Development of a robust soft-SAFT model for protic ionic liquids using new high-pressure density data

Emanuel A. Crespo a, Liliana P. Silva a, Cristina I.P. Correia a, Mônia A.R. Martins a, Ramesh L. Gardas b, Lourdes F. Vega c, Pedro J. Carvalho a,* João A.P. Coutinho a

a CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
b Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
Chemical Engineering Department, Research and Innovation Center on CO2 and H2 (RICH), and Center for Catalysis and Separation (CeCaS), Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates

A R T I C L E   I N F O
Article history:
Received 12 February 2021
Revised 24 March 2021
Accepted 29 March 2021
Available online 5 April 2021

Keywords:
Protic ionic liquids
High pressure density
Equation of state
Soft-SAFT
Derivative properties

A B S T R A C T

New experimental density data in a wide range of temperatures (283–363) K and pressures (0.1–95) MPa is here reported for five protic ILs based on the N,N-diethylethanolammonium ([DEEA]) cation, combined with the following anions: acetate ([Ace]), propanoate ([Prop]), butanoate ([But]), pentanoate ([Pent]) and hexanoate ([Hex]) in a 1:1 acid/base proportion. The molar volumes of the different ILs and derivative properties such as the isothermal compressibility and isobaric thermal expansivity were determined from the experimental density data. Moreover, considering the importance of having a robust and transferable thermodynamic model of these ILs that can be used in further studies including CO2 capture, the new experimental data was used to develop a coarse-grain molecular model of the studied ILs, in the framework of the soft-SAFT EoS, employing a 2/2 association scheme to account for the hydrogen bonding character of the ILs. The proposed model was found to provide an excellent description of the experimental pρT data with average relative deviations lower than 0.11% for all the ILs, while still providing reasonable predictions of the second-order derivative properties. Furthermore, the optimized molecular parameters were found to be correlated with the ILs molecular weight, highlighting the physical meaning and consistency of the parameters obtained.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

The increased human and industrial activity since mid-20th century have resulted in major changes in biological communities worldwide, harming biodiversity and ecosystems function, natural resources or the climate, whose scientific evidences are now undeniable [1–3]. In order to mitigate the anthropogenic impact on the environment, rapid and global transformations in different aspects of our society are required, namely in the industry, energy, and transport sectors [4]. Important steps towards achieving climate change neutrality is being enforced in Europe with increasing and challenging targets for greenhouse gases (GHG) emissions, energy deployment and energy efficiency [5]. Nonetheless, the successful achievement of these targets are deeply dependent on the development and optimization of existent or new solvents, technologies and ultimately, processes.

GHG contributing to the global warming are mainly attributed to carbon dioxide (CO2), nitrous oxide (N2O), methane (CH4), and the hydrofluorocarbons (HFCs) because of their greenhouse effect into the atmosphere. Among these, CO2 contributes with over 80% of energy-related emissions, mostly due to the burning of fossil fuels (e.g. at power plants) that have resulted in a considerable increase of the CO2 concentration in the atmosphere over the last decades [6]. Several technologies can be used to capture CO2 reducing the correspondent emissions, the most promising being post-combustion techniques since they are considered as a mature technology and have the additional benefit that they can easily retrofit the existent power plants. Absorption processes using amines are the current state of art technology for this purpose [7,8], with different amines (or amine blends) being used as solvents. The most used formulations typically include monoethanolamide, diethanolamine, diglycoamine, methyldiethanolamine and piperazine [9,10]. Although these solutions of aminokalanolamines are efficient in capturing CO2 from the post-combustion streams, this process still possesses significant drawbacks such as a high energy consumption (and consequently cost),
corrosion, oxidative and thermal degradation and environment pollution [11]. Aiming at overcoming some of these drawbacks, and ultimately develop new sustainable processes, the development of more sustainable solvents than aqueous amines for capturing CO₂ by absorption has become a very active area of research.

