Applied Energy 220 (2018) 536–544

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Molecular dynamics simulations of the local structures and thermodynamic properties on molten alkali carbonate K_2CO_3

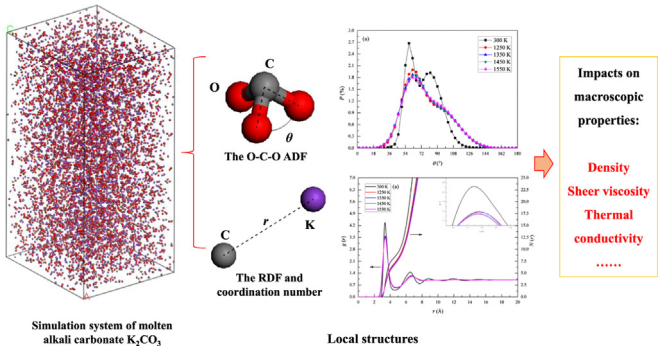
Jing Ding[a], Lichan Du[a], Gechuanqi Pan[a], Jianfeng Lu[a], Xiaolan Wei[b], Jiang Li[c], Weilong Wang[a,*], Jinyue Yan[d,e]

[a] School of Engineering, Sun Yat-Sen University, Guangzhou 510006, China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China
[c] National Supercomputer Center in Guangzhou, Guangzhou 510006, China
[d] School of Business, Society and Energy, Mälardalen University, Västerås, Sweden
[e] Energy Process Division, Royal Institute of Technology, Stockholm, Sweden

HIGHLIGHTS

- Local structures and thermodynamic properties were systematically reported.
- Sheer viscosity and thermal conductivity were simulated by the NEMD simulations.
- Accuracy and reliability of MD simulations were verified for molten carbonate salts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Molecular dynamics simulation
Molten alkali carbonates
Local structures
Thermodynamic properties

ABSTRACT

Molten carbonate salts have received particular attention for high-temperature thermal energy storage and heat transfer applications due to desirable thermal characteristics, such as wide operating temperature range, low causticity and excellent thermal stability. In this study, molecular dynamics (MD) simulations were performed on molten alkali carbonate K_2CO_3 based on an effective pair potential model, a Born-Mayer type combined with a Coulomb term. The radial distribution functions (RDF) and coordination number curves of the molten salt were characterized to explore the temperature dependences of macroscopic properties from microscopic view. The results suggest that the distance between K_2CO_3 particles is getting larger with temperature increasing, resulting in the increase of molar volume and the diminished ability of resistance to shear deformation and heat transfer by vibration between ions. Besides, it can be concluded that the structure of CO_3^{2-} is inferred reasonably to be ortho-triangular pyramid from the comprehensive analysis of local structures including the angular distribution functions (ADF). Moreover, the thermodynamic properties were simulated in detail from 1200 to 1600 K including the density, thermal expansion coefficient, specific heat capacity, sheer viscosity, thermal conductivity and ion self-diffusion coefficient, which was hard to be measured from experiments under high-temperature extreme conditions. All the simulation results are in satisfactory agreement with available experimental data with high accuracy, and the minimum simulation error is as low as 1.42%.

* Corresponding author.
E-mail address: wwlong@mail.sysu.edu.cn (W. Wang).

https://doi.org/10.1016/j.apenergy.2018.03.116
Received 15 August 2017; Received in revised form 26 March 2018; Accepted 27 March 2018
Available online 31 March 2018

1. Introduction

With the rapid development of global economy, enormous energy consumption has brought about serious energy shortage and environment pollution. Solar energy, as a prospective renewable energy, has been receiving extensive attentions worldwide [1,2]. Developing efficient energy storage and heat transfer technology for concentrating solar power plants is required urgently due to its intermittence and instability [3–6]. Molten salts have been studied extensively for thermal energy storage and heat transfer applications due to desirable thermal characteristics such as wide operating temperature range, low vapor pressure, moderate heat capacity, low viscosity and excellent thermal stability [7–10]. Currently, only nitrate salts have been employed widely as thermal energy storage and heat transfer media for concentrating solar power plants below 773 K [11–15], while other molten salts are temporally limited to be used in commercial applications due to the lack of properties data over their entire operating temperature range at higher temperature. However, it's because of their high working temperature that relevant properties such as sheer viscosity and thermal conductivity are difficult, if not impossible, to be obtained accurately under high-temperature extreme conditions, which are of great significance for thermal energy storage and heat transfer system design. Therefore, it is desirable to seek for an alternative way to accurately predict thermodynamic properties of molten salts instead of experimental measurements.

