

A spectroscopic study on the formation of Cm(III) acetate complexes at elevated temperatures

Supporting information

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Calculation of the free ligand concentration

The free ligand concentration is calculated as performed in our previous studies treating the interaction of Cm(III) with propionate.^{21,22} There, we showed that the complexation of Na⁺ by propionate is negligible.^{21,22} Due to the similar chemical properties, NaAc is also assumed to be fully dissociated under the present experimental conditions. Following these approximations, the free acetate concentration in NaCl and NaClO₄ solution is calculated according to the following equation which has been deduced in a previous work:²¹

$$[Ac^-]_{eq}(T) = \frac{-\left([H^+]_{total} - [Ac^-]_{total} + K'_{HAc}(T)\right)}{2} + \frac{\sqrt{\left([H^+]_{total} - [Ac^-]_{total} + K'_{HAc}(T)\right)^2 + 4 \cdot [Ac^-]_{total} \cdot K'_{HAc}(T)}}{2}$$

$[H^+]_{total}$ and $[Ac^-]_{total}$ are the total concentrations of protons and acetate, respectively. $K'_{HAc}(T)$ is the conditional dissociation constant of acetic acid as a function of temperature at a given ionic strength and is calculated according to the following equation:

$$K'_{HAc}(T) = K^0_{HAc}(T) \cdot \frac{\gamma_{HAc}(T)}{\gamma_{H^+}(T) \cdot \gamma_{Ac^-}(T)}$$

$K^0_{HAc}(T)$ at a given temperature is calculated from $\log K^0_{HAc}(25\text{ }^\circ\text{C}) = -4.757$ and $\Delta_r H^0_m = -0.41$ kJ/mol (both values given in the NIST database 46.6)²⁴ using the integrated Van't Hoff equation. The activity coefficients ($\gamma(T)$) are determined according to the specific ion interaction theory which is recommended in the NEA thermodynamic database (TDB).⁷ Within the SIT-approach, ion interaction coefficients (ϵ) are introduced to describe the non-electrostatic, short-range interaction between ions of opposite charge. This procedure is valid for ionic strengths up to 4 mol/kg H₂O. Within the temperature range studied in the present work it is appropriate to use temperature-independent coefficients for 25 °C.⁷ The required ϵ -values ($\epsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$, $\epsilon(H^+, Cl^-) = 0.12 \pm 0.01$ and $\epsilon(Na^+, Ac^-) = 0.08 \pm 0.01$) are tabulated in the NEA-TDB.⁷

In the case of CaCl₂ as background electrolyte, the interaction between Ca²⁺ and Ac⁻ has to be taken into account. The required conditional stability constants $K'_{CaAc^+}(T)$ is calculated from $\log K^0_{CaAc^+}(25\text{ }^\circ\text{C}) = 1.18$ and $\Delta_r H^0_m = 4$ kJ/mol (both values given in the NIST database 46.6)²⁴. Considering CaAc⁺ formation, the free acetate concentration in solution is a function of the initial Ca²⁺ concentration and $K'_{CaAc^+}(T)$. The mathematical expression to calculate the free ligand concentration in CaCl₂ solution has already been deduced in our previous work on Cm(III)-propionate complexation.²² In the context of this work, the required ion interaction coefficients $\epsilon(Ca^{2+}, Ac^-) = 0.27 \pm 0.20$ and $\epsilon(CaAc^+, Cl^-) = 0.21 \pm 0.10$ were derived.²² $\epsilon(Ca^{2+}, Cl^-) = 0.14 \pm 0.01$ is tabulated in the NEA TDB.⁷

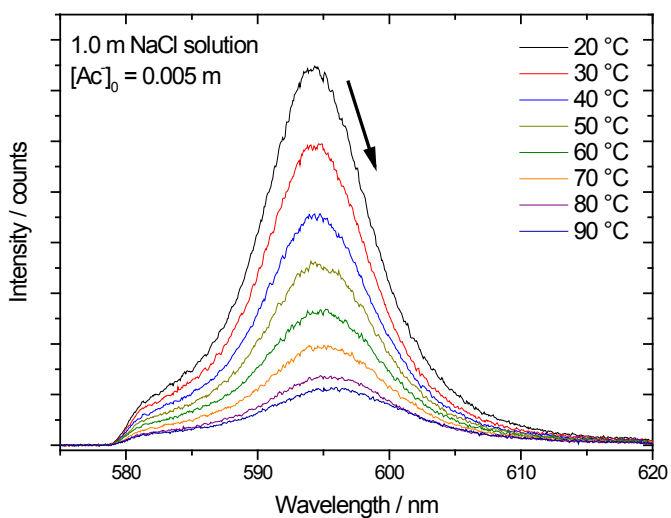


Figure S1. Emission spectra of Cm(III) in 1.0 m NaCl solution in the presence of 0.005 m acetate as a function of temperature (20-90 °C).

