Cyclic voltammetry of samarium ions in the molten LiCl-KCl eutectic for diffusion coefficient analysis

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Abstract

Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of SmCl_3 when it is solvated in the molten LiCl-KCl eutectic at 773 K. An experimental method obtained from the literature was adjusted to produce repeatable current responses attributed to the $\text{Sm}^{3+}/\text{Sm}^{2+}$ reaction couple and to determine working electrode surface area. The effect of solvating SmCl_3 at high concentration was investigated as it relates to electrochemical reversibility and diffusion coefficient analysis. An electrochemically reversible region was identified using correlations between the current response and the scan rate along with peak current ratio measurements. In these, the reversibility was unaffected by increasing concentration. The correlation between current response and concentration was less linear than expected, suggesting the effects of additional modes of diffusion, solution resistance, and charge transfer kinetics may be contributing more at high concentrations. The measurement errors associated with peak current response, working electrode surface area, and melt temperature were used to estimate the associated uncertainties of the reported diffusion coefficients of Sm^{3+} in the molten LiCl-KCl eutectic. These diffusion coefficient values were found to be relatively consistent with values for Sm^{3+} reported in the literature for lower concentrations.

1. Introduction

Molten salt media have been developed for a variety of electrochemical processing schemes including used nuclear fuel (UNF) reprocessing, plutonium refining, rare-earth metal recycling, and the electrolysis of lithium, magnesium, and titanium [1-4]. The pyrochemical reprocessing scheme relies on the molten LiCl-KCl eutectic electrolyte to electrochemically separate uranium, plutonium, and other transuranic (TRU) elements from UNF [5, 6]. After being anodically solvated into the molten eutectic, uranium is consolidated on a solid stainless steel cathode, while plutonium and TRU elements are co-deposited on a liquid cadmium cathode [1]. The pyrochemical reprocessing scheme is an alternative to the tradition plutonium uranium redox extraction (PUREX) method and offers some valuable advantages. A pyrochemical facility would be more compact in terms of space requirements and produce an impure and more proliferation-resistant plutonium product [7]. The pyrochemical process is also compatible with the fast reactor fuel cycle, utilizes simple waste processing operations, and exhibits lower criticality risks than the PUREX method [5]. Several nations are pursuing pyrochemical reprocessing development including France, India, Japan, Russia, South Korea, and the United States [8, 9]. Figure 1 provides a proposed flowsheet for a commercial pyrochemical reprocessing installation outfitted to reprocess existing light water reactor (LWR) fuel stockpiles and fast reactor fuel [10].

Figure 1: Proposed processing flowsheet for a commercial pyrochemical reprocessing installation equipped to reprocess LWR oxide and fast reactor metallic fuel [10]. Figure courtesy of Dr. J. Zhang.

Figure 1 illustrates the disconnected nature of unit operations associated with the pyrochemical process. Product and waste materials exiting each unit operation are handled as separate packages and transferred between unit operations in such a manner that could pose nuclear material holdup and accountancy problems [8]. Furthermore, the electrorefining operation is subject to constantly shifting actinide and lanthanide concentrations that require real-time and nondestructive monitoring to ensure optimized process control and accurate safeguards measurements [7].

Since there is no commercial pyrochemical reprocessing facility in a non-weapons nation state subject to the International Atomic Energy Agency's (IAEA) safeguards agreement, there is a need for the development of real-time and nondestructive nuclear material accountancy (NMA) approaches before any such facility can be constructed [11]. Although Idaho National Laboratory (INL) currently operates an electrorefiner for the consolidation of breeder reactor fuel, NMA methods are heavily reliant on destructive analyses which are both time consuming and offer no real-time data for process optimization or control [6]. Traditional safeguarding approaches using radiation detection and spectroscopic methods fall short in efficacy due to the high-temperature and extreme nature of the molten salt environment [12]. Electroanalytical methods are ideal for NMA in these systems as they are resistant to high radiation fields, compatible with remote handling and inert gas environments, and make available valuable information regarding electrochemical or kinetic behavior of dissolved analytes that can be used to optimize the unit operations [7, 8, 10].

