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Article

Insights into the Chloride versus Bromide Effect on the Formation of Urea-Quaternary Ammonium Eutectic Solvents

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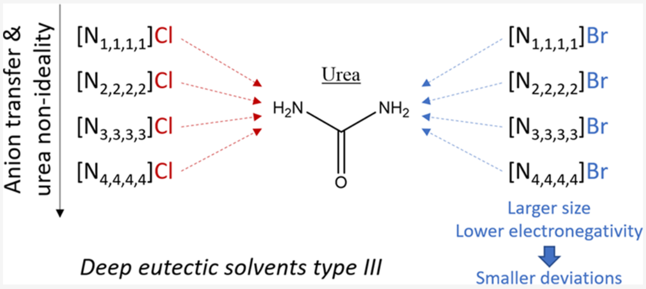
ABSTRACT: The intermolecular interactions of urea and quaternary ammonium salts relevant to their thermodynamic nonideality were here investigated by measuring the solid−liquid equilibria of their binary mixtures. The experimental data revealed that the anion transfer between the quaternary ammonium salt and urea increases with increasing alkyl chain lengths, leading to negative deviations from ideality in the urea-rich side for $[N_{4,4,4,4}]$-based systems. However, the use of bromides instead of chlorides dampens the nonideality of urea because of larger size and lower electronegativity of the anion. The behavior of urea when mixed with ChCl or ChBr was found to be remarkably different, indicating that its nonideality in the ChCl/urea eutectic solvent is governed by urea−chloride rather than hydroxyethyl−urea interactions. The conclusions presented highlight the contribution of charge delocalization in the formation of deep eutectic solvents of type III.



1. INTRODUCTION

Deep eutectic solvents or systems (DES) are a class of potentially green solvents that gained attention during the past decade.[1−4] Contrary to most types of solvents (including ionic liquids), DES are not pure substances but mixtures of compounds that, when combined, form a liquid phase at the desired operating temperature without chemical reactions. From a thermodynamics perspective, the prefix *deep* should be reserved for systems whose components show significant negative deviations from ideality, that is, activity coefficients inferior to unity.[5] In other words, negative deviations indicate that the molecular interactions between the components of the mixture are stronger than those found in the liquid phases of pure substances. When these molecular interactions are similar or weaker to those of pure substances, leading to ideal mixtures or positive deviations from ideality, the well-known eutectic mixture denomination should be used.[5]

When first introducing the term DES, Abbott et al.[6] focused on the system choline chloride/urea which, since then, has been the most widely studied DES.[7−15] According to the prevailing understanding of the molecular interactions present in this system,[16−19] the negative deviations from ideality presented by urea arise from a favorable interaction established between two of its protons (each from each nitrogen) and a chloride anion (NH···Cl), in a geometry resembling the head-to-tail interaction of two urea molecules. On the other hand, the hydroxyl group of choline may be competing for chloride anions with the amine groups of urea, decreasing the prevalence of NH···Cl contacts, which is supported by the thermodynamically ideal behavior of choline chloride in this system.[5,19] These observations suggest that the negative deviations from ideality displayed by urea (and, thus, its melting temperature depression) can be heightened by designing hydrogen bond acceptors that are better *chloride donors* (i.e., stronger hydrogen bond acceptors) than choline chloride.

In recent work,[20] we observed that mixtures of tetramethylammonium chloride and tetraethylammonium chloride, tetrapropylammonium chloride, or tetrabutylammonium chloride present negative deviations from thermodynamic ideality. This behavior was unexpected because both components possess the same anion and electrostatic repulsion should hinder any favorable cation−cation interactions. It was shown, however, that the observed negative deviations from ideality were caused by a chloride transfer mechanism occurring from the bulkier cation to the more densely charged tetramethylammonium cation. This suggests that, in virtue of their highly shielded positive charge, bulky alkylammonium cations, namely, tetrabutylammonium, may be excellent chloride donors.

Understanding the dominant molecular interactions between the components of eutectic systems is of utmost

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importance and provides relevant information for the design of novel and *deeper* eutectic solvents for specific applications.[21,22] In this context, the purpose of this work is to further explore the interactions between urea and different tetraalkylammonium halide salts by measuring their solid−liquid equilibrium (SLE) phase diagrams. The use of different anions will provide insights into their impact on the nonideality of the compounds in the liquid phase. Additionally, aiming to increase the number of NH···Cl contacts, by removing the competitive hydroxyl group of the cholinium cation, it will be possible to explore the resulting interactions between the constituents.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The name, source, and purity of the chemicals used are reported in Table 1, and their chemical structures are depicted in Figure 1. Compounds were purified under vacuum (0.1 Pa) at room temperature (298 K) for at least 72 h. After this procedure, the water content of each substance was measured using a Metrohm 831 Karl-Fischer coulometer, with the analyte Hydranal Coulomat AG from Riedel-de-Haën, and found to be lower than 600 ppm in all cases.