Computer simulations can be a complementary tool for predicting the macroscopic and microscopic properties of ionic crystal materials, among which molecular dynamics (MD) simulation has proved its value for the study of local structures and thermodynamic properties of molten salts [16]. Dixon and Sangster [17–19] simulated the radial distribution functions (RDF), velocity autocorrelation functions (ACF) and mean square displacements (MSD) of a series of pure molten alkali halides (RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr and CsI) by MD simulations using the Born-Mayer-Huggins potential model, and verified the suitability of the model for molten alkali halides. Galamba et al. [20–23] calculated the sheer viscosity and thermal conductivity of pure molten NaCl and KCl through the equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations within the framework of the Born-Mayer-Huggins ionic potential, and the simulation results of the two molecular dynamics simulation methods were all much overestimated but in agreement with experimental data in terms of the development trend with temperature. Pan et al. [24,25] performed MD simulations on a series of molten alkali chlorides (LiCl, NaCl, KCl and NaCl-KCl) with the verified Born-Mayer-Huggins pair potential. The systematic properties such as the density, sheer viscosity, thermal conductivity, the RDF and angular distribution functions (ADF) were all presented in detail. Tissen and Janssen [26] reported MD simulations on molten carbonates Li_2CO_3, Na_2CO_3, and K_2CO_3 in the NVT ensemble at 1200 K. A significant change in structure of the melt was observed on going from Li_2CO_3 to K_2CO_3, and the rotation of CO_3^{2-} was substantially easier in K_2CO_3 than in Li_2CO_3. Of all the previous MD simulations, most investigations focused on molten alkali halides, and few systematical studies worked on the internal relation between macroscopic properties and microscopic structures.

Recently, molten carbonate salts have received particular attentions for high-temperature thermal energy storage and heat transfer applications owing to their excellent characteristics of wide working temperature range, low causticity, low unit cost and excellent thermal stability up to 1273 K [27–29]. In this paper, local structures and thermodynamic properties of molten alkali carbonate K_2CO_3 in liquid state were systematically reported by means of MD simulations with an effective pair potential model, a Born-Mayer type combined with a Coulomb term. The RDF and coordination number curves of molten alkali carbonate K_2CO_3 were characterized to analyse the temperature dependences of macroscopic properties from microscopic view. Besides, the ADF was calculated to study the structure of CO_3^{2-} combined with the RDF and coordination number simulations. Thermodynamic properties were calculated from 1200 to 1600 K including the density, thermal expansion coefficient, specific heat capacity, sheer viscosity, thermal conductivity and ion self-diffusion coefficient, and their temperature dependences were also investigated in detail.

2. Molecular dynamics simulations

2.1. Simulation details

The effective pair potential used in MD simulations was a Born-Mayer type combined with a Coulomb term. This form of potential model is initially developed for applications on molten alkali halides [30,31] and has been successfully used for molten alkali carbonates [26]. The interionic potential is described as follows,

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + b\left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}\right)\exp[\alpha(\sigma_i + \sigma_j - r_{ij})] \quad (1)$$

where r_{ij} is the distance between the centres of two particles i and j, e is the electronic charge unit, z_i is the valence of ion i, n_i is the number of electrons in the outer shell of the ion, σ_i is the effective radius of the ion, α is the softness parameter and b is a pre-exponential term, where α and b are constants, and they are 3.45 $Å^{-1}$ and 4.865 kcal/mol, respectively. The parameters used for the potential model in this study were collected in Table 1, which were obtained by Janssen and Tissen [32].

All the MD simulations on molten alkali carbonate K_2CO_3 were performed using the open source molecular simulation package LAMMPS from 1200 to 1600 K. The MD simulations reported here were performed on a simulation system consisting of 9216 atoms, and the numbers of K, C and O were distributed as the proportion of 2:1:3. The initial crystal cell was generated by using the parameters of solid state at 800 K provided by Becht and Struikmans [33], and then expanded to the simulation box by the supercell method. The periodic boundary conditions were adopted to keep the number of particles constant in simulation system and eliminate the boundary effect. The cut-off distance of short-range interactions was set to be 20 Å, which was almost equal to half of the smallest side length of the simulation box after relaxation. While the long-range interaction calculations were computed in K-space using the PPPM solver [34] to eliminate the truncation errors, and the accuracy of calculated forces was 1.0×10^{-6}. The initial velocities were randomly assigned and obeyed the Gaussian distribution. The Verlet algorithm was used to solve Newton's equations of motion with a timestep of 1.0 fs.

In the MD simulations, the simulation system was first heated to 1600 K and then cooled to desired temperatures from 1200 to 1600 K with an interval of 50 K. After that, the system was sufficiently equilibrated in the NPT ensemble for 200 million timesteps at corresponding temperature with the atmospheric pressure, and the temperature and stress damping parameters were set to be 100 and 500 fs separately. Subsequently, the system was in NVT ensemble lasting for at least 500 million timesteps to ensure good statistics for computing desired properties and structures such as the sheer viscosity and thermal conductivity.

Table 1
Parameters of molten alkali carbonate K_2CO_3 for the potential model in MD simulations.

Atom	z (e)	n	σ (Å)
K	1.00	8.00	1.39
C	1.54	2.46	1.10
O	−1.18	7.18	1.33