Cyclic voltammetry (CV) is one electroanalytical technique that has been employed in the molten LiCl-KCl eutectic to investigate the electrochemical, diffusion, and kinetic behavior of solvated actinide and lanthanide chlorides [4, 13-20]. Actinide chloride data is more abundant, as actinides pose greater proliferation risk and are the main analytes of interest in the electrorefiner. The effects of concentration on electroanalytical measurements are a focus of current studies and the high concentration regime (> 3 wt. %) is generally less understood [4, 7, 14, 21]. Low concentration lanthanide data is available and

preliminary studies of NdCl_3 have explored concentrations up to 9 wt. % [22, 23]. Samarium electroanalytical data is primarily available for the low concentration regime [18-20, 24]. Understanding lanthanide electrochemical behavior is vital, as these species have negative neutronic effects on nuclear fuel and must therefore be effectively monitored and removed throughout the pyrochemical reprocessing scheme.

In this work, the effect of high concentration SmCl_3 solvated in the molten LiCl-KCl eutectic at 773 K was investigated using CV. A method developed for actinide systems was adjusted and employed to produce repeatable current response and determine the working electrode (WE) surface area. The electrochemical reversibility characteristics were investigated through scan rate correlation and peak current ratio analysis across a high concentration range [13, 14]. The concentration regime of interest was approximately 5 to 17 wt. % SmCl_3 . Based on the results, diffusion coefficients were calculated across the concentration range and compared with the literature. Additionally, cylindrical and migration diffusion effects were investigated. By conducting these analyses at high concentrations of SmCl_3 , this work will help elucidate the implications of conducting CV in high concentration process conditions and develop a path forward to further mitigating uncertainties associated with this concentration region.

2. Experimental

2.1 Chemicals and Materials

The eutectic salt was prepared by baking the individual eutectic components, LiCl (Alfa Aesar 99.9 % pure) and KCl (Alfa Aesar 99.9 % pure), for extended periods of time to ensure moisture impurities were minimized. The eutectic salt components were each baked under vacuum for over 72 hours as Fourier-transform infrared spectroscopy (FTIR) analysis suggested the presence of moisture in the salt up until the 72-hour time point. Figure 2 shows the FTIR spectra obtained from as received, 24- hour baked, and 72- hour baked salts. The spectral features associated with moisture contamination are mitigated only after

72 hours of baking; however, residual moisture impurities are assumed to still be present and result in some oxychloride or oxide formation during experiments [18]. Once baked, the eutectic components were then mixed at a 59:41 (LiCl:KCl) mole ratio.

Figure 2: FTIR spectra of eutectic salt components as received, 24-hour baked, and 72-hour baked.

SmCl_3 (Alfa Aesar 99.99 % pure) was solvated in the molten LiCl-KCl eutectic at various concentrations and agitated using an alumina rod (McMaster-Carr, 1/16" diameter) before the electrodes were immersed in the molten salt solutions. Tungsten rods were employed as the working electrode (WE, ESPI metals 99.95 % pure, 1/16" diameter) and counter electrode (CE, ESPI metals 99.95 % pure, 1/8" diameter). A highly-stable Ag|AgCl reference electrode (RE) consisted of silver wire (ESPI metals 99.95 % pure, 1/16" diameter) immersed in 5 mol % AgCl (Alfa Aesar 99.99 % pure) LiCl-KCl solution. The reference electrode was encased in a Pyrex tube with a thinned bottom wall to provide ionic contact with the sample melts. This reference design was obtained from Tylka *et al.* [13, 14]. The working electrode (WE), counter electrode (CE), and reference electrode (RE) were gently polished with SiC pads and rinsed with anhydrous methanol (99.9 % pure Alfa Aesar) between experiments to prevent cross contamination of samples. All molten salt solutions were contained inside alumina crucibles (GraphiteStore) that were fired at 1273 K, along with the alumina agitation rods, to remove any contaminants and organic binders.

