Status and Priorities re Solubility / Speciation of Long-Lived Radionuclides

WBS 1.2.3.4.1.3.1/2
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OUTLINE

- I. Bulk Solubility
  - A. Approach
  - B. Sample Experiment
  - C. Summary of Current Results
  - D. Status
- II. Speciation / Thermodynamic Database Developments
  - A. Approach
  - B. Examples
    1. NMR
    2. PAS
    3. NpO_2^+ hydrolysis study
  - C. Conclusions
- III. Research Priorities / Summary

First Priority Elements (from Inventory):

U, Np, Pu, Am, Tc

Second Priority:

Se, Ni, Zr, Sn, Nb

Overall Approach to Evaluate Solubility Barrier

1. Bulk Solubility Measurements

a. nature of expt's

i. long-term expt's

ii. from under- and over-sat.

iii. solid-liquid phase separation

iv. solid ppt analysis required

v. solution speciation needed

b."Bounding Conditions" approach

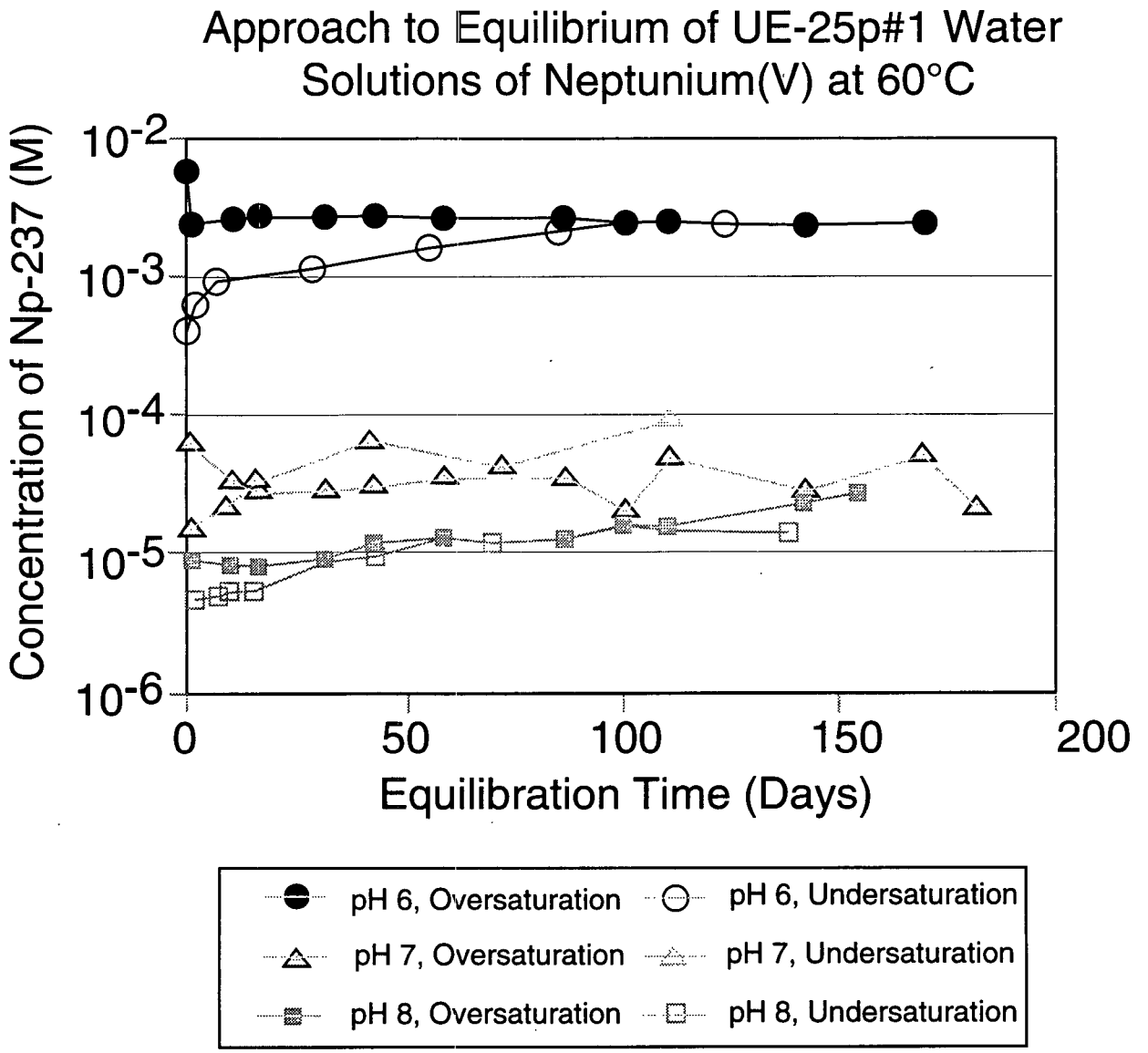
CO_3^{2-} top priority ligand

no carbonate - baseline

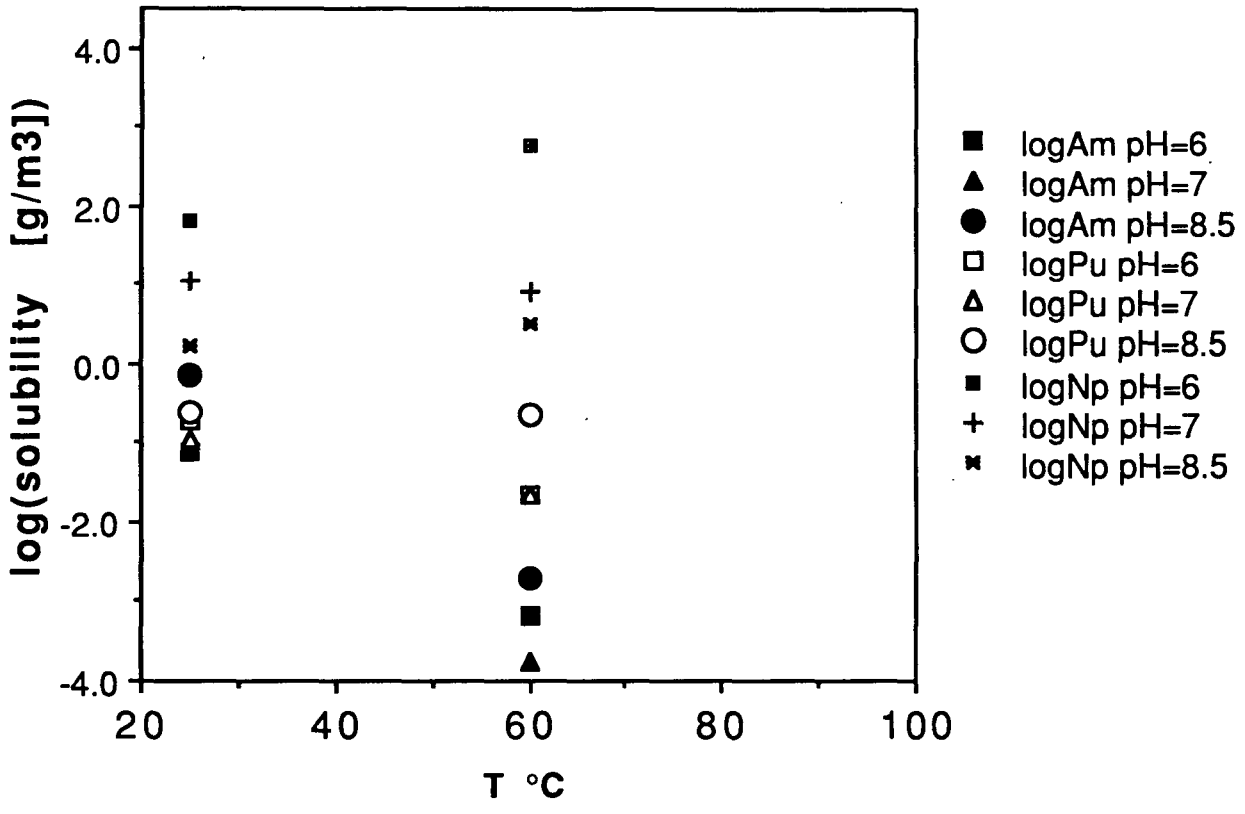
J-13 levels (2.8 mM) - "typical"

UE25p#1 (11 mM) - upper bound

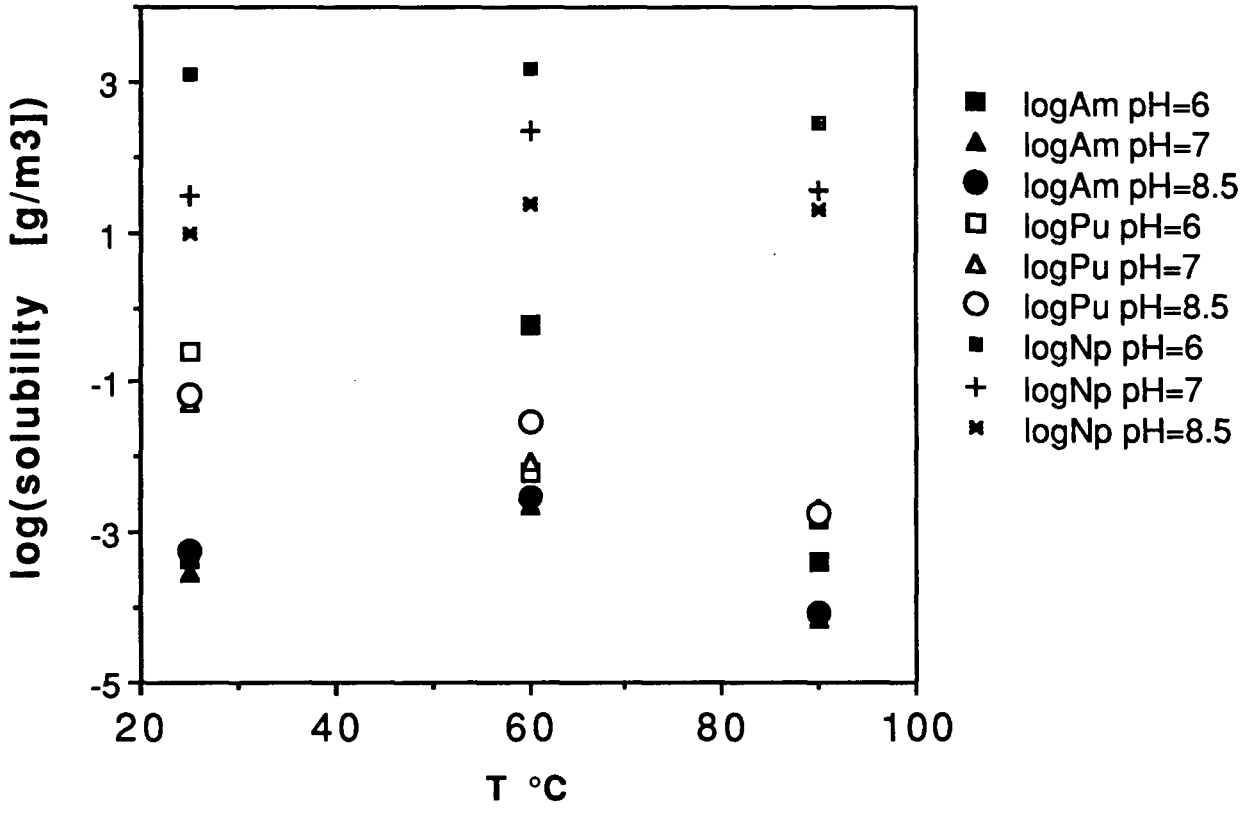
T, pH, E_h also key variables


