7, and 9.8 with 0.01 M $HClO_4$ (doubly distilled, G.F. Smith Chem. Co.) or 0.01 M NaOH (prepared from NaOH pellets "low in carbonate," J.T. Baker Chem. Co., and carbonate-free double-distilled H_2O). The cells were shaken and opened daily to allow air to contact the solution and to accelerate the establishment of equilibrium conditions in the solutions. The solution pH was measured at least twice a week, using a combination glass electrode (Ag/AgCl/3 M NaCl/glass) and a Beckman Model 4500 pH meter. The pH meter and the electrode were recalibrated with standard buffer solutions (Mallinckrodt, Inc.) before each measurement.

The approach to steady-state conditions for americium was monitored by analyzing aliquots of the solution phases for their americium concentration by measuring the 74.67 keV ^{243}Am γ-ray line with a planar intrinsic germanium detector coupled to amplifiers (both LBL design) and to a multichannel analyzer (Tracor Northern, Inc., Model TN 1710). A

waiting period of several weeks was necessary to determine accurately the americium concentration in the samples. The ^{243}Am daughter nuclide $^{239}Np(t_{1/2} = 2.3$ days), is significantly more soluble than the ^{243}Am parent. The relatively small γ-line of the ^{243}Am at 74.67 keV is positioned on a large Compton edge of the 106.13 keV γ-line and of the Pu *K* X-rays coming from the ^{239}Np decay. Accurate analysis of the americium was obtained only after the ^{239}Np had decayed to near equilibrium with the ^{241}Am.

The efficiency of the separation of solid and solution phases depends strongly on the method of separation. Ultrafiltrations with Centricon Microconcentrators (Amicon Corp., MW cut-off 30,000 daltons, calculated pore size 4.1 nm) are stated to provide effective separation [3, 10]. For all filtrations, possible adsorption of soluble material onto the filters was minimized by first filtering an aliquot of the sample in order to saturate possible adsorption sites on the filter material. Then, after discarding the filtrate, a second sample was filtered for analysis. A sufficient amount of 9 M HCl (15–100 µl) was always added to the filtrate-collecting vial before filtration to acidify the filtrate. This prevents possible adsorption of radioactive material onto the container walls, which would lead to erroneous results.

At the end of each solubility experiment, four aliquots of the aqueous phase were taken. The first aliquot was filtered through the 4.1 nm Amicon filter as described previously. The second was filtered through a 15 nm polycarbonate membrane filter (Nuclepore Corp.). The third was filtered through a 220 nm cellulose ester membrane filter (Millipore Corp.). The fourth was centrifuged at 15,000 rpm for 15 minutes. For this centrifuge system (Eppendorf Microcentrifuge, Model 5412) it was estimated that particles approximately 0.1 µm in diameter and larger should be precipitated [4]. The filtrates and the supernatant were analyzed for americium. The solid phases were studied by X-ray powder diffraction analysis at the end of the solubility experiments.

RESULTS AND DISCUSSION

The results of the solubility measurements for the dissolution of crystalline $AmOHCO_3$ as a function of time are given in Table 1, together with the solutions' pH values at the time of sampling. The average pH values for the solutions during the 98-day duration of the experiment were calculated to be 6.18 ± 0.16, 7.38 ± 0.48, and 9.84 ± 0.18. Although it was attempted to control the pH as tightly as possible, adjustments made even every other day resulted in considerable pH fluctuation, especially for the pH 7.38 solution. The results of the X-ray diffraction analyses on the solids phases at the end of

each experiment, given in Table 2, show that the crystalline $AmOHCO_3$ starting material did not undergo any significant change during the experiments in the pH 6.18 (phase 1) and the pH 9.84 (phase 2) solutions. The $AmOHCO_3$ from the pH 7.38 solution, however, was converted to an unidentified americium compound of very low crystallinity as indicated by the few and weak diffraction lines. This change of the solid may have caused the relatively large pH fluctuation of 0.5 pH unit during the experiment in addition to possible radiolytically-induced pH changes for all three solutions.