2.2 Experimental Apparatus

All experiments were conducted in an argon atmosphere glovebox with moisture and oxygen levels maintained below 1 ppm. Chemicals and materials were stored in this atmosphere to mitigate the formation of moisture and oxygen induced impurities. AgCl was stored in a dark bottle to prevent light-induced chemical degradation. A Gamry REF3000AE potentiostat was employed for electroanalytical measurements. The potentiostat cabling was fed directly into the glove box to prevent any extension wire induced resistance. The molten salt samples contained in alumina crucibles were placed inside a stainless-steel Faraday cage to prevent electrical frequency noise created by the furnace from affecting electroanalytical measurements. The alumina crucible and Faraday cage were placed inside a Watlow ceramic tube furnace with ± 1 K temperature control. The electrodes were mounted onto a micron-resolution translation stage for accurate and repeatable positioning in the molten salt melt. The electrodes were aligned in a perpendicular fashion with respect to the melt using alumina tubing, stainless-steel alignment plates, and alignment holes drilled into the ceramic furnace cap. The electrode translation stage and furnace were remotely operated using National Instruments LabVIEW software. Figure 3 illustrates the experimental setup employed for the electroanalytical investigations.

Figure 3: Illustration of experimental setup.

2.3 Electroanalytical Measurement Methodology

After temperature calibration, component bakes, melting of the components, and agitation of the molten salt solutions, the electrodes were immersed and allowed to equilibrate for an extended period of time. Specifically, enough time must be allotted for the melting of the RE solution and establishment of ionic contact with the melt. Open circuit potential (OCP) measurements were taken for up to 7 hours to confirm the establishment of this ionic contact. After the RE was equilibrated, the WE was anodically polarized and left to establish a clean surface, free of any passivating films [4]. In order to obtain repeatable CV curves and current response, an electroanalytical sequence previously published by Tylka

et al. for UCl_3 studies was adjusted and applied to the SmCl_3 system [13, 14]. This adjusted sequence can be found in Table 1.

Sequence Step	Description	Duration (seconds)
1	CV acquisition	1 – 5
2	Hold at Open Circuit Potential (OCP)	15-30
3	Hold at oxidative potential to ensure all reduced species return to original valence state and the WE surface is restored	45 – 60
4	Hold at OCP	30-60

Table 1: Electroanalytical sequence obtained from Tylka *et al.* and adjusted for SmCl_3 analysis

The Randles-Sevcik relationship for soluble-soluble electrochemical couples was used to analyze the CV data in terms of electrochemical reversibility, and calculating the diffusion coefficients. Equation 1 reports the Randles-Sevcik relationship used for CV analysis [25].

$$i_p = 0.4463 \cdot n \cdot F \cdot A \cdot C_i \cdot \left(\frac{n \cdot F}{R \cdot T}\right)^{1/2} \cdot v^{1/2} \cdot D^{1/2} \quad (1)$$

Here, i_p is the peak current response in A, n is the number of electrons being transferred in the electrochemical couple of interest, F is the Faraday constant in C mol^{-1} , A is the WE surface area in cm^2 , C_i is analyte concentration in mol cm^{-3} , R is the ideal gas constant in $\text{J mol}^{-1} \text{K}^{-1}$, v is the potential scan rate in V s^{-1} , and D is the analyte diffusion coefficient in cm^2/s . The concentration of dissolved analyte was measured through inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of molten salt samples complexed with deprotonated ethylene diamine tetra acetic acid (EDTA) solution. The peak cathodic current was analyzed for use in diffusion coefficient determination as it is associated with the diffusion of dissolved Sm^{3+} species. A broad range of scan rate values were analyzed with respect to peak current to establish an electrochemically reversible region for diffusion coefficient analysis. Furthermore, cathodic to anodic peak current ratio analysis helped narrow the scan rate region of interest. The WE surface area was determined using an adjusted differential method previously reported in the literature

[13, 14]. Instead of calculating differential current response, the WE was stepped out of the molten salt solution at regular intervals (giving regular steps in surface area) using the high resolution translation stage. The anodic and cathodic peak current responses were then linearly analyzed with respect to immersion and used to back-calculate a WE surface area and associated uncertainty.

