Molecular Dynamics Simulations of the Thermal and Transport Properties of Molten NaNO₂–NaNO₃ Systems

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ABSTRACT

The thermodynamic and transport properties of nitrite and nitrate salts, which are candidates for thermal energy storage, were investigated by differential scanning calorimetry (DSC), high-temperature pulse-field NMR, and molecular dynamics (MD) simulations. The potential parameters of NO₂ for the MD simulations were newly developed by ab initio calculations and empirical approaches. The MD results for molten xNaNO₂–(1–x)NaNO₃ salts (x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0) were comparable to the experimental density and Na self-diffusion coefficients. Moreover, the temperature-averaged heat capacities of the molten xNaNO₂–(1–x)NaNO₃ systems were calculated from the changes in the energy and volume versus the temperature, which reproduced the results obtained from the DSC measurements well.

Keywords : High-Temperature Pulse-Field NMR, Molecular Dynamics, Nitrite and Nitrate Salts, Heat Capacities

1. Introduction

Solar thermal energy (STE) systems using solar power have received a considerable amount of attention for the effective use of natural energy resources. The key to the success of STE is the selection of the heat reservoir media, which have good thermal properties and a competitive cost. A variety of melts have been proposed thus far and tested for practical use. Since the suitable thermal properties are different at the STE site, optimization of the chemical composition is strongly demanded on the engineering side.

Heat transfer salts have a long history for heat storage. It is well-known that molten salts are good media for thermal conduction and storage. Several mixtures of alkali nitrates and nitrates have a low melting temperature. For example, a eutectic mixture containing 40 wt% NaNO₂, 7 wt% NaNO₃, and 53 wt% KNO₃ melts at 142°C and has been used for a long time as a heat transfer medium because of its low cost and good compatibility with common structural materials. This mixture is called HTS (heat transfer salt), HTS I, or Hitec (Du Pont trade name) because of its use for heat transfer. Although the thermal properties of alkali nitrates and nitrate mixtures have been reported, the reported values were not in good agreement with each other because of the difficulties associated with high-temperature experiments. Generally, molten salts with multicomponent systems are utilized to achieve the desired properties. Because of these experimental difficulties and the extremely large number of combinations of multicomponent molten salts, the development of an optimized composition is complicated and time-consuming.

A computational approach for material design is a good way to determine the best composition much faster. Suitable techniques for predicting the thermal properties of alkali nitrates and nitrate mixtures include molecular dynamics (MD) simulations. The development of the force-field parameters is the central procedure for the achievement of accurate simulations and predictions. A potential parameters of NaNO₂, NaNO₃ and their eutectic with rigid molecular was used in previous MD study. The force-field parameters for predicting the thermal properties of alkali nitrate salts (LiNO₂, NaNO₂, and KNO₃) have also been reported by Saiwenkataraman et al. The results for the viscosity and thermal conductivity of these three salts were comparable to their experimental values. Further, the computed heat capacities were also in reasonable agreement with the experimental values. Although reproducible simulations for pure alkali nitrate salts have been achieved by MD simulation, it has not been extended to multicomponent systems. Therefore, it is worthwhile to develop force-field parameters that are transferable to multicomponent systems.

As a first step toward being able to simulate multicomponent mixtures of nitrate salts, we targeted the development of the force-field parameters for sodium-nitrite–sodium-nitrate salt mixtures. It is known that sodium nitrite is an important salt for controlling the melting point and thermal properties. However, the densities and heat capacities of the binary xNaNO₂–(1–x)NaNO₃ system are not available in the literature. In the present study, these properties were newly measured by a conventional dilatometric method and differential scanning calorimetry (DSC). In addition, the Na self-diffusion coefficient, which is an important property related to the viscosity and thermal conductivity, was also obtained from in-situ high-temperature pulse-field-gradient NMR experiments. By comparing these experimental results with those from the MD simulation, we discuss the validity of the prediction of the thermal properties of the binary xNaNO₂–(1–x)NaNO₃ system.

2. Experimental

2.1 Materials

Analytical reagent-grade NaNO₂ and NaNO₃ salts were used. Solid mixtures (xNaNO₂–(1–x)NaNO₃; x = 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared by mixing two salts with known weights, dehydration, melting, and then cooling to room temperature. Melting was carried out at the melting point plus 50 K following dehydration at the melting point minus 50 K for at least 6 h. A dilatometric method was employed to measure the volume of the weighed sample. The apparatus was similar to that used by Iwadate. The cell was calibrated with distilled water at room temperature according to the density data reported by Kell.

