Absorption Spectroscopy for Quantitative Prediction of Lanthanide Concentrations in 3 LiCl – 2 CsCl Eutectic at 723 K

Cynthia A. Schroll,^a Amanda M. Lines,^b William R. Heineman,^{a*} and Samuel A. Bryan^{b*}

^aDepartment of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172

^bEnergy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

* Correspondence email: <u>sam.bryan@pnnl.gov</u>, <u>heinemwr@ucmail.uc.edu</u>

Absorption spectra of erbium(III) chloride were obtained at different concentrations ranging from 0 mM to 112 mM in 3 LiCl – 2 CsCl. The spectrum of ErCl₃ shows that there are four peaks in the absorbance which have been attributed to multiple f^5 - f^5 transitions.^[1,2] When the spectra are plotted on the same graph (Figure S-1A), it can be seen that as the concentration is increased there is an increase in absorbance at several wavelengths. The absorbances at 367, 380 and 523 nm were graphed vs. concentration in Figure S-1B. Using the slope of the best fit line for each wavelength the molar absorptivities were calculated and are presented in Table S-1 along with the known molar absorptivities for ErCl₃ in 3 LiCl – 2 KCl for comparison.^[3]



Figure S-1 (A) Spectra of erbium(III) chloride at (—) 0, (—) 28.4, (—) 42.2, (—) 56.3, (—) 70.3, (—) 85.5, (—) 99.6 and (—) 112 mM in 3 LiCl – 2 CsCl. (B) Beer's Law plot of Absorbance vs. Concentration (mM) at (•) 367 ($y = 0.0006x M^{-1} + 0.007$; $R^2 = 0.990$), (**n**) 380 ($y = 0.0072x M^{-1} + 0.039$; $R^2 = 0.986$) and (**a**) 523 nm ($y = 0.0050x M^{-1} + 0.026$; $R^2 = 0.985$).

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λ, nm	367	380	523
ϵ , M ⁻¹ cm ⁻¹ (this study)	0.64 ± 0.03	7.2 ± 0.4	5.0 ± 0.2
ϵ , M ⁻¹ cm ⁻¹ (ref [3] _{3 LiCl - 2 KCl})	0.3	9.55	6.3

Table S-1 Molar absorptivities listed as a function of wavelength for erbium(III) chloride from this study as well as values from reference [3].

Absorption spectra of holmium(III) chloride in 3 LiCl – 2 CsCl were obtained at different concentrations from 0 mM to 114 mM. The spectrum of HoCl₃ shows five peaks in the absorbance at 362, 421, 451, 460 and 540 nm which have been assigned to multiple f^5-f^5 transitions.^[2,4] Figure S-2A shows spectra for HoCl₃ at various concentrations and the absorbance peaks are graphed vs. concentration in Figure S-2B. Using the slope of the best fit line for each wavelength and Beer's law the molar absorptivities were calculated and are presented in Table S-2 along with previously known values in 3 LiCl – 2 KCl. ^[3]



Figure S-2 Spectra of holmium(III) chloride at (-) 0, (-) 28.3, (-) 42.7, (-) 57.0, (-) 70.8, (-) 85.3, and (-) 101 in 3 LiCl - 2 CsCl. (B) Beer's Law plot of Absorbance vs. Concentration (mM) at (\diamond) 362 (y = 0.0026x M⁻¹ + 0.012; R² = 0.995), (-) 421 (y = 0.0005x M⁻¹ + 0.0005; R² = 0.992), (-) 451 (y = 0.0065x M⁻¹ + 0.015; R² = 0.999), (-) 460 (y = 0.0081x M⁻¹ + 0.018; R² = 0.999) and (\diamond) 540 nm (y = 0.0004x M⁻¹ + 0.0002; R² = 0.988).

Table S-2 Molar absorptivities listed as a function of wavelength for holmium(III) chloride from this study as well as values from reference [3].