The results of the filtration and centrifugation experiment after 98 days are also included in Table 1. The solution concentrations after separation by centrifugation were significantly higher than those measured after separation by filtration. The americium concentration in each solution increased as the filter size changed from 4.1 nm (Amicon) to 15 nm (Nuclepore). However, the concentration decreased again when the 220 nm filter (Millepore Corp.) was used. It seems rather puzzling that a presaturated filter with a pore size 15 times larger than that of another should retain more material. The data in Table 1 show a dramatic drop in concentration between days 14 and 28, e.g., the pH 6.18 solution concentration decreased by almost four orders of magnitude. This fact and the unorthodox filtration behavior suggests that effects other than a mere particle size distribution must control the measured changes in solution concentration. This result suggests that soluble americium species might have been adsorbed onto the filter or its PVC-housing material, although the active sites should have become saturated during the prefiltering step. The solution concentrations after the separation by centrifugation were rather high, suggesting that most of the soluble americium species are smaller than 0.1 μm and larger than 4.1 nm. This is in contradiction to published results on the solubility of $AmOHCO_3$ by dissolution of crystalline material at pH 6.14 in 0.1 M $NaClO_4$ [3]. In that experiment, the americium solution concentration changed only by a factor of about 2 after 30 days, when the separation method was changed from centrifugation to filtration through filters of 0.2 μm and 0.015 μm pore size. Comparison of the solution concentrations given in reference [3] with the values for the pH 6.2 solution reported here shows the values to be in quite good agreement until day 28 of this study. At that time the concentration dropped strikingly by more than four orders of magnitude from 7.5×10^{-6} M to 5×10^{-10} M. One possible explanation for this fact is a sudden increase in particle size. This hypothesis is reinforced by the result of the filtering experiment after 98 days. The value of 1.1×10^{-5} M is in acceptable agreement with the value of 7.5×10^{-6} M at day 14.

Figure 1 shows the results of modeling calculations for the solubility of $AmOHCO_3$ under atmospheric CO_2 pressure as a function of pH [3, 4]. Also included in the graph are the steady-state concentrations determined in this study. The values are five orders of

magnitude lower at pH 6.2 and nearly two orders of magnitude lower at pH 9.8 than the values calculated from the model. The concentration at pH 7.4 is about one order of magnitude lower than the modeling prediction, but it cannot be compared with the model since the solid was amorphous, not crystalline $AmOHCO_3$. Although I have no plausible explanation for the discrepancy in results, it is apparent that $AmOHCO_3$ is indeed the solubility-controlling solid at pH values of 6.2 and 9.8 under the influence of air.

While this work was in progress, a report was published on the solubility of $Am(OH)_3$ in bicarbonate-carbonate mixtures under argon [3]. The solubility-controlling solid phase in that system was determined to be $AmOHCO_3$ in the pH range from 6 to10. The conclusion that the solid formed was $AmOHCO_3$ was based on an experiment with the homologous $EuOHCO_3$. A suspension of $Eu(OH)_3$ was sparged with 1% CO_2 gas and the resulting solid identified as $EuOHCO_3$ by infrared spectroscopy. Then Am^{3+} was precipitated in 0.1 M $NaHCO_3$ solution. The resulting precipitate was assumed to be $AmOHCO_3$. It was contacted with air for 2 weeks in batch experiments using 0.1 M $NaClO_4$ at pH values between 6 and 8.3. The americium concentrations, from the batch experiment that was conducted in air, agreed with the americium concentrations of the $Am(OH)_3/HCO_3^-/CO_3^{2-}$ experiment at the corresponding carbonate concentrations. Unfortunately, it is not known if the solid material was crystalline or amorphous, nor was the solution concentration for either experiment reported as a function of equilibration time. The reported solubilities for $AmOHCO_3$ between pH 6 and 7 agree with the modeling calculations of Silva [4,5]. Above pH 7, the experimental values are larger than the calculated values, with a difference of up to 2.3 orders of magnitude at pH 10.

CONCLUSION

Further careful study of the $AmOHCO_3$ system in aqueous solution is required to resolve the discrepancies between the results reported in this paper, the solubility studies of $Am(OH)_3$ in bicarbonate-carbonate solutions, and the modeling calculations.

