Molecular Dynamics of Choline Chloride: Phase Behavior, Structural Evolution, and Transition Mechanisms in Deep Eutectic Solvents

Inderdip Shere[ab], Magali Duvail[ac], Jean-François Dufrêche[ad]

[a] Institut de Chimie Séparative de Marcoule (ICSM), [b] Centre national de la recherche scientifique (CNRS), [c] Commissariat à l'énergie atomique et aux énergies alternatives (CEA), [b] University of Montpellier (UM)

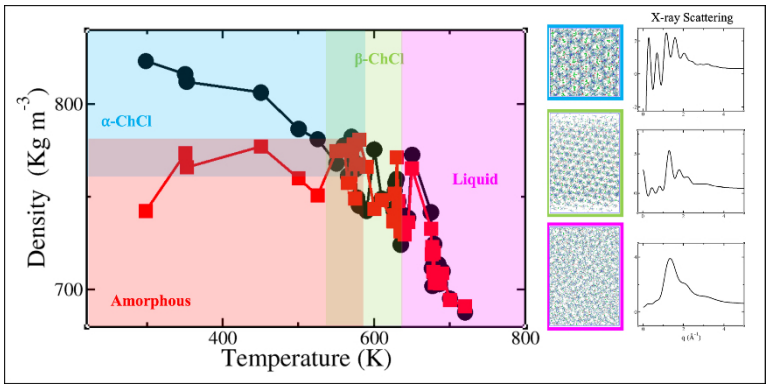
inderdip.shere@cea.fr

Deep eutectic solvents (DES) represent a new class of complex ionic fluids with tunable properties and emerging applications in separative chemistry and biomaterials.[1] Choline chloride (ChCl) - a key component in DES formulations including ethaline (ChCl + ethylene glycol) and reline (ChCl + urea), serves as an ideal model system for understanding the fundamental dynamics and phase behavior of DES.[2] While binary ChCl mixtures are technologically important, the difficulty in precisely locating their eutectic points indicates they are not true eutectics in the thermodynamic sense, yet this distinction has minimal practical consequence. Understanding ChCl's intrinsic molecular-level thermodynamics is essential for rational design of DES with optimized phase stability and transport properties for industrial separative applications.

Using comprehensive molecular dynamics simulations with optimized force fields,[3] we characterize ChCl's complete phase diagram across three interconnected investigations. **1-Structural Characterization:** We establish baseline metrics for amorphous and crystalline α-ChCl including density, density fluctuations, octahedral order parameters (Q_4, Q_6), radial distribution functions, coordination numbers, hydrogen bonding network topology, rotational dynamics, survival probabilities, and complementary SAXS/structure factor analysis. **2-Temperature-Dependent Thermodynamics:** Coexistence simulations reveal spontaneous formation of a previously uncharacterized metastable β-phase and subsequent melting, with extraction of temperature-dependent density, heat capacity, and transition enthalpies. All metrics are recomputed for β-phase and liquid states. **3-Phase Transition Mechanisms:** Real-time trajectory analysis, hydrogen bonding network evolution, and molecular mechanism investigation elucidate the three observed transitions: amorphous↔α (crystallization), α↔β (solid-state transformation), and β↔liquid (melting).

Key Findings: The β-phase exhibits intermediate structural order between crystalline and amorphous states, with anomalously high local density fluctuations explaining its metastability. Transition mechanisms reveal distinct pathways: nucleation-and-growth kinetics for crystallization, geometric reorganization and H-bond network restructuring for α↔β transformation, and diffusion-driven disordering for melting. These results establish ChCl's complete phase diagram at atomic resolution, reconcile computational-experimental discrepancies, and provide molecular design principles for engineering DES with optimized thermal stability, and transport properties for separative chemistry applications.

Keywords:
DES, ChCl, Phase transition



ChCl Phase Diagram and X-ray Diffraction Analysis. Density evolution across four phases (amorphous, α-crystalline, β-phase, liquid) validated by XRD patterns showing sharp Bragg peaks (crystalline), intermediate diffraction (β-phase), and diffuse scattering (liquid).

References:

[1] Smith, E. L.; Abbott, A. P.; Ryder, K. S. *Chem. Rev.* **2014** , *114* , 11060–11082.
[2] Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun.* **2003** , *1* , 70–71.
[3] Doherty, B.; Acevedo, O. *J. Phys. Chem. B.* **2018** , *122* , 9982–9993