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DFT Analysis of the Gas Phase Interactions of Choline Chloride with Urea

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Abstract Choline chloride and urea interact to form a Deep Eutectic Solvent widely used as a green solvent in several applications such as electrochemistry, chemical substance separation and reactions. We searched for the equilibrium geometries, charges distributions of model compounds of their respective associated complexes of 1:1, 1:2 and 1:3 ratios. The calculated interaction energies indicate that several stable conformers of the DES may form and coexist in the solvent medium. Beside coulombic interactions, NBO analysis shows that the through bond interactions between occupied orbitals and empty antibonding molecular orbitals contribute to spread the electronic charge and stabilize the systems. These interactions involve mainly the lone pairs of the electronegative elements Cl, N and O so that H-bonds of the type C=O---H-O, Cl---H-N, Cl---H-C and C=O---H- link the various neutral and ionic fragments in the model compounds of the solvent. Calculated Wiberg bond indices revealed the partial covalent nature of these H-bonds.

Keywords Density functional theory calculations, Choline chloride-urea compounds, Deep eutectic solvents, NBO analysis, H-bonds

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1. Introduction

The investigations on safe solvents that protect ecosystems nowadays have paved the way to the synthesis in 2001 by Abbott and coworkers [1-2] of novel mediums called deep eutectic solvents (DES) or low temperature transition mixtures (LTTM). Since then, these solvents have gained great interest and continuing research is done on their development and the understanding of the physical and chemical properties that they display. They are liquid over a certain range of temperatures, have negligible volatility as compared to traditional solvents such as organic solvents and show good thermal stability and electrical conductivity. As such, they are candidates for reaction mediums in the fields of material science, electrochemistry and biochemistry [3-7]. These important fields of application of DESs require that their geometric structures and their electronic charge distributions as well as their physico-chemical properties be well defined in order to offer optimal conditions for their use.

A deep eutectic solvent (DES) is defined as a mixture of two or more components which has a temperature of its eutectic point significantly below that of its ideal mixture. Studies done on the solid-liquid phase diagrams have shown that such mixtures present negative deviation from ideality at their eutectic point with specific ratio of the components and are liquid at operating temperatures over a certain range of composition [2,8-9]. They are mainly mixtures of Lewis or Bronsted acids and bases, which may be neutral or ionic. DESs that do not contain metal ions or metal free DES [10] are well established and an example of this category of solvents is the mixture of choline chloride and urea in a 1:2 ratio. This solvent contains a quaternary ammonium salt and urea as interacting agents. It is argued that the lowering of the eutectic point below the ideal one is due to interaction between the species through H-bonding so that the preparation of these solvents implies appropriate selection of the H-bond donor and acceptor.

For the particular case of the metal-free DES made of choline chloride (ChCl) and urea (U), several experimental and theoretical studies have been done in attempts to characterize it and to understand its properties. Abbot and al. [2] have studied the phase diagram constructed from measurements of freezing points and showed that the eutectic point of the solution has a temperature of 12 ℃ with a composition of 1:2 ratio of respectively choline chloride and urea. At this composition, the mixture is referred to as reline. By using DSC technique, Morrisson et al. [11] have obtained an eutectic point of 17 ℃ and a similar composition of the mixture. Later on, Meng and coworkers [12] have done a more extensive study on the phase diagram of this DES by measuring the melting point of different mixtures

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containing known amounts of water via DSC and optical microscopy techniques. Their results indicate that the presence of water greatly influences the interactions between the two components and therefore the physico-chemical properties of the DES. At the eutectic composition ratio of Abbot and al., their measured melting temperature was 25 ℃. The difference in the various measured eutectic temperatures is explained by the presence of water in the DES, as the constituents are hygroscopic. Water induces formation of new interactions with the polar constituents and therefore affects the density, viscosity and electrical conductivity of the mixture. These authors suggested that properties of DESs be measured on water free samples. The formation of H-bond in water free mixtures has been suggested from the liquid phase neutron diffraction measurements of isotopically substituted samples by Hammond et al. [13] and the IR and NMR investigations of Perkins et al. [14-15]. Ashworth et al. [16] have done a theoretical study of pairwise interactions between the constituents and of clusters of Cl^- with urea. This extensive work on conformers of pairs of species by DFT has revealed a network of H-bonding within the pairs of neutral and ionic species. They calculated interaction energies of these conformers in order to understand the basis of the H-bond formation. In this interesting analysis of the interactions of pairs of fragments of the DES, geometries and charge distributions have not been detailed to link the structures to the observed H-bonding. The present work is a continuation of the study on the interactions between choline chloride and urea based on model systems composed of several ratios of these constituents. We report calculated geometrical structures of urea, choline chloride and their associated compounds. We search for the gas phase optimal geometries and charge distributions of the constituents and the model compounds of reline that would enlighten our understanding of their structural, bonding and physico-chemical properties.

2. Computational Methodology

The work consists of a DFT [17] study of the geometries, energies and electronic structures of the fragments choline chloride and urea as well as those of their successive associations to form model compounds of reline. The GaussView06 software [18] was used to construct and visualize the various systems. Then optimized geometrical parameters, energies and charge distributions were carried out by the Gaussian 09 software package [19] by using the gradient corrected hybrid functional BYL3P [17] along with the standard 6-31+G(d,p) basis set which is a split valence band basis with polarization and diffuse functions to well describe bond formation and charge delocalization. No symmetry constraints were maintained during the optimization of the compounds. Vibrational frequencies were calculated at each optimized structure to characterize it as a minimum. The total energies are all ZPE corrected. The mechanism of charge delocalization through bonds in these systems was studied by performing NBO calculations on the optimized structures with the NBO codes provided by the Gaussian 09 package. Atomic charges were also calculated by using the NBO subroutine. The covalent nature of the bonds was analyzed by calculating Wiberg bond indices in the optimized species.

3. Results and Discussion

3.1. Geometries and Energies

The model compounds of the DES reline were investigated by starting with a search of the minimum structures of the fragments urea and choline chloride. Table 1-3 contain respectively the energies and optimized geometrical parameters of urea $CO(NH_2)_2$ (or U), its dimers, the choline cation $[(CH_3)_3N(CH_2)_2OH]^+$ (or Ch^+), choline chloride $[(CH_3)_3N(CH_2)_2OH]Cl$ (or ChCl) and experimental results on urea. Figure 1-3 display their respective optimized structures.

a. Urea monomers and dimers

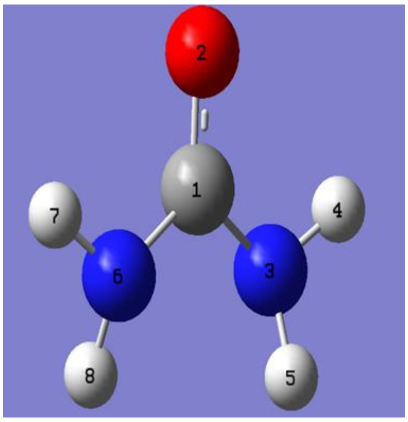
The equilibrium structure of urea is basis set dependent and our results in Table 1 and Figure 1a-c indicate that the conformation of C2 symmetry is its stationary structure while the others of C2V and Cs symmetries are respectively second and first order saddle points. The dihedral angles OCN_3H_4, OCN_3H_5 and $N_6CN_3H_4$ in the C2 minimal energy conformer have respective values of 11.8°, 152.3° and -168.2°. These parameters along with the calculated bond lengths and bond angles reproduce quite well the microwave results of Godfrey and al. [20] as well as the gas phase data obtained at the MP2/6-31G(d, p) and MP2/6-311G(d,p) by Raptis and coworkers [21]. This attests of the good quality of the basis set used in our approach. Oher experimental geometries of urea from neutron diffraction and X-rays analysis gave a planar structure with C-O and C-N bond lengths of 1.265Å and 1.349 Å respectively [22-24]. This CO bond length obtained in solid state is longer than our calculated gas phase value and may be due to intermolecular interactions. The structures of dimers of urea have been also explored and are shown on figure 1.d-f. They are true minima and the interaction energies, which range from -50.6 to -37.8 $kJ.mol^{-1}$ indicate that they are stable gas phase structures. One may notice that the interactions between two urea molecules cause elongation of the C-O and N-H bonds and opening of the C-N-H angles of interacting groups. The structural arrangements of these dimers in figure 1d-f well illustrate the proton donor and acceptor ability of urea through its N-H bonds and the lone pairs of electrons on its N and O atoms. One therefore expects urea to play a central role in the formation of compounds with choline chloride.

Table 1. Energies and geometries of optimized urea monomers and dimers

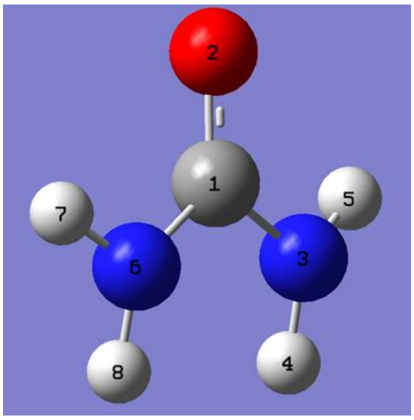
System	Energy (H)	Geometric parameters$^{(a)}$							
		d_{C-O}(Å)	d_{C-N}(Å)	d_{N-H}(Å)	Θ_{N-C-N}(°)	Θ_{O-C-N}(°)	Θ_{C-N-H}(°)	Θ_{H-N-H}(°)	DE kJ.mol^{-1}
Urea, C_{2v}	-225.2902636	1.227	1.377	1.007	115.3	122.3	116.9;124.1	119.0	-
Urea, Cs	-225.2905297	1.226	1.381	1.008	115.3	122.3	115.1;121.9	117.0	-
Urea C_2	(-225.2917616) -225.228116	1.225	1.386	1.010	114.4	122.8	113.6;118.9	115.2	-
Urea C2^{ref}	-224.645238	1.225	1.390	1.008	112.9	123.5	111.9;116.0	113.6	-
Urea experim	-	1.221	1.378	1.021; 0.998	114.7	122.6	112.8; 119.2	118.6	-
Urea dimer (d) C1	-450.475503	1.240 1.240	1.385; 1.361	1.01; 1.027	116.2 116.2	120.6 120.6	117.4; 120.0	115.4;117.4	-50.593
Urea dimer (e) C1	-450.470352	1.227 1.238	1.367;1.408 1.368;1.379	1.019;1.015 1.010 (2.158)	113.9 116.0	124.5;121.6 122.6;121.4	120.0;115.5 120.5;116.0	119.0;113.5 117.7;116.0	-37.072
Urea dimer (f) C1	-450.470237	1.227; 1.238	1.366;1.409 1.368;1.379	1.018;1.015 1.010	113.9 116.2	124.5;121.6 122.5;121.3	119.9;115.4 115.9;114.5	119.0;113.5 117.5;116.1	-36.770

