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CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

Molecular dynamics simulations and thermodynamic modeling of NaCl–KCl–ZnCl$_2$ ternary system

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A B S T R A C T

The NaCl–KCl–ZnCl$_2$ ternary system is examined and modeled using the CALPHAD methodology in conjunction with molecular dynamics (MD) simulations. In particular, MD simulations are used for calculating liquid enthalpies of mixing as a function of composition for the ternary and its binary sub-systems. In addition, key structural features are obtained from MD that is then used for informing the employed two-sublattice ionic liquid model (Na^{+1}, K^{+1}: Cl^{-1}, ZnCl$_2$), which describes the ternary liquid phase. The structure of the simulated liquid systems show that Zn^{+2} cations primarily exhibit 4-fold coordination in addition to a smaller percentage of 5-fold followed by 3-fold coordination; in contrast, the coordination of both Na+ and K+ cations are distributed between 2- and 4-fold states. The optimized self-consistent thermodynamic model parameters show good agreement with MD data obtained in this work and available experimental literature data.

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1. Introduction

The NaCl–KCl–ZnCl$_2$ molten salt mixtures are investigated as potential candidate materials for high temperature heat transfer fluids in concentrated solar power (CSP) plants. The heat transfer fluids in CSPs require low liquidus temperatures (< 250 °C) and high thermal stability (> 800 °C) besides other thermo physical properties such as corrosion resistance, thermal conductivity, viscosity, etc. [1,2]. The NaCl–KCl–ZnCl$_2$ ternary with low liquidus points (as low as ~ 200 °C) and vapor pressures (lower than 1 atm) up to ~ 800 °C is a promising system as it satisfies the basic criterion of thermodynamic stability of the molten salts for CSPs. In the present work we report the thermodynamic modeling of the entire NaCl–KCl–ZnCl$_2$ ternary. We focus on the thermal stability of the liquid in the entire compositional space.

Thermodynamic modeling of the NaCl–KCl–ZnCl$_2$ ternary has earlier been reported by Robelin and Chartrand [3], who used a modified quasichemical model for the liquid phase. Robelin and Chartrand [3] predicted the thermodynamics of the NaCl–KCl–ZnCl$_2$ ternary from the binary subsystems with no ternary excess parameters. Romero-Serrano et al. [4] in their calculations of MCl–ZnCl$_2$ (M – Li, Na, K) phase diagrams, reported the thermodynamic modeling of the binary subsystems – NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ – using

a different structural model based on a depolymerization reaction, for the liquid phase. However, in both of these studies the modeling of the liquid phase was limited by the lack of experimental enthalpies of mixing in the binaries (except for NaCl–KCl) and in the ternary. In the modeling reported by Robelin and Chartrand [3], they estimated the enthalpies of mixing in the NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ liquids at 40 mol% ZnCl$_2$ from the linear regression of the available experimental data pertaining to NaCl–MCl$_2$ and KCl–MCl$_2$ (M – Ca, Mg, Sr, Mn, Fe Co and Ni) melts at 1083 K. The experimental thermochemical data pertaining to the NaCl–KCl–ZnCl$_2$ ternary is also incomplete for accurate parameterization of the models. A brief review of the available literature data pertaining to the NaCl–KCl–ZnCl$_2$ systems is presented in Section 2.

Addressing the dearth of the thermochemical data pertaining to the liquid phase on the binary subsystems and the ternary, we performed classical molecular dynamics (MD) simulations to predict the enthalpies of mixing in the liquid phase on the NaCl–KCl–ZnCl$_2$ system. We employed Born–Mayer–Huggins type pair potentials that are available in literature [5,6] for pure components of NaCl, KCl and ZnCl$_2$. The parameters for alkali halides reported by Adams and McDonald [5] characterize the interactions among ions as predominately coulombic. In their work the charge on each ion is the corresponding nominal charge and no effects of electronic polarization are incorporated. Additionally, the inclusion of dispersion forces of van der Waals type were included due to significant contribution to thermodynamic properties. This addition of non-coulombic terms is commonly referred to as the

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Huggins–Mayer potential which is based on the Born model for ionic solids. The parameters reported for the Huggins–Mayer terms were adapted from the works of Tosi and Fumi [7,8] which parameterize all alkali halide systems having the rock-salt structure. The parameterization of zinc chloride by Gardner and Heyes [6] followed similar methodology. Employing Lorentz–Berthelot mixing relations [9] for the NaCl–KCl–ZnCl$_2$ mixtures, we predicted the structure and enthalpies of mixing of the liquid phase at several different compositions in the binary and ternary composition space.

The structure of the liquid phase from the MD simulations is characterized in this work in order to choose an appropriate model to describe that phase. Based on this analysis, we employed an ionic 2-sublattice model to describe the liquid phase; (Na^{+1}, K^{+1}: Cl^{-1}, ZnCl$_2$) which is different from the earlier published models [3,4]. All the solid phases in the ternary system, except the solid solution on the NaCl–KCl binary, are stoichiometric and their free energies are either optimized in this work or taken from literature [3,10–12]. The gas phase is modeled as an ideal solution of the various gaseous species; NaCl, Na$_2$Cl$_2$, KCl, K$_2$Cl$_2$, ZnCl$_2$, Zn$_2$Cl$_4$, NaZnCl$_3$, KZnCl$_3$.

2. Review of experimental literature data

Robelin and Chartrand [3] reported a critical assessment of the NaCl–KCl–ZnCl$_2$ ternary phase diagram containing the stoichiometric intermediate compounds, Na$_2$ZnCl$_4$, KZn$_2$Cl$_5$, K$_2$ZnCl$_4$, and K$_5$Zn$_4$Cl$_{13}$. The phase diagrams of the NaCl–KCl, NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ systems have been investigated experimentally by several researchers [13–19]. The NaCl–KCl binary is a congruently melting isomorphous system with a miscibility gap in the solid-solution phase [12,20,21]. The NaCl–ZnCl$_2$ system has one intermediate compound, Na$_2$ZnCl$_4$ with an orthorhombic crystal structure (Space group: Pnma) [18,22]. On the KCl–ZnCl$_2$ pseudo-binary there are three intermediate compounds; KZn$_2$Cl$_5$, K$_2$ZnCl$_4$, and K$_5$Zn$_4$Cl$_{13}$ [13–16]. The compound K$_2$ZnCl$_4$ exhibits three different allotropic forms; a monoclinic structure (Space group: C1c1) below 143 K, an orthorhombic structure (Space group: Pna2$_1$) between 143 and 403 K and an orthorhombic structure (Space group: Pnam) above 403 K up to its melting point [23]. There is no available thermodynamic data pertaining to these polymorphic phase transitions and hence the low temperature allotropic forms are not included in this work. Concerning the ternary phase diagram, Nikonova et al. [24] reported the measured liquidus curves along 11 different isopleths using the method of cooling curves.

