

PAPER



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Impact of water on the melting temperature of urea + choline chloride deep eutectic solvent

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Deep eutectic mixtures are considered as promising green, cheap and easy-to-prepare solvents for applications in catalysis, extraction or material design. In the present work we focus on the urea:choline chloride system. Our aim was to establish its phase diagram and to quantify the impact of naturally present water on the melting temperature for this highly hygroscopic system. The phase diagram of dried urea:choline chloride was established using three complementary apparatuses: a thermostated bath, an optical microscope and a differential scanning calorimeter. Due to limited thermal stability, only mixtures with urea mole fractions between 0.50 and 0.80 were studied. The eutectic point was found for a urea mole fraction of 0.67 at 25 °C and its enthalpy of melting is 93 J g⁻¹. Water can be easily absorbed from the atmosphere, which decreases the melting temperature of eutectic compositions below room temperature. This is quantified in this paper by a systematic study of the melting temperature of a eutectic mixture containing different quantities of water up to 10 wt%. The presence of water should be taken into account for any physico-chemical characterization as well as for applications of this type of eutectic system.

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Introduction

According to the 5th principle of green chemistry, safer solvents should be preferred. The research for alternative liquids that could be used in synthesis or separation has been very active for several years. An acceptable solvent should be not only non-toxic but also biodegradable or easily recycled. In addition it should be cheap and fulfill the technical requirements of the process.

Among the possible alternatives, the so-called 'eutectic mixtures' are of great interest. In the isobaric solid-liquid phase diagram of a binary system, a eutectic point is a particular point displaying an equilibrium between two crystalline phases and a liquid phase.¹ It corresponds to the minimum in the liquidus curve (curve above which the system is liquid), in other words, at the eutectic composition the system can be used as liquid solvent at the lowest temperature. In 2003, Abbott *et al.*² noticed that different mixtures composed of quaternary ammonium salts and urea (two solids at ambient temperature) were liquid at ambient temperature. Even if the concept of eutectic is well known for years, it is relatively new to find eutectic points near ambient temperatures.

Abbott *et al.* introduced the concept of 'deep eutectic solvent' as a system composed of a hydrogen bond acceptor and a

hydrogen bond donor liquid at ambient temperatures. In these mixtures, the decrease of the melting point can be explained by strong H-bonds that limit the crystallization of the salt. Since this work of Abbott, many papers have been published on similar mixtures referred to as deep eutectic solvents (DES), eutectic-based ionic liquids or low transition temperature mixtures (LTTM). Most of the publications concern the preparation of the eutectic liquid or its possible applications in various domains: electrochemistry, synthesis and catalysis, separation and material preparation.³⁻⁷

Eutectic solvents are sometimes presented as alternatives to ionic liquids or considered as a whole new class of ionic liquids themselves. One reason for this comparison comes from their similar low melting points, typically below 100 °C. Moreover, they can be considered as tunable solvents since it is possible to combine numerous H-bond donors and acceptors. When compared to ionic liquids, they are generally far less expensive, easy to prepare, non-toxic, biodegradable⁶ and thus more attractive as green media. However, high viscosities and limited thermal and chemical stabilities are the main drawbacks of these liquids.⁴ At the molecular level, ionic liquids are purely ionic whereas the H-bond donor of eutectic liquids is generally not ionic.

The decreased melting point of DES is explained by strong H-bond interactions between the donor and the acceptor.⁷ These interactions were studied by molecular dynamics simulations and experimentally by spectroscopy. Using molecular dynamics simulations, Perkin *et al.*⁸ and Shah *et al.*⁹ observed, in the case

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of urea:choline chloride, strong interactions between the NH_2 moiety of urea and the chloride anion. IR and NMR spectroscopy have also confirmed the presence of these H-bonds.^{8,10,11} For urea:choline chloride, the maximum number of H-bonds are obtained with the 2:1 molar ratio leading to the lowest melting point. At this particular composition the urea:choline chloride mixture is named reline.

To optimize the use of eutectic solvents, physico-chemical characterization of these systems would be helpful. A careful review of the literature shows a lack of thermodynamic studies on DES systems. For example, only a few references describe the phase behavior of the most studied eutectic system urea:choline chloride. Abbott *et al.*² established the first phase diagram for this system in 2002. In this pioneer paper, the liquidus curve is obtained from freezing temperatures. The eutectic composition and temperature were found at 2:1 molar ratio and 12 °C. Later on, using differential scanning calorimetry, Shah *et al.* observed a melting point of the same 2:1 sample at 12 °C.⁹ With the same experimental technique, Morrisson *et al.*¹² have also identified 2:1 as the mole fraction of the eutectic composition melting point at 17 °C.