In this sense, ionic liquids (ILs) have been proposed as an attractive alternative to conventional solvents used in the physical sorption of CO₂ [12]. Among their unique properties, the well-known tunability of their thermophysical properties, their low vapor pressure and high solvating ability contributes to make them good candidates for the desired task [13,14]. In a recent work, based on a COSMO-RS [15] screening of more than two hundred systems, mixtures of [C₄C₁im][DMF] or [C₄C₁im][NTf₂] with carboxylate-based protic ILs were found to have considerably excess volumes, and are thus expected to have an enhanced CO₂ solubility due to the free volume increase [16]. It was also found that the combination of the bis(trifluoromethylsulfonyl)imidide ([NTf₂])⁺ or dimethyl phosphate ([DMF]⁻) anions with the imidazolium cation ([C₄C₁im]⁺), generally improves the CO₂ selectivity and results in a higher overall solubility [12,17]. In contrast, one of the main disadvantages of imidazolium-based ILs is their high viscosity that hinders their industrial application in absorption processes due to the resulting low mass transfer coefficients. However, it has been shown that the addition of carboxylate-based protic ILs to imidazolium-based ones allows for a significant decrease of their viscosity, while preserving their solvation potential [16].

While imidazolium-based ILs are among the most studied families of ILs, [18] experimental data for pure carboxylate-based protic ILs is still scarce [19]. Even though different properties, at the atmospheric pressure, have been reported for a number of these compounds and their mixtures with water [20,21], experimental measurements of thermophysical properties for pure PILs, at different (T, P) conditions, are much seldom [22,23], despite their importance for the correct parameterization of thermodynamic models. Such gap in the literature hinders further studies on the potential of these mixtures as solvents for CO₂ capture technologies, despite the potential demonstrated so far [24,25]. Therefore, a first step towards the evaluation of these new solvents is to provide an extensive thermophysical characterization of the pure ILs and their mixtures, allowing the development of robust and accurate thermodynamic models of the different solvents that can later be used in process simulators to provide an accurate design, simulation and economic analysis of different industrial processes and configurations.

Equations of State (EoSs) are the most versatile methods to provide fast calculations of thermophysical properties and phase equilibrium data required by process simulators. Although a first effort towards the modeling of ILs using EoSs was carried out using simple Cubic EoSs [26], these models not only require the critical properties of the pure components (that are normally unavailable for ILs) but they also usually fail to correctly capture the anisotropy and hydrogen bonding ability often exhibited by ILs. Conversely, molecular-based EoS, derived from the Statistical Associating Fluid Theory (SAFT) [27–30], are able to explicitly account for different structural and energetic effects such as the molecular shape, chain length, the presence of short-range and highly directional forces, and electrostatics on the systems behavior, being often suggested as the most appropriate method for the modeling of IL-containing systems [31].

In this work, aiming at providing an accurate thermophysical characterization of protic ILs suitable for CO₂ capture, the density as a function of temperature – (283-363) K – and pressure – (0.1-95) MPa – was measured for five different carboxylate-based protic ILs, namely N,N-diethylcarboxylic acid, N,N-diethylcarboxylic acid acetate, [DEEA][Ace], N,N-diethylcarboxylic acid propanoate, |[DEEA][Prop], N,N-diethylenetramino-7-methanobutanoate, [DEEA][But], N,N-diethylenetramino-5-methanopyranoate, [DEEA][Pen], and N,N-diethylenetramino-6-methanopyranoate, [DEEA][Hex]. The selected compounds allow to investigate the effect of the anions chain length on the compounds’ density and second-order derivative properties (i.e. isothermal compressibility and isobaric thermal expansivity). The new experimental data is then used to propose a new coarse-grained (CG) molecular model of these ILs, in the framework of the soft-SAFT EoS [32,33] that has previously shown to be one of the best SAFT variants for the thermodynamic modeling of ILs and their mixtures with CO₂ [34–38].

2. Experimental section

2.1. Chemicals

The protic ILs were prepared using N,N-diethylenetraminoamine as base and acetic acid, propionic acid, butyric acid, pentanoic acid or hexanoic acid. The precursors were used as received from the supplier without further purification. Their characteristics are summarized in Table S1. The resulting protic ILs are described in Table 1, along with their acid-base proportion, molecular weight, molar percentage purity and mass percentage of water. The water content of the protic ILs was determined by a Metrohm 831 Karl Fischer couloumeter using the analyte Hydranal® - Coulomat AG from Riedel-de Haën. The purity of each synthesized IL was estimated from the 1H NMR spectra available in Supporting Information – Figures S1–S5.