Approach to Equilibrium of UE-25p#1 Water Solutions of Neptunium(V) at 60°C
Concentration of Np-237 (M)
10-2
10-3
10-4
10-5
10-6
0
50
100
150
200
Equilibration Time (Days)
pH 6, Oversaturation
pH 6, Undersaturation
pH 7, Oversaturation
pH 7, Undersaturation
pH 8, Oversaturation
pH 8, Undersaturation

Summary of Solubility from Oversaturation: UE25p#1



Summary of Solubility from Oversaturation: J-13 water



Status of Bulk Solubility Studies

Oversaturation Expt's For Top Priority Elements (except Tc) Finished

Solid ppt characterization from these expt's performed, although some questions still remain (e.g. Np carbonate solids)

Solubilities from undersaturation started for UE25p#1 water, need to start for J-13 and neutral electrolyte solutions

Remaining radionuclides: non-actinides such as Se, Ni, Zr, Sn, Nb

2. Thermodynamic Database Development (Speciation)

Justifications:

A. Bulk solubility alone only gives a few, discrete points

For general case, need thermodynamic data for calculations

ex. "bounding waters" may not bound

e.g. after boiling (~5% water left), pH and [CO_3^{2-}] could increase (Bill Murphy, DOE-NRC Technical Exchange Meeting, LANL, 10/93)