Confusion exists in the literature, as the freezing points measured by Abbott *et al.* are referred to as melting points by some authors.^{4,6} In many systems, supercooled liquids can exist leading to differences between the freezing and melting temperatures. In order to establish the phase diagram, melting should be preferred to freezing, as it is independent of the experimental conditions.¹³

Both choline chloride and urea are hygroscopic. The presence of water may impact their use in further applications and will modify the interactions between the two components. Using molecular simulations, Shah *et al.*⁹ have shown a decrease of urea-anion interactions in the presence of water. With NMR spectroscopy, a similar tendency was observed in other eutectic mixtures.¹¹ Using solvatochromic probes on urea:choline chloride mixtures with water Pandey *et al.*¹⁴ have shown an increased dipolarity/polarizability and a decrease of the H-bond acceptor basicity. Furthermore, the strong organization of DES (partly explained by the H-bond network) can be advantageous for selective catalysis or nanoparticle synthesis.^{5,15,16} The addition of water will disturb the molecular structure and thus limit these applications. This effect was investigated in gold nanoparticles in reline DES.¹⁷

At 30 °C, the density of pure reline was measured to be 1.1945, 1.1952 and 1.216 g cm⁻³, respectively, by Yadav *et al.*,¹⁸ Xie *et al.*¹⁹ and Shah *et al.*⁹ With the addition of water a systematic decrease of the density (1% for the addition of 5 wt% of water) was observed.¹⁸ Large discrepancies were also observed for the viscosities of reline: measured at 30 °C, 527 mPa s, 552 mPa s and 954 mPa s, respectively, by Yadav *et al.*,¹⁸ Shah *et al.*⁹ and Xie *et al.*¹⁹ These deviations may be due to different quantities of water in the neat eutectic mixtures, which have not been quantified in any of these studies. When water is added, there is a dramatic decrease of the viscosity. For example, an addition of 5 wt% of water leads to a viscosity divided by a factor of 6.¹⁸ The presence of water modifies the volumetric and transport properties of

reline whereas its influence on the melting point of reline has not yet been considered.

In this work, we determined the solid-liquid phase diagram for the urea:choline chloride system. For that purpose, three complementary techniques were implemented: (i) visual determination of the melting point of samples of a few grams using a thermostated bath, (ii) optical microscopy of smaller samples of typically 20–200 mg using polarized light that allows the detection of amorphous and crystalline particles and, (iii) DSC (differential scanning calorimetry) that can also provide the heat associated with the phase transitions. Furthermore, this work includes a study of the effect of naturally present water, in these highly hygroscopic mixtures, on the melting point using the same three techniques.

Materials and methods

Materials

Choline chloride (ChCl) and urea were purchased from Sigma-Aldrich with purities higher than 98%. Both powders were dried under vacuum (0.1 mbar) for at least 24 hours at room temperature. Urea:ChCl mixtures were prepared by weight. The samples of any composition, under mechanical stirring, became liquid and perfectly transparent within few minutes at 80 °C.

When heating a dry urea sample at 5 °C min⁻¹ in the DSC, the decomposition temperature which is very close to its melting point (130–135 °C) is observed as reported in the literature.²⁰ If the heating rate is reduced to 1 °C min⁻¹, the decomposition peak is shifted to 105 °C. To avoid the possible decomposition of the samples, only mixtures with liquidus temperature below 80 °C were studied. Eight compositions between $x_{\text{urea}} = 0.50$ and 0.80 have been investigated (urea:ChCl molar ratio = 50:50, 55:45, 60:40, 65:35, 67:33, 70:30, 75:25 and 80:20). Given the precision of the balance and the presence of residual water in the powders, the uncertainty of the mole fraction is estimated to be 0.2%.

The water content of all mixtures was measured using a coulometric Karl-Fischer titrator (Mettler Toledo, DL31). Quantities were around 1000 ppm and systematically below 2000 ppm for dried mixtures.

Thermostated bath

1 gram of the urea:ChCl mixture is inserted in a vial together with a magnetic stirring bar under a nitrogen atmosphere. The vial is heated up to 80 °C and kept at this temperature for 30 minutes for homogenizing the sample. It is then quickly cooled down with liquid nitrogen to obtain a solid transparent sample. The vial is then immersed in the thermostated bath equipped with two insulated glass windows (Julabo 18V). The bath was previously cooled down to 5 °C using an immersion cooler (Julabo FT200). While heating to 5 °C, a transition is observed for all samples from a transparent to white solid. Samples are left at 5 °C for 30 minutes for equilibration before use. In a typical experiment, the bath is heated from 5 °C to 80 °C at a scanning rate of 0.25 or 0.025 °C min⁻¹ using the controller on the thermostated bath. The temperature is measured using a 100 Ω platinum resistance

thermometer immersed in the bath between the different samples. A webcam (Logitech C920) is fixed in front of one of the windows of the thermostated bath. Images of the samples are taken automatically every 0.5 °C using Yawcam software. The phase transitions of the samples were studied by analyzing the brightness of each image using home-made software.

