A methodology to parameterize SAFT-type equations of state for solid precursors of deep eutectic solvents: the example of cholinium chloride†

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Given the recent boom of applications for deep eutectic solvents (DES), there is a need for robust and accurate thermodynamic models that are able to describe them. Recent works have used molecular-based equations of state, derived from the Statistical Associating Fluid Theory (SAFT), to model DES due to their ability to explicitly account for hydrogen bonding, which is thought to govern the formation of a DES. However, the application of these association models to DES is a non-trivial task, because pure fluid data for several DES precursors are not available to be used in the model parameterization. The alternative parameterization procedures currently employed have evident flaws including the use of oversimplified association schemes, lack of transferability, inability to provide fundamental solid–liquid equilibrium data, and an overall poor accuracy. This work highlights the disadvantages of the current approaches while providing a novel methodology for the development of coarse-grained models applicable to DES. By proposing a more realistic association scheme and regressing the model parameters from experimental data that can be easily measured for a representative DES, a new coarse-grained model for [Ch]Cl, the most used DES precursor, was developed for soft-SAFT. The good performance and versatility of the new model were then successfully demonstrated through the modelling of a wide variety of [Ch]Cl-based DES, providing accurate descriptions of densities, vapor–liquid equilibria and solid–liquid equilibria data, for both binary and ternary systems. Furthermore, the novel approach can easily be applied to other SAFT-type models and extended to other solid DES precursors such as urea.

1. Introduction

Over the last few decades, and especially due to issues such as global warming, the general rising of the sea level, or high indexes of atmospheric pollution, society seems to be more aware of the impact that most human activities have upon our planet's resources and ecosystems. To stress the importance of finding novel approaches for an efficient and sustainable environmental management, the Organization of the United Nations outlined in 2015 a sustainability-oriented development plan entitled “Transforming Our World: the 2030 Agenda for Sustainable Development”. This is composed of several goals and tasks tackling a wide range of issues in which green and sustainable chemistry is expected to play a vital role.1

Accordingly, chemists and chemical engineers are now focusing on the development of alternative greener and more sustainable chemical processes that can be further implemented in large-scale industries. In any chemical process, the choice of the right solvent is crucial as they can make up to 80% of the total volume of chemicals used and present numerous environmental, health, and waste management issues, while being responsible for a large share of the overall energy consumption and greenhouse gas emissions of a process.2,3 Thus, many researchers have focused on the design, characterization and applicability of alternative solvents such as the use of water, supercritical fluids (e.g. CO2), ionic liquids (ILs), and deep eutectic solvents (DES).

First reported by Abbott and co-workers⁴ in 2003, DES are a new class of green solvents that consist of eutectic mixtures of...
two or more compounds that due to strong and highly complex hydrogen-bond interactions between a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) exhibit a considerable freezing temperature depression, resulting in an eutectic temperature lower than that expected for an ideal liquid phase, allowing the formation of stable liquids at relatively low temperatures with interesting solvent properties. The most common DES precursors are quaternary ammonium salts as HBAs, cholinum chloride ([Ch]Cl) being the most common due to its low cost and biodegradability, combined with different HBDs such as carboxylic acids,\textsuperscript{5,6} glycols,\textsuperscript{7} sugars,\textsuperscript{8} urea and its derivatives,\textsuperscript{4} amino acids,\textsuperscript{9} amines,\textsuperscript{10} amides,\textsuperscript{4} alcohols and polyols.\textsuperscript{11}

One of the most attractive properties of DES is their ‘designer solvent’ character, as their thermophysical properties can be tailored aiming at a specific application through an appropriate selection of the HBDs and HBAs used in the mixture, combined with the HBD to HBA molar ratio employed. Moreover, their ease of preparation, operation under mild conditions, inexpensive and readily available starting materials, and water compatibility are often acknowledged and might have contributed to the boom of DES within industry and academia over the last decade with a wide range of applications for DES being reported over the years.\textsuperscript{12,13} Though DES have been primarily investigated as reaction or separation media,\textsuperscript{12} several works have reported the emergence of DES in other fields such as organic synthesis or catalysis,\textsuperscript{14,15} biomass conversion,\textsuperscript{16} metal processing,\textsuperscript{17} gas separation,\textsuperscript{18} drug vehicles,\textsuperscript{19} or biodiesel purification.\textsuperscript{20}

Prior to their industrial application at large-scale, a reliable knowledge of their thermophysical properties and phase behavior is required for the proper simulation and design of new processes, or optimization of existing ones, and to perform trustworthy economic evaluations for different process conditions and configurations. This requires the development of accurate thermodynamic models or equations of state (EoSs) able to provide such data in an extrapolative manner, if not predictive, and to grant the existence of an attractive framework to screen different DES.

Surprisingly, studies on the thermodynamic modelling of DES by suitable activity coefficient models or EoSs are rather scarce. This is in part due to the complexity of the hydrogen bond networks thought to be established in DES that are still far from being fully understood,\textsuperscript{21} and consequently are not well described by current models. Only recently, advanced molecular-based EoSs, derived from the Statistical Associating Fluid Theory (SAFT),\textsuperscript{22,23} able to explicitly account for the association phenomenon, have been proposed to deal with the complexity of DES-based systems.\textsuperscript{24–34}

Most of those works\textsuperscript{25–28,32,34} report the use of a pseudo-pure component approach to model DES, which is a crude simplification that should be avoided, as DES are mixtures of two or more individual components, significantly different from each other. This approach has several limitations, the most obvious being its inability to describe the solid–liquid phase behavior of DES which is of utmost importance for a better understanding of the nature of DES. Moreover, when using a pseudo-pure component approach, a set of molecular parameters needs to be fitted individually to each HBD to HBA ratio, \textit{i.e.} the model becomes compositional dependent. Consequently, if binary interaction parameters with other species (\textit{e.g.} CO\textsubscript{2} or H\textsubscript{2}O) happen to be required, they also become compositional dependent.