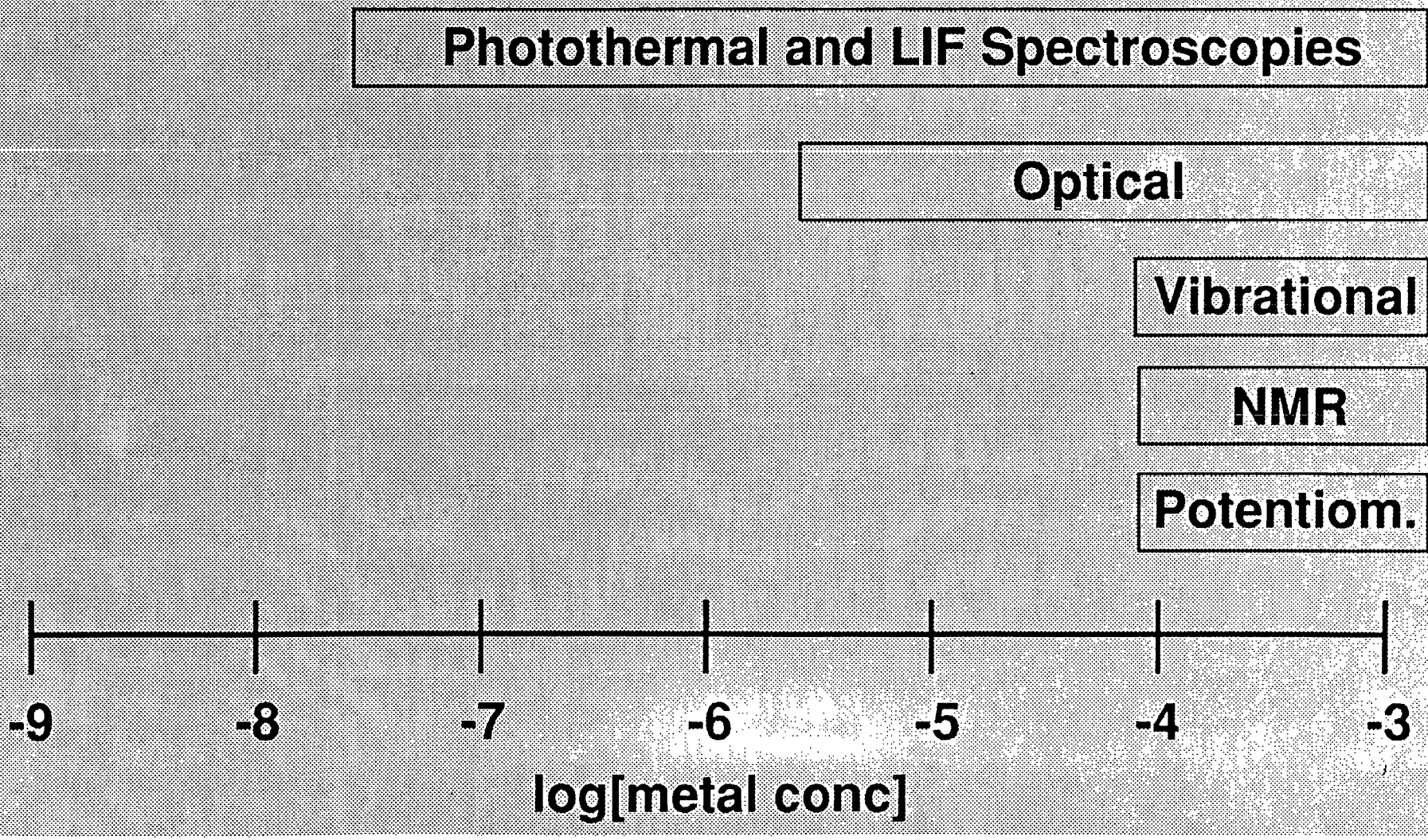
B. Speciation Information (overall species charge, ligands attached, nuclearity, ...)

i. prerequisite info for thermodynamic modeling

ii. input to repository design (e.g. in response to species' charge or redox state, as per R.A. Van Konynenburg's talk])

