ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

# Insight into the viscosity enhancement ability of $Ca(NO_3)_2$ in molten nitrate salts

Haiou Ni, Jie Wu, Ze Sun*, Guimin Lu*, Jianguo Yu

*1 East China University of Science and Technology, Shanghai, China*

**Corresponding author: zsun@ecust.edu.cn ; gmlu@ecust.edu.cn*

***Highlights***

- Precise experimental results for viscosity of molten salts under high temperature.
- Analysis of molten salt structure under atomic scale.
- Find the inherent reason of viscosity enhancement ability of $Ca(NO_3)_2$.

## 1. Introduction

Molten salts are used as heat-transfer-fluid (HTF) in concentrating solar power (CSP) plant. Among various formulas of HTF, nitrate salts are the most common components for their relatively low melting point. The most commonly used HTF in solar thermal power plants is the binary mixture of $NaNO_3$ and $KNO_3$, known as Solar Salt. However, the relatively high melting point of Solar Salt results in high maintenance cost of the entire system. Thus, new molten salt formulas should be studied to obtain a molten salt mixture with low melting point. $Ca(NO_3)_2$ is one of the salts which can lower the melting point of Solar Salt. However, the addition of $Ca(NO_3)_2$ can cause a rise of viscosity of molten salt mixtures[1], which is detrimental to the heat exchange ability of molten salt.

Though it is known that the addition of $Ca(NO_3)_2$ can cause a rise of viscosity, the inherent reason of this phenomenon is still not clear. With the rapid development of computer science, molecular dynamics simulation method has become an important method to study materials from atomic scale. Corradini[2] and Wilding[3] have found network forming effect of trivalent metal halides and sodium carbonate, which may cause high viscosity.

In this work, the influence of $Ca(NO_3)_2$ on the viscosity of binary salts is studied through both experimental and molecular simulation methods. The inherent reason of viscosity enhancement ability of $Ca(NO_3)_2$ is studied through structure analyze from molecular dynamics simulation results.

## 2. Methods

Different amount of $Ca(NO_3)_2$ was added to Solar Salt and their viscosity were tested with a Anton Paar EC TWIST 502 viscometer, which can test viscosity at temperature up to 1000°C.

For molecular dynamics simulation, Buckingham potential was used as inter-molecular pair potential. Flexible nitrate iron model was used with intra-molecular potentials calculated from vibration spectrum. A reverse none-equilibrium molecular dynamics (r-NEMD) method was used to calculate the viscosity of molten salts. All the simulation was conducted using Lammps software package.

## 3. Results and discussion

Fig.1(a) shows the simulation and experimental results of viscosity. The difference between the two results is within 10%. Viscosities of different $Ca(NO_3)_2$ ratios are plotted in Fig.1(b). The viscosity decreases as the temperature increase, and increases as $Ca(NO_3)_2$ ratio increase. The viscosity increases remarkably as the $Ca(NO_3)_2$ ratios increase at lower temperature, while at higher temperature, the difference between the viscosities of different $Ca(NO_3)_2$ ratios becomes less obvious.

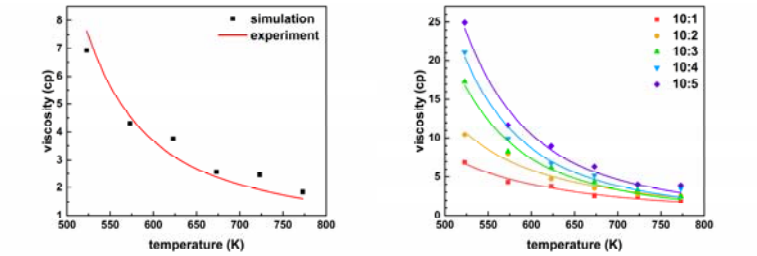


**Figure 1.** (a) Simulation and experimental viscosity of the 10:1 mixture; (b) Simulation results of the viscosity of all the mixtures.

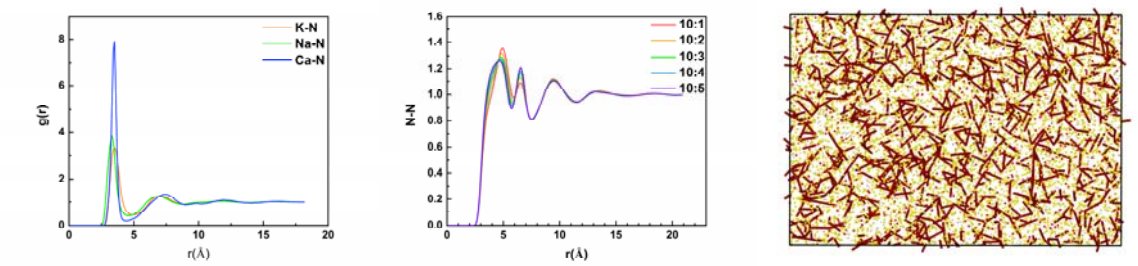


**Figure 2.** (a) RDF of the cation-anion pair of the 10:1 ratio at 573K; (b) RDF of the anion-anion pair of different $Ca(NO_3)_2$ ratios at 573K; (c) N-N chain in a snapshot of the 10:5 mixture

Cation-anion radio distribution function (RDF) of 10:1 ratio at 573K is plotted in Fig.2(a). The height of the first peak of K-N and Na-N pair is similar while for Ca-N, the height is remarkably higher. This denotes that Ca-$NO_3$ interaction is much stronger than that of K-$NO_3$ and Na-$NO_3$. The difference arises from the difference between the charge of $Ca^{2+}$ and $k^+/Na^+$. For RDF curves with different $Ca(NO_3)_2$ ratio, the N-N pair charges most remarkably. A small shoulder can be observed at r≈3.5Å for the 10:1 mixture. As $Ca(NO_3)_2$ ratio increases, the shoulder becomes stronger while the first peak becomes lower. This can also be observed in the snapshots of the simulation box in Fig.2(c). The red chain in the snapshots are between pairs of N atoms separated by r ≤ 3.5Å. It can be observed that N-N network are formed in the mixture.

## 4. Conclusions

- Viscosities of the molten salts are measured and simulated and the results agree well. The addition of $Ca(NO_3)_2$ causes the viscosity increase.
- N-N network can be observed in the molten salt and as the $Ca(NO_3)_2$ ratio increases, the network grows as well.

## References

[1] Gomez JC, Calvet N, Starace AK, Glatzmaier GC, Journal of Solar Energy Engineering. 135(2013) 21016.
[2] Corradini D, Madden PA, Salanne M, FARADAY DISCUSS. (2016)
[3] Wilding MC, Wilson M, Alderman OLG, Benmore C, Weber JKR, Parise JB, et al., SCI REP-UK. 6(2016) 24415.

***Keywords***
Molten salt; molecular dynamics simulation; viscosity