2.2. Synthesis of the protic ILs

The synthesis of the carboxylate-based protic ILs was based on the Brønsted acid-base neutralization method, as reported in previous publications by Sharma et al. [39] and Chennuri et al. [40] Briefly, the acid is added dropwise to an equimolar quantity of base at room conditions. After, the reaction mixture is constantly stirred at room temperature for at least 2 hours, under nitrogen atmosphere. To avoid the formation of azoetropes during distillation that leads to acid:base proportions different from the expected 1:1, as observed in our previous publication [16], no additional purification steps were performed. The structure of all compounds synthesized was evaluated by ¹H and ¹³C NMR spectroscopy, Figures S1 to S5 of Supporting Information.

2.3. High- pressure density measurements

The densities of the five protic ILs synthesized in this work were measured in the (283-363) K temperature and (0.1-95) MPa pressure ranges using an Anton Paar high pressure densimeter (DMA-HPD) coupled to an mPDS 5 unit. The standard uncertainty on density was found to be of 5×10⁻⁴ g cm⁻³. A thermostat bath circulator (Julabo MC), with a temperature uncertainty of 0.01 K, is used to ensure the circulation of a thermo-regulated heat transfer fluid, in order to control the temperature of the measuring cell, whose uncertainty was previously found to be of 0.1 K [41]. The pressure is measured by a piezoresistive silicone pressure transducer (Kulite HEM 375) with an accuracy better than 0.2%. The transducer is directly fixed in the ¼" stainless steel line, placed between the cell and the movable piston to reduce the existence of dead volumes. A more detailed description of the methodology, apparatus, and its calibration procedure can be found in previous publications [42].

3. Soft-SAFT EoS

The progress towards more sophisticated EoSs has been accomplished through the use of statistical thermodynamics in the de-
development of molecular-based EoSs that can explicitly account for the influence that the molecular structure/shape and the occurrence of different kinds of interactions have on the fluids’ physical behavior. Chapman and co-workers in the late 80’s [27–30], proposed the Statistical Associating Fluid Theory (SAFT) which, based on the thermodynamic perturbation theory of first order (TPT1) presented by Wertheim a few years earlier [43–46], included a term to explicitly account for the associating interactions. Within SAFT, molecules are represented as a number of spherical segments covalently bonded to each other forming chains that interact with each other according to a given intermolecular potential and, if representing associating compounds, might associate at specific square-well bonding sites embedded in the core of some of the chains’ segments. The residual Helmholtz energy of the fluid (A\text{res}) is then obtained as a sum of different contributions, starting from the energy of a chosen reference monomeric fluid to which different perturbation terms can be added, each accounting for a specific structural or energetic effect, according to Eq. (1):

\[
A^{\text{res}} = A^{\text{total}} - A^{\text{ideal}} = A^{\text{id}} + A^{\text{chain}} + A^{\text{assoc}} + ... 
\] (1)

In Eq. (1), the superscripts id, res, and total represent the ideal, residual and total Helmholtz energy of the system. A^{\text{id}} denotes the energy of the reference fluid accounting for the monomer-monomer interactions, A^{\text{chain}} is the contribution due to the formation of chains from the individual segments, and A^{\text{assoc}} is a term explicitly accounting for the presence of anisotropic, short range and strong interactions such as hydrogen bonding. Considering the additive nature of SAFT-type EoSs, additional terms can be added, depending on the systems nature/complexity, to better represent their physical nature.

Several modifications to the original model have been proposed over the last decades, mainly changing how to express the physical interactions (i.e. the reference term) while both the A^{\text{chain}} and A^{\text{assoc}} terms, derived from Wertheim’s TPT1 theory, remain essentially unchanged [47]. In this work the soft-SAFT EoS variant is used, as it has previously been shown to provide an accurate description of the thermophysical properties and phase equilibria of IL/gas systems that are particularly relevant for the aim of this study [34–38].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Acid:Base proportion</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEEA][Ace], 1:1</td>
<td>N,N-diethylethanolammonium acetate</td>
<td>Mw = 177.24 g mol⁻¹; mol% &gt; 97%; w_H2O% = 0.4×</td>
</tr>
<tr>
<td>[DEEA][Prop], 1:1</td>
<td>N,N-diethylethanolammonium propanoate</td>
<td>Mw = 191.27 g mol⁻¹; mol% ≈ 97%; w_H2O% = 0.3×</td>
</tr>
<tr>
<td>[DEEA][But], 1:1</td>
<td>N,N-diethylethanolammonium butanoate</td>
<td>Mw = 205.30 g mol⁻¹; mol% &gt; 98%; w_H2O% = 0.3×</td>
</tr>
<tr>
<td>[DEEA][Pent], 1:1</td>
<td>N,N-diethylethanolammonium pentanoate</td>
<td>Mw = 219.33 g mol⁻¹; mol% ≈ 99%; w_H2O% = 0.4×</td>
</tr>
<tr>
<td>[DEEA][Hex], 1:1</td>
<td>N,N-diethylethanolammonium hexanoate</td>
<td>Mw = 233.35 g mol⁻¹; mol% ≈ 99%; w_H2O% = 0.5×</td>
</tr>
</tbody>
</table>

