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NEPTUNIUM (IV) OXALATE SOLUBILITY

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ABSTRACT

The equilibrium solubility of neptunium (IV) oxalate in nitric/oxalic acid solutions was determined at 22°C, 45°C, and 60°C. The concentrations of nitric/oxalic acid solutions represented a wide range of free oxalate ion concentration. A mathematical solubility model was developed which is based on the formation of the known complexes of neptunium (IV) oxalate. The solubility model uses a simplified concentration parameter which is proportional to the free oxalate ion concentration. The solubility model can be used to estimate the equilibrium solubility of neptunium (IV) oxalate over a wide range of oxalic and nitric acid concentrations at each temperature.

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THE SOLUBILITY OF NEPTUNIUM (IV) OXALATE

INTRODUCTION

The Savannah River Plant recovers neptunium-237 by precipitation as neptunium (IV) oxalate. It is then calcined to neptunium oxide, mixed with powdered aluminum, and pressed into billets for fabrication into reactor targets. The targets are irradiated to produce plutonium-238 for use as heat sources in radioisotopic power generators.

Neptunium (IV) oxalate solubility data are necessary for proper control of the precipitation process and for optimizing filtrate recovery operations. The purpose of this work is to provide a simple method to estimate the equilibrium solubility of neptunium (IV) oxalate over a wide range of temperatures and acid concentrations.

EXPERIMENTAL METHODS

Equilibrium Solubility Methods

The equilibrium solubility of neptunium (IV) oxalate in nitric/oxalic acid solutions was determined at 22°C, 45°C, and 60°C. Two methods were used:

1. Neptunium (IV) oxalate was precipitated from solutions containing a mixture of known oxalic acid and nitric acid concentrations. After equilibration, the solutions were analyzed to determine the concentration of neptunium.

2. Excess solid neptunium (IV) oxalate was equilibrated with solutions containing a mixture of known oxalic acid and nitric acid concentrations. After equilibration, the solutions were analyzed to determine the concentration of neptunium.

The solubility measurements at 45°C and 60°C were thermostated during equilibration. Solubility samples were then immediately quenched and diluted in strong acid before neptunium analysis.

Preparation of Reagents

A stock solution of purified neptunium-237 was prepared by anion exchange.[1] Solutions of neptunium (V) were eluted from the column.

For the solubility measurements, a portion of the eluate was used. Neptunium (VI) in the eluate was reduced[2] to neptunium (V) by heating the eluate to 55°C in the presence of 0.1M hydrazine. The solution was cooled to room temperature and the neptunium (V) was further reduced to neptunium (IV) using 0.03M excess ascorbic acid as reducing agent.

Solid neptunium (IV) oxalate was prepared by precipitation. Excess oxalic acid was added to a small portion of adjusted eluate. The solution was filtered and the precipitate washed several times with a dilute cake wash. The precipitate was then washed with distilled water to remove excess oxalate and nitrate ion.

Equilibrium Solubility Determination

In the first method, neptunium (IV) oxalate was precipitated from solution by addition of adjusted neptunium (IV) nitrate to precipitant solutions containing oxalic and nitric acids of predetermined concentrations. The precipitant solution concentrations ranged from 0.01M to 0.8M oxalic acid and 0.4M to 8.0M nitric acid. Hydrazine was used to stabilize the neptunium (IV) valence state from oxidation due to nitric acid radiolysis products.

In the second method, pure neptunium (IV) oxalate was dissolved in solutions containing oxalic acid and nitric acid of predetermined concentrations. The solutions were the same concentrations as those used in the first method. These tests were conducted only at room temperature.

In both methods, the solutions were equilibrated for 24 hours and then filtered and sampled using a 0.25 μm micropore filter on a 5.0 cc syringe. The filtered samples were immediately diluted in strong nitric acid to prevent post precipitation. Neptunium analysis was performed using standard alpha counting techniques.

SOLUBIITY OF NEPTUNIUM (IV) OXALATE

Equilibrium Parameter

The neptunium (IV) oxalate solubility data are shown in Tables 1 through 3. The data are tabulated to show actual oxalic acid and nitric acid concentrations and a solubility parameter, R_s.

