

Computational Analysis of Rehydration During the Solid-to-Liquid Transition in Molten Salts

Hyeonwoo Kim^a, Sangtae Kim^{a*}

^aDepartment of Nuclear Engineering, Hanyang University, Seoul 04763

*Corresponding author: sangtae@hanyang.ac.kr

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1. Introduction

Residual water in molten chlorides is a critical initiator of corrosion because its thermal dissociation yields highly aggressive species that attack structural materials. Industrial practice mitigates this by annealing salts slightly below their melting points, with effective dehydration verified by Karl–Fischer titration. Nevertheless, we observe apparent “rehydration” upon melting, raising the unresolved question of whether this signal reflects artifact or intrinsic thermodynamics. Here, we address this gap by combining targeted experiments with atomistic simulations to quantify the mixing enthalpy of trace water in both solid and liquid chlorides. We then translate these calculations into a rehydration-propensity metric, $\Delta H_{\text{rehyd}} = \Delta H_{\text{mix}}^{\text{liquid}} - \Delta H_{\text{mix}}^{\text{solid}}$, whose sign and magnitude predict the preference of rehydration across salts, providing a theoretical basis for experimentally observed trends.

2. Methods and Results

This section outlines the computational workflow used to quantify the thermodynamic drivers of salt rehydration across the solid–liquid transition and summarizes the key outcomes.

2.1 Simulation Framework

All atomistic calculations employed Matlantis [1], a machine-learning interatomic potential trained across diverse chemistries and phases, for minimization and molecular dynamics (MD). Energy minimizations used BFGS until the maximum residual force fell below 0.01 eV/Å. For MD simulations, NPT calculations were performed for sufficient time to ensure the convergence of both volume and energy. The MD simulations used a 1 fs timestep with Nosé–Hoover thermostating, and all subsequent analysis was based on data collected after this convergence was achieved.

2.2 Solid-Salt Model

This study focuses on the intrinsic thermodynamic properties of ideal bulk and surface structures. The influence of microstructural features such as grain

boundaries or pores, while important for overall kinetics, is considered beyond the scope of this initial thermodynamic analysis. For monovalent chlorides (KCl, NaCl, LiCl), we built anhydrous slab models (rocksalt, representative low-index surfaces) and randomly adsorbed trace H₂O on surface sites to emulate uptake in the absence of definitive bulk hydrate phases (Fig. 1a). For divalent salts, hydration was modeled using well-established crystalline hydrates as initial structures — Mg(ClO₃)₂·6H₂O, CaCl₂·6H₂O, and Zn₂Cl₄·9H₂O — to capture bulk water incorporation. All configurations were then energy-minimized and the resulting energies were compared to compute per-molecule hydration mixing enthalpies in solid-state.

2.3 Liquid-Salt Model

Liquid systems were prepared by randomly placing salt ions and H₂O molecules within a periodic box at experimental densities before subsequent equilibration (Fig 1b). We then ran NPT MD at T=T_m+50K to obtain equilibrated densities/volumes. All subsequent timesteps after both energy and volume had converged were individually energy-minimized to remove thermal noise. The liquid-state energy for thermodynamic comparisons was taken as the average of these minimized potential energies.

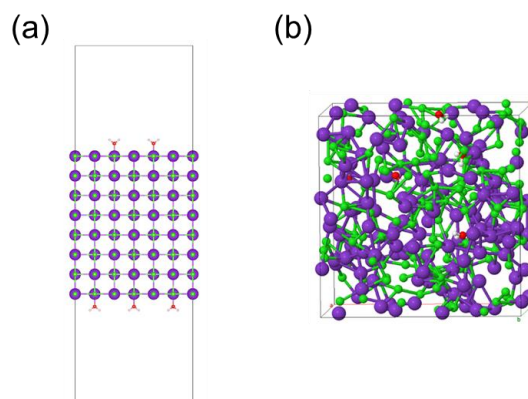


Fig. 1. Representative atomistic models used in this work. (a) Solid model: a rocksalt slab with trace H₂O molecules adsorbed on the surface. (b) Liquid model: formed by randomly mixing salt ions and H₂O

2.4 Hydration enthalpy and rehydration metric

The mixing enthalpy of hydration per water molecule was computed as

$$\Delta H_{\text{mix}} = \frac{1}{n} [E(\text{salt} + n\text{H}_2\text{O}) - E(\text{Salt}) - nE(\text{H}_2\text{O})]$$

where n is the number of water molecules and all E are minimized potential energies. We then defined a rehydration-propensity metric

$$\Delta H_{\text{rehyd}} = \Delta H_{\text{mix}}^{\text{liquid}} - \Delta H_{\text{mix}}^{\text{solid}}.$$

A negative ΔH_{rehyd} indicates that hydration is thermodynamically more favorable in the liquid than in the solid, consistent with rehydration upon melting. While Gibbs free energy, which includes entropy, determines the ultimate spontaneity, this study focuses on enthalpy. This is because the primary factor differentiating the salts' behavior is the large enthalpic change associated with structural differences which dominates the overall thermodynamic trend."

