ORNL/TM-XXXX/XXX

ATOMISTIC SIMULATIONS FOR THERMOPHYSICAL PROPERTIES OF URANIUM-CONTAINING HALIDE MOLTEN SALTS

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Chemical Sciences Division

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831
managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ABBREVIATIONS AND ACRONYMS

ORNL	Oak Ridge National Laboratory
MSR	Molten Salt Reactor
AIMD	Ab-Initio Molecular Dynamic
RDF	Radial Distribution Function

ACKNOWLEDGMENTS

This work is funded by the US Department of Energy's Office of Nuclear Energy Molten Salt Reactor (MSR) Campaign under the Advanced Reactor Technology (ART) program. The authors would like to thank Joanna McFarlane, N. Dianne Bull Ezell, and Kevin Robb for their insights and expertise regarding molten salt chemistry, handling, and experimental considerations. The authors would also like to acknowledge Bill Phillips and Jacob Yingling at Idaho National Laboratory for synthesis and compositional analysis of the NaCl-UCl_3 mixture studied in this work.

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1. INTRODUCTION

Characterizing the thermophysical properties in both fuel and coolant salts are critical in modeling, developing, process optimizing and utilizing molten salt reactors (MSRs), as these properties directly relate to operation metrics and can inform on the selection of candidate salts. The demand for consistent, accurate and publicly available thermophysical property data has become more apparent in recent years as interests have increased from molten salt reactor developers. There are a number of challenges in experimentally measuring properties such as thermal conductivity, viscosity, density and heat capacity , which have led to sparse and often times conflicting data points or molten salts in general.[1, 2] Additionally, there are a number of hazards to consider when synthesizing, storing, using, treating and disposing of molten salts.[3]

With the advances in computational capabilities over the last 10 years, the use of atomistic simulations can be implemented to support these efforts.[4-6] The primary objective of this work is characterize the thermophysical transport properties in a number of molten chloride salts, and in particular NaCl-UCl_3 using ab-initio molecular dynamic (AIMD) simulations. In this binary salt the UCl_3 acts as the primary fissile material and NaCl acts as a carrier salt due with its' high solubility for actinides[7, 8]

A number of studies on the thermophysical properties of NaCl-UCl_3 have been published[2, 8] but there is not a vast amount of viscosity data for this system. In 1975, Desyatnik, et al[9] published a study reporting dynamic viscosities that were calculated from kinematic viscosity measurements, and using the coefficients provided the viscosity in a 70:30 NaCl:UCl_3 mixture is 2.29 cP and 2.88 for a 60:40 mixture. Termini et al.[1] recently reported viscosities in the range of 2.75 – 3 cP for the 63:37 NaCl-UCl_3 mixture in the same temperature range using rolling ball viscosity measurements. Computational viscosity of a similar mixture (64:36) can be obtained from the work Andersson et al.[2] using the reported diffusion coefficients, and the hydrodynamic radius from the pair-radial distribution functions (RDFs). Using Eq (1) (vida infra), the viscosity would be 2.50 cP at 1100K. This is not to say that these values are incorrect due to the varying reported values, but aims to highlight the necessity of this work. The data reported in this ongoing work are computations on a 64:36 mixture of NaCl-UCl_3 at 987K. This work is likely to be expanded into varying concentrations of this mixture along with the inclusion of other salt candidate mixtures.

1.1 Computational Methods

1.1.1 Ab Initio Molecular Dynamic Simulation Details

The binary molten chloride salt NaCl-UCl_3 was generated based on "RK estimated density". The densities were used in obtaining the cell dimension that are used in the subsequent optimizations and simulations. All computations were carried out using CP2K version 2023.2.[10] We've employed the Perdew-Burke-Ernzerhof (PBE)[11] density functional with the VandeVondele and Hutter's MOLOPT basis set[12] and Goedecker-Teter-Hutter (GTH) pseudopotentials[13] for density functional theory calculations (geometry optimization and ab-initio molecular dynamics). Ab initio Molecular Dynamics Simulations (AIMD) were conducted within the NVT ensemble, where the temperatures were maintained 987 K with a Nose-Hoover thermostat,[14, 15] with 1 femtosecond timesteps.

1.1.2 Viscosity and Diffusion Coefficients

Diffusion coefficients were obtained from Einstein's relation[16] through mean square displacement (MSD) in the molecular trajectory (Eq. 1 & 2), where D_i is the diffusion coefficient of ion i and $r_i(t)$ is ion i's position at time t and $r_i(0)$ is that ion's initial position.

$$D_i = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\langle|r_i(t) - r_i(0)|^2\rangle \quad (1)$$

$$\text{Slope} = \lim_{t\to\infty}\frac{d}{dt}\langle|r_i(t) - r_i(0)|^2\rangle \quad (2)$$

A multi-component salt's diffusion coefficient can be obtained through the summation of all individual diffusion coefficients multiplied by their respective molar ratio (X_i)[17]. (Eq. 3)

$$D = \sum_i^n D_i X_i \quad (3)$$

Finally, the viscosity was obtained through the approximated Stokes-Einstein relation (Eq. 4), where d is the hydrodynamic radius calculated from the sum of each ion-pair's first minimum in the radial distribution function[18] (Eq. 5 for the binary NaCl-UCl_3).

$$\eta = \frac{k_b T}{2\pi D d} \quad (4)$$

$$d = (d_{Cl-Cl} + d_{Na-Na} + d_{U-U} + (2d_{Na-Cl} + 2d_{U-Cl})/7 \quad (5)$$

2. EXPERIMENTAL AND COMPUTATIONAL RESULTS

2.1 AIMD SIMULATIONS

AIMD simulations have been conducted on the NaCl-UCl_3 mixture using the computational protocol detailed above. A simulation cell of 20.312 angstroms in each dimension was used, based on the mixtures density and the mass of the system with 100 molecules total (64 NaCl molecules and 36 UCl_3 molecules). The pair-RDFs of this system, displayed in **Error! Reference source not found.**, are used to describe the average local structure around each ion over the course of the simulation. They all feature well-defined and relatively sharp peaks followed by oscillations that decay over distance, where the sharp peaks indicate the nearest neighbor distance and the decaying oscillations are indicative of finite ligand exchange between the successive coordination shells of the liquid. The height of the positions is indicative of the uranium atoms being more tightly bound, they are likely to play a more dominant role in the structure, whereas the sodium atoms exhibit more diffuse behavior with higher mobility. The first U-U peak appears at a very short r(Å), and will need to be monitored closely throughout this simulation. The diffusion coefficients for each ion and the total mixture, along with the viscosity are displayed in **Error! Reference source not found.**

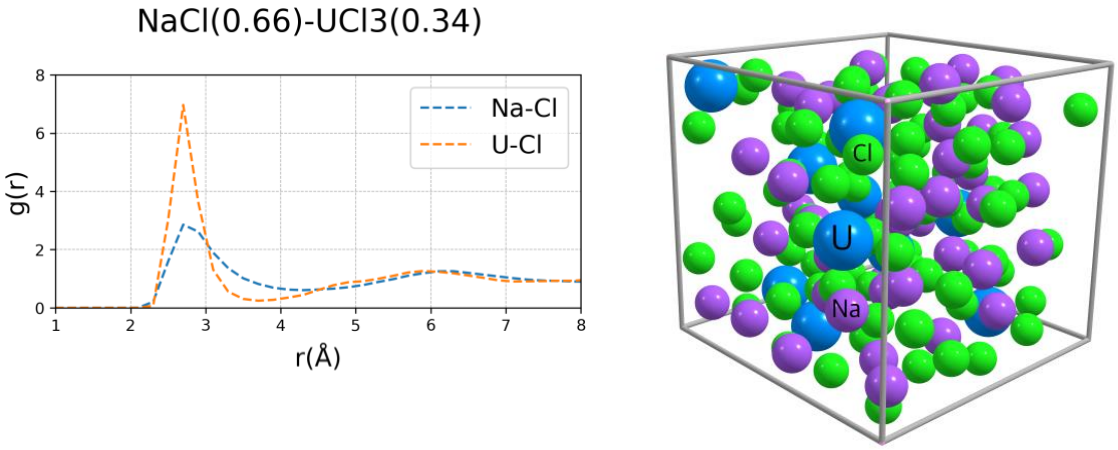


Figure 1. RDF of the cation-anion pairs (left) for the NaCl-UCl_3 mixture and a basic representation of the simulation cell used (right).

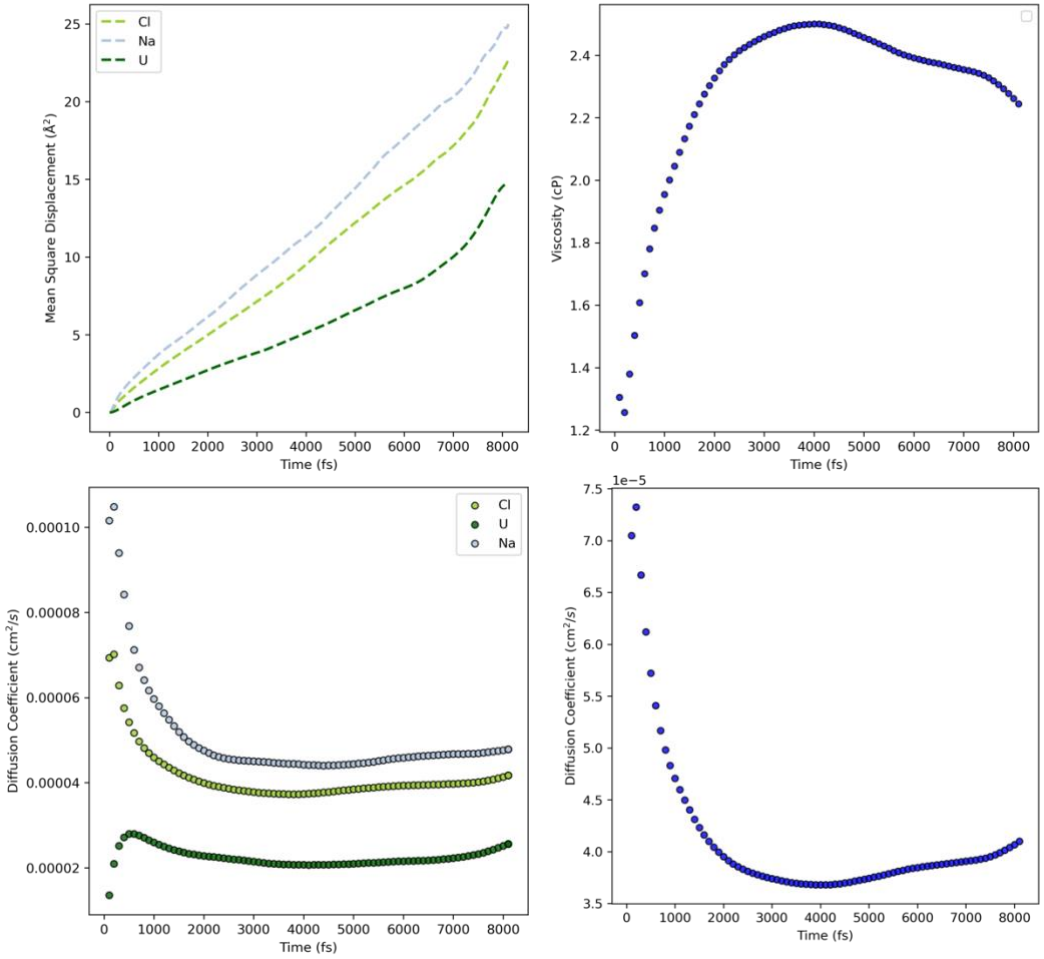
Source	Method	Temp (K)	$\chi(UCl_3)$	D_{Na}	D_{Cl}	D_U	D_{mix}	η_{mix} (cP)
This work	AIMD Simulation	987	0.36	4.79	4.18	2.57	4.09	2.30
Andersson[2]	AIMD Simulation	1100	0.36	3.1	1.4	0.6	4.5	2.50[A]
Li[19]	Experimental Fitting	987	0.36	4.75	2.25	1.5	2.92	1.51[B]
Termini[1]	Rolling-Ball Viscosity	1025	0.36	---	---	---	---	3
Desyatnik[20]	Kinematic Viscosity Fitting	987	0.3	---	---	---	---	2.29[C]
Desyatnik[20]	Kinematic Viscosity Fitting	987	0.4	---	---	---	---	2.88[C]

Table 1. Diffusion coefficients (D_i where i =Na,Cl or U) given in units of $10^{-5}cm^2/s$, viscosity (η_{mix}) given in units of cP, temperature in K and the mole fraction of UCl_3 for this work along with other relevant values reported in the literature. [A]Viscosity values were calculated using Stokes-Einstein relation with the data reported in reference 2. [B,C]Viscosity values were calculated using the viscosity equations and coefficients reported in references 19 and 20.

