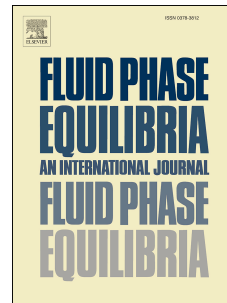


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# Can Cholinium Chloride form Eutectic Solvents with Organic Chloride-based Salts?

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## ABSTRACT

The high melting point of a large number of organic salts with potential ionic liquid-like properties, hinders their applicability as solvents. Considering the success of cholinium chloride on lowering the melting temperature of several substances and its success on forming deep eutectic solvents, this work studies its mixing with organic chlorides to lower their melting points producing eutectic ionic liquids.

The solid-liquid phase diagrams for binary mixtures composed of cholinium chloride and ten organic halides were experimentally measured. Surprisingly, cholinium chloride presented, for all these systems, significant positive deviations from ideal liquid behaviour that restricted its ability to lower the melting points of these mixtures. Only for mixtures with ammonium chloride, tetramethylammonium chloride, bis(2-hydroxyethyl)dimethylammonium chloride or cholinium bromide was cholinium chloride able to significantly lower the melting point of the mixture, but without reaching values close to room temperature (298 K). For a better understanding of the results obtained, the solid-liquid phase diagrams of four alkylammonium chloride-based mixtures were experimentally assessed and used to show that these compounds are better than cholinium chloride at inducing negative deviations from ideality, leading to greater melting point depressions.

**KEYWORDS:** Cholinium Chloride, Ionic Liquids, Ionic Liquid Mixtures, Eutectic Solvents, Solid-liquid equilibria

## 1. Introduction

During the last decades, the study of ionic liquids attained a high degree of maturity[1–10]. They present an immense potential for tunability due to their ionic nature. Since they are composed of a cation and an anion, a judicious choice of their combination may help to design a compound with a set of desired properties. Nevertheless, in some cases, the relatively high melting point of the resulting compound may hinder its applicability, especially as a solvent to be used at or near room temperature (298 K).

Recently there has been a growing interest for ionic liquid mixtures[11,12]. Not only does the use of mixtures of ionic liquids increase their *designer* capability, it also allows for the reduction of the melting point of some ionic solids, allowing the preparation of eutectic ionic liquids from ionic solids. This concept was clearly addressed by Maximo et al.[13] showing that the melting point of hexafluorophosphate-based salts could be successfully lowered by preparing binary mixtures of them, and yet it has been explored only by few authors[14–18].

Cholinium chloride is an ionic solid commonly used in the preparation of deep eutectic solvents[19–21] since it not only forms biodegradable mixtures[22], but also acts as a hydrogen bond acceptor with a low melting enthalpy (4.3 kJ/mol)[23], which contributes to substantial melting-point depression of its mixtures. As such, in this work, the feasibility of using cholinium chloride to lower the melting point of organic chlorides, with a melting point too high to be useful as a solvent, is explored.

When organic salts with a common ion are mixed, the resulting system is usually of the eutectic type, in some cases inducing the formation of intermediate compounds that may originate peritectic points. The common-ion specification is necessary to ensure that only the original salts may crystallize from the liquid mixture. If instead of 3 ions, a mixture of 4 ions is considered, the phase diagram becomes much more complex, with at least 4 different solid compounds precipitating from solution depending on the relative concentration of the ions present and the temperature of the system. For this reason, in this work only chloride-based salts are used, with the single exception of cholinium bromide that is used to evaluate the effect of a common cation upon the phase behaviour of cholinium chloride.

The eutectic-type solid-liquid equilibrium phase diagram of a mixture between two common-ion salts, when no solid-phase transitions are present, may be computed by describing each individual component melting curve using the following equation[24]:

$$\ln(x_i \cdot \gamma_i) = \frac{\Delta_m h_i}{R} \cdot \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) + \frac{\Delta_m C p_i}{R} \cdot \left( \frac{T_{m,i}}{T} - \ln \frac{T_{m,i}}{T} - 1 \right) \quad (1)$$

where  $x_i$  is the mole fraction of the general salt  $i$ ,  $\gamma_i$  its activity coefficient,  $\Delta_m h_i$  its melting enthalpy,  $T_{m,i}$  its melting temperature and  $\Delta_m C p_i$  its heat capacity change upon melting, while  $R$  is the ideal gas constant and  $T$  is the absolute temperature of the system. Equation 1 is not practical to use since the heat capacity change upon melting is not simple to measure and is not readily available in the literature. However, this term can, for most substances, be neglected in comparison with the other terms of the equation[24,25], leading to:

$$\ln(x_i \cdot \gamma_i) = \frac{\Delta_m h_i}{R} \cdot \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) \quad (2)$$

Equation 2 may be used to estimate the activity coefficients from the experimental phase diagrams. Moreover, to evaluate the non ideality of the liquid phase, the experimental results can also be compared with the prediction of Equation 2 when setting the activity coefficient value to 1. In this work the solid-liquid phase diagrams of mixtures of cholinium chloride with ten organic chloride salts are measured and their non ideality discussed.