2.5 Results

Calculated ΔH_{rehyd} indicates negative values for KCl, NaCl, LiCl, MgCl₂ and CaCl₂, indicating more exothermic hydration in the liquid and thus a propensity for rehydration upon melting. ZnCl₂ is the sole exception, giving slightly positive ΔH_{rehyd} , consistent with no rehydration (Fig. 2). These computational predictions are in excellent agreement with our experimental findings from Karl-Fischer titration, confirming that the rehydration phenomenon is not an artifact but a composition-dependent thermodynamic preference. A detailed report on these experimental results will be presented separately by our collaborators.

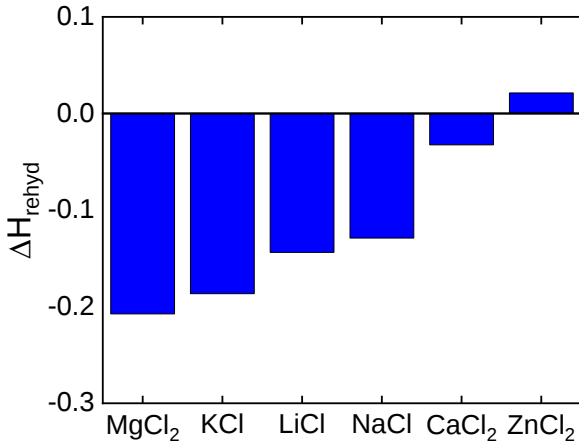


Fig. 2. Calculated rehydration enthalpy ΔH_{rehyd} for each salt

To understand the origin of this distinct behavior, we analyzed the local structure of the molten salts (Fig. 3). The cation–Cl radial distribution function (RDF) for ZnCl₂ exhibits a significantly sharper and more intense first peak than those for MgCl₂ and CaCl₂. This feature, along with a Zn–Cl integrated coordination number of 4, indicates a well-defined tetrahedral coordination. This

continuous network of corner-sharing tetrahedra is visually represented in Fig. 4. These findings confirm that molten ZnCl₂ is not a simple ionic liquid but a “network-forming” liquid, characterized by a robust, polymeric network of corner-sharing tetrahedra in good agreement with previous experimental and computational reports [2, 3]. We therefore hypothesize that accommodating water requires breaking the strong Zn–Cl–Zn bridges of this network. The significant enthalpic penalty associated with this bridge-breaking offsets the stabilization gained from hydration, resulting in the observed positive ΔH_{rehyd} .

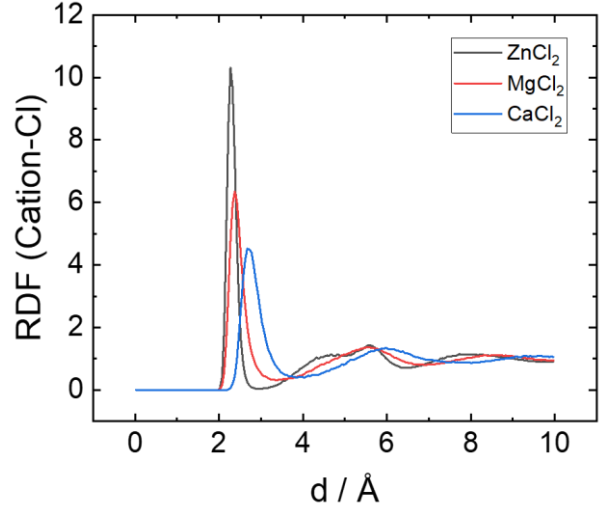


Fig. 3. Cation–Cl radial distribution function (RDF) for molten ZnCl₂, MgCl₂, and CaCl₂.

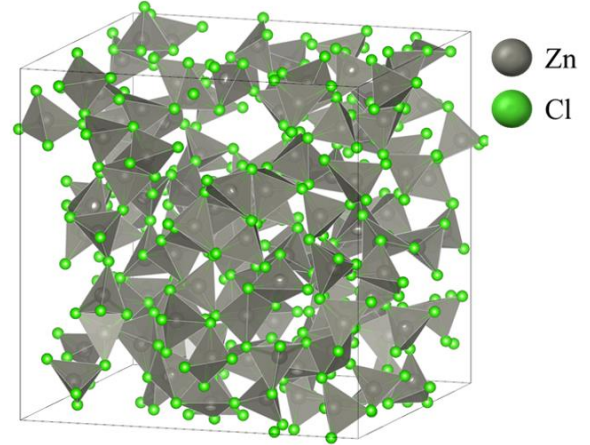


Fig. 4. Snapshot of the local structure of molten ZnCl₂. The gray polyhedra represent ZnCl₄ tetrahedra, with gray spheres at their centers representing Zn atoms and green spheres at the vertices representing Cl atoms.

3. Conclusions

We combined experiments with atomistic simulations to test whether apparent post-melting “rehydration” of chlorides is an artifact or an intrinsic thermodynamic effect. Our calculations, in excellent agreement with experimental trends, predict rehydration for most

chlorides (KCl, NaCl, LiCl, MgCl₂, CaCl₂) but not for ZnCl₂. Crucially, our structural analysis reveals that the exceptional behavior of ZnCl₂ stems from its robust, polymeric network of bridged tetrahedra, which imposes a significant enthalpic penalty on water incorporation. These results establish that rehydration is a thermodynamically driven and composition-dependent phenomenon, not a measurement artifact. The proposed metric provides a practical screen to guide salt selection and minimize corrosion consequences. Future work should build on these findings by considering the effects of microstructural defects, entropic contributions, and kinetic factors.

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