

Density of Molten Salt Mixtures of Eutectic LiCl-KCl Containing UCl_3 , CeCl_3 , or LaCl_3

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Densities of molten salt mixtures of eutectic LiCl-KCl with UCl_3 , CeCl_3 , or LaCl_3 at various concentrations (up to 13 wt%) were measured using a liquid surface displacement probe. Linear relationships between the mixture density and the concentration of the added salt were observed. For LaCl_3 and CeCl_3 , the measured densities were significantly higher than those previously reported from Archimedes' method. In the case of LiCl-KCl- UCl_3 , the data fit the ideal mixture density model very well. For the other salts, the measured densities exceeded the ideal model prediction by about 2%.

Keywords: Pyroprocessing, Molten salt, Density, Fuel cycle

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1. Introduction

To support future expansion of nuclear power, closing the nuclear fuel cycle via actinide recycling is currently of high interest for a number of countries. To support this recycling objective, it is critical to improve fuel separation technologies. Pyroprocessing is widely accepted as the optimal method to separate actinides from spent fuel from fast reactors, because of its compatibility with high burnup fuel with minimal cooling time and relatively compact processing space requirements. It is compatible with processing both oxide and metal spent fuel. Functionally, it recovers metallic actinides, U and Pu, together to minimize the attractiveness of proliferation [1,2]. Electrorefining using a molten eutectic LiCl-KCl is the key separation step within the pyroprocessing scheme. To support safeguarding electrorefiners, there needs to be a way to frequently and non-obtrusively determine the inventory of fissile material in the molten salt [3]. The molten salt electrolyte used for electrorefining has a high solubility for actinide chlorides and can, thus, be an attractive target for proliferation. Electrochemical sensors show great promise for measuring actinide concentrations in electrorefiner salt in real time [4-7]. They typically are calibrated based on concentrations in weight fraction or percentage. To calculate the total amount of a given actinide in the salt, the total mass of the salt is also needed. Since the salt mass cannot be directly measured in large, remotely-operated electrorefiners, it would have to be inferred from a salt level measurement. If the shape of the electrorefiner vessel is precisely known, the salt level can be directly converted into a volume. That volume value can then be multiplied by the density of the salt mixture to determine mass. The problem, however, is that the salt density is not fixed. It varies with composition of the salt. LiCl and KCl have relatively low densities with the eutectic mixture having a density of about 1.62 g·cm⁻³ [8]. Rare earth and actinide chlorides, however, have much higher liquid densities in the range of 3-6 g·cm⁻³. As the concentrations of these components go up with processing of spent

fuel, the salt mixture density is expected to rise. Researchers at Idaho National Laboratory (INL) have addressed this problem by assuming an ideal mixing density model [9]. The formula for the density of an ideal mixture is as follows.

$$\frac{1}{\rho_{\text{salt,calc}}} = \sum \left(\frac{w_i}{\rho_i} \right) \quad (1)$$

Where ρ is density, w is weight fraction, and i is a component in the mixture.

Sridharan et al. reported measurements of salt density in eutectic LiCl-KCl with varying concentrations of LaCl₃, CeCl₃, and NdCl₃ [10]. They used the Archimedes method to measure the molten salt densities and found the measured values to be much less than predicted based on the ideal mixture formula. This result indicates there is a problem with accountancy measurements in the electrorefiner even if U and Pu concentration can be measured electrochemically. If the density of the electrorefiner salt cannot be modeled, then it will somehow need to be measured. The only known feasible method for in-situ density measurements in an electrorefiner is the double bubbler which is currently being developed by Idaho National Laboratory [11].

For the purpose of further evaluating the ideal mixing model for density, we performed a series of density measurements for molten eutectic LiCl-KCl based mixtures using a more direct approach. The height of the salt in a dimensionally calibrated crucible was precisely measured with a computer controlled electrode-based probe. As incremental amounts of UCl₃, CeCl₃, or LaCl₃ were added to the salt, changes in the salt height were measured. Results are compared to the ideal mixture density model to provide additional insight into its applicability for different mixtures similar to ER salt.

