Supporting Information

Extensive Characterization of Choline Chloride and its Solid-Liquid Equilibrium with Water

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### S1 X-ray powder diffraction

Table S1.1. X-ray data collection, crystal data and structure refinement details for the partially-hydrated ChCl structure at 358 K.

| Data Collection |       |
|-----------------|-------|
| Diffractometer  | Empyrean PANalytical |
| Wavelength (Å)  | Cu Kα1,2 X-radiation |
| Temperature (K) | 358   |
| Geometry        | Bragg-Brentano para-focusing optics |
| 20 range (º)    | 10.00 to 60.00 |

| Unit Cell       |       |
|-----------------|-------|
| Formula         | C$_5$NO$_{1.1}$Cl |
| Crystal system  | Triclinic |
| Space group     | P1     |
| a / Å           | 5.82   |
| b / Å           | 6.85   |
| c / Å           | 8.62   |
| α / º           | 55.71  |
| β / º           | 56.64  |
| γ / º           | 59.15  |
| Volume/Å$^3$    | 226.72 |
| Z               | 1      |
| $D_c$/g cm$^{-3}$ | 1.86  |

| Profile parameters |       |
|--------------------|-------|
| Profile function   | Fundamental parameters approach |
| Zero shift [2θº]   | -0.031 |

| Refinement details |       |
|--------------------|-------|
| No. of independent reflections | 136 |
| No. of global refined parameters | 108 |
| $R_p$               | 1.58  |
| $R_{wp}$            | 2.36  |
| $R_{exp}$           | 0.89  |

Structure Reliability Factors

\[ R_{\text{Bragg}} = 5.80 \]

where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated profile intensities, $I_{i,o}$ and $I_{i,c}$ the observed and calculated intensities, respectively. The summations run over $i$ data points or $n$ independent reflections. Statistical weights $w_i$ are usually taken as $1/y_{i,o}$. 
2 Differential Scanning Calorimetry

The temperatures and the standard molar enthalpies of transition ChCl were measured in a power compensation differential scanning calorimeter, PERKIN ELMER model Pyris Diamond DSC, using a heating rate of 0.0833 K·s⁻¹ (5 K·min⁻¹) and a constant flow of high purity (99.999%) gaseous nitrogen as protective gas. The samples were enclosed in hermetically sealed aluminum crucibles (50 µL). The temperature and heat flux scales calibrations of the device were performed by measuring the temperature and the enthalpy of fusion of some reference materials: benzoic acid, o-terphenyl, perylene, anthracene, naphthalene, 1,3,5-triphenylbenzene, diphenyl ether, 1,3-difluorobenzene, 1-heptanol and 1-hexanol. Sample loading into the crucibles was performed in a glove box under dry nitrogen. Thermal behavior of crystalline ChCl was evaluated following the same experimental procedure used in the calibration runs (Figure SI.1) and the experimental results are presented in Table SI.2. The temperatures of the phase transitions were determined as the onset temperatures of the peaks.

![Figure SI.1. – Thermograms for ChCl heat flow versus time (Exp IV). Sample mass = 7.4055 mg.](image)

| Exp. | \( m_{\text{sample}}/\text{mg} \) | \( \Delta_{\text{ss}}f^e_{\text{exp}} \) / J·g⁻¹ | \( T_{\text{ss}}/\text{K} \) | \( \Delta_{\text{ss}}H_m^o \) / kJ·mol⁻¹ | \( \Delta_{\text{ss}}S_m^o \) / J·K⁻¹·mol⁻¹ |
|------|-------------------------------|----------------------|-----------------|------------------|------------------|
| I    | 4.6825                        | 110.0                | 353.2           | 16.2             | 45.9             |
| II   | 7.7654                        | 110.0                | 352.1           | 16.2             | 46.0             |
| III  | 7.8727                        | 111.1                | 351.7           | 16.4             | 46.5             |
| IV   | 7.4055                        | 112.1                | 351.9           | 16.5             | 46.9             |
The kinetics of decomposition of ChCl was followed by DSC (Figure SI.2). Samples of pure ChCl were enclosed in aluminum crucibles with a hole in the lid. In Table SI.3 are presented the temperatures of decompositions, $T_{dec}$, at different scanning rates. In Figure SI.3 are given the experimental and estimated decomposition temperatures as function of scanning rates.