3. Results and Discussion

3.1 Electrochemical Characteristics of SmCl_3

The CV curves displayed in Figure 4 were obtained from 1) a melt containing only the molten LiCl-KCl eutectic and 2) another melt with SmCl_3 solvated in the molten LiCl-KCl eutectic at a concentration of $6.69 \cdot 10^{-4} \text{ mol cm}^{-3}$. The observed standard reduction potential of the $\text{Sm}^{3+}/\text{Sm}^{2+}$ electrochemical reaction (give the potential) is consistent with the literature [18-20].

Figure 4: Cyclic voltammograms from a molten LiCl-KCl (eutectic) and $\text{SmCl}_3(6.69 \cdot 10^{-4} \text{ mol cm}^{-3})$ -LiCl-KCl(eutectic) sample at 773 K and 250 mV s^{-1} .

These literature studies have attributed the cathodic and anodic peaks near -0.90 V vs. Ag|AgCl to the reduction of Sm^{3+} to Sm^{2+} and the oxidation of Sm^{2+} to Sm^{3+} , respectively. The relatively symmetric nature

of the samarium features is a consequence of the $\text{Sm}^{3+}/\text{Sm}^{2+}$ electrochemical couple being a soluble-soluble valence state transition and its electrochemical reversibility. The sharp features at the limits of the electrochemical window are attributed to the breakdown of the LiCl-KCl eutectic. The cathodic and anodic features near -2.65 V vs. Ag|AgCl are attributed to the reduction of Li^+ to metallic Li and the oxidation of metallic Li to Li^+ , respectively. The feature observed at approximately 1.05 V vs. Ag|AgCl is the oxidation of Cl^- and resulting evolution of chloride gas. These features (characterized to be the breakdown of the molten LiCl-KCl eutectic) are also in agreement with the literature [22].

3.2 Repeatability, Immersion, and ICP-OES Results

The repeatability of CV curves and associated current response measurements was established using the electroanalytical sequence detailed in Table 1. Five repeat CV scans from a melt at 250 mV s^{-1} and 773 K containing $5.65 \cdot 10^{-4} \text{ mol cm}^{-3} \text{ SmCl}_3$ are overlaid in Figure 5.

Figure 5: Five overlaid CV scans from a $\text{SmCl}_3(5.65 \cdot 10^{-4} \text{ mol cm}^{-3})$ -LiCl-KCl(eutectic) melt at 250 mV s^{-1} and 773 K with calculated peak cathodic current standard deviation (WE area = 0.840 cm^2).

Using the proposed electroanalytical CV acquisition sequence, the standard deviation of current response across all scan rates and concentrations tested was generally under 1%. CV curves acquired using the

immersion step method from a melt containing $5.65 \cdot 10^{-4} \text{ mol cm}^{-3} \text{ SmCl}_3$ at 773 K and 250 mV s^{-1} are overlaid in Figure 6.

Figure 6: Overlaid CV scans from a $\text{SmCl}_3(5.65 \cdot 10^{-4} \text{ mol cm}^{-3})\text{-LiCl-KCl(eutectic)}$ melt at 250 mV s^{-1} and 773 K acquired using the immersion step method.

The shape of the CV curves displayed in Figure 6 remains consistent across the different immersion depths, and the curves appear to space consistently as the WE is stepped out of the melt in 2 mm increments. Figure 7 illustrates this linear spacing of the CV curves with respect to peak cathodic and anodic current responses plotted as a function of WE electrode immersion depth.

Figure 7: Peak cathodic and anodic current response plotted as a function of WE immersion from a $\text{SmCl}_3(5.65 \cdot 10^{-4} \text{ mol cm}^{-3})$ - LiCl-KCl (eutectic) melt at 250 mV s^{-1} and 773 K .

The immersion step method for determining WE surface area produced and linear current response data that could then be used to back calculate a surface area value and associated range of error. Both the anodic and cathodic peak current correlations were used to back calculate this surface area value. Table 2 summarizes the molten salt samples analyzed in this work, their measured concentrations using ICP-OES, and the WE surface area values determined for each sample using the immersion step method.