2. Experimental

All salt handling and experiments were carried out in an argon atmosphere glove box (PureLab HE, Inert Technol-

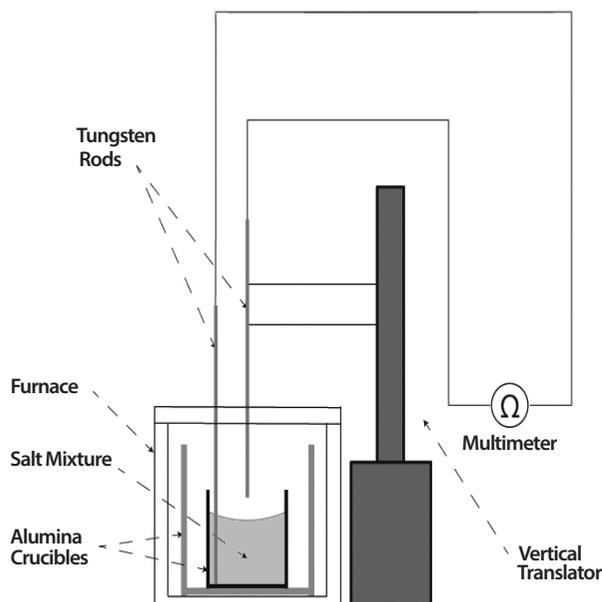


Fig. 1. Experimental setup.

ogy) with H_2O and O_2 concentrations controlled at less than 1 ppm each. For each salt mixture, pure salts were weighed and placed into a small alumina crucible (AdValue Technology, 99.6%, 17.9 mm ID). This crucible was placed in a large secondary alumina crucible (AdValue Technology, 99.6%, 55 mm ID), which acted as a protective liner. Mass of each salt was measured by a precision balance (Mettler Toledo, NewClassic MF) with detection limit of 0.1 mg. The crucible was heated by a Kerr Auto Maxi Electromelt Furnace. The temperature was measured by insisting a thermocouple into the salt mixture periodically. The salt mixture temperature was maintained at 773 ± 1 K. The thermal expansion of alumina from room temperature to 773 K is only 0.4% [12], therefore the volume increase during heating can be neglected. Liquid salt volumes were calculated from the measured height of the salt mixture in the crucible. At first the crucible was modeled height versus volume with known volumes of ultrapure water. A 1-mm tungsten rod (99.95%, Alfa Aesar) was inserted completely into the crucible. A second 1-mm tungsten rod was then attached to a vertical translator (Velmex Inc., Part No.

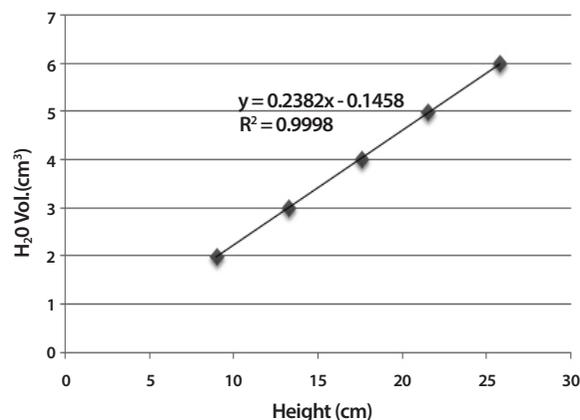


Fig. 2. Crucible volume calibration model.

XN10-0012-M02-71). The vertical translator allowed the second rod to move vertically at 0.005 mm per step. The two tungsten rods were then connected by a digital multimeter (Agilent, 34450A), which monitored the resistance. The second rod was first suspended above the solution, and then it was moved down toward the liquid slowly (Fig. 1). The multimeter initially read zero because the second rod was suspended above the liquid. When the rod finally made contact with the liquid surface, the multimeter showed a finite, positive resistance reading. This step change was used to indicate the level of liquid salt surface.

Three sets of experiments were performed, each set with one of the three tri-chloride salts of interest. The three tri-chloride salts are LaCl_3 (99.99% anhydrous, Alfa-Aesar), CeCl_3 (99.99% anhydrous, Alfa-Aesar), and UCl_3 (anhydrous, synthesized via reacting anhydrous HCl and H_2 with DU metal). There were two sets of experiments for each tri-chloride salt. For each such experiment, the crucible first contained only pure LiCl-KCl eutectic (99.99% anhydrous, SAFC Hitech), and then three additions of the tri-chloride salt were made. The salt mixtures were stirred and allowed to equilibrate for one hour before the heights of the salt mixtures were recorded. The height increase was converted to volume increase by using the crucible calibration model shown in Fig. 2.

