TEMPERATURE DEPENDENCE TRANSPORT PROPERTIES OF MOLTEN THALLIUM HALIDES FROM EQUILIBRIUM MOLECULAR DYNAMICS CALCULATIONS

H. B. KAVANOZ

Department of Physics, Yıldız Technical University, Davutpaşa Campus
Esenler-Istanbul 34210, Turkey

Transport properties depending on temperature of TlCl, TlBr and TLI in molten state have been calculated by means of equilibrium molecular dynamics simulation (EMD). The potentials used for the calculations have the same functional form as the semi empirical potential originally proposed by Vashistha and Rahman (VR) [1].The results obtained from the velocity correlation function method and those measured by mean-square displacement are in line with each other. The diffusion coefficient and ionic conductivity for these molten salts at various temperatures are also estimated by using a equilibrium molecular dynamics simulation. The results for thallium halides are similar to experimental data.

1. Introduction

Molten salts have been studied for many years; however, renewed interest in them has currently increased, largely owing to their use as electrolytes in high-temperature carbonate fuel cells. Under those high-temperature conditions, it is extremely difficult, if not impossible, to accurately measure transport properties, and data regarding measurement in high temperatures are very limited. A major premise of this work is that, because of the experimental problems encountered at high temperature, it may be possible to simulate those properties more accurately than they can be measured.

Thallium halides crystals are used in infrared optics and optical fiber. In the last years, TlBr crystals are employed in γ- , x-ray and α-particles detectors. Molten thallium halides exhibit several features which distinguish them from the alkali halides. The local structure of these melts exhibit a behavior intermediate between those of the noble-metal halides and the alkali halides [2,3]. All three TlX compounds have CsCl-type crystal structure near their melting points [4]. They have low melting temperature and relatively high ionic conductivity which increases exponentially with temperature [2]. This work deals with the effects of temperatures on the diffusion coefficient and ionic conductivity of the molten thallium halides (TlCl, TlBr and TlI) between 700K-1000K at 20K intervals. The potentials used here are the same as those proposed by Vashistha and Rahman in that, by using their potential formalism, it is possible to learn the diffusion mechanisms in the different thermodynamic states through the mean-square displacements $\langle r_\alpha^2(t) \rangle$ and the velocity autocorrelation functions $C_\alpha(t)$ (VACF) of the component species.

The following section presents briefly parameterization of the potentials [2] as well as giving minimal information about the molecular dynamics code used in this study. Section 3 reveals the results of the study, which are then followed by a few relevant conclusions.

2. Simulation procedure

The simulation was done using MOLDY code [5]. The system under study was represented by NVE micro canonical ensemble. The Beeman algorithm was used for calculation of the particle motion, and the Ewald method was applied for the calculation of the electrostatic interaction. The molecular dynamics simulations were carried out using system made up of N=216 ions which, in case of TlX compounds under study, included 108 anions, 108 cations placed in a cubic box of volume V, with periodic boundary conditions. The positions and velocities were computed using Beeman`s integration algorithm with a time step of 1.0×10^{-15} s and the pair potentials were described as given below. The Ewald summation method was used to account for the long range Coulomb contributions. Once equilibrium was reached, the properties of interest by averaging over 1.0×10^{5} time steps were calculated considering that such a large number of time steps minimize the statistical fluctuations in the structure factors. The temperature is varied from 700K-975K at 20K intervals.

A semi-empirical potential based on the functional form originally proposed by Vashishta and Rahman (VR) [1] which is expressed as follows was used;

$$\phi(r) = \frac{H_{\alpha\beta}}{r^{\eta_{\alpha\beta}}} + \frac{Z_\alpha Z_\beta}{r} - \frac{P_{\alpha\beta}}{r^4} - \frac{C_{\alpha\beta}}{r^6} \qquad (1)$$

The first term models the repulsion between the ions arising from the overlap of the outer shell of electrons; the second is the Coulomb interaction between effective charges $Z_{\alpha,\beta}$; the third term is the monopole-induced dipole attractive interaction, and last is the dipole-dipole or van der Waals contribution. Generally, model potentials have provided useful information in solid phase as the parameters were fit to the properties of solid state. It was concluded that they are not capable to reproduce some basic properties at high temperature. As it is presented below, VR potential model parameters determined in this study is the only one that is efficient to model the interactions in solid and liquid phase by estimating the structural transition and the melting at about the correct experimental temperatures.

The set of potential parameters employed in the simulation is listed in Table 1.

Table 1. Parameters of the pair potentials.