Sample Number	Concentration of SmCl_3 Wt. %	Concentration of SmCl_3 (mol/cm^3)	Electrode Area (cm^2)
1	4.66	$3.08 \cdot 10^{-4}$	0.636 ± 0.025
2	6.30	$4.21 \cdot 10^{-4}$	0.858 ± 0.049
3	8.39	$5.65 \cdot 10^{-4}$	0.840 ± 0.032
4	9.73	$6.69 \cdot 10^{-4}$	0.782 ± 0.001
5	11.9	$8.19 \cdot 10^{-4}$	0.865 ± 0.039
6	13.5	$9.45 \cdot 10^{-4}$	0.760 ± 0.018
7	16.3	$11.5 \cdot 10^{-4}$	0.691 ± 0.039

Table 2: Summary of the molten SmCl_3 - LiCl-KCl samples analyzed in this work, their respective SmCl_3 concentrations measured using ICP-OES, and WE surface area values determined using the immersion step method.

The peak current responses with respect to scan rate and immersion measurements were very repeatable; however, accounting for anodic and cathodic current response in immersion tests creates a level of uncertainty associated with the measurement of WE surface area that will consequentially affect peak current density versus concentration correlations and diffusion coefficient calculations. This uncertainty is likely the result of molten salt surface tension effects which have been previously reported to produce similar error in the literature [4, 13, 14].

3.3 Scan Rate Results

A broad range of scan rates were tested and analyzed with respect to peak current response and peak current ratio. The results of these two analyses helped establish an electrochemically reversible scan rate range that also produced the most repeatable CV curves. A broad range of 25 to 500 mV s^{-1} scan rate values were tested for all samples. CV curves obtained from a melt solvated with $6.69 \cdot 10^{-4} \text{ mol cm}^{-3} \text{ SmCl}_3$ at 773 K across the broad scan rate range are overlaid in Figure 8.

Figure 8: Overlaid CV scans from a $\text{SmCl}_3(6.69 \cdot 10^{-4} \text{ mol cm}^{-3})$ -LiCl-KCl(eutectic) melt at 773 K acquired across the broad range of scan rates (WE surface area = 0.782 cm^2).

The magnitude of peak cathodic and anodic current response is observed to increase as a function of increasing scan rate in Figure 8, consistent with the Randles-Sevcik relationship for soluble-soluble

electrochemical couples. The CV curves also exhibit a small level of peak broadening across the scan rate range. This broadening can be attributed to a variety of phenomena such as increased resistance between the WE and CE, diffusion layer growth on the WE, or an increased effect of charge transfer kinetics on the reactions occurring at the WE surface [4, 21]. It is difficult to attribute the observed broadening to just one phenomenon as they are interrelated. Diffusion layer growth or surface effects on the WE can affect the uncompensated resistance. Charge transfer kinetics corrections are dependent on uncompensated solution resistance and the activity of the dissolved analyte. Fick's second law assumes the analyte activity is equivalent to its concentration; however, this assumption may lose applicability at higher concentrations [4, 11].

Both the anodic and cathodic peak current responses exhibit relative linearity with respect to the square root of the potential scan rate, as dictated by the Randles-Sevcik relationship. Figure 9 displays the peak current versus square root of scan rate correlation for both anodic and cathodic peak current values from a $6.69 \cdot 10^{-4} \text{ mol cm}^{-3} \text{ SmCl}_3$ melt at 773 K.

Figure 9: Peak cathodic and anodic current response plotted as a function of the square root of scan rate from a $\text{SmCl}_3(5.65 \cdot 10^{-4} \text{ mol cm}^{-3})\text{-LiCl-KCl(eutectic)}$ melt at and 773 K (WE surface area = 0.782 cm^2).

The cathodic peak current response exhibits a more linear response to the square root of scan rate, as indicated by the 0.9958 R^2 value (versus 0.9795 for anodic) in Figure 9. This difference in linearity, along with the plotted peak current ratios as a function of scan rate in Figure 9, suggests the system is not fully reversible but rather quasi-reversible [7]. This quasi-reversibility further validates the need for the oxidative step in the electroanalytical sequence reported in Table 1, as all of the reduced species are most likely not being oxidized back to their original valence states.

Figure 10: Peak cathodic and anodic current response ratio plotted as a function of scan rate from a $\text{SmCl}_3(5.65 \cdot 10^{-4} \text{ mol cm}^{-3})$ - $\text{LiCl-KCl}(\text{eutectic})$ melt at and 773 K (WE surface area = 0.782 cm^2).