This approach has been used mainly because of the nature of HBAs which typically consist of salts with considerably high melting temperatures (\textit{e.g.} [Ch]Cl has an estimated melting temperature of 597 K).\textsuperscript{15} Thus, vapor pressures and liquid densities of pure salts are not available and the traditional parameterization method of SAFT-type EoSs cannot be applied.

Other authors have used a more realistic individual-component approach to model DES with the parameters describing the HBA being regressed using experimental data from diluted aqueous solutions in which the interactions governing the system are likely to be much different from those observed in a DES. Zubier \textit{et al.}\textsuperscript{25} applied such an approach to derive a coarse-grained (CG) model of [Ch]Cl in the framework of PC-SAFT.\textsuperscript{36} However, although five molecular parameters for [Ch]Cl and a temperature-dependent binary parameter with water were fitted simultaneously to the densities and osmotic coefficients at different molalities, significant deviations from the experimental data were still observed.

Llovell and co-workers\textsuperscript{32,33} explored two different approaches to model DES within the soft-SAFT framework: treating the DES as a pseudo-pure compound, and a second approach describing the DES as a mixture of two independent constituents. In the first case, the authors fixed four molecular parameters and left only the chain length parameter, \textit{m}, of the DES to become composition dependent to account for the different possible ratios, finding a linear relation with the average molecular weight of the eutectic mixture. In the second case, a molecular model for each salt (X) and for the other components (Y) is required. Taking into account that a robust molecular model and parameters are usually available for component Y, the molecular parameters for the salt \textit{X} were obtained from density data,\textsuperscript{37} for a binary mixture with a component \textit{Y} at all the available ratios. While a very good description of the density and solubility of CO\textsubscript{2} was obtained, the mixtures used were often very diluted in the target component \textit{X}, and, in some cases, an indirect regression was required (see Fig. 2 of Lloret \textit{et al.}\textsuperscript{32}). Moreover, using only density data may prevent the model from capturing most of the system physical features as density is mainly influenced by size-related parameters, and should always be complemented with some kind of phase equilibrium data which are greatly influenced by energy-related parameters.

A limitation of these individual-component approaches is the use of a 2B association scheme (according to the nomenclature of Huang and Radosz\textsuperscript{29}) that, although commonly used to model ionic liquids and salts, may be too simplistic to capture the highly complex hydrogen-bonding character of [Ch]Cl (and other salts) in DES. This complex behavior was previously evidenced through molecular dynamics (MD) simulations and \textit{ab initio} calculations performed on such systems.\textsuperscript{39–41}

This work aims at overcoming these limitations, proposing an alternative methodology for the systematic parameterization of DES precursors under an individual-component approach using SAFT-type EoSs. The approach here proposed is illustrated through the development of a CG model for [Ch]Cl, the most
common HBA used in DES formulations, in the framework of the soft-SAFT EoS. The model performance is then evaluated for the description of different sets of experimental data corresponding to a variety of [Ch]Cl-based eutectic mixtures in a wide range of temperature, pressure and compositional conditions.

2. Experimental section

2.1. Materials

[Ch]Cl was acquired from Acros Organic with a mass purity of 98% and purified under vacuum (0.1 Pa and 298 K) and constant stirring for at least 3 days. Ethylene glycol (EG) was acquired from Sigma Aldrich with a mass purity of 99.5% and was dried using 3 Å molecular sieves. The DES [Ch]Cl: EG (1 : 2) was prepared inside a dry-argon glovebox to avoid contamination, and the masses were weighed using an analytical balance ALS 220-4N from Kern (accuracy of 0.002 g). The water content of the eutectic mixture was measured using a Metrohm 831 Karl Fischer coulometer with the analyte Hydranal Coulomat AG from Riedel-de Haën and was found to be 388 ppm.

2.2. Vapor–liquid equilibrium (VLE) measurements

The VLE of the binary mixture [Ch]Cl: EG (1 : 2) was determined at two different pressures (0.1 and 0.07 MPa) – values reported in Table S1 (ESI†) – using an in-house isobaric microebulliometer developed and optimized in our laboratory. A detailed description of the apparatus is given in previous publications where its adequacy to measure this type of systems was established.42,43

3. Theory: the soft-SAFT EoS

The description of thermophysical properties and phase equilibria of all fluids involved in a process remains highly important in the field of chemical engineering and physical chemistry. To accomplish this, algebraic methods based on suitable EoSs are desirable and convenient. Traditional cubic EoSs such as Peng-Robinson (PR) or Soave–Redlich–Kwong (SRK) have been the standard in industry for decades but their inaccuracy when used to describe fluids of higher complexity like those exhibiting associating or polar interactions is acknowledged and has driven the development of more sophisticated EoSs with a stronger physical foundation. Among such models, molecular-based equations developed within the framework of SAFT have been increasingly applied over the last few decades and are already included in common process simulation software.