Table 1. Name, CAS Number, Supplier, and Mass Fraction Purity (Declared by the Supplier) of the Compounds Used in This Work

	chemicals	CAS	supplier	purity/wt %
$[N_{1,1,1,1}]Cl$	tetramethylammonium chloride	75-57-0	Sigma-Aldrich	97
$[N_{2,2,2,2}]Cl$	tetraethylammonium chloride	56-34-8	Alfa Aesar	98
$[N_{3,3,3,3}]Cl$	tetrapropylammonium chloride	5810-42-4	Alfa Aesar	98
$[N_{4,4,4,4}]Cl$	tetrabutylammonium chloride	1112-67-0	Sigma-Aldrich	97
MeChCl	*β*-methylcholine chloride	2382-43-6	TCI	≥98
ChBr	choline bromide	1927-06-6	TCI	≥98
$[N_{1,1,1,1}]Br$	tetramethylammonium bromide	64-20-0	Fluka	99
$[N_{2,2,2,2}]Br$	tetraethylammonium bromide	71-91-0	Alfa Aesar	98
$[N_{3,3,3,3}]Br$	tetrapropylammonium bromide	1941-30-6	Aldrich	98
$[N_{4,4,4,4}]Br$	tetrabutylammonium bromide	1941-30-6	Fluka	98
Urea		57-13-6	Analar	99.5

2.2. Experimental Procedure. Binary mixtures were prepared at different proportions covering the full range of composition (at mole fraction intervals of 0.1). Urea was initially weighed at room conditions in an analytic balance Mettler Toledo XP205 (repeatability of 0.015 mg). Thereafter, vials containing urea were transferred to a dry argon glovebox, and the ionic compounds were weighed using an analytical balance model ALS 220-4N from Kern (repeatability of 0.2 mg). Mixtures were molten, recrystallized, and homogenized with a mortar and pestle, and the powder was transferred to glass capillaries. The full procedure was performed inside the glovebox to avoid moisture absorption by the hygroscopic ionic compounds under study. The melting point of the resulting mixtures was measured with an automatic glass capillary device model M-565 from Buchi, with a temperature resolution of 0.1 K. For each system, an initial fast run at 5 K min^{-1} was carried out. Then, the measurement was repeated, in triplicate, applying a heating rate of 0.2 K min^{-1}. The melting temperature was taken when the last solid disappears.

The melting point of certain samples (indicated in Table S1) with a pastelike consistency after recrystallization was measured using a visual technique. In this approach, the mixtures were heated in an oil bath under stirring using a heating plate until complete melting. The temperature was controlled with a Pt100 probe with a precision of ±0.1 K, and the procedure was repeated at least three times. The melting temperatures recorded correspond to the last crystal disappearance. The PT100 probe was previously calibrated against a platinum resistance thermometer, SPRT100 (Fluke-Hart Scientific 1529Chub-E4), traceable to the National Institute of Standards and Technology (NIST).

The experimental methodologies herein applied for the measurement of SLE phase diagrams are well established and validated in the literature, and benchmarks against other techniques are available.[20,23−25]

All ^{1}H and ^{13}C NMR spectra were recorded at room temperature using a Bruker Avance 300 instrument operating at 75 MHz with deuterated water as the solvent.

2.3. Thermodynamic Framework. The SLE curves of a eutectic-type liquid mixture whose individual components solidify into pure and immiscible solid phases can be described using the simplified equation:[26]

$$\ln(x_i\gamma_i^l) = \frac{\Delta_m H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{\Delta_{m,trs} H}{R}\left(\frac{1}{T_{m,trs}} - \frac{1}{T}\right) \quad (1)$$

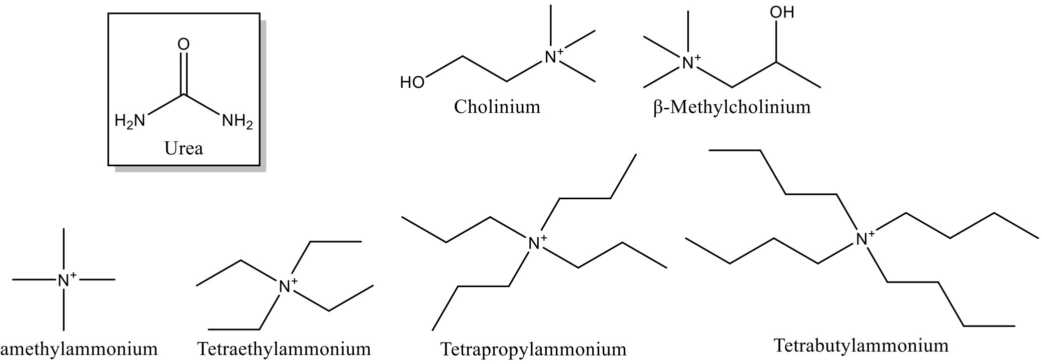

Figure 1. Chemical structures of urea and the cations of the chloride and bromide-based salts investigated in this work.