	H	P	C	η	$|Z_{eff}|$
Tl-Tl	216.4	0.0	0.0	7	
Cl-Cl	1921.1	22.9	83.5	7	0.68
Tl-Cl	701.8	11.4	0.0	7	

	H	P	C	η	$|Z_{eff}|$
Tl-Br	137.9	0.0	0.0	6	
Br-Br	896.3	31.5	131.0	6	0.7
Tl-Br	378.1	15.7		6	

	H	P	C	η	$|Z_{eff}|$
Tl-Tl	46.0	0.0	0.0	5	
I-I	67959.7	44.3	273.5	9	0.65
Tl-I	1408.9	22.1	0.0	7	

in unit of $e^2/A = 14{,}399$ eV

2.1 Diffusion coefficients

The temperature dependences of the diffusion constant for Tl halides have been obtained by using the same potential as were by Vashistha-Rahman and the simulation method. Transport coefficients calculated using the Green-Kubo integral formulas require appropriate correlation functions which can, in principle be calculated by molecular dynamics computer simulation. The diffusion coefficients can be computed by two different ways. One is via the mean square displacement $\langle r^2(t) \rangle$, and the other is via the velocity autocorrelation function $C(t)$. The former is computed from the positions of the particles $r_i(t)$, as follows:

$$\langle r_\alpha{}^2(t) \rangle = \frac{1}{N} \left\langle \sum_{i=1}^{N} \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle \tag{2}$$

Where $\vec{r}_i(t)$ is the absolute position of particle i at a time t after an arbitrary defined time origin and $\langle ... \rangle$ denotes the time average from which the self-diffusion coefficients D can be evaluated using both the Kubo and Einstein formulas.

The self-diffusion coefficient of particle i can be obtained directly from molecular dynamics computer simulation from the linear region of the mean-square displacement (MSD) as

$$D = \lim_{t \to \infty} \frac{\left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle}{6t} \tag{3}$$

This formula is known as Einstein formula [6,7,8].

The velocity correlation function is computed from the of the particles $\vec{v}_i(t)$ in terms of

$$C(t) = \left\langle \sum_{i=1}^{N} (\vec{v}_i(t) \cdot \vec{v}_i(0)) \right\rangle \tag{4}$$

The self-diffusion coefficient D can be obtained trough the Green-Kubo formula

$$D = \frac{1}{3} \int_0^\infty \left\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \right\rangle dt \tag{5}$$

Here the integrand of equation is called the VAC function which is obtained with very high statistical accuracy by time-averaging over N particles of the system.

2.2 Partial conductivities of molten salts

An equivalent molten salt with the density $n^+ = n^- = n_0 (= N/V_0)$ and charge $z^+ = -z^- = z$ was considered, where N is the total number of cations or anions in the volume V_0. The current density at the time t can be written as [9,10],

$$\vec{J}(t) = \vec{J}^+(t) + \vec{J}^-(t)$$

$$\vec{J}^+(t) = \sum_{i=1}^{n^+} z^+ e \vec{v}_i^+(t)$$

$$\vec{J}^-(t) = \sum_{k=1}^{n^-} z^- e \vec{v}_i^-(t) \tag{6}$$

According to linear response theory, the dc conductivity in such a molten salt is given by;

$$\sigma = \sigma^+ + \sigma^-$$

$$\sigma^+ = \sigma^{++} + \sigma^{+-}$$

$$\sigma^- = \sigma^{-+} + \sigma^{--} \tag{7}$$

where conductivity coefficients σ^{++}, σ^{+-} and σ^{--} are expressed as follows,

$$\sigma^{++} = \frac{1}{3k_BT} \int_0^\infty \langle \vec{J}^+(t) \cdot \vec{J}^+(0) \rangle dt$$

$$\sigma^{--} = \frac{1}{3k_BT} \int_0^\infty \langle \vec{J}^-(t) \cdot \vec{J}^-(0) \rangle dt$$

$$\sigma^{+-} = \sigma^{-+} = \frac{1}{3k_BT} \int_0^\infty \langle \vec{J}^+(t) \cdot \vec{J}^-(0) \rangle dt \tag{8}$$

All current correlation functions in these integrations are then replaced by the form of

$$< \vec{v}_j^\alpha(t) \cdot \vec{v}_j^\beta(t) > (\alpha, \beta = +,-).$$

3. Results and discussion

All three thallium halides were studied at the temperatures ranging between 700K-975K at 20K intervals. The melting temperatures are 702K, 732K and 713K for TlCl, TlBr and TlI respectively. The results of $\langle r^2(t) \rangle$, are shown in Fig.1,2,3 at selected three temperatures as representative samples of calculations.
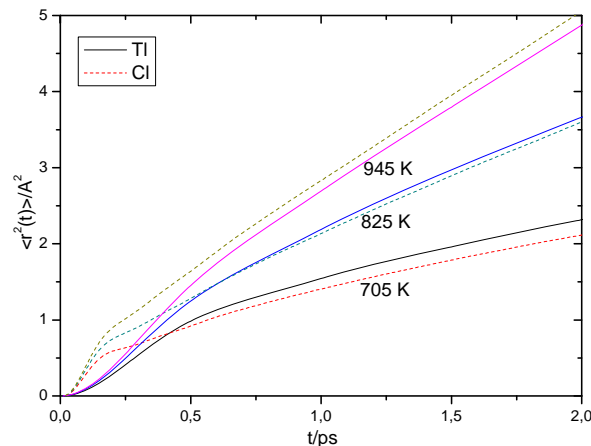

Fig.1. The mean square displacement of TlCl at three temperatures.

