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Prediction of Formation Constants of $NdHB_4O_7^{2+}$ up to 200°C

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INTRODUCTION

- Recent experimental work indicates that borate could form a relatively strong complex with Nd(III) (log $\beta_1 = 4.99 \pm 0.30$) at 25°C (Borkowski et al., 2010), an analog to Am(III).
- Borosilicate glass is proposed as a waste form for high-level radioactive waste.
- Up to 65 mmol/L of boron can be leached out in long-term alteration experiments of a simulated nuclear-waste borosilicate glass in water at 90°C (Advocat et al., 2001; Curti et al., 2009).
- Therefore, dissolved borate could be important to complexation with Am(III) at elevated temperatures.

Advocat, T., Jollivet, P., Crovisier, J.L., del Nero, M., 2001. Long-term alteration mechanisms in water for SON68 radioactive borosilicate glass. Journal of Nuclear Materials 298, 55-62.

Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. Radiochimica Acta 98, 577-582.

Curti, E., Dahn, R., Farges, F., and M. Vespa, M., 2009. Na, Mg, Ni and Cs distribution and speciation after long-term alteration of a simulated nuclear waste glass: A micro-XAS/XRF/XRD and wet chemical study. Geochimica et Cosmochimica Acta 73, 2283-2298

Objective of This Study

The objective of this study is to estimate the formation constant of $NdHB_4O_7^{2+}$ to 200°C using the one-term isocoulombic approach.

- **To guide and stimulate further experimental work on borate complexation with Nd(III) and actinide(III)**

One-Term Isocoulombic Approach

- One-term isocoulombic extrapolation (Gu et al., 1994):

$$\Delta G^{o}_{T} = \Delta G^{o}_{Tr} = -RT \times \ln K_{T}$$

- This extrapolation method is found to have an average error of ±0.5 logarithmic units (10-based logarithmic units) to temperature of 200°C.
- Theory behind this approach: A well-balanced isocoulombic reaction should minimize the changes in both heat capacity and entropy, leaving a free energy of reaction which is nearly constant.

Gu, Y., Gammons, C., Bloom, M.S., 1994, A one-term extrapolation method for estimating equilibrium constants of aqueous reactions at elevated temperatures. Geochimica et Cosmochimica Acta 58, 3545-3560.

Isocoulombic Reactions

The following are ideal isocoulombic reactions:

$$NH_4^+ \leftrightarrows NH_3(aq) + H^+$$

$$H_2O + Ac^- \leftrightarrows HAc + OH^-$$

$$H_2O + HS^- \leftrightarrows H_2S + OH^-$$

$$H_2O + F^- \leftrightarrows HF + OH^-$$

$$H_2O + HCO_3^- \leftrightarrows H_2CO_3(aq) + OH^-$$

The following are semi-ideal isocoulombic reactions:

$$H_2O + CO_3^{-2} \leftrightarrows HCO_3^- + OH^-$$

$$H_2O + SO_4^{-2} \leftrightarrows HSO_4^- + OH^-$$

Isocoulombic Reaction Used by This Study

$HB_4O_7^- + NdAc^{2+} \leftrightarrows Ac^- + NdHB_4O_7^{2+}$

which is the combination of the following reactions:

$Nd^{3+} + Ac^- \leftrightarrows NdAc^{2+}$ (1)

$Nd^{3+} + HB_4O_7^- \leftrightarrows NdHB_4O_7^{2+}$ (2)