The peak current ratio (cathodic to anodic) levels off at approximately 1.5 in Figure 10, and this trend was consistent across all analyzed samples. This ratio suggests that approximately 66% of the reduced Sm^{2+} is oxidized back to Sm^{3+} during the CV's reverse sweep. Generally, low scan rates are used for diffusion coefficient and concentration analysis to ensure reversibility of kinetics; however, faster scan rates minimize surface effects on the WE which may explain the large peak current ratios in the low scan rate region [11, 13, 14, 21]. Furthermore, it can prove difficult in elucidating a clear peak current in the lower scan rate regions as the peaks do not manifest as sharply.

The broad range Randles-Sevcik scan rate correlation, peak current ratio analysis, and the effects of charge transfer kinetics were all taken into account when establishing a narrower scan rate region for concentration and diffusion coefficient analysis. The 200 – 300 mV s⁻¹ was selected for the continuing analyses. This region is consistent with results available in the literature regarding high concentration soluble-insoluble electrochemical couples [11]. The broad and narrow peak cathodic current density versus square root of scan rate correlation results are displayed in Figure 11.

Figure 11: Peak cathodic current density versus the square root of scan rate correlations for the broad (left) and narrow (right) scan rate regions.

Narrowing the scan rate region slightly increased the level of peak current versus the square root of scan rate linearity for some concentrations, while leaving some relatively unaffected. The system is assumed to be relatively reversible in this narrow region, and this reversibility does not seem to be affected by increasing concentration when considering the R² values reported in Figure 11.

3.4 Concentration and Diffusion Coefficient Results

The peak cathodic current density versus concentration correlation was analyzed for linearity. Figure 12 reports the results of this analysis with and without the highest concentration data point.

Figure 12: Peak cathodic current density plotted as a function of SmCl₃ concentration with (left) and without (right) the highest concentration data point.

Both correlation results reported in Figure 12 are less linear than would be expected according to the Randles-Sevcik relationship. Removing the highest concentration data point noticeably increases linearity as illustrated by the R² values in Figure 12. WE surface area and peak current error, cylindrical diffusion effects, migration effects, charge transfer kinetics effects, uncompensated resistance, approaching the solubility limit, or concentration dependence of the diffusion coefficient all provide potential explanations for the lower levels of linearity in Figure 12. The error associated with repeat peak current response and WE surface area discussed in section 3.1 were taken into account when reporting the peak cathodic current density as a function of SmCl₃ concentration and Sm³⁺ diffusion coefficient results. Diffusion coefficient values were calculated at 200 mV s⁻¹ as it is the lowest scan rate in the narrowed region of interest. This minimum scan rate was chosen to maximize the reversibility of kinetics [13, 14, 21]. The diffusion coefficient results and their associated error values are reported in Table 3 and were found to be in agreement with the available samarium literature [18, 20, 24].

Sample Number	Concentration of SmCl_3 Wt. %	Concentration of SmCl_3 ($\cdot 10^{-4}$ mol/cm ³)	Diffusion Coefficient of SmCl_3 ($\cdot 10^{-5}$ cm ² /s)
Cordoba et al. [20]	0.77 – 2.02	0.49 – 1.3	0.98 – 1.30
Castrillejo et al. [18]	1.54 – 1.87	0.99 – 1.2	0.77 – 1.44
Yamada et al. [24]	0.24	0.15	1.80
1	4.66	3.08	1.16 ± 0.14
2	6.30	4.21	0.859 ± 0.14
3	8.39	5.65	0.860 ± 0.10
4	9.73	6.69	1.07 ± 0.01
5	11.9	8.19	0.830 ± 0.12
6	13.5	9.45	0.806 ± 0.07
7	16.3	11.5	0.672 ± 0.12

Table 3: Diffusion coefficient results and associated error values from this study compared with the available literature.

A visual representation of diffusion coefficient values as a function of SmCl_3 concentration and their associated errors is displayed in Figure 13.

Figure 13: Diffusion coefficient of Sm^{3+} values and their respective errors versus SmCl_3 concentration.