$^{(a)}$(distances in Å)

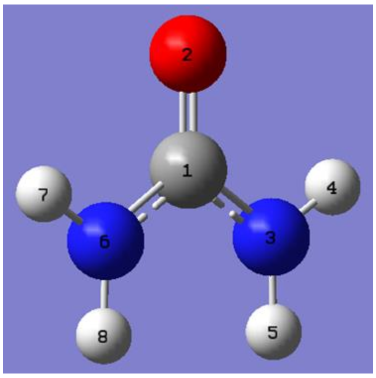
Torsional angles: OCN_3H_4 =0.0 ° and OCN_3H_5 =180.0 ° for urea $C_{2V;}$
Torsional angle: OCN_3H_4=11.836 ° and OCN_3H_5 =152.325 °; $N_6CN_3H_4$ = -168.2 for urea C2
Torsional angle: OCN_3H_4= 164.594 ° and OCN_3H_5= 12.461 ° for urea Cs
Dimers:
- Conf 1 : $d_{O6---H13}$ = $d_{O14---H8}$ =1.859 Å
- Conf 2 : $d_{N3—H13}$ = 2.158Å; $d_{O14----H4}$ =1.990Å; $d_{O14----H7}$ = 2.708Å
- Conf 3 : $d_{N2---H13}$ =2.159 Å; $d_{O14---H4}$ = 2.676 Å; $d_{O14---H7}$ = 1.993 Å



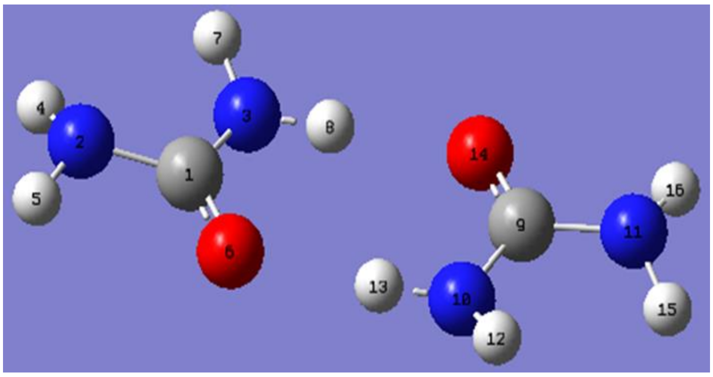
a) Urea (C2)



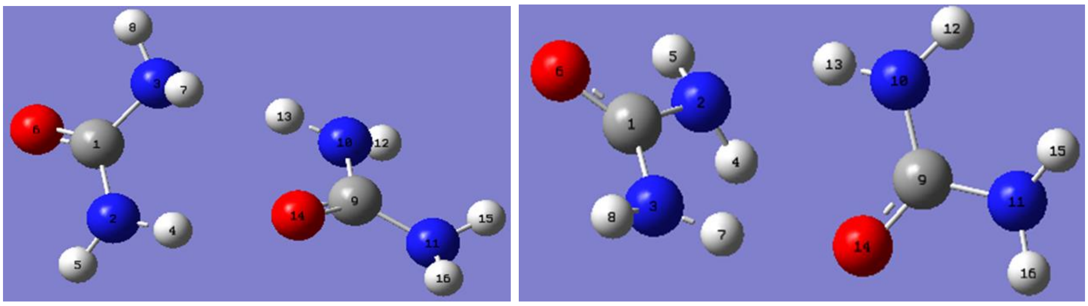
b) Urea (Cs)



c) Urea (C2v)



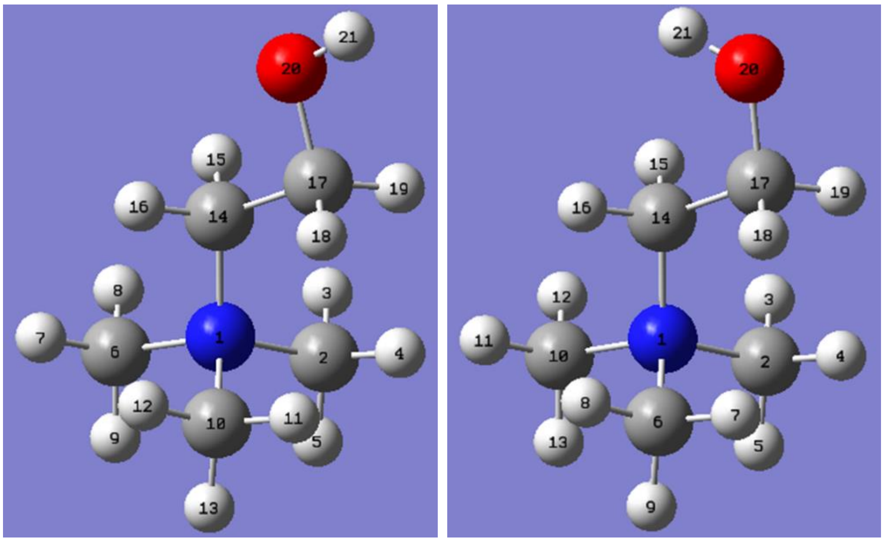
d) Urea Dimer (Conformer 1)



e) Urea Dimer (Conformer 2)

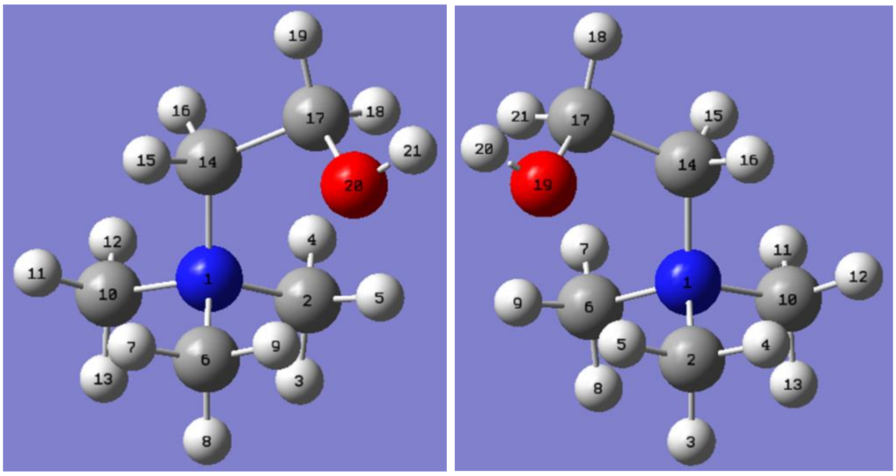
f) Urea Dimer (Conformer 3)

Figure 1. Optimized structures of urea monomers and dimers



a) T1

b) T2



c) G1

d) G2

Figure 2. Optimized structures of Conformers of the cholinium cation

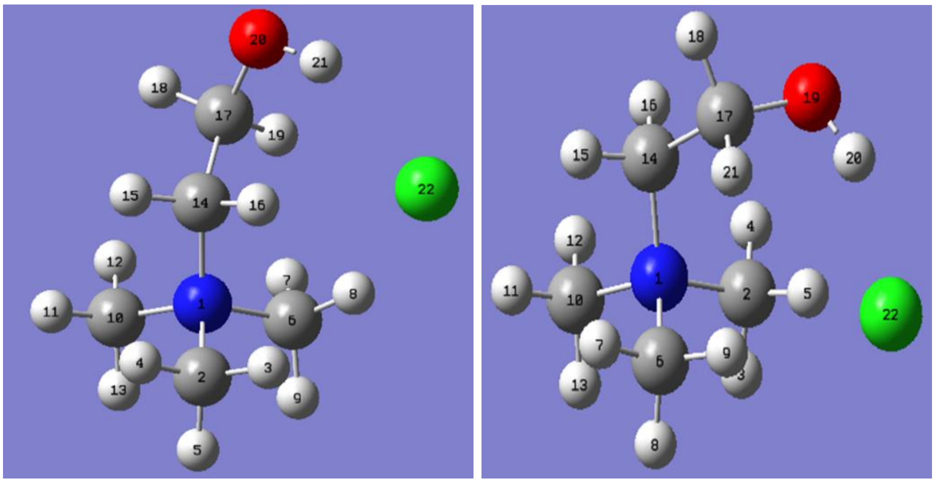
b. Choline cation and model compounds of choline chloride

Choline cation Ch^+

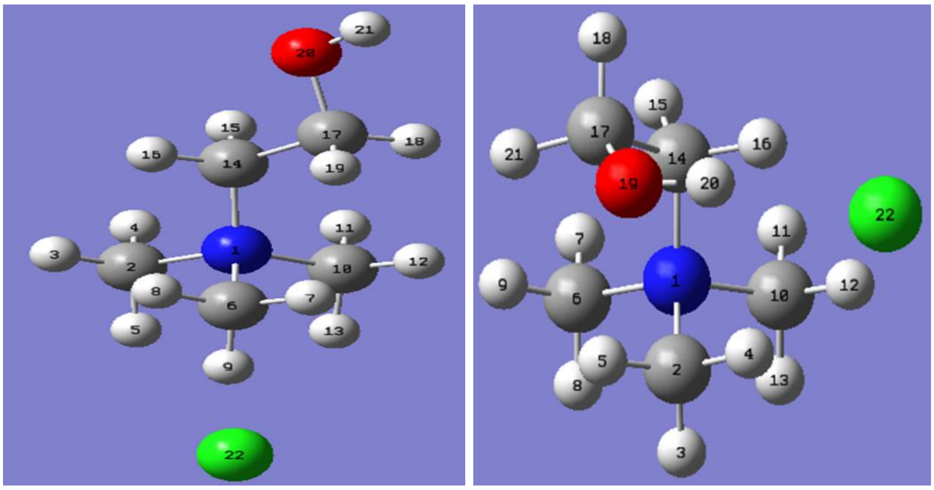
Three conformations of the equilibrium structures of the choline cation noted Trans T1, Gauche G1 and Gauche G2 are found in our work and are pictured in Figure 2. The Trans conformer T2 with OH rotated is a first order saddle point. Table 2 presents their geometries and energies. The notation Trans and Gauche is related to the position of the C-O and C-N bonds with respect to the ethyl C-C chain. These conformational isomers differ also by the N-C-C-O torsional angle, which is 58.2 ° in the Gauche but 180 ° in the Trans suggesting that the C-N and C-O bonds are coplanar in the Trans isomers. The gauche conformers G1 and G2 are lower in energy and are found here as mirror images of one another as indicated by the opposite values of the dihedral angles C-N-C-C, C-C-O-H and N-C-C-O. The results for the bond length C-O (1.415-1.419Å), C-N (1.510-1.534 Å), C-C (1.523-1.534 Å), O-H (0.967 Å) and C-H (1.087-1.098 Å) and those of the bond angles obtained in these minimum structures are typical of standard organic compounds.