The behavior of the msd in all cases is similar to each other. However, there are some important differences when considered in detail. Thallium ions show the diffusive behavior after about 0.5 ps while the negative ions start diffusing through the surrounding ions at about t=0.13, 0.2 and 0.35 ps for Cl, Br and I, respectively. Before the diffusive regime of both anions and cations, it appears that they experience a rattling motion in the cages formed by the neighboring like ions.

The mass ratio affects the starting time of diffusion of anions; as the mass ratio increases, the time of the rattling motion of anions becomes shorter compared to that of cations. The slope of msd of anions also increases with increasing the mass ratio after they become diffusive. It is also observed that when the temperature increases, there is an increase in the diffusion of both ions. The rate of increase clearly depends on the mass ratio. Consequently, the diffusive behavior of anions in TlX is mainly determined by the mass, since diffusive behavior is related to size ratio of anion and cation.
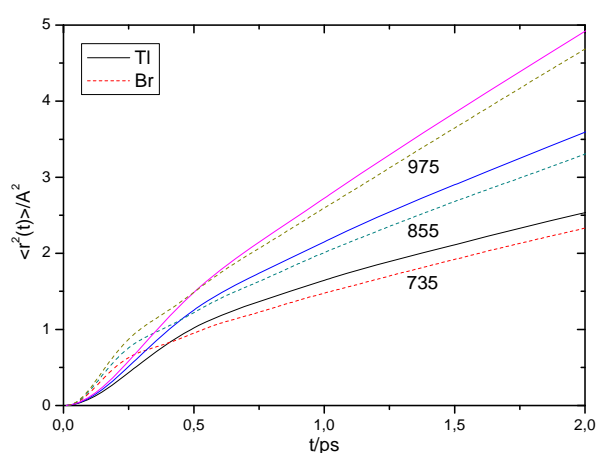

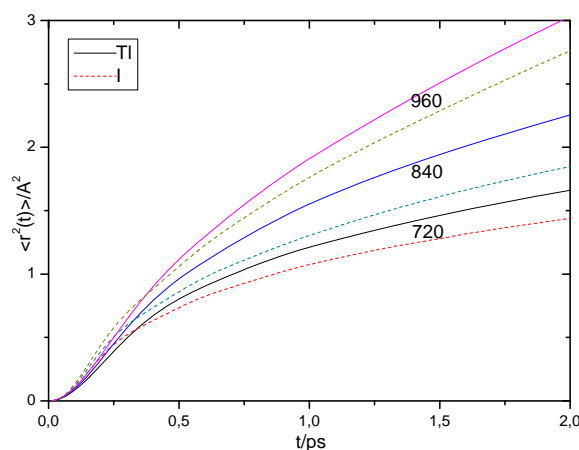*Fig.2. The mean square displacement of TlBr at three temperatures.*

Fig.3. The mean square displacement of TlI at three temperatures.

3.1 Diffusion coefficient

The diffusion coefficient was calculated by the Einstein formula from root mean-square displacement of ionic positions [11]. Diffusion coefficients of Tl and Cl, Br , I ions in molten Thallium halides are plotted in Fig 4,5,6.
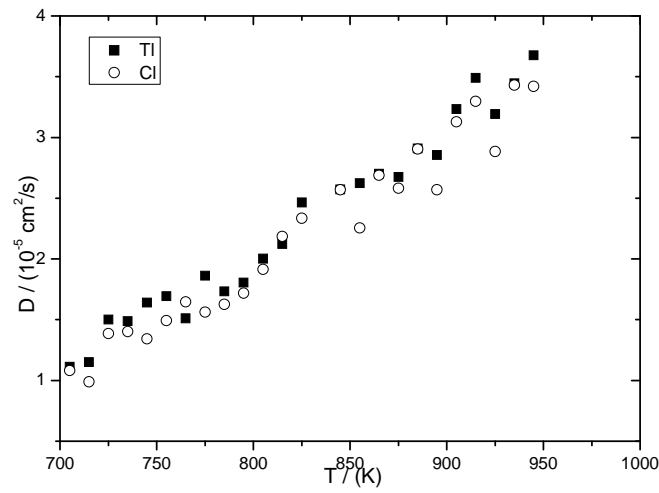
Fig.4. The change of temperature dependences of diffusion coefficients of Tl and Cl.
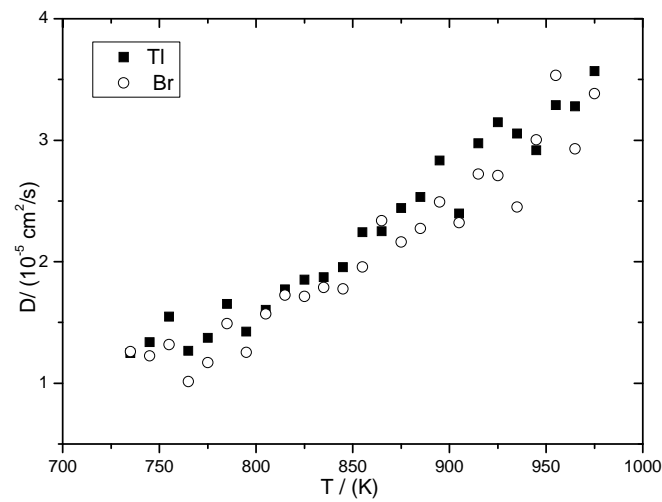