Microscope

A few drops of the liquid mixture are placed on a glass slide and immediately covered by a glass coverslip to avoid water absorption. The glass slide is placed on the hot stage (Linkam LTS420) of the thermostated optical microscope (Leica DM2500M). A typical temperature program analysis of the sample is: (i) heat from room temperature to 80 °C at 20 °C min⁻¹; (ii) hold for 1 minute at 80 °C; (iii) cool down to -60 °C at 10 °C min⁻¹; (iv) hold for 10 minutes at -60 °C and (v) heat up to 80 °C at either 0.10 or 0.25 °C min⁻¹. During the experiment, the hot stage containing the sample is continuously purged with nitrogen to keep the sample dry. To follow the phase transitions of the sample, images were recorded every 0.5 °C and the brightness of each image was analyzed using home-made software. There was no evolution of the samples during our experiments. This was verified by performing two successive cycles on the same sample.

Differential scanning calorimetry

A differential scanning calorimeter mDSC 2920 from TA-Instruments was used. It was calibrated in temperature and energy using standard indium and lead. The validation of the calibration was realized by fusion of water and naphthalene. The maximum deviation from the literature of temperature obtained for those two compounds was below 0.2 °C. The maximum deviation in enthalpy was below 1%. About 5 to 10 mg of the liquid mixture is weighed in a hermetic sealed crucible. The sample and reference crucibles are placed inside the calorimeter. The atmosphere of the calorimeter oven is continuously flushed with nitrogen to increase the homogeneity of the temperature and evacuate any volatile compound that may be produced during heating. Experiments were conducted as follows: (i) fast increase of the temperature up to 80 °C; (ii) isotherm at this temperature for 10 minutes; (iii) decrease of the temperature to -55 °C at a scanning rate of 10 °C min⁻¹; (iv) isotherm at this temperature for 10 minutes; (v) increase of the temperature with a scanning rate of 0.1, 0.25 or 1 °C min⁻¹, up to 80 °C; (vi) isotherm at this temperature

for 10 minutes; and (vii) return to room temperature at a scanning rate of 10 °C min⁻¹. The first and the last steps are not recorded as they are used to initialize the sample and finish the experiment, respectively.

Results and discussion

Determination of the liquid–solid phase diagram

Thermostated bath. The transition temperatures of all urea:ChCl mixtures were first determined using a thermostated bath as illustrated in Fig. 1 in the case of 55 : 45 and 67 : 33 mixtures.

While heating the reline sample (67 : 33), a rapid transition from a white solid to a transparent liquid is observed between 30 and 35 °C. In the case of the 55 : 45 sample, the mixture is crystalline up to 30 °C. Above 60 °C, it is a transparent liquid. Between 30 and 60 °C, a white solid–liquid biphasic system is observed. This temperature range corresponds to the domain between the solidus (temperature below which the mixture is a solid) and the liquidus temperatures.

To precisely build the phase diagram of the urea:ChCl system, the brightness of all samples was automatically analyzed as illustrated in Fig. 2 for the reline and the 55 : 45 samples. At the lowest temperatures, below 30 °C, the mixtures are crystalline, the brightness is the most stable. The variations in the signals are similar for all samples. They correspond to changes in the overall luminosity and not to a physical modification of the sample. Then, around 30 °C, the brightness quickly decreases. The beginning of this transition corresponds to the solidus temperature. At higher temperatures, strong oscillations of the brightness are observed which correspond to the movement of the stirrer bar. Thus, it was not possible to precisely determine the liquidus temperature with this technique. This part of the diagram will be obtained using the optical microscopy and DSC experiments.

The solidus temperatures obtained after the brightness analysis of the eight samples at two different heating rates (0.25 and 0.025 °C min⁻¹) are presented in Table 1. An average value of 30 °C was obtained. We cannot exclude a small effect of the scanning rate as the values obtained at 0.25 °C min⁻¹ are slightly higher than those obtained at 0.025 °C min⁻¹. The average deviation of all the results is 1.5 °C that will be considered as the global uncertainty of this method.