## 2. Experimental

### 2.1 Chemicals

The ionic solids used in this work and their abbreviations, along with their source and purity, are reported in Table 1, while their structures are depicted in Figure 1. Previous to being used, all salts were thoroughly dried under vacuum (0.1 Pa), at room temperature (298 K) and constant stirring, for at least 72 hours. Their water content 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 instances.

### 2.2 Phase Diagrams Measurement

Binary mixtures of the ionic solids were prepared for the entire composition range of each system inside a dry-argon glove-box, by weighting the amounts of each pure substance using an analytical balance (model ALS 220-4N from Kern) with an accuracy of  $\pm 0.002$  g. After being molten and recrystallized, each mixture was crushed in a mortar inside a dry-argon glove-box and part of the powder was transferred to a glass capillary. Its melting point was measured using the melting point device model M-565 from Buchi, with a temperature resolution of 0.1 K, as previously described[22], and a temperature gradient of  $0.1 \text{ K} \cdot \text{min}^{-1}$ .

This procedure was repeated at least three times and the measurements have an estimated reproducibility better than 2 K.

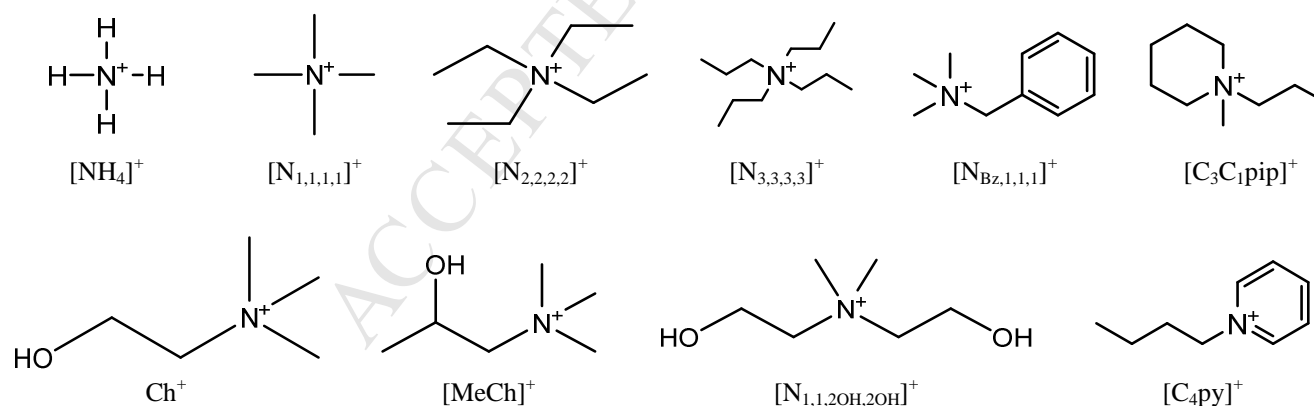
In a few cases, a mixture with a paste-like consistency was obtained after the initial melting and recrystallization. In those cases, a visual method with an oil bath, described elsewhere[22], was employed instead. The mixtures were gradually heated until complete melting and the temperature was controlled with a Pt100 probe possessing a precision of  $\pm 0.1$  K, which was previously calibrated against a calibrated platinum resistance thermometer, SPRT100 (Fluke-Hart Scientific 1529Chub-E4), traceable to the National Institute of Standards and Technology (NIST). This procedure was also repeated at least three times, presenting the same reproducibility as before (better than 2 K).

The melting temperatures and enthalpies of [MeCh]Cl and [C<sub>4</sub>py]Cl were measured using differential scanning calorimetry (DSC) in a Hitachi DSC7000X model working at atmospheric pressure. Samples of approximately 2 – 5 mg tightly sealed in aluminium pans were prepared inside the dry-argon glove-box and submitted to 3 repeated cooling–heating cycles at 5 K min<sup>-1</sup> (cooling) and 2 K min<sup>-1</sup> (heating). The thermal transition temperatures were taken as the peak temperature. The equipment was calibrated with several standards (heptane, octane, decane, 4-nitrotoluene, naphthalene, benzoic acid, diphenylacetic acid, indium, tin, caffeine, lead, zinc, potassium nitrate, water and anthracene) with weight fraction purities higher than 99 %. Due to the degradation upon melting, it was not possible to measure the melting properties of [N<sub>Bz,1,1,1</sub>]Cl, [N<sub>1,1,2OH,2OH</sub>]Cl, [C<sub>3</sub>C<sub>1</sub>pip]Cl, [NH<sub>4</sub>]Cl and ChBr.