A×: Molar percentage purity evaluated by ¹H NMR spectroscopy
b×: Mass percentage of water measured by Karl-Fisher titration.

In soft-SAFT, the monomer-monomer interactions are described using a version of the Modified Benedict-Webb-Rubin (MBWR) EoS, whose parameters were adjusted to describe a Lennard-Jones (LJ) spherical fluid, accounting for both the repulsive and attractive interactions between the segments in a single term. This term defines the monomers using two molecular parameters: the diameter of the monomeric segments, σ, and the dispersive energy of interaction between them, ε. These two parameters along with the chain length parameter m (i.e. the total number of monomeric segments constituting the chainlike molecule) are used to fully describe a non-associating, non-polar, component. If any component is able to hydrogen bond (e.g. ILs), an association scheme specifying the number/type of association sites added to the molecule and the type of site-site interactions allowed to occur in the system has to be defined a priori and values for the association energy, ε_HH, and association volume, x_HH, characterizing the site-site interactions has to be provided in order to obtain A^{assoc}.

Both the proper selection of a coarse-grain model/association scheme, capable of representing most of the molecules’ physical features, and the selection of adequate properties to be used in the parameterization procedure of the pure-component parameters are crucial for a good performance of the EoS, and to enhance its extrapolative/predictive ability. Therefore, for the carboxylate-based protic ILs investigated in this work we have decided to apply a 2/2 association scheme to account for the hydrogen bonding character of the ILs. Hence, two positive (A) association sites are used to mimic the H-atom of the cation’s hydroxyl group and the delocalized positive charge surrounding the N-atom in the cation while two negative (B) sites are used to represent the lone electron pairs of the O-atom in the cation’s hydroxyl group and the negative charge surrounding the anion. Only A-B interactions can occur between different ILs in the system and, to reduce the number of adjustable parameters, all site-site interactions were considered equivalent, thus sharing the same value of association energy and volume. A sketch of the association scheme for [DEEA][But] is depicted in Fig. 1.

The five pure-component parameters required to describe an associating fluid, such as the ILs studied in this work, are typically regressed from experimental VLE data of the pure fluid, namely
the vapor pressure and saturated densities. As this data is typically unavailable for ILs, due to their negligible (or very low in the case of protic ILs) vapor pressures, part of the \( p\rho T \) data measured in this work was used in the parameterization procedure, additional details being provided in the next section.

4. Results and discussion

The density of five synthesized carboxylate-based protic ILs, namely [DEEA][Ace], [DEEA][Prop], [DEEA][But], [DEEA][Pent], and [DEEA][Hex], were measured in the 283–363 K temperature and 0.1–95 MPa pressure ranges.

The use of these compounds in the formation of IL mixtures suitable for CO\(_2\) capture has been suggested by us in a recent publication [16]. In there, densities and viscosities at atmospheric pressure for [DEEA][Ace], [DEEA][Prop] and [DEEA][Hex] at a 2:1 (acid:base) proportions and [DEEA][But] and [DEEA][Pent] at a 1:1 (acid:base) proportions were reported for the first time. To the best of our knowledge these are the only density data available in literature for the studied compounds, therefore high-pressure density data is here reported for the first time for all the studied ILs.

In Fig. 2, the atmospheric pressure density data reported in the previous work [16] is compared with those obtained here using the high-pressure densimeter in terms of percentage average relative deviation (\%ARD) and density differences. Due to the different acid:base proportions of the synthesized ILs, experimental data can only be directly compared for [DEEA][But] and [DEEA][Pent] – same 1:1 acid:base proportion, for which a good agreement between the two sets of data is observed. The values obtained in the previous work are systematically higher than those obtained here, but the absolute density differences are always lower than 0.008 g\(\cdot\)cm\(^{-3}\). Such small discrepancies can be explained by the presence of additional monomeric or oligomeric species resulting from the purification processes performed in our previous work [16], as discussed by us recently [48].