3. Results

3.1 Density model

The melting points for all three tri-chloride salts are higher than 773 K. Therefore, the densities of each tri-chloride salt at 773 K are extrapolated from the density of the pure molten phase at higher temperatures. The densities are from Molten Salts Handbook [13] as listed in Table 1. The formula for density of each pure salt is based on Equation 2. Equation 1 was then used to calculate the density of the mixture.

$$\rho = A + B \cdot T(K) \text{ g} \cdot \text{cm}^{-3} \quad (2)$$

3.2 Density Measurements

The measured densities are shown in Fig. 3, 4, and 5 for LiCl-KCl-LaCl₃, LiCl-KCl-CeCl₃, and LiCl-KCl-UCl₃, respectively. The overlaid ideal mixing density models lines for each plot were computed using Equation 1 and the pure salt density data from Table 1 along with Equation 2. Notice that in all cases the measurements appeared to have excellent repeatability. In other words, there was very little deviation between each set of measurements for a given type of salt mixture. This repeatability was quantified by calculating the % difference between measured densities in each Test 1 versus densities measured from Test 2 linearly extrapolated to the exact same concentration. These calculations are summarized in Tables 2-4. The average errors of the LaCl₃, CeCl₃, and UCl₃ mixtures are 0.477%, 0.334%, and 0.936%, respectively. However, only in the case of LiCl-KCl-UCl₃ was the data in good agreement with the model. Table 5 gives the average relative error for each salt mixture compared to the ideal mixing model.

Notice that in each set of measurements that the eutectic LiCl-KCl density matches the model very well. For the six measurements made using pure eutectic LiCl-KCl, the average deviation from the calculated value of 1.6227 g·cm⁻³

is 0.44%. The reported density of eutectic LiCl (58 mol%)-KCl (42 mol%) at 773 K is 1.6226 g·cm⁻³ [8].

4. Discussion

It was hypothesized that the difference between modeled and measured density values might be attributed to the meniscus of the molten salt surface (illustrated in Fig. 1). The tungsten rod used to probe for the surface of the salt may be positioned differently for each measurement, putting it in different positions relative to the meniscus. If a meniscus causes the salt level to be higher or lower than the average across the entire crucible, it effectively introduces a Δh into the measurement. This error in height should be constant for each experiment, since the position of the vertical translator does not change during a given experiment. Therefore, the Δh values are the same for each individual experiment. As a way of estimating what the value of Δh should be, the density of eutectic LiCl-KCl was used as a reference point. Every experiment started with pure eutectic LiCl-KCl, which has been reported to have a density of 1.6226 g·cm⁻³ [8]. All of the other points in a given experiment were shifted by the same vertical distance. In Fig. 6, 7, and 8, the reported measured densities have been adjusted to match the eutectic LiCl-KCl density. Data from each experiment for a given salt mixture were combined

Table 1. Pure molten salt density correlations from literature [13]

Salt	A	B	Density at 773 K (g·cm ⁻³)
KCl	2.1359	5.83x10 ⁻⁴	1.6852
LiCl	1.8842	4.33 x10 ⁻⁴	1.5496
LaCl ₃	4.0895	7.77 x10 ⁻⁴	3.4886
CeCl ₃	4.248	9.20 x10 ⁻⁴	3.5368
UCl ₃ *	6.3747	1.52 x10 ⁻³	5.1982

*UCl₃ density is from Desyatnik et al. [14]

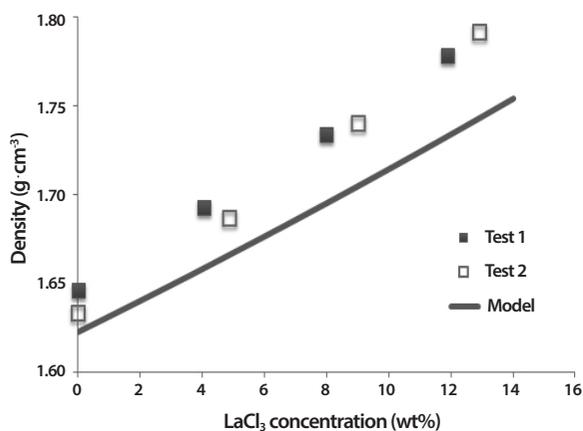


Fig. 3. Density of LiCl-KCl-LaCl₃ mixtures at 773 K.

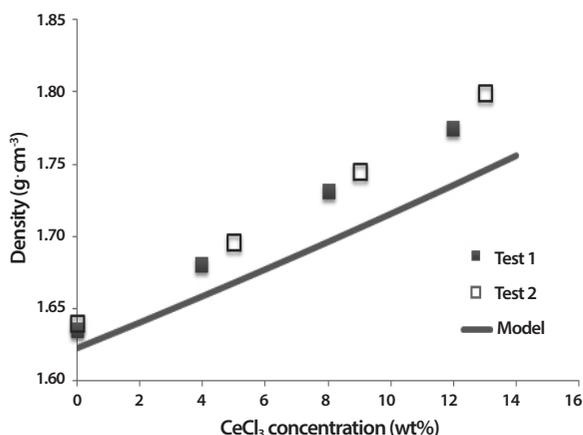


Fig. 4. Density of LiCl-KCl-CeCl₃ mixtures at 773 K.