SAFT23,25 is an elegant thermodynamic approach written in the form of an engineering EoS based on the thermodynamic perturbation theory of first order (TPT1) presented by Wertheim in a series of papers in the mid-80s.14-47 In the framework of SAFT, molecules are interpreted as a number of equally sized spherical segments covalently bonded to each other forming chains that interact with each other through a given intermolecular potential and might associate at specific association sites. The free energy of the fluid is then obtained in the form of a sum of perturbation terms starting with the energy of a chosen reference monomeric fluid and then adding contributions corresponding to different structural or energetic effects according to eqn (1).

\[
A_{\text{res}} = A^{\text{total}} - A^{\text{id}} = A^{\text{ref}} + A^{\text{chain}} + A^{\text{assoc}} + A^{\text{polar}}
\]

In eqn (1), the superscripts res, total and id represent the residual, total and ideal Helmholtz energy of the system. \(A^{\text{ref}}\) is the reference term contribution due to the monomer–monomer interactions that, in the case of the soft-SAFT variant of Vega and collaborators,37 are described using a version of the Modified Benedict–Webb–Rubin (MBWR) EoS whose parameters describe a Lennard-Jones (LJ) fluid48 that accounts for both repulsive and attractive forces. \(A^{\text{chain}}\) is the contribution due to the formation of chains from the individual segments, while \(A^{\text{assoc}}\) is a term describing the presence of strong, short range and highly directional forces like hydrogen-bonding by embedding association sites in the core of some of the chainlike molecule’s segments. These two terms are derived from Wertheim’s theory and kept essentially unchanged between the different SAFT variants. When polar molecules are present in the system, an additional term is included (\(A^{\text{polar}}\)) to account for polar and multipolar interactions.

In this work we use the soft-SAFT EoS, which has been proven to provide a very accurate description of the thermophysical properties and phase equilibria of systems containing a wide variety of compounds (e.g. water,59 nitriles,50 polyethers,51 amines,52,53 ionic liquids,54,55 refrigerants,56 CO2,57) as well as DES.32,33 An adequate coarse-grained model capturing the basic physical features of the compounds is crucial for the good performance of the equation. Therefore, for non-associating species, soft-SAFT requires three molecular parameters: \(m\), the number of segments making up the molecule, or chain length parameter; \(\sigma\), the LJ diameter of the segments; and \(\varepsilon\), the LJ dispersive energy governing the segment–segment interactions. For associating species, an association scheme defining the number and type of association sites is chosen \textit{a priori}, and values for the association energy \((\varepsilon^{\text{HB}})\) and volume \((\kappa^{\text{HB}})\) characterizing the associating site–site interactions are required to provide the Helmholtz energy contribution of the association term.37,58 For systems containing quadrupolar molecules, the polar contribution requires two additional parameters, \(Q\) and \(x_p\), that correspond to the effective quadrupole moment and the fraction of segments in the chain containing the quadrupole, respectively.59 These pure-component parameters are usually regressed from experimental liquid density and vapor pressure data for the pure fluid but, if unavailable as it is the case for solid DES precursors, alternative approaches are needed.

The chain and association terms are specifically written for mixtures; hence, only the reference term needs to be extended. This is usually done by applying the van der Waals one-fluid theory with the unlike size and energy parameters of the LJ fluid obtained from the generalized Lorentz–Berthelot mixing rules:

\[
\sigma_{ij} = \eta_i \sigma_i + \sigma_j \quad (2)
\]

\[
\varepsilon_{ij} = \xi_i \sqrt{\varepsilon_i \varepsilon_j} \quad (3)
\]
In eqn (2) and (3), \( \eta_{ij} \) and \( \xi_{ij} \) are the size and energy binary adjustable parameters between species \( i \) and \( j \) that can be fitted to binary experimental data if predictions from the pure-component parameters (\( \eta_{ij} = \xi_{ij} = 1 \)) are not satisfactory.

In a similar manner, when cross-association energies and volumes between a site type \( z \) in component \( i \) and a site type \( \beta \) in component \( j \) are required, the following mixing rules are applied:

\[
e_{ij}^{\beta} = \sqrt[3]{e_i^a e_j^d} \tag{4}
\]

\[
\kappa_{ij}^{\beta} = \left(\frac{\sqrt[3]{\xi_i^a} + \sqrt[3]{\xi_j^d}}{2}\right)^3 \tag{5}
\]

For further details about the soft-SAFT EoS, the reader is referred to the original contributions and subsequent extensions of the equation.\(^{37,59,60}\)

4. Results and discussion

Development of a coarse-grained model for [Ch]Cl

In the association models currently employed in the thermodynamic modelling of DES, most DES precursors like [Ch]Cl have been modelled using the simple ‘2B’ association scheme.\(^{24-34}\) This association scheme contains one proton-donor site ‘A’ and one proton-acceptor site ‘B’ with only ‘A–B’ interactions being allowed in the system. However, it seems too simplistic to capture the highly complex hydrogen-bonding character of [Ch]Cl in these solvents. In fact, \textit{ab initio} calculations performed by Ashworth \textit{et al.}\(^{41}\) revealed that, in contrast to traditional solvents, many different types of H-bonds can form in the archetypal mixture of [Ch]Cl + urea (1:2) that cannot be well captured by oversimplified models. An example is the formation of the complexed anions and cations thought to be responsible for the eutectic melting point occurring at a ratio of 1:2 ([Ch]Cl:urea) that would require more than one proton acceptor site.\(^{41}\)

Therefore, considering the MD simulations and \textit{ab initio} calculations available in the literature for [Ch]Cl-based DES,\(^{39,41}\) we propose in this work to model the salt using a 5-site association scheme. This scheme is sketched in Fig. 1, and comprises

- One pair of sites ‘A’ + ‘B’ mimicking the hydrogen atom and the lone electron pairs in the oxygen atom of the hydroxyl group as commonly considered for alkane-1-ols.\(^{61}\)
- One pair of sites ‘C’ + ‘D’ mimicking the cation–anion interactions as typically done for salts and ionic liquids.\(^{25,32,33,62,63}\)
- One additional ‘E’ site representing the hydrogen bond donor character of the methyl groups that, as observed by Ashworth \textit{et al.},\(^{41}\) are able to establish important hydrogen bonds such as strongly doubly ionic hydrogen bonds ‘CH–Cl’ in a tripodal arrangement.

Given these association sites’ distribution and the fact that association energies and volumes must be defined pairwise, a total of six association parameters (three association energies and three association volumes) are required in order to describe the interactions involving the hydroxyl group, cation/anion pair, and the methyl groups within the SAFT association term. To decrease this high number of unknown parameters to be regressed from experimental data, one can use the molecular nature of soft-SAFT EoS, based on the transferability of the association parameters between chemical families as they usually describe interactions involving the same functional group. As an example, Pedroza \textit{et al.}\(^{55}\) fitted the association parameters accounting for the hydrogen bond interactions through the hydroxyl end groups to the experimental data of monoethylene glycol (EG) that were later transferred to the modelling of the remaining oligomers\(^{59}\) and polyethylene glycols.\(^{64}\) In other works, Lloret \textit{et al.}\(^{65}\) and Pereira \textit{et al.}\(^{32}\) used soft-SAFT transferability to capture the multifunctional nature of alkanolamines and describe the effects of the functional groups and their interactions in water; the required parameters being transferred from the study of monofunctional molecules and their respective aqueous solutions. Thus, in this work, the association parameters required to describe [Ch]Cl are also transferred from previous contributions. Those necessary to describe the hydroxyl group (‘A’ and ‘B’ sites) are transferred from the alkane-1-ols family reported by Pámites,\(^{60}\) while those describing the cation–anion interactions (‘C’ and ‘D’ sites) are transferred from the work of Lloret \textit{et al.}\(^{32}\) on the modelling of symmetrical tetralkylammonium chlorides ([TXA]Cl). The definition of association parameters for the methyl groups is less trivial as no evident transferability is possible. Therefore, we apply here an empirical approach similar to that proposed by Folas \textit{et al.}\(^{66}\) to account for solvation, but in which it is the volume of interaction that is kept fixed to the association volume of the other association site involved in the H-bond, while the energy of association is taken as half of the association energy of the other site. As an example, the association parameters mediating the interactions between a site type ‘E’ and any other site ‘X’ are obtained as follows:

\[
\epsilon_{E-X}^{\text{HB}} = \frac{\epsilon_{X-X}^{\text{HB}}}{2} \tag{6}
\]

\[
\kappa_{E-X}^{\text{HB}} = \kappa_{X-X}^{\text{HB}} \tag{7}
\]

Nonetheless, given the nature of the site ‘E’ assigned to [Ch]Cl, this site type engages only in self-associating interactions with other [Ch]Cl ions (H-bonds with the chloride anion or with the lone electron pairs of the oxygen atom – ‘D’ and ‘B’ sites, respectively) while cross-association interactions with other molecules are forbidden given its unlikely occurrence.\(^{41}\) The self- and cross-interactions allowed to occur in a hypothetical [Ch]Cl-based DES are summarized in Table 1 along with the approach followed to obtain the corresponding association parameters.

![Fig. 1](https://example.com) Sketch of the associating sites proposed in this work for [Ch]Cl.
Another issue arising when modelling [Ch]Cl and other salts used in DES formulations is that they are solid at room temperature, and thus, vapor pressures and liquid densities of the pure fluid (the properties commonly used to regress SAFT pure-component parameters) are not available, so alternative approaches must be used. In the work of Lloret et al., this fact was circumvented by estimating the molecular parameters of the salt first departing from the data of the DES that this salt forms with another compound for which the pure component is well characterized (i.e. tetraethylene glycol). The molecular parameters of the salt were fitted to the density of the mixture at available ratios and used to predict the behavior of the salt with other compounds but, as mentioned, limited experimental data were used at this time. In another recent work, we showed that coarse-grained models developed using aqueous solution data, as suggested in the literature, often yield inaccurate results when those models are later applied to the thermodynamic modelling of DES due to the unique behavior exhibited by most aqueous systems and the difficulty of most models in describing them, but also due to the low concentration region considered in the fitting. Alternatively, we propose in this work to regress the three remaining parameters of [Ch]Cl (m, σ, and ε) from experimental data obtained for another DES containing this salt, namely [Ch]Cl + EG (1:2). Hence, the experimental dataset used for the fitting consists of the high-pressure liquid densities reported in our previous work, and, given the importance of including phase equilibrium data, the solid–liquid equilibrium (SLE) data for this DES, as reported by Silva et al.

Ethylene glycol (EG) is modelled using a 2-site model as proposed by Pedrosa et al. whose parameters are given in Table 2. The regression of the model parameters was carried out using the ‘Isqnomm’ routine of the MATLAB® software using the Levenberg–Marquardt algorithm. The results of the fitting are depicted in Fig. 2, while the [Ch]Cl pure-component parameters obtained under this approach are also reported in Table 2. The molecular parameters obtained for [Ch]Cl under this approach were found to be in good agreement with those reported by Lloret et al. for [TXA]Cl salts, as the number of segments and segment’s diameter are in between those obtained for tetramethylammonium chloride and tetraethylammonium chloride, as expected given the size of the different salts. Furthermore, a higher dispersive energy was obtained here for [Ch]Cl, namely ε/σ_B = 376.64 K, compared to the value of 360.8 K reported for [TXA]Cl salts, which is also expected given the much stronger hydrogen bonding character of [Ch]Cl. Notice that in these coarse-grained models the associating energy and the dispersive energy are not completely independent of each other, as both contribute to the overall energy of the molecule.