Since oxalic acid is a weak diprotic acid, the concentration of free oxalate ion is given by:

$$[C_2O_4{}^{2-}] = \frac{k_1\ k_2\ [H_2C_2O_4]}{[H^+]^2 + k_1[H^+] + k_1\ k_2} \qquad (1)$$

where k_1 and k_2 are the consecutive dissociation constants[3] of oxalic acid.

$k_1 = 5.9 \times 10^{-2}$ and $k_2 = 6.4 \times 10^{-5}$

In a system with a strong acid such as nitric acid, the free oxalate ion concentration can be approximated by:

$$[C_2O_4{}^{2-}] \sim \frac{k_1\ k_2\ [H_2C_2O_4]}{[H^+]^2} \sim \frac{k_1\ k_2\ [H_2C_2O_4]}{[HNO_3]^2} \qquad (2)$$

therefore

$[C_2O_4{}^{2-}]$ is proportional to $[H_2C_2O_4]/[HNO_3]^2$.

R_s, the solubility parameter tabulated in Tables 1 through 3, is given by

$$R_s = \frac{[H_2C_2O_4]}{[HNO_3]^2} \qquad (3)$$

Equilibrium Solubility Data

The equilibrium solubility data are shown in Figures 1 through 3. The data show that the equilibrium solubility of neptunium (IV) oxalate can be represented as a function of the solubility parameter, R_s, for each temperature.

Equilibria between neptunium (IV) oxalate complexes can account for the varying solubility. Four oxalate complexes have been reported,[3-6] in the literature. Minimum solubility results when the formation of the highly insoluble dioxalate complex is favored. Increased solubility results from the formation of cationic or anionic complexes as the free oxalate ion concentration is varied from optimum values.

Equilibrium Solubility Model

The following complex equilibria can be used to develop a mathematical model of the equilibrium solubility of neptunium (IV) oxalate as a function of the solubility parameter, R_s.

$$Np(C_2O_4)_2\ 6H_2O\ (solid) \leftrightarrow Np(C_2O_4)_2{}^{\circ}\ (soln) \qquad (4)$$

$$K_1 = [Np(C_2O_4)_2{}^{\circ}]$$

$$Np(C_2O_4)_2{}^{\circ} + 2H+ \leftrightarrow Np(C_2O_4)^{2+} + H_2C_2O_4 \qquad (5)$$

$$K_2 = \frac{[Np(C_2O_4)^{+2}]\ [H_2C_2O_4]}{[Np(C_2O_4)_2{}^{\circ}]\ [H^+]^2}$$

$$Np(C_2O_4)_2{}^{\circ} + H_2C_2O_4 \leftrightarrow Np(C_2O_4)_3{}^{2-} + 2H^+ \qquad (6)$$

$$K_3 = \frac{[Np(C_2O_4)_3{}^{-2}]\ [H^+]^2}{[Np(C_2O_4)_2{}^{\circ}]\ [H_2C_2O_4]}$$

The neptunium (IV) oxalate equilibrium solubility can be expressed as the sum of all the neptunium species in solution (assuming that the free metal ion concentration is negligible):

$$[Np^{4+}]\ total = [Np(C_2O_4)^{2+}] + [Np(C_2O_4)_2{}^{\circ}] + + [Np(C_2O_4)_3{}^{2-}] \qquad (7)$$

Using the equilibrium expressions in equations 1 through 3:

$$[Np^{4+}]\ total = [Np(C_2O_4)_2{}^{\circ}]\left(1 + K_2 \frac{[HNO_3]^2}{[H_2C_2O_4]} + K_3 \frac{[H_2C_2O_4]}{[HNO_3]^2}\right) \qquad (8)$$

or

$$[Np^{4+}]\ total = K_1 + K_1K_2/R_s + K_1K_3R_s \qquad (9)$$

Equation (9) forms the basis of a least-squares model of the form:

$$Y = a_0 + a_1/X + a_2X \qquad (10)$$

where

$Y = [Np^{4+}]$ total, $X = R_s$

$$\begin{aligned} a_0 &= K_1 \\ a_1 &= K_1K_2 \\ a_3 &= K_1K_3 \end{aligned}$$

R_s is proportional to the free oxalate ion concentration; a_0, a_1, and a_2 are least-squares coefficients based on the solubility data.