A crystallization experiment on dried reline was also conducted by decreasing the temperature from 35 to 5 °C at a scanning rate

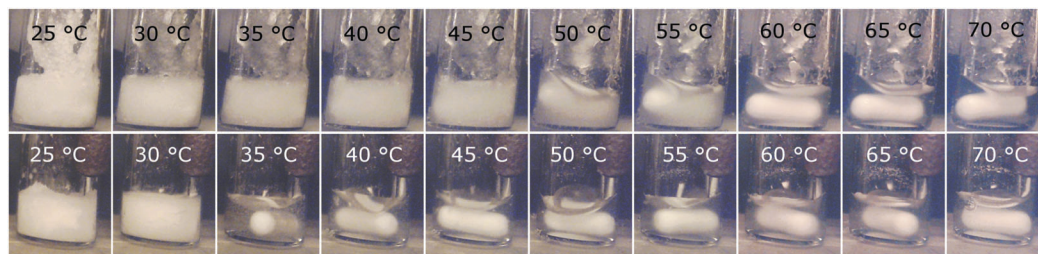


Fig. 1 Photographs of 55 : 45 (top) and 67 : 33 (bottom) urea : ChCl mixtures taken in the thermostated bath during an experiment at a scanning rate of 0.25 °C min⁻¹. After the melting, the stirrer bar is clearly visible in both liquid mixtures.

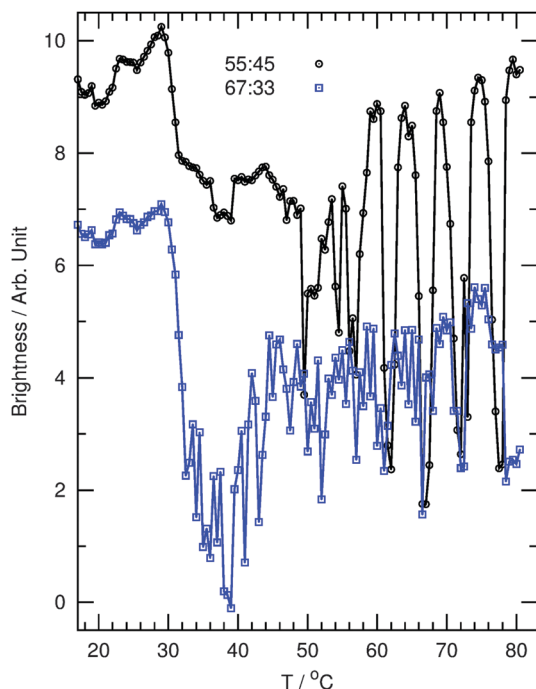


Fig. 2 Evolution of the brightness of the 55 : 45 and 67 : 33 samples during an experiment in the thermostated bath at a heating rate of $0.25\text{ }^{\circ}\text{C min}^{-1}$. For readability reasons, the brightness of the two samples has been shifted from each other.

of $-0.025\text{ }^{\circ}\text{C min}^{-1}$ under stirring. The beginning of the crystallization occurs at $20\text{ }^{\circ}\text{C}$. This value is lower than the melting temperature of $30\text{ }^{\circ}\text{C}$. This is different from the data measured by Abbott *et al.*² ($12\text{ }^{\circ}\text{C}$). This deviation can be partially explained by different crystallization conditions.

Polarized microscopy. The phase transitions of the same eight samples were analyzed by optical microscopy using polarized light to enhance the sensitivity to crystalline structures. Experiments were conducted using scanning rates of 0.10 and $0.25\text{ }^{\circ}\text{C min}^{-1}$. Examples of the images of the 67 : 33 and 50 : 50 mixtures are given in Fig. 3.

At $10\text{ }^{\circ}\text{C}$, the reline sample presents a spherulitic crystalline structure (Fig. 3a) characteristic of a eutectic mixture. All the eutectic crystals melt between 24 and $30\text{ }^{\circ}\text{C}$, resulting in a liquid above this temperature (Fig. 3c). In contrast, the 50 : 50 mixture presents several types of crystals (Fig. 3b). The whiter crystals melt at the same temperature as the solid particles in the reline sample. The elongated needle shaped crystals are still