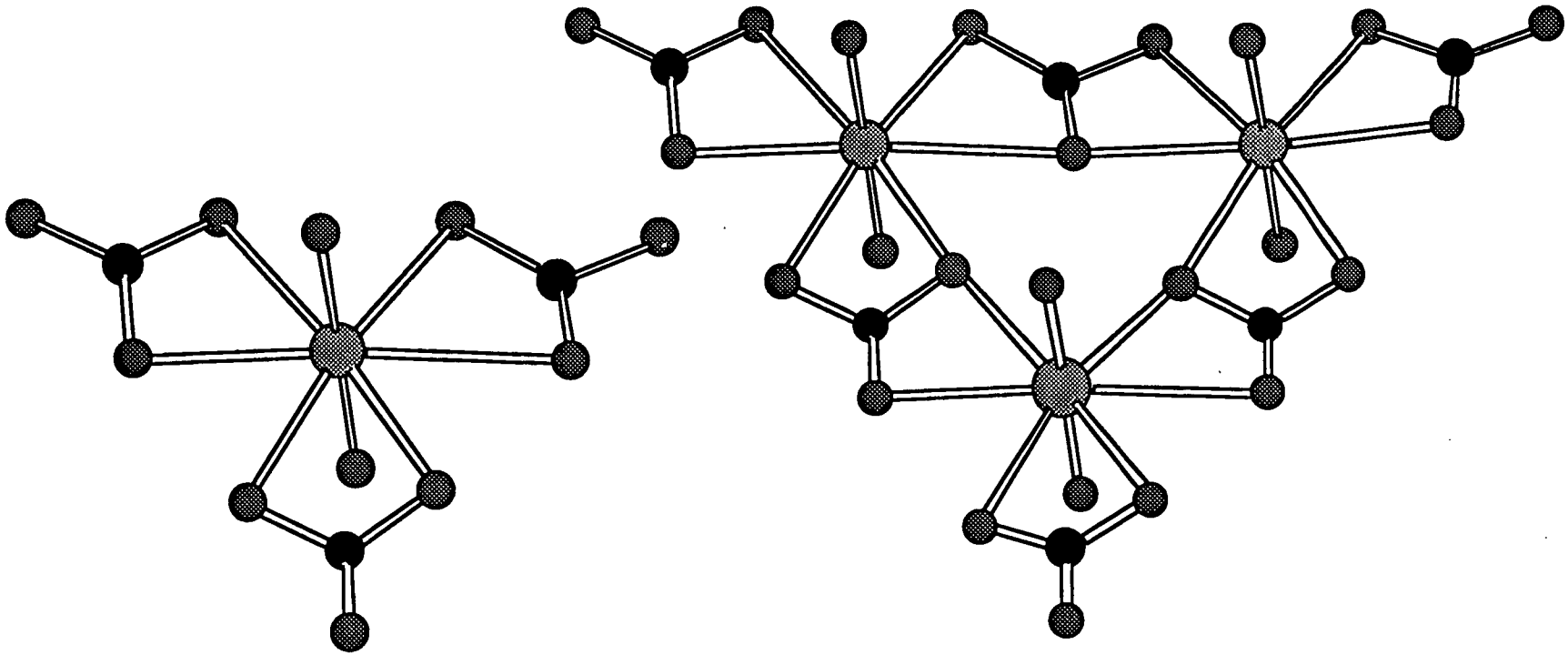
iii. input to PA models

Environmental Concentrations
Repository domain
minimum radiolysis



Proposed Monomer and Trimer Structures in the Actinyl Carbonate System

$$3\,NpO_2(CO_3)_3^{4-} + 6\,H^+ \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-} + 3\,CO_2 + 3\,H_2O$$



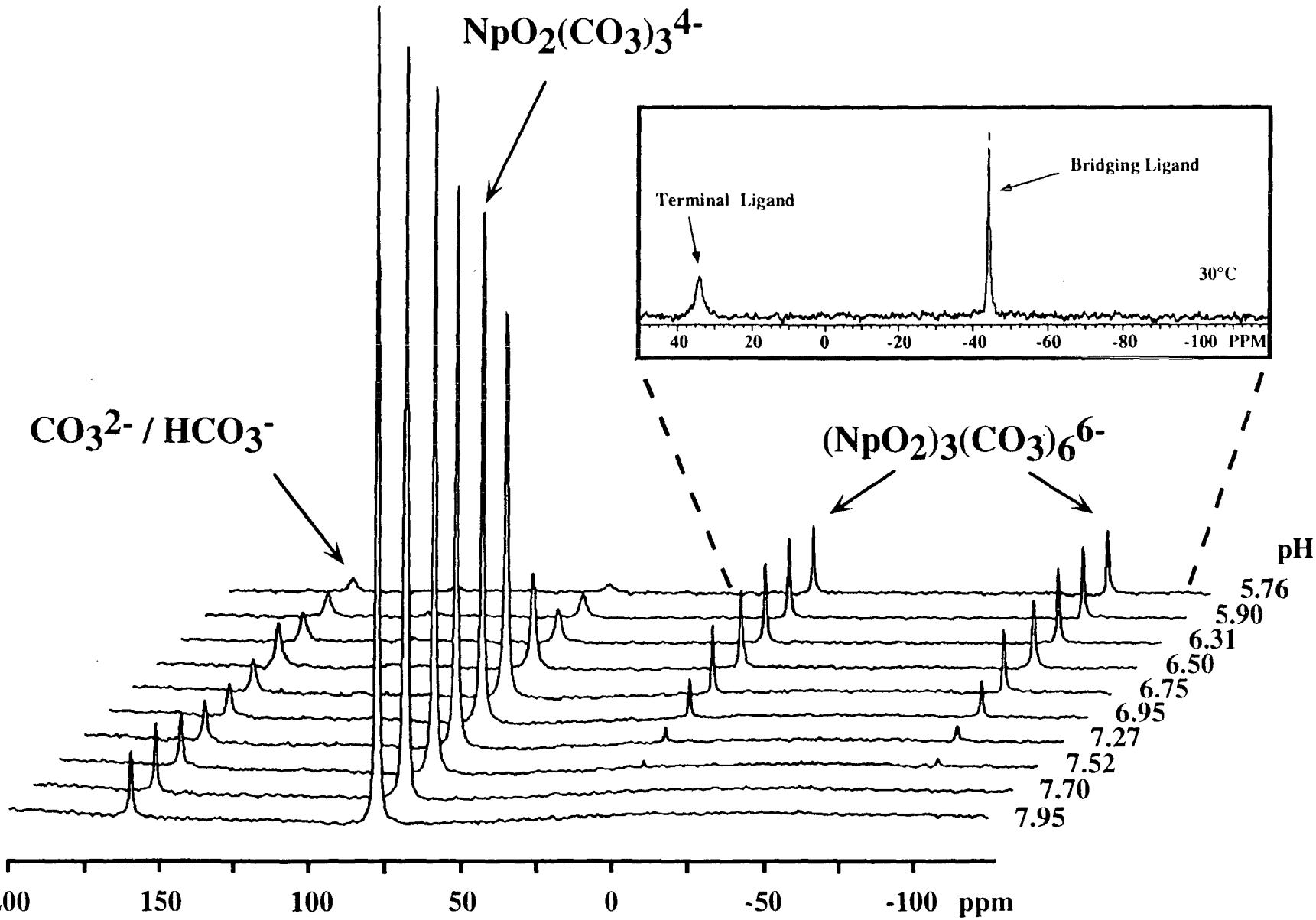
$NpO_2(CO_3)_3^{4-}$ $(NpO_2)_3(CO_3)_6^{6-}$