Fig.5. The change of temperature dependences of diffusion coefficients of Tl and Br.
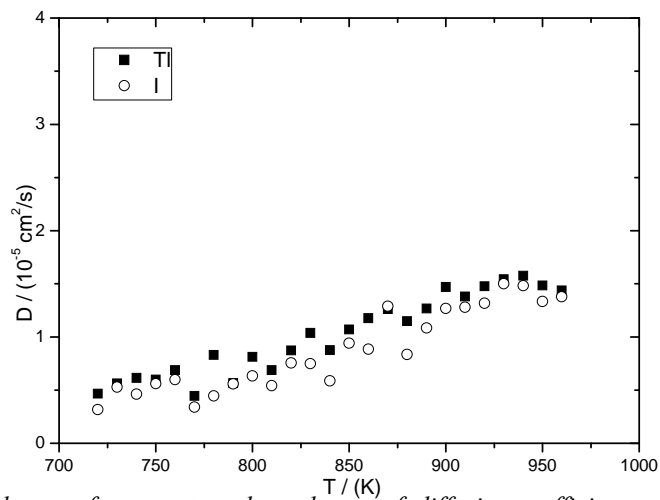

Fig.6. The change of temperature dependences of diffusion coefficients of Tl and I.

3.2 Ionic conductivity

The results measured at melting temperatures are 1.1, 1.2 and 0.25 $(1/\Omega cm)$ and the experimental results of ionic conductivities are 1.52, 1.07 and 0.64 for TlCl, TlBr and TlI respectively [12]. In addition, electronegativity and electron affinity differences are TlCl<TlBr<TlI. Similarities and differences observed in diffusion coefficients are also seen ionic conductivity. That is, while ionic conductivity increases linearly, TlCl and TlBr show almost similar properties whereas TlI seems to divert a little from them as Fig 7 demonstrates. In the molten phase, it may be noteworthy that the total conductivities and partial conductivities increase linearly with the rise in temperature.

Furthermore, it seems that the conductivities and partial conductivities have a constant ratio to each other in spite of increasing temperature. In the molten binary system, it is known that the ratio of the partial conductivities is in inverse proportion to their mass ratio [13]. Mass and size ratio are $m_+ / m_- = 5.77$, 2.56, 1.61 and $d_- / d_+ = 1.2$, 1.3, 1.5 for TlCl, TlBr and TlI respectively.
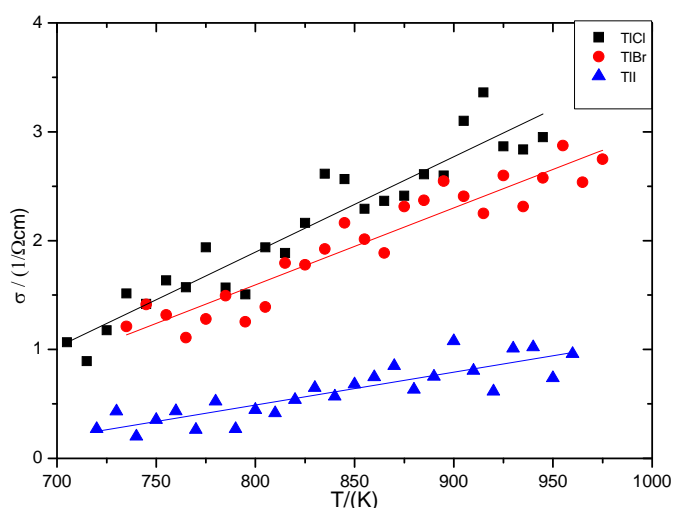

Fig.7. The change of temperature dependences of ionic conductivities of TlCl, TlBr and TlI.

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