λ, nm	362	421	451	460	540
ϵ , M ⁻¹ cm ⁻¹ (this study)	2.6 ± 0.1	0.52 ± 0.02	6.5 ± 0.3	8.1±0.4	0.43 ± 0.02
ϵ , M ⁻¹ cm ⁻¹ (ref [3] _{3 LiCl - 2 KCl})	4.05			12.1	0.62

Absorption spectra of praseodymium(III) chloride in 3 LiCl – 2 CsCl were obtained at different concentrations from 0 mM to 225 mM. The spectrum of PrCl₃ shows that there are four peaks in the absorbance which have been attributed to multiple $f^{5}-f^{5}$ transitions.^[2,4] When the spectra at different concentrations are plotted on the same graph (Figure S-3A) it can be seen that as the concentration is increased there is an increase in absorbance. The absorbances at 450, 473, 486 and 594 nm were graphed vs. concentration in Figure S-3B and using the slope of the best fit line for each wavelength the molar absorptivities were calculated and are presented in Table S-3 with the molar absorptivities obtained from Banks *et al.* in 3 LiCl – 2 KCl.^[3]



Figure S-3 (A) Spectra of praseodymium(III) chloride at (—) 0, (—) 28.2, (—) 56.4, (—) 85.2, (—) 113, (—) 142, (—) 168, (—) 196 and (—)225 mM in 3 LiCl – 2 CsCl. (B) Beer's Law plot of Absorbance vs. Concentration (mM) at (\blacklozenge) 450 (y = 0.0010x M⁻¹ + 0.005; R² = 0.992), (\blacksquare) 473 (y = 0.0009x M⁻¹ + 0.005; R² = 0.992), (\blacktriangle) 486 (y = 0.0012x M⁻¹ + 0.009; R² = 0.992) and (\blacklozenge) 594 nm (y = 0.0002x M⁻¹ + 0.004; R² = 0.966).

Table S-3 Molar absorptivities listed as a function of wavelength for praseodymium(III) chloride from this study and values from reference [3].

λ, nm	450	473	486	594
ϵ , M ⁻¹ cm ⁻¹ (this study)	1.0 ± 0.1	0.90 ± 0.04	1.2 ± 0.1	0.24 ± 0.01
$\epsilon, M^{-1}cm^{-1}(ref [3]_{3 LiCl-2 KCl})$	0.87	1.30	1.45	0.28

Absorption spectra of samarium(III) chloride were obtained at different concentrations from 0 mM up to 112 mM in 3 LiCl – 2 CsCl. The spectrum of SmCl₃ shows that there are five absorbance peaks that have been attributed to multiple f^5-f^5 transitions.^[2,5] When the spectra for the various concentrations are plotted on the same graph (Figure S-4A), it can be seen that the absorbance increases with concentration. The absorbances at 348, 365, 380, 408, and 427 nm were graphed vs. concentration in Figure S-4B and using Beer's law and the slope of the best fit

line for each wavelength the molar absorptivities were calculated and are listed in Table S-4 along with the molar absorptivities in 3 LiCl - 2 KCl.^[3]



Figure S-4 (A) Spectra of samarium(III) chloride at(—) 0, (—) 28.2, (—) 42.3, (—) 56.7, (—) 70.4, (—) 84.8, (—) 98.6 and (—) 112 mM in 3 LiCl – 2 CsCl. (B) Beer's Law plot of Absorbance vs. Concentration (mM) at (\diamond) 348 (y = 0.0002x M⁻¹ + 0.002; R² = 0.988), (**■**) 365 (y = 0.0004x M⁻¹ – 0.001; R² = 0.992), (**▲**) 380 (y = 0.0005x M⁻¹ – 0.001; R² = 0.993), (**■**) 408 (y = 0.0016x M⁻¹ – 0.004; R² = 0.995) and (**▲**) 427 nm (y = 0.0003x M⁻¹ + 0.0005; R² = 0.987).

Table S-4 Molar absorptivities are listed as a function of wavelength for samarium(III) chloride from this study and values from reference [3].