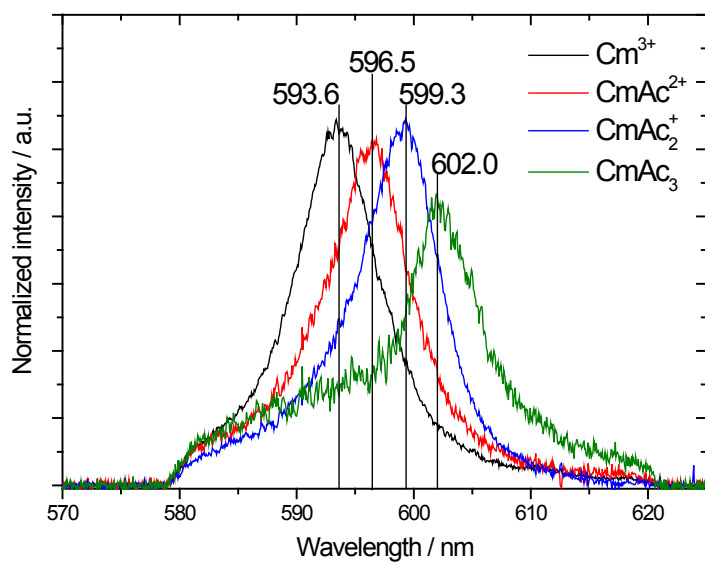


Figure S2. Pure component spectra of $\text{Cm(III)}_{\text{aq}}$ and Cm(Ac)_n^{3-n} ($n = 1-3$) obtained by peak deconvolution.