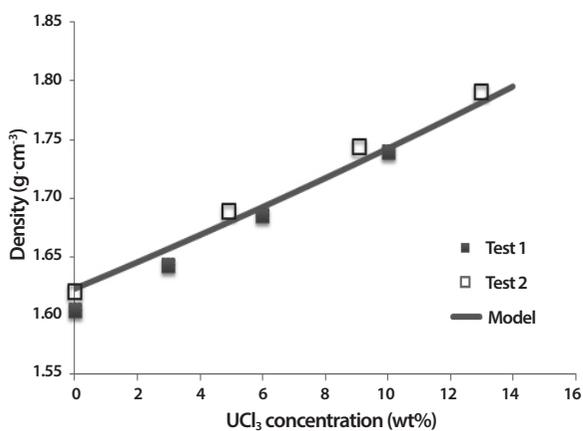


Fig. 5. Density of LiCl-KCl-UCl₃ mixtures at 773 K results.

Table 2. Experimental errors of LiCl-KCl-LaCl₃ mixtures at 773 K

Conc.(wt%)	Density (g·cm ⁻³)		Error
	Test 1	Test 2	
0	1.6464	1.6333	0.801%
4.0470	1.6928	1.6804*	0.733%
7.9681	1.7338	1.7286*	0.299%
11.9047	1.7784	1.7770*	0.075%
Average error:			0.477%

*Density data are linearly extrapolated

Table 3. Experimental errors of LiCl-KCl-CeCl₃ mixtures at 773 K

Conc. (wt%)	Density (g·cm ⁻³)		Error
	Test 1	Test 2	
0	1.6348	1.6398	0.301%
3.9665	1.6799	1.6855*	0.330%
8.0290	1.7314	1.7351*	0.213%
11.9844	1.7746	1.7833*	0.492%
Average error:			0.334%

*Density data are linearly extrapolated

Table 4. Experimental errors of LiCl-KCl-UCl₃ mixtures at 773 K

Conc. (wt%)	Density (g·cm ⁻³)		Error
	Test 1	Test 2	
0	1.6046	1.6204	0.990%
2.9684	1.6434	1.6613*	1.090%
5.9887	1.6862	1.7009*	0.868%
10.0295	1.7399	1.7538*	0.797%
Average error:			0.936%

*Density data are linearly extrapolated

Table 5. Average deviation between measured densities and calculated densities using ideal mixing model for salts in eutectic LiCl-KCl

Salt	Average Deviation from Model (%)
LaCl ₃	1.90
CeCl ₃	1.81
UCl ₃	0.55

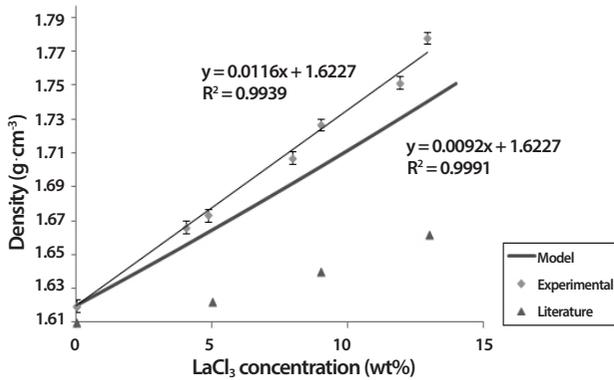


Fig. 6. Adjusted LaCl_3 density test results compared with ideal mixing density model and literature data [14].

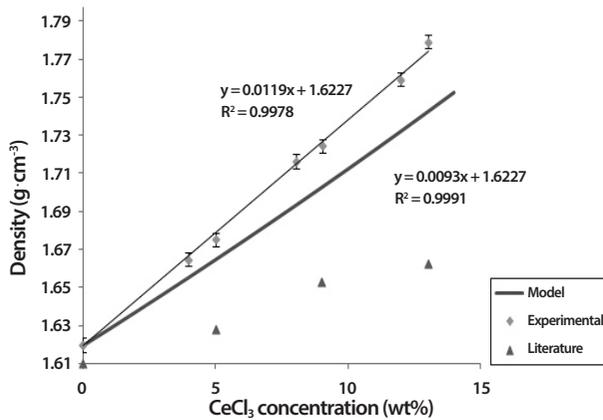


Fig. 7. Adjusted CeCl_3 density test results compared with ideal mixing density model and literature data [6].