The new experimental pressure-density-temperature (\( p\rho T \)) data for the carboxylate-based ILs is shown in Fig. 3 and is reported in Tables S2–S6 in the Supporting Information. As expected, the IL densities were found to increase with increasing pressure and to decrease with increasing temperatures, while the molar density of the different ILs seems to decrease with increasing chain length of the anion. To further confirm this behavior and to analyse the consistency of the new experimental data across the different ILs, the molar volumes were calculated at different \((T, P)\) conditions and results are reported in Fig. 4.

According to Fig. 4, the molar volumes of the studied ILs present minor temperature and pressure dependencies, with a slight increase with temperature and decrease with pressure, as previously observed for other compounds [41,42]. Concerning the influence of the anion’s chain length, a linear increase of the molar volume with the ILs molecular weight was observed in all cases (\( R^2 \) higher than 0.9998 for all cases), suggesting a constant increase of the molar volume with the increase of the anions chain length i.e., through the addition of \( CH_2 \) groups. The experimental data plotted in Fig. 4 result in a molar volume increase of 17.84 and 17.17 cm\(^3\)\(\cdot\)mol\(^{-1}\) at 0.1 and 50 MPa, respectively.

From the experimental density data, two second-order derivative properties, namely the isothermal compressibility, \( k_T \), and the isobaric thermal expansivity, \( \alpha_p \), were determined. \( k_T \) is a measure of the fluids compressibility, i.e. the response of the volume to a change in pressure, at constant temperature. This property can be obtained from the pressure derivative of density using Eq. (2).

\[
k_T = \left( \frac{\partial \log(\rho)}{\partial p} \right)_T
\]

The values obtained are shown in Fig. 5 and, as observed for other compounds [41,42], \( k_T \) was found to decrease with increasing pressure and to increase with increasing temperature, although the temperature effect tends to become less pronounced at higher pressures.

\( \alpha_p \) is the response of volume to a change in temperature at constant pressure and can be obtained from the temperature derivative of density using Eq. (3).

\[
\alpha_p = -\left( \frac{\partial \log(\rho)}{\partial T} \right)_p
\]

The values obtained from the experimental data are plotted in Fig. 6 and show a similar behavior to that exhibited by \( k_T \), decreasing with pressure and increasing with temperature.
Considering the importance of having a robust and accurate thermodynamic model for the studied carboxylate-based protic ILs that can be used for predictive calculations or screening purposes, a coarse-grain molecular model of these ILs, is here developed in the framework of the soft-SAFT EoS. As mentioned in the previous section, the pure-component parameters required by soft-SAFT to fully describe an associating compound \((m, \sigma, \varepsilon, \varepsilon_{HB}, \text{and } \kappa_{HB})\) are usually obtained by regression to the available pure fluid VLE data, namely vapor pressure and the saturated liquid densities. In addition, some works have also pointed out the importance of including additional data such as vaporization enthalpies, monomer fractions, and derivative properties, in the fitting procedure whenever they are available \([49–51]\), making the model more robust, at the expense of being less predictive. Once those parameters are known, they can then be used to predict a number of thermophysical properties, under different thermodynamic conditions, or applied to the modeling of binary and multicomponent mixtures.

The performance of the EoS (i.e., accuracy; the need for considerable binary interaction parameters to accurately describe mixtures, etc.) relies on the proper development of a CG model (association scheme + molecular parameters) for each of the compounds, capturing the main features of their molecular structure, and on the type and quantity of experimental data used in the parameterization. Since VLE data is unavailable for ILs, their parameters are usually fitted only to the atmospheric pressure densities in a wide range of temperatures \([34,35,52,53]\), or optimized to reproduce specific binary experimental data \([54,55]\). While the former approach suffers from using only one type of experimental data in
the parameterization and from only accounting for the temperature effect on the fluids behavior, the parameters obtained using binary experimental data are necessarily affected by the presence of the other component, which may result in a diminished transferability of the parameters to different systems than the one initially considered, and a consequent lower accuracy of the model in those situations.