**Table 1.** Name, abbreviation and CAS number of the salts experimentally used in this work, along with the corresponding supplier and purity. The melting temperatures and enthalpies, when available, are also included.

Name	Abbreviation	CAS Number	Supplier	Purity (%)	$T_m$ /K	$\Delta h$ /kJ/mol
<b>Cholinium Chloride</b>	ChCl	67-48-1	Acros Organics	98	597[23]	4.3[23]
<b>beta-Methylcholine Chloride</b>	[MeCh]Cl	2382-43-6	TCI	>98	442.0 <sup>a</sup>	6.72 <sup>a</sup>
<b>Tetramethylammonium Chloride</b>	[N <sub>1,1,1,1</sub> ]Cl	75-57-0	Sigma-Aldrich	97	614.7 <sup>b</sup>	20.49[12]
<b>Tetraethylammonium Chloride</b>	[N <sub>2,2,2,2</sub> ]Cl	56-34-8	Alfa Aesar	98	535.4 <sup>b</sup>	51.24[12]
<b>Tetrapropylammonium Chloride</b>	[N <sub>3,3,3,3</sub> ]Cl	5810-42-4	Sigma-Aldrich	98	502.4 <sup>b</sup>	66.58[12]
<b>Benzyltrimethylammonium Chloride</b>	[N <sub>Bz,1,1,1</sub> ]Cl	56-93-9	Acros Organics	98	509.2 <sup>b</sup>	—
<b>Bis(2-hydroxyethyl)dimethylammonium Chloride</b>	[N <sub>1,1,2OH,2OH</sub> ]Cl	38402-02-7	Acros Organics	99	563.7 <sup>b</sup>	—
<b>1-Methyl-1-Propylpiperidinium Chloride</b>	[C <sub>3</sub> C <sub>1</sub> pip]Cl	1383436-85-8	Iolitec	99	498.4 <sup>b</sup>	—
<b>Ammonium Chloride</b>	[NH <sub>4</sub> ]Cl	12125-02-9	JMGS	99.5	632.2 <sup>c</sup>	10.38 <sup>c</sup>
<b>1-Butylpyridinium Chloride</b>	[C <sub>4</sub> py]Cl	1124-64-7	Iolitec	98	405.4 <sup>a</sup>	26.13 <sup>a</sup>
<b>Cholinium Bromide</b>	ChBr	1927-06-6	TCI	98	581.6 <sup>b</sup>	—