To achieve good agreement with the experimental data observed in Fig. 2, a binary interaction parameter, ε_HB, to correct the mixture’s dispersive energy, was fitted simultaneously with the three non-associating [Ch]Cl parameters. Contrarily to what was observed in the work of Zubeir et al., where PC-SAFT parameters for [Ch]Cl were regressed from aqueous solution data, the binary interaction parameter fitted to the selected data is temperature independent and its value is reported in Table 3. Notice that a value of unity means no fitting to binary data. Additional optimizations (not shown here) revealed that the binary parameter is required not only due to the negative deviations from the ideal behavior observed in the solid–liquid phase diagram but also mostly due to the fully predictive association matrices considered in the association term (see Tables S2 and S3, ESI†). Similar results without a binary interaction parameter could have been obtained if one of the
association parameters, e.g. the association energy for the hydroxyl group, was reoptimized for [Ch]Cl instead of directly transferred from previous works. Aiming at an increased transferability and considering the good results obtained, we opted for the first approach, and as can be observed in Fig. 2a, considering the extended temperature (283–363) K and pressure (0.1–95) MPa ranges where experimental densities were measured, the effect of temperature and pressure on the DES densities is remarkably captured by the model with a percentage average absolute relative deviation (%AARD – eqn (8)) of only 0.181%. Greater deviations are observed at high temperatures–low pressures and low temperatures–high pressures.

\[
\%\text{AARD} = \frac{100}{\frac{1}{n-1} \sum \left( \frac{|\rho_{\text{calc}} - \rho_{\text{exp}}|}{\rho_{\text{calc}}} \right)}
\]

Concerning the solubility data, the solid–liquid phase diagram reported for [Ch]Cl + EG shows that the solid–solid transition of [Ch]Cl previously reported in the literature has an impact on the phase diagram of the mixture. Therefore, the modelling of the phase diagram was carried out both neglecting and accounting for the existence of such phase transition, using eqn (9) or eqn (10), respectively:

\[
x_{k}^{\text{lg}} = \exp \left[ \frac{\Delta H_{\text{sl}}}{RT_{m,k}} - \frac{T - T_{m,k}}{T} \right]
\]

\[
x_{k}^{\text{lg}} = \exp \left[ \frac{\Delta H_{\text{sl}}}{RT_{m,k}} - \frac{T - T_{m,k}}{T} + \frac{\Delta H_{\text{trs}}}{RT_{\text{trs}}} - \frac{T - T_{\text{trs}}}{T} \right]
\]

where \( x_k \) is the solubility of a solid solute \( k \), \( \gamma_k^l \) its activity coefficient in the liquid phase, \( T \) the absolute temperature, \( R \) the ideal gas constant, and \( T_{m,k} \) and \( \Delta H_{\text{sl}}^k \) the melting temperature and enthalpy of the pure compound \( k \). The \( T_{\text{trs}} \) and \( \Delta H_{\text{trs}}^k \) required in eqn (10) represent the transition temperature and transition enthalpy for the solid–solid transition, which for [Ch]Cl have the values of 352.92 K and 17 190 J mol\(^{-1}\), respectively. Both expressions neglect the effect of the heat capacity difference between the solid and liquid phases, as previously suggested by Martins et al.\(^{21}\)

The values of \( T_{m,k} \) and \( \Delta H_{\text{sl}}^k \) used in this work are given in Table 4.

The results depicted in Fig. 2b show that when the solid–solid transition is explicitly considered in the modelling, an excellent description of the solubility of [Ch]Cl is achieved with only small deviations in the near-transition region, probably due to the two different experimental techniques used to measure the two regions (i.e., visual vs. DSC). Nonetheless in the large temperature range where the solubility of [Ch]Cl was measured (280–597) K, the average absolute deviation as given by eqn (11) is only 6.89 K.

\[
\text{AAD} (K) = \left| T_{\text{calc}} - T_{\text{exp}} \right|
\]

### Table 3 Binary interaction parameters used in this work

<table>
<thead>
<tr>
<th>Compound ( i )</th>
<th>Compound ( j )</th>
<th>( \xi_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ch]Cl</td>
<td>EG</td>
<td>1.040</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>TriEG</td>
<td>1.000</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>Phenol</td>
<td>1.000</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>Glycerol</td>
<td>1.022</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>Ethanol</td>
<td>1.000</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>Water</td>
<td>1.250</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>Lactic acid</td>
<td>1.040</td>
</tr>
<tr>
<td>EG</td>
<td>( H_2O )</td>
<td>1.130(^{36})</td>
</tr>
<tr>
<td>Glycerol</td>
<td>( H_2O )</td>
<td>1.000</td>
</tr>
<tr>
<td>[Ch]Cl</td>
<td>CO(_2)</td>
<td>1.100</td>
</tr>
<tr>
<td>EG</td>
<td>CO(_2)</td>
<td>0.832(^{59})</td>
</tr>
<tr>
<td>Glycerol</td>
<td>CO(_2)</td>
<td>0.960</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>CO(_2)</td>
<td>0.760</td>
</tr>
</tbody>
</table>