where x_i is the mole fraction of compound i, γ_i^l its activity coefficient, T_m and $\Delta_m H$ are the melting temperature and enthalpy of the pure compound, respectively, $T_{m,trs}$ and $\Delta_{m,trs}H$ are the solid−solid transition temperature and enthalpy of the pure compound, respectively, T is the absolute temperature, and R is the universal gas constant. Whenever available, the melting properties of the pure compounds are displayed in Table 2. This equation neglects the difference between the molar heat capacity of compound i in the liquid and solid states when a small difference between the equilibrium temperature and the melting temperature of the pure compounds is verified.[27,28] Using the SLE data, the experimental activity coefficients can be calculated through eq 1.[29] When assuming ideality, the activity coefficients in the liquid phase are equal to one, $\gamma_i^l = 1$, and the ideal solubility curves can be directly obtained from eq 1.

Table 2. Melting Properties of the Investigated Compounds

chemicals	T_m/K	$\Delta_m H$/kJ·mol^{-1}	$T_{m,trs}$/K	$\Delta_{m,trs}H$/kJ·mol^{-1}
$[N_{1,1,1,1}]Cl$	612.9[23]			
$[N_{2,2,2,2}]Cl$	535.4[24]			
$[N_{3,3,3,3}]Cl$	503.1[23]			
$[N_{4,4,4,4}]Cl$	344.0[20]	14.69[20]		
ChCl	597[31]	4.3[31]	352.92[34]	17.19[34]
MeChCl	442.0[24]	6.72[24]	425.02[a]	9.60[a]
ChBr	581.6[24]			
$[N_{1,1,1,1}]Br$	645.7[30]			
$[N_{2,2,2,2}]Br$	568.3[20]			
$[N_{3,3,3,3}]Br$	535.0[20]			
$[N_{4,4,4,4}]Br$	390.5[a]	14.80[a]	367[35]	15.10[35]
Urea	406.5[36]	14.79[36]		

[a] Measured in this work using differential scanning calorimetry. Procedure described elsewhere.[20]

3. RESULTS AND DISCUSSION

The SLE phase diagrams data for the urea-based systems investigated in this work are listed in Table S1 of the Supporting Information, along with the activity coefficients calculated (when possible) using eq 1 and the melting properties listed in Table 2.

The melting properties of quaternary ammonium salts are very scarce in the literature, in particular, the melting enthalpies, because of the decomposition of these compounds upon melting. Most of the data available has been estimated from experimental solid−liquid phase diagrams, either by modeling the nonideality of the liquid phase using equations of state[23,30] or by selecting quasi-ideal systems and assuming unity activity coefficients.[24,31] This was successfully accomplished by us for choline chloride.[31] Because of the dispersion on the melting enthalpy values for $[N_{1,1,1,1}]Cl$, $[N_{2,2,2,2}]Cl$, $[N_{3,3,3,3}]Cl$, ChBr, $[N_{1,1,1,1}]Br$, $[N_{2,2,2,2}]Br$, and $[N_{3,3,3,3}]Br$,[30] these were not considered in this work. Additionally, when available, the solid−solid transitions of the pure components, Table 2, were considered.

Given the fact that urea, when pure, slowly decomposes upon melting,[32] the ^{1}H NMR spectra of mixtures of urea with ChBr, $[N_{2,2,2,2}]Br$, or $[N_{2,2,2,2}]Cl$ at 30:70 mole ratios, whose melting points are 459.1, 451.8, and 428.1 K, respectively, were measured along with the spectra of the pure components; Figures S1−S3 of the Supporting Information. Results show no additional signals in urea or in the ionic salt, demonstrating that no decomposition occurred after melting and recrystallization.