Interpretation of the Solubility Model

Using the solubility model, the contribution to the overall equilibrium solubility from the formation of a particular complex species can be associated with a single least square coefficient. For example, the contribution to the overall equilibrium solubility from the formation of the neutral species, $Np(C_2O_4)_2{}^{\circ}$, is given by the magnitude of a_0. Likewise, a_1 is associated with the formation of the cationic species, $Np(C_2O_4)^{2+}$, and a_2 is associated with the formation of the anionic species, $Np(C_2O_4)_3{}^{2-}$.

The model shows, that for small values of R_s, (i.e., $R_s < 0.01$), the equilibria involving the cationic complex predominates. This gives rise to enhanced solubility at low concentrations of free oxalate ion. This region of the solubility curve is known as the oxalic-lean region.[7]

As R_s increases (i.e., $0.01 < R_s < 0.2$) the solubility minimum is reached when the formation of the highly insoluble dioxalate complex is favored. The equilibria involving the formation of the neutral complex species predominates in this region.

However, as R_s further increases (i.e., $R_s > 0.2$), the equilibria involving the anionic complex begins to predominate. The solubility increases because of the formation of the highly soluble anionic complex. This region of the solubility curve is known as the oxalic-rich region.[7]

Data Analysis

Figures 1 through 3 show the actual solubility data at each temperature. The solid curve through the data points in each figure is the least square curve generated from the data using the solubility model at the particular temperature.

Table 4 summarizes the experimentally determined least square coefficients at 22, 45, and 60°C. Table 4 also shows the correlation coefficient and standard deviation of the least square fit of the solubility model to the solubility data at each temperature.

Using the model, the predicted solubility in milligrams of neptunium per liter is given by Equation 10, viz.

$$Y = a_0 + a_1/X + a_2X \pm\sigma$$

where

$Y = [Np^{4+}]$ total; $X = R_s$

σ = standard deviation in Table 4

and

a_0, a_1, and a_2 are least-squares coefficients

Considering the wide range of nitric acid concentrations and oxalic acid concentrations used in this work, the simple solubility model correlates the data very well at each temperature.

Results Using the Solubility Model

Figure 4 shows the predicted equilibrium solubility curves at each temperature using the solubility model.

In the region of high free oxalate ion concentration, the predicted solubility curve at 60°C intersects and actually falls below the predicted solubility curve at 45°C. This behavior suggests high temperature instability of the anionic complex, $Np(C_2O_4)_3^{2-}$. That is, as the temperature rises, the anionic complex becomes unstable due to the increased kinetic energy and begins to dissociate. Solubility enhancement from temperature effects alone are not enough to compensate for the reduced solubility from the dissociation of the anionic complex.

Another result from the solubility model becomes evident if the solubility minimum is examined as a function of temperature. Mathematically, the solubility minimum occurs at:

$$R_s = \sqrt{a_1/a_2} \tag{11}$$

Using the experimental determined coefficients, the solubility minimum shifts to higher free oxalate ion concentrations as the temperature increases. This has direct application to high temperature two-stage semi-continuous precipitation processes.

Equilibrium Constants

The equilibrium constants for the reactions shown in Equations 4 through 6 can be estimated using the least-squares coefficients. Table 5 shows the equilibrium constants calculated for the least square coefficients at each temperature.

Table 6 shows the best literature[5] values of the equilibrium constants available for qualitative comparison. However, the literature values are for a hydrochloric acid-oxalic acid system at 19°C with an ionic strength of 0.1 to 1.0. Comparison of the equilibrium constants show the same qualitative trends.