Choline chloride ChCl

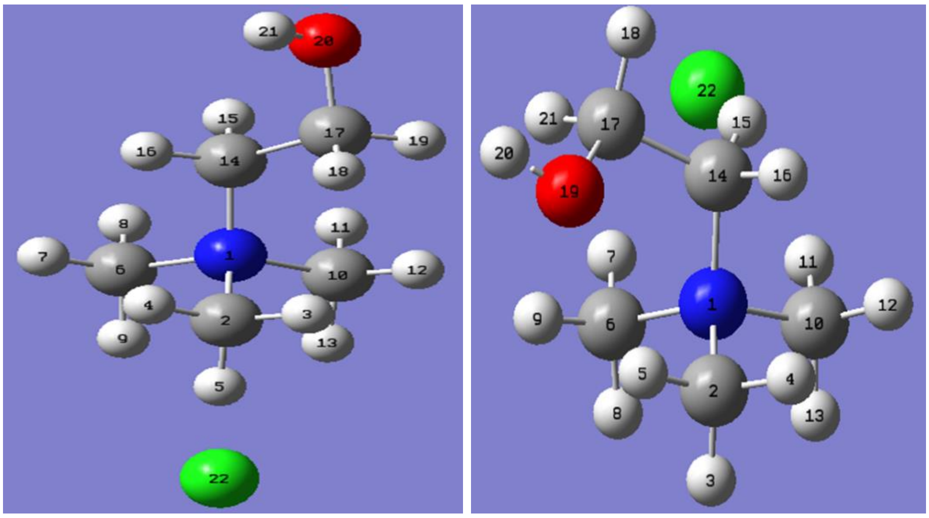
Addition of the chloride ion by positioning it at different locations around the Ch$^+$ cation of Trans and Gauche conformations has given five (5) minimum energy model compounds of choline chloride of each conformer noted T1a-e and G1a-e. Table 3 gives their geometrical parameters, energies, and figure 3 displays the minimum structures. These equilibrium structures of the choline chloride agree with the theoretical B3PYP/6-311+G(d, p) results of Ashworth and coworkers [16]. However, our study revealed two more minimum energy structures noted T1d and T1e. These conformational isomers of choline chloride are very close in energy and the most stable conformer G1a lies 40.288 kJ.mol^{-1} below the least stable T1e. The position of Cl$^-$ relative to the choline cation is crucial in the stabilization of each of these systems. As the geometrical parameters indicate, the most stable compounds are those where Cl$^-$ interacts with the hydroxyl group along with its closed approach to H atoms of the methyl or ethyl groups. The closest d$_{OH---Cl}$ distances are 2.079Å for G1a, 2.222 Å for G1b and 2.335Å for T1a. These OH---Cl interactions cause distortion of the dihedral angle N-C-C-O. In all these ten (10) structures, Cl$^-$ sits at locations where it interacts closely with at least 3H atoms of the choline cation, causing the lengthening of the C-H and O-H bonds of the methyl, the ethyl and the hydroxyl groups relative to those found in the choline cation. However, contraction of the C-O bonds is observed where Cl---HO interactions occur. The reported B3LYP/6-31+G(d,p) value of 2.391 Å for CH$_{meth}$----Cl in choline chloride of Cs symmetry of Davis and coworkers [25] correlates well with the present values for T1b, T1c and G1e of C1 symmetry. The interaction energies of Cl$^-$ with Ch$^+$ are respectively -392.6 and -396.4 kJ.mol^{-1} for the most stable compounds T1a and G1a (Table 6). As pointed out by other authors [26], these values are typical for gas phase ionic salts containing organic cations and have mainly coulombic contribution. Intramolecular interactions also exist within the choline cation involving its oxygen atom and surrounding nearest H atoms.as indicated by the O---H distances varying from 2.02 to 2.52Å.



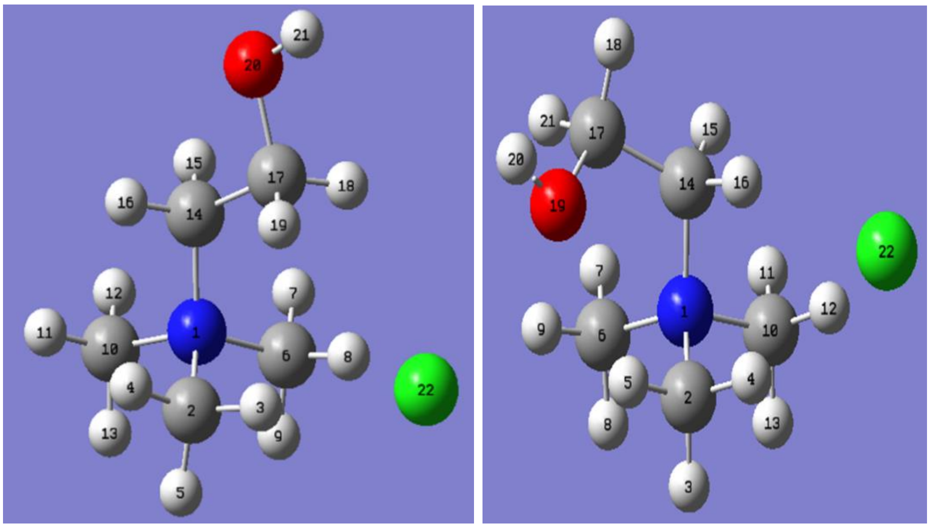
a) T1a *f) G1a*



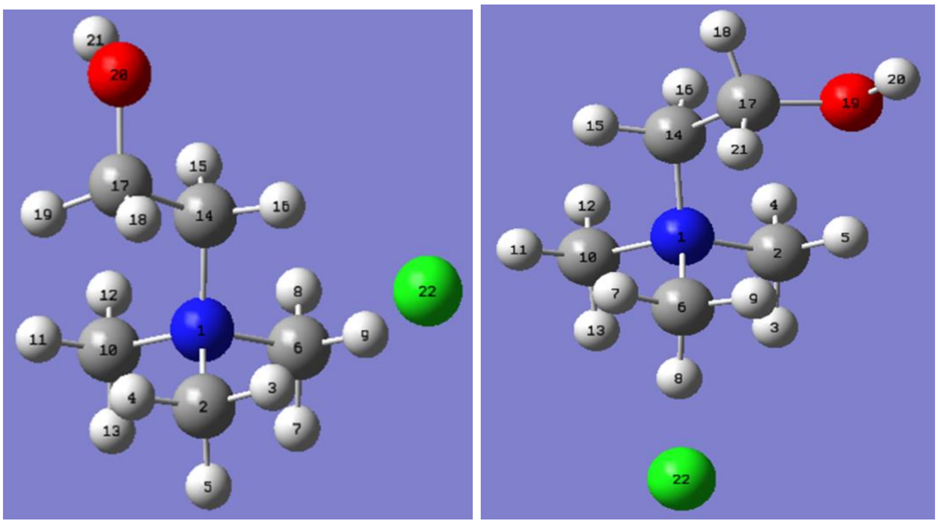
b) T1b *g) G1b*



c) T1c *h) G1c*



d) T1d *i) G1d*



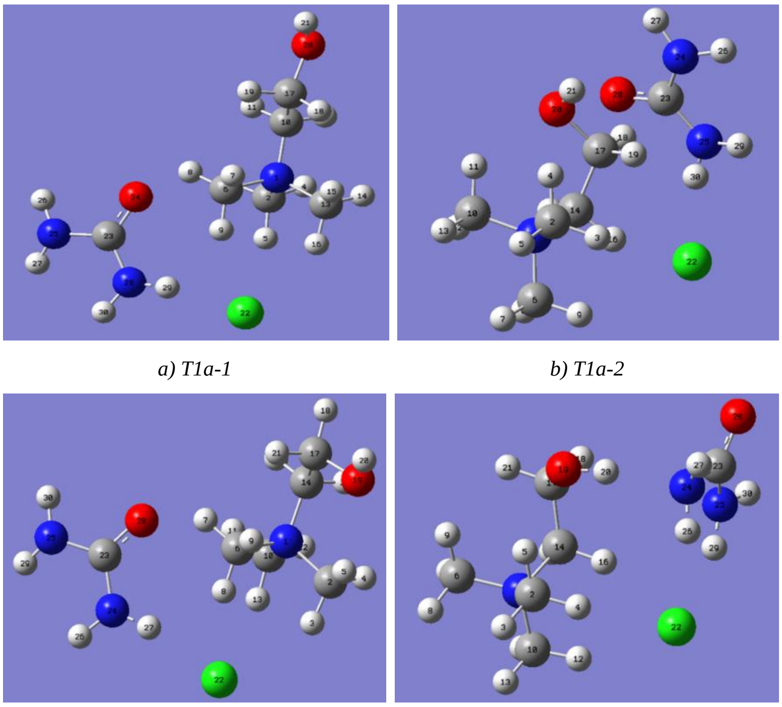
e) T1e *j) G1e*

Figure 3. Optimized structures of conformers of choline chloride

Table 2. Energies and geometries of optimized choline cation monomers

System	Energie (H)	Geometric parameters$^{(a)}$									
		$d_{C\text{-}H\ meth}$	$d_{C\text{-}Heth}$	$d_{N\text{-}Cmet}$	$d_{N\text{-}Cet}$	$d_{C\text{-}O}$	$d_{O\text{-}H}$	$d_{C\text{-}C}$	C-N-C-C	C-C-O-H	N-C-C-O
Conformer 1 Trans (T1)	-328.515532	1.090	1.092 1.098	1.512	1.524	1.415	0.967	1.532	61.1 ° -61.2 ° 180.0 °	180 °	180.0 °
Conformer 2 Trans (T2) O-H rotated	-328.7032084 (one imaginary frequency)	1.090	1.094 1.096	1.511	1.528	1.416	0.966	1.533	61.0 ° -61.1 ° 180.0 °	-0.013 °	180.0 °
Conformer 1 Gauche (G1)	-328.521938	1.090 1.087	1.092 1.098	1.510 1.516	1.534	1.419	0.967	1.523	-43.1 ° 78.7 ° -162.8 °	-167.3 °	-58.2 °
Conformer 2 Gauche (G2)	-328.521938	1.091 1.087	1.092 1.098	1.510 1.516	1.534	1.419	0.967	1.523	-78.7 ° 43.1 ° 162.8 °	167.3 °	58.2 °

$^{(a)}$(distances in Å)



a) T1a-1 *b) T1a-2*

c) G1a-1 *d) G1a-2*

Figure 4. Optimized conformers of 1:1 complexes of choline chloride and urea

c. Model compounds of choline chloride and urea

Systems of one urea and one choline chloride

The present work explored several positions of one molecule of urea around the previous structures of choline chloride and this gave several model systems very close in energy. The conformers T1a and G1a, led to many minimal structures among which were the four most stable ones noted T1a-1, T1a-2, G1a-1 and G1a-2 shown in figure 4. Table 4 contains their ZPE corrected energies and geometrical parameters. The main NCCO backbone of Ch^+ is retained. However, a main change occurs on the T1a-2 structure where the torsional N-C-C-O angle approaches that of the gauche conformers (-50.6 °instead of -155.4 °in T1a). One may also observe that urea assures a perfect link to each of the two ions by interacting with them via either its carbonyl or its amino end. The choline cation is associated to Cl^- through at least three H atoms and to urea by one or two H atoms. The pairwise interactions of the three fragments occur therefore through the H atoms. In the two lowest energy structures T1a-2 and G1a-2 for instance, one observes CO_{ur}---HO and CN_{ur}---HO respective close approach of 1.93Å and 1.91Å. The data in Table 6 show that the attachment energies of urea to choline chloride (DE) are respectively -70.631 and -59.972 kJ.mol^{-1} for T1a-2 and G1a-2. The higher absolute value for T1a-2 may be due to the observed change in conformation.

Table 3. Energies and geometries of optimized choline chloride monomers [(a)]

Model system	Conformer	Energy (H)	$d_{H\text{---}Cl}$	$d_{C\text{-}H\ meth}$	$d_{C\text{-}Heth}$	$d_{N\text{-}Cmet}$	$d_{N\text{-}Cet}$	$d_{C\text{-}O}$	$d_{O\text{-}H}$ ($d_{O\text{-}Het}$)	$d_{C\text{-}C}$	C-N-C-C	C-C-O-H	N-C-C-O	$d_{N\text{---}Cl}$
Choline chloride trans from Choline cation Trans T1	T1a	-788.939787	2.335(OH) 2.364(1H_{et}) 3.279(H_{et}) (2.389(1H_{met})) 3.313(H_{met})	1.091 1.100	1.093 1.097	1.498 (1.516) 1.506	1.536	1.408	0.986 (2.071; 2.022)	1.541	166.6 ° 49.1 ° -73.8 °	66.5 °	-155.4 °	3.770
	T1b	-788.936030	2.376 2.389	1.090 1.100	1.092 1.097	1.514 1.516	1.509	1.424	0.966	1.529	180.0 ° 61.2 ° -61.3 °	180.0 °	180.0 °	3.597
	T1c	-788.934819	2.369 2.377 2.388	1.090 1.100	1.093 1.096	1.513 1.516	1.512	1.422	0.966 (2.088; 2.015)	1.536	61.2 ° -179.8 ° -61.0 °	81.6 °	175.5 °	3.592
	T1d	-788.933829	2.321(2H_{met}) 2.902(2H_{et})	1.101 1.091	1.093	1.515 1.502	1.519	1.433	0.966 (2.523)	1.528	60.8 ° -32.8 ° 180.0 °	-180.0 °	180.0 °	3.783
	T1e	-788.932304	2.356 2.372 2.406(H_{et})	1.100 1.091	1.100 1.092	1.514 1.500	1.531	1.419	0.966 (2.081; 2.006)	1.536	-54.6 ° -172.4 ° 68.108 °	68.4 °°	-169.1 °	3.568
Choline chloride Gauche from choline cation G1	G1a	-788.947649	2.079(OH) 2.875(H_{et}) 2.431(1H_{met}) 2.401(1H_{met})	1.091 1.098	1.093 1.101	1.517 1.511 1.501	1.533	1.400	0.996	1.532	-63.9 ° 58.0 ° 177.1 °	-108.5 °	71.3 °	3.860
	G1b	-788.946468	2.222(OH) 2.362(1H_{et}) 2.453(1H_{met}) 2.798(1H_{met})	1.091 1.094	1.095 1.103	1.517 1.498 1.510	1.539	1.405	0.991 (2.024; 2.083)	1.529	-44.643 ° 77.715 ° -162.978 °	39.1 °	68.6 °	3.649
	G1c	-788.942874	2.350(1H_{et}) 2.419(1H_{met}) 2.470(1H_{met})	1.091 1.098	1.095 1.100	1.502 1.510 1.512	1.535	1.434	0.966 (2.263H_{met})	1.513	-78.7 ° 44.0 ° 162.0 °	175.7 °	60.4 °	3.580
	G1d	-788.937192	2.581(H_{met}) 2.394(1H_{met}) 2.364(1H_{et})	1.091 1.099	1.094 1.100	1.519 1.514 1.496	1.533	1.426	0.965 (2.262H_{met})	1.521	-80.8 ° 41.8 ° 162.3 °	157.2 °	55.3 °	3.609
	G1e	-788.936976	2.453(H_{met}) 2.361(H_{met}) 2.365(H_{met})	1.091 1.100	1.093 1.100	1.518 1.511 1.515	1.516	1.422	0.966 (2.331H_{met})	1.522	-73.5 ° 48.9 ° 168.0 °	176.6 °	62.3 °	3.614

[(a)](distances in Å)

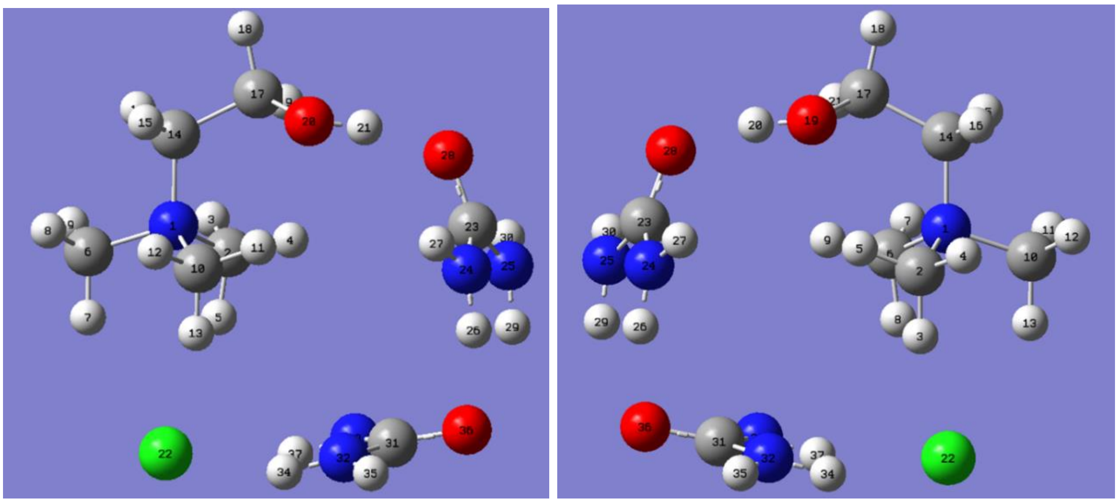
Table 4. Energies and geometries of optimized systems of choline chloride and 1 urea

Model system	Conformer	Energy (H)	Geometrical parameters [(a)]										
			d_{H---Cl}	$d_{C-Hmeth}$	d_{N-Cmet}	d_{N-Cet}	d_{C-O}	d_{O-H}	d_{C-Nur}	d_{N-Hur}	d_{C-Our}	$d_{COur---}$	C-O_{ur}-	N-C-C-O
Choline chloride Trans + 1 urea	T1a + U = T1a-1	-1014.186290	2.454 2.431 2.507 2.251(H_{ur})	1.088 1.095	1.518 1.514 1.510	1.509	1.425	0.965 (**2.462;** **2.642** O--H_{et}C)	1.357 1.390	1.009 1.029	1.241	2.338; 2.371 (HC_{met})	2.54 ° (CH_{me}) faced	169.9 °
	T1a + U = T1a-2	-1014.194805	2.356 2.655 2.916 2.260(H_{ur})	1.088 1.094	1.514 1.505 1.503	1.537	1.423	0.975 **(2.312** O--H_{met}C)	1.353 1.385	1.009 1.030	1.245	1.930 (HO)	68.6 ° (HO)	-50.6 °
Choline chloride Gauche + 1 urea	G1a + U = G1a-1	-1014.188262	2.732 2.413 2.434 (2.243)H_{ur}	1.088 1.095	1.512 1.512 1.517	1.517	1.425	0.966 (**2.330** O--H_{met}C)	1.356 1.391	1.009 1.030	1.242	2.273; 2.300 (HC_{met})	2.33 ° (CH_{me}) faced	65.5 °
	G1a + U = G1a-2	-1014.198607	2.585 2.525 (2.482) Het (2.388; 2.337)H_{ur}	1.088 1.094	1.516 1.497 1.510	1.535	1.410	0.988 (2.280 O--H_{met}C) **(1.911** O-H--N_{ur})	1.410 1.372	1.014 1.023 1.027	1.227	.	93.4 ° (HO)	63.1 °

