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X-Ray structure and ionic conductivity study of an anhydrous and hydrated choline chloride and oxalic acid deep eutectic solvent

Lorenzo Gontrani^{*a}, Matteo Bonomo^{*b}, Natalia V. Plechkova^c, Danilo Dini^b, Ruggero Caminiti^b

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In this study, we report the structural, thermodynamics and electrochemical properties of the Deep Eutectic Solvents constituted by choline chloride and oxalic acid, in anhydrous and di-hydrated form in a 1:1 molar ratio.. As far as we are aware, the employment of X-ray diffraction technique to analyze the structural features of DESs is here reported for the first time.

The combination of alkylammonium salts with metal salts and/or hydrogen bond donor like organic acids¹, is known for producing new phases (DESs²⁻⁴) with values of melting point, density, viscosity, surface tension, solubilizing action, optical transmission and electrical conductivity that are remarkably different with respect to the parent components⁵⁻⁹. For this reason, DESs have attracted enormous interest from the materials scientists community since their discovery reported by Abbott and his team in 2001².

The possibility of modulating the remarkable chemical-physical properties of DESs upon addition of controlled amounts of water^{10,11} and/or upon dissolution of inert gases has further motivated the researchers to define and prepare new formulations of DESs for innovative, green and inexpensive procedures to be adopted in materials processing, mass production of chemicals and chemical sensing at various scales of detection. Another added value of DESs is their generally scarce toxicity, a feature which marks DESs as the solvents of next generation with respect to ionic liquids (ILs)¹². From these considerations it is easy to conclude that DESs represent the most advanced choice of solvents in terms of sustainability, biodegradability, versatility, capability of stabilizing/suspending solutes.

Throughout this paper, physical (viscosity, density) and electrochemical (conductivity) properties will be investigated and they will be discussed in view of the DES structure obtained from XRD measurements. The Energy Dispersive variant, EDXD¹³⁻¹⁶ that allows gathering high-level diffraction patterns with large q range ($0.5-24 \text{ \AA}^{-1}$) using lab instruments, was used [see Supporting Information for details]. This leads to both a substantial cost reduction and a greater amount of data with large repeatability compared to Synchrotron large-scale facilities. XRD data are further strengthened by theoretical calculations (i.e. molecular dynamics), that were found to be in excellent agreement with each other. All the techniques employed converged to the same result and point out the key-role of water as additional component of DES structure. As far as we are aware, this is the first example of determination of DES

structure with X-ray diffraction in the liquid state, coupled to other techniques in a synergic approach. All the chemicals were purchased from Sigma Aldrich or Carlo Erba. Before utilization, Choline Chloride, ChCl (Oxalic Acid, OA, Oxalic Acid dihydrate, OA*2H₂O) was heated at 90 (80) °C for 24 hours to prevent the adsorption of water molecules. The temperature is sufficiently low as not to provoke the degradation of the starting material¹⁷.

Three different preparative approaches were developed: i) 30 mmol of anhydrous oxalic acid (M.W. 90 g/mol from Sigma Aldrich) were mixed with 30 mmol of ChCl to form DES termed A; ii) to verify the influence of water crystallization molecules in the formation of DES, 30 mmol of di-hydrated oxalic acid (OA*2H₂O, M.W 126 g/mol from Carlo Erba) were mixed with an equimolar amount of ChCl: the DES obtained was named M; iii) the samples obtained from preparation ii) were processed with a RotaVapor system for different timespans (i.e. 3, 24, 36, 48, 72 hours). After 72 hours the DES (named B) reached a constant weight. Very interestingly, the loss in weight (1.08 g) exactly corresponds to 60 mmol of water. This led us to hypothesize that the DES named A and B possess the same structure following on from the complete removal of the crystallization water molecules.

Table 1 Crystallization temperatures (K) and densities (kg*L⁻¹) of ChClOx DES at 298.15 K.

	Crystallization Temperature (K)	Density [§] (Kg L ⁻¹) at 298.15 K
ChClOx_A	285	1.282
ChClOx_B	286	1.280
ChClOx_M	267	1.228

§ Densities measured with an U-tube densimeter (details in Supporting Information) and by weighing given volumes of sample agree within 0.5%

