

Models for the thermodynamic properties of molten salt systems: Perspectives for ionic liquids



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ABSTRACT

Over the past several years, the Modified Quasichemical Model for short-range ordering has been used successfully to obtain a quantitative thermodynamic description of various multicomponent high temperature inorganic molten salt systems. In the present paper, it was applied to the $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ ternary system and the $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ binary system (where $[\text{C}_2\text{mim}]\text{Cl}$ refers to 1-ethyl-3-methyl-imidazolium chloride), which both involve some ionic liquid compounds. Those two systems were selected as prototypes since experimental data were available for them in the literature. The $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ liquid displays relatively little short-range ordering, and the experimental ternary eutectic at $T = 309 \text{ K}$ or 312 K was satisfactorily reproduced by using solely the optimized binary parameters along with a standard symmetric interpolation method. The $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ liquid displays strong negative deviations from ideality, and two different compositions of maximum short-range ordering (near the $[\text{C}_2\text{mim}]\text{AlCl}_4$ and $[\text{C}_2\text{mim}]\text{Al}_2\text{Cl}_7$ compositions) were introduced. All available experimental data (phase diagram, *emf* measurements, partial enthalpies of mixing) were satisfactorily reproduced by the model. The Volume-based Thermodynamics (VBT) from Glasser and Jenkins was used to assess the missing thermodynamic data for $[\text{C}_2\text{mim}]\text{Cl}$, and it was also tested on several ionic liquid compounds of the methyl-imidazolium type.

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1. Introduction

Over the past several years, we have developed thermodynamic databases for multicomponent high temperature inorganic molten salt systems such as $(\text{LiCl} + \text{NaCl} + \text{KCl} + \text{MgCl}_2 + \text{CaCl}_2 + \text{MnCl}_2 + \text{FeCl}_2 + \text{FeCl}_3 + \text{CoCl}_2 + \text{NiCl}_2 + \text{AlCl}_3)$ [1–5] and $(\text{NaF} + \text{AlF}_3 + \text{CaF}_2 + \text{Al}_2\text{O}_3)$ [6], using the Modified Quasichemical Model in the quadruplet approximation [7] which takes into account simultaneously first-nearest-neighbour (cation-anion) and second-nearest-neighbour (cation–cation and anion–anion) short-range ordering. All thermodynamic data (enthalpy of mixing, *emf* measurements, etc.) and phase equilibrium data available in the literature for the binary and ternary subsystems are collected and critically evaluated, and model parameters are obtained through an optimization of the selected data. These assessed binary and ternary parameters combined with standard interpolation methods permit an estimation of the thermodynamic properties (including phase equilibria) of multicomponent salt systems. These

calculations are important for the understanding and control of the corresponding industrial processes.

It is proposed to apply the Modified Quasichemical Model to common-ion (*i.e.* common-cation or common-anion) ionic liquid ternary mixtures. Ionic liquids are usually composed of a large organic cation and a small inorganic anion, and they melt at relatively low temperatures (below $T = 373.15 \text{ K}$, and often below room temperature). They have a very low volatility and are involved in numerous potential applications (solvents and catalysts [8], electrochemistry [9], materials science [10], etc.). Since 2000 [11] the research on ionic liquids has grown dramatically and it has focused on the design of single compounds with “tailor-made” properties. As suggested by Plechkova and Seddon [11], ionic liquid ternary mixtures may be considered, where the first component would control and define the chemistry of the system, the second component would allow fine tuning of the physical properties (such as density and viscosity) of the system, and the third component would be cheap and inert, thus lowering the global cost of the system through a dilution of the other two components. Ionic liquid mixtures have been studied relatively little, and most of the existing studies correspond to binary

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mixtures [12]. Clearly, modelling the phase diagram of ionic liquid systems is of interest only if the pure compounds have melting temperatures significantly above room temperature. Common-ion ionic liquid ternary mixtures may have a liquidus temperature substantially lower than the melting temperatures of the three pure compounds. For instance, the CH_3COOLi , CH_3COOK and CH_3COOCs pure compounds have relatively high melting temperatures (between 463 K and 579 K) and in principle they should not be regarded as ionic liquids. The corresponding ternary system is predicted to exhibit a ternary eutectic at $T = 368$ K [13]. Our current liquid model [7,14,15], which assumes the distribution of cations and anions on two different sublattices (where each ion occupies one site on the corresponding sublattice), may have to be modified since the cations (and sometimes also the anions) in ionic liquid systems are large. Moreover, specific short-range interactions such as hydrogen bonding, van der Waals and π - π stacking interactions are not being considered yet. A preliminary literature search was conducted in 2012, and very few thermodynamic data (such as phase diagrams) were available for ionic liquid systems at that time. More recently, the phase diagrams of some common-ion binary ionic liquid systems were measured: $([\text{C}_4\text{mim}]\text{Cl} + [\text{C}_2\text{mim}]\text{Cl})$ [16,17], $([\text{C}_2\text{mim}]\text{PF}_6 + [\text{C}_2\text{mim}]\text{NO}_3)$ [17], $([\text{C}_2\text{mim}]\text{PF}_6 + [\text{C}_2\text{mim}]\text{Cl})$ [17], and nine common-anion binary systems with PF_6^- as the common anion [18] (where $[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$ refer to the 1-ethyl-3-methyl-imidazolium and 1-butyl-3-methyl-imidazolium cations, respectively).