**Figure SI.2.** Thermogram for ChCl, heat flow versus temperature until complete sample decomposition, at different scanning rates: --- 5 K·min$^{-1}$; --- 10 K·min$^{-1}$; --- 20 K·min$^{-1}$; --- 90 K·min$^{-1}$; --- 200 K·min$^{-1}$.

**Table SI.3.** Decomposition temperatures, $T_{dec}$, of ChCl, measured by DSC, at different scanning rates.

| Scanning rate/K·s$^{-1}$ | $T_{dec}$/ K |
|--------------------------|--------------|
| 0.0833 (5 K·min$^{-1}$)  | 583 ± 5      |
| 0.1666 (10 K·min$^{-1}$) | 592 ± 5      |
| 0.3333 (20 K·min$^{-1}$) | 603 ± 5      |
| 1.5000 (90 K·min$^{-1}$) | 619 ± 5      |
| 3.3333 (200 K·min$^{-1}$)| 629 ± 5      |
Figure SI.3. – Plot of decomposition temperature, $T_{\text{dec}}$, versus scanning rate, of the DSC experiments of ChCl. ● – experimental $T_{\text{dec}}$; ● – estimated $T_{\text{dec}}$.

S3 High-precision heat capacity drop calorimeter at 298.15 K

The calorimeter was calibrated with sapphire ($\alpha$-Al$_2$O$_3$ pellets, NIST-RM 720), based on a single drop temperature step procedure of $\Delta T = 10.00$ K, from the initial temperature $T_i = 303.15$ K to the final temperature $T_f = 293.15$ K, and using the respective standard molar heat capacity at 298.15 K reported in the literature, $C_{p,m}(\alpha$-Al$_2$O$_3$) = 79.03 ± 0.08 J·K$^{-1}$·mol$^{-1}$.1 The calibration constant of the calorimeter was found to be $\varepsilon = 6.6541 \pm 0.0206$ W·V$^{-1}$.

Benzoic acid (Calorimetric Standard NIST 39j) and hexafluorobenzene were used as test substances to evaluate the accuracy of the apparatus for the measurements of the heat capacities of solid and liquids compounds.2–4 Additionally, the ionic liquid [C$_6$C$_1$im][NTf$_2$] was used to check the accuracy of the calorimeter for the measurements of the heat capacities of ionic liquids: recommended value of $C_{p,m}([\text{C}_6\text{C}_1\text{im}][\text{NTf}_2], \text{l}, 298.15 \text{ K}) = 631.6 \pm 1.3$ J·K$^{-1}$·mol$^{-1}$.5 The determined value achieved as the average of two independent experimental runs was $C_{p,m}([\text{C}_6\text{C}_1\text{im}][\text{NTf}_2], \text{l}, 298.15 \text{ K}) = 629.6 \pm 2.3$ J·K$^{-1}$·mol$^{-1}$, which is in excellent agreement with the literature recommend value.4 The high-precision heat capacity drop calorimeter incorporates a fully automatic setup and data treatment, providing reliable high-quality heat capacity data for several compounds, liquid and solid samples.1–3,6–9
The detailed results of the heat capacities of the liquid binary mixtures of chloride choline and water (molar fraction $x_{ChCl} < 0.4$) at $T=298.15$ K, are presented in Table SI.4.