In the case of thermochemical data, none of the intermediate compounds on the ternary system have C_p data reported from experiments. Similarly, as mentioned earlier, there are no available enthalpies of mixing in the liquid phase. Bloom et al. [25] measured the activities and vapor pressures in the molten NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ systems from the transpiration method at two different temperatures. Alabyshev and Lantratov [26] and Tarasov and Guldin [27] have also reported the activities of ZnCl$_2$ in the NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ systems as a function of composition and temperature. The reported activities of ZnCl$_2$ in the NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ melts as a function of composition are available in the range of 673–923 K and 673–1048 K, respectively. In the case of NaCl–KCl–ZnCl$_2$ melts, the activity of ZnCl$_2$ along an isopleth with 30 mol% ZnCl$_2$ is measured at two different temperatures by Markov [28] and Tarasov and Guldin [27].

3. Details of molecular dynamics simulations

MD simulations were carried out using the Born–Huggins–Meyer (BHM) potentials reported by Adams and McDonald [5] and

Gardner and Heyes [6] for NaCl/KCl and ZnCl$_2$ respectively. In order to ensure consistency between the respective potentials, the interactions between the dissimilar cation–cation pairs as well as the anion–anion (i.e., Cl–Cl) pairs were estimated as follows: the Lorentz–Berthelot mixing relations were used for describing dissimilar cation–cation interactions, which has been shown to be accurate [9]. On the other hand, the Cl–Cl interaction-parameter in the binary and ternary solutions was obtained by a weighted average scheme, with the respective weights corresponding to atomic fractions of each constituent. This scheme was initially validated based on its ability to reproduce the experimental densities of select binary solutions. The MD simulations were carried out by using the LAMMPS software package [29]. Employing periodic boundary conditions, simulation cells of 24576–32768 atoms were used for the calculations. The simulations for enthalpies of mixing were performed under isobaric/isothermal conditions at zero pressure and 1100 K for 2 ns (time-step = 1 fs). We employed a Nose–Hoover thermostat and barostat in our simulations with the damping parameters being 1.0 fs and 10.0 fs, respectively. The error bars (given by standard deviation) on the enthalpies are calculated by using the method of block averages as described by Flyvbjerg and Petersen [30]. The obtained error bars on the enthalpies of mixing are smaller than 0.1 kJ/mol. The structure of the liquid was characterized by calculating the pair distribution functions (PDFs) of different pairs and the radial coordination numbers. The radial coordination numbers ($n_{ij}(r)$) of different ions are obtained from the pair distribution functions as given by Eq. (1):

$$n_{ij}(R) = 4\pi\rho_i \int_0^R r^2 g_{ij}(r)dr \tag{1}$$

where $g_{ij}(r)$ is pair distribution function for the i–j pair, ρ_i is the number density, and R is the distance to the minimum of the first peak in the PDF.

4. Thermodynamic modeling

4.1. Solid phases

Thermochemical data for the stoichiometric NaCl, KCl, ZnCl$_2$ as shown in Table 1 are taken from the literature [3,10,11]. For the stoichiometric intermediate compounds (e.g., Na$_2$ZnCl$_4$) the heat capacity is approximated to be the sum of the heat capacities of the binary compounds with H$_{298}$ and S$_{298}$ taken from Robelin and Chartrand [3]. However, the approximate H$_{298}$ and S$_{298}$ of these intermediate compounds were further optimized in this work. The excess free energy of the only solid solution phase on the NaCl–KCl binary is taken from Sangster and Pelton [12] (see Table 1).

4.2. Liquid phase

The liquid phase is described by using a 2-sublattice ionic liquid model [31,32]: (Na^{+1}, K^{+1})$_P$ (Cl^{-1}, ZnCl$_2$)$_Q$. The electro neutrality is maintained by varying P and Q as shown in Eqs. (2) and (3).

$$P = 1 \, y_{cl^{-1}} \tag{2}$$

$$Q = 1y_{Na^{+1}} + 1y_{K^{+1}} \tag{3}$$

where y_i is the site fraction of species i in a given sublattice. In the ionic 2-sublattice model the cations occupy the 1st sublattice and, the anions and the neutral species occupy the 2nd sublattice. In the liquid phase Zn primarily exhibits a tetrahedral coordination (ZnCl$_4^{-2}$) with smaller fractions of 3-fold and 5-fold coordinations. For convenience, within the liquid model, we restricted our choice to a single-species namely ZnCl$_2$ as an approximation of the predominantly single-type coordination of Zn (see Section 5.1).

Table 1

Thermodynamic model parameters of NaCl–KCl–ZnCl$_2$ ternary system (in J/mol). The parameters that were taken from literature are shown along with the references.