Several authors have successfully applied different SAFT variants to the description of high-pressure density data and second-order derivative properties of ILs [56–61], suggesting the importance of including such data in the parameterization and performance assessment of new SAFT-type models. Therefore, in this work, we have taken advantage of having available experimental density data in wide temperature and pressure range, hence, high-pressure densities and the isothermal compressibility measured at 323 K were combined with the atmospheric pressure densities (in the whole temperature range), to obtain the molecular parameters of the CG model of the various ILs with soft-SAFT. As previously observed for glycols and glycol ethers [41,42], the inclusion of a single isotherm of high-pressure data is expected to improve the prediction of the pressure effect on the fluids behavior and, consequently, to better reproduce the derivative properties. Therefore, the non-associating pure-component parameters characterizing each of the five protic ILs \((m, \sigma, \text{and} \ \varepsilon)\) were obtained by minimizing the following objective function:

\[
\text{OF} = \frac{\sum_{i=1}^{N_T} \left( \frac{\rho_{\text{calc}}}{\rho_{\text{exp}}^1} - \left( \frac{\rho_{\text{exp}}^1}{\rho_{\text{exp}}^{0.1 \text{MPa}}} \right) \right)}{N_T} + \frac{1 - \theta}{N_P} \left[ 0.90 \sum_{i=1}^{N_P} \left( \frac{p_T^{123} K - p_T^{0.1 \text{MPa}} K}{p_T^{0.1 \text{MPa}} K} \right) \right]_{p=p_T} + 0.10 \sum_{i=1}^{N_T} \left( \frac{\rho_{\text{calc}}^{0.1 \text{MPa}} - \rho_{\text{exp}}^1}{\rho_{\text{exp}}^1} \right)_{T=T_i} \tag{4}
\]

where \(\theta\) is the coupling factor (equal to 0.5 as suggested in the literature [49]), \(N_T\) is the number of different temperatures at which the density was measured, and \(N_P\) is the number of pressure levels at which the \(p_T\) data was measured in this work. The weights 0.90 and 0.10 were used in a previous publication [41], and found to ensure an excellent description of the experimental \(p_T\) data while still providing a good description of the isothermal compressibility data.

Concerning the association term, as previously mentioned, a 2/2 association scheme was employed to account for the hydrogen bonding character of all the studied ILs. The required association parameters are, in SAFT-type EoSs, usually kept constant within a homologous family of compounds as they are intended to capture the same type and number of hydrogen bonds, involving the same functional groups [42,62]. Hence, in this work, the association parameters were regressed only to the lowest \(M_w\) IL, [DEEA][Ace], along with its non-associating parameters, and used in a transferable manner to the modeling of its higher chain homologues. The optimal soft-SAFT pure-component parameters obtained for the studied ILs are reported in Table 2 along with the deviations from the experimental data.

As can be observed in Fig. 3, the selected molecular model using the optimized pure-component parameters, reported in Table 2, allow for an excellent description of the compounds’ density in the whole temperature and pressure ranges with percentage average absolute relative deviations %AARD (Eq. (5)) lower than 0.11% for all the studied ILs. Remarkably, using only one single isotherm of high-pressure densities (at 323 K), the model is able to correctly predict the pressure effect on density at all temperatures, while still providing a very good description of the temperature effect.

\[
\text{%AARD} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\rho_{\text{calc}}^i - \rho_{\text{exp}}^i}{\rho_{\text{exp}}^i} \right| \tag{5}
\]

Furthermore, it can be observed from the deviations to the experimental data reported in Table 2, that as the association parameters were fitted to the experimental data of [DEEA][Ace], it presents very low deviations from the experimental data, as expected. Nevertheless, the deviations observed for the other ILs with association parameters transferred from [DEEA][Ace] are kept very small and do not follow any trend with the compounds chain length, suggesting the absence of systematic deviations and the model robustness.

It is worth to note that, as can be observed in Table 2, the protic ILs investigated here are characterized by an association volume parameter that is considerably lower than those previously obtained when investigating aprotic ILs, such as the symmetrical tetraalkyl ammonium halides [63]. This may be due to the much stronger directionality of the H-bond interactions that are thus much more localized in protic ILs than in their aprotic counterparts [64,65].

Nevertheless, an additional set of parameters, with an increased value of the association volume, was obtained and is also reported.
in Table S7. However, as depicted in Figure S6 for [DEEA][Pent], although the description of the $p\rho T$ data is very similar using both sets of parameters, the behavior exhibited by the second-order derivative properties are clearly better described by using a lower association volume. This reinforces the importance of carrying high-pressure data measurements and considering the second-order derivative properties for the selection of the most appropriate set of molecular parameters of ILs, especially considering that vapor pressures, vaporization enthalpies and other properties often used in the parameterization are unavailable for this type of components.