**Table SI.4.** Molar heat capacity values at $T = 298.15$ K for different mixtures of chloride choline and water. The calibration constant used to calculate the $C_p$ values was the one derived from the sapphire [NBS, SRM 720, (α-Al₂O₃)] calibration, $(6.6734 ± 0.0167 \text{ W·V}^{-1})$.

| $x_{ChCl}$ | $M$/g·mol⁻¹ | $m$ _sample_/g | $N_{\text{drop}}$ | $<T_{\text{furnace}}>/K$ | $<T_{\text{calorimeter}}>/K$ | $<T>/K$ | $C_p^0$,J/K⁻¹·mol⁻¹ |
|------------|--------------|-----------------|------------------|--------------------------|--------------------------|---------|---------------------|
| 0.060      | 24.0493      | 0.51750         | 33               | 303.32                   | 293.18                   | 298.25  | 80.7 ± 0.2          |
| 0.100      | 30.1634      | 0.51307         | 14               | 303.37                   | 293.18                   | 298.28  | 87.5 ± 0.3          |
| 0.150      | 36.2040      | 0.51766         | 86               | 303.33                   | 293.18                   | 298.26  | 95.6 ± 0.3          |
| 0.175      | 39.3839      | 0.50710         | 10               | 303.32                   | 293.17                   | 298.25  | 100.0 ± 0.5         |
| 0.197      | 41.9262      | 0.51696         | 23               | 303.30                   | 293.18                   | 298.24  | 103.5 ± 0.3         |
| 0.224      | 45.2582      | 0.49880         | 11               | 303.33                   | 293.18                   | 298.25  | 108.7 ± 0.3         |
| 0.248      | 48.2071      | 0.49649         | 78               | 303.37                   | 293.18                   | 298.26  | 113.1 ± 0.3         |
| 0.272      | 51.1140      | 0.53522         | 15               | 303.38                   | 293.17                   | 298.28  | 117.6 ± 0.3         |
| 0.299      | 54.3203      | 0.55606         | 56               | 303.31                   | 293.18                   | 298.25  | 121.8 ± 0.3         |
| 0.322      | 57.1297      | 0.56960         | 22               | 303.34                   | 293.18                   | 298.26  | 126.0 ± 0.3         |
| 0.356      | 61.2531      | 0.56628         | 52               | 303.34                   | 293.17                   | 298.26  | 132.5 ± 0.4         |

$N_{\text{drop}}$ = number of drop experiments; $T_{\text{furnace}}$ = average temperature of the furnace; $T_{\text{calorimeter}}$ = average temperature of the calorimeter; the uncertainty reported is twice the standard deviation of the mean and the calibration uncertainty ($\varepsilon$) is included.

$\Delta T$ is calculated as $T_{\text{furnace}} - T_{\text{calorimeter}}$. Temperature sensors (Pt100) were calibrated by comparison with a certified platinum resistance thermometer, PTR100 (Fluke – Hart Scientific, Model 5626), traceable to the National Institute of Standards and Technology (NIST) based on the ITS-90 temperature scale, with an uncertainty smaller than 0.002 K. The temperatures is typically controlled to within ±$(3\cdot10^{-3})$ K and measured with a resolution better than $1\cdot10^{-3}$ K and um uncertainty of $2\cdot10^{-2}$ K in the temperature range.
S4 Heat capacities measurements of ChCl by DSC and HC-DSC Calorimetry

The experimental heat capacities as a function of temperature were measured based on the step method procedure, using two different calorimeters. A heat conduction differential scanning type microcalorimeter (HC-DSC) SETARAM model (microDSC III) was used to measure the heat capacity in the temperature range of 283 to 333 K. A power compensation differential scanning calorimeter, PERKIN ELMER model (Pyris Diamond DSC) used to measure the heat capacity in the temperature range of 273 to 423 K.