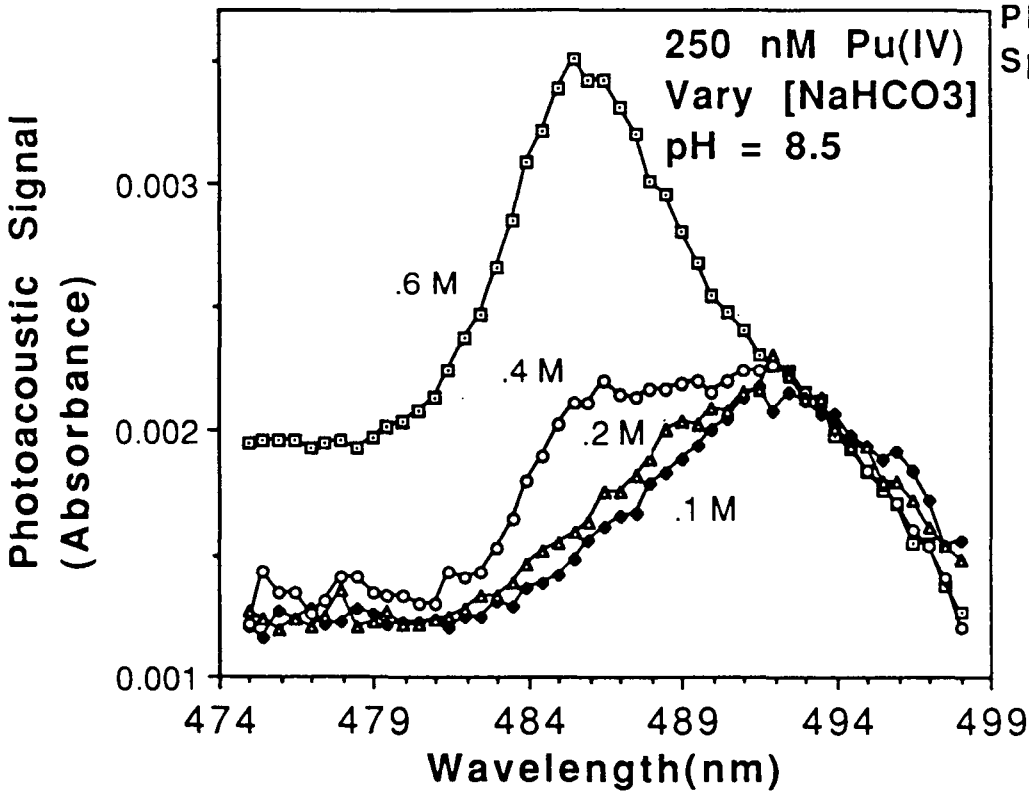
Np C O

* M. Aberg, D. Ferri, J. Glaser, I. Grenthe, *Inorg. Chem.*, **22** (1983) 3981.

^{13}C NMR Spectra of Neptunyl Carbonate at 0°C

$3NpO_2(CO_3)_3^{4-} + 6H^+ \text{ <---> } (NpO_2)_3(CO_3)_6^{6-} + 3CO_2 + 3H_2O$





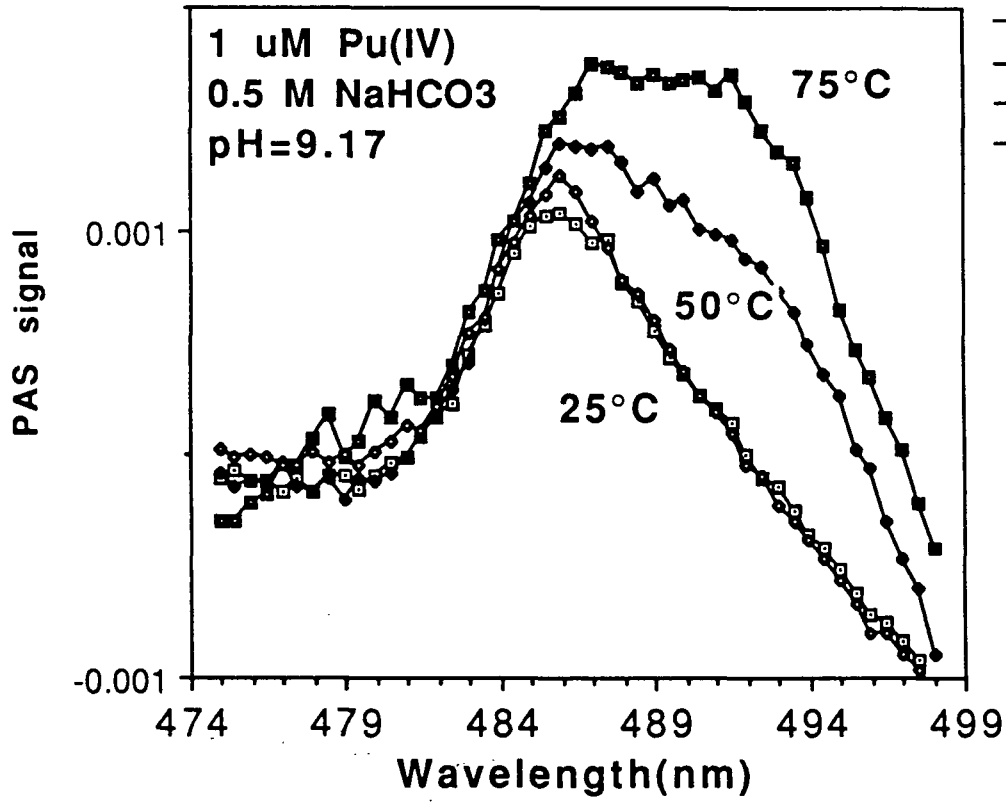
Photoacoustic Spectroscopy

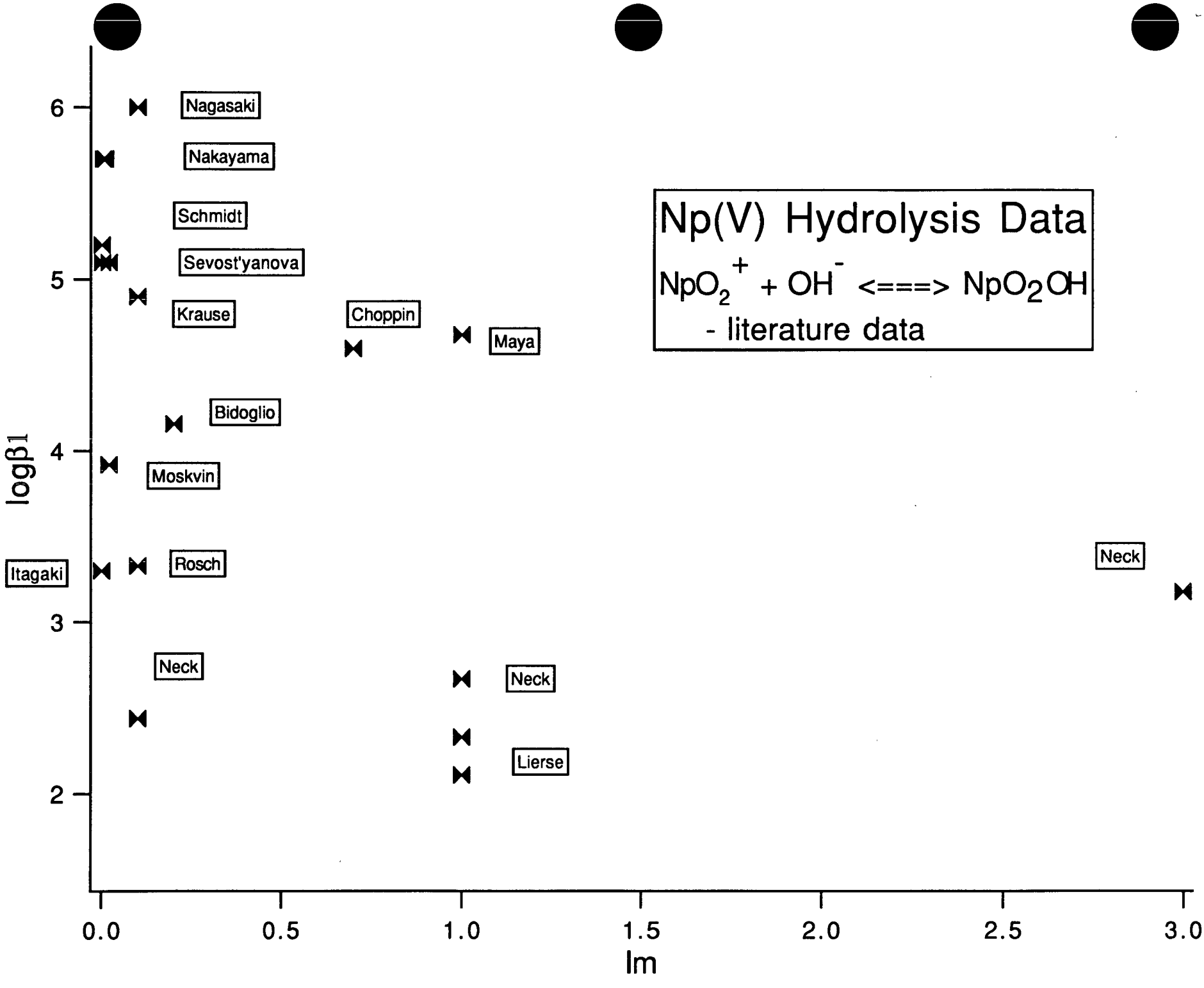
High Sensitivity for Low Actinide Concentrations