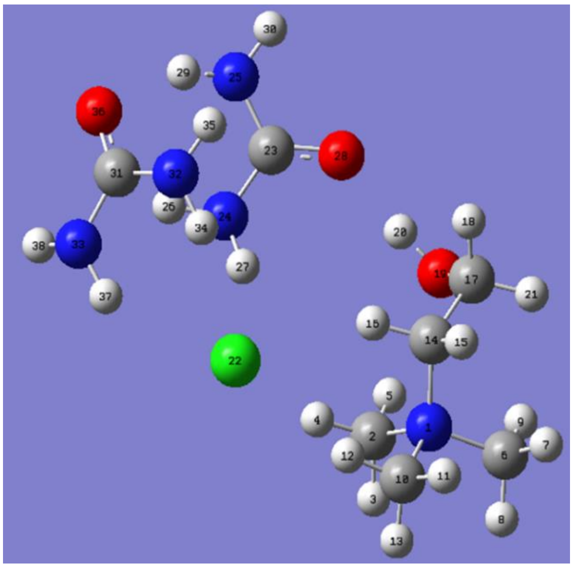
[(a)](distances in Å)

Systems of two urea molecules and one choline chloride

Experimental studies suggest that choline chloride and urea combine to form a complex of 1:2 ratio, used in liquid form as a green solvent for several purposes. We have therefore modelled this system and explored potential locations for H-bonding of urea with T1a-2 and G1a-2. Many optimized systems with positive vibrational frequencies were obtained and the two most stable in energy are displayed in Figure 5a-b. This shows that the first molecule of urea (by following the numbering of the atoms) interacts with the hydroxyl group of the choline cation Ch^+ while the second urea is connected to it and Cl^-. The chain of fragments is closed by the interaction of Cl^- with three H atoms of the methyl groups of Ch^+. These resulting two minimal structures of lowest energy formed from T1a-2 and G1a-2 with one additional urea molecule are mirror images as indicated by the NCCO, CO_{ur2}---CO_{ur1} and OC_{ur2}---Cl---N_{Ch} torsional angles in Table 5. As previously noted, the Trans T1a conformer of choline chloride adopts a gauche conformation upon addition of a urea molecule (T1a-2). This may also result from the presence of the two mirror images G1 and G2 of the gauche choline cation shown earlier in Figure 2. All the traditional C-C, C-N, C-O and C-H bonds are equivalent in both structures. Interestingly, one may notice that H-bonding imposes the four fragments to interact in such a manner that the entire model has a «wheel »form. We found a third conformer pictured in Figure 5c lying just 6.59 $kJ.mol^{-1}$ above the two lowest energy structures and which has a geometry where Cl^- is « sandwiched » by the urea molecules and the choline cation through the NH and CH bonds with a C=O---OH link between Ch^+ and one molecule of urea. The association energy of the second urea molecule to T1a-2 and G1a-2 are respectively -71.377 and -61.397 $kJ.mol^{-1}$ for the two most stable models of the DES and are very close to the previous ones of the 1:1 ratio model systems (Table 6).



a) T1a-2 + Urea *b) G1a-2 + Urea (Conf 1)*



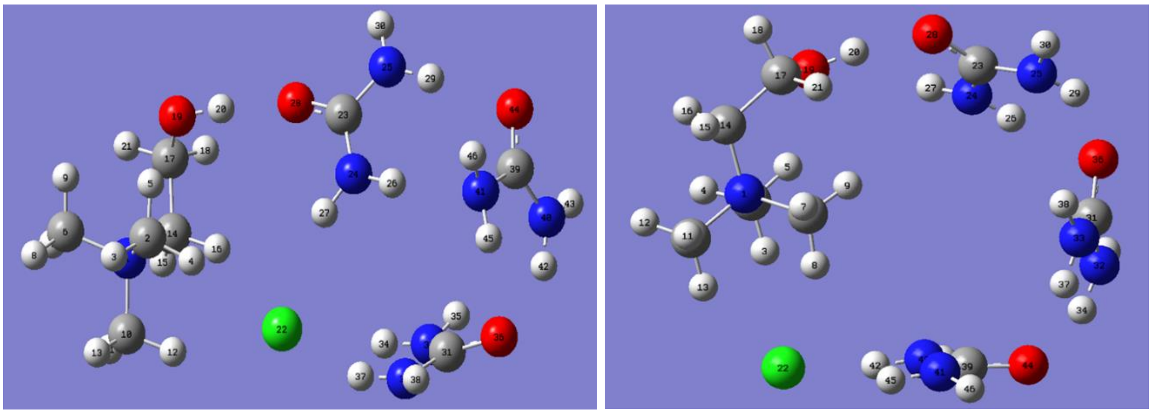
c) G1a-2 + urea (Conf 2)

Figure 5. Choline chloride complexes with 2 ureas

Table 5. Energies and geometries of optimized systems of choline chloride with 2 or 3 ureas [(a)]

System	Energy (H)	$d_{H\text{---}Cl}$	$d_{C\text{-}Hmeth}$	$d_{N\text{-}Cmet}$	$d_{N\text{-}Cet}$	$d_{C\text{-}O}$	$d_{O\text{-}H}$ ($d_{O\text{-}H\text{—}OCur1}$)	$d_{C\text{-}Nur}$	$d_{N\text{-}Hur}$	$d_{C\text{-}Our}$	$d_{COur2\text{---}HNur1}$	CO_{ur2}-CO_{ur1}	OC_{ur2}---Cl--N_{ch}	N-C-CO_{ch}
T1a-2 + urea	-1239.450107	(2.534 2.601 2.608) H_{ch} (2.353; 2.347)H_{ur1}	1.087 1.093	1.508 1.510 1.515	1.525	1.408	0.994 (1.686)	(1.362; 1.363) $_{ur1}$ (1.364; 1.364) $_{ur2}$	(1.007; 1.017) $_{ur1}$ (1.007; 1.022) $_{ur2}$	1.252$_{ur1}$ 1.252$_{ur2}$	2.065 2.080	-11.4 °	0.469 °	-61.6 °
G1a-2 + urea Conf1	-1239.450108	(2.608 2.534 2.601) Hmet (2.353; 2.347)H_{ur2}	1.088 1.093	1.515 1.508 1.510	1.525	1.408	0.994 (1.686)	(1.362; 1.363) $_{ur1}$ (1.364; 1.364)$_{ur2}$	(1.007; 1.017) $_{ur1}$ (1.007; 1.022)$_{ur2}$	1.252$_{ur1}$ 1.252$_{ur2}$	2.065 2.080	11.4 °	-0.469	61.6 °
G1a-2 + urea Conf2	-1239.447589	(2.562; 2.569) Hmet (2.557) H_{et} (2.491; 2.532) H_{ur2} (2.545)H_{ur1}	1.088 1.094	1.517 1.498 1.509	1.536	1.407	0.994 (1.688)	(1.369; 1.367) $_{ur1}$ (1.372; 1.371) $_{ur2}$	(1.009; 1.020) $_{ur1}$ (1.009; 1.019)$_{ur2}$	1.249$_{ur1}$ 1.245$_{ur2}$	2.088	-64.3 °	36.1 °	58.4 °
G1a-2 + 2ureas Conf1	-1464.701126	(2.594)1H_{et} (2.558; 2.551)2H_{met} (2.378; 2.443)2H_{ur2} (2.505)H_{ur1}	1.088 1.094	1.517 1.498 1.508	1.536	1.406	0.993 (1.668)	(1.356; 1.366) $_{ur1}$ (1.364; 1.365) $_{ur2}$	(1.016; 1.020) $_{ur1}$ (1.020; 1.019$_{ur2}$ (1.020; 1.017)$_{ur3}$	1.254$_{ur1}$ 1.252$_{ur2}$ 1.239$_{ur3}$	(1.967; 2.143)$_{ur23}$	(-22.5 °)$_{ur3}$	13.2 °	56.2 °
G1a-2 + 2ureas Conf2	-1464.699833	(2.620; 2.535; 2.519) Hmet (2.328: 2.359)H_{ur2}	1.089 1.094	1.516 1.509 1.510	1.525	1.407	0.995	(1.359; 1.366) $_{ur1}$ (1.361; 1.365) $_{ur2}$ (1.359; 1.368)$_{ur3}$	(1.008; 1.019) $_{ur1}$ (1.007; 1.018) $_{ur2}$ (1.007; 1.022)$_{ur3}$	1.251$_{ur1}$ 1.253$_{ur2}$ 1.252$_{ur3}$	(2.002 : 2.030)$_{ur12}$ (2.037; 2.021)$_{ur23}$	(8.8 °) $_{ur12}$ (-18.8 °)$_{ur23}$	-2.8 °	60.7 °

[(a)](distances in Å)