Phase Solid phases	Model	Phase description	
SS_NaCl-KCl	(NaCl,KCl)	$^0G^{SS\_NaCl-KCl}_{KCl} = -448523.0835 + 191.0005433T - 40.0158T\ln T - 182424.0T^{-1} - 0.012734T^2$	[10,11]
		$^0G^{SS\_NaCl-KCl}_{NaCl} = -425542.16405 + 240.422492T - 0.0081588T^2 - 45.9403T\ln T$	[10,11]
		$^0L^{Ionic\ Liquid}_{Na^{+1},K^{+1}:Cl^{-1}} = 15972 + 32.796T - 5.598T\ln T$	[12]
		$^1L^{Ionic\ Liquid}_{Na^{+1},K^{+1}:Cl^{-1}} = -1639$	[12]
ZnCl$_2$	(Zn)$_1$:(Cl)$_2$	$^0G^{ZnCl_2}_{Na:Zn:Cl} = -435688.942 + 62.941T + 0.0143325T^2 + 260.5597T - 62.941\ T\ln T - 0.028665T^2$	[3]
Na$_2$ZnCl$_4$	(Na)$_2$:(Zn)$_1$:(Cl)$_4$	$^0G^{Na_2ZnCl_4}_{Na:Zn:Cl} = -1300271.2899100 + 801.9854241T - 0.0306501T^2 - 154.8216T\ln T$	This work (Optimized [3])
KZn$_2$Cl$_5$	(K)$_1$:(Zn)$_2$:(Cl)$_5$	$^0G^{KZnCl_5}_{K:Zn:Cl} = -1300278.0979099 + 741.3957195T - 165.8978T\ln T - 182422.5T^{-1} - 0.041399T^2$	This work (optimized [3])
K$_2$ZnCl$_4$	(K)$_2$:(Zn)$_1$:(Cl)$_4$	$^0G^{K_2ZnCl_4}_{K:Zn:Cl} = -1336712.1832498 + 762.80643T - 159.9136T\ln T - 364845.0T^{-1} - 0.025468T^2$	This work (optimized [3])
K$_5$Zn$_4$Cl$_{13}$	(K)$_5$:(Zn)$_4$:(Cl)$_{13}$	$^0G^{K_5Zn_4Cl_{13}}_{K:Zn:Cl} = -4080841.8367113 + 2248.329163T - 451.8429T\ln T - 912112.0T^{-1} - 0.121T^2$	This work (optimized [3])
Ionic liquid	(Na^{+1},K^{+1})$_p$: (Cl^{-1},ZnCl$_2$)$_q$	$^0G^{Ionic\ Liquid}_{Na^{+1}:Cl^{-1}} = -417806.2629 + 442.5091T + 0.0037656T^2 - 77.7638T\ln T$	[10,11]
		$^0G^{Ionic\ Liquid}_{K^{+1}:Cl^{-1}} = -443767.9 + 406.3978T - 73.5966T\ln T$	[10,11]
		$^0G^{Ionic\ Liquid}_{ZnCl_2} = -416867.4132 + 308.4871T - 0.0115645T^2 - 65.8350T\ln T$	[3]
		$^0L^{Ionic\ Liquid}_{Na^{+1},K^{+1}:Cl^{-1}} = -2186.1 + 0.1*T$	This work (optimized [40])
		$^1L^{Ionic\ Liquid}_{Na^{+1},K^{+1}:Cl^{-1}} = -136 + 0.0649*T$	This work (optimized [40])
		$^0L^{Ionic\ Liquid}_{Na^{+1}:Cl^{-1},ZnCl_2} = -30893 + 4.3425T$	This work
		$^1L^{Ionic\ Liquid}_{Na^{+1}:Cl^{-1},ZnCl_2} = -14759.9 + 5.1960T$	This work
		$^2L^{Ionic\ Liquid}_{Na^{+1}:Cl^{-1},ZnCl_2} = 2435.2 + 0.8401T$	
		$^0L^{Ionic\ Liquid}_{K^{+1}:Cl^{-1},ZnCl_2} = -56071.1 - 4.5044T$	This work
		$^1L^{Ionic\ Liquid}_{K^{+1}:Cl^{-1},ZnCl_2} = -21510.5 + 13.7134T$	This work
		$^2L^{Ionic\ Liquid}_{K^{+1}:Cl^{-1},ZnCl_2} = 6905.2 + 9.1568T$	This work
		$^2L^{Ionic\ Liquid}_{K^{+1},Na^{+1}:Cl^{-1},ZnCl_2} = 12000$	This work
Gas	(NaCl,Na$_2$Cl$_2$,KCl,K$_2$Cl$_2$, ZnCl$_2$,Zn$_2$Cl$_4$,NaZnCl$_3$, KZnCl$_3$)		
		$^0G^{Gas}_{NaCl} = -193113.5205 + 21.3477T - 0.0003681169T^2 - 37.3339T\ln T + 79277T^{-1}$	[10]
		$^0G^{Gas}_{KCl} = -193113.5205 + 21.1282T - 0.0003681169T^2 + 79277T^{-1} - 37.3339T\ln T$	[10]
		$^0G^{Gas}_{ZnCl_2} = -283396.4 + 139.40387T + 240807T^{-1} - 62.3201T\ln T$	[3]
		$^0G^{Gas}_{Zn_2Cl_4} = -727486.6273 + 534.1130681T - 133.0083T\ln T + 481617.0T^{-1}$	[3]
		$^0G^{Gas}_{KZnCl_3} = -663770.719 + 300.3493065T - 108.0752T\ln T + 291739.5T^{-1}$	This work (optimized [3])
		$^0G^{Gas}_{NaZnCl_3}$ $= -589148.7451 - 64.38T + 341.0447623T - 108.0769T\ln T + 347374.0T^{-1} - 955272.6667T^{-2}$	This work (optimized [3])
		$^0G^{Gas}_{Na_2Cl_2} = -26616.896 + 232.879T - 83.0656T\ln T + 191245.0T^{-1} - 0.0002153627T^2$	[10]
		$^0G^{Gas}_{K_2Cl_2} = -26077.14787 + 205.039T - 83.1229T\ln T + 100777.5T^{-1} - 0.000004437335T^2$	[10]

4.3. Gas phase

The gas phase is modeled by using an ideal solution of different gaseous species. The species, NaCl, Na$_2$Cl$_2$ KCl, K$_2$Cl$_2$ ZnCl$_2$, Zn$_2$Cl$_4$, NaZnCl$_3$, and KZnCl$_3$ are considered for the gas phase. Thermochemical data of all the gaseous species are taken from the literature [3,10].

5. Results and discussion

5.1. MD simulations of liquid phase

As a first step in this work, we carried out a brief structural analysis of the simulated systems. Towards this end, we present the pair distribution functions (PDFs) and coordination numbers of Na–Cl, Zn–Cl and Na–Zn pairs in the pure NaCl and ZnCl$_2$ liquids as well as a representative binary NaCl–ZnCl$_2$ melt (NaCl+40 mol%ZnCl$_2$), obtained at 1100 K, as shown in Fig. 1a and b. The choice of this temperature was to ensure that the temperature was greater than the melting points of NaCl and KCl in order to obtain pure liquid phases, while ensuring that the obtained ZnCl$_2$ and ZnCl$_2$-based liquids were still stable, despite the fact that this temperature was greater than the boiling point of ZnCl$_2$. This is demonstrated by the liquid-like PDFs of pure ZnCl$_2$ and NaCl+40 mol%ZnCl$_2$ liquids, which show a Zn–Cl peak at 2.7 Å.