Given the enhanced physical meaning of soft-SAFT molecular parameters, the non-associating pure-component parameters characterizing a homologous series of compounds can usually be correlated with the compounds molecular weight, yielding relationships that allow the prediction of the thermodynamic behavior of other members, for which no experimental data is available, this being particularly useful for future screening purposes. Those correlations are shown in Fig. 7 for the studied ILs and exhibit linear dependencies ($R^2 > 0.9912$) of the molecular parameters on the compounds chain length. Such dependencies can be expressed by the following expressions:

\[ m = 0.0159M_w + 3.6232 \]  
\[ \sigma^3 = 0.0190M_w - 0.7636 \]  
\[ \varepsilon/k_B = 0.0059M_w + 0.6719 \]

On these expressions, $\sigma^3$ can be seen as the volume occupied by a single chainlike molecule while $\varepsilon/k_B$ is a measure of
Fig. 6. Isobaric thermal expansivity, $\alpha_P$, as function of temperature and pressure for the carboxylate based protic ILs. Symbols represent the values obtained from the experimental data while the solid lines depict the soft-SAFT results.

Table 2
Soft-SAFT pure-component parameters for the carboxylate-based protic ILs using a 2/2 association scheme.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$m$</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon/k_B$ (K)</th>
<th>$\epsilon^{118}/k_B$ (K)</th>
<th>$\kappa^{118}$ (Å$^3$)</th>
<th>%AARD$_{pT}$</th>
<th>%AARD$_{\mu_T}$</th>
<th>%AARD$_{\mu_P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEEA][Ace]</td>
<td>6.401</td>
<td>3.4450</td>
<td>268.35</td>
<td>3740</td>
<td>515</td>
<td>0.054</td>
<td>3.44</td>
<td>2.21</td>
</tr>
<tr>
<td>[DEEA][Prop]</td>
<td>6.705</td>
<td>3.4920</td>
<td>268.79</td>
<td>3740</td>
<td>515</td>
<td>0.108</td>
<td>3.85</td>
<td>5.92</td>
</tr>
<tr>
<td>[DEEA][But]</td>
<td>6.916</td>
<td>3.5680</td>
<td>271.64</td>
<td>3740</td>
<td>515</td>
<td>0.048</td>
<td>3.78</td>
<td>2.58</td>
</tr>
<tr>
<td>[DEEA][Pent]</td>
<td>7.100</td>
<td>3.6340</td>
<td>275.68</td>
<td>3740</td>
<td>515</td>
<td>0.050</td>
<td>4.23</td>
<td>1.53</td>
</tr>
<tr>
<td>[DEEA][Hex]</td>
<td>7.319</td>
<td>3.6890</td>
<td>280.58</td>
<td>3740</td>
<td>515</td>
<td>0.075</td>
<td>4.04</td>
<td>3.18</td>
</tr>
</tbody>
</table>

the van der Waals interaction energy per molecule (IL). Both these properties and the number of segments were found to linearly increase with the successive addition of CH$_2$ groups to the IL anion. Such result not only confirms the consistency of the molecular parameters obtained for the different ILs but, along with the fixed association parameters, can be used to predict the thermophysical properties of any other carboxylate-based protic IL based on the same cation.

A stringent test to any molecular-based EoS is to evaluate its ability to provide data at conditions different than those considered in the parameterization procedure or its ability to provide different thermophysical properties. As an example, obtaining an
accurate description of derivative properties like $k_T$ and $\alpha_p$ that are second-order derivative properties of the EoS (i.e. second-order derivatives of the fluids Helmholtz energy) is particularly difficult as these properties usually present some experimental singularities and are very sensitive to model inaccuracies [66].

