The Origin of the LCST on the Liquid–Liquid Equilibrium of Thiophene with Ionic Liquids

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Supporting Information

ABSTRACT: Mixtures of thiophene with two ionic liquids, namely, [C₄C₈im][SCN] and [C₄C₈im][NTf₂], were chosen as prototypes of systems presenting lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior, respectively. This distinct behavior is due to different interactions between the constituting species which are investigated here by means of experimental and computational studies. Experimentally, density measurements were conducted to assess the excess molar volumes and ¹H and ¹³C NMR spectroscopies were used to obtain the corresponding nuclear chemical shifts with respect to those measured for the pure ionic liquids. Computationally, molecular dynamics simulations were performed to analyze the radial distribution neighborhoods of each species. Negative values of excess molar volumes and strong positive chemical shift deviations for [C₄C₈im][SCN] systems, along with results obtained from MD simulations, allowed the identification of specific interactions between the anion and the molecular solvent (thiophene), which are not observed for [NTf₂]⁻. It is suggested that these specific thiophene interactions are responsible for the LCST behavior observed for mixtures of thiophene with ionic liquids.

INTRODUCTION

Ionic liquids (ILs) are a novel class of salts possessing unique physical and chemical properties, which have been in recent years the focus of great interest for both academic and industrial researchers. They are usually composed by a large asymmetric organic cation and by an anion that can be organic or inorganic. The intricate polar/apolar structure of these species makes their crystallization difficult and minimizes the cation–anion interaction conferring the ILs unique properties, such as a wide liquid temperature range, negligible vapor pressure, high thermal and chemical stabilities, good solvating capacity for both organic and inorganic compounds, and, among others, the ability to tune their properties for specific applications, through innumerous combinations between their ions.¹,² These properties make ILs an excellent choice to replace common molecular organic solvents in several applications, namely, extractive solvents in the petrochemical industry for aromatic–aliphatic separations³,⁴ and in the desulfurization of refined products.⁵–⁷

The reduction of the sulfur content in fuels has been a major worldwide concern during the past decades.⁶,⁸,⁹ The most common desulfurization process is the hydrodesulfurization (HDS), that uses catalysts based on CoMo and NiMo, and high temperatures (300–400 °C) and pressures (20–100 bar of H₂). These operation conditions are costly and have the disadvantage of removing aliphatic compounds, along with the sulfur ones, and which are important for fuel performance. Alternative processes have been studied to replace or complement HDS such as the oxidative desulfurization, reactive adsorption, biodesulfurization, membranes, and extractive desulfurization which is an attractive process due to its mild and clean conditions, and efficiency.⁵,⁷,⁸,¹⁰,¹¹ Several ILs have been studied for evaluation of their performance to remove sulfur compounds such as imidazolium¹²–¹⁹ and pyridinium-based²⁰,²¹ and also Lewis and Brønsted acidic ILs or oxidative ILs.¹⁴,²²–²⁵

While measuring the binary¹,²,²⁶ and ternary⁵,⁶,¹¹,²⁷ phase diagrams, required to evaluate the capacity of ILs to be used in the extractive desulfurization, it was observed that systems of ILs and thiophene present different types of liquid–liquid equilibrium behavior, which mainly depends on the IL anion. In most cases, these systems display the most common upper critical solution temperature (UCST) behavior, with their mutual miscibilities increasing with a temperature increase, while some others display a lower critical solution temperature (LCST).¹,² Examples of these behaviors are presented in Figure 1 for thiophene combined with [C₄C₈im][NTf₂] (UCST) or...
The interaction between ILs and thiophene was investigated by molecular dynamics (MD) simulation using the GROMACS 4.5.4 molecular dynamics package. These simulations were carried out in the constant temperature and constant pressure (NPT) ensemble. Constant temperature (298.15 K) was maintained by using the Nose–Hoover thermostat, while the pressure (1 bar) was maintained by using the Parrinello–Rahman barostat. All systems (each one considering 80 pairs of IL ions and 40 molecules of thiophene) were prepared by randomly placing all species in the simulation boxes. In each of these simulations, the equations of motion were integrated with the Verlet-Leapfrog algorithm and a time step of 2 fs. A 10 000 step energy minimization was performed, and the systems were equilibrated (at least 150 000 steps). Further, quite long simulations were carried out, with 25 000 000 steps for \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) with thiophene and 50 000 000 steps for \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\) with thiophene (50 ns). The intermolecular interaction energy between pairs of neighboring atoms was calculated using the Lennard-Jones potential to describe dispersion/repulsion forces, and the point-charge Coulomb potential was used for electrostatic interactions. Long-range electrostatic interactions were accounted for using the particle-mesh Ewald method with a cutoff of 1.0 nm for the real-space part of the interactions. A cutoff radius of 1.2 nm was used for the Lennard-Jones potential, and long-range dispersion interactions were added to both energy and pressure. Rigid constraints were enforced on all bond lengths.

All-atom force fields for \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) were obtained from the works of Cadena and Maginn for the cation and for the anion, respectively, as in the work of Tomé et al. The charges for the cation and the anion were recalculated with the CHelpG scheme using an optimized geometry for the \(\text{C}_4\text{C}_1\text{im}-\text{NTf}_2\) dimer in the gas phase. The calculations considered the B3LYP/6-311+G(d) approach as included in the Gaussian 03 code, i.e., using the same computational strategy employed by Morrow and Maginn for the \([\text{C}_4\text{C}_1\text{im}][\text{PF}_6]\) ionic liquid. The total charges on the cation and anion are +0.797 and −0.797, respectively. The estimation of partial charges for an IL from calculations of an ion pair in a vacuum can be a problematic treatment, and this issue has been addressed and discussed in other works. Nevertheless, it has been demonstrated that models with total charges on each ion in the range ±0.7–0.8 yield a better description of both structural and (most noticeably) dynamic properties of ionic liquids. Furthermore, we have also performed calculations considering a pair of ions surrounded by other IL ions and no significant differences were found in the results obtained. The full set of atomic charges is supplied as

![Figure 1. Phase diagram of temperature as a function of mole fraction of \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\) and \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\). Lines are guides to the eye.](image)
 Supporting Information (Tables S.1–S.3). The calculated density and enthalpy of vaporization for \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) are 1486 kg/m\(^3\) and 131.74 kJ/mol, respectively, which compare well with the range of experimental results, i.e., [1429; 1437.4] kg/m\(^3\) [46,47 and 134–155 kJ/mol, respectively. In the case of \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\), we have used the all-atom force field from the work of Cadena and Maginn\(^{37}\) for the cation and we have adapted standard Gromos potential parameters for the anion (additional details given in Tables S.4–S.7 supplied as Supporting Information). The CHelpG total charges on the cation and anion are +0.791 and −0.791 au, respectively. These values were also calculated using a B3LYP/6-311+G(d) optimized geometry (minimum energy from several initial configurations) for the \(\text{C}_4\text{C}_1\text{im}-\text{SCN}\) dimer in the gas phase. It was quite encouraging to see that the charges above are close to those computed for the central cation/anion pