Titre: Title:	Extending the kinetic theory-based thermal conductivity model to reciprocal molten salt mixtures with short-range ordering via the Modified Quasi-chemical Model in the Quadruplet Approximation. Supplément
Auteurs: Authors:	Huiqiang Yang, Anh Thu Phan, Aimen E. Gheribi, & Patrice Chartrand
Date:	2025
Type:	Article de revue / Article
Référence: Citation:	Yang, H., Thu Phan, A., Gheribi, A. E., & Chartrand, P. (2025). Extending the kinetic theory-based thermal conductivity model to reciprocal molten salt mixtures with short-range ordering via the Modified Quasi-chemical Model in the Quadruplet Approximation. Solar Energy Materials and Solar Cells, 292, 113724 (16 pages). https://doi.org/10.1016/j.solmat.2025.113724

Titre de la revue: Journal Title:	Solar Energy Materials and Solar Cells (vol. 292)
Maison d'édition: Publisher:	Elsevier BV
URL officiel: Official URL:	https://doi.org/10.1016/j.solmat.2025.113724

Supplementary materials for : Extending the kinetic theory-based thermal conductivity model to reciprocal molten salt mixtures with short-range ordering via the Modified Quasi-chemical Model in the Quadruplet Approximation

Huiqiang Yang[a,*], Anh-Thu Phan[a], Aïmen E. Gheribi[a], Patrice Chartrand[a]

[a]*CRCT - Center for Research in Computational Thermochemistry, Department of Chemical Eng., Polytechnique Montréal (Campus de Université de Montréal), Box 6079, Station Downtown, Montréal, Québec, Canada H3C 3A7*

1. Sound velocity

In a previous study [1], the thermal conductivity of pure molten salt was estimated based on sound velocity at its melting temperature. In this work, we modified the sound velocity as a temperature dependent parameter based on the thermal conductivity of each molten salts. The analysis was conducted over a temperature range from 300 [K] below the melting point to 600 [K] above it. The FTsalt Database of Factsage^{TM} 8.4 was used to estimate the temperature-dependent sound velocity. To validate the accuracy of the predicted sound velocity, comparisons were made with available experimental datasets for both pure molten salts and molten salt mixtures (including common-anion mixture and reciprocal mixtures), as shown in the following figures. The predicted sound velocities exhibit excellent agreement with experimental data for most salts, accurately capturing the trends with composition. This is true when compared with the most recent works reported by Stepanov [2, 3]. The only notable discrepancies are a 10% error for CsI and three binary mixtures, LiBr-LiCl, NaF-NaBr and NaF-NaI.

*Corresponding author: huiqiang.yang@polymtl.ca

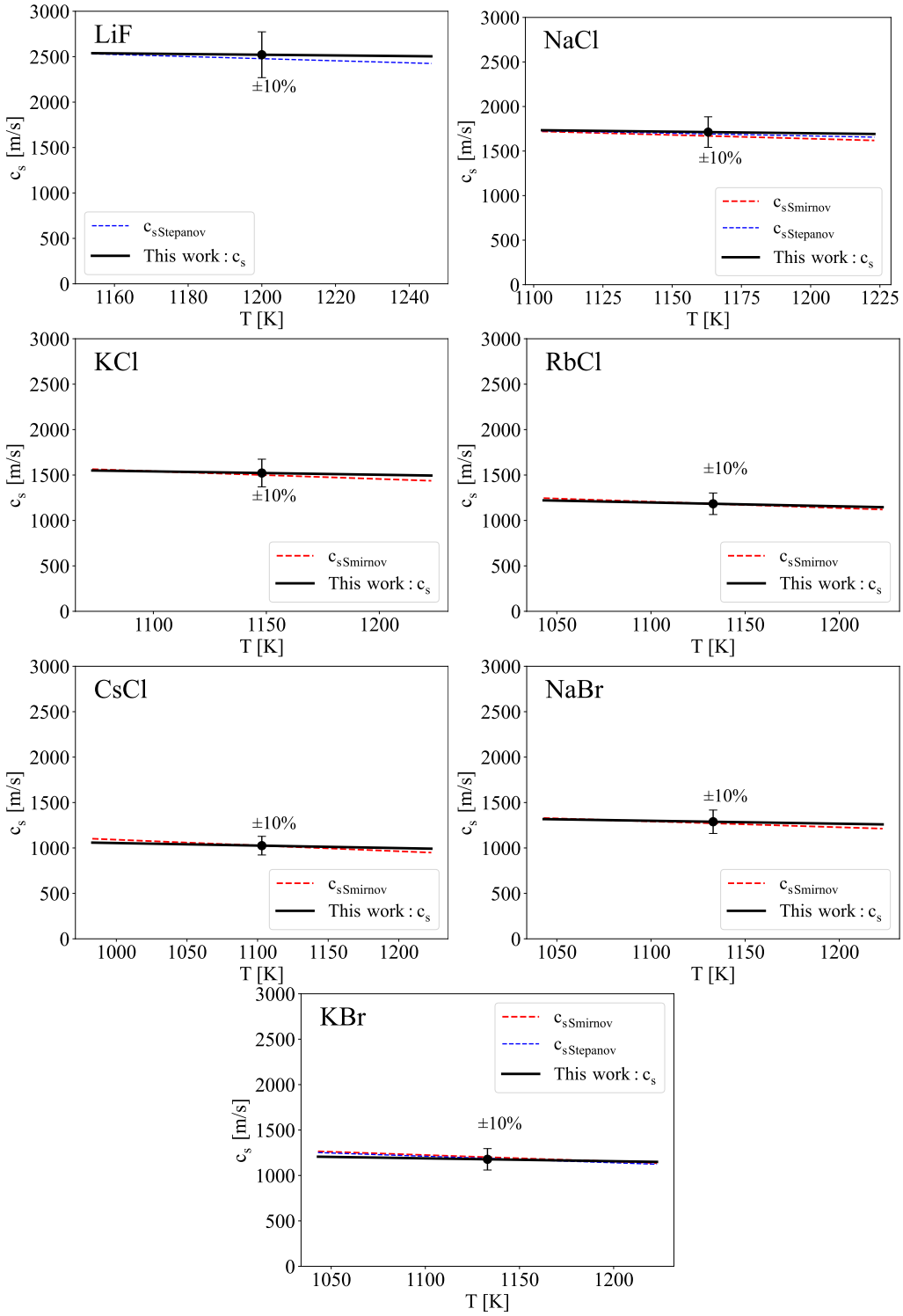

Figure S.1. Comparison of the predicted sound velocities for pure molten salts with available experimental data [2, 4].

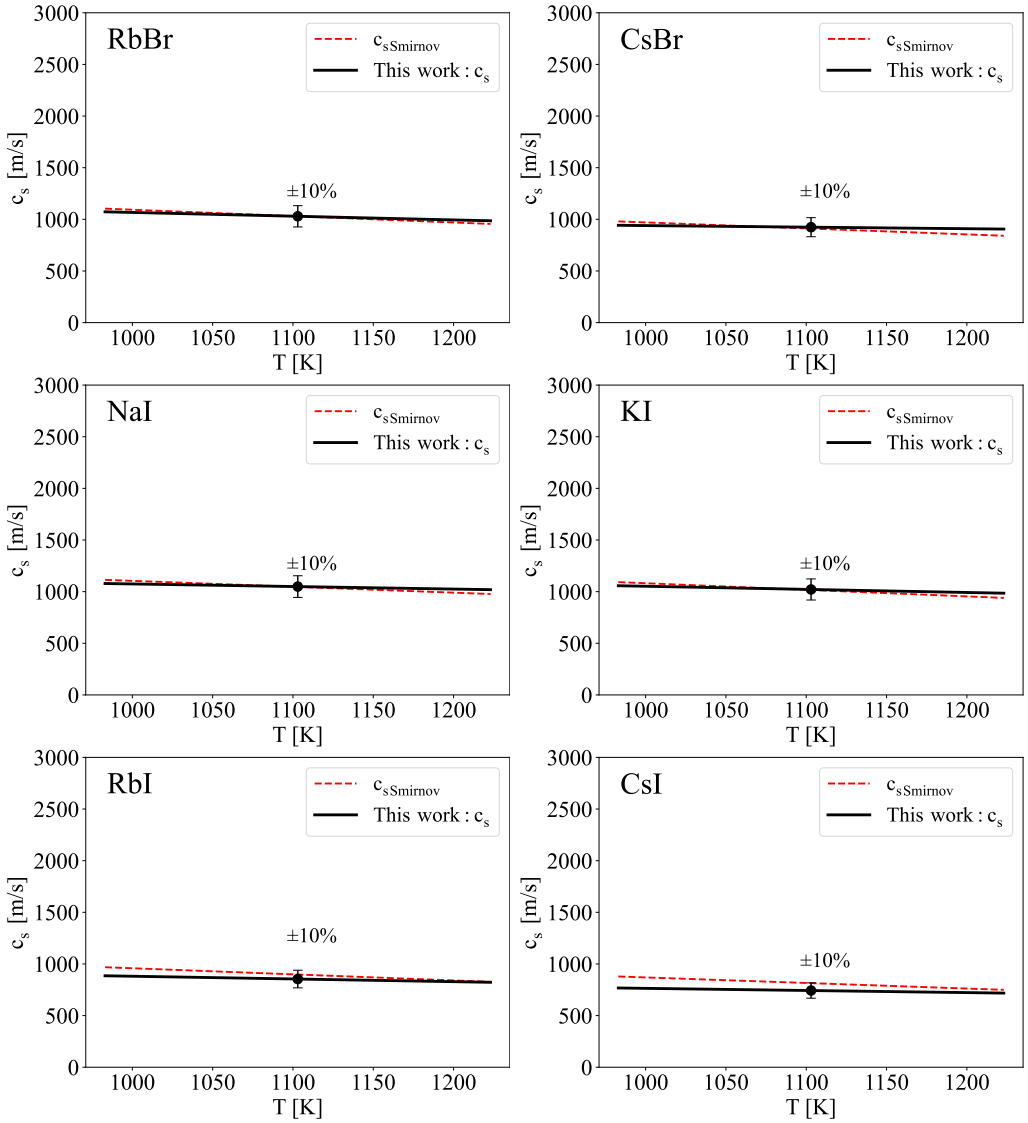

Figure S.2. Comparison of the predicted sound velocities for pure molten salts with available experimental data [2, 4].

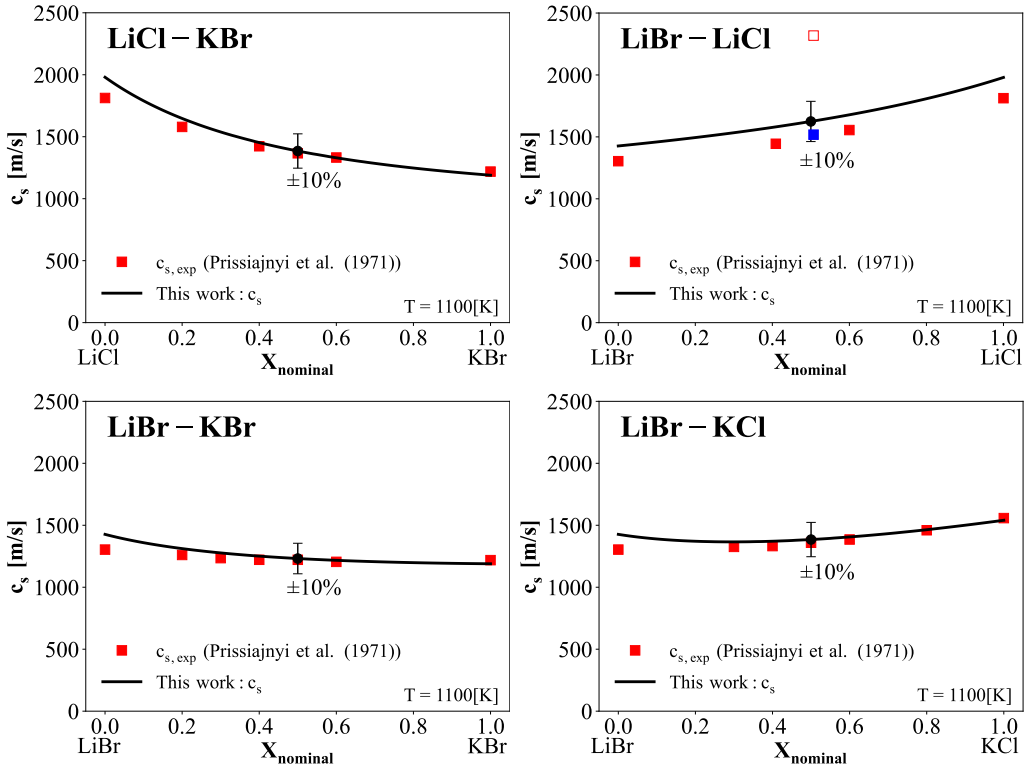

Figure S.3. Comparison of the predicted sound velocities for reciprocal and common-ion molten salt mixtures as a function of composition with the experimental data reported by Prissiajnyi et al. [5] at 1100 [K]. The composition at $(LiBr)_{0.493}$-$(LiCl)_{0.507}$ exhibited a significant deviation from the predicted values, as well as from the trend observed in the experimental data. The reported value of $c_{s0} = 2905$[m/s] appears to be a manuscript error for this composition, with the likely correct value being $c_{s0} = 2105$[m/s]. Accordingly, the corrected data point is highlighted in blue.

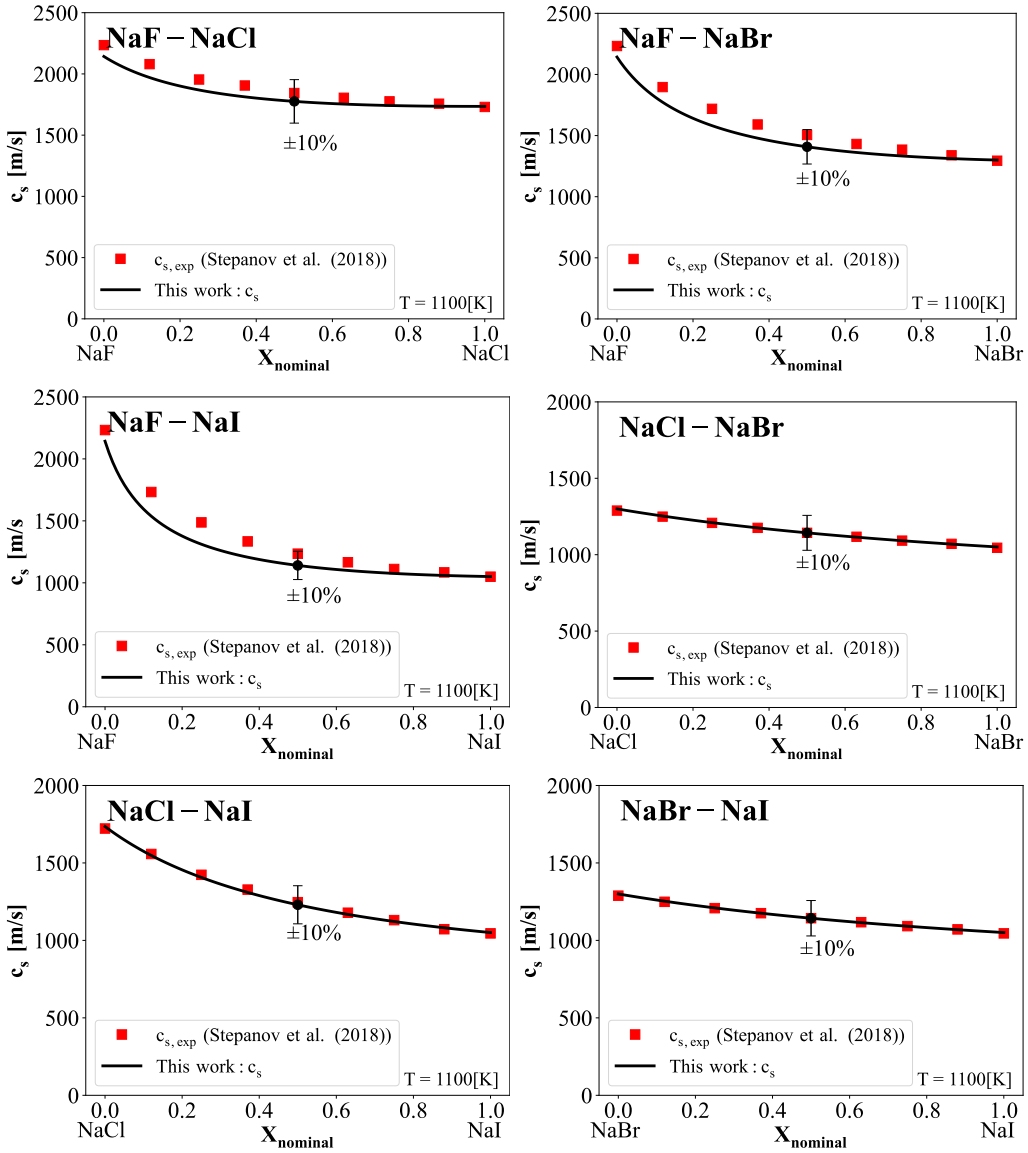

Figure S.4. Comparison of the predicted sound velocities for reciprocal and common-ion molten salt mixtures with the experimental data reported by Stepanov [2] at 1100 [K].

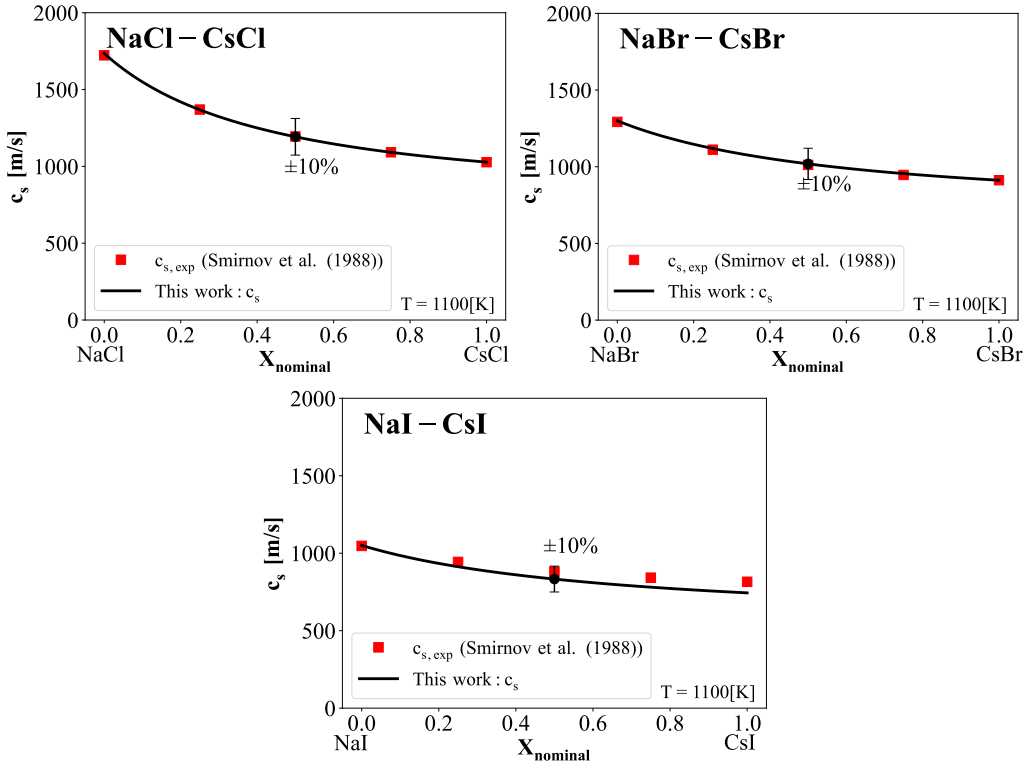

Figure S.5. Comparison of the predicted sound velocities for common-anion molten salt mixtures with the experimental data reported by Smirnov et al. [4] at 1100 [K]

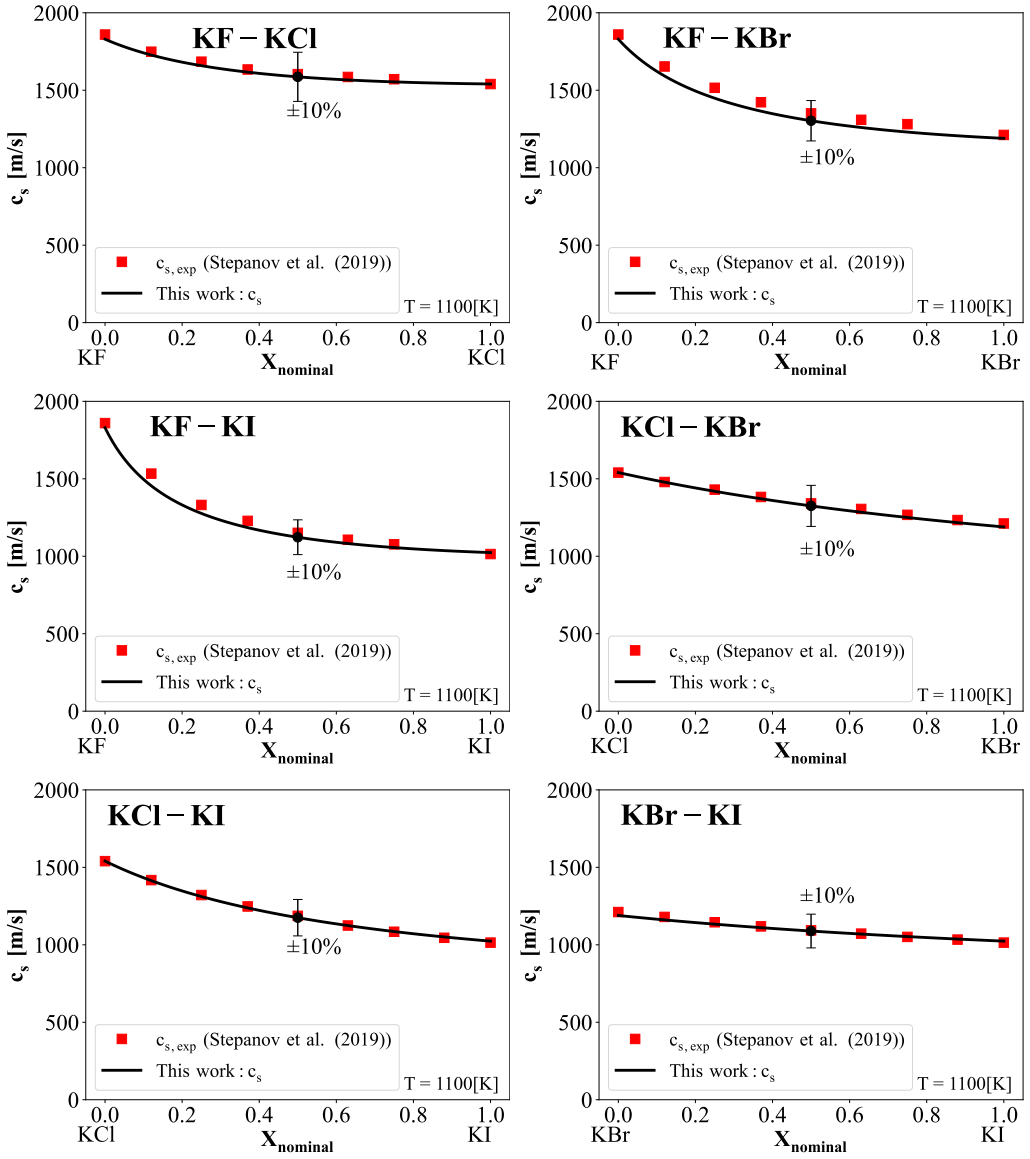

Figure S.6. Comparison of the predicted sound velocities for common-anion molten salt mixtures with the experimental data reported by Stepanov [3] at 1100 [K]

2. Modeling the thermal conductivity of common-cation molten salt mixtures

In our previous work [6], we validated a thermal conductivity model only for simple common-anion molten salt mixtures. In this study, we have simulated numerous common-cation mixtures using equilibrium molecular dynamics (EMD) to verify the predictivity of the present model for common-cation molten salt mixtures, specifically LiF-LiCl, LiF-LiBr, LiF-LiI, LiCl-LiBr, LiCl-LiI, NaF-NaCl, NaF-NaBr, and KF-KCl at 1300 [K]. Unfortunately, no experimental data sets can be found related for the common-cation molten salt mixtures in the literature.

Figure S.7 shows the thermal conductivity predictions (red dashed line) of

the common-cation binary mixtures as a function of composition in comparison to the EMD results, which the end members were calibrated to the EMD results. Meanwhile, the predicted values (black solid line) are compared to the experimental datasets. It can be observed that the predictions of the current model are well in agreement with the EMD results for most common-cation mixtures (LiF-LiCl, NaF-NaCl and KF-KCl). However, the heavier anions Br^- and I^- of EMD results displayed less stable and discretely, which could be attributed to the significant mass difference between the ions and the errors in the potentials within the Br^- / I^- solutions. Therefore, the obtained values showed slightly larger, for instance the binary mixture of LiF-LiBr and LiF-LiI. On the other hand, we applied the framework of the polariable ion model (PIM) for the EMD simulation, since LiF is no polarizable, the value obtained of LiF is larger than experimental works, with more scatterings. However, the results of EMD for Na^+ and K^+ binary common-cation mixtures displayed a perfect tendency. The current model predicted in perfect agreement with the EMD results for NaF-NaCl, NaF-NaBr and KF-KCl. Similarly to the common-anion solutions, the reduction of the thermal conductivity regarding to the mass fluctuation played an important role. The larger difference in mass of anions and thermal conductivity of the pure compound, the larger deviation from the linearity presents.

A comparison of the end-member of pure molten salt between reliable experimental works and the current model were shown in the same figure. It can be observed that the predictions of this current model are in good agreement with reliable works. Since the EMD simulation were performed at 1300 [K], the experimental works are mostly done close to the melting points. Thus, some of these works shown slightly difference to the predictions as the values were obtained by the extrapolation to the same temperature.

In summary, these common-cation mixtures demonstrated that the present model is capable of predicting the thermal conductivity of simple monovalent reciprocal molten salt mixtures with reliable accuracy. Furthermore, we are confident that it can also predict the behavior of common-cation with polyatomic anion mixtures, such as nitrates, carbonates, and others.

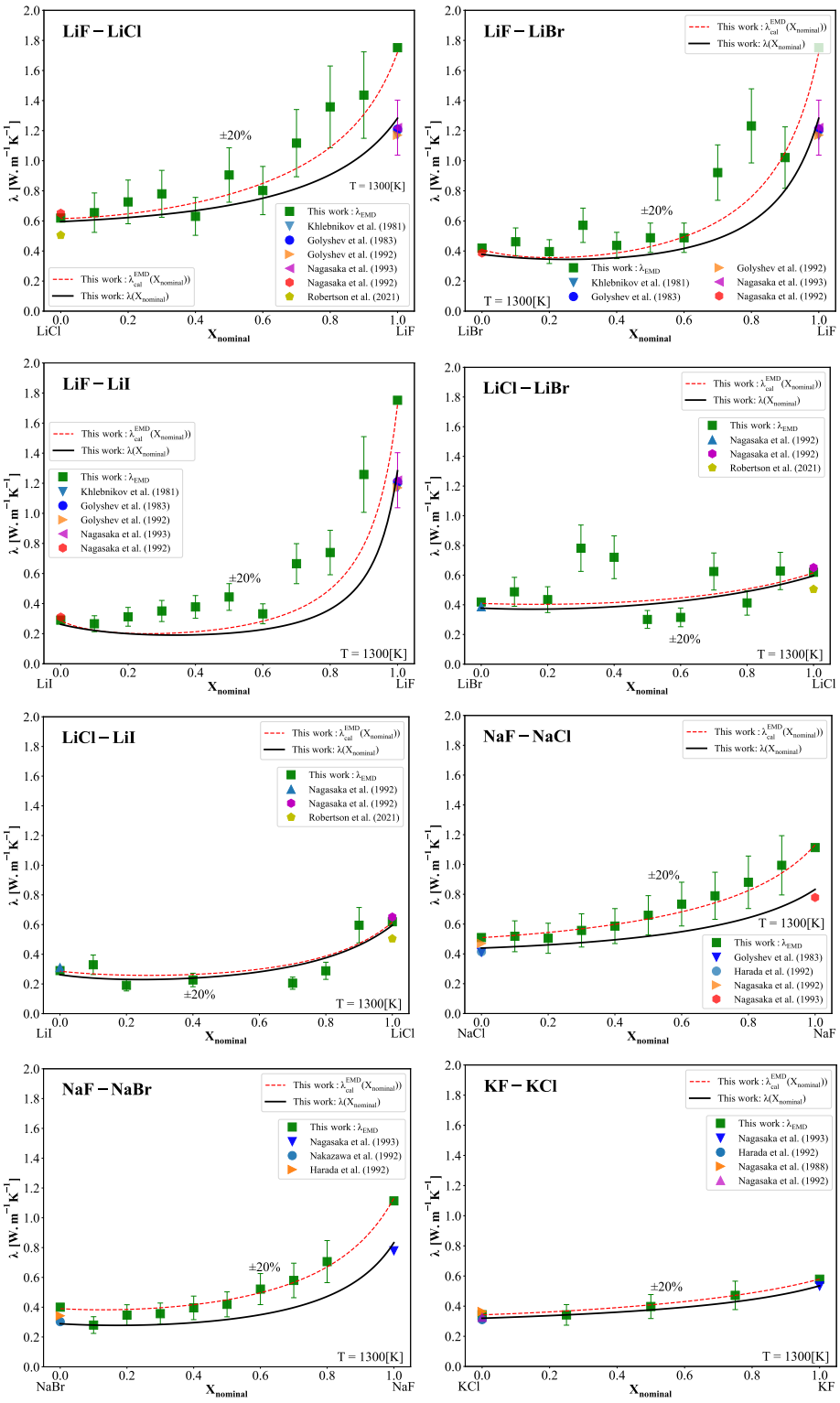

Figure S.7. Predicted thermal conductivity values of common-cation of binary molten salt mixtures in comparison to EMD results of this work and to recommended experimental values at 1300 [K].

References

[1] H. Yang, R. Gallagher, P. Chartrand, A. E. Gheribi, Development of a molten salt thermal conductivity model and database for advanced energy systems, Solar Energy 256 (2023) 158–178. doi:https://doi.org/10.1016/j.solener.2023.04.009.

[2] P. Stepanov, Speed of sound and adiabatic compressibility of binary sodium halide mixtures, High Temperature 56 (2018) 689–693.

[3] V. P. Stepanov, Speed of sound in binary molten mixtures of potassium halides, High Temperature 57 (2019) 842–847.

[4] M. Smirnov, V. Minchenko, A. Bukharov, Sound absorption in molten alkali chlorides, bromides, iodides and their mixtures, Electrochimica acta 33 (2) (1988) 213–220.

[5] V. Prissiajnyi, V. Vasilescu, S. Sternberg, Ultrasonic velocity and compressibility in reciprocal fused salt pairs (cd, k, cl, br) and (li, k, cl, br), The Journal of Chemical Thermodynamics 3 (6) (1971) 867–876.

[6] H. Yang, R. C. Gallagher, A.-T. Phan, P. Chartrand, A. E. Gheribi, A predictive approach for the compositional and temperature representation of thermal conductivity in multicomponent molten salt systems for advanced energy applications, Materials Today Energy 38 (2023) 101441. doi:https://doi.org/10.1016/j.mtener.2023.101441.