### Table 4 Melting properties used in this work

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_{m}/K )</th>
<th>( \Delta H_{\text{sl}}^k /[J\text{ mol}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ch]Cl</td>
<td>597(^{75})</td>
<td>4300(^{35})</td>
</tr>
<tr>
<td>EG</td>
<td>260.15(^{73})</td>
<td>9958(^{73})</td>
</tr>
<tr>
<td>Glycerol</td>
<td>291.33(^{73})</td>
<td>18 280(^{73})</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>289.82(^{74})</td>
<td>11 340(^{74})</td>
</tr>
</tbody>
</table>
Given the nature of SAFT-type equations, several pure-component parameters can yield similar results when evaluating a small experimental dataset like those usually considered during model parameterization. Therefore, the coarse-grained model proposed here for [Ch]Cl was then validated through the description of the boiling temperatures of the [Ch]Cl + EG (1 : 2) DES measured in this work, and reported in Table S1 (ESI†). As shown in Fig. 3, using the pure-component parameters from Table 2 and the binary interaction parameter fitted to the densities and SLE of the eutectic solvent (Table 3), excellent predictions of the VLE data were obtained with a %AARD of 0.229% corresponding to an overall AAD of 1.08 K. The small deviations observed in the glycol-rich phase can be attributed to the overestimation of the boiling temperature of pure EG.

Performance assessment for the [Ch]Cl CG model

Once the new CG model for [Ch]Cl was established, its performance was evaluated through the modelling of different [Ch]Cl-based DES. In our previous work, we showed that when CG models available in the literature are used to model DES, a good description of density could not be achieved even at atmospheric pressure. Therefore, we first used the new model to describe the atmospheric pressure densities of [Ch]Cl + triethylene glycol (TriEG) at a 1 : 2 molar ratio in the (303–353) K temperature range, reported by Mjalli et al. As can be observed in Fig. 4a, using the model for [Ch]Cl proposed in this work and the model for TriEG reported by Pedrosa et al., whose parameters are given in Table 2, an excellent prediction of the experimental density was obtained with a %AARD of 0.106%.

Considering that DES have also been used at compositions other than the eutectic point, aiming at an increased tunability of the solvent, the effect of composition on thermophysical properties, e.g. density, must also be well described by thermodynamic models. Guo et al. measured the atmospheric pressure densities of binary mixtures composed of [Ch]Cl and phenol at different HBD/HBA molar ratios in the (293–318) K temperature range. As no CG model for phenol in the framework of the soft-SAFT EoS was available in the literature, new molecular parameters based on a “2B” association scheme were regressed in this work from pure fluid VLE data. The good results of the fitting (%AARD of 0.436% and 1.58% for the liquid densities and vapor pressures, respectively) are shown in Fig. S1 in ESI† and the parameters obtained are presented in Table 2. Using these parameters and those proposed for [Ch]Cl, an excellent agreement between the soft-SAFT predictions and the experimental data from Guo et al. is achieved with a %AARD of 0.073%. These results are depicted in Fig. 4b and highlight the ability of soft-SAFT to correctly capture the effect of composition on the DES densities.

One of the most typical [Ch]Cl-based DES is its binary mixture with glycerol at a 1 : 2 molar ratio, for which we have recently reported densities in wide temperature and pressure ranges.
Similarly to phenol, no soft-SAFT parameters were available in the literature, and thus molecular parameters for glycerol were here regressed from pure fluid VLE data. The results of the fitting, using the “2B” association scheme, are shown in Fig. S2 in ESI,† while the pure-component parameters obtained are given in Table 2. Despite the existence of small deviations between the soft-SAFT results and the experimental liquid densities at higher temperatures, well beyond the typical temperature range of interest for DES applications, an overall good agreement with the experimental data was found with %AARD of 1.03% and 1.75% for the liquid densities and vapor pressures, respectively. Although glycerol has a higher number of hydroxyl groups when compared to alkan-1-ols and phenol, suggesting the use of additional association sites, the “2B” association scheme yielded better results than the 4-site or 6-site association schemes tested in our preliminary calculations (results not shown here). This is probably due to the relatively small size of glycerol molecules and the consequent steric hindrance induced when bonds with other molecules are established preventing bonding at the other free sites.

Once the CG models for the two compounds are established, soft-SAFT was applied to the prediction of the $p_T$ data in the entire temperature (283–363) K and pressure (0.10–95) ranges, and, as depicted in Fig. 5a, a remarkable agreement with the experimental data was achieved (%AARD = 0.226%), showing that soft-SAFT is also able to capture the effect of pressure on the DES densities, even though only atmospheric pressure density data were used in the parameterization of the HBD’s model, reinforcing the robustness of the model proposed here for [Ch]Cl when used to predict densities.

Abbott et al. and Silva et al. reported the solid–liquid phase diagram for this DES, and as previously observed for the mixture with EG, considerable negative deviations from the ideal behavior were observed by the different authors, especially as we approach the eutectic region. Consequently, when the CG models developed in this work were used to describe the solubility of [Ch]Cl in glycerol (Fig. 6), a binary interaction parameter (see Table 3) was required in order to obtain a good agreement with the experimental data. Contrarily to what was observed in the mixture with EG, the solid–solid transition of the pure salt had no visible influence on the phase diagram of the mixture; hence, accurate results were only obtained when the solubility was calculated through eqn (9). The binary parameter required to accurately describe these data has a value only slightly different from the one used in the mixture with EG and was found to have a negligible impact on the DES densities, as shown in Fig. 5b.