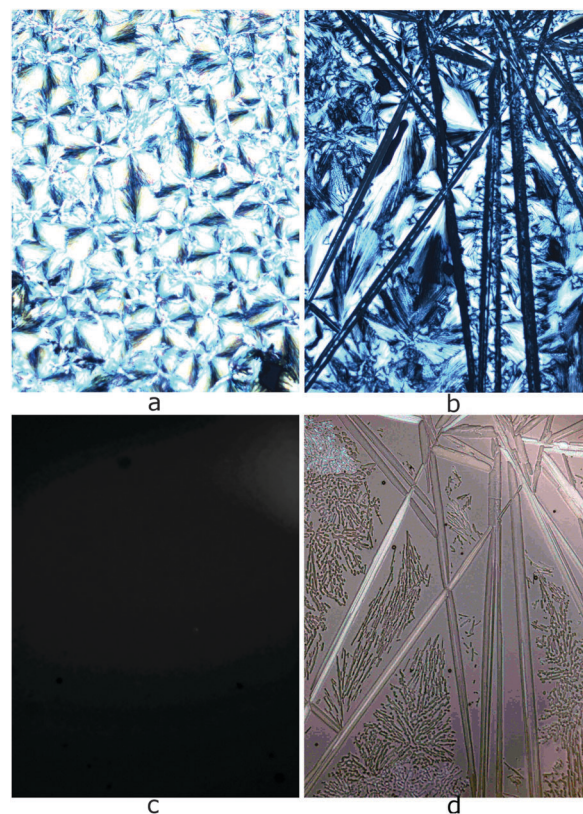


Fig. 3 Microscope images of a eutectic composition (67 : 33, left) and a 50 : 50 mixture (right) at $10\text{ }^{\circ}\text{C}$ (a and b) and $30\text{ }^{\circ}\text{C}$ (c and d) at a scanning rate of $0.10\text{ }^{\circ}\text{C min}^{-1}$. The contrast of the pictures taken at $30\text{ }^{\circ}\text{C}$ has been improved to help the reader to see the particles still present at this temperature in the non-eutectic composition (d). The size of all pictures is around 1 mm^2 .

visible at $30\text{ }^{\circ}\text{C}$ (Fig. 3d) and melt continuously when increasing the temperature up to the liquidus transition.

Using brightness analysis it is difficult to determine the initial point of melting. Thus, the solidus temperature cannot be precisely determined with this technique. Analysis of all the images permits the estimation of the liquidus temperature. This is defined as the temperature of the first image without any particles. The results are presented in Table 2 for the two scanning rates studied. Similar temperatures (average deviation of $2\text{ }^{\circ}\text{C}$) are obtained with the two sets of experiments. This average deviation is considered as the global uncertainty of this technique. The composition corresponding to the minimum of the liquidus curve ($29\text{ }^{\circ}\text{C}$) is the 67 : 33 molar ratio.

Differential scanning calorimetry. The solidus and liquidus temperatures were also determined using differential scanning calorimetry (DSC). Experiments were conducted at different scanning rates (0.10 , 0.25 and $1\text{ }^{\circ}\text{C min}^{-1}$).

Sample thermograms obtained for two mixtures at 3 scanning rates are presented in Fig. 4. The general behavior of the thermograms at reline composition (left Fig. 4) can be described as the following:

- Exothermic peaks are associated with the crystallization of the sample. The crystallization does not happen during the cooling

Table 1 Solidus temperatures (in $^{\circ}\text{C}$) obtained in the thermostated bath at two heating rates

Sample	$0.025\text{ }^{\circ}\text{C min}^{-1}$	$0.25\text{ }^{\circ}\text{C min}^{-1}$
50 : 50	—	27.9
55 : 45	28.3	28.9
60 : 40	28.3	29.7
65 : 35	—	29.7
Reline	28.3	29.7
70 : 30	28.3	31.2
75 : 25	33.7	32.7
80 : 20	—	32.7

Table 2 Liquidus temperatures (in °C) obtained with the microscopy experiments at two scanning rates

Sample	0.10 °C min ⁻¹	0.25 °C min ⁻¹
50 : 50	71.3	73.2
55 : 45	61.1	61.8
60 : 40	39.9	40.7
65 : 35	31.1	28.6
Reline	30.1	28.5
70 : 30	31.9	31.5
75 : 25	63.0	57.5
80 : 20	78.5	78.2

step but during the heating of the sample. This phenomenon is named cold crystallization. It is generally observed in strongly metastable systems such as ionic liquids or polymers. The temperature associated with this phenomenon is drastically dependent on the scanning rate.²¹

- An endothermic peak is associated with the melting of the eutectic crystals. The solidus temperature is the onset temperature of this peak, which is defined as the intersection between the baseline just before the peak and the tangent of the peak at the point with the maximum slope as illustrated in Fig. 4. This temperature is characteristic of the beginning of the melting of the eutectic crystal.

In the case of the 60 : 40 mixture (right graphs in Fig. 4), as well as for all the mixtures with compositions different from the reline, a last event can be identified. Its related temperature is determined from the intersection of the straight lines obtained from the thermal flux after the solidus peak and the line to return to the baseline (see Fig. 4). This temperature corresponds to the end of the melting of non-eutectic crystals (liquidus temperature).