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TABLE 1

Neptunium (IV) Oxalate Solubility in Oxalic Acid/Nitric Acid Solutions at 22°C

$H_2C_2O_4$, M	HNO_3, M	R_s*	Np(IV) Solubility, mg/L
0.014	0.4	0.09	6.1
0.078	0.4	0.49	8.7
0.158	0.4	1.00	12.8
0.397	0.4	2.48	29.2
0.80	0.4	5.00	37.4
0.623	0.5	2.49	31.6
0.370	0.6	1.02	14.0
0.243	0.7	0.49	9.9
0.640	0.8	0.99	20.8
0.047	1.0	0.047	4.0
0.097	1.0	0.097	5.9
0.498	1.0	0.498	9.4
0.017	2.0	0.004	4.4
0.037	2.0	0.009	4.6
0.197	2.0	0.049	5.9
0.398	2.0	0.099	5.9
0.460	3.0	0.051	4.1
0.014	4.0	0.0008	35.6
0.084	4.0	0.005	5.5
0.158	4.0	0.010	5.1
0.123	5.0	0.005	7.7
0.034	6.0	0.0009	35.6
0.242	7.0	0.005	10.6
0.062	10.0	0.0006	35.9

---

* R_s is the solubility parameter, $[H_2C_2O_4]/[HNO_3]^2$.

TABLE 2

Neptunium (IV) Oxalate Solubility in Oxalic Acid/Nitric Acid Solutions at 45°C

$H_2C_2O_4$, M	HNO_3, M	R_s*	Np(IV) Solubility, mg/L
0.013	0.4	0.08	45.5
0.077	0.4	0.48	35.5
0.157	0.4	0.98	94.0
0.397	0.4	2.48	92.5
0.799	0.4	5.00	295.0
0.623	0.5	2.49	133.0
0.242	0.7	0.49	34.5
0.640	0.8	0.996	73.5
0.046	1.0	0.046	22.5
0.096	1.0	0.096	25.5
0.497	1.0	0.497	83.5
0.016	2.0	0.004	38.5
0.036	2.0	0.009	26.0
0.397	2.0	0.099	44.0
0.456	3.0	0.051	19.0
0.016	4.0	0.001	373.5
0.083	4.0	0.005	76.5
0.157	4.0	0.010	41.5
0.023	5.0	0.0009	162.5
0.122	5.0	0.005	74.5
0.036	6.0	0.001	362.5
0.242	7.0	0.005	101.0
0.063	10.0	0.0006	330.0

---

* R_s is the solubility parameter, $[H_2C_2O_4]/[HNO_3]^2$.

TABLE 3

Neptunium (IV) Oxalate Solubility in Oxalic Acid/Nitric Acid Solutions at 60°C

$H_2C_2O_4$, M	HNO_3, M	R_s*	Np(IV) Solubility, mg/L
0.013	0.4	0.08	74.9
0.077	0.4	0.48	60.2
0.157	0.4	0.98	74.5
0.390	0.4	2.48	172.4
0.789	0.4	5.00	263.7
0.622	0.5	2.49	118.9
0.367	0.6	1.00	106.6
0.241	0.7	0.49	61.9
0.640	0.8	0.995	84.9
0.046	1.0	0.046	68.3
0.097	1.0	0.097	49.6
0.497	1.0	0.497	84.4
0.017	2.0	0.004	76.2
0.036	2.0	0.009	54.8
0.196	2.0	0.049	36.4
0.396	2.0	0.099	32.4
0.456	3.0	0.051	36.7
0.016	4.0	0.001	378.1
0.083	4.0	0.005	104.6
0.156	4.0	0.009	53.8
0.123	5.0	0.005	198.2
0.036	6.0	0.001	420.1
0.242	7.0	0.005	104.6
0.063	10.0	0.0006	369.8

---

* R_s is the solubility parameter, $[H_2C_2O_4]/[HNO_3]^2$.

TABLE 4

Statistical Parameters for Neptunium (IV) Oxalate Equilibrium Solubility Model*

	Temperature		
	22°C	45°C	60°C
Least-Squares Coefficient			
a_0	4.2 (±0.7)	14.3 (±6.5)	41.9 (±5.3)
a_1	0.030 (±0.002)	0.34 (±0.02)	0.35 (±0.02)
a_2	8.2 (±0.7)	60.1 (±5.4)	43.9 (±4.9)
Correlation Coefficient	0.96	0.97	0.97
Standard Deviation of Y(x)	±3.6 mg/L	±28.8 mg/L	±26.5 mg/L

TABLE 5

Comparison of Equilibrium Formation Constants for Neptunium (IV) Oxalate Solubility Data*

Reaction Step	Literature* (19°C)	Calculated (22°C)
Neutral complex	2.9×10^{-5}	1.8×10^{-5}
Cationic complex	3.0×10^{-8}	1.3×10^{-7}
Anionic complex	3.0×10^{-4}	3.5×10^{-5}

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* The literature data is for a hydrochloric acid-oxalic acid system. Note also the temperature difference between the literature and calculated values.