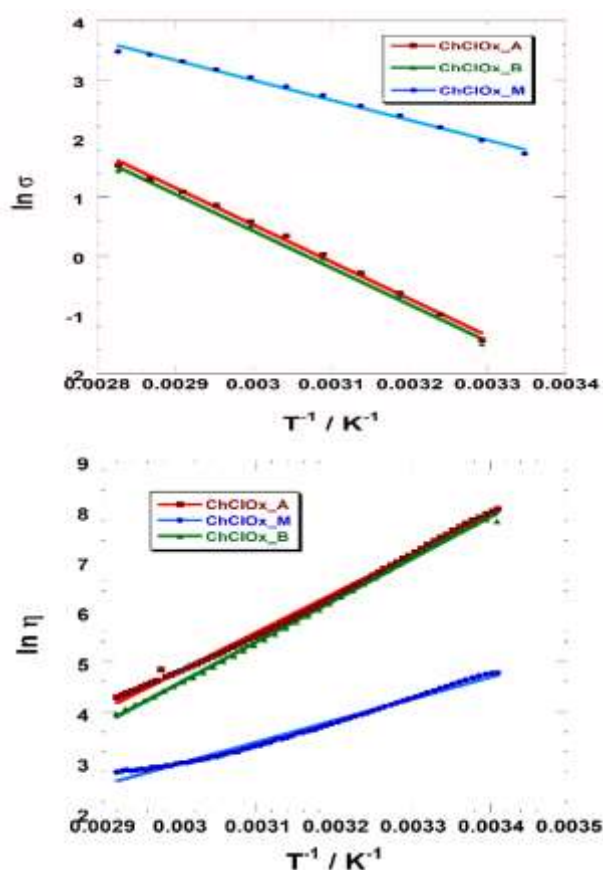


Figure 1. Conductivity (left) and viscosity (right) trends of the three different DES (ChClOx_A, red squares; ChClOx_B, green triangles; ChClOx_M, blue dots) as a function of the inverse of absolute temperature. Straight lines refer to the interpolation of experimental data. Conductivity was measured by electrochemical impedance spectroscopy as previously made for similar compounds as ILs in²⁰.

These three different approaches led in every case to the formation of colorless and odorless liquids, that appear to be stable at room temperature, as it can be seen in Fig. S2, at least for the time needed for X-Ray, density, viscosity and conductivity measurements. Considering the studies by Abbott *et al.*² and very recently by Gilmore *et al.*¹⁸, we cannot rule out completely that these systems remained undercooled. Yet, the weight loss, the conductivity studies (Fig. 1) and the infrared spectroscopy analyses (additional material, Fig. S3) make us confident that the water content was negligible and kept to a minimum. Very interestingly, the complete production of DES is quicker when OA*2H₂O is employed. In more detail, using di-hydrated oxalic acid, the DES is completely formed after a couple of hours, whereas anhydrous OA required more than 48 hours. The latter evidence stressed that the presence of two molecules of water somehow speeds up the kinetics of the eutectic mixture formation. A first proof of the similarity between samples named A and B was obtained by the analyses of crystallization curves (Table 1): ChClOx_A and ChClOx_B showed similar crystallization temperatures (i.e. 285 K and 286 K, respectively), while the value drops at 267 K for ChClOx_M. A whole explanation of these findings requires a thorough assessment of the interactions that are established between the building blocks of DES structures, molecules and ions¹⁹. Generally speaking, the greater the number of the intermolecular interactions established in DESs (e.g. hydrogen bonds) and their magnitude, the lower the crystallization temperature. Very interestingly, this point was also confirmed by the different values recorded for the ChClOx density.

Both conductivity and viscosity data (in their logarithmic form) were interpolated using a linear fitting², where $\sigma(\eta)$ is the measured conductivity (viscosity), σ_0 (η_0) is a constant value, R is the gas constant, T is the absolute temperature (in K) and E_A (E_η) is the activation energy for conduction (activation of viscous flow, see table 2):

$$\ln\sigma = \ln\sigma_0 - \frac{E_A}{RT} \quad \text{and} \quad \ln\eta = \ln\eta_0 + \frac{E_\eta}{RT}$$

The goodness of the linear interpolation is slightly lacking for ChClOx_M at temperatures higher than 343 K. This evidence is probably due to the presence of the crystallization water molecules than at relatively high temperature tend to partially evaporate: the higher the occurrence of such phenomenon, the lower the conductivity and the higher the viscosity of the DES. Similar deviations were not recorded for the anhydrous DES. Parameters obtained by the linear fitting are reported in table 2.

The significantly higher values of E_A recorded for ChClOx_A and ChClOx_B compared to ChClOx_M refer to the larger energy required to activate the conduction in anhydrous DESs as well as their higher viscosity. Probably, the two crystallization water molecules remain partially frozen in their crystallization positions, leading to a weaker complexation between choline/acid moieties and chloride ions, that are consequently freer to flow throughout the DES structure, with lower hindrance to the conduction²¹. Such “frozen” water molecules cannot act as a solvent, as suggested by the higher conduction values (and lower E_η) observed when liquid water is added to the anhydrous salt (data not shown). To further strengthen this hypotheses we performed coupled XRD-MD experiments. The qualitative effect of water on DES structure can be rapidly assessed from the analysis of raw diffracted intensity data from the two systems, shown in Fig. 2. While ChClOx_A and ChClOx_B exhibit very similar patterns, the intensity in ChClOx_M is much lower.