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2.2 DSC measurements

A Rigaku Thermo plus EVO II DSC8230 differential scanning calorimeter was used to estimate the heat capacity. α-Al2O3 was used as a reference material. The samples were prepared by placing small amounts of the samples on a weighed sample pan, covering it with a lid, and keeping them melted for 30 min to obtain good contact with the pan. The temperature range for the heat capacity (C_p) measurement was 623–723 K. The temperature dependence of C_p was within 5% in the temperature range. Therefore, we estimated the average C_p in the measured temperature range for comparison with the simulation results.

2.3 High-temperature NMR

NMR measurements were performed in situ in the liquid phase from 550 to 750 K. High-temperature PFG NMR (HT-NMR) spectra were recorded using a Bruker Avance WB 400-MHz spectrometer operating at 9.4 T. The NMR probe is a 10-mm liquid probe equipped with a z-axis gradient coil and adapted to high temperatures at CEMHTI (Orleans, France). The experimental details of high-temperature PFG NMR are available in a previous paper,

2.4 Computational method

The force-field parameters were developed by a combination of ab initio calculations and empirical approaches. The potential functions used in this study are based on a previous MD study for pure alkali nitrates. The following function employing the Buckingham and Coulombic potentials, E, was utilized:

\[ E = \sum_{fi} \exp \left( -\frac{r_{ij}}{\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6} + \frac{z_i z_j e^2}{4 \pi \epsilon_0 r_{ij}} \right) \]

where \( A_{ij} \), \( \rho_{ij} \), and \( C_{ij} \) are ionic-pair-dependent parameters, and \( r \) is the ionic distance. \( z_i \) and \( z_j \) are the partial charges of each ion. In order to ensure compatibility with the force-field parameters, the ionic-pair-dependent parameters were calculated from the following mixing rules:

\[ A_{fi} = \sqrt{A_i \cdot A_f} \]

\[ \frac{1}{\rho_{fi}} = \frac{1}{\rho_i} + \frac{1}{\rho_f} \]

\[ C_{fi} = \sqrt{C_i \cdot C_f} \]

where \( A_i, \rho_i, \) and \( C_i \) are ionic-dependent parameters.

The interionic bond and angle potentials (\( E_b \) and \( E_a \)) of NO2- and NO3- were employed with harmonic functions as follows:

\[ E_b = k_b (r - r_0)^2 \]

\[ E_a = k_a (\theta - \theta_0)^2 \]

Further, we used an improper quadruplet O-N-O-O potential \( E_\phi \) to maintain planar nitrate species. The improper angle \( \phi \) corresponds to an angle between the plane O-N-O and the plane O-N-O:

\[ E_\phi = k_\phi (\phi - \phi_0)^2 \]

All of the force-field parameters of the NaNO3- system were taken from the literature. For the development of the NaNO2 force-field parameters, a molecular orbital (MO) calculation with a B3LYP/6-31+G** level was carried out to obtain the relaxed structure and to determine the partial charges. MO calculations were performed by using the Gaussian 98 suite of programs. The partial charges on the nitrogen and oxygen atoms in NO2- were −0.1 and −0.45, respectively, which were calculated from the electrostatic potential partial charge (ESP). The potential parameters for a N-O bond and an O-N-O angle were determined from a fitting of the change in the MO energy, which was calculated from the derivative of the optimized NO2- structures. The fitted results obtained from the developed parameters are presented in Fig. 1. The interatomic potential parameters of NO2- were determined from the changes in the energies for random molecular configurations of Na, NO2-, and NO3-. Furthermore, fine-tuning was also carried out to reproduce the crystal structures of NaNO3 and NaNO2. All simulation parameters are summarized in Table 1.

All MD simulations were performed with the NPT ensemble (a constant number of particles, a constant pressure, and a constant temperature) with a variable temperature. The temperature was kept constant by using the Nosé–Hoover thermostat. The electrostatic interactions were calculated using the particle–particle–particle mesh method and a relative error in the force of 0.0001 and a real-space cutoff of 11 Å. The same cutoff was used for short-range interactions. The initial structures were a random distribution of Na+ and NO3- ions, and NO2- with the desired composition (xNaNO2–(1–x)NaNO3; x = 0.2, 0.4, 0.6, 0.8, and 1.0) and were composed of approximately 5000 atoms. Eutectic composition (67.4NaNO2–32.6NaNO3) was also calculated for a comparison of experimental data. The atomic trajectories were generated by the Verlet algorithm with a time step of 1.0 fs. After achieving energy equilibrium, the atomic configurations, total energy, and volume were sampled to calculate the heat capacity and the mean squared displacement of Na atoms for 1 ns. Variable-temperature simulations were carried out to estimate \( C_p \) and the density. As described in DSC measurement, the temperature dependence was negligibly small in the experimental...
temperature range. Therefore, we calculated the temperature-averaged $C_p$ using the following equation:

$$C_p = \frac{\Delta U}{\Delta T} + P \frac{\Delta V}{\Delta T}$$  (8)

where $P$ is the pressure (1 atom), and $\Delta U$ and $\Delta V$ are the time-averaged total energy and volume in the equilibrium state. $\Delta U/\Delta T$ and $\Delta V/\Delta T$ were obtained from a linear regression of the results with variable-temperature MD simulations.