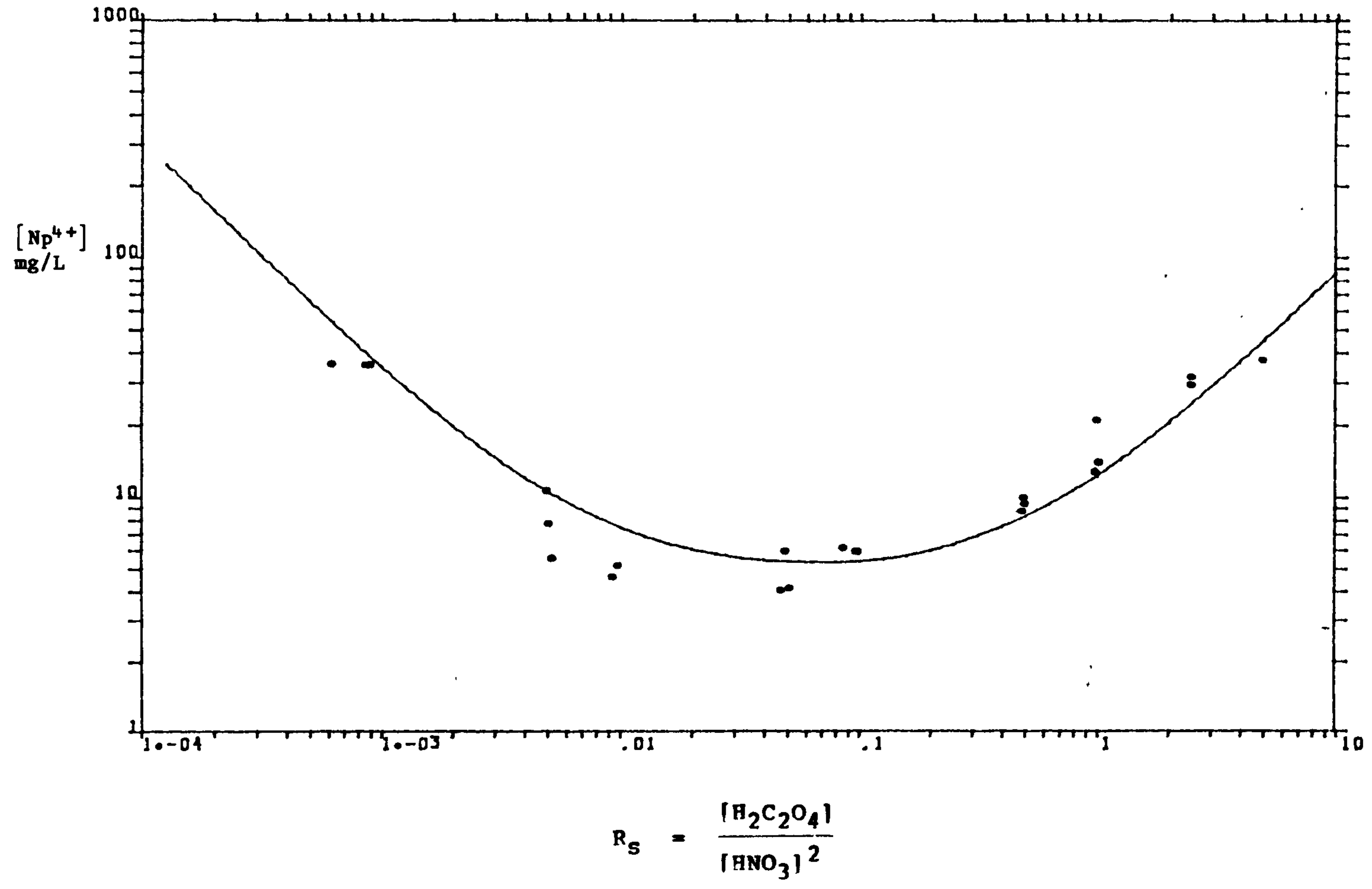

FIGURE 1. Neptunium(IV) Oxalate Solubility at 22°C