The heat capacity results are presented in Tables SI.5 and SI.6. For the HC-DSC measurements, \( \Delta T_{\text{step}} = 10 \text{ K} \), at 0.3 \( \text{K} \cdot \text{min}^{-1} \), \( t_{\text{isothermal}} = 2400 \text{ s} \) and for the DSC measurements, \( \Delta T_{\text{step}} = 5 \text{ K} \), at 5 \( \text{K} \cdot \text{min}^{-1} \), \( t_{\text{isothermal}} = 600 \text{ s} \). For the DSC measurements, the sample was kept in hermetically sealed 50 \( \mu \text{L} \) aluminum crucibles. In the HC-DSC runs, the sample was kept in a 1 cm\(^3\) Hastelloy C276 cell, hermetically sealed with a Viton o-ring. The HC-DSC samples were weighted in a Mettler Toledo AT201 analytical balance, with a resolution of \( \pm 0.00001 \text{ g} \). The DSC samples were weighted in a Mettler Toledo UMT5 micro balance, with a resolution of \( \pm 0.0001 \text{ mg} \).

To test the fidelity of the DSC measurements, the heat capacity of the \( \alpha \) crystalline phase was also evaluated. For this, in the first DSC experiment (Experiment 1 in Table SI.7) runs were made including a temperature interval where the choline chloride was in the \( \alpha \) crystalline phase (between 280 and 340 K). In order to extend the temperature interval, a second experiment (Experiment 2 in Table SI.8) was done with choline chloride in the \( \alpha \) crystalline phase, but at a lower temperature interval (between, 280 and 310 K). The same step temperature change (\( \Delta T_{\text{step}} \)), scanning rate, and isothermal step duration (\( t_{\text{isothermal}} \)) was used in all DSC experiments. In both calorimeters the calibration was done using highly pure synthetic sapphire (\( \alpha \)-\( \text{Al}_2\text{O}_3 \), NBS SRM-720\(^1 \)) using blanks experiments correction. A typical thermogram and the temperature program of one of the DSC runs is presented in Figure SI.4.
Table SI.5. Experimental heat capacity data obtained for each run through Tian-Calvet type differential scanning microcalorimetry (HC-DSC).

**Experiment 1** \( (m_{\text{sample}} = 0.64132 \text{ g}) \)

| \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) | \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) | \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) |
|------------------|---------------------------------|------------------|---------------------------------|------------------|---------------------------------|
| **Run 1**        |                                 | **Run 3**        |                                 | **Run 5**        |                                 |
| 283.34           | 201.26                          | 283.34           | 201.11                          | 283.34           | 201.01                          |
| 293.38           | 206.72                          | 293.38           | 206.50                          | 293.38           | 206.44                          |
| 303.42           | 212.06                          | 303.42           | 211.87                          | 303.42           | 211.84                          |
| 313.45           | 217.67                          | 313.45           | 217.13                          | 313.45           | 216.85                          |
| **Run 2**        |                                 | **Run 4**        |                                 | **Run 6**        |                                 |
| 283.34           | 201.23                          | 323.47           | 222.87                          | 323.47           | 222.52                          |
| 293.38           | 206.70                          | 333.50           | 227.96                          | 333.50           | 228.48                          |
| 303.42           | 212.19                          | 293.38           | 206.34                          | 293.38           | 206.34                          |
| 313.45           | 217.44                          | 303.42           | 211.91                          | 303.42           | 211.82                          |
| 323.47           | 223.11                          | 313.45           | 217.11                          | 313.45           | 216.95                          |
| 333.50           | 228.48                          | 323.47           | 222.64                          | 323.47           | 222.49                          |
|                  |                                 | 333.50           | 227.62                          | 333.50           | 227.40                          |