The mean squared displacement, ionic diffusion, molar diffusion and viscosity over the course of the simulation are displayed in Figure 2. Examining these transport properties as they evolve over time is useful in identifying the equilibration behavior of the simulation and its' relation to those properties. The mean squared displacement is particularly useful in this, because generally linear behavior is an indication of high-fidelity simulation data in the context of transportation properties, the behavior of shown in the plot above indicates a fair degree of linearity, but more simulation time is likely required. This is reflected in the tail of both the molar diffusivity and viscosity plots, where we can observe a decrease in diffusion, and

as a result an increase in viscosity. These plots are indicative of good behavior over time and with sufficient equilibration time will provide accurate results.

Figure 2. Various transport properties over the course of the simulation. The top left plot shows the mean square displacement of each ion, and the bottom left plot shows each ions diffusion coefficient over time. The top right plot shows the viscosity of the mixture and the bottom right plot shows the mixture's diffusion coefficient over time.



The diffusion and viscosity data obtained so far is promising it is lining up to similarly to the established experimental data (see Table 1 for details), the values appear to be "leveling-out" as simulation time proceeds and there is fair agreement between the simulated properties and the measured properties.

2.2 SUMMARY OF EXPERIMENTAL RESULST

This work has been in collaborative conducted with Anthony Birri and his team, the experimental work they've done on the NaCl-UCl_3 system is briefly summarized here, for additional details consult reference [[1]]

NaCl-UCl_3 (63:37 mol%) was measured over the temperature range of 825–1,025 K. The salt was acquired from Idaho National Laboratory (INL); the salt synthesis process is proprietary, but some details may be found in Abou-Jaoude et al.[21]. Analysis at INL performed with ICP-MS and ICP-OES indicated that the sample had a purity of >99.96 %, on a trace metal basis. The salt was loaded and sealed in an inert glovebox, transferred to the furnace setup, heated to 325◦C under Ar for 4 hours, and held at 675◦C for another 8 hours before starting the measurement.

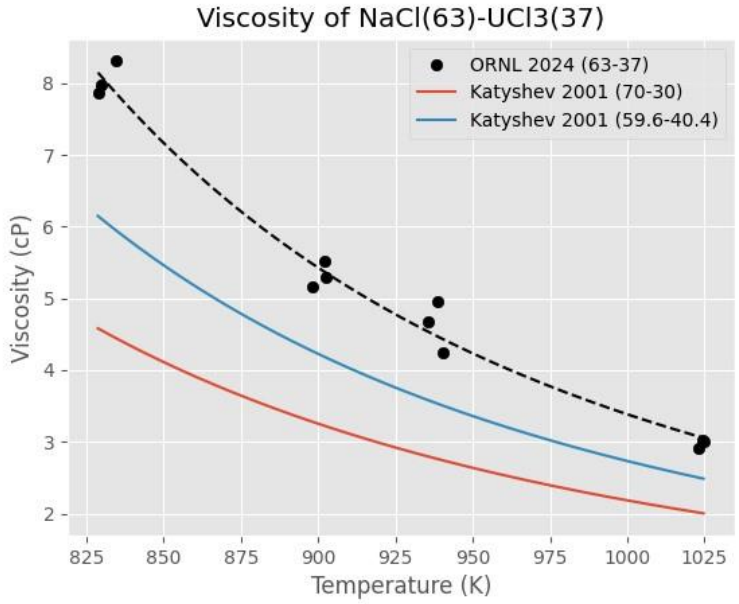


Figure 3. Viscosity of NaCl-UCl_3 (63:37 mol%) molten salt measured by rolling ball viscosity compared to MSTDB-TP reference correlations.