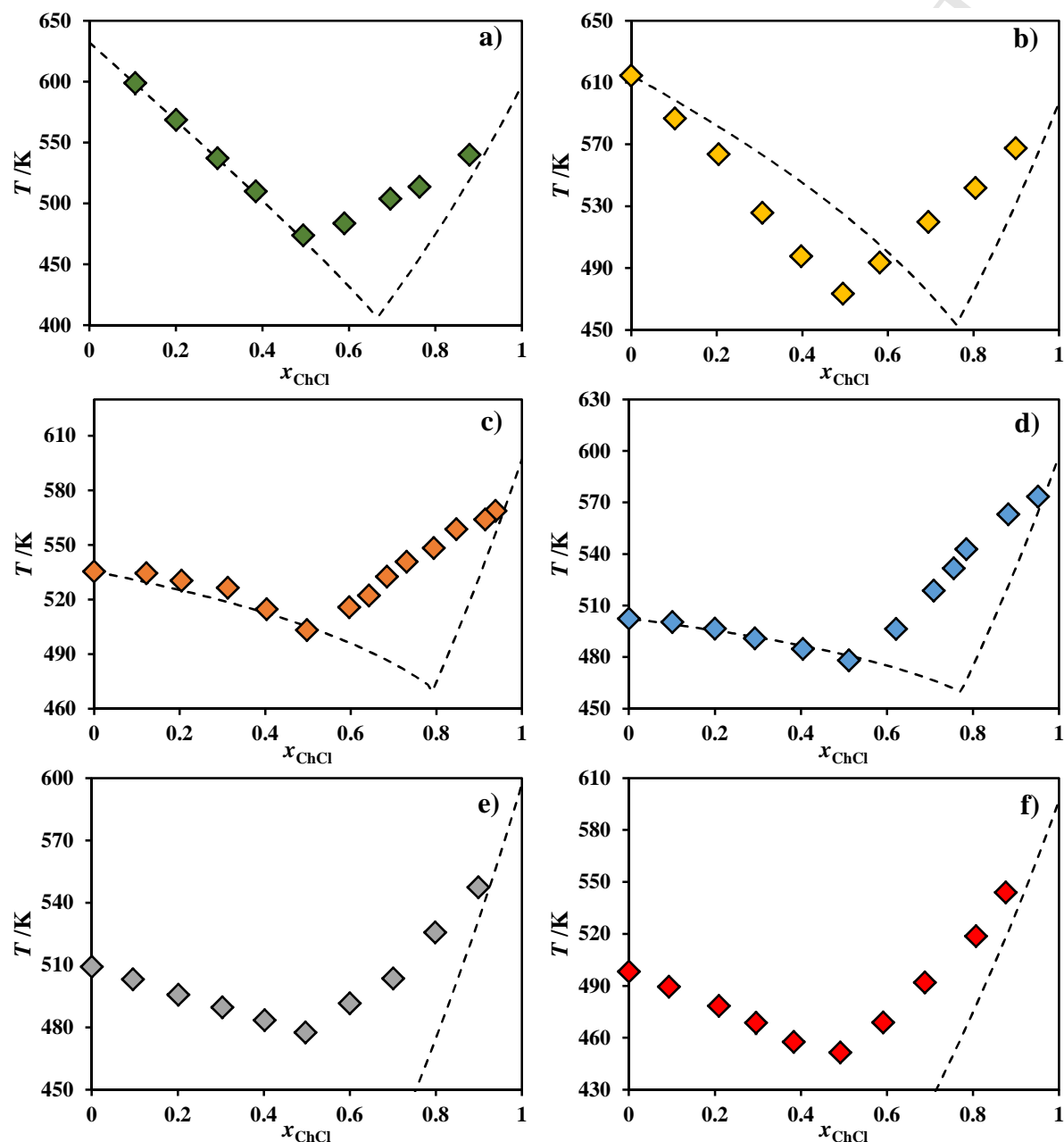
a) Measured in this work through DSC. b) Measured in this work through the capillary-visual method. c) Estimated in this work using experimental SLE data (see Supporting Information)



**Figure 1.** Chemical structure of the cations composing the ionic solid investigated in this work. Each abbreviation matches that used in Table 1.

### 3. Results

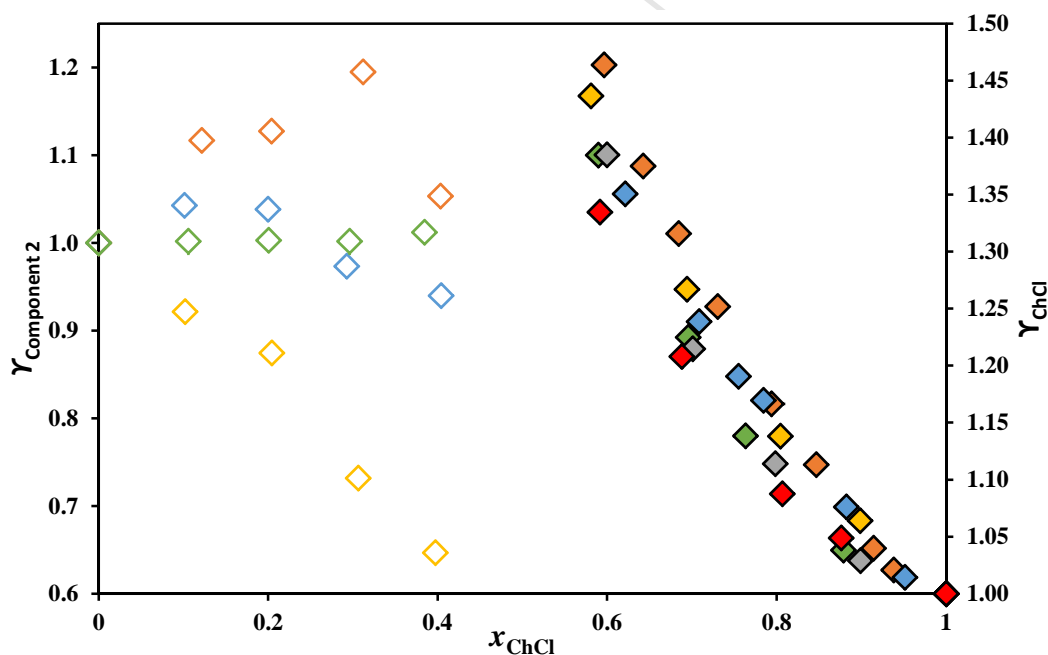
The alkylammonium-based systems are herein first analysed (the experimental data is given in Tables S1 to S3, as Supporting Information). Figure 2 presents the experimental solid-liquid equilibrium (SLE) data along with the ideal liquid mixture phase diagram calculated by setting  $\gamma_i$  equal to 1 in Equation 2 and using the fusion properties reported in Table 1.