In the present article, some results, based on the experimental data available in the literature in 2012, are presented for the phase diagrams of the $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ ternary system and its three binary subsystems (where $\text{N}(\text{FSO}_2)_2$ is the bis(fluorosulfonyl)amide anion), and for the thermodynamic properties (phase diagram, *emf* measurements, partial enthalpies of mixing) of the $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ binary system, which exhibits strong negative deviations from ideality (due to short-range ordering in the liquid phase). The $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ ternary system is discussed in Section 3. The three $\text{AN}(\text{FSO}_2)_2$ compounds (with $A = \text{Li}, \text{K}, \text{Cs}$) are not organic since they do not contain any carbon. However, they have low melting temperatures (between 375 and 403 K, according to [19]) and exhibit a ternary eutectic at about $T = 309$ K [20] or 312 K [21]. The three binary subsystems are simple eutectic systems, and it will be shown that the characteristics of the experimental ternary eutectic are very satisfactorily reproduced by using solely the optimized binary model parameters along with a symmetric interpolation method (Section 3). The $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ binary system, which involves an inorganic compound (AlCl_3) and a “common” ionic liquid ($[\text{C}_2\text{mim}]\text{Cl}$), is presented in Section 5. By analogy with the $(\text{NaCl} + \text{AlCl}_3)$ and $(\text{KCl} + \text{AlCl}_3)$ liquids which were previously modelled using the Modified Quasichemical Model in the pair approximation [4], two different compositions of maximum short-range ordering (near the $[\text{C}_2\text{mim}]\text{AlCl}_4$ and $[\text{C}_2\text{mim}]\text{Al}_2\text{Cl}_7$ compositions) were introduced for the $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ binary liquid. Satisfactory results are obtained for the latter binary system, but it will be shown that the current thermodynamic model would fail to reproduce the experimental [22] $\{[\text{C}_2\text{mim}]\text{AlCl}_4 + \text{NaAlCl}_4\}$ section of the $(\text{NaCl} + [\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ phase diagram due to the large size difference between the inorganic Al^{3+} and organic $[\text{C}_2\text{mim}]^+$ cations (Section 5).

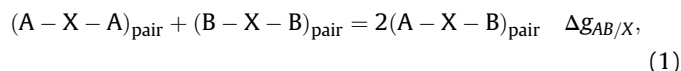
Although comprehensive compilation tables such as JANAF [23] and Barin [24] exist for the thermodynamic properties ($\Delta H_{298.15\text{K}}^\circ$, $S_{298.15\text{K}}^\circ$ and $C_p(T)$) of pure inorganic compounds, no such compilation tables exist currently for ionic liquid compounds. Therefore, methods of estimation such as the Volume-based Thermodynamics (VBT) from Glasser and Jenkins [25–31] need to be used in order to assess the missing thermodynamic

data for the pure ionic liquid compounds. The VBT and its applicability to ionic liquids of the methyl-imidazolium type are discussed in Section 4.

The present article is concerned with the thermodynamic evaluation and optimization of the $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ ternary system and of the $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ binary system, which both involve some ionic liquid compounds. Those two systems were selected as prototypes since experimental data were available for them in the literature. The experimental study of some common-ion ionic liquid systems was initiated recently. Measurements of the phase diagrams of some common-cation ionic liquid systems are under way.

2. Thermodynamic model for the liquid phase

The liquid solution was modelled using the Modified Quasichemical Model [14,15] which takes into account short-range ordering between nearest-neighbours on a lattice or sublattice. The $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ and $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ systems are both common-anion systems and, therefore, the pair approximation is sufficient. Short-range ordering is treated by considering the relative numbers of second-nearest-neighbour cation–cation pairs. The parameters of the model are the Gibbs free energy changes $\Delta g_{AB/X}$ for the following pair exchange reactions:



where A and B are two different cations, and X is the common anion. As $\Delta g_{AB/X}$ becomes progressively more negative, reaction (1) is shifted to the right, (A-X-B) pairs predominate, and the solution becomes progressively more ordered. In Refs. [14,15], the model was developed in terms of nearest-neighbour pairs (A-B) for species mixing on one lattice. In the present case, since the anionic sublattice is occupied only by one type of anions, the model can be used directly to treat cation–cation pairs on the cationic sublattice. The parameter $\Delta g_{AB/X}$ is the parameter Δg_{AB} (or Δg_{mn}) of [14] (or [15]). When $\Delta g_{AB/X}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of cations on the cationic sublattice. This is the case for the three binary subsystems of the $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ system. On the other hand, the $([\text{C}_2\text{mim}]\text{Cl} + \text{AlCl}_3)$ liquid exhibits extensive short-range ordering. As explained in Section 5, the *emf* measurements of Hussey et al. [32] show the existence of two different compositions of maximum short-range ordering (near the $[\text{C}_2\text{mim}]\text{AlCl}_4$ and $[\text{C}_2\text{mim}]\text{Al}_2\text{Cl}_7$ compositions). The Modified Quasichemical Model was used in the present work since it is suitable for liquids exhibiting either small or extensive short-range ordering, and also for liquids displaying positive deviations from ideality. For simple liquids such as the $(\text{LiN}(\text{FSO}_2)_2 + \text{KN}(\text{FSO}_2)_2 + \text{CsN}(\text{FSO}_2)_2)$ system, the Bragg-Williams (random-mixing) model may also be used. This model is described in detail in Ref. [33]. For a common-ion binary liquid such as $\{\text{AN}(\text{FSO}_2)_2 + \text{BN}(\text{FSO}_2)_2\}$ (where A, B = Li, K, Cs), cations A and B are assumed to be distributed randomly over the sites of the cationic sublattice, and the molar configurational entropy of mixing and enthalpy of mixing are given by:

$$\Delta S^{\text{config}} = -R(x_A \ln(x_A) + x_B \ln(x_B)) \quad (2)$$

$$\Delta h = x_A x_B \omega_{BW} \quad (3)$$

where x_A and x_B are the mole fractions of cations A and B on the

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