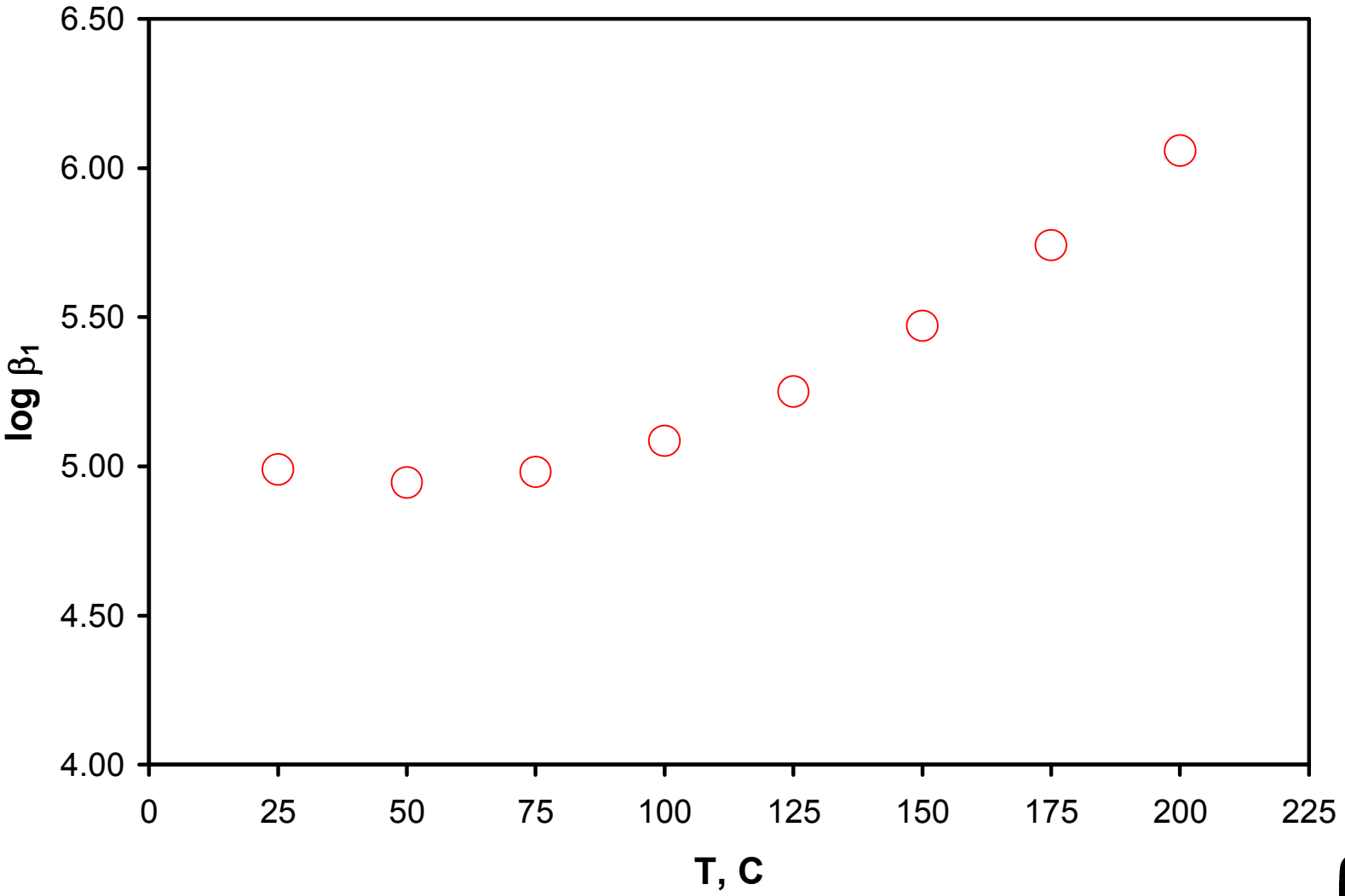
- log β_1's for Reaction (1) at elevated temperatures are from Wood et al. (2000).
- log β_1 for Reaction (2) at 25°C, which is 4.99, is from Borkowski et al. (2010).

Wood, S.A., Wesolowski, D.J., and Palmer, D.A., 2000. The aqueous geochemistry of the rare earth elements IX. A potentiometric study of Nd^{3+} complexation with acetate in 0.1 molal NaCl solution from 25°C to 225°C. Chemical Geology 167, 231-253.