At fast scanning rates (1 °C min⁻¹), melting begins before the end of the crystallization peak which prevents the precise determination of the solidus temperature (Fig. 4). When the scanning rate is slow (0.1 °C min⁻¹) the crystallisation and the melting point are well separated but the effect associated with the liquidus temperature is difficult to distinguish from the baseline. The solidus temperatures are then obtained from the 0.1 °C and 0.25 °C min⁻¹ experiments. An average value of 25 °C is obtained with a global uncertainty (calculated as the average deviation) of ± 2 °C. The liquidus temperatures are obtained from the 0.25 and 1.0 °C min⁻¹ experiments. All characteristic temperatures determined by DSC are reported in Table 3.

In addition to the melting temperatures, it is possible to calculate the enthalpy of melting of the eutectic crystals, by integration of the thermal flux *versus* time. This calculation is done at the reline composition. Using the experiments conducted with scanning rates of 0.1 °C min⁻¹ and 0.25 °C min⁻¹, the enthalpy of melting is determined to be 88 ± 2 J g⁻¹.

Phase diagram. The phase diagram obtained is presented in Fig. 5. For the solidus line, a discrepancy was observed between the data obtained from the DSC and the thermostated bath. The temperatures measured using the thermostated bath are systematically higher than those obtained using the DSC. The sizes of the samples are different in the two apparatus (5–10 mg in the DSC and 1 g in the thermostated bath). In the thermostated bath, the melting temperatures obtained at the two scanning rates (0.25 and 0.025 °C min⁻¹) are not significantly different. These experiments are not sufficient to confirm the possible heat transfer limitations in the thermostated bath. Another possible explanation for the deviations between the two techniques could be the sensitivity to detect the start of the

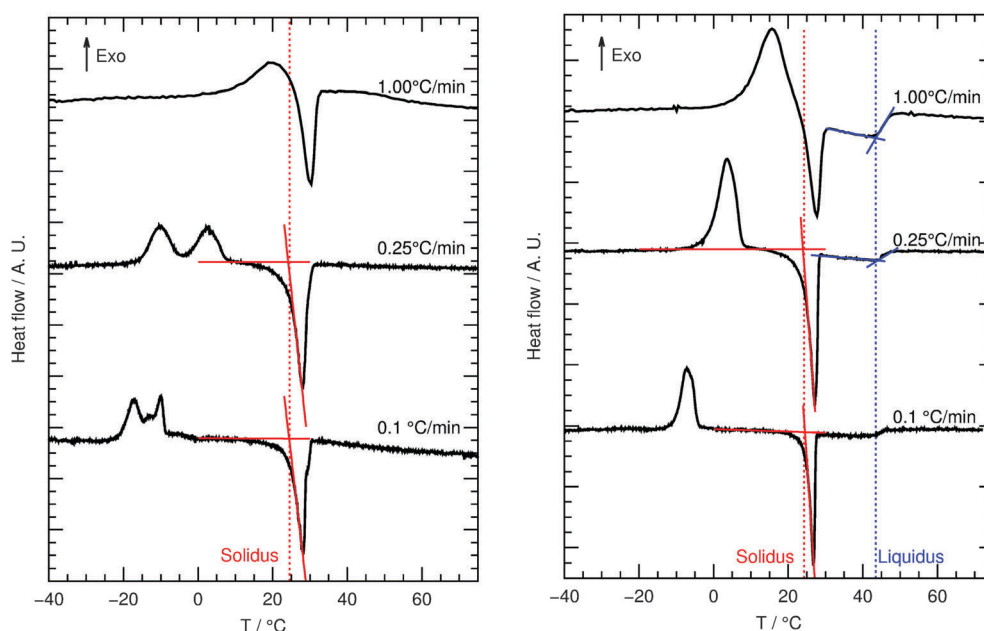
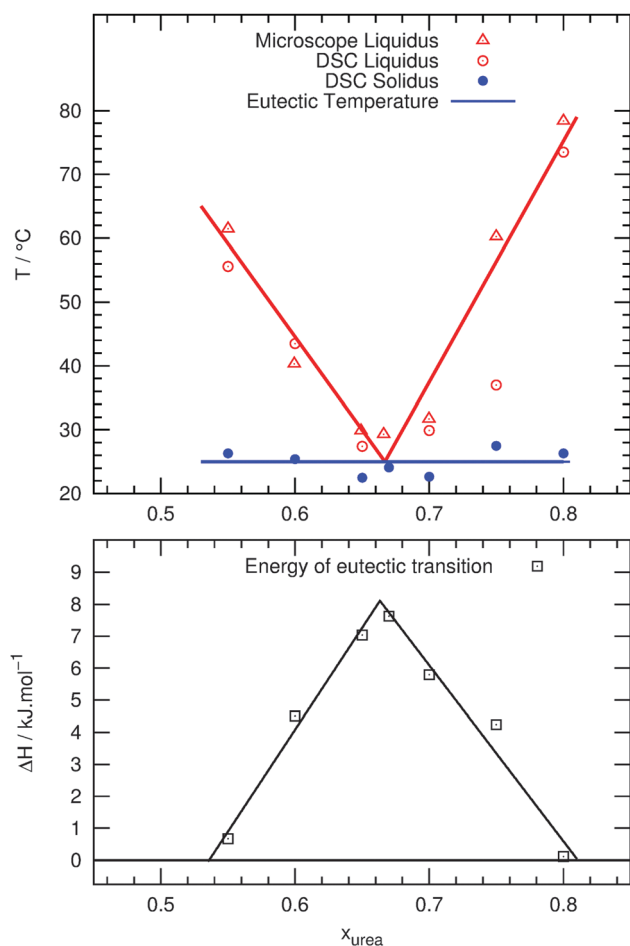