Fig. 1b shows the Zn–Cl coordination number (n_{Zn-Cl}) as a function of distance for the ZnCl$_2$ and NaCl+40 mol% ZnCl$_2$ liquids; clearly, the coordination number of Zn in NaCl+40 mol% ZnCl$_2$ displays similar characteristics to Zn in pure ZnCl$_2$, with a demonstrable plateau between 4 and 5. In this context, it is worth
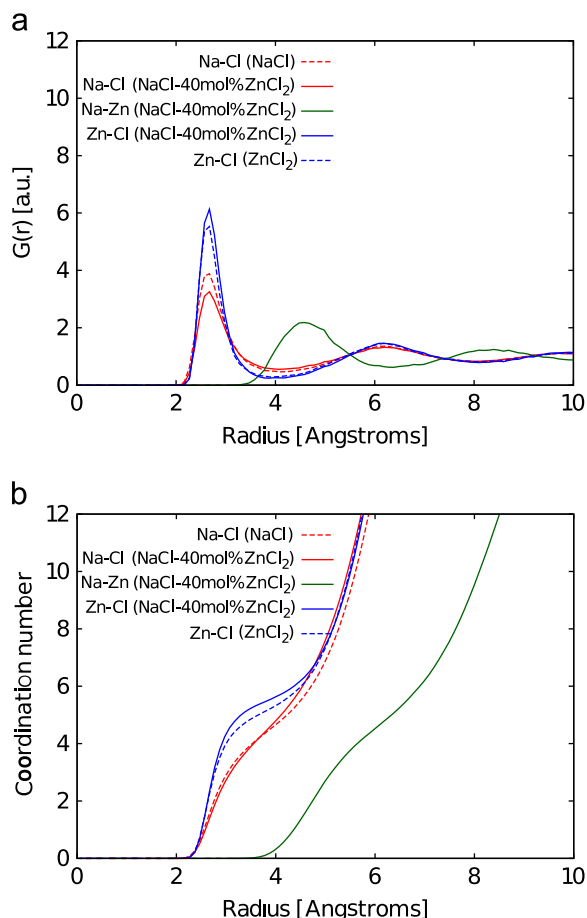
Fig. 1. MD simulated NaCl–ZnCl$_2$ liquids (a) the pair distribution functions (PDFs) and (b) the coordination numbers ($n_{ij}(r)$) of different cations.

Fig. 2. MD simulated KCl–ZnCl$_2$ liquids (a) the pair distribution functions (PDFs) and (b) the coordination numbers ($n_{ij}(r)$) of different cations.

pointing out that previous experimental and MD simulations have shown that Zn in ZnCl$_2$ liquids exhibits tetrahedral coordination (ZnCl$_4^{-2}$) in addition to 3-fold and 5-fold coordinations [33–35]. In this study, for the simulated ZnCl$_2$ liquid at 1100 K, we obtain 52% of the Zn ions to be coordinated tetrahedrally to neighboring Cl ions, while 36% of Zn ions are 5-fold coordinated; the rest of the Zn ions have coordinations that are either 2- and 3-fold. Here, we chose the minimum in the first cation–anion PDF peak as the cutoff distance to calculate coordination.

An examination of the variation in the coordination number (n_{Na-Cl}) as a function of distance (Fig. 1b) shows that variations in n_{Na-Cl} are much smoother for both NaCl and NaCl+40 mol% ZnCl$_2$. Specifically, n_{Na-Cl} shows a distribution between 2, 3- and 4-fold coordinations with the relative distributions equaling 19%, 47% and 29 % respectively. This analysis reveals that the distribution of Cl ions around Na is different from that of the Zn.

Fig. 2 shows the PDFs and coordination numbers of the KCl–ZnCl$_2$ liquids, which are similar to that of the NaCl–ZnCl$_2$ liquids. The n_{Zn-Cl} shows a distribution (between 4 and 5), in KCl+40 mol% ZnCl$_2$, similar to that of NaCl+40 mol% ZnCl$_2$. The K and Na ions in the KCl–ZnCl$_2$ and NaCl–ZnCl$_2$ liquids respectively, have identical coordination numbers ($n_{Na-Cl} \approx n_{K-Cl}$, and $n_{Na-Zn} \approx n_{K-Zn}$) and influence the structure of the liquid in the same fashion (comparing Figs. 2 and 1b). The structure of the liquid for the third binary, NaCl–KCl is also characterized and depicted in Fig. 3. The overlapping PDFs of Na–K, K–K and Na–Na (Fig. 3a) and the nearly same cation-anion ($n_{Na-Cl} \approx n_{K-Cl}$) and cation-cation ($n_{Na-Na} \approx n_{K-K} \approx n_{Na-K}$) coordination numbers (Fig. 3b) reveal that Na and K ions in the NaCl–KCl liquid are randomly mixed.
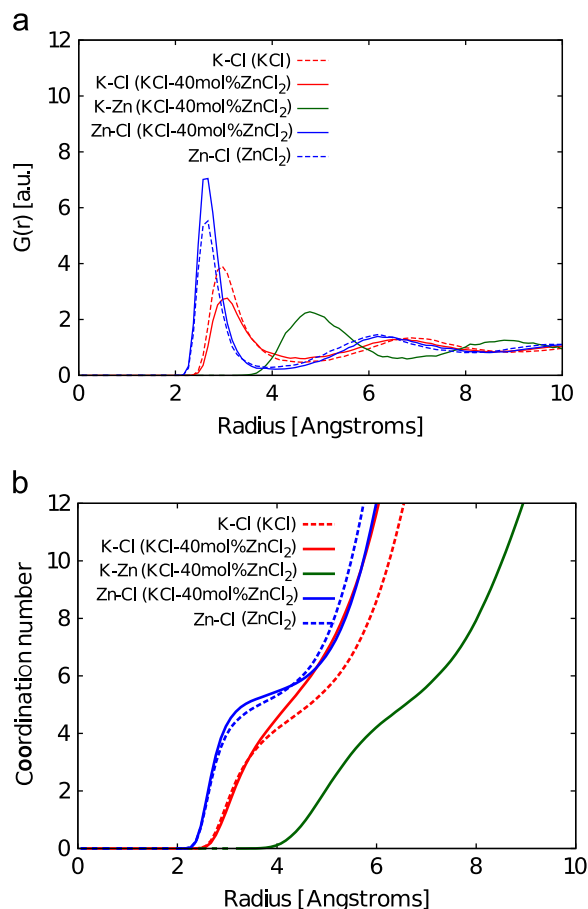
In summary, our structural analysis of the binary liquids on the NaCl–KCl–ZnCl$_2$ ternary revealed that

1. Cation–anion coordinations: the Na and K exhibit identical first neighbor coordinations which is different from the coordination of Zn.
2. Dissimilar cation–cation coordinations: Na and K have the same coordination numbers ($n_{Na-K}=n_{K-Na}$) with respect to each other and an analysis of structural configurations in this binary exhibit random mixing. However, the mixing of Na and Zn or K and Zn does not show similar random configuration (as in the case of Na and K mixing).