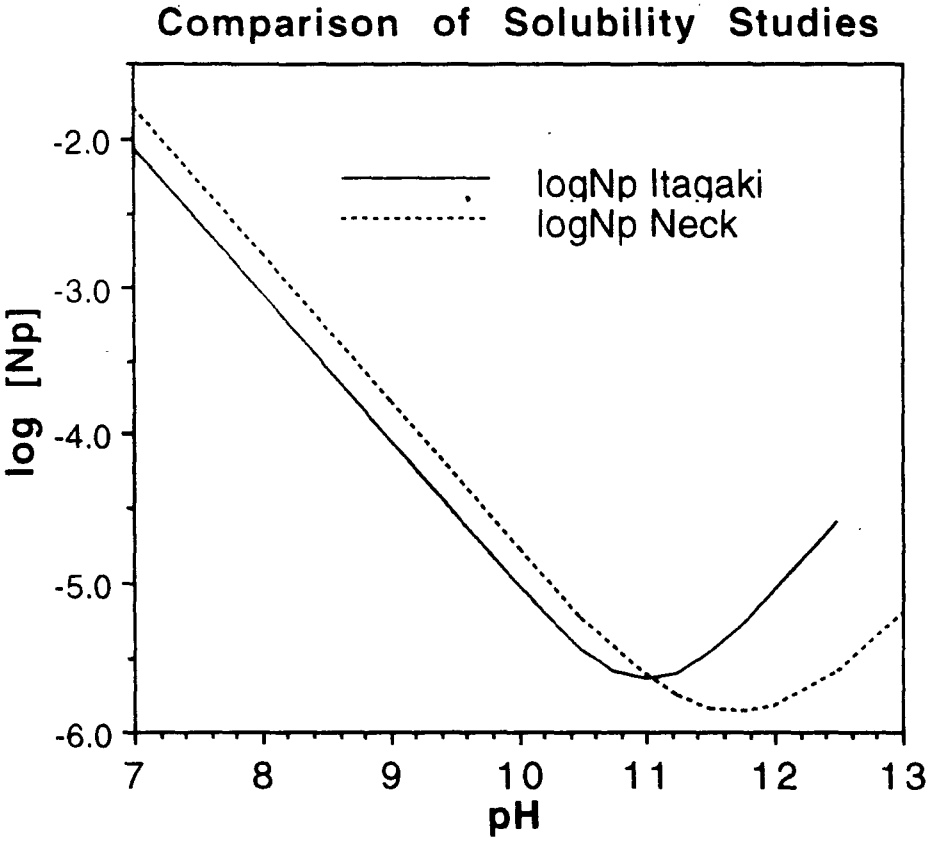
$Pu(OH)_x(CO_3)_y + H_2O <=> Pu(OH)_{x+1}(CO_3)_y + H^+$ pQ=8.14