3. Results and Discussion

3.1 Structures and molar volume

All simulations of the crystal phase were performed using a supercell with a size of $10 \times 10 \times 10$. The crystal simulations of NaNNO2 started from the crystal structures obtained by X-ray diffraction. Independent fluctuations were allowed along the three orthogonal dimensions of the crystal ($a$, $b$, and $c$), but the cell angles were fixed at 90°. As such, the simulations can provide a test of whether the force-field parameters result in a stable structure. A comparison of the simulated and experimentally determined lattice parameters is presented in Table 2. The simulated lattice parameters are agreement with experimental data within 10%.

The experimental structure factors $Q_i(Q)$ and the molten NaNNO3, NaNNO3 and eutectic composition (67.4NaNNO2–32.6NaNNO3) were calculated to compare experimental neutron20 and X-ray studies. The neutron and X-ray total scattering structure factors were calculated (Fig. 2) from the partial scattering structure factors, which can be obtained from the partial radial distribution functions. All partial scattering structure factors were summed after multiplying by appropriate coefficients for neutron and X-ray experiments, respectively. The equation and coefficients used can be found elsewhere. Good agreements of phase (peak positions) between experimental simulated $Q_i(Q)$ were obtained over a wide $Q$ range. On the other hand, small-mismatch of peak intensity was confirmed. This may be due to the fact that experimental $Q_i(Q)$ were obtained from data of finite $Q$ ranges via various treatments such as smoothing and Fourier and back-Fourier transforms.

| Table 1. Interatomic and intra-atomic force-field parameters for the sodium-nitrate–sodium-nitrite system used in this study. |
|-----------------|-----------|-------------|-------------|
| Atom            | $q_i$ (e) | $A$ (kcal/mol) | $\rho$ (Å) | $C$ (kcal/mol Å$^6$) |
| Na              | 1.00      | 9778.06     | 0.317       | 24.18          |
| N(NO$_2^-$)     | 0.95      | 35682.18    | 0.2645      | 259.1          |
| O(NO$_2^-$)     | -0.65     | 64542.47    | 0.2392      | 259.3          |
| N(NO$_3^-$)     | -0.10     | 33652.7     | 0.2646      | 259.1          |
| O(NO$_3^-$)     | -0.45     | 62142.9     | 0.2393      | 259.4          |

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<td>116.8</td>
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<td>O-N-O-O (NO$_3^-$)</td>
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\[ V_m(x, T) = \sum_{i=0}^{x}a_i x^i + \left( \sum_{i=0}^{2} b_i x^i \right) T \]

where $T$ is temperature in degrees Kelvin, and $a_i$ and $b_i$ are fitting parameters. The values obtained for $a_i$ and $b_i$ are summarized in Table 2.

\[ V_m(x, T) = \sum_{i=0}^{x}a_i x^i + \left( \sum_{i=0}^{2} b_i x^i \right) T \]

Figure 2. Simulated neutron (bottom) and X-ray (upper) structure factors of 67.4NaNNO2–32.6NaNNO3 (Eutectic), NaNNO2 and NaNNO3–NO$_3^-$._\textendash\textendash NO$_3^-$.

\[ V_m(x, T) = \sum_{i=0}^{x}a_i x^i + \left( \sum_{i=0}^{2} b_i x^i \right) T \]

Figure 3. Molar volumes of NaNNO$_3$, NaNNO$_2$, and their mixtures at various temperatures. Triangles: MD simulation and Circles: experiment.

The molar volumes of NaNNO$_3$, 20NaNNO$_2$–80NaNNO$_3$, 80NaNNO$_2$–20NaNNO$_3$, and NaNNO$_3$ obtained from the experiments and MD simulations are shown as a function of the temperature in Fig. 3. From the experimental results, we expressed the molar volume ($V_m(x)$) of the molten $x$NaNNO$_2$–(1–$x$)NaNNO$_3$ systems by empirical polynomial functions with eight parameters as follows:

\[ V_m(x, T) = \sum_{i=0}^{x}a_i x^i + \left( \sum_{i=0}^{2} b_i x^i \right) T \]
Table 3. Parameters for the empirical polynomial molar volume function of the molten $x\text{NaNO}_2-(1-x)\text{NaNO}_3$ system.