In view of the above structural information, we chose Na and K ions to be randomly mixed on the cation sublattice i.e., on the first sublattice, while approximating the presence of Zn in the form of a distinct structural unit: ZnCl$_2$, leading to the 2-sublattice ionic liquid model, (Na^{+1}, K^{+1})$_P$ (Cl^{-1}, ZnCl$_2$)$_Q$, for which the parameters are obtained from MD-predicted enthalpies of mixing of the binary and ternary liquids.

5.2. NaCl–ZnCl$_2$ binary

The optimization of the model parameters and the thermodynamic calculations are performed using the Thermocalc software [36]. Table 1 shows the optimized model parameters of the solid, liquid and gas phases. The MD predicted enthalpies of mixing of the liquid phase (shown in Fig. 4) along with the experimental activity (of ZnCl$_2$) and vapor pressure data are used for the evaluation of the model parameters pertaining to the
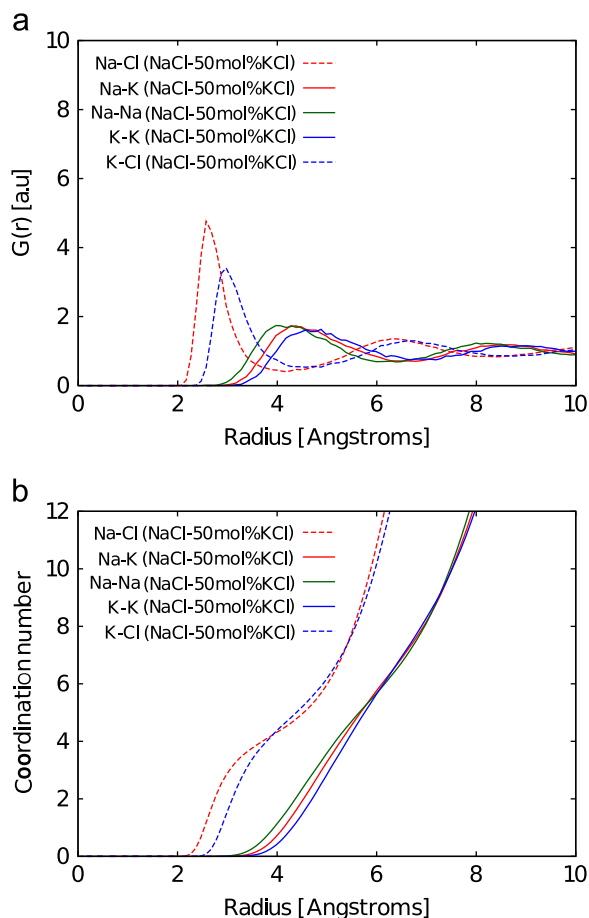
a

b

Fig. 3. MD simulated KCl–NaCl liquids (a) the pair distribution functions (PDFs) and (b) the coordination numbers ($n_{ij}(r)$) of different cations.
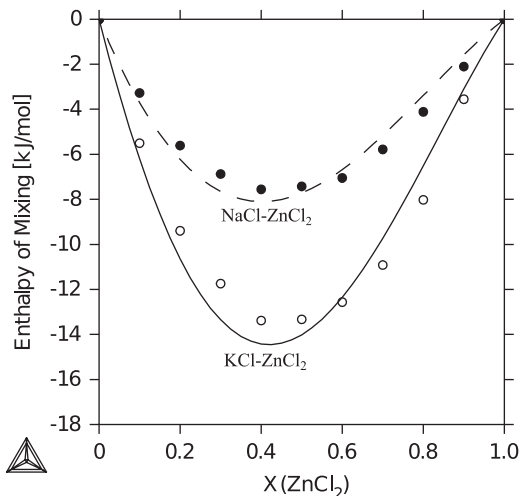

Fig. 4. Calculated enthalpies of mixing in the NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ liquids at 1100 K. The solid and the dashed curves are from CALPHAD and symbols are from the MD simulations. The solid circles and the open circles are for NaCl–ZnCl$_2$ and KCl–ZnCl$_2$, respectively. The estimated error bars on the MD-predicted enthalpies of mixing using the method of block averages [30] are smaller than 0.1 kJ/mol.

liquid. The enthalpies of mixing in the ionic-liquid model are allowed to change during the optimization and as shown in Fig. 4, the modeled enthalpy of mixing of the liquid shows good agreement with the MD data within ± 0.73 kJ/mol.

Robelin and Chartrand [3] estimated the enthalpies of mixing in the NaCl–ZnCl$_2$ liquid at 40 mol% ZnCl$_2$ from the linear regression of

the available experimental data pertaining to NaCl–MCl$_2$ (M – Ca, Mg, Sr, Mn, Fe, Co and Ni) melts at 1083 K, and used a value of −6.86 kJ/mol in their modeling. At 40 mol% ZnCl$_2$ the MD simulations in this work predicted an enthalpy of mixing of −7.6 ± 0.085 kJ/mol at 1100 K, while the Ionic-Liquid model in this work yields a value of −8.1 kJ/mol (Fig. 4). It is also interesting to note that the enthalpy of mixing in NaCl–ZnCl$_2$ shows a minimum at ∼40 mol% ZnCl$_2$ as exhibited by the other NaCl–MCl$_2$ melts [37,38] and as suggested by Robelin and Chartrand [3]. It is evident from this analysis that the BMH potentials of NaCl and ZnCl$_2$ we employed in our MD simulations predicted accurate mixing enthalpies in the liquid. The CALPHAD calculated vapor pressures of the liquid are shown in Fig. 5. Fig. 6 shows the calculated NaCl–ZnCl$_2$ binary phase diagram with the superimposed experimental data [17–19,24]. The calculated eutectic and peritectic points are in good agreement with the reported experimental data [17–19,24]. In the case of liquidus temperatures on the NaCl-rich region, this work shows a good agreement with the liquidus data reported by Shaw and Perry [18] and Nikonova et al. [24]. The calculated liquidus temperatures in the ZnCl$_2$-rich region, especially around the composition X(ZnCl$_2$)=0.55, however shows a significant deviation from the available experimental data [17–19,24].
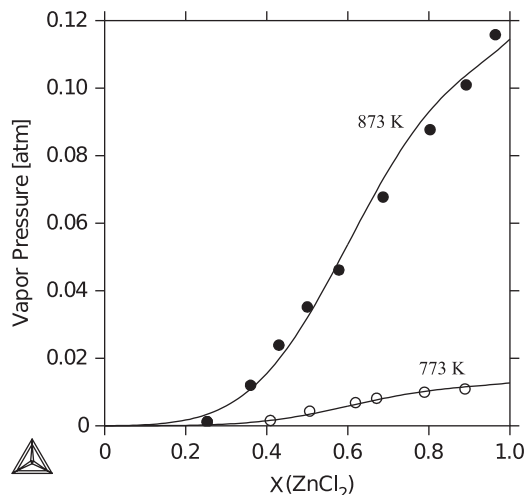