A more quantitative appraisal is provided by the comparison of structure functions $I(q)$ -Fig. 3- and of their Fourier transform, total radial distribution functions (Supplementary Material) with the analogous patterns calculated from molecular dynamics trajectories for ChClOx_A and ChClOx. Functions definition and simulation details are given as supplementary material. The agreement between experiment and simulations is very satisfactory at all ranges of q

(structure functions) and r (Radial distribution function), suggesting that the model built is highly descriptive of the liquid structure. Once the model was confirmed by comparison with experimental data, the simulation trajectory was used to gather some features useful to shed light on the structural interactions occurring in the liquid phase. First, the partial radial distribution functions (pair distribution function, $g(r)$) of the contacts between chloride anion and the oxygen atoms of choline, and oxalic acid, which are shown in Fig. 5 in black, and red for the di-hydrated sample, and in grey/magenta for the anhydrous one, respectively. Cl-water oxygen and water-oxygen/water oxygen contacts are shown in green and blue. All the distributions point out the pivotal role of chloride ion in tearing apart the structure of the solids, by lowering their lattice energy and by forming a liquid structure in which the ion is mutually solvated by the other partners, forming strong cooperative interactions. Notably, chloride-oxalic acid interactions (black and red lines of Fig. 5) occur at larger distances in the hydrated model than in the anhydrous system (grey and magenta lines of Fig. 5) and the peak intensities are greater. Water molecules take part actively to DES structure, and the first-shell correlations peak of bulk water (blue line of Fig. 5) is reduced to a very broadened peak, signalling that water-water interactions are often mediated by other fragments. These $g(r)$ patterns comply with the main peak of $I(q)$ shift at lower q (Fig. 3, inset), sign of the system swelling induced by water. Thus, water molecules seem to take part actively to the DES structure. This feature does not comply entirely with a recently published study by Hammond *et al.*²² describing the substantial preservation of DES nanostructure upon hydration in malicine (choline-chloride plus malic acid); this could be ascribed to the effect of the strong chelating attitude of hydroxyl substituted acids.

A pictorial representation of the interactions in anhydrous and hydrated DES can be identified in the typical structural motifs that can be identified in the trajectory, like those shown in Fig. 4. Obviously, this structural picture is to be intended in a statistical sense, and the distance between the atoms vary continuously over time along the simulation.

Table 2 Limit conductivity (σ_0) and viscosity (η_0) for ChCl-OX DES from data fitting (see Fig. 1).

	$\ln \sigma_0$	$E_A / \text{kJ mol}^{-1}$	R^2	$\ln \eta_0$	$E_\eta / \text{kJ mol}^{-1}$	R^2
ChClOx_A	19.4	52.3	0.99	-18.1	63.3	0.998
ChClOx_B	19.2	52.1	0.99	-20.5	69.3	0.999
ChClOx_M	13.1	28.2	0.99	-9.46	34.4	0.985

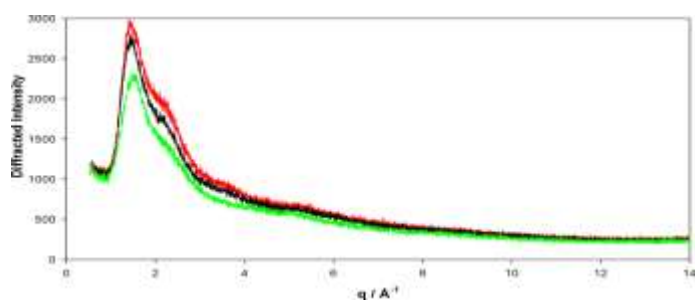


Figure 2 X-Ray Diffracted Intensity of ChCl-OX DES. ChClOx_A (red) ChClOx_B (black) ChClOx_M (green)