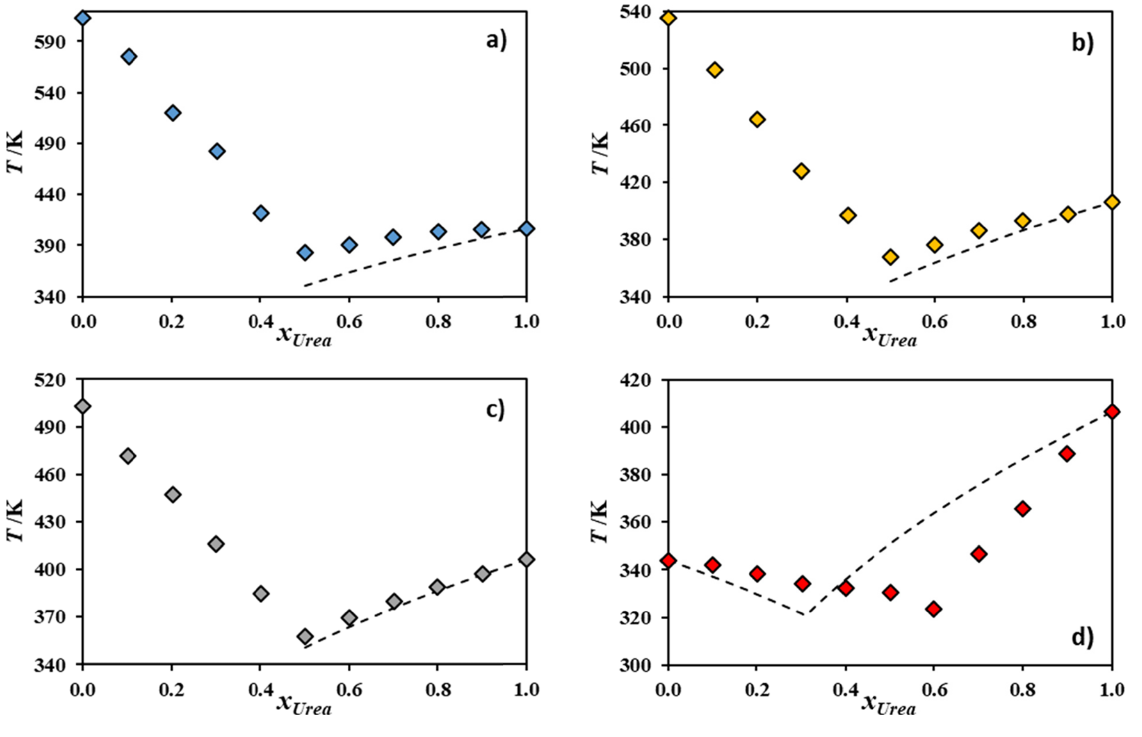

Figure 2. Solid−liquid equilibrium phase diagrams for the binary systems composed of urea and (a) $[N_{1,1,1,1}]Cl$, (b) $[N_{2,2,2,2}]Cl$, (c) $[N_{3,3,3,3}]Cl$, or (d) $[N_{4,4,4,4}]Cl$. Symbols represent the data experimentally measured in this work, while the dashed lines represent the ideal solid−liquid equilibrium.