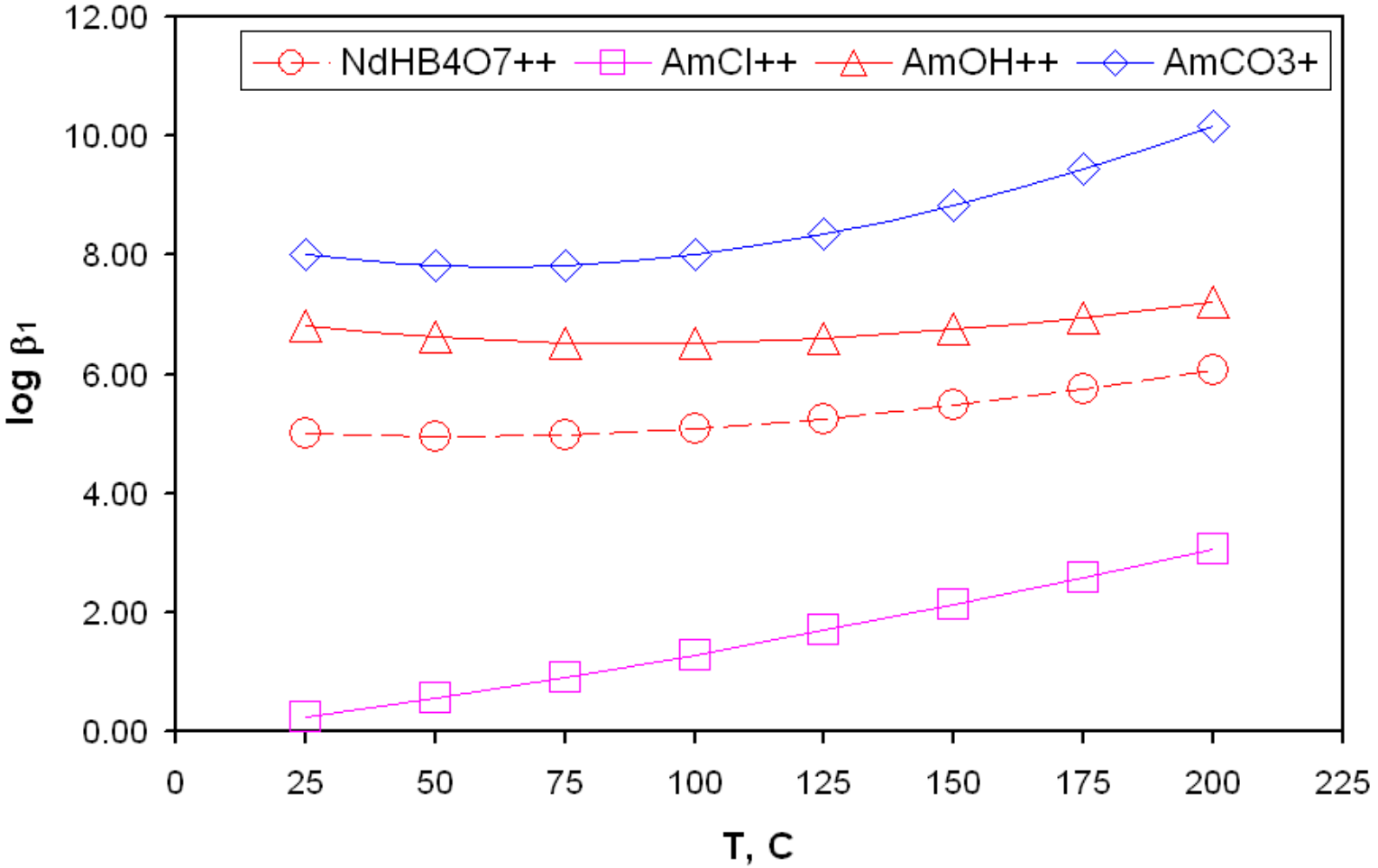
log β_1's for Reaction (1) from Wood et al. (2000)

T, K	T, C	log β_1
298.15	25	2.61
323.15	50	2.75
348.15	75	2.94
373.15	100	3.18
398.15	125	3.47
423.15	150	3.80
448.15	175	4.16
473.15	200	4.56

Results for $Nd^{3+} + HB_4O_7^- \leftrightarrows NdHB_4O_7^{2+}$



Comparison with Other Inorganic Complexes



Simplified Alteration Solution

Element	M
Li	2.90E-02
Na	2.06E-02
K	4.00E-04
ΣB	6.50E-02
ΣSi	4.60E-03
OH^-	8.00E-04
MoO_4^{2-}	7.00E-04
HPO_4^{2-}	2.00E-05
C(total)	1.00E-05
CO_3^{2-}	1.50E-06
pH	9.10

Simplified solution resulting from alteration of simulated borosilicate waste in pure water at 90°C (from Curti et al., 2009)

Implications

- It is expected that borate would play an important role in complexation with Am(III) because of its potentially high concentrations in solution.
- Although β_1 for the carbonate complex is about four orders of magnitude higher than β_1 for the borate complex, the latter is expected to compete with the carbonate complex owing to its much higher concentrations.

CONCLUSIONS

- The formation constants of the neodymium-borate complex are estimated up 200°C by using the isocoulombic approach.
- The strength of this complex is stronger than $AmCl^{2+}$ by about four orders of magnitude, and is similar to that of $AmOH^{2+}$, at 200°C.
- This complex is expected to strongly compete with $AmCO_3^+$ because of the potentially higher concentrations of borate anticipated in solutions resulting from alteration of borosilicate waste forms.