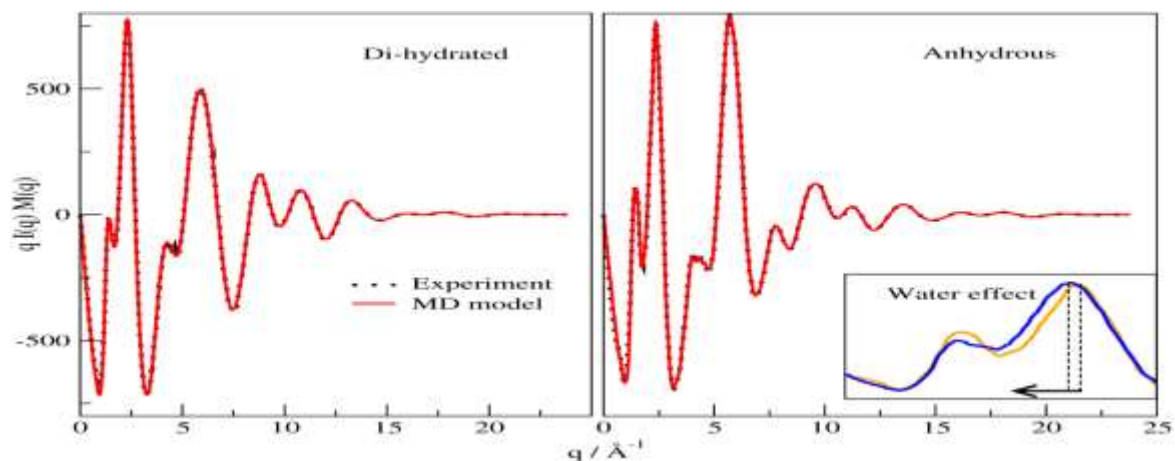


Figure3 X-Ray Structure function of ChClOx_M(left) and ChClOx_A (right) Dotted: experiment; continuous, red: MD model

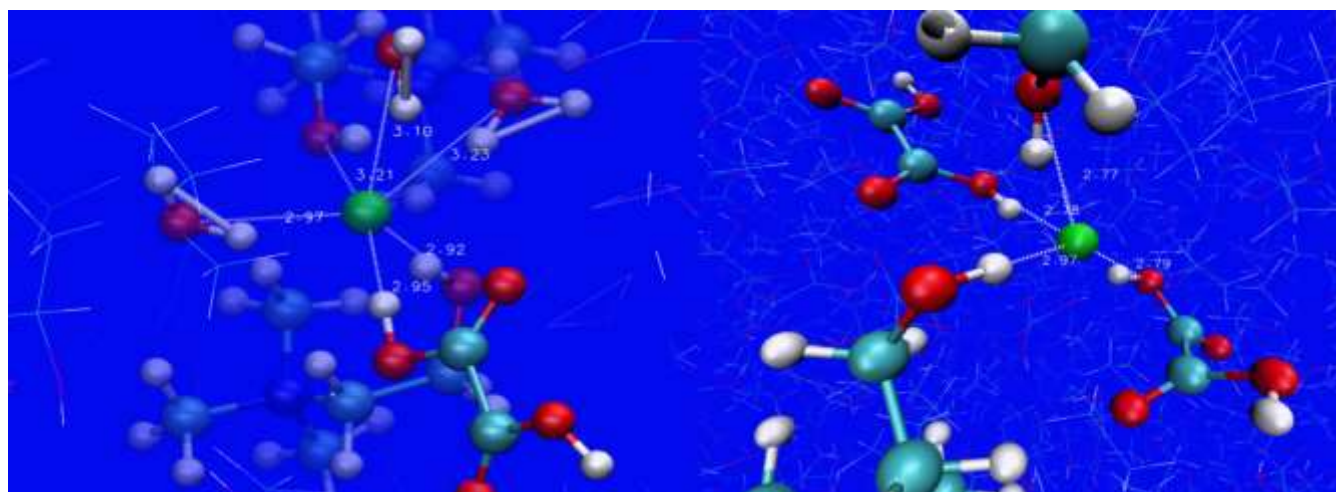


Figure 4 Typical coordination of chloride anion in ChClOx_M (left) and ChClOx_A (right), taken from a trajectory frame.

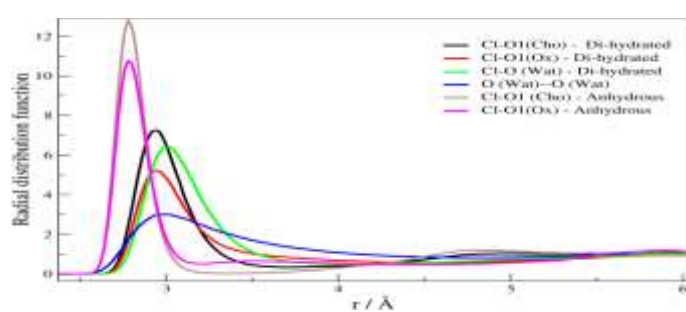


Figure 5 Chloride-oxygen Radial Distribution Functions: ChClOx_M (black, red, green), ChClOx_A (grey, red) and water-water of ChClOx_M

Conclusions

Summarizing, in this work we have employed Energy Dispersive X-Ray diffraction to investigate on the structure, and performed density, viscosity and conductivity measurements to assess the properties of the liquid Deep Eutectic Solvent formed by choline chloride and oxalic acid, both with and without crystal waters. The observed rather high

conductivity and the relatively good thermal stability observed in these liquids, particularly when hydrated oxalic acid is used, could foreshadow their effective application as electrolytes in (photo)electrochemical devices in place of ionic liquids.

Notes and references

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