One of the most challenging systems involving [Ch]Cl is its aqueous solution. As previously mentioned, Zubeir et al. regressed the five pure-component parameters of a PC-SAFT CG model for [Ch]Cl (“2B” association scheme) from the data of its aqueous solutions, namely VLE data, in the form of
osmotic coefficients, and densities at different salt concentrations \( (x_{\text{salt}} < 0.33) \) along with a temperature-dependent binary parameter, but significant deviations from the experimental data were still observed. In this work, using the molecular model developed for \([\text{Ch}]\text{Cl}\), and the 4-site CG model for water proposed by Vega et al.\(^69\) (see Table 2), a reasonable agreement with the experimental boiling temperatures measured by Carvalho et al.\(^42\) (%AARD = 0.328% and AAD = 1.22 K) and the densities at atmospheric pressure reported by Francisco et al.\(^78\) (%AARD = 0.161%) can be obtained, as shown in Fig. 7.

Although an accurate prediction of the experimental densities could have been obtained solely from the pure-component parameters (see dashed lines in Fig. 7a), a binary interaction parameter, \( \xi = 1.25 \), was necessarily fitted to the boiling temperatures at 0.10 MPa, being successfully transferred to the description of the other two isobars at lower pressures and to the description of atmospheric pressure densities (Fig. 7a). In fact, similarly to what was previously observed in the system with glycerol, the binary interaction parameter had a negligible impact upon the system’s density despite its considerably high value. This is because the \( \xi \) parameter modifies the cross-energy interaction but does not affect the volume interactions, which mostly dictate the density behavior.

In the same work, Carvalho et al.\(^42\) also reported the boiling temperatures for the binary mixture \([\text{Ch}]\text{Cl} + \text{ethanol (EtOH)}\) at three different pressure levels (0.10, 0.07, and 0.05 MPa). We used the CG model developed for \([\text{Ch}]\text{Cl}\) and the soft-SAFT model for ethanol proposed by Pámiész,\(^60\) based on a “2B” association scheme, to predict the experimental data. As shown in Fig. 8a, an excellent agreement with the experimental data was observed although a very narrow composition range was investigated.

Fig. 7 (a) Densities and (b) boiling temperatures of aqueous solutions of \([\text{Ch}]\text{Cl}\). The symbols represent experimental data\(^42,78\) while the solid and dashed lines represent the soft-SAFT results using \( \xi = 1.25 \) and \( \xi = 1 \), respectively.

Fig. 8 (a) Boiling temperatures for \([\text{Ch}]\text{Cl} + \text{EtOH}; \) (b) water activities at 298.2 K in the aqueous solution of \([\text{Ch}]\text{Cl}\). The symbols represent experimental data\(^42,79\) while the lines depict the soft-SAFT predictions.
Khan et al.\textsuperscript{79} reported the water activities of aqueous solution of [Ch]Cl at 298.2 K. Using the binary interaction parameter between [Ch]Cl and water previously fitted to one of the isotherms in Fig. 7b, a reasonable prediction of water activities at a much lower temperature was obtained. These results are depicted in Fig. 8b where the soft-SAFT predictions show the same trend as the experimental data, highlighting the ability of the model to describe VLE data.

Having a CG model for [Ch]Cl, one could use this model to obtain the density of a hypothetical pure liquid in the temperature range of interest (Fig. 9a) and compare such value with an extrapolation of the density data of its aqueous solution. Using the experimental data reported by Francisco et al.\textsuperscript{78} and neglecting the most diluted data point, the density predicted by the CG model developed in this work captures well the trend observed experimentally, reinforcing the model’s robustness. Furthermore, as shown in Fig. 9b, a linear relationship between ln(\rho) and 1/x_{H2O} can be proposed, allowing a very good prediction of the density of aqueous solutions of [Ch]Cl in the entire composition range.

As can be observed in Fig. 9a, the density of pure [Ch]Cl, as predicted by soft-SAFT, using the CG model proposed in this work, exhibits an anomalous behavior, displaying a maximum around 256.15 K. Some numerical pitfalls of SAFT models are known to produce unphysical behavior and unrealistic phenomena under particular thermodynamic conditions.\textsuperscript{80–82} Considering that [Ch]Cl melts at 597 K, the results shown in Fig. 9a derive from calculations performed for a hypothetical fluid well below its melting point, at a very low reduced temperature where numerical issues are prone to appear. Therefore, although there are no experimental data corroborating or denying this behavior, the model proposed here should not be used at temperatures lower than 256.15 K which, nonetheless, is below the temperature range for most DES applications, usually carried out at room temperature.

Once the new model was successfully applied to the aqueous solutions of [Ch]Cl, it can be used to describe the effect of water on the thermophysical properties of DES. This information is of key interest, not only because water absorption by DES is known to significantly influence their thermodynamic behavior\textsuperscript{83,84} but also because water can be deliberately added to DES in order to tune their properties, an example being the addition of water to decrease their viscosities.

Leron et al.\textsuperscript{85} reported the densities of the [Ch]Cl + EG and [Ch]Cl + glycerol DES, both at a 1:2 molar ratio, at temperatures ranging from 298.15 to 333.15 K. Using the pure-component parameters from Table 2 and the binary parameters from Table 3, excellent predictions of the ternary mixture’s densities were obtained, as shown in Fig. 10. The %AARD values of the soft-SAFT predictions from the experimental data are 0.449% and 0.216% for the mixture with EG and glycerol, respectively, being similar to those observed in pure DES and lower than those observed when soft-SAFT is used to describe pure water.\textsuperscript{49,69}

Finally, an area of great interest involving DES is their use in gas separation,\textsuperscript{18} including their use as physical solvents for CO\textsubscript{2}. Leron and co-workers\textsuperscript{86,87} have measured the solubility of CO\textsubscript{2} in the [Ch]Cl-based DES with EG or glycerol as HBD with the latter exhibiting the highest affinity towards CO\textsubscript{2}. The experimental solubility data in the two DES are plotted in Fig. 11 along with the soft-SAFT EoS modelling.