**Figure 2.** Experimental SLE data (■) along with the ideal liquid mixture SLE phase diagram (---) for the systems composed of cholinium chloride and a)  $[\text{NH}_4]\text{Cl}$ , b)  $[\text{N}_{1,1,1,1}]\text{Cl}$ , c)  $[\text{N}_{2,2,2,2}]\text{Cl}$ , d)  $[\text{N}_{3,3,3,3}]\text{Cl}$ , e)  $[\text{N}_{\text{Bz},1,1,1}]\text{Cl}$  and f)  $[\text{C}_3\text{C}_{\text{pip}}]\text{Cl}$ .

It was not possible to calculate the complete ideal liquid mixture SLE curves for the systems with components  $[N_{Bz,1,1,1}]Cl$  and  $[C_3C_1pip]Cl$  since their melting enthalpies are not available as these compounds decompose before melting. The  $[NH_4]Cl$  ideal curve was calculated using melting properties estimated in this work from experimental SLE data (see section S2 of the supporting information). Except for  $[N_{1,1,1,1}]Cl$ , no significant melting-point depressions were observed upon mixing the ionic solids with cholinium chloride.

The most striking feature of these results is that, unlike observed for the phase diagrams of cholinium chloride-based (deep) eutectic systems published in the literature[26–28], for which the cholinium chloride melting curves present a near ideal behaviour, or a small negative deviation to ideality, here, for all systems studied, positive deviations from ideality are observed. However, there is no evident relationship between the magnitude of these deviations and the chemical structure of the second component of the mixture. The experimental activity coefficients reported in Figure 3 show very similar values and behaviour for all systems studied.