**Experiment 2** \( (m_{\text{sample}} = 0.67630 \text{ g}) \)

| \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) | \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) | \( T / \text{K} \) | \( C_{p,m}^{o} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) |
|------------------|---------------------------------|------------------|---------------------------------|------------------|---------------------------------|
| **Run 1**        |                                 | **Run 3**        |                                 | **Run 5**        |                                 |
| 283.34           | 200.93                          | 283.34           | 200.86                          | 283.34           | 200.79                          |
| 293.38           | 206.34                          | 293.38           | 206.26                          | 293.38           | 206.16                          |
| 303.42           | 211.29                          | 303.42           | 211.23                          | 303.42           | 211.17                          |
| 313.45           | 216.45                          | 313.45           | 216.43                          | 313.45           | 216.24                          |
| 323.47           | 222.11                          | 323.47           | 221.99                          | 323.47           | 221.76                          |
| 333.50           | 227.59                          | 333.50           | 227.30                          | 333.50           | 227.14                          |
| **Run 2**        |                                 | **Run 4**        |                                 | **Run 6**        |                                 |
| 283.34           | 200.85                          | 283.34           | 200.67                          | 283.34           | 200.67                          |
| 293.38           | 206.22                          | 293.38           | 206.12                          | 293.38           | 206.00                          |
| 303.42           | 211.17                          | 303.42           | 211.00                          | 303.42           | 211.16                          |
| 313.45           | 216.25                          | 313.45           | 216.16                          | 313.45           | 216.16                          |
| 323.47           | 221.76                          | 323.47           | 221.71                          | 323.47           | 221.71                          |
| 333.50           | 227.12                          | 333.50           | 227.02                          | 333.50           | 227.02                          |
Table SI.6. Experimental heat capacity data obtained for each run through differential scanning calorimetry (DSC).

**Experiment 1** ($m_{\text{sample}} = 12.8670 \text{ mg}$)

| $T / K$ | $C_{\text{p,m}}^\alpha / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ | $T / K$ | $C_{\text{p,m}}^\alpha / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ | $T / K$ | $C_{\text{p,m}}^\alpha / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ |
|---------|-----------------|---------|-----------------|---------|-----------------|
| **Run 1** | | **Run 2** | | **Run 3** | |
| 363.6 | 261.7 | 322.9 | 219.5 | 404.2 | 274.8 |
| 368.6 | 263.6 | 328.0 | 221.9 | 409.2 | 275.4 |
| 373.7 | 264.6 | 333.1 | 224.1 | 414.3 | 278.4 |
| 378.8 | 266.4 | 338.1 | 225.0 | 419.4 | 279.8 |
| **α to β transition** | | | | |
| 383.9 | 267.8 | 368.6 | 262.5 | 404.2 | 275.6 |
| 389.0 | 269.5 | 373.7 | 264.0 | 409.2 | 276.1 |
| 394.0 | 271.7 | 378.8 | 267.1 | 414.3 | 277.5 |
| 399.1 | 273.6 | 383.9 | 267.3 | 419.4 | 278.2 |
| 404.2 | 274.5 | 399.1 | 272.1 | | |
| **Run 4** | | **Run 5** | | **Run 5** | |
| | | 322.9 | 219.0 | 338.1 | 224.9 |
| | | 368.6 | 262.0 | 368.6 | 262.5 |
| | | 373.7 | 263.6 | 373.7 | 264.0 |
| | | 388.9 | 269.0 | 388.9 | 269.0 |
| | | 394.0 | 271.6 | 394.0 | 271.6 |
| | | 399.1 | 274.0 | 399.1 | 274.0 |
| | | 404.1 | 275.6 | | |
| **α to β transition** | | | | | |
| 368.6 | 264.0 | 322.9 | 219.0 | 404.1 | 275.6 |
| 373.7 | 265.0 | 328.0 | 221.9 | 409.2 | 275.9 |
| 378.8 | 268.2 | 333.0 | 224.0 | 414.3 | 279.2 |
| 383.9 | 269.2 | 338.1 | 225.0 | 419.3 | 278.1 |
| | | **α to β transition** | | | |
| 389.0 | 270.8 | 368.6 | 261.9 | 389.0 | 270.8 |
| 394.0 | 270.9 | 373.7 | 263.4 | 394.0 | 270.9 |
| 399.1 | 271.9 | 378.8 | 265.5 | 399.1 | 271.9 |
| 404.2 | 273.9 | 383.9 | 266.5 | 404.2 | 273.9 |
| 409.2 | 275.7 | 388.9 | 269.8 | 409.2 | 275.7 |
| 414.3 | 276.9 | 394.0 | 272.6 | 414.3 | 276.9 |
| 419.4 | 277.6 | 399.1 | 273.4 | 419.4 | 277.6 |
Experiment 2 ($m_{\text{sample}} = 3.7922 \text{ mg}$)