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<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$b_0$</th>
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<td></td>
<td>0.3535</td>
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<td>164.3</td>
<td>-32.09</td>
<td>0.2309</td>
<td>3.498</td>
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3.2 $^{23}\text{Na}$ self-diffusion coefficient

The self-diffusion coefficient is a representative dynamical property of molten salts. Thanks to HT-NMR, we now have accurate $^{23}\text{Na}$ self-diffusion coefficients at various temperatures. The self-diffusion coefficients in the MD simulations were obtained from fittings of the mean square displacement with a linear time region over 500 ps. The temperature-dependent experimental and simulated $^{23}\text{Na}$ self-diffusion coefficients are shown in Fig. 4 as Arrhenius plots. The diffusivity of Na in $\text{NaNO}_3$ is higher than that in $\text{NaNO}_2$ when compared at the same temperature. This trend is the same as that obtained from the results of $^{23}\text{Na}$ high-temperature NMR and MD simulations. For all molten $x\text{NaNO}_2-(1-x)\text{NaNO}_3$ systems, the simulated $^{23}\text{Na}$ self-diffusion coefficients are in agreement with the experimental data within 25%. This discrepancy reflects the limitation of MD; however, the general trends in the experimental data are reproduced by the simulations. The activation energy ($E_a$) of Na was also calculated from a linear regression of the temperature-dependent Na self-diffusion coefficients ($D$) using

\[
D = D_0 \exp \left( -\frac{E_a}{RT} \right)
\]

where $R$ and $T$ are the gas constant and temperature. The activation energy is plotted as a function of the $\text{NaNO}_2$ content ($x$) in Fig. 5. The composition dependence of $E_a$ is within a range of 10 kJ/mol, which is comparable with $E_a$ of the electrical conductivity with a difference of about 5 kJ/mol. Although our developed force-field parameters exhibit fairly good reproducibility, fine-tuning and consideration of the polarized potential models might provide better results.

The diffusivity coefficients of ions in the molten $\text{NaNO}_3$, $\text{NaNO}_2$, and eutectic composition ($67.4\text{NaNO}_2-32.6\text{NaNO}_3$) were also compared with experimental and previous MD studies. All data were summarized in Table 4. It is clear that our developed potential model can reproduce experimental diffusivity compared with previous MD study.

3.3 Heat capacity

The heat capacities were computed using the procedure described in the experimental section. Good linear relationships for the total energy and molar volume versus the temperature are confirmed in the calculated temperature range, as shown in Fig. 6. The slopes of

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Table 4. Comparison of self-diffusion coefficients ($\times 10^{-9}$ m$^2$/s) obtained from experimental ($D^{\text{exp}}$) and MD ($D^{\text{MD}}$) studies. $D^{\text{MD}}_{\text{ref1}}$ and $D^{\text{MD}}_{\text{ref2}}$ were taken from references $^{6,24}$.

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<th>Temperature/K</th>
<th>Ion</th>
<th>$D^{\text{exp}}$</th>
<th>$D^{\text{MD}}$</th>
<th>$D^{\text{MD}}_{\text{ref1}}$</th>
<th>$D^{\text{MD}}_{\text{ref2}}$</th>
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<td>$\text{NaNO}_3$</td>
<td>$\text{Na}^+$</td>
<td>1.29</td>
<td>1.04</td>
<td>6.12</td>
<td>2.33</td>
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<tr>
<td></td>
<td>$\text{NO}_3^-$</td>
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<td>4.61</td>
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<td>$\text{Na}^+$</td>
<td>1.55</td>
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<td>$\text{NO}_2^-$</td>
<td>1.68</td>
<td>1.68</td>
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<td>2.96</td>
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<tr>
<td>Eutectic</td>
<td>$\text{Na}^+$</td>
<td>1.21</td>
<td>8.78</td>
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<td>$\text{NO}_2^-$</td>
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<td>$\text{NO}_3^-$</td>
<td>0.865</td>
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NaNO\textsubscript{3} system were developed by ab initio calculations and empirical methods to reproduce the NaNO\textsubscript{2} crystal structure. The densities for the solid crystal and molten state obtained from the MD simulations were within 5% of the experimental values for all systems. The $^{23}\text{Na}$ self-diffusion coefficients were measured with high-temperature $^{23}\text{Na}$ HT-NMR from the melting temperature to the melting temperature plus 100 K. The simulated Na self-diffusion coefficients and activation energies were in fairly good agreement with the experimental results. The temperature-averaged heat capacities were computed from linear regressions of the total energy and volume as a function of the temperature. The results obtained from the MD simulation were approximately 5% higher than experimental data, but the composition dependence was in very good agreement for the $x\text{NaNO}_2-(1-x)\text{NaNO}_3$ system. The force field developed in this study is reasonable for predicting the thermal properties of the molten $x\text{NaNO}_2-(1-x)\text{NaNO}_3$ system.

References