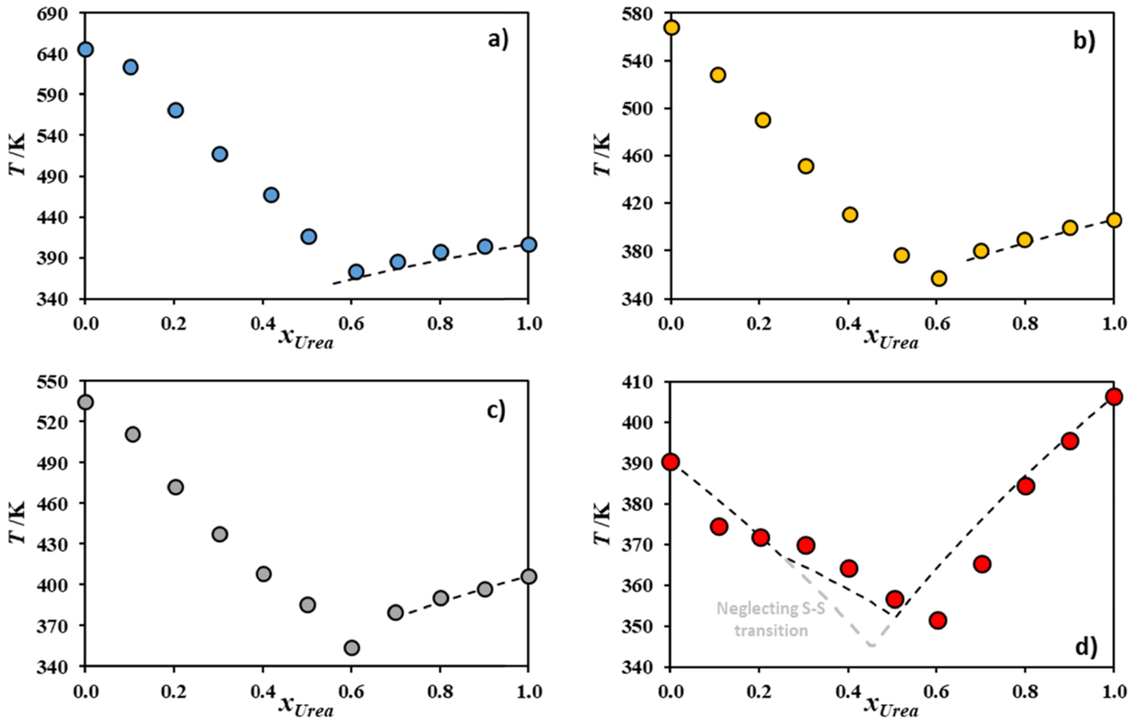

Figure 3. Solid–liquid equilibrium phase diagrams for the binary systems composed of urea and (a) $[N_{1,1,1,1}]$Br, (b) $[N_{2,2,2,2}]$Br, (c) $[N_{3,3,3,3}]$Br, or (d) $[N_{4,4,4,4}]$Br. Symbols represent the data experimentally measured in this work while the dashed lines represent the ideal solid–liquid equilibrium.

Additionally, because quaternary ammonium salts with short alkyl chain lengths are known to decompose upon melting,[33] ^{1}H and ^{13}C-NMR analysis of pure $[N_{2,2,2,2}]$Br and $[N_{2,2,2,2}]$Cl were performed after melting with slow and fast heating to verify the extent of degradation, along with the spectra of the salts at room temperature for comparison; Figures S4 and S5 of the Supporting Information. No differences in the spectra or new NMR signals were observed when melting $[N_{2,2,2,2}]$Cl with slow heating, when compared with the pure salt, indicating that no decomposition products are formed. When fast heating is applied, the salt shows signs of decomposition at the melting temperature (535 K), and the ^{1}H-NMR analysis indicates approximately 3 mol % decomposition. For $[N_{2,2,2,2}]$Br, a strong yellowing of the solution was observed along with some mass loss when slowly approaching the melting temperature (568.3 K), and ^{1}H-NMR analysis indicated full degradation. Similar to the chloride analogue, when fast heating is applied, the salt shows signs of decomposition at the melting temperature (568.3 K) and ^{1}H-NMR analysis indicates approximately 14 mol % decomposition. It was also observed that when using fast heating, both compounds do not melt, even using very high temperatures (around 100 K above the melting). Based on those results, and as stated before, for some mixtures containing ammonium salts,[20] we advise caution on the part of the reader when considering the reported data for pure ammonium salts with short alkyl chain lengths. The indicated temperatures should be seen as guides, having in mind the decomposition, partial or even full, upon melting.

The $[N_{X,X,X,X}]$-chloride-based systems are herein first analyzed (Figure 2). All exhibit a phase behavior characterized by a single eutectic point, with significant temperature depressions when compared to the melting temperature of the pure quaternary ammonium salt used. Urea presents slight positive deviations when mixed with $[N_{1,1,1,1}]$Cl, $[N_{2,2,2,2}]$Cl, and $[N_{3,3,3,3}]$Cl, indicating that the interactions in the mixture are weaker (or less favorable) than those present in the liquid phase of pure urea. Although the nonideality of these salts cannot be rigorously evaluated because of the lack of melting properties described above, the results available clearly indicate that they, indeed, display negative deviations from ideality, as debated in Section II of the Supporting Information. This thermodynamic asymmetry can be explained by considering the formation of new $[N_{X,X,X,X}]\cdots O$ contacts at the expense of $NH\cdots O$ contacts. This trade-off is favorable for the quaternary ammonium salts (as it stabilizes cation–cation repulsion) but unfavorable for urea and is supported by (i) the negative deviations from ideality due to chloride transfer reported for $[N_{1,1,1,1}]$Cl/$[N_{4,4,4,4}]$Cl mixtures,[20] (ii) the activity coefficient pattern for urea seen in Figure S6, where its positive deviations are dampened by the increase in the alkyl chain length of $[N_{X,X,X,X}]$, which shield the positive charge of the cation and decrease the driving force for $[N_{X,X,X,X}]\cdots O$ contact formation, and (iii) the analogous behavior observed before for mixtures of chloride ammonium salts with carboxylic acids[23] and ionic liquids with water.[37]