| $T / \text{K}$ | $C_{p,m}^0 / \text{J K}^{-1} \text{mol}^{-1}$ |
|---------------|---------------------------------|
| Run 1         |                                 |
| 282.9         | 205.1                           |
| 287.9         | 207.1                           |
| 292.9         | 208.5                           |
| 297.9         | 211.9                           |
| 303.0         | 214.9                           |
| 308.0         | 215.1                           |

Figure SI.4. Thermogram (blue) and temperature program (red) of one of the ChCl scans for the determination of heat capacity through the isothermal step method with DSC (Experiment 1).
**S5 Sample preparation**

Binary mixtures of chloride choline and water [ChCl + H\textsubscript{2}O] of approximately 2 g with different compositions were prepared gravimetrically using an analytical balance, Mettler Toledo, model AG245, with a mass resolution of ± 0.01 mg. All mixtures were prepared in a glove box under nitrogen atmosphere and kept in sealed glass bottles under nitrogen to avoid contamination. The mixtures of different composition (molar fraction between 0.0 and 1.0 in 0.1 mol fraction steps, and whenever was necessary additional binary mixtures were prepared in order to increase the resolution of the phase diagrams or heat capacities measurements) were heated (≈ 353 K), mixed and kept for 72 h in order to obtain a homogeneous solution. The overall uncertainty of the experimental mole fraction was estimated to be approximately ± 1 × 10\textsuperscript{−3}. Sample handling and preparation for the calorimetric measurements was always performed in a glove box (Captair pyramid 2200) under dry nitrogen atmosphere.

**S6 ChCl + H\textsubscript{2}O solid-liquid phase diagram**

For the study of the solid-liquid equilibrium of the binary mixtures of ChCl + H\textsubscript{2}O the following thermal procedure was done: first an isothermal step of 1 min at 298 K, followed by a heating step until 368 K and another isothermal step of 1 min. After this isothermal step the sample was cooled using scanning rate of 10 K·min\textsuperscript{−1} until 178 K and it was done another isothermal step of 5 min; a heating step of 5 K·min\textsuperscript{−1} was performed until 200 K, with the annealing of the sample during 20 min at 200 K. This step was followed by another scanning step at 10 K·min\textsuperscript{−1} until 178 K, followed by another isothermal of 10 min. The sample was now heated at 5 K·min\textsuperscript{−1} until 368 K followed by an isothermal step of 1 min. The thermograms for the chloride choline and ChCl + H\textsubscript{2}O mixtures at different compositions are presented in Figure SI.5. A detailed plot of the solid-solid transition of ChCl for pure choline chloride and binary mixtures of ChCl + H\textsubscript{2}O \(x_{\text{ChCl}} = 0.9\) and \(x_{\text{ChCl}} = 0.8\) is presented in Figure SI.6. The eutectic temperatures, \(T_{\text{eutectic}}\), solid-solid transition temperatures, \(T_{\text{ss}}\), melting temperatures, \(T_{\text{melting}}\), for the different compositions (molar fraction of ChCl, \(x_{\text{ChCl}}\)) of the binary mixtures ChCl + H\textsubscript{2}O are given in Table SI.7.
Table SI.7. Different compositions (molar fraction of ChCl, $x_{\text{ChCl}}$) of the binary mixtures ChCl + H$_2$O, eutectic temperatures, $T_{\text{eutectic}}$, solid-solid transition temperatures, $T_{\text{ss}}$, melting temperatures, $T_{\text{melting}}$ and enthalpies of the solid-solid transitions.$^a$