Table 1. Results of solubility measurements at $AmOHCO_3$ in 0.1 M $NaClO_4$ at 23 ± 1°C in contact with air.

Equil. time	–log concentration		–log concentration		–log concentration	
days	M	pH	M	pH	M	pH
1	(5.237 ± 0.008)	5.95	(8.62 ± 0.02)	8.03	(9.34 ± 0.08)	9.97
5	(5.061 ± 0.005)	6.02	(8.82 ± 0.03)	7.45	(9.30 ± 0.04)	9.95
7	(5.061 ± 0.005)	6.04	(9.10 ± 0.05)	7.44	(9.49 ± 0.08)	9.96
14	(5.125 ± 0.006)	6.14	(8.89 ± 0.07)	7.04	(8.04 ± 0.02)	9.89
28	(9.30 ± 0.08)	6.18	(9.64 ± 0.08)	7.58	(9.48 ± 0.07)	9.30
82	(9.8 ± 0.2)	6.13	(10.6 ± 1.5)	7.59	(9.99 ± 0.16)	9.50
91	(10.05 ± 0.10)	6.50	(9.08 ± 0.05)	7.85	(9.89 ± 0.16)	9.85
98	(10.00 ± 0.05)	6.54	(9.45 ± 0.07)	7.86	(10.04 ± 0.16)	9.65
	(8.22 ± 0.02)[a]		(9.2 ± 0.06)[a]		(9.36 ± 0.09)[a]	
	(9.92 ± 0.08)[b]		(9.3 ± 0.06)[b]		(9.68 ± 0.09)[b]	
	(4.962 ± 0.008)[c]		(6.13 ± 0.01)[c]		(6.52 ± 0.01)[c]	

[a]With 15 nm filter.
[b]With 220 nm filter.
[c]Centrifugation.

Table 2. Comparison of X-ray powder diffraction patterns of Am solid phases in 0.1 M $NaClO_4$ at 23 ± 1°C and pH 6.18 (phase 1), pH 7.38 (phase 2), and pH 9.84 (phase 3) with patterns reported in the literature.

Phase 1 d(Å) I[a]	Phase 2 d(Å) I[a]	Phase 3 d(Å) I[a]	$AmOHCO_3$[c] d(Å) I[a]	$Nd_2(CO_3)_3 \cdot 3H_2O$[c] d(Å) I[a]	$Am(OH)_3$[d] d(Å) I[b]
		7.21 w		7.56 m	
				5.68 s	
					5.57 4
5.51 m		5.54 w	5.51 w		
				4.67 s	
	4.40 w				
4.30 s		4.29 s	4.28 s		
				3.93 s	
				3.83 s	
3.69 m		3.67 s	3.67 m		
				3.62 m	
3.31 m		3.31 m	3.31 m		
					3.21 10
					3.11 10
				3.09 s	
				3.02 s	
			2.94 w	2.98 w	
2.91 m		2.92 m	2.92 m		
2.84 w		2.86		2.87 w	
		2.81 w			
					2.78 1
	2.77 w			2.75 w	
2.64 w		2.64 w	2.64 w		
				2.58 s	
2.49 w		2.49 w	2.48 w		
					2.44 1
		2.36 w	2.40 w		
			2.33 m		
2.24 w	2.26 m			2.25 w	2.24 7
2.16 w	2.13 w			2.17 w	
				2.08 w	2.10 3
2.06 w		2.06 w	2.05 w		
					2.02 m
1.99 w		1.99 w	1.98 w	1.98 w	
	1.96 w				
			1.89 w	1.87 m	1.86 7
			1.84 w	1.83 m	1.83 7
				1.78 m	1.77 1
				1.74 w	1.62 1
					1.61 1
				1.56 m	1.55 1
					1.43 1
					1.40 5
					1.32 2
					1.28 2
					1.21 1

[a]Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak.
[b]Relative intensities by diffractometer in percent.
[c]Reference [4].
[d]Reference [11].