In sharp contrast with the systems based on $[N_{1,1,1,1}]$Cl, $[N_{2,2,2,2}]$Cl, and $[N_{3,3,3,3}]$Cl, mixtures of urea and $[N_{4,4,4,4}]$Cl also show an asymmetrical behavior but with the salt having positive and urea negative deviations from thermodynamic ideality (Figure 2d). This same behavior was observed before for $[N_{4,4,4,4}]$Cl+ fatty acids or fatty alcohols,[25] as depicted in Figure S7, and $[N_{1,1,1,1}]$Cl + $[N_{4,4,4,4}]$Cl,[20] where, while $[N_{4,4,4,4}]$Cl presents either a near-ideal behavior or weak positive deviations from ideality, negative deviations from ideality are seen in the second component. This can be rationalized by considering the chloride donating ability of $[N_{4,4,4,4}]$Cl.[20,25] The large size of its alkyl chains shield the

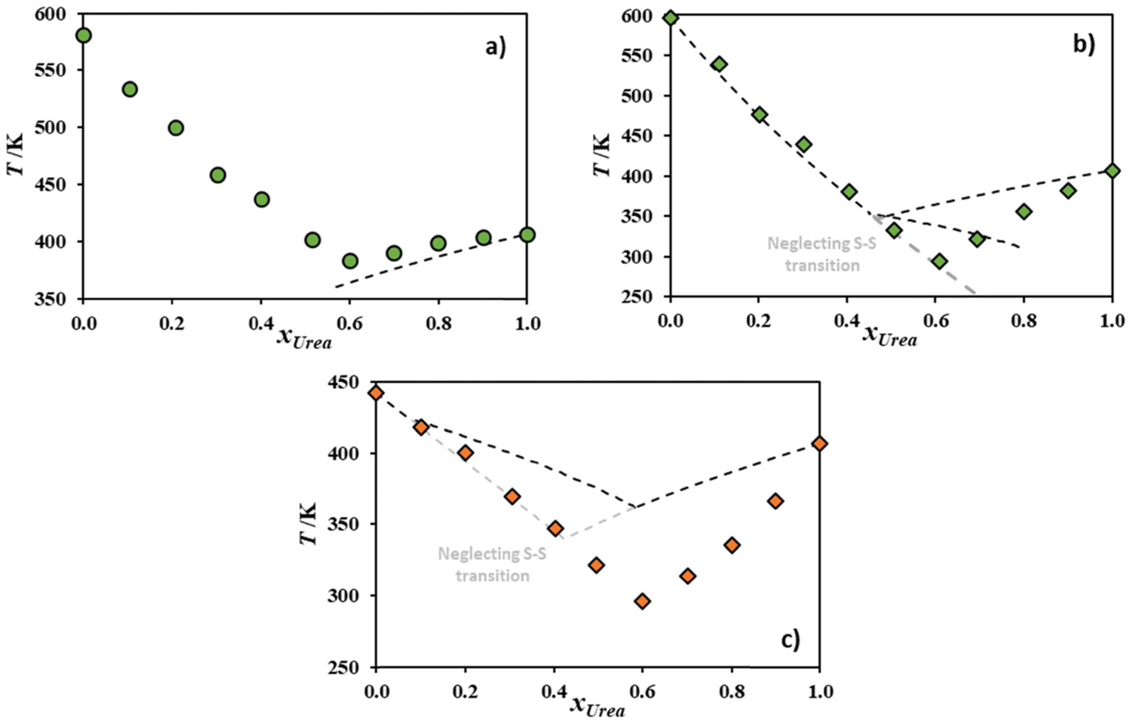

Figure 4. Solid−liquid equilibrium phase diagrams for the binary systems composed of urea and (a) ChBr, (b) ChCl,[19] or (c) MeChCl. Symbols represent the data experimentally measured in this work or taken from the literature, while the dashed lines represent the ideal solid−liquid equilibrium.

positive charge of $[N_{4,4,4,4}]$, leading to weaker $[N_{4,4,4,4}]\cdots Cl$ interactions, and add an important van der Waals component to cation−cation interactions, decreasing their Coulombic repulsion. Both effects permit the transfer of chloride anions to urea. Because NH···Cl interactions are stronger than NH···O, this leads to negative deviations from ideality for urea. On the other hand, the loss of $[N_{4,4,4,4}]\cdots Cl$ contacts (even if they are replaced by new, weaker $[N_{4,4,4,4}]\cdots O$ interactions) leads to the positive deviations seen for $[N_{4,4,4,4}]Cl$.