| $x_{\text{ChCl}}$ | $m_{\text{sample}}$/mg | $T_{\text{eutectic}}$ / K | $T_{\text{ss}}$ / K | $T_{\text{melting}}$ / K | $\Delta H_m^o$ / kJ·mol$^{-1}$ |
|---------------------|-------------------------|--------------------------|----------------------|-------------------------|-----------------------------|
| 0.100               | 11.1213                 | 203.1                    |                      | 249.0                   |                             |
| 0.150               | 10.5021                 | 204.5                    |                      | 230.2                   |                             |
| 0.197               | 17.9522                 |                          |                      |                         |                             |
| 0.248               | 16.9899                 | 200.2                    |                      | 238.4                   |                             |
| 0.299               | 17.9518                 | 204.5                    |                      | 264.8                   |                             |
| 0.322               | 16.4122                 | 204.5                    |                      | 275.3                   |                             |
| 0.356               | 14.3214                 | 204.6                    |                      | 292.1                   |                             |
| 0.395               | 6.1127                  | 204.7                    |                      | 304.2                   |                             |
| 0.495               | 41.2497                 | 204.7                    | 341.0                | 337.0                   | 0.8 ± 1.0                   |
| 0.603               | 22.4682                 | 204.7                    | 340.5                |                         | 3.7 ± 1.0                   |
| 0.700               | 6.1908                  | 204.2                    | 340.0                |                         | 8.4 ± 1.0                   |
| 0.791               | 12.7892                 | 204.2                    | 340.0                |                         | 10.1 ± 1.0                  |
| 0.901               | 4.3247                  | 204.5                    | 340.0                |                         | 14.0 ± 1.0                  |

$^a$The uncertainty of the experimental results $\sigma$ (temperature) was estimated as ± 1.0 K for the temperature.
Figure SI.5. – Thermograms for the chloride choline (ChCl) and ChCl + H₂O mixtures at different compositions.

- ChCl, \( x_{\text{ChCl}} = 0.9 \),  
- \( x_{\text{ChCl}} = 0.8 \),  
- \( x_{\text{ChCl}} = 0.7 \),  
- \( x_{\text{ChCl}} = 0.6 \),  
- \( x_{\text{ChCl}} = 0.5 \),  
- \( x_{\text{ChCl}} = 0.4 \),  
- \( x_{\text{ChCl}} = 0.35 \),  
- \( x_{\text{ChCl}} = 0.325 \),  
- \( x_{\text{ChCl}} = 0.3 \),  
- \( x_{\text{ChCl}} = 0.15 \),  
- \( x_{\text{ChCl}} = 0.1 \).

The experimental results obtained by procedures 1 and 3 are compiled in Table SI.8, while in Figure SI.7 a comparison to the literature data is given.
Table SI.8. Melting temperatures in binary mixtures ChCl + H₂O at different water mole fraction \( x_{\text{ChCl}} \) and the solubility of ChCl in water at different temperatures.

| Procedure 1 | \( x_{\text{ChCl}} / K \) | \( T_{\text{melting}} / K \) | \( x_{\text{ChCl}} / K \) | \( T_{\text{melting}} / K \) | \( x_{\text{ChCl}} / K \) | \( T_{\text{melting}} / K \) |
|------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.007      | 271.7                   | 0.054                   | 261.6                   | 0.127                   | 239.6                   |
| 0.014      | 270.5                   | 0.066                   | 258.3                   | 0.166                   | 223.3                   |
| 0.023      | 269.1                   | 0.083                   | 253.9                   | 0.302                   | 261.3                   |
| 0.032      | 267.3                   | 0.090                   | 251.8                   | 0.321                   | 266.6                   |
| 0.042      | 264.2                   | 0.117                   | 243.3                   | 0.329                   | 268.5                   |