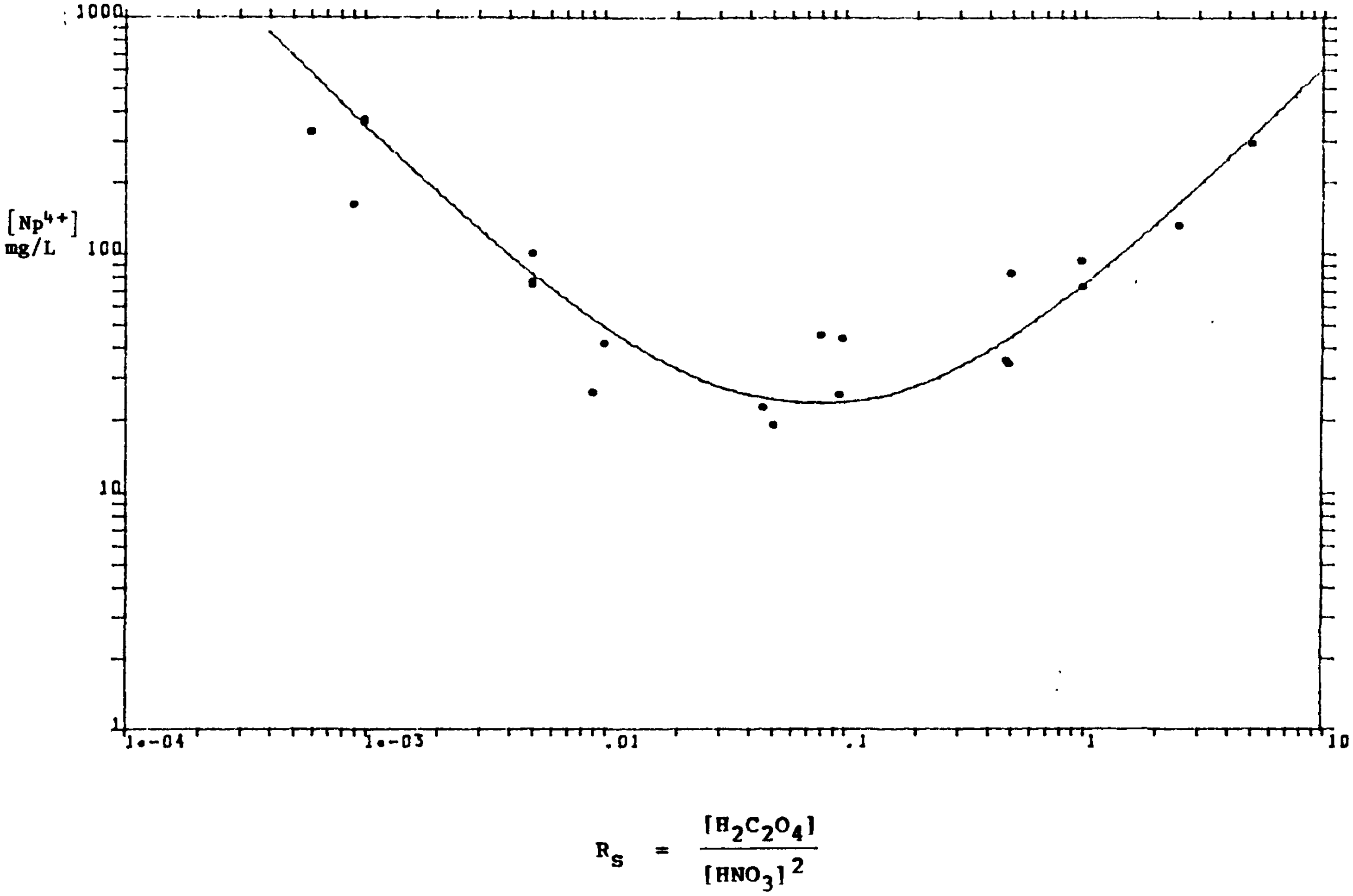

FIGURE 2. Neptunium(IV) Oxalate Solubility at 45°C

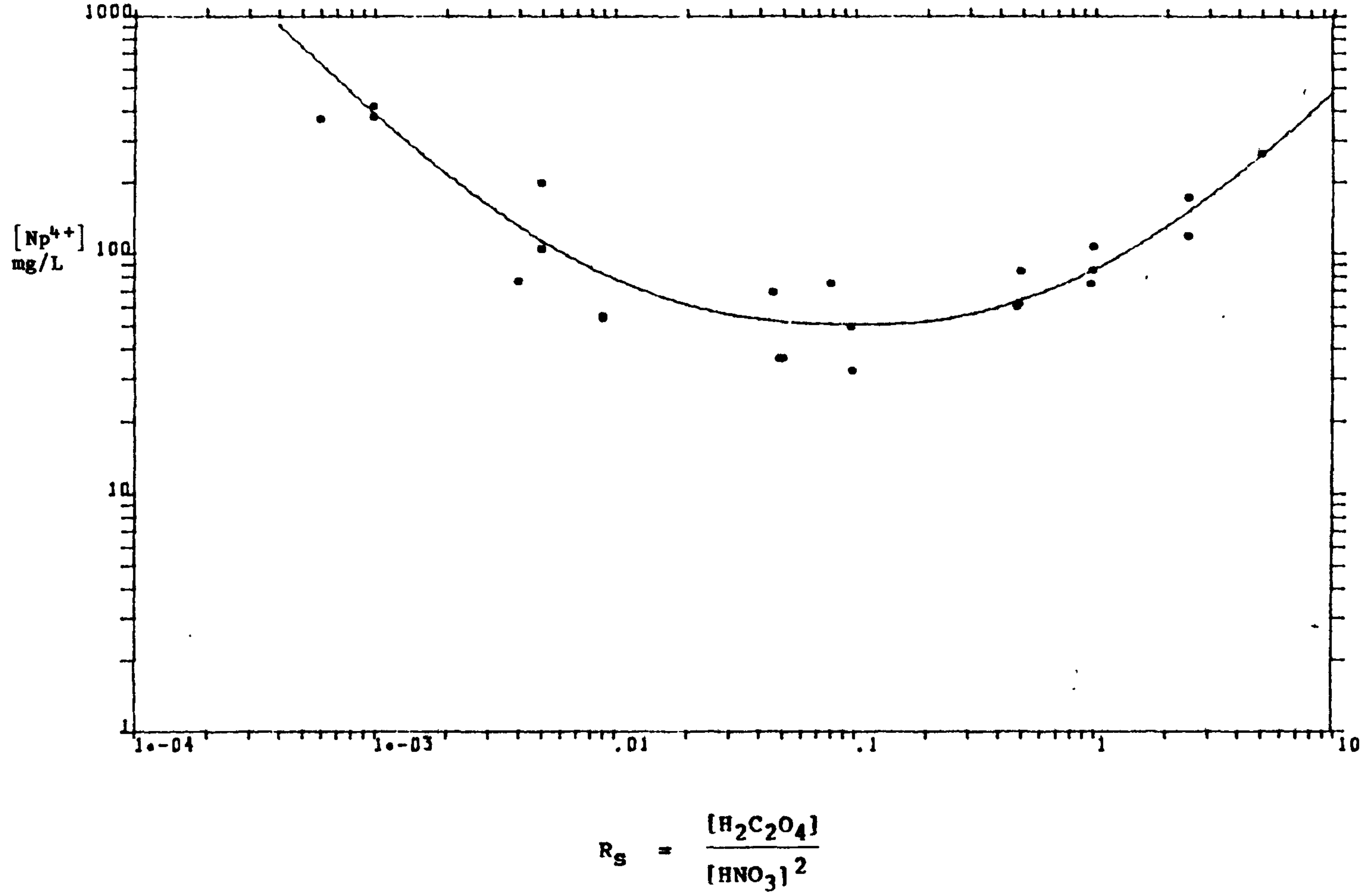