$Pu(OH)_x(CO_3)_y + H_2O + CO_2 <=> Pu(OH)_x(CO_3)_{y+1} + 2H^+$ pQ=15.72

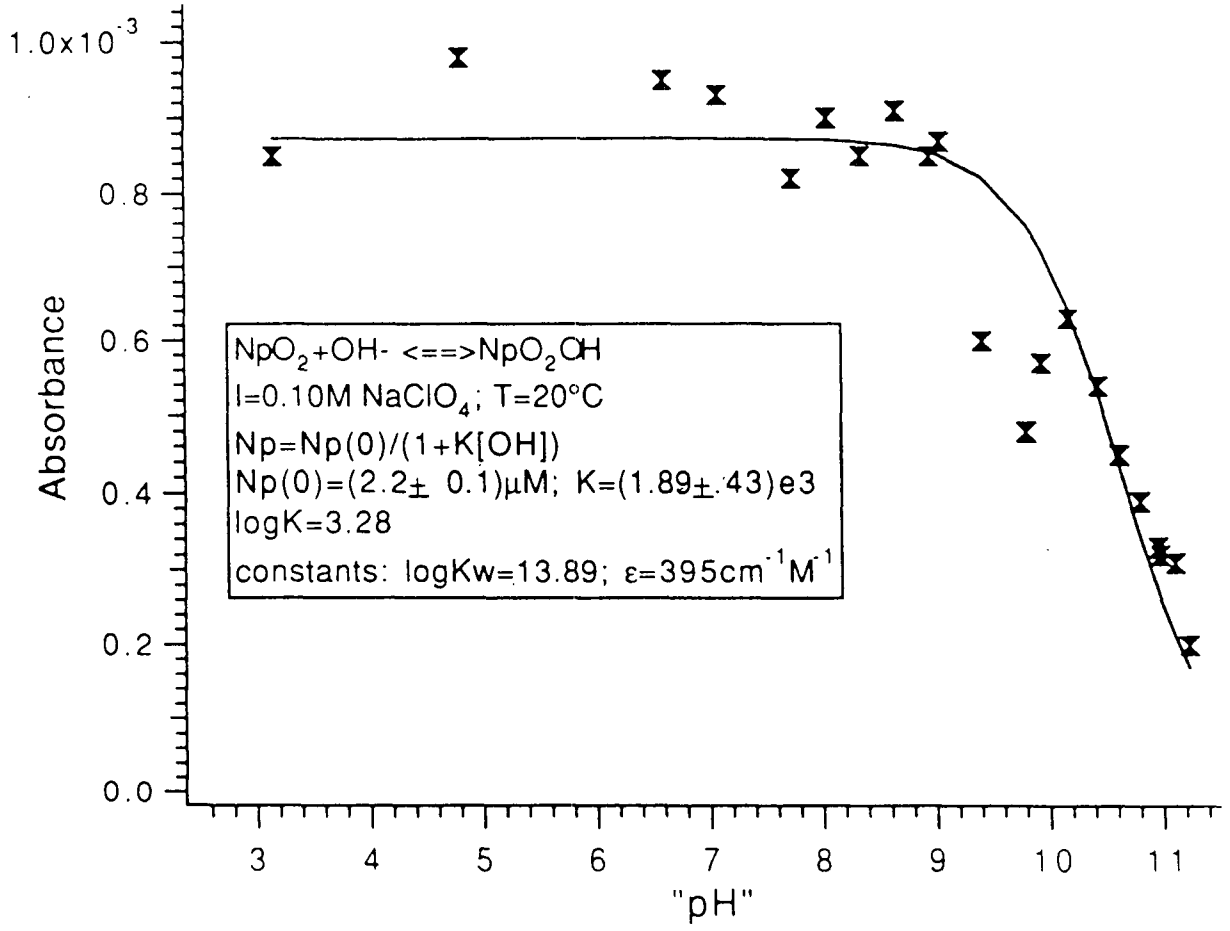
Temperature Dependence Experiment

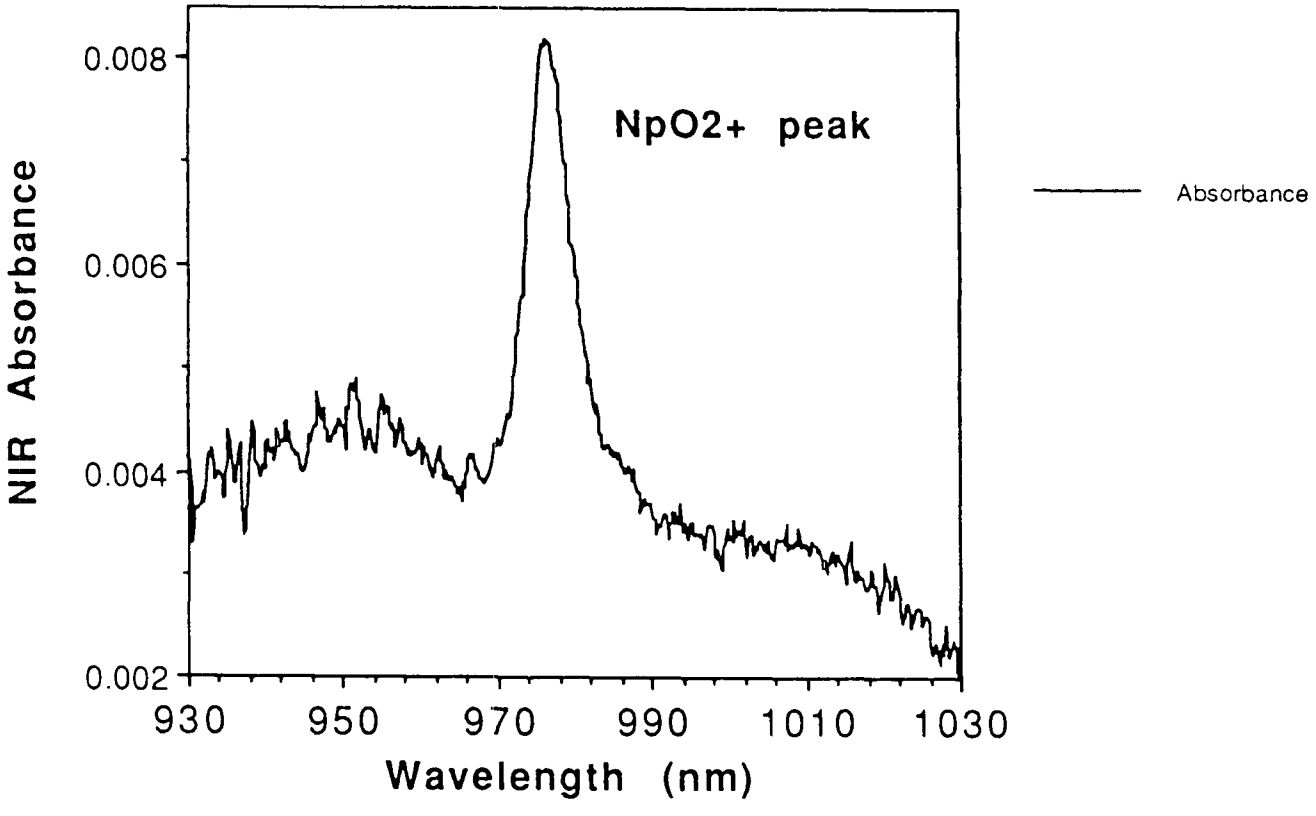


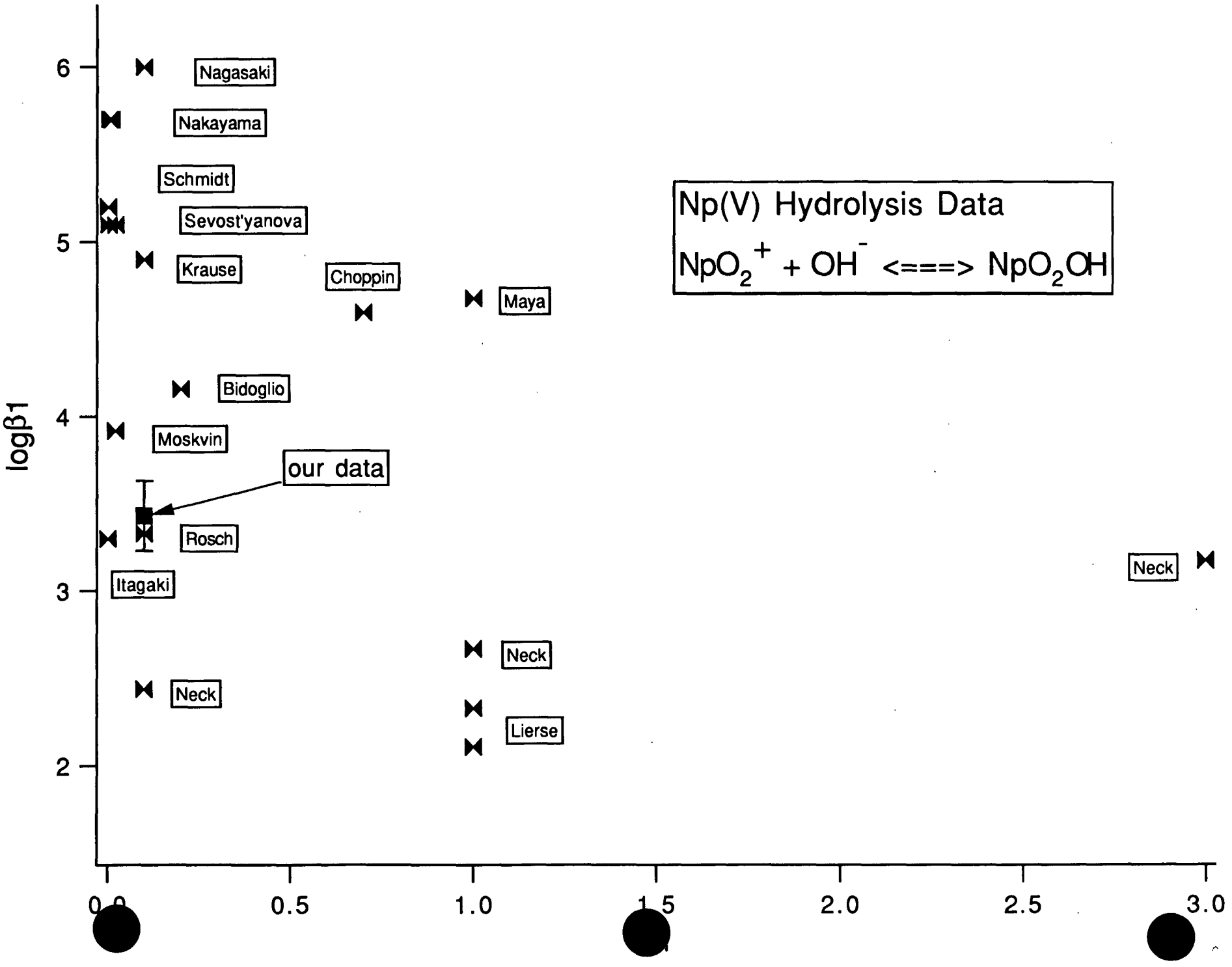

Np(V) Hydrolysis Data
NpO2+ + OH- <===> NpO2OH
- literature data
Nagasaki
Nakayama
Schmidt
Sevost'yanova
Krause
Choppin
Maya
Bidoglio
Moskvin
Itagaki
Rosch
Neck
Neck
Lierse
Neck
log β1
Im
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0


Comparison of Solubility Studies
logNp Itagaki
logNp Neck
log [Np]
-2.0
-3.0
-4.0
-5.0
-6.0
7
8
9
10
11
12
13
pH

Neptunium Hydrolysis






Np(V) Hydrolysis Data
NpO2+ + OH- <===> NpO2OH
logβ1
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Nagasaki
Nakayama
Schmidt
Sevost'yanova
Krause
Choppin
Maya
Bidoglio
Moskvin
our data
Rosch
Itagaki
Neck
Neck
Lierse
Neck

Summary from Speciation Studies (fundamental input to Solubility and Sorption)

Development, Implementation and Verification of Advanced Techniques to Give Integrated Approach

ex. ^{13}C and ^{17}O NMR application to UO_2^{2+}-carbonate monomer/trimer system, comparison to NEA data

Pu(IV) - OH - CO_3^{2-} System

Combined conventional and PAS absorption measurements: model

$Pu(OH)_x(CO_3)_y + H_2O <=>$
$Pu(OH)_{x+1}(CO_3)_y + H^+$ pQ=8.14

$Pu(OH)_x(CO_3)_y + H_2O + CO_2 <=>$
$Pu(OH)_x(CO_3)_{y+1} + 2H^+$ pQ=15.72

(from comparison to Yamaguchi; x= 1, y=2)

Np(V)O_2 - OH - CO_3^{2-} System

hydrolysis: $\log\beta 1 = 3.43 \pm 0.20$ at room T
higher T experiments underway

carbonate complexation: T-dependent NIR absorption, ^{13}C and ^{17}O NMR experiments underway