The effect of anion electronegativity was explored by replacing the anion chloride with bromide. Because of its lower electronegativity and larger size, the charge transfer of bromide to the second precursor (i.e., urea) is expected to be less extensive than the chloride as NH···Br interactions are weaker than NH···Cl. This was observed before for mixtures of $[N_{1,1,1,1}]Cl$ with $[N_{2,2,2,2}]Cl$ or $[N_{2,2,2,2}]Br$, and $[N_{3,3,3,3}]Cl$ or $[N_{3,3,3,3}]Br$.[20] In these cases, the tetramethylammonium salt presents negative deviations from ideality when mixed with chloride-based salts but a near-ideal behavior when mixed with bromide-based salts.

Figure 3 depicts the binary solid−liquid phase diagrams of mixtures of urea and tetraalkylammonium bromides, and the corresponding activity coefficients are represented in Figure S8.

The use of bromide-based salts also leads to significant melting point depressions, as can be observed in Figure 3. However, while urea presented slight positive deviations from ideality when mixed with $[N_{1,1,1,1}]Cl$, $[N_{2,2,2,2}]Cl$, and $[N_{3,3,3,3}]Cl$, Figure 3 shows that it behaves ideally when mixed with the bromide counterparts of these salts. Although these differences are small and of little importance to the overall soup of interactions present in the eutectic systems, they are most likely caused by the larger size of the bromide anion, which increases the distance between cations, minimizing their repulsion and, thus, the driving force for the formation of $[N_{X,X,X,X}]\cdots O$ contacts (which resulted in the urea positive deviations identified for the chloride systems). On the other hand, $[N_{4,4,4,4}]Br$ is able to induce negative deviations from ideality in urea, albeit to a lesser extent than those seen in the $[N_{4,4,4,4}]Cl$/urea system, as expected because of the lower electronegativity of bromide. In other words, all intermolecular interactions identified for chloride-based systems (Figure 2) seem to occur in bromide-based systems as well, but to a much lesser extent, leading all thermodynamic deviations (negative or positive) to be dampened, with all components behaving closer to thermodynamic ideality.

As in the chloride-based systems, the nonideality of the bromide salts cannot be rigorously evaluated because of the lack of melting enthalpies. However, the estimated values available in the literature[30] clearly indicates that the bromide salts also behave nonideally when mixed with urea (Section II of the Supporting Information).

It is worth noting that the solid−solid transition of $[N_{4,4,4,4}]Br$ has an important impact on the phase diagram of the mixture with urea. The results depicted in Figure 3d show that when the solid−solid transition is considered, the salt behaves almost ideally; otherwise, positive deviations from ideality would be assumed. Despite its enormous challenge and the need to combine different techniques for solid-phase experimental studies, this calls for improvements in the availability of reliable experimental melting property data of the pure compounds. Alternatively, well-founded thermodynamics procedures can be used to predict or estimate those properties. Both approaches are crucial to help prevent precipitated and often wrong conclusions.

The impact of introducing a hydroxyethyl group in the salt cation is here evaluated by investigating the SLE phase diagrams of ChCl, MeChCl, or ChBr + urea (Figures 4 and

S9). Starting with the system ChCl/urea (Figure 4b), the salt behaves ideally while urea shows strong negative deviations from ideality. This is surprising as despite the similarity between the $[N_{1,1,1,1}]$ and choline cations (Figure 1), the thermodynamic behavior of the system ChCl/urea is much closer to that seen in $[N_{4,4,4,4}]$/urea rather than $[N_{1,1,1,1}]$/urea mixtures. Note that the presence of the hydroxyl group of choline, initially thought to compete with urea for the chlorides available in the liquid mixture, appears to favor the nonideality of urea. This suggests that much like $[N_{4,4,4,4}]$Cl, ChCl can stabilize its cation−cation repulsion (likely due to hydrogen bonding between hydroxyethyl groups, as identified by Knorr et al.[38] and Gilmore et al.[39]) and behave as a chloride donor when mixed with urea, NH···Cl contacts being the key interaction underpinning the thermodynamic behavior of the system. Of course, urea−hydroxyethyl hydrogen bonds also contribute to the overall nonideality of urea, as identified in previous studies,[16−19] but this appears to be a minor contribution when compared to NH···Cl interactions, as will be further explored below.

The dominant role of NH···Cl over urea−hydroxyethyl interactions is supported by the results obtained for ChBr/urea mixtures. In this case, in stark contrast to ChCl/urea mixtures, urea shows slight positive deviations from ideality (Figure S9) despite the possibility of establishing urea−hydroxyethyl interactions in both cases. In other words, the thermodynamic behavior of ChCl/urea is similar to that of $[N_{4,4,4,4}]$Cl/urea, while the behavior of ChBr/urea is more closely related to that of $[N_{1,1,1,1}]$Cl/urea. This clearly shows that the formation of the prototypical ChCl/urea DES is governed by urea−chloride interactions, and, in their absence, the nonideality of urea is lost.