FIGURE 3. Neptunium(IV) Oxalate Solubility at 60°C

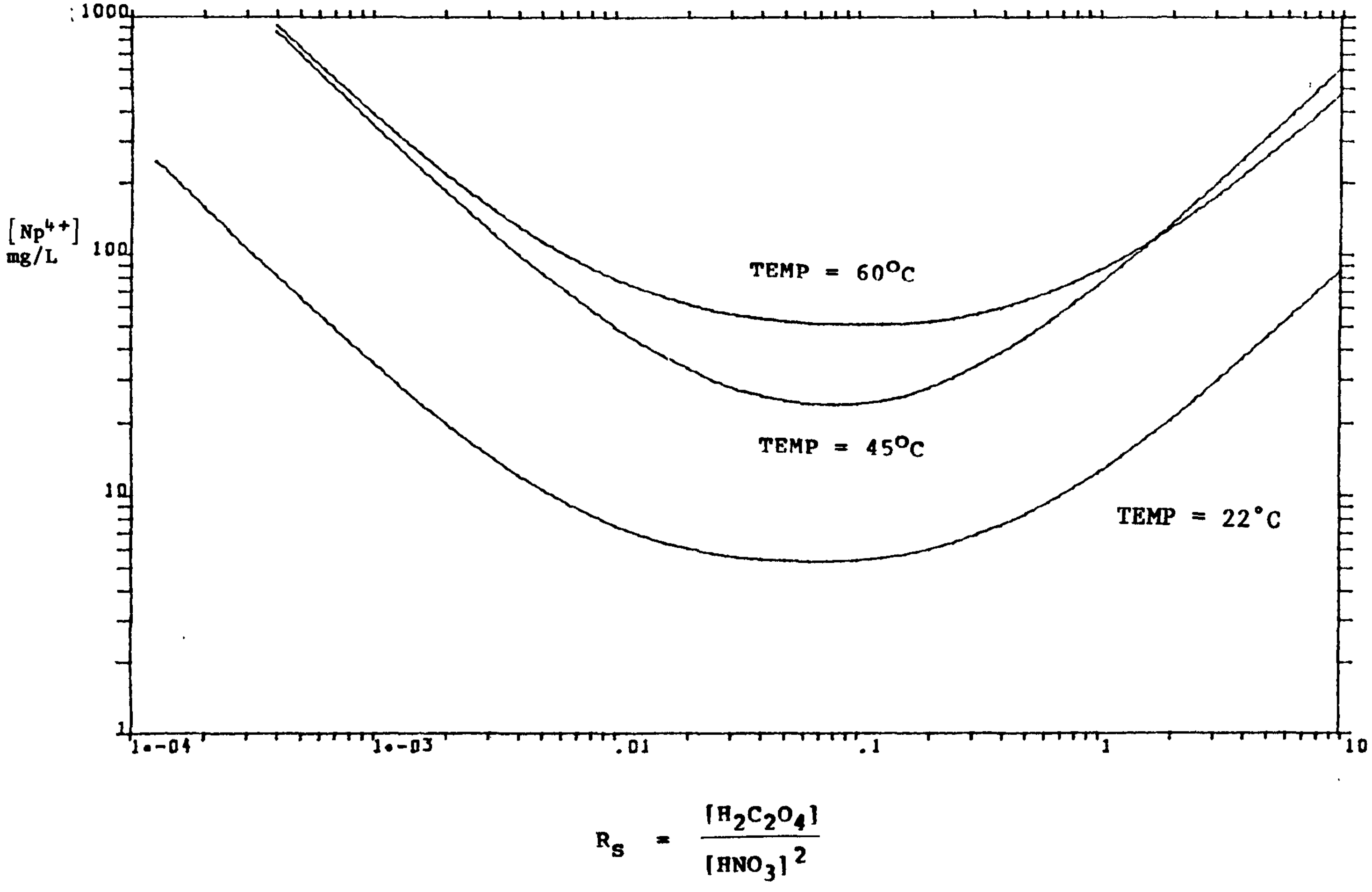

FIGURE 4. Predicted Solubility of Neptunium(IV) Oxalate Using the Least-Squares Solubility Model