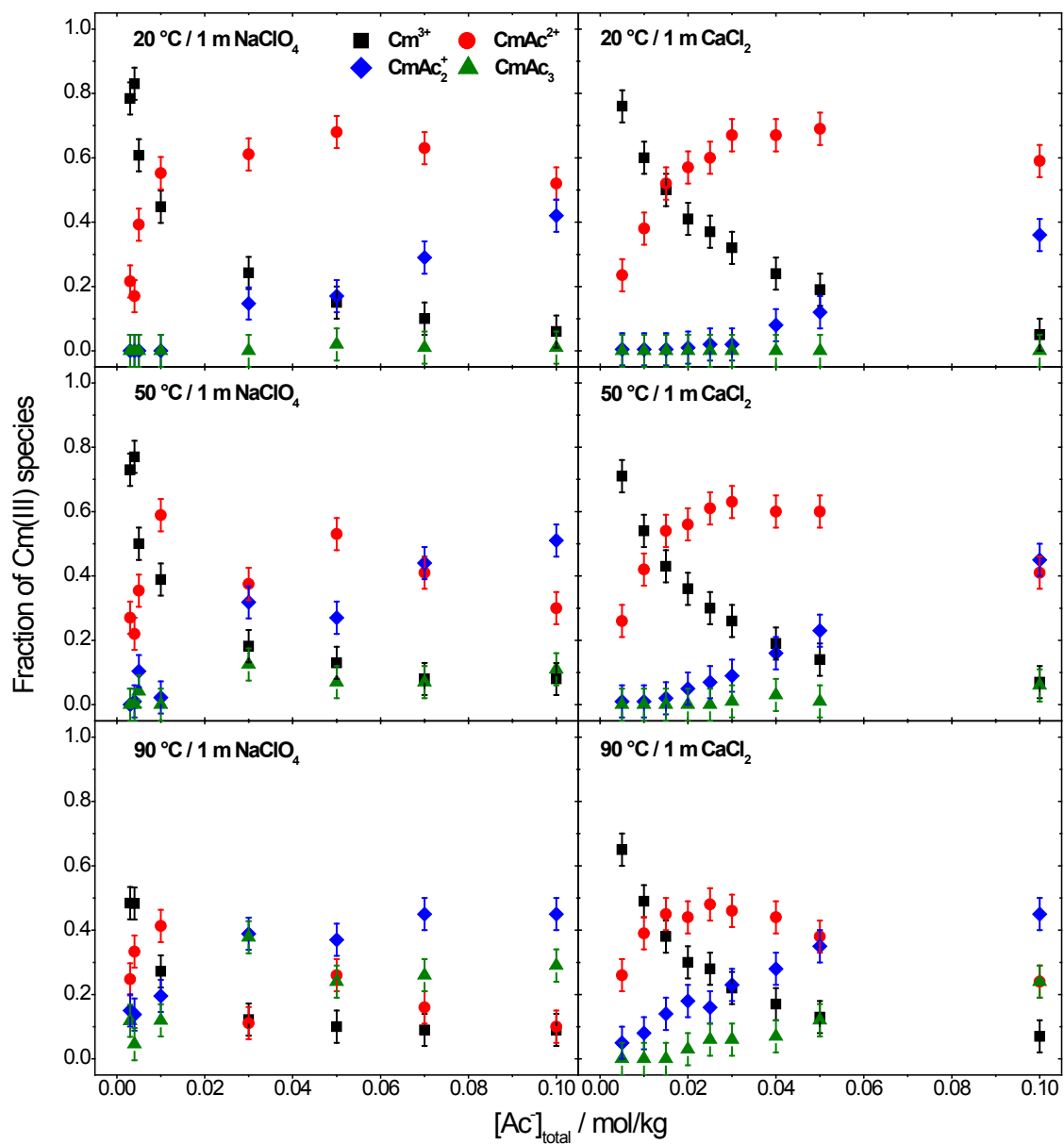


Figure S3. Cm(III) speciation as a function of the initial acetate concentration and temperature (20, 50, 90 °C) in 1 m NaClO₄ and CaCl₂ solution. The error bars equal an absolute error of 5% for each species.

