Supplementary Information
Isocompositional Liquid-Liquid Transition in Dilute Aqueous LiCl Solutions

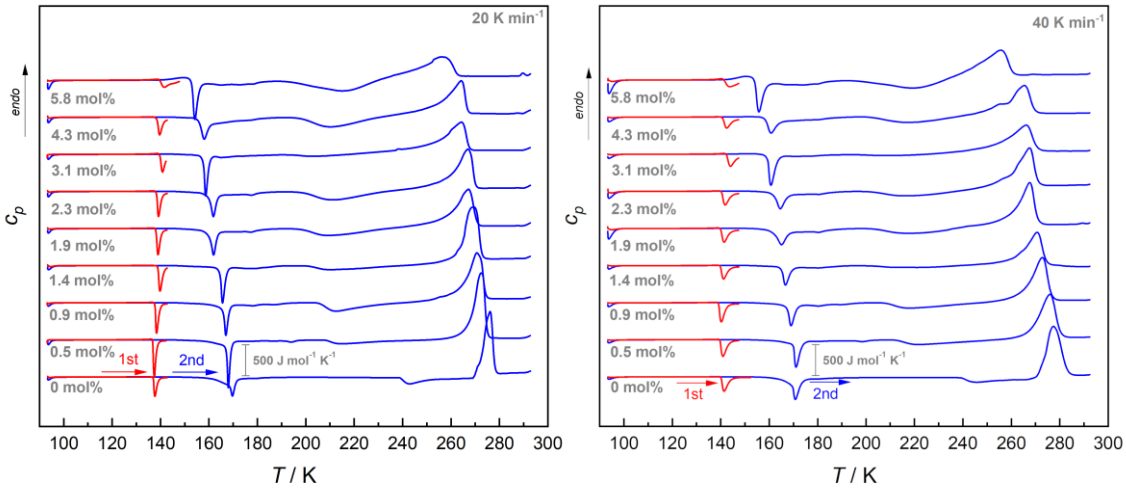
Johannes Giebelmann, Johannes Bachler, Thomas Loerting*

Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria

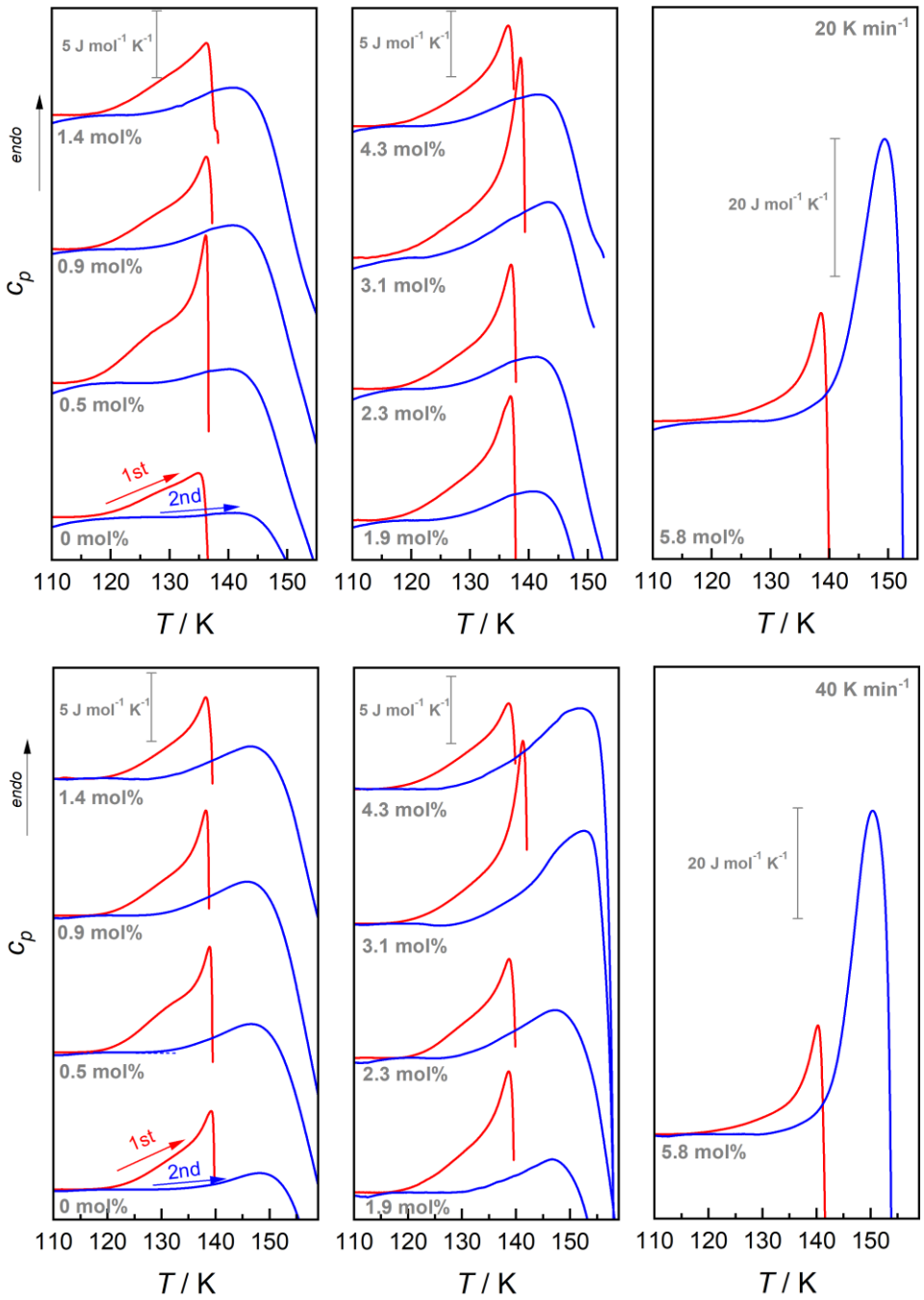
*Author to whom correspondence should be addressed: thomas.loerting@uibk.ac.at