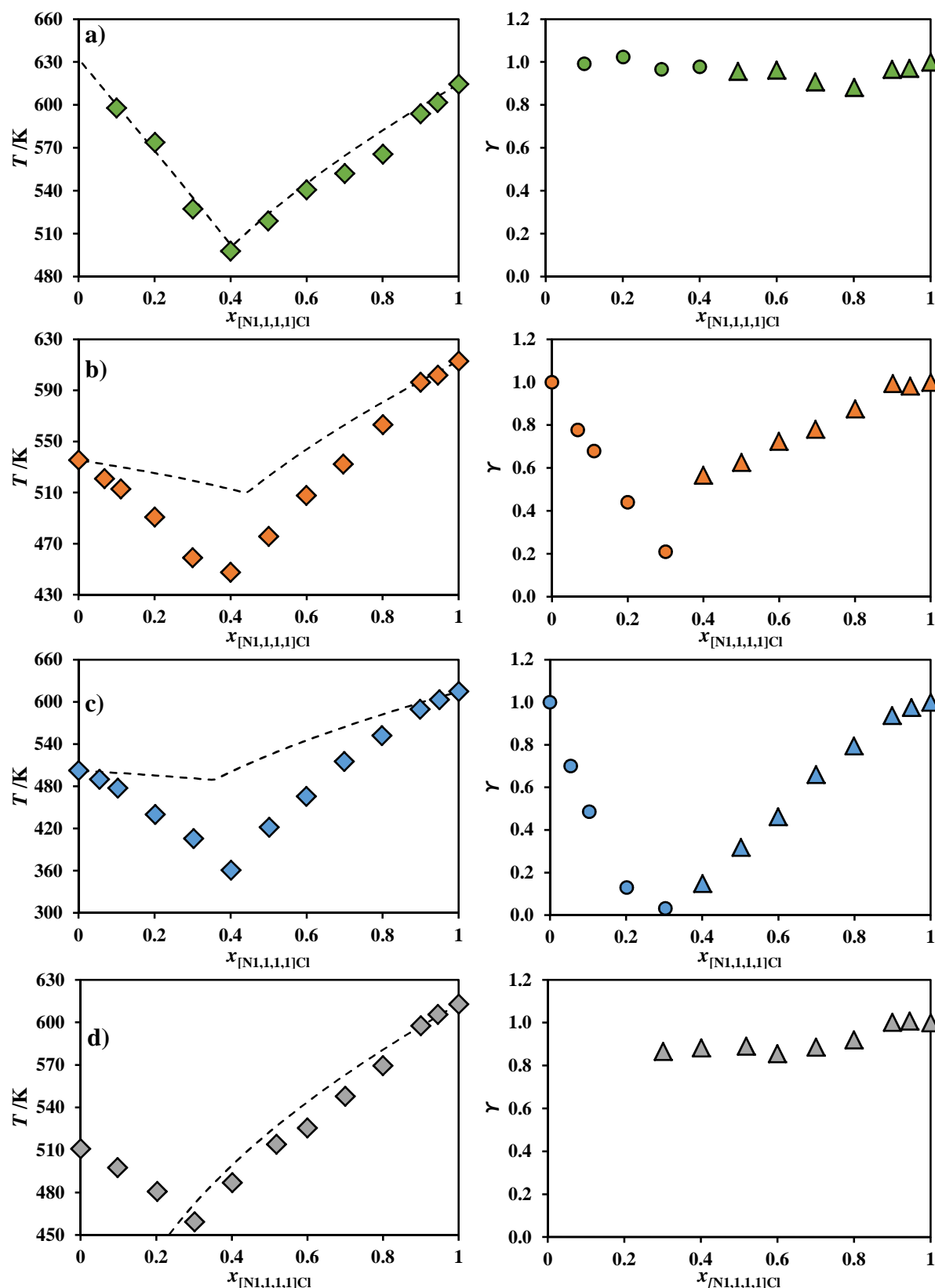


**Figure 3.** Experimental activity coefficients for cholinium chloride (full marker, right axis) and the second component (empty marker, left axis) in the binary mixtures herein studied ( $ChCl + NH_4Cl$ ,  $[N_{1,1,1,1}]Cl$ ,  $[N_{2,2,2,2}]Cl$ ,  $[N_{3,3,3,3}]Cl$ ,  $[N_{Bz,1,1,1}]Cl$ , and  $[C_3C_1pip]Cl$ ), calculated using the experimental data presented in Table S1 and the melting properties included in Table 1.



Another interesting feature to note in Figure 3, and in Figure 2b as well, is the negative deviation from ideality presented by  $[N_{1,1,1,1}]Cl$ , in contrast with the near ideal behaviour of  $[NH_4]Cl$ ,  $[N_{2,2,2,2}]Cl$  and  $[N_{3,3,3,3}]Cl$ . The ionic liquid  $[N_{4,4,4,4}]Cl$  was also previously shown to behave ideally when mixed with choline chloride[23]. The explanation for the behaviour of  $[N_{1,1,1,1}]Cl$  is not yet clear. Since it cannot form hydrogen bonding nor any other specific interaction with  $ChCl$ , entropic effects may be the cause for its strong negative deviations from ideality.

To aid in explaining the phenomenon introduced in the last paragraph and to investigate the role of cholinium chloride's hydroxyethyl group on the deviations from ideality reported in Figure 3,  $ChCl$  was replaced with  $[N_{1,1,1,1}]Cl$ . Note that  $ChCl$  and  $[N_{1,1,1,1}]Cl$  are structurally very similar (Figure 1), the difference being that one of the latter methyl groups is replaced by a hydroxyethyl group in the former. The new SLE phase diagrams were experimentally assessed and are shown in Figure 4.



**Figure 4.** Experimental SLE data points ( $\blacklozenge$ ), ideal liquid mixture SLE phase diagram (---) and activity coefficients ( $\blacktriangle$  for component 1 and  $\bullet$  for component 2) for the systems composed of  $[\text{N}_{1,1,1,1}]\text{Cl}$  and a)  $[\text{NH}_4]\text{Cl}$ , b)  $[\text{N}_{2,2,2,2}]\text{Cl}$ , c)  $[\text{N}_{3,3,3,3}]\text{Cl}$  and d)  $[\text{NBz}_{1,1,1,1}]\text{Cl}$ .