Like the NaCl-KCl measurement, salt creep caused issues at the start of the measurement, but alterations to the insulation allowed the frozen section to remelt and incorporate back into the main melt. Unlike the akali chlorides/halides, actinide salts attenuate clearly using x-rays (Figure 4). Three trial ball drops were performed at each temperature step (823, 898, 948, and 1,000 K). Figure 4 shows the ball moving through the actinide salt in the test section. These images oppose the images associated with the alkali chloride salts because the ball is less x-ray absorptive than the salt, so they will appear as light spots instead of dark spots. The results compared to the closest compositional MSTDB-TP correlations are shown in Figure 3

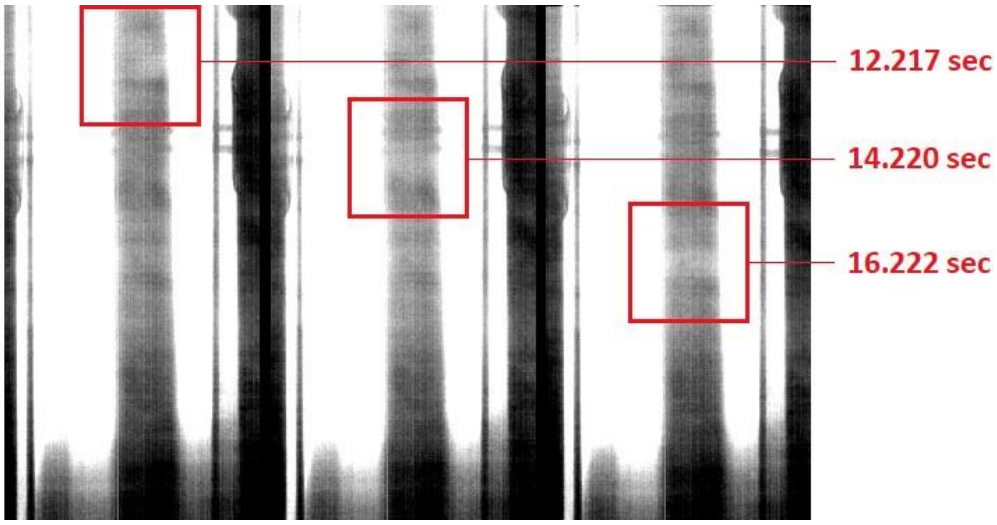


Figure 4. X-ray images collected during NaCl-UCl_3 viscosity test.

Although the measurement is overestimating comparatively, a very clear expected temperature trend (Arrhenius) can be seen. The calculation of the viscosity was adjusted in two ways compared to the normal calculation. Velocities from the regions of the crucible without the wire constriction issue were chosen for terminal velocity calculations, for both the calibrations in determining *K* so the measurement could avoid unknown effects from the abnormality in the crucible.

3. CONCLUSION

Understanding the thermophysical properties, namely thermal conductivity, diffusivity and viscosity, of actinide-bearing molten salt mixtures is essential for advancing molten salt reactor (MSR) technologies. This report focuses on the thermophysical properties of NaCl-UCl_3, namely the viscosity and diffusivity, and how atomistic simulations can further elucidate the underlying nature of these properties. The computational data collected is compared to both experimental and computational values from the literature where available. Notably, the addition of UCl_3 to alkali chloride solvents has been shown to produce significant changes in viscosity, with outcomes varying based on temperature. From a computational standpoint, AIMD simulations have provided key insights into viscosity trends. These simulations showcase that even in these high temperature, dynamically changing environments, uranium maintains a well-defined immediate (first coordination shell) compared to the more labile alkali metal ions (Na+), leading to reduced diffusion coefficients for uranium and a high barrier for ligand exchange. In contrast,

lithium ions show enhanced mobility across various melts,[1] indicating that LiCl can potential be used to lower viscosity. Future work will expand into varying temperatures, salt composition and simulating actinide fluoride–bearing molten salt systems, combining both experimental and AIMD approaches. The findings from this study will inform refinements to experimental methodologies, with particular attention to optimizing crucible and containment design to minimize uncertainties and improve measurement accuracy.

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