a) G1a-2 + 2 urea (Conf1) *b) G1a-2 + 2 urea (Conf2)*

Figure 6. Choline chloride complexes with 3 ureas

Table 6. Reactions energies and quantum chemical parameters

Model System	Energy(H)	E_{HOMO} (H; eV)	E_{LUMO} (H; eV)	ΔE(kJ.mol^{-1})	μ (H;eV)	χ (H;eV)	η (H;eV)	ω (H;eV)	Dipole moment (D)
Cl^-	-460.2747259	-0.02825 -0.7687	0.21658 5.8934	-	-0.094165 -2.562	0.094165 2.562	0.122415 3.331	0.985	-
Urea (C2)	-225.228116	-0.26897 -7.3191	-0.01283 -0.3491	-	-0.1409 -3.834	0.1409 3.834	1.12807 3.485	2.109	3.981
Urea+urea C1,conf1	-450.475503	-0.26373 -7.1765	-0.00810 -0.2204	-50.596	-0.135915 -3.698	0.135915 3.698	0.127815 3.478	1.966	0.2922
Urea+urea C1,conf2	-450.470352	-0.25934 -7.0570	-0.02114 -0.5752	-37.072	-0.14024 -3.816	0.14024 3.816	0.1191 3.241	2.247	6.165
Cholinium Trans C1	-328.515532	-0.43081 -11.7229	-0.14899 -4.0542	-	-0.2899 -7.889	0.2899 7.889	0.14091 4.057	7.670	3.683
Cholinium Gauche C1	-328.521938	-0.44356 -12.0699	-0.14449 -3.9318	-	-0.294025 -8.001	0.294025 8.001	0.149535 4.069	7.866	1.942
Choline chloride T1a (C1)	-788.939787	-0.20491 -5.5759	-0.03809 -1.0365	-392.589	-0.1215 -3.306	0.1215 3.306	0.08341 2.270	2.487	13.5628
Choline chloride G1a (C1)	-788.947649	-0.20799 -5.660	-0.03584 -0.9753	-396.411	-0.121915 -3.317	0.121915 3.317	0.086075 2.342	2.349	13.080
T1a+urea = T1a-2 (C1)	-1014.194805	-0.20594 -5.6039	-0.01968 -0.5355	-70.631	-0.11281 -3.070	0.11281 3.070	0.09313 2.534	1.860	6.670
G1a+urea = G1a-2 (C1)	-1014.198607	-0.22850 -6.2178	-0.03424 -0.9317	-59.972	-0.13137 -3.575	0.13137 3.575	0.09713 2.643	2.418	11.794
T1a-2+urea (C1)	-1239.450107	-0.22609 -6.1522	-0.02725 -0.7415	(-142.008) -71.377	-0.12667 -3.447	0.12667 3.447	0.09942 2.705	2.196	7.3462
G1a-2+urea (C1) conf1	-1239.450108	-0.22608 -6.1520	-0.02725 -0.745	(-121.369) -61.397	-0.126665 -3.447	0.126665 3.447	0.099415 2.705	2.196	7.3467
G1a-2+urea (C1) conf2	-1239.447589	-0.23547 -6.4075	-0.03115 -0.8476	(-114.755) -54.784	-0.13331 -3.628	0.13331 3.628	0.10216 2.780	2.367	11.3138
G1a-2+2urea (C1) conf1	-1464.701126	-0.23892 -6.5013	-0.02945 -0.8014	(-181.498) -60.129	-0.134185 -3.651	0.134185 3.651	0.104735 2.850	2.339	10.6872
G1a-2+2urea (C1) conf2	-1464.699833	-0.22739 -6.1876	-0.02650 --0.7211	(-178.103) -56.734	-0.126945 -3.454	0.126945 3.454	0.100445 2.733	2.183	7.7468

Table 7. Atomic charges (in u.a) of the most stable compounds

System	**Cl^-**	**Urea**				**cholinium ion**						
		N	**C**	**O**	**H**	**N**	**C_{met}**	**C_{eth}**	**H_{met}**	**H_{et}**	**O**	**$H_{(O)}$**
Cl^-	-1											
Urea(C2)		-0,.21 -0.921	0.787	-0.658	0.437;0.419 0.437;0.419							
Urea+Urea C2+C2 Conformer 1		-0.914; -0.908 -0.908; -0.914	0.799 0.799	-0.714 -0.714	0.418;0.435 0.417;0.466 0.417;0.466 0.418;0.435							
Ch^+ (gauche) Conformer G1						-0.342	-0.491 -0.486 -0.485	-0.281 -0.150	0.273;0.267; 0.279 0.266;0.264;0.297 0.272;0.269;0.273	0.278; 0.277 0.226; 0.255	-0.797	0.535
Ch^+ (gauche) Conformer G2						-0.342	-0.486 -0.491 -0.485	-0.281 -0.150	0.273;0.267;0.279 0.266;0.264;0.297 0.272;0,269;0.273	0.278; 0.277 0.226; 0.255	-0.797	0.535
Ch^+(trans) Conformer T1						-0.330	-0.482 -0.482 -0.480	-0.283 -0.131	0.271;0.272;0.268 0.272;0.271;0.268 0.272;0.272;0.270	0.279; 0.279 0.217; 0.217	-0.764	0.525
ChCl (gauche) G1a	-0.828					-0.346	-0.488 -0.497 -0.477	-0.277 -0.148	0.242;0.254; **0.305** 0.244;0.252; **0.306** 0.256;0.260; 0.260	0.249; 0.260 0.231; **0.242**	**-0.819**	**0.519**
ChCl(trans) T1a	-0.865					-0.344	-0.498 -0.483 -0.478	-0.309 -0.136	0.250;**0.311**; 0.244 **0.295**;0.256; 0.250 0.258;0.264;0.256	**0.305**; 0.246 0.217; 0.220	-0.786	0.528
ChCl+U G1a-2)	-0.849	-0.974 -0.923	0.790	-0.668	**0.445**;0.436 **0.444**;0.432	-0.345	-0.495 -0.480 -0.489	-0.303 -0.145	0.238;**0.298**;0.278 0.255;0.257;0.267 0.247;**0.306**;0.249	0.250;**0.298** 0.244;0.219	-0.809	0.527

System	**Cl^-**	**Urea**				**Cholinium ion**						
		N	**C**	**O**	**H**	**N**	**C_{met}**	**C_{eth}**	**H_{met}**	**H_{et}**	**O**	**$H_{(O)}$**
ChCl+U (T1a-2)	-0.868	-0.912 -0.894	0.802	-0.759	0.419;0.435 0.423;0.458	-0.344	-0.499 -0.485 -0.481	-0.283 -0.156	0.295;0.275;0.236 0.248;0.249;0.298 0.291;0.247;0.248	0.242;0.304 0.231;0.252	-0.818	0.543
ChCl+2U (G1a-2+U)	-0.856	-0.897; -0.897 -0.912; -0.912	0.796 0.792	-0.748 -0.761	**0.451**;0.432 **0.453**;0.432 **0.451**;0.431 **0.451**;0.430	-0.345	-0.488 -0.494 -0.489	-0.277 -0.139	**0.289**;0.243;0.275 0.243;**0.296**;0.264 0.248;0.249;**0.305**	0.257;0.262 0.229;0.224	-0.828	**0.540**
ChCl+3U (G1a-2+2U)	-0.866	-0.904; -0.904 -0.898; -0.899 -0.906; -0.940	0.806 0.796 0.790	-0.777 -0.760 -0.715	0.434;**0.450** **0.450**;0.432 **0.447**;0.425 **0.450**;0.429 **0.456**;0.437 **0446**;0.435	-0.344	-0.493 -0.484 -0.487	-0294 -0.144	0.236;**0.293**;0.284 0,.54;0.255;**0.276** 0.246;**0.304**;0.249	0.250;**0.300** 0.248;0.213	-0.824	**0.548**

Table 8. Second order perturbation energy $E^{(2)}$ in kcal.mol^{-1} for the most important charge transfer interactions in the most stable model of choline chloride plus two urea ($E^{(2)} \geq 2$ kcal.mol^{-1})

Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcalmol^{-1})	Donor occupancy	Acceptor occupancy
Intra cholinium Ch$^+$				
BD(1) C2-H3	BD*(1) N1-C14	2.83	1.9892	0.0420
BD(1) C2-H4	BD*(1) N1-C6	2.63	1.9901	0.0197
BD(1) C2-H5	BD*(1) N1-C10	2.49	1.9895	0.0163
BD(1) C6-H7	BD*(1) N1-C2	2.59	1.9903	0.0179
BD(1) C6-H8	BD*(1) N1-C14	3.03	1.9884	0.0420
BD(1) C6-H9	BD*(1) N1-C10	2.52	1.9899	0.0163
BD(1) C10-H11	BD*(1) N1-C2	2.39	1.9909	0.0179
BD(1) C10-H12	BD*(1) N1-C6	2.51	1.9907	0.0197
BD(1) C10-H13	BD*(1) N1-C14	2.64	1.9894	0.0420
BD(1) C14-H15	BD*(1) N1-C2	2.58	1.9800	0.0179
BD(1) C14-H15	BD*(1) C17-O19	4.05	1.9800	0.0123
BD(1) C14-H16	BD*(1) N1-C6	2.85	1.9826	0.0197
BD(1) C14-H16	BD*(1) C17-H21	2.29	1.9826	0.0231
BD(1) C17-H18	BD*(1) N1-C14	6.51	1.9752	0.0420
BD(1) C17-H21	BD*(1) C14-H16	2.75	1.9855	0.0132
BD(1) O19-H20	BD*(1) C14-C17	2.19	1.9874	0.0251
LP(1) O19	BD*(1) C17-H21	4.25	1.9761	0.0231
LP(2) O19	BD*(1) C2-H5	2.22	1.9404	0.0123
LP(2) O19	BD*(1) C14-C17	4.27	1.9404	0.0251
LP(2) O19	BD*(1) C17-H18	8.36	1.9404	0.0291
From Cl$^-$ to cholinium Ch$^+$				
LP(3) Cl22	BD*(1) C2-H3	2.81	1.9543	0.0217
LP(3) Cl22	BD*(1) C6-H8	4.58	1.9543	0.0255
LP(3) Cl22	BD*(1) C10-H13	3.65	1.9543	0.0205
From Cl$^-$ to U_2				
LP(2) Cl22	BD*(1) N32-H34	3.14	1.9674	0.0416
LP(2) Cl22	BD*(1) N33-H37	2.36	1.9674	0.0421
LP(4) Cl22	BD*(1) N32-H34	8.06	1.9356	0.0416
LP(4) Cl22	BD*(1) N33-H37	8.74	1.9356	0.0421
From U_1 to cholinium Ch$^+$				
BD(2) C23-O28	BD*(1) O19-H20	2.36	1.9826	0.0642
LP(1) O28	BD*(1) O19-H20	9.50	1.9551	0.0642
LP(2) O28	BD*(1) O19-H20	17.41	1.8610	0.0642
Intra U_1				
BD(1) C23-N24	BD*(1) N25-H30	2.11	1.9929	0.0071
BD(1) C23-N25	BD*(1) N24-H27	2.06	1.9920	0.0070
BD(2) C23-O28	BD*(2) C23-O28	4.12	1.9826	0.4135
BD(1) N24-H26	BD*(1) C23-O28	4.91	1.9852	0.0597
BD(1) N24-H27	BD*(1) C23-N25	4.87	1.9877	0.0562
BD(1) N25-H29	BD*(1) C23-O28	4.80	1.9844	0.0597
BD(1) N25-H29	BD*(2) C23-O28	2.06	1.9844	0.4135
BD(1) N25-H30	BD*(1) C23-N24	5.04	1.9873	0.0578
CR(1) N24	RY*(2) C23	2.49	1.9995	0.0092
CR(1) N25	RY*(2) C23	2.52	1.9995	0.0092
CR(1) O28	RY*(1) C23	5.81	1.9997	0.0152
LP(1) O28	RY*(1) C23	13.17	1.9551	0.0152

Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcalmol^{-1})	Donor occupancy	Acceptor occupancy
LP(1) N24	BD*(1) C23-O28	3.00	1.7662	0.0597
LP(1) N24	BD*(2) C23-O28	46.58	1.7662	0.4135
LP(1) N25	BD*(1) C23-O28	3.16	1.7714	0.0597
LP(1) N25	BD*(2) C23-O28	44.50	1.7714	0.4135
LP(1) O28	BD*(1) C23-N24	6.08	1.9551	0.0578
LP(2) O28	BD*(1) C23-N24	14.49	1.8610	0.0578
LP(2) O28	BD*(1) C23-N25	21.83	1.8610	0.0562
From U_2 to U_1				
BD(2) C31-O36	BD*(1) N24-H26	2.70	1.9848	0.0274
LP(1) O36	BD*(1) N24-H26	2.44	1.9633	0.0274
LP(1) O36	BD*(1) N25-H29	3.16	1.9633	0.0265
LP(2) O36	BD*(1) N25-H29	2.68	1.8731	0.0265
Intra U_2				
BD(1) C31-N32	BD*(1) N33-H38	2.08	1.9924	0.0080
BD(1) C31-N33	BD*(1) N32-H35	2.05	1.9925	0.0079
BD(2) C31-O36	BD*(2) C31-O36	3.41	1.9848	0.4436
BD(1) N32-H34	BD*(1) C31-O36	5.95	1.9867	0.0213
BD(1) N32-H35	BD*(1) C31-N33	4.82	1.9864	0.0596
BD(1) N33-H37	BD*(1) C31-O36	6.00	1.9865	0.0213
BD(1) N33-H38	BD*(1) C31-N32	4.82	1.9866	0.0591
CR(1) N32	RY*(2) C31	2.55	1.9995	0.0094
CR(1) N33	RY*(2) C31	2.62	1.9995	0.0094
CR(1) O36	RY*(1) C31	5.81	1.9998	0.0159
LP(1) O36	RY*(1) C31	14.88	1.9633	0.0159
LP(1) N32	BD*(2) C31-O36	60.33	1.7693	0.4436
LP(1) N33	BD*(2) C31-O36	60.73	1.7679	0.4436
LP(1) O36	BD*(1) C31-N32	2.10	1.9633	0.0591
LP(1) O36	BD*(1) C31-N33	2.43	1.9633	0.0596
LP(2) O36	BD*(1) C31-N32	21.11	1.8731	0.0591
LP(2) O36	BD*(1) C31-N33	20.83	1.8731	0.0596

Systems of three urea molecules and one choline chloride

To further our understanding of the composition of the solvent, the present study has also considered the 1:3 ratio model systems of choline chloride and urea by starting with the minimal energy structure of Fig.5b obtained from G1a-2. The reactions are also exoergic and Figure 6a-b show the two lowest minimum energy models. The geometry of the most energetically stable conformer (Figure 6a) shows an arrangement in which two of the urea molecules still interact with the choline cation. The third urea tends to form a second shell of urea molecules around choline chloride. In the second model compound, the third urea is just between the two formers, maintaining the «wheel» form. One therefore observes that in each of these two model compounds, the four main components of the solvent, that is, the choline cation Ch^+, the chloride anion and two urea molecules remain in contact through H-bonding. These interactions of choline chloride with urea preserve the 1:2 ratio of these constituents in the solvent.

3.2. Charge Distributions

a. Atomic charge

In the natural atomic orbital (NAO) basis, the natural population on an atom (A) is the sum over all contributing NAOs of the natural population $q_i(A)$ of orbital $\varphi_i(A)$. The difference between its atomic number and its natural population is its atomic charge Q(A). According to the Pauli principle, $0 \leq q_i(A) \leq 2$. Table 7 displays the calculated atomic charges given by the present analysis. One may note the negative charge carried by the carbon atoms of the choline cation and which increases upon addition of Cl^- and urea due to the interactions. The results also indicate the charges on the electronegative elements N and O, which follow the same trend as the carbon atoms. Concurrently, there is a decrease in charge on the chlorine atom from -1.0 a.u to -0.856 au in the most stable 1:2 ratio model system. The H atoms are all polarized and those of the methyl groups nearest to the chloride ion have up to +0.305 au in the most stable model of reline.

b. Natural bond orbital (NBO) analysis

Natural bond orbitals (NBO) are localized orbitals constructed from natural atomic orbitals (NAO) and well describe the electron distribution in chemical substances. One often uses NBO analysis [27] to understand intra and intermolecular electronic charge transfer from occupied NBOs of an electron donor group into vacant ones of an acceptor. The second order perturbation energy $E^{(2)}$ given by the analysis of the Fock matrix in the NBO basis provides an estimation of the strength of the interactions that lead to the charge delocalization and is expressed as:

$$E^{(2)} = q_i \frac{F_{ij}^2}{E_j - E_i} \qquad (1)$$

$F_{ij,}$ are Fock matrix elements, E_i and E_j are the NBO energies and q_i is the donor NBO occupancy. Table 8 presents the results of an NBO analysis with $E^{(2)} \geq 2$ kcal.mol^{-1} of the most stable model of the mixture containing ChCl and two molecules of urea. The data suggest that the interactions intra and inter fragments involve occupied C-H, N-H, O-H, C-O and C-N bonds, lone pairs on O, N and Cl with vacant antibonding C-C, C-H, C-O, N-C, N-H, and Rydberg orbitals of C atoms. The data also indicate that Cl^- interacts with Ch^+ and the nearest urea U_2 through its lone pairs. Clearly, three C-H and two N-H empty acceptor orbitals receive electronic charge. The same observation is made of donor NBOs of the carbonyl group of urea U_2 with two vacant σ^*(N-H) of urea U_1 as well as for the donor lone pair LP(O) of U_1 with the empty σ^*(O-H) of Ch^+. The stronger charge transfers of 10 to 60 kcal.mol^{-1}are mainly observed between the lone pairs of N, O and Cl with vacant antibonding NBOs that show some occupancy. The interactions through bonds contribute therefore to spread the electronic charge within the system and to stabilize it.

Table 9. Wiberg bond Indices in the urea molecule (C2)

Bond	Bond index	Bond	Bond index between distant atoms
C1-O2	1.6372	O2-H4	0.0037
C1-N3	1.1235	O2-H5	0.0185
C1-N6	1.1235	O2-H7	0.0037
N3-H4	0.7925	O2-H8	0.0185
N3-H5	0.8037	N3-N6	0.0400
N6-H7	0.7925	N3-H7	0.0119
N6-H8	0.8037	N6-H4	0.0119
		O2-N3	0.1363
		O2-N6	0.1363

Table 10. Wiberg bond indices in the cholinium cation Gauche and Trans (C1)

Cholinium Gauche (G1)		Cholinium Trans (T1)		Cholinium Gauche (G2)	
Bond	**Bond Index**	**Bond**	**Bond index**	**Bond**	**Bond index**
N1-C2	0.8926	N1-C2	0.8908	N1-C2	0.8830
N1-C6	0.8830	N1-C6	0.8896	N1-C6	0.8926
N1-C10	0.8953	N1-C10	0,.908	N1-C10	0.8953
N1-C14	0.8701	N1-C14	0.8789	N1-C14	0.8701
C2-H3; H4; H5	0.9127; 0.9161; 09079	C2-H3; H4; H5	0.9130; 0.9148; 0.9136	C2-H3; H4; H5	0.9173; 0.9167; 0.8924
C6-H7; H8; H9	0,9167; 0.9173; 0.8924	C6-H7; H8; H9	0.9129; 0.9129; 0.9146	C6-H7; H8; H9	0.9161; 0.9127; 0.9079
C10-H11; H12; H13	0.9133; 0.9151; 0.9129	C10-H11; H12; H13	0.9148; 0.9130; 0.9136	C10-H11; H12; H13	0.9151; 0.9133; 0.9129
C14-H15; H16	0.8950; 0.989	C14-H15; H16	0.8946; 0.8946	C14-H15; H16	0.8989; 0.8950
C17-H18; H19	0.9059; 0.8915	C17-H18; H19	0.9122; 0.9122	C17-H21; H18	0.9059; 0.8915
C14-C17	1.0240	C14-C17	1.0041	C14-C17	1.0240
C17-O20	0.9427	C17-O20	0.9606	C17-O19	0.9427
O20-H21	0.7027	O20-H21	0.7133	O19-H20	0.7027
Between distant atoms					
C2-C6; C10; C14	0.0105; 0.0107; 0.0098	C2-C6; C10; C14	0.0109; 0.0108; 0.0111	C2-C6; C10; C14	0.0105; 0.0109; 0.0101
C6-C10; C14	0.0109; 0.0101	C6-C10; C14	0.0109; 0.0100	C6-C10; C14	0.0107; 0.0098
C14-O20	0.0182	C14-O20	0.0266	C14-O19	0.0182
O20-H18; H19	0.0277; 0.0232	O20-H18; H19	0.0270; 0.0270	O19-H21; H18	0.0277; 0.0232
N1-H19	0.0110	-	-	N1-H18	0.0110