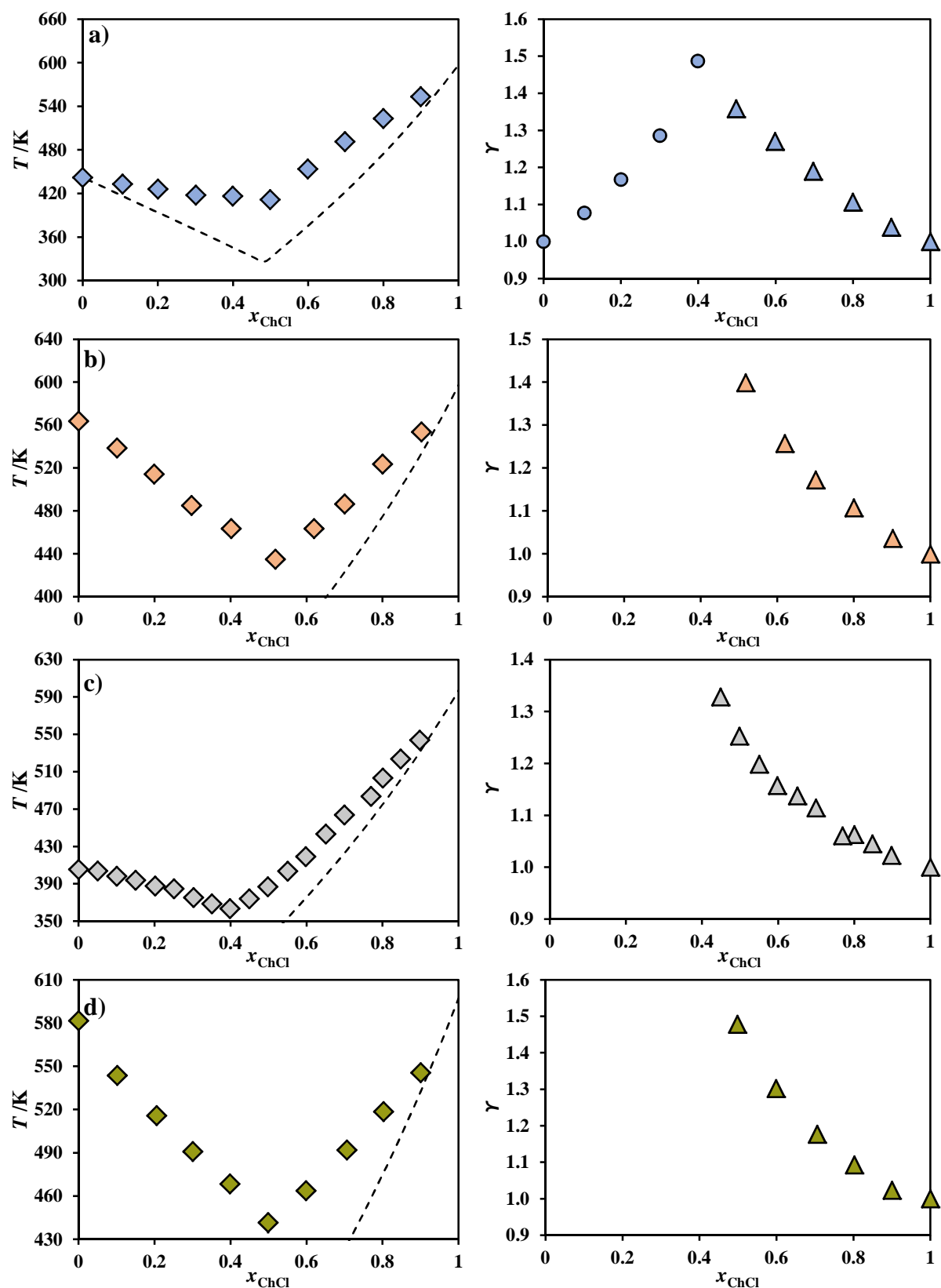
While cholinium chloride revealed positive deviations from ideality in all systems, as shown in Figures 2 and 3,  $[N_{1,1,1,1}]Cl$  reveals negative deviations from ideality, similar to what was shown in Figure 2b, or a near-ideal behaviour. This suggests that the hydroxyethyl group present in cholinium chloride allows for stronger interactions in the pure substance, either in the form of OH-Cl interactions between cation and anion, as suggested by Hammond[29] et al., or in the form of hydrogen bonding between cations (OH-OH), as recently proposed by Knorr[30] et al. and Gilmore[31] et al. This explains cholinium chloride positive deviations from ideality, while the cations in the alkylammonium-based ionic solids cannot participate in hydrogen bonding nor offer any other type of specific interactions. Particularly, the  $[N_{1,1,1,1}]Cl$  salt used in the four systems above has no centres capable of specific interactions other than coulombic.

Bearing in mind the objective of lowering the melting point of ionic solids, mixtures  $[N_{1,1,1,1}]Cl/[N_{2,2,2,2}]Cl$  (Figure 4b) and  $[N_{1,1,1,1}]Cl/[N_{3,3,3,3}]Cl$  (Figure 4c) are remarkable. The strong negative deviations from ideality revealed by all components in these mixtures leads to an eutectic temperature of around 175 K in the first case, about 60 K below the ideal eutectic temperature, and 88 K in the second case, about 130 K below the ideal eutectic temperature, making of this a true eutectic ionic liquid. This suggests that the use of quaternary alkyl ammonium chlorides may be a better approach to produce eutectic ionic liquids, by decreasing the eutectic temperature well below the melting temperature of the pure constituents, than the cholinium chloride used in this work. This approach will be object of a future work.