| Procedure 3 | \( T / K \) | \( x_{\text{ChCl}} / K \) | \( T / K \) | \( x_{\text{ChCl}} / K \) | \( T / K \) | \( x_{\text{ChCl}} / K \) |
|------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 298.2\(^{b}\) | 0.364                   | 323.2\(^{b}\)           | 0.430                   | 353.2                   | 0.490                   |
| 303.2\(^{b}\) | 0.376                   | 328.2\(^{b}\)           | 0.443                   | 358.2                   | 0.491                   |
| 308.2\(^{b}\) | 0.389                   | 333.2\(^{b}\)           | 0.460                   | 368.2                   | 0.500                   |
| 313.2\(^{b}\) | 0.403                   | 338.2\(^{b}\)           | 0.476                   | 378.2                   | 0.508                   |
| 318.2\(^{b}\) | 0.416                   | 343.2\(^{b}\)           | 0.486                   | 388.2                   | 0.515                   |

\(^{a}\)The uncertainty of the experimental results \( \sigma \) (temperature) was estimated as ± 0.5 K for the temperature. \(^{b}\) Reference 10.
**Figure S1.6.** Detailed thermogram for the chloride choline (ChCl) and ChCl + H₂O mixtures at the following compositions: — ChCl, — $x_{\text{ChCl}} = 0.9$, — $x_{\text{ChCl}} = 0.8$.

**Figure S1.7.** Overview of the available solid-liquid equilibrium data for the binary system chlorine chloride and water: from this work, □ — procedures 1-3; ■ — solid–solid transition of binary ChCl + H₂O mixtures; ■ — solid–solid transition of ChCl; ◊ — eutectic transition; ◆ — Vilas-Boas et al.;□ — Zhang et al.;○ — Petrouleas and Lemmon (solid-solid transition of ChCl);○ — Fernandez et al. (melting of ChCl, estimated);◆ — Asare (eutectic transition);○ — Rahman and Raynie (eutectic transition).
S7 Calculation of the activity coefficients

The solubility of a solid compound \((i)\) in a liquid, under some assumptions, can be described by:\(^{16}\)

\[
\ln (x_i \cdot \gamma_i) = \frac{\Delta_m H_i}{R} \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) + \frac{\Delta_m C_p_i}{R} \left( \frac{T_{m,i}}{T} - \ln \frac{T_{m,i}}{T} - 1 \right) 
\]

(S1)

in which \(x\) and \(\gamma\) are the mole fraction and the activity coefficient of component \(i\) in the liquid phase, respectively, \(\Delta_m H\) is the melting enthalpy, \(T_m\) its melting point, \(\Delta_m C_p\) its heat capacity change upon fusion, \(T\) is the absolute temperature, and \(R\) is the ideal gas constant. Since the heat capacity change upon melting is often unavailable and has a negligible impact on the equilibrium calculations, the heat capacity term in Eq. (S1) can be neglected, resulting in a simpler expression that allow the calculation of the experimental activity coefficient from solid-liquid equilibrium data:

\[
\gamma_i = \frac{1}{x_i} \exp \left[ \frac{\Delta_m H_i}{R} \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) \right]
\]

(S2)

COSMO-RS

The COnductor like Screening MOdel for Real Solvents (COSMO-RS) is a statistical thermodynamics-based model that predicts the chemical potential of individual components in a mixture.\(^{17,18}\) To do so, it takes as input the so-called \(\sigma\)-profile of each component and, through pair-wise screened charge contacts, estimates their overall intermolecular interactions. The COSMOtherm software package (BP_TZVP_18 parametrization),\(^{19,20}\) which is a direct implementation of COSMO-RS, was used in this work to estimate the activity coefficients of water and choline chloride at different compositions. The \(\sigma\)-profile of water was taken from the software database while that of choline chloride was obtained using TURBOMOLE,\(^{21}\) with a def-TZVP basis set, a BP-86 DFT functional, and the COSMO solvation model (infinite permittivity). In this context, choline chloride was treated as a neutral ionic pair with a conformation akin to that used in previous works.\(^{10,22}\)
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