Fig. 4 Thermograms of 67 : 33 (left) and 60 : 40 (right) samples obtained with scanning rates of 0.1, 0.25 and 1 °C min⁻¹. Exothermic peaks (signal up) correspond to crystallization and endothermic ones (signal down) to melting. For readability reasons, the thermograms have been shifted from each other. Construction lines used to obtain the solidus (in red) and liquidus (blue) temperatures are added to the thermograms.

Table 3 Transition temperatures obtained with the DSC experiments at two scanning rates

Sample	Solidus temperature/°C		Liquidus temperature/°C	
	0.1 °C min ⁻¹	0.25 °C min ⁻¹	0.25 °C min ⁻¹	1.0 °C min ⁻¹
50 : 50	—	—	65.0	62.0
55 : 45	27.0	25.6	57.0	54.2
60 : 40	24.8	25.8	43.6	43.4
65 : 35	22.0	23.0	27.4	—
Reline	23.5	24.5	—	—
70 : 30	23.0	22.1	28.3	31.5
75 : 25	26.5	28.5	38.0	36.0
80 : 20	—	26.3	73.5	—

**Fig. 5** Solid–liquid phase diagram of the urea:ChCl system as a function of the urea mole fraction. For clarity reasons, only the average temperature is shown when experiments were repeated with two scanning rates. The red lines are only added to help the reader. On the bottom, Tamman's plot of the enthalpy of the eutectic transition is also given.

melting with the thermostated bath. Due to the thickness of the sample, a difference in the brightness cannot be detected before a sufficient quantity has melted. It can be observed in the thermostated bath experiments (for example, see Fig. 1, 55 : 45 mixture, at 30 °C) that small solid particles are present on the glass surface of the vial, and they melt a few degrees before the

bulk phase. This is consistent with the results of the DSC analysis. All these reasons could explain why a higher solidus temperature is found with the thermostated bath than with the DSC experiments. For the solidus, only the DSC data are then presented on the phase diagram in Fig. 5.

The liquidus temperatures obtained using the microscopy and the DSC are similar as observed in Fig. 5, except in the particular case of the 75 : 25 sample. At this composition, using the microscope, most of the non-eutectic crystals melt quickly but a small quantity of them remains dispersed in the liquid up to 60 °C. The energy associated with the melting of the last crystals cannot be detected by DSC due to sensitivity limitation.

The lowest melting temperatures were measured for urea mole fractions between 0.65 and 0.70, in agreement with the literature (eutectic composition of 67 : 33^{2,12}). Following the discussion on the possible overestimation of the solidus temperatures in the thermostated bath, we finally estimate the eutectic temperature to be 25 °C using the DSC experiments. This is a higher value compared to the results of Morrison *et al.*¹² and Shah *et al.*⁹ This difference could be explained by different water quantities.

Tamman's graph is also given in Fig. 5. It shows the enthalpy of melting of the eutectic crystals (in kJ mol⁻¹) versus the composition of the mixture. As expected, this representation shows that the enthalpy is maximum at the eutectic composition and decreases linearly when moving far from this particular composition. With this representation, the eutectic composition can be precisely obtained at 0.67 and with an enthalpy of melting of 93 J g⁻¹ or 8.1 kJ mol⁻¹ (24.3 kJ mol⁻¹ of reline). Morrison *et al.* found a lower value (71.09 J g⁻¹) for their reline mixture melting at 17 °C. Finally, the thermal effect associated with the melting of the eutectic temperature disappears at urea mole fractions of 0.53 and 0.81.

Effect of water on the melting temperature of reline

The eutectic mixture is highly hygroscopic, so, inevitably water will always be present in the sample. As already reported in the literature, its presence will modify the interactions between the two components of the eutectic system and impact its physico-chemical properties.^{9,18,19} In this work, we propose to (i) evaluate the typical water quantity that can be absorbed from atmosphere and (ii) quantify the impact of this residual water on the melting point.