Fig. 5. Vapor pressures of the NaCl–ZnCl$_2$ liquid from the CALPHAD modeling in comparison to the experimental data (symbols) [25].
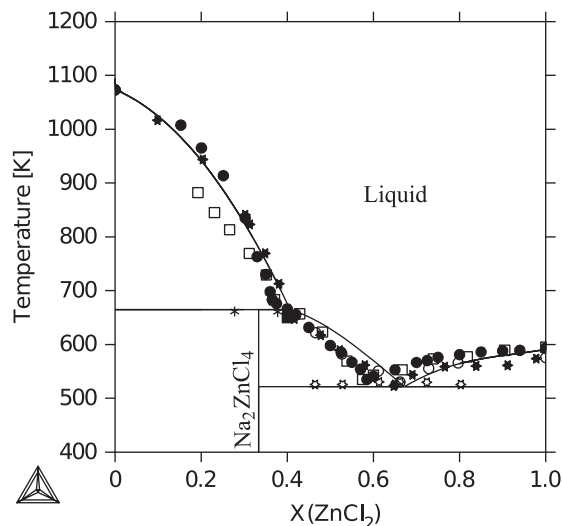

Fig. 6. Calculated NaCl–ZnCl$_2$ pseudo-binary phase diagram. The symbols are the experimental data ((□ – [19]) (○,✳,∗ – [17]) (● – [24]) (★,■ – [18])).

A similar disagreement was also observed in the calculated NaCl–ZnCl$_2$ reported by Robelin and Chartrand [3].

5.3. KCl–ZnCl$_2$ binary

Fig. 4 shows the enthalpies of mixing of the KCl–ZnCl$_2$ liquids from MD and the CALPHAD modeling in this work. The optimized enthalpies of mixing from the Ionic-Liquid model are in good agreement with the MD data within ± 1.39 kJ/mol. As in the case of NaCl–ZnCl$_2$ (this work) and as observed with the KCl–MCl$_2$ (M – Ca, Mg, Sr, Mn, Fe, Co and Ni) liquids [3], the mixing enthalpy of the liquid from MD shows a minimum at ~40 mol% ZnCl$_2$. The MD simulations at 40 mol% ZnCl$_2$ in this work predicted a value −13.48 ± 0.077 kJ/mol at 1100 K. The estimated enthalpy of mixing (−14.94 kJ/mol) by Robelin and Chartrand [3] from the linear regression of the available KCl–MCl$_2$ (M – Ca, Mg, Sr, Mn, Fe, Co and Ni) experimental data at 1083 K, is in slight variance with respect to our MD data.

The calculated vapor pressures of the KCl–ZnCl$_2$ liquids with the superimposed experimental data are shown in Fig. 7. The self-consistent set of model parameters, which shows a good agreement with the experimental data also validate the MD predictions in this work.

The calculated KCl–ZnCl$_2$ phase diagram along with the experimental data [13–16,24,39] is shown in Fig. 8. The invariant reactions are listed in Table 2. The calculated liquidus temperatures and the invariant reactions are in good agreement with the experimental phase diagram data [13–16,24,39]. On this binary, the compound KZn$_2$Cl$_5$ decomposes into K$_5$Zn$_4$Cl$_{13}$ and ZnCl$_2$ by a eutectoid reaction at 393 K, in agreement with Robelin and Chartrand [3], who also calculated its decomposition according to the eutectoid reaction but at 430 K.

5.4. KCl–NaCl–ZnCl$_2$ ternary

The CALPHAD and MD calculated mixing enthalpies in the ternary liquid along three sections (as shown on the composition triangle) are shown in Fig. 9. A ternary excess parameter (see Table 1) has been used for the liquid, and the predicted invariant reactions (Table 2) and the liquidus temperatures are in reasonable agreement with the experimental data [24].

Fig. 10 shows the calculated isothermal section of the NaCl–KCl–ZnCl$_2$ ternary phase diagram at 523 K. The isothermal section shows the single-phase liquid region (marked by number 8) and
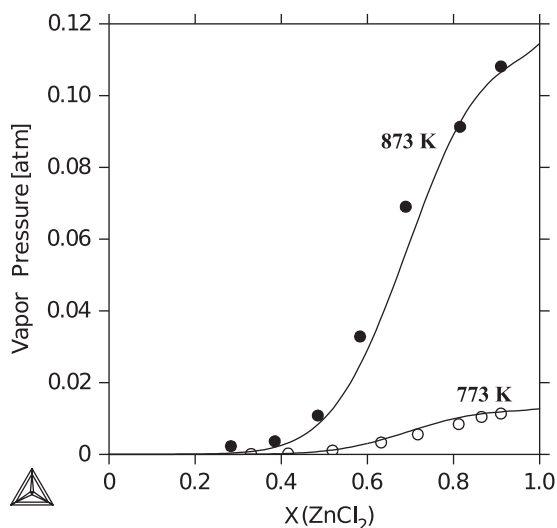

Fig. 8. Calculated KCl–ZnCl$_2$ pseudo-binary phase diagram. The symbols are the experimental data [] ((∘,●,□ – [13]) (◇ – [15]) (✳,△ – [16]) (∗ – [39]) (∇ – [24]).

Table 2
List of invariant reactions in the NaCl–KCl–ZnCl$_2$ ternary and its subsystems.