Alternatively to the alkylammonium chlorides, ChCl was also combined with  $[MeCh]Cl$ ,  $[N_{1,1,2OH,2OH}]Cl$ ,  $[C4py]Cl$  or ChBr. The experimental SLE phase diagrams for these binary systems are displayed in Figure 5, along with the calculated ideal liquid mixture SLE curves, whenever the melting properties of the pure components are available. The positive deviations from ideality of cholinium chloride, albeit less severe, are analogous to those reported in the previous section for alkylammonium-based salts. Nevertheless, cholinium chloride was able to successfully lower the melting point of  $[N_{1,1,2OH,2OH}]Cl$  and of ChBr, in the first case with an eutectic temperature close to 160 K.

The eutectic mixtures of cholinium chloride with quaternary ammonium or ionic-liquid analogues of high melting points, unlike other eutectic ionic liquids based on mixtures with a common anion previously studied[14–18], show important deviations to ideality. In

particular, the hydroxyl group of cholinium chloride seems to induce specific interactions between these cations and a strong interaction with the anion that induce strong positive deviations to ideality in most mixtures. This is clearly shown in the study of the four binary systems formed by  $[N_{1,1,1,1}]Cl$ , where removing the hydroxyl group induces strong negative deviations, on analogous binary mixtures, evidencing the role of the hydroxyl group on the cholinium interactions. But not only the nature of the hydrogen bonding between hydroxyl groups seems to matter as the  $ChBr-ChCl$  system also presents positive deviations that seem to be induced by the different nature of the cation-anion interactions in the two compounds. The results here reported reinforce the idea that the ability of the cholinium chloride to induce the formation of low melting point eutectic mixtures is probably more connected to its low melting enthalpy than to the formation of donor:acceptor hydrogen bonding complexes commonly accepted. In particular, the results from this work suggest that cholinium chloride is not the best choice to prepare eutectic ionic liquids, by mixing it with other organic salts, but instead tetra-alkyl ammonium chlorides show an interesting potential for that purpose, that will be explored in a future work.



**Figure 5.** Experimental SLE data points ( $\blacklozenge$ ), ideal liquid mixture SLE phase diagram (---) and activity coefficients ( $\blacktriangle$  for component 1 and  $\bullet$  for component 2) for the systems composed of cholinium chloride and a) [MeCh]Cl, b) [N<sub>1,1,2OH,2OH</sub>]Cl, c) [C<sub>4</sub>py]Cl and d) ChBr.

#### 4. Conclusions

In this work, the feasibility of using cholinium chloride to lower the melting point of ionic substances, unfit for the definition of ionic liquid, was studied. The SLE phase diagrams of ten cholinium chloride-based mixtures were experimentally measured and are herein reported and discussed. Although cholinium chloride presented positive deviations from ideality in all systems investigated, its small melting enthalpy alleviated this problem and led to useful melting point depressions in four substances: cholinium bromide, ammonium chloride, tetramethylammonium chloride and bis(2-hydroxyethyl)dimethylammonium chloride.

To better understand the thermodynamic behaviour of mixtures of cholinium chloride and alkylammonium-based ionic salts, ChCl was replaced with  $[N_{1,1,1,1}]Cl$  and the SLE phase diagram measurements were repeated. The replacement of the hydroxyethyl group of the cholinium cation by a methyl group in  $[N_{1,1,1,1}]Cl$  led to negative deviations from the ideal behaviour. These results suggest that the cholinium chloride hydroxyethyl group plays a significant role on its interactions with other cholinium chloride pairs, and seem to be the basis of its positive deviations from ideality when mixed with alkylammonium-based ionic solids.

This study also showed that the mixtures  $[N_{1,1,1,1}]Cl/[N_{2,2,2,2}]Cl$  and  $[N_{1,1,1,1}]Cl/[N_{3,3,3,3}]Cl$  presented large negative deviations from ideality, leading to remarkable melting point depressions. The eutectic temperature of the mixture  $[N_{1,1,1,1}]Cl/[N_{3,3,3,3}]Cl$  is around 90 K, 140 K below the melting point of  $[N_{3,3,3,3}]Cl$  and 250 K below the melting point of  $[N_{1,1,1,1}]Cl$ . This suggests that tetralkyl ammonium chlorides may be better at producing eutectic ionic liquids and should prompt further investigation on the nature of these mixtures.

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