To further test our molecular model, we applied the soft-SAFT EoS to describe both properties in the whole temperature and pressure ranges investigated, although only one single isotherm of $k_T$ at 323 K was used in the parameterization procedure. As can be observed in Fig. 5, an excellent description of $k_T$ was obtained for all the studied ILs, with the model being able to correctly describe this property at temperatures other than 323 K. Although no systematic deviations with temperature were observed, it is clear from Fig. 5 that the deviations from the experimental data increase at higher pressures, with the model having an excellent performance to pressures up to 50 MPa, after which it starts to overestimate the fluids compressibility. Nonetheless, %AARD lower than 4.23% were obtained for all the compounds, which are significantly lower than the deviations previously obtained for other molecules [41,42]. Concerning $\alpha_p$, the soft-SAFT predictions are shown in Fig. 6 in overall excellent agreement with the experimental data without systematic deviations with temperature, pressure or the ILs molecular weight. An exception is the [DEEAA][Prop] for which considerably higher deviations from the experimental data were observed. This is due to the surprisingly much higher temperature effect observed experimentally while, instead, the model predicts a similar temperature dependency to that observed for the other homologues.

Different authors have estimated the expanded uncertainty of $k_T$ and $\alpha_p$ data derived from high-pressure density data measurements of ILs to be in the range 2.5-5% [67,68]. Hence, the model predictions discussed previously can be considered to be accurate, given that the %AARD values obtained are of the same order of the data uncertainty.

Both the good description of the second-order derivative properties and the consistency of the obtained molecular model parameters (linear dependencies with the ILs molecular weight) suggest the robustness and transferability of the proposed model that can be used in future studies such as to provide a screening of CO$_2$ solubilities, as a function of the IL molecular weight.

5. Conclusions

Aiming at providing an experimental characterization and to develop a molecular model for the carboxylate-based protic ILs that have been recently suggested as suitable candidates for CO$_2$ capture, new experimental $p\rho T$ data for five different ILs were measured in wide temperature (283–363 K) and pressure (0.1–95 MPa) ranges. The density data measured in this work exhibited the expected trends, increasing with pressure and decreasing with temperature, while the ILs molar volume was found to increase linearly with the anions chain length, due to the successive addition of CH$_2$ groups. From the experimental density data, using appropriate derivatives, the isothermal compressibilities and isobaric thermal expansivities were determined and discussed.

Given the importance for further studies of having a robust and transferable molecular model available for the studied ILs, a coarse-grain model was proposed for these ILs for the first time in the framework of the soft-SAFT EoS, which was previously shown to be a suitable model for gas/IL systems. Due to the relevance of the hydrogen bonding character of ILs, a 2/2 association scheme was employed to all the ILs and its correspondent pure-component parameters were then regressed from experimental data, using a single isotherm at 323 K of the high-pressure densities and isothermal compressibility, in addition to the usual atmospheric pressure densities.

The thermodynamic model proposed was then used to describe the $p\rho T$, $k_T$ and $\alpha_p$ data in the whole temperature and pressure ranges investigated. An excellent description of the density data was obtained for all the ILs, without systematic deviations with either temperature, pressure, or the IL molecular weight, while still providing excellent predictions of the very sensitive second-order derivative properties, highlighting the robustness of the proposed model. Furthermore, as typically observed in most SAFT-type models, when applied to describe a homologous series of compounds, the optimized non-associating parameters of the different ILs were found to correlate with the ILs molecular weight, while the association parameters were fitted to one IL and transferred to the other members of the family without loss of accuracy. This highlight both the consistency of the parameters obtained and the transferability of the proposed model that can be used for screening purposes, predicting the thermophysical properties of similar ILs for which experimental data is not currently available.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement

Emanuel A. Crespo: Investigation, Formal analysis, Visualization, Writing - original draft. Liliana P. Silva: Methodology, Investigation, Visualization, Data curation. Cristina I.P. Correia: Investigation, Visualization, Writing - original draft. Mónica A.R. Martins: Methodology, Data curation, Supervision. Ramesh L. Gar- das: Conceptualization, Funding acquisition, Project administration. Lourdes F. Vega: Resources, Validation, Supervision, Writing - review & editing. Pedro J. Carvalho: Conceptualization, Validation, Supervision, Writing - review & editing. João A.P. Coutinho: Conceptualization, Funding acquisition, Writing - review & editing.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 &
Supplementary materials

Supplementary text associated with this article can be found in the online version, at doi:10.1016/j.fluid.2021.113036.

References


Fluid Phase Equilibria 539 (2021) 113036


[57] I. Polishuk, Implementation of Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT), Generalized (G)/SAFT-Cubic, and Cubic-Plus-Association (CPA) for modeling thermophysical properties of selected 1-Alkyl-3-