Research Priorities / Summary

Drivers:

a. Develop thermodynamically defensible input to PA for effectiveness of solubility barrier
- won't have to rely on most conservative (higher) estimates

b. Provide speciation / thermodynamic data for other tasks
Solubility <--> Sorption : $Np(V)O_2^+$
Solubility <--> Sorption, EBS: Tc(VII) vs. Tc(IV)

1. $Np(V)O_2^+$ Studies

a. bulk solubility
i. better identification of solid ppts
ii. finish expt's from undersat.

b. Speciation
i. finish determination of equilibrium constants for T-dependent hydrolysis and carbonate-complexation

2.non-Actinide Radionuclides

a. Tc

TcO_4^- --> $TcO(OH)_2$

11.3 m ($\sim 10^{-8}$ m)

- bulk solubility under reducing or near-field conditions
- database for hydrolysis and carbonate complexation, with E_h key variable

b. bulk solubility and basic speciation of Se, Ni, Zr, Sn

3. Plutonium-carbonate studies

• sorption studies (see I. Triay's talk) may refine K_d soon such that Pu becomes less of a problem as a soluble (non-colloid) species

Pu still on list because:

- K_d value still not known with a high degree of certainty
- solubility may provide barrier despite flow path

a. Bulk Solubility

Finish expt's from undersat.

b. Speciation

T-dependent equilibrium
constant determinations for
Pu(V) and Pu(VI) hydrolysis
and carbonate
complexation reactions

c. Colloids
overall charge
stability
mechanism of formation
Pu(IV) (and non- Pu)

4. Modeling and Database Evaluation
Test self-consistency of
database to determine
reliability of solubililty (and
sorption) predictions in
general cases
Predictions of solubility and
feedthrough to PA