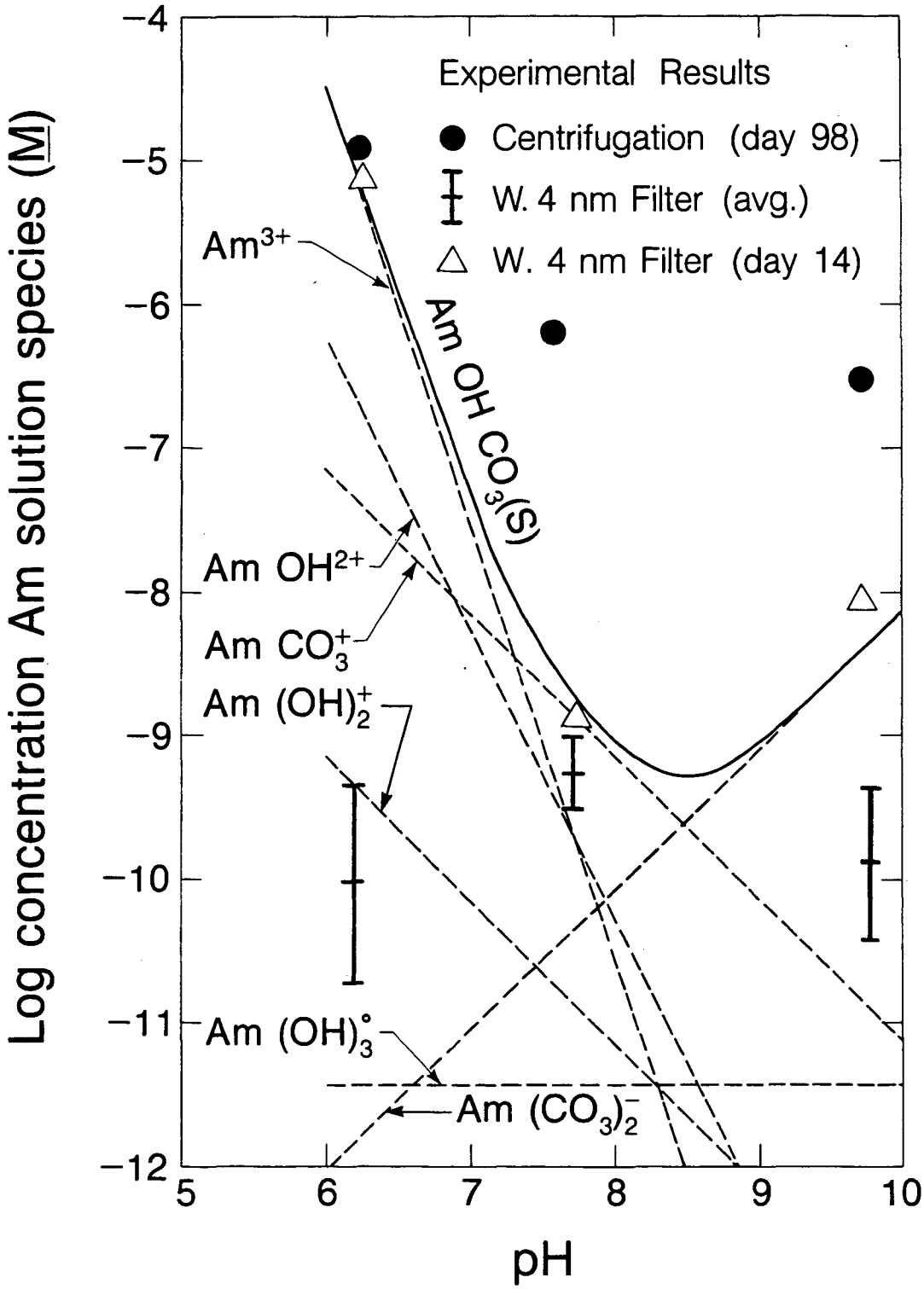

Figure 1. Sums of calculated concentrations of americium (solid curve is the controlling solid phase) for 0.1 M ionic strength, oxic Eh conditions and a CO_2 partial pressure of $10^{-3.5}$ atmospheres (from reference [4]). Also included are experimentally determined data points from this study. [XBL 839-3276A]

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