Table 11. Wiberg bond Indices in choline chloride G1a et T1a plus 2 urea molecules (C1)

choline chloride G1a +U_1+U_2		**choline chloride T1a +U_1+U_2**	
Bond	**Bond Index**	**Bond**	**Bond index**
In Ch$^+$			
N1-C2	0.8804	N1-C10	0.8804
N1-C6	0.8863	N1-C2	0.8864
N1-C10	0.8938	N1-C6	0.8938
N1-C14	0.8806	N1-C14	0.8806
C2-H3; H4; H5	0.8804; 0.9276; 0.9004	C10-H13; H12; H11	0.8804; 0.9276; 0.9005
C6-H7; H8; H9	0.9272; 0.8703; 0.9142	C2-H3; H5; H4	0.9272; 0.8704; 0.9142
C10-H11; H12; H13	0.9252; 0.9247; 0.8727	C6-H9; H8; H7	0.9252; 0.9247; 0.8727
C14-H15; H16	0.9076; 0.9021	C14-H16; H15	0.9076; 0.9021
C17-H18; H21	0.8935; 0.9106	C17-H18; H19	0.8935; 0.9106
C14-C17	1.0168	C14-C17	1.0168
C17-O19	0.9641	C17-O20	0.9641
O19-H20	0.6026	O20-H21	0.6026
C2-C6; C10; C14	0.0100; 0.0105; 0.0107	C10-C2; C6; C14	0.0100; 0.0105; 0.0107
C6-C10; C14	0.0103; 0.0105	C2-C6; C14	0.0103; 0.0105
C14-O19	0.0266	C14-O20	0.0266
O19- H5; H15; H18; H21	0.0115; 0.0099; 0.0342; 0.0208	O20-H11; H16; H18; H19	0.0115; 0.0099; 0.0342; 0.0209
N1-H18	0.0112	N1-H18	0.0112
In Urea (U_1)			
C23-N24; N25	1.2031; 1.2021	C23-N24; N25	1.2031; 1.2020
N24-N25	0.0605	N24-N25	0.0605
N24-H26; H27; H30	0.7483; 0.7963; 0.0118	N24-H26; H27; H30	0.7482; 0.7963; 0.0118
N25-H26; H27; H29; H30	0.0004; 0.0111; 0.7483; 0.7961	N25-H26; H27; H29; H30	0.0004; 0.0111; 0.7483; 0.7961
O28-C23; N24; N25	1.4612; 0.1265; 0.1216	O28-C23; N24; N25	1.4613; 0.1265; 0.1216
O28-H26; H29	0.0132; 0.0122	O28-H26; H29	0.0132; 0.0122
In Urea (U_2)			
C31-N32; N33	1.1991; 1.1994	C31-N32; N33	1.1991; 1.1993
N32-N33	0.0588	N32-N33	0.0588
N32-H34; H35; H38	0.7283; 0.7961; 0.0116	N32-H34; H35; H38	0.7283; 0.7961; 0.0116
N33-H37; H38; H35	0.7274; 0.7966; 0.0117	N33-H37; H38; H35	0.7274; 0.7966; 0.0117
O36-C31; N32; N33	1.4713; 0.1260; 0.1253	O36-C31; N32; N33	1.4713; 0.1260; 0.1253
O36-H34; H37	0.0127; 0.0128	O36-H34; H37	0.0127; 0.0128
Between Ch$^+$ and Cl$^-$			
Cl22-C2; C10	0.0139; 0.0141	Cl22-C10; C6; C14	0.0139; 0.0141
Cl22-H3; H8; H13	**0.0246; 0.0310; 0.0236**	Cl22-H13; H5; H7	**0.0246; 0.0310; 0.0236**
Between Ch$^+$ and urea (U_1)			
O19-O28	**0.0247**	O20-O28	**0.0247**
O28-H20	**0.0947**	O28-H21	**0.0947**
Between Cl$^-$ and urea (U_2)			
Cl22-N32; N33	**0.0202; 0.0207**	Cl22-N32; N33	**0.0203; 0.0207**
Cl22-H34; H37	**0.0531; 0.0541**	Cl22-H34; H37	**0.0532; 0.0540**
Between urea (U1) and urea (U2)			
H26-O36	**0.0289**	H26-O36	**0.0289**
H29-O36	**0.0285**	H29-O36	**0.0285**

c. Wiberg bond indices

The NBO analysis also provide Wiberg bond indices, which give estimates of the bond orders between pairs of atoms. Table 9-11 list these data for pure urea (C2), the conformers G1, G2 and T1 of the choline cation and of the most stable model of reline. They show that the formal covalent C-O, C-N, C-C, C-H, N-H and O-H bonds have calculated bond orders ranging from 1.6 for C=O in pure urea to 0.6 for O-H in the model of reline. It is important to note the formation of partial covalent bonds between the four fragments of the model of reline. The highest bond orders between H-bond acceptors and donors are respectively 0.0947 for C=O---H-O, 0.0541 and 0.0531 for Cl---H-N, 0.031, 0.0246 and 0.0236 for Cl---H-C and 0.0289, 0.0285 for C=O---H-N. One may also observe that these H-bonds join the pairs of fragments urea$_1$/Ch$^+$, Cl$^-$/ urea$_2$, Cl$^-$/Ch$^+$ and urea$_1$/urea$_2$. Even though these values of the calculated bond orders may contain errors, they correlate well with the strength of the through bond interactions presented in table 8. They may also explain the depletion of charge on the H atoms and the increase in charge on the C, N and O atoms involved in these H-bonds shown in table 7. The data show that the spread of the electronic charge in the compounds induces bond order between pairs of distant atoms. The bond orders also indicate that five closest H atoms of urea and Ch$^+$ surround Cl$^-$. As expected, urea plays the double role of H-bond donor and acceptor in the formation of the DES.

3.3. Quantum Chemical Parameters of the Model Compounds

The electronic chemical potential μ, the electronegativity χ, the chemical hardness η and the global electrophilicity index ω of the model compounds were determined in our study from the energies of the frontier orbitals E_{HOMO} and E_{LUMO} using the following expressions as suggested by other authors [28-30].

$$\mu = \frac{E_{HOMO}+E_{LUMO}}{2} = -\chi \quad (2)$$

$$\eta = \frac{E_{LUMO}-E_{HOMO}}{2} \quad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

Electronic charge flows naturally from a substance of higher chemical potential to another of lower chemical potential or from an electron donor to an acceptor, which, beside this property has higher electronegativity and higher index of electrophilicity. Table 6 presents the calculated quantum chemical parameters. The choline cation has the lowest chemical potential (-8.0 eV for the conformer Gauche) compared to urea (-3.834 eV) and Cl$^-$ (-2.562 eV). This favors the formation of choline chloride and its subsequent compounds with urea. Upon addition of two urea molecules, there is a notable decrease in the electrophilicity index of the mixture from that of the cation. However, this index starts to increase with the addition of a third molecule of urea and this may explain the combination ratio of 1:2 of choline chloride and urea in the solvent.

4. Conclusions

We report Density Functional Theory calculations for urea, Cl$^-$, the choline cation, choline chloride and model compounds of the DES reline that may result from their association. The total ZPE corrected energies; detailed structural parameters, interaction energies, charge distribution and some quantum chemical parameters of all these systems are presented. Our results predict minimum energy structures for the DES in which partial covalent H-bonds link the ions and the molecules of urea in accord with previous work. Our study reveals the presence in the model solvent of H-bonds of the type C=O---H-O, Cl---H-N, Cl---H-C and C=O---H-N that result from the interactions of the fragments. Formation of these H-bonds maximizes the intra and intermolecular interactions and stabilize the system. Our data do not show evidence of a specific speciation of Cl$^-$ with urea although such geometries may minimize coulombic interactions. Our calculated quantum chemical parameters and the geometrical arrangement of the fragments in the model compounds also predict the 1:2 ratio in which choline chloride and urea combine in the DES.

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REFERENCES

[1] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrayah, *Chem., Commun.*, 2001, 2010-2011.

[2] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrayah, *Chem., Commun.*, 2003, 70-71.

[3] M. A. Martins, S. P. Pinho, J. A. P. Coutinho, *J. Sol. Chem*, 2019, 48, 7, 962-982.

[4] D. Lindberg, M. D. L. F. Revenga, M. Widersten, *J. Biotechnol* 147, 169-171.

[5] J. T. Gorke, F. Srienc, R. J. Kazlauskas, *Chem Commun*, 2008, 1235-1237.

[6] E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chemical Reviews*, 2014, 114, 21, 11060-11082.

[7] a) F. Soma, Q. Rayé, M. Bougouma, C. Baustart, C. Buess-Herman, T. Doneux, Electrochim Acta, 345, (2020), 136165. b) K. Adama, B. Moussa, S. Fousseni, S. Alassane, J. Mater. Environ. Sci., 12, (2021), 1293-1309.

[8] J. Zhang, T. Wu, S. Chen, P. Y. Fen, X. H. Bu, Angew. Chem. Int. Ed. 2009, 48, 3486-3490.

[9] M. Francisco, A. vanden Bruinhorst and M. C.Kroon, Angew. Chem. Int. Ed. 2013, 52, 3074-3085.

[10] B. Gurkan, H. Squire, E. Pentzer, J. Chem. Phys. Lett. 2019, 10, 7956-7964.

[11] H. G. Morrison, C. C. Sun, S. Neervannan, Int. J. Pharmaceutics, 2009, 378; 136-139.

[12] X. Meng, K. Ballerat-Busserolles, P. Husson, and J.-M. Andanson, New J. Chem, 2016, 40(5); 4492-4499.

[13] O. S. Hammond, D. T. Bowron, and K. J. Edler, Green Chem, 2016, 18, 2736.

[14] S. L. Perkins, P. Painter, and C. M. Colina, J. Phys. Chem. B 2013, 117, 10250-10260.

[15] S. L. Perkins, P. Painter, and C. M. Colina, J. Chem Eng. Data, 2014, 59(11); 3652-3662.

[16] C. R. Ashworth, R.P. Matthews, T. Welton, and P. A. Hunt, Chem Chem Phys., 2016,18(27), 18145-18160.

[17] C. Lee, W. Yang, and r. g. p arr, Phys. Rev. B. 37(2), 785-789, (1988).

[18] R. Dennington, T. Keith, J. Millan, Semichem Inc., Shawnee Mission, K. S. (2019).

[19] G09.

[20] P. D. Godfrey, R. D. Brown, A. N. Hunter, J. Mol. Struct. 413/414:405, (1997).

[21] S. G. Raptis, J. Anastasopoulou, T. Theophanides, Theor. Chem. Acc. (2000), 105:156-164.

[22] M. R. Andrews, D. Hyndman, Proc. Phys. Soc. A, 1953, 66, 1187.

[23] J. E. Worsham, H. A. Levy, S. W. Peterson, Acta Cryst. 1957, 10, 319.

[24] S. Swaminathan, B. M. Craven, R. K. McMullan, Acta Cryst. 840,301, (1984).

[25] A. S. Davies, W. O. George and S. T. Howard, Phys. Chem. Chem. Phys. 2003, 5, 4533-4540.

[26] S. Zahn, F. Uhlig, J. Thar, C. Spickermann and B. Kirchner, Angew. Chem. Int. Ed. 2008, 47, 3639-3641.

[27] A. E. Reed, l. A. Curtiss, F. Weinhold, Chem. Rev. 88(6), 899-926 (1988).

[28] Z. Zhou, R.G. Parr, J. Am. Chem. Soc. 111, (1989), 7371-7379.

[29] R. G. Pearon Inorg. Chim. Acta, 1992, 198-200: 781-786.

[30] R. G. Parr, R.G. Pearson, J. Am. Chem. Soc.105, (1983) 7512-7516.