The nonideality of ChCl and ChBr is explored in Section II of the Supporting Information. The melting enthalpy of ChCl was estimated assuming that the system ChCl + urea herein measured behaves ideally and is very close to the value presented by us before[31] and significantly inferior to the values predicted using PC-SAFT and COSMO-RS.[30] Regarding ChBr, the melting enthalpy herein estimated assuming that the system ChBr + urea measured behaves ideally is very close to the values predicted with PC-SAFT and COSMO-RS,[30] indicating that ChBr behaves ideally when mixed with urea.

Despite the many studies performed for the ChCl/urea system[16−19] (and references therein), there is still debate in the literature about the thermodynamic behavior of this system, particularly the claim that ChCl behaves ideally (Figure 4b). This is due to the fact that ChCl decomposes upon melting, precluding the experimental measurement of its fusion properties,[31] which are key in interpreting thermodynamic behavior from SLE phase diagrams (see Section 2.3). One way to settle this debate is to choose a structurally similar compound whose melting properties are known experimentally, such as MeChCl (see Figure 1). Figure 4c shows the SLE of MeChCl/urea, where, as already described for ChCl/urea, MeChCl behaves ideally (when neglecting its solid−solid transition). It is worth noting that, in contrast to $[N_{4,4,4,4}]$Br whose solid−solid transition has a strong impact on its phase diagram with urea, the solid−solid transitions of ChCl and MeChCl are not observed in their experimental phase diagrams with urea (no inflection points in the liquidus line). The absence of this transition is commonplace across the literature of ChCl-based DESs and may be connected with Ostwald's rule.[40,41] In other words, the remarkably low melting enthalpy of the higher-temperature polymorph of ChCl and MeChCl (β) favors its crystallization even at temperatures, where the low-temperature polymorph (α) is the most stable.

Bearing in mind the objective of lowering the melting point of the pure compounds used in the mixture, and hence generate DESs, the mixtures investigated here are quite promising. Although none is liquid at room temperature, the melting point depressions are considerably high with values up to 272 and 110 K corresponding to the salt in $[N_{1,1,1,1}]$Br/urea and urea in MeChCl/urea. Of course, in a direct comparison of their eutectic temperatures, the system choline chloride/urea reported before[19] still presents the highest depression (302/112 K salt/urea) and the lowest eutectic temperature. This fact is in part attributed to the small melting enthalpy of this prototypical DES-forming component (4.3 kJ/mol)[31] rather than to the actual interactions between the DES precursors.

The results discussed in this work show that anion transfer, promoted by minimizing cation−cation repulsion and increasing the strength of urea−anion interactions, is key in understanding the nonideality of urea/quaternary ammonium eutectic solvents, which is in line and complements previous studies regarding choline chloride/urea mixtures.[16−19] Although the sustainable character of the salts used here is questionable, these results can be easily extended to more promising alternatives. Particularly, the insights provided here contextualize the recent success in forming betaine/urea DESs[42] (note the similarity of betaine with ChCl and $[N_{1,1,1,1}]$Cl) and call for more systematic studies on the impact of charge transfer in DES formation.

4. CONCLUSIONS

The solid−liquid phase diagrams of eutectic systems composed of ammonium chlorides or bromides and urea were measured. The experimental data show that these systems present a eutectic temperature far from the melting temperature of the pure precursors. The nonideality seen in the urea-rich side shows that chloride transfer can be heightened by increasing the alkyl chain length of the salt. Upon replacing chloride by bromide, this thermodynamic behavior is attenuated due to the bromide larger size and lower electronegativity.

The introduction of a hydroxyethyl group in the tetramethylammonium cation, that is, cholinium cation, leads to two very different behaviors depending on the anion. When mixed with ChCl, urea displays strong negative deviations to ideality, while it shows small positive deviations when mixed with ChBr. This indicates that anion-urea interactions, rather than cation-urea, govern the formation of urea-based DESs, particularly the prototypical ChCl/urea. The use of MeChCl, whose melting properties are experimentally known, supports previous analysis of the thermodynamic behavior in the ChCl/urea system.

This contribution is part of a series of studies that aim to provide insights into the donor−acceptor interactions that lead to DES formation, and data on eutectic systems solid−liquid phase equilibria and thus information on the operation window (range of compositions and temperatures) of these systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c01274.

Solid−liquid equilibrium data; NMR spectra of urea mixtures and pure $[N_{2,2,2,2}]Cl$ and $[N_{2,2,2,2}]Br$; and activity coefficients of binary systems and salts non-ideality study (PDF)

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Notes

The authors declare no competing financial interest.

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