Concerning the mixture with EG, the binary interaction parameter between EG and CO\textsubscript{2} was retrieved from the work of Pedrosa et al.\textsuperscript{59} where the CG models for the two compounds were first proposed, while the binary interaction parameter between [Ch]Cl and CO\textsubscript{2}, reported in Table 3, was fitted to the isotherm at 303 K and used to predict the remaining isotherms. As can be observed in Fig. 11a, a reasonable agreement with the experimental data was achieved although larger discrepancies were observed at high temperatures. The results can however be easily improved by using a temperature-dependent binary parameter between CO\textsubscript{2} and either the salt or the HBD, if a higher accuracy is required. In fact, temperature-dependent binary parameters between glycols and CO\textsubscript{2} have already been

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**Fig. 9** (a) Density of pure [Ch]Cl as predicted by soft-SAFT. (b) Density of aqueous solutions of [Ch]Cl at 303.15 K. Blue circles represent experimental data from the literature\textsuperscript{78} while the red triangle represents the density of pure [Ch]Cl predicted by soft-SAFT at 303.15 K.
used in soft-SAFT to better describe the interactions between glycols (e.g. diethylene glycol) and CO$_2$.$^{29}$

Once the binary parameter between [Ch]Cl and CO$_2$ is available, it can be used to describe the gas solubility in the mixture with glycerol. In this system, the binary parameter between glycerol and CO$_2$, reported in Table 3, was fitted to the isotherm at 303 K and used to predict the data at higher temperatures. As depicted in Fig. 11b, an excellent agreement with the experimental data was observed with deviations lower than those observed in the system with EG, although for the latter no binary interaction parameters between the HBD and the gas were fitted to the experimental data.

Another [Ch]Cl-based DES commonly suggested as a physical solvent for CO$_2$ capture is [Ch]Cl mixed with lactic acid (LA) at 1:2 molar ratio. Considering that a molecular model within the framework of soft-SAFT was recently proposed for LA by Lloret et al.$^{32}$, we could apply the CG model developed here for [Ch]Cl to the modelling of the SLE phase diagram measured for this system by Crespo and co-workers$^{31}$ and the densities reported by Francisco et al.$^{88}$ measured for different HBD:HBA molar ratios. By fitting a temperature-independent binary parameter between [Ch]Cl and LA (see Table 2), an excellent description of the SLE phase diagram for this mixture is achieved although no experimental data near the eutectic region are available – Fig. 12a. In contrast, a poor description of the mixture's densities was obtained either with or without such a binary parameter. Given the good results obtained with the model proposed here for [Ch]Cl when used to describe the densities of different mixtures, including its challenging aqueous solution, we believe that such discrepancies may be related to the CG model of lactic acid whose parameters were obtained from an indirect fitting using mixtures’ density data.$^{32}$ As we mentioned in the introduction section, this simplified approach may hinder a correct description of the compound's physical features resulting in a lower accuracy. This is corroborated by the soft-SAFT results.
shown in Fig. 12b, as the deviations of the soft-SAFT predictions from the experimental densities of the mixture increase as the molar fraction of LA is increased.

Francisco et al.\textsuperscript{88} reported the solubility of CO\textsubscript{2} in the DES [Ch]Cl + LA (1:2) in the form of isopleths with a CO\textsubscript{2} mole fraction ranging from 0.025 to 0.100. As the binary parameter between the salt and the HBD was defined through modelling of the SLE data of the correspondent binary mixture, only the binary parameter between LA and CO\textsubscript{2} was directly fitted to the experimental solubility data. The results of the fitting are depicted in Fig. 13 along with the experimental data and show that the model is able to provide a good description of the experimental data with a %AARD of 4.95\%, although deviations increase with increasing temperatures and gas contents. However, the absorption capacity of DES seems rather limited, so higher CO\textsubscript{2} contents than those reported by Francisco et al.\textsuperscript{88} are unlikely to occur.

5. Conclusions

In this work, a new methodology for the parameterization of solid DES precursors in the framework of SAFT-type EoSs was proposed, overcoming the limitations of the current approaches, while achieving a better performance. The new approach was successfully illustrated for the most used DES precursor, the cholinium chloride salt, using the soft-SAFT EoS.

Firstly, using information from MD simulations and \textit{ab initio} calculations available in the literature about the type and magnitude of the hydrogen-bonding interactions present in some [Ch]Cl-based DES, a more realistic association scheme with five associating sites was proposed to describe the hydrogen bonding character of [Ch]Cl. Then, the molecular parameters characterizing the associating sites were transferred from the literature or obtained through an empirical approach proposed in this work without further fitting, while the non-associating pure-component parameters were obtained from fitting to experimental data that can be easily measured for an archetypal [Ch]Cl-based DES, namely high-pressure liquid densities and SLE data.

The accuracy and robustness of the new CG model were then demonstrated through the successful description of a wide variety of [Ch]Cl-based DES with seven different HBDs and experimental data comprising densities, VLE, and SLE of pure DES and their mixtures with water and CO\textsubscript{2} in wide temperature, pressure and composition ranges. The new approach is easily applicable to other solid DES precursors, e.g. urea, enabling the correct thermodynamic modelling of other typical DES such as [Ch]Cl + urea which should be the aim of future works. Moreover, the use of a SAFT-type EoS allows the easy coupling with different theories such as the free volume theory (FVT) or the density gradient theory (DGT) for the calculation of transport or interfacial properties, respectively.

Conflicts of interest

There are no conflicts to declare.
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