A dry 67 : 33 eutectic mixture was exposed to atmosphere (21 °C, 50% relative humidity) under stirring for three weeks. An aliquot was regularly taken from the sample. The water content was quantified by Karl-Fisher titration and its evolution as a function of time is presented in Fig. 6. A first linear increase of the water quantity is observed. Absorption of 5.5 wt% of water is measured after 48 hours corresponding to 1150 ppm per hour. After a week under our experimental conditions, a plateau is obtained at 18–20 wt% of water.

Water can be easily present in the reline sample, if powders are not initially dried or if the mixing is not performed under a dried atmosphere. To understand the impact of this residual water on melting, different water quantities were systematically added to dry reline samples, up to 10 wt%. The eutectic temperatures of

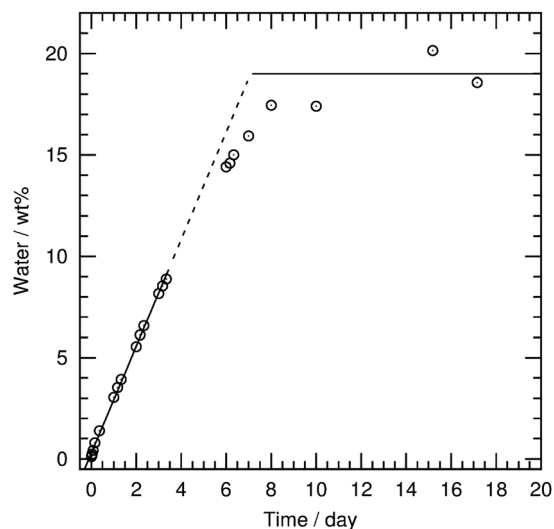


Fig. 6 Evolution of the water quantity (expressed in weight percent) in a reline sample in contact with atmosphere (under mixing), as a function of time. The average temperature and the atmospheric relative humidity are, respectively, 21 °C and 50%.

the wet samples are measured using the same techniques used to build the solid–liquid phase diagram.

A linear decrease of the melting temperature to 15 °C was observed for a mixture containing 5 wt% of water, as shown in Fig. 7. Similar values were obtained with the three techniques. Given the melting point of water, this tendency was expected. However this effect was never quantified. This could explain some discrepancies observed in the literature in which the water quantity is not always controlled. The higher temperatures found

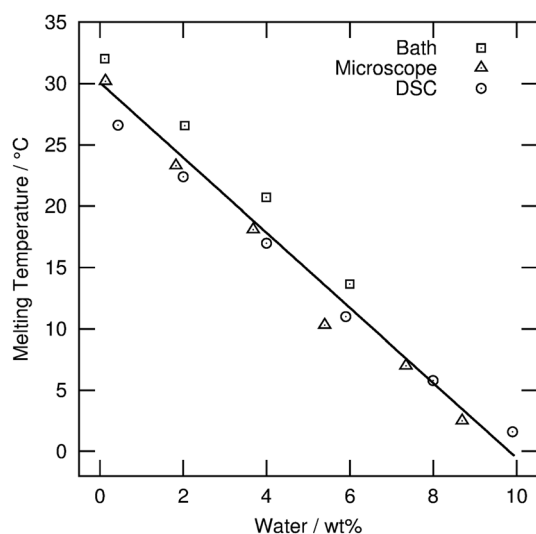


Fig. 7 Evolution of the melting point of a 67 : 33 mixture as a function of the water quantity expressed in wt%. In the thermostated bath, the temperature determined is obtained from the beginning of the decrease of the brightness. With the microscope, it corresponds to the first image without any crystals. With the DSC, the temperature is obtained at the end of the melting determined similarly to the liquidus temperature of the dried samples.

in the present study may be due to smaller water quantities than in previous published data.

Conclusions

The phase diagram of the binary system urea:choline chloride was established using complementary tools. The thermostated bath permits working with samples on the gram scale, which are representative of practical applications. The sensitivity to observe the last particles (determination of the liquidus temperature) is much higher when using optical microscopy compared to the thermostated bath. Over the determination of the phase transition, DSC experiments also give access to the energy associated with the phase transition. The melting temperature at eutectic composition (two molecules of urea per choline chloride) is 25 °C, a value higher than the previously reported data. This difference is mainly due to the presence of water. Its impact on the melting temperature was studied in detail for the first time. After 48 hours in contact with atmosphere, the sample absorbed 5.5 wt% of water. This quantity leads to a decrease of more than 15 °C of the melting temperature. This result could explain the discrepancies observed in the literature on the melting temperatures of eutectic systems. Quantification of the water content in DES should be done systematically for any physico-chemical characterization as well as for applications.

Acknowledgements

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