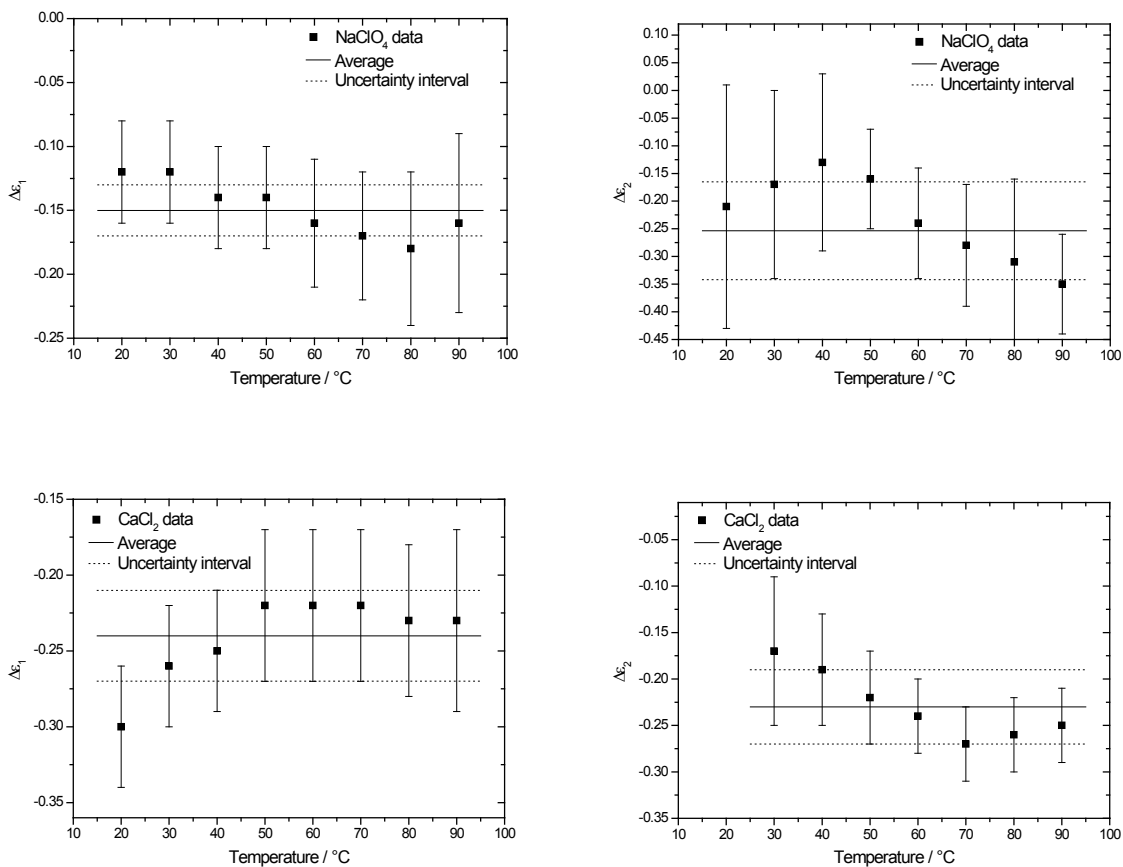


Figure S4. $\Delta\epsilon_n$ values ($n = 1, 2$) for the formation of $[\text{Cm}(\text{Ac})_n]^{3-n}$ in NaClO_4 and CaCl_2 solution as a function of the temperature. The error bars equal the 2σ errors of the linear regressions.

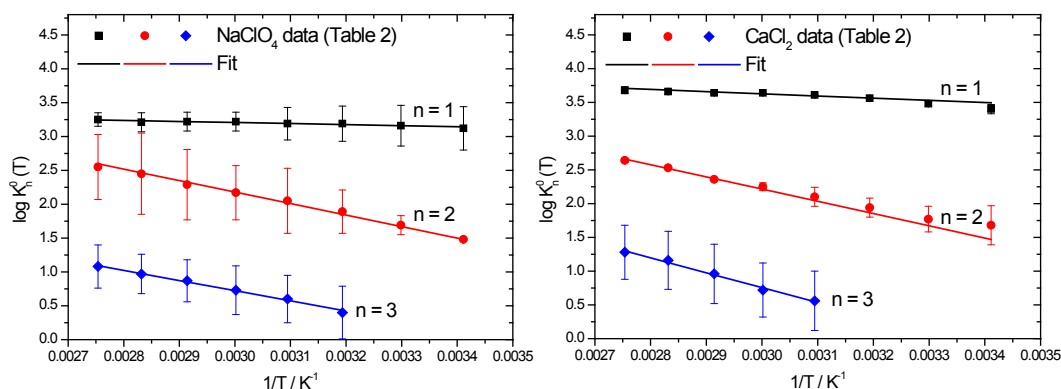


Figure S5. Arrhenius plot of $\log K_n^0$ ($n = 1-3$) obtained in NaClO_4 and CaCl_2 solution (values and errors given in Table 2) to determine the thermodynamic data ($\Delta_r H_m^0$ and $\Delta_r S_m^0$).

Table S1. Result of the slope analysis for the formation of $[\text{Cm}(\text{Ac})_n]^{3-n}$ ($n = 1-3$) in NaClO_4 , NaCl and CaCl_2 solution in the temperature range of 20-90 °C.

T / °C	Result of slope analysis for the formation of $[\text{Cm}(\text{Ac})_n]^{3-n}$							
	NaClO_4			NaCl			CaCl_2	
	n = 1	n = 2	n = 3	n = 1	n = 2	n = 3	n = 1	n = 2
20	1.09 ± 0.11	-	-	0.97 ± 0.08	-	-	1.02 ± 0.10	-
30	1.11 ± 0.11	1.09 ± 0.17	-	0.98 ± 0.08	-	-	1.03 ± 0.10	-
40	1.09 ± 0.12	1.01 ± 0.13	-	0.99 ± 0.08	1.13 ± 0.44	-	1.05 ± 0.11	-
50	1.07 ± 0.12	0.84 ± 0.13	0.84 ± 0.50	1.00 ± 0.08	1.08 ± 0.15	0.88 ± 0.29	1.00 ± 0.11	1.18 ± 0.17
60	0.89 ± 0.13	0.89 ± 0.19	0.75 ± 0.26	1.00 ± 0.10	1.15 ± 0.16	0.78 ± 0.22	0.96 ± 0.11	1.13 ± 0.15
70	0.90 ± 0.14	0.76 ± 0.21	0.69 ± 0.40	0.92 ± 0.10	0.92 ± 0.15	0.88 ± 0.20	0.91 ± 0.11	1.21 ± 0.15
80	0.95 ± 0.17	1.06 ± 0.15	0.80 ± 0.38	0.87 ± 0.11	0.99 ± 0.20	0.60 ± 0.17	0.84 ± 0.11	1.04 ± 0.14
90	0.80 ± 0.19	0.90 ± 0.14	0.76 ± 0.38	0.83 ± 0.12	0.91 ± 0.08	0.65 ± 0.17	0.85 ± 0.12	0.95 ± 0.14