Invariant reaction	T (K)	X_{NaCl}	X_{KCl}	X_{ZnCl_2}
NaCl–ZnCl$_2$				
Liquid + NaCl = Na$_2$ZnCl$_4$	665	0.593	–	0.407
Liquid = ZnCl$_2$ + Na$_2$ZnCl$_4$	522	0.328	–	0.672
KCl–ZnCl$_2$				
Liquid = KCl + K$_2$ZnCl$_4$	701	–	0.696	0.304
Liquid + K$_2$ZnCl$_4$ = K$_5$Zn$_4$Cl$_{13}$	528	–	0.514	0.486
Liquid = KZn$_2$Cl$_5$ + K$_5$Zn$_4$Cl$_{13}$	493	–	0.432	0.568
Liquid = KZn$_2$Cl$_5$ + ZnCl$_2$	528	–	0.261	0.739
NaCl–KCl–ZnCl$_2$				
Liquid = Na$_2$ZnCl$_4$ + K$_5$Zn$_4$Cl$_{13}$ + KZn$_2$Cl$_5$	486	0.070	0.376	0.554
Liquid = Na$_2$ZnCl$_4$ + KZn$_2$Cl$_5$ + ZnCl$_2$	475	0.216	0.147	0.637
Liquid + K$_2$ZnCl$_4$ = Na$_2$ZnCl$_4$ + K$_5$Zn$_4$Cl$_{13}$	520	0.130	0.425	0.445
Liquid + SS_NaCl–KCl = Na$_2$ZnCl$_4$ + K$_2$ZnCl$_4$	527	0.160	0.407	0.433
Liquid + SS_NaCl–KCl = SS_NaCl–KCl + K$_2$ZnCl$_4$	661	0.129	0.582	0.289

Fig. 7. Vapor pressures of the KCl–ZnCl$_2$ liquid from the CALPHAD modeling. The symbols are the experimental data [25].

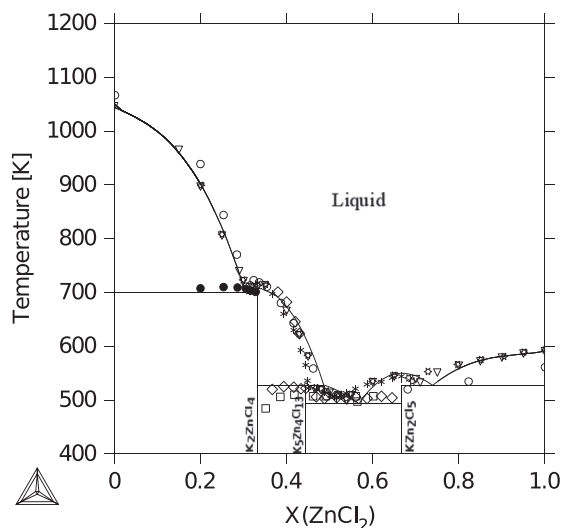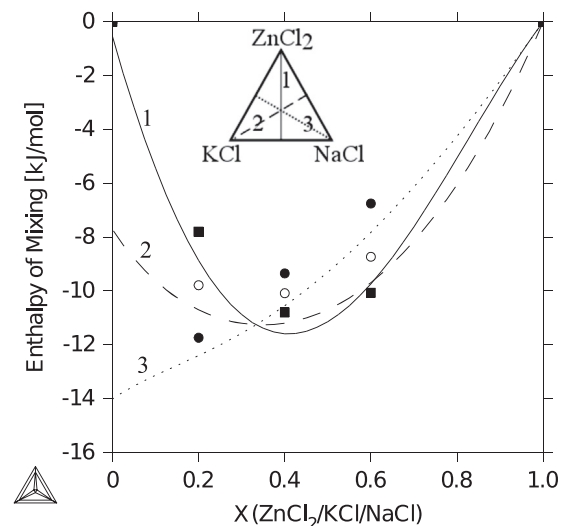**Fig. 9.** Calculated enthalpies of mixing in the NaCl–KCl–ZnCl2 ternary liquid at 1100 K. The lines are from CALPHAD and the symbols are from MD simulations. ■ – belong to line 1, ∘ – belong to line 2 and, ● – belong to line 3. The estimated error bars on the MD-predicted enthalpies of mixing using the method of block averages [30] are smaller than 0.1 kJ/mol.
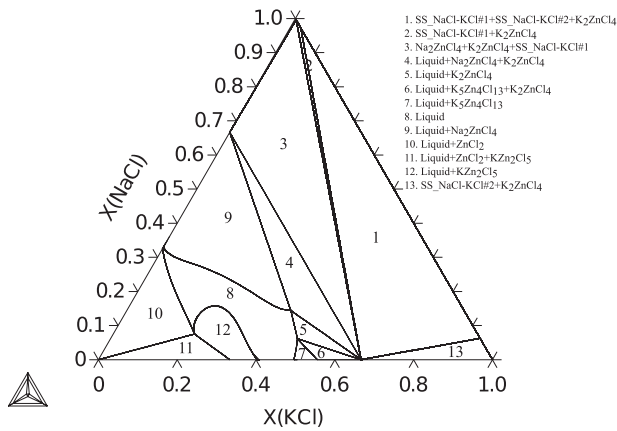
Fig. 10. Calculated isothermal section of the NaCl–KCl–ZnCl$_2$ ternary phase diagram at 523 K. The region 8 shows the single-phase liquid at 523 K. This ternary systems offers the molten salt solutions that can function as heat transfer fluids in concentrating solar power plants between 523 and 1073 K.
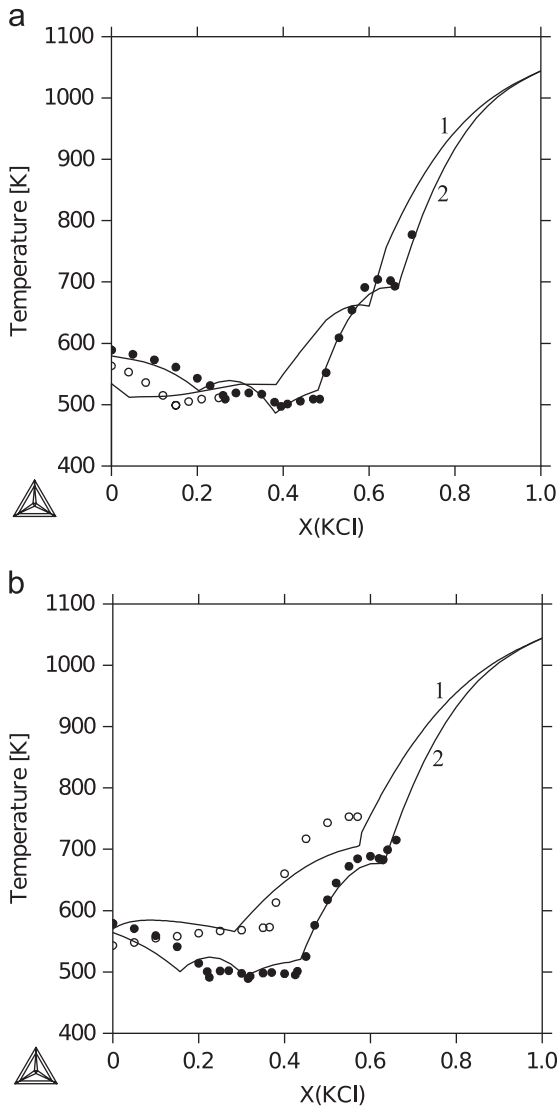