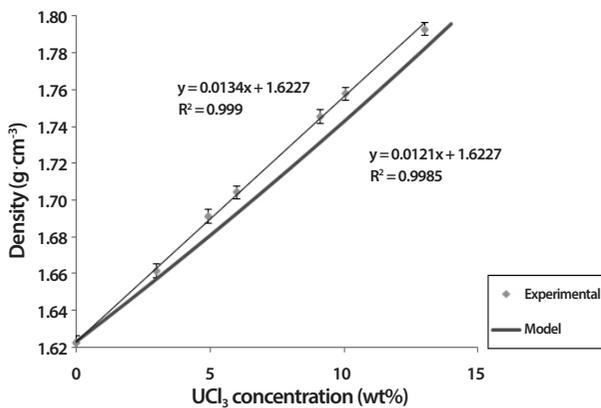


Fig. 8. Adjusted UCl_3 density test results compared with ideal mixing density model. Literature data not available.

and fit to a linear function. Error bars have been added based on the standard derivation of the measurements for each data point. Density data reported by Sridharan et al. has also been added as the “literature” values.

From these figures, it is evident that the estimated correction due to meniscus height does not have an appreciable affect on the measured density values. The fit to the LiCl-KCl-UCl_3 density model was slightly worsened, while the other fits were only slightly improved. The data measured in this study is a much closer match to the ideal model than the data reported by Sridharan et al. for LaCl_3 and CeCl_3 mixtures.

All of the corrected density measurements and corresponding model predictions are given in Table 6, and average deviations from models are shown in Table 7. For each type of salt, the relative error tends to increase with increasing concentration. Note that in a spent fuel electrorefiner that the UCl_3 concentration would be capped at about 10 wt%, and each rare earth chloride would likely be present at less than 5 wt%. Thus, the model is perhaps tested more severely in this study than it would in a real electrorefiner. It is, thus, recommended that the ideal mixing model continue to be used until more data can be collected to develop a more advanced model. Because of the many interactions possible in an electrorefiner salt pool, it may be impractical to attempt any model development that is more complex. Notably, the concentration measurements are likely to have at least 2% error, making it less meaningful to achieve perfect density predictions.

5. Conclusions

We have reported new experimental data on densities of molten eutectic LiCl-KCl with added LaCl_3 , CeCl_3 , or UCl_3 using a vertical displacement method to measure salt volume in an inert atmosphere glove box. The results show that there are small (0.5 to 2%) discrepancies between measured densities and modeled densities based on ideal fluid mixing. The measured densities are slightly higher than

Table 6. Measured (corrected) and modeled densities of CeCl₃, LaCl₃, and UCl₃ in LiCl-KCl eutectic at 773 K

LaCl ₃				CeCl ₃				UCl ₃			
Wt %	Density (g·cm ⁻³)			Wt %	Density (g·cm ⁻³)			Wt %	Density (g·cm ⁻³)		
	Meas.	Model	Error		La	Model	Error		U	Model	Error
4.0470	1.6690	1.6586	0.63%	3.9665	1.6678	1.6583	0.57%	2.9684	1.6615	1.6565	0.30%
4.8794	1.6761	1.6662	0.60%	4.9893	1.6782	1.6677	0.63%	4.9069	1.6913	1.6793	0.71%
7.9681	1.7101	1.6949	0.89%	8.0290	1.7192	1.6964	1.33%	5.9887	1.7044	1.6924	0.70%
9.0139	1.7297	1.7049	1.44%	9.0229	1.7274	1.7060	1.24%	9.0820	1.7459	1.7308	0.86%
11.905	1.7546	1.7330	1.23%	11.984	1.7624	1.7352	1.55%	10.0295	1.7581	1.7429	0.86%
12.944	1.7809	1.7434	2.11%	13.025	1.7824	1.7457	2.06%	13.0008	1.7933	1.7820	0.63%

Table 7. Average deviation between corrected measured densities and calculated densities using ideal mixing model for salts in eutectic LiCl-KCl

Salt	Average Deviation from Model (%)
LaCl ₃	1.15
CeCl ₃	1.23
UCl ₃	0.68

ideal mixing densities for all three mixtures and substantially higher than densities for mixtures containing LaCl₃ and CeCl₃ previously reported by other researchers. While more data is needed on additional rare earth and other fission product chlorides in eutectic LiCl-KCl, the relative error of the ideal mixing model may be considered satisfactory for the purpose of estimating inventory of U and Pu in the electrorefiner salt. The model prediction appears to be at least as accurate if not more so than in-situ density measurement using a double bubbler [11].

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