The error in the diffusion coefficient values make it difficult to determine any dependence of the diffusion coefficient on SmCl_3 with certainty, but it remains feasible that the coefficient decreases with increasing analyte concentration.

Cylindrical diffusion's contribution is assumed to be less than 5% if the relationship detailed in Equation 2 holds true [4, 7, 11].

$$\frac{4D\tau}{d^2} \leq 3 \cdot 10^{-3} \text{ where } \tau = \frac{RT}{nFv} \quad (2)$$

Here d is the WE diameter in cm. An average cylindrical diffusion factor of $4.8 \cdot 10^{-4}$ was calculated for the 200 mV s⁻¹ data, indicating the effects of cylindrical diffusion are minimal but not necessarily negligible.

The contribution of Sm³⁺ migration was calculated using the relationship detailed in Equation 3 and is reported for all analyzed samples in Table 4 [4].

$$t_i = \frac{|z_i|\mu_i C_i}{\sum_k |z_k|\mu_k C_k} \text{ where } \mu = \frac{zFD}{RT} \quad (3)$$

Here, t is the transference number fraction of the ion of interest, z is the species' ionic charge, and μ is the species' mobility value.

Sample Number	Concentration of SmCl ₃ Wt. %	Concentration of SmCl ₃ ($\cdot 10^{-4}$ mol/cm ³)	Sm ³⁺ Transference Number (%)
1	4.66	3.08	2.34
2	6.30	4.21	2.37
3	8.39	5.65	3.16
4	9.73	6.69	4.60
5	11.9	8.19	4.36
6	13.5	9.45	4.87
7	16.3	11.5	4.94

Figure 14: Migration contribution results with respect to Sm³⁺ transference for all sample concentrations.

The migration contribution approaches 5% at the highest concentrations analyzed in this study, suggesting that the contribution is negligible [4]. Migration effects increase with decreasing supporting electrolyte and increasing applied potential. Molten salts such as LiCl-KCl serve as both the solvent and supporting electrolyte, meaning that migration will play an increasing role as a direct function of increasing analyte concentration. However, it is not clear whether the dissolved lanthanide species migrate in their trivalent states. Spectroscopic studies have suggested lanthanides form [LnCl₆]⁻³ complexes when solvated in the

molten LiCl-KCl eutectic [26]. The migration effect is heavily dependent the behavior of these solvated complexes and requires further investigation [4].

Errors associated with WE surface area determination and peak current response measurement undoubtedly introduce uncertainty to the diffusion coefficient results. The contribution of cylindrical diffusion and migration are small, but likely nonnegligible as previously reported in the literature for high concentration actinide [4, 7, 21]. The dependence of diffusion coefficient on concentration may play a larger role at these higher concentrations, along with the effects of approaching analyte solubility limits. Uncompensated resistance and charge transfer kinetics undoubtedly affect the CV results; however, developing a numerical method for positive feedback resistance compensation and charge transfer kinetics correction is non-trivial and would require considerable investment in adjusting the numerical solution to diffusion laws that is at the foundation of the Randles-Sevcik relationship.

4. Conclusion

CV was employed for high concentration electrochemical reversibility and diffusion analysis of SmCl_3 solvated in the molten LiCl-KCl eutectic at 773 K. Published methods for repeatable CV acquisition and WE surface area determination were adjusted and applied to the SmCl_3 reaction couples of interest, producing repeatable current response data. Peak current versus the square root of scan rate correlations, along with peak current ratio analysis, was employed to determine a scan rate region with high current response repeatability, minimal WE surface effects, and maximized reversibility characteristics. The scan rate region was then utilized to conduct concentration analysis as it relates to peak current density response and the calculation of diffusion coefficients. The diffusion coefficient results were in agreement with the available literature; however, the concentration results indicated some sources of uncertainty. Peak current response error, WE surface area error, concentration dependence of the diffusion coefficient, cylindrical diffusion effects, migration effects, uncompensated resistance, and charge transfer kinetics effects were all determined to play some role in creating the observed uncertainty. Further work

is required to develop accurate and reliable CV numerical methods that incorporate the effects of these phenomena before the technique can be applied to processing facilities on a commercial scale.

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6. Conflicts of Interest

There are no conflicts to declare.

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