Fig. 11. Calculated liquidus curves along different sections of the NaCl–KCl–ZnCl$_2$ ternary (a) 1: (30 mol% NaCl + 70 mol% ZnCl$_2$) – KCl, 2: (10 mol% NaCl + 90 mol% ZnCl$_2$) – KCl (b) 1: (40 mol% NaCl + 60 mol% ZnCl$_2$) – KCl, 2: (20 mol% NaCl + 80 mol% ZnCl$_2$) – KCl. The symbols are the experimental data [24].
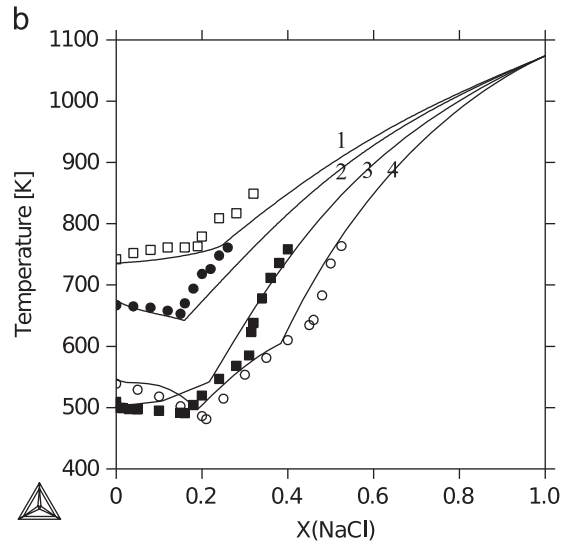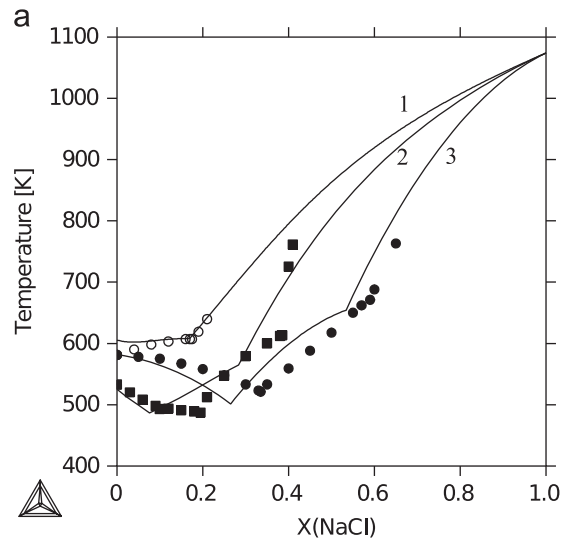

Fig. 12. Calculated liquidus curves along different sections of the NaCl–KCl–ZnCl$_2$ ternary (a) 1: (55 mol% KCl + 45 mol% ZnCl$_2$) – NaCl, 2: (40 mol% KCl + 60 mol% ZnCl$_2$) – NaCl, 3: (10 mol% KCl + 90 mol% ZnCl$_2$) – NaCl (b) 1: (71 mol% KCl + 29 mol% ZnCl$_2$) – NaCl, 2: (60 mol% KCl + 40 mol% ZnCl$_2$) – NaCl, 3: (45 mol% KCl + 55 mol% ZnCl$_2$) – NaCl, 4: (30 mol% KCl + 70 mol% ZnCl$_2$) – NaCl. The symbols are the experimental data [24].
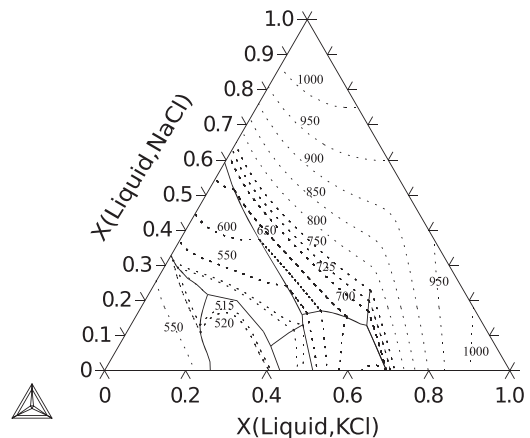

Fig. 13. Calculated liquidus projection of NaCl–KCl–ZnCl$_2$ ternary (the indicated temperatures are in kelvin).

offers the molten salt compositions which can be used as heat transfer fluids in CSPs at $250\,°C \leq T \leq \sim 800\,°C$. The vapor pressures (not shown in the figure) calculated using the developed thermodynamic database show the high temperature stability of the molten salt compositions of interest. The only available experimental data for the ternary liquidus temperatures is reported by Nikonova et al. [24]. The calculated liquidus curves along different sections of the ternary phase diagram are compared with Ref. [24] data in Figs. 11 and 12. In view of the deviations of the liquidus data reported in Ref. [24] as compared to other experiments examining the NaCl–ZnCl$_2$ and KCl–ZnCl$_2$ binaries, the calculated liquidus temperatures on the ternary in this work, depict a reasonable agreement with Ref. [24]. Fig. 13 shows the calculated liquidus projection of the NaCl–KCl–ZnCl$_2$ ternary system.

6. Summary

Thermodynamic modeling of the NaCl–KCl–ZnCl$_2$ system is performed by combining MD simulations and CALPHAD approach. MD simulations predicted the enthalpies of mixing in the liquid phase on the entire NaCl–KCl–ZnCl$_2$ system, addressing the lack of the experimentally measured data. The liquid phase is described by employing a two-sublattice Ionic-Liquid model and MD data is used to assess the thermodynamics of the molten salts. The calculated phase diagrams of the ternary and binary subsystems are in good agreement with the experimental data.

The calculated NaCl–KCl–ZnCl$_2$ ternary revealed compositions which are liquids in the temperature range of 250–800 °C and offers potential heat transfer fluids for CSPs. A further lowering of the liquidus temperatures (to $< 200\,°C$) while retaining or increasing the high temperature stability may be achieved by adding quaternary additives to this ternary.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.calphad.2014.04.004.

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