Supplementary Information

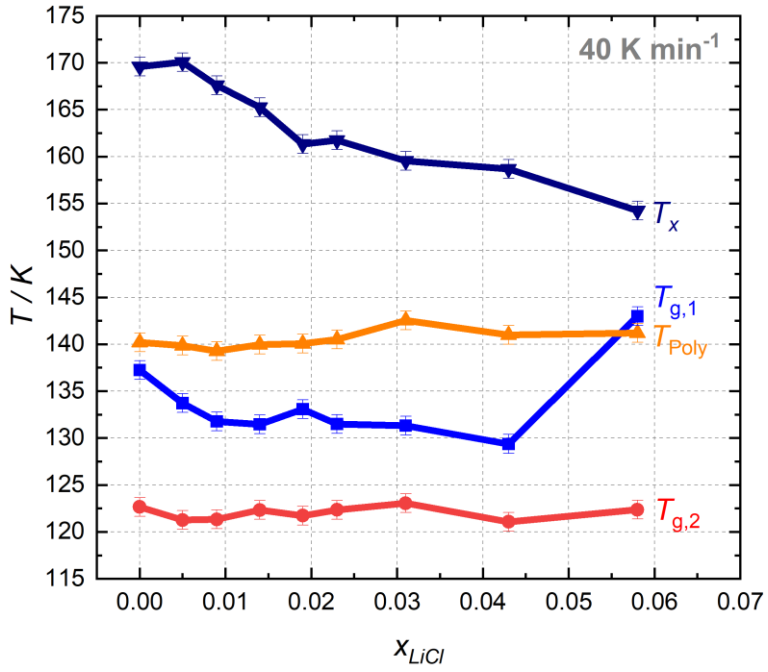
This supplementary material contains 3 additional figures showing additional calorimetric data. The data depicted in each figure are described and interpreted in the corresponding caption.



Supplementary Figure 1: First (red) and second (blue) calorimetric heating traces at 20 K min^{-1} (left panel) and 40 K min^{-1} (right panel) showing the full temperature range between 93 and 298 K. The curves are shifted vertically for clarity and are normalized using the enthalpy of fusion (large endotherm between 240 and 280 K in second heating traces). The pronounced exotherm at around 140 K seen in all first heating scans is assigned to the polyamorphic transition from a high-density to a low-density state as discussed in the main text. The exotherm between 150 and 170 Kin all second traces stems from the cold-crystallization of the low-density liquid to ice I_{sd}.



Supplementary Figure 2: Zoom of the traces shown in Figure S1 between 110 and 160 K. The first heating traces are truncated for clarity. All traces show the discussed in the main text except the ones of the 5.8 mol% sample. In this case, $T_{g,2}$ (in the red traces) is barely visible while the spike is very pronounced (note the larger scale bar in the panels on the right side). Additionally, $T_{g,1}$ (in the blue traces) is shifted to higher onset temperatures. The difference in heat capacity between the extrapolated baseline and the maximum of the endotherm increases by roughly a factor of 20 compared to all samples at < 5mol%. At 5.8 mol% $T_{g,1}$ exceeds T_{Poly}, and no liquid-liquid transition is observable anymore.



Supplementary Figure 3: Glass transition temperatures $T_{g,1}$ and $T_{g,2}$, the onset temperature of the polyamorphic transition T_{Poly} and the onset temperature of the cold-crystallization to ice I_{sd} T_x as a function of the molar fraction of LiCl x_{LiCl} at a heating rate of 40 K min^{-1}. The general trends of these temperatures are almost identical to the ones observed for 20 K min^{-1} but shifted to slightly higher temperatures. One exception, however, is the mole fraction at which $T_{g,1}$ exhibits its minimum: For 40 K min^{-1} heating rate it is found at 4.3 mol% whereas it is observed at 3.1 mol% for 20 K min^{-1}. This indicates that said minimum is rather broad and more data points would be needed to localize it more precisely.