λ, nm	348	365	380	408	427
ϵ , M ⁻¹ cm ⁻¹ (this study)	0.19 ± 0.01	0.41 ± 0.02	0.49 ± 0.02	1.6	0.28
				± 0.1	± 0.02
ϵ , M ⁻¹ cm ⁻¹ (ref [3] _{3 LiCl - 2 KCl})	0.50	0.93	0.90	2.65	

Absorption spectra of thulium(III) chloride were obtained at different concentrations ranging from 0 mM up to 148 mM in 3 LiCl – 2 CsCl. The spectrum of TmCl₃ shows that there are peaks in the absorbance at 475, 695 and 800 nm which have been attributed to multiple f^5-f^5 transitions.^[2,6] Figure S-5A shows the spectrum for TmCl₃ at six different concentrations. The absorbances at 475, 695 and 800 nm were graphed vs. concentration in Figure S-5B. Using the slope of the best fit line for each wavelength the molar absorptivities were calculated and are presented in Table S-5 and comparison the molar absorptivities for the same peaks in LiCl – KCl eutectic have been included.^[3]



Figure S-5 (A) Spectra of thulium(III) chloride at (—) 0, (—) 50.6, (—) 74.1, (—) 99.7, (—) 123 and (—) 148 mM in 3 LiCl – 2 CsCl. (B) Beer's Law plot of Absorbance vs. Concentration (mM) at (◆) 475 (y = 9.0 x $10^{-5}x M^{-1} + 0.004$; R² = 0.984), (■) 695 (y = 0.0002x M⁻¹; R² = 0.988) and (▲) 800 nm (y = 0.0005x M⁻¹ + 0.003; R² = 0.984).

Table S-5 Molar absorptivities are listed as a function of wavelength for thulium(III) chloride from this study and values from reference[3].

λ, nm	475	695	800
ε, M ⁻¹ cm ⁻¹ (this study)	0.11 ± 0.005	0.18 ± 0.01	0.48 ± 0.02
ε, M ⁻¹ cm ⁻¹ (ref [3] _{3 LiCl - 2 KCl})	0.07	0.37	0.7



The plots in Figure S-6 convey the wavelengths used in molar absorptivity calculations and chemometric analysis. Table 2 (main manuscript) details the wavelength range used for chemometric analysis.

Figure S-6 Plot of the molar absorptivity $(M^{-1}cm^{-1})$ vs. wavelength (nm) for (A) erbium(III) chloride, (B) holmium(III) chloride, (C) neodymium(III) chloride, (D) praseodymium(III) chloride, (E) samarium(III) chloride and (F) thulium(III) chloride in 3 LiCl – 2 CsCl.

Sample	ErCl₃	HoCl₃	NdCl₃	PrCl₃	SmCl₃	TmCl₃
c1	0	0	0	0	0	0
c2	28.4	0	0	0	0	0
c3	42.2	0	0	0	0	0
c4	56.3	0	0	0	0	0
c5	70.3	0	0	0	0	0
c6	85.5	0	0	0	0	0
c7	99.6	0	0	0	0	0
c8	112.4	0	0	0	0	0
c9	0	0	0	0	0	0
c10	0	28.3	0	0	0	0
c11	0	42.7	0	0	0	0
c12	0	57	0	0	0	0
c13	0	70.8	0	0	0	0
c14	0	85.3	0	0	0	0
c15	0	101.3	0	0	0	0
c16	0	114	0	0	0	0
c17	0	0	0	0	0	0
c18	0	0	28.3	0	0	0
c19	0	0	56.7	0	0	0
c20	0	0	84.8	0	0	0
c21	0	0	112.7	0	0	0
c22	0	0	146.1	0	0	0
c23	0	0	171.3	0	0	0
c24	0	0	0	0	0	0
c25	0	0	0	28.2	0	0
c26	0	0	0	56.4	0	0
c27	0	0	0	85.2	0	0
c28	0	0	0	113.4	0	0
c29	0	0	0	141.5	0	0
c30	0	0	0	168.1	0	0
c31	0	0	0	196.2	0	0
c32	0	0	0	225.3	0	0
c33	0	0	0	0	0	0
c34	0	0	0	0	28.2	0
c35	0	0	0	0	42.3	0
c36	0	0	0	0	56.7	0

Table S-6 Concentration matrix (mM) for single-component mixtures used as a training data set for the PLS models.

c37	0	0	0	0	70.4	0
c38	0	0	0	0	84.8	0
C39	0	0	0	0	112.5	0
c40	0	0	0	0	0	0
c41	0	0	0	0	0	50.6
c42	0	0	0	0	0	74.1
c43	0	0	0	0	0	99.7
c44	0	0	0	0	0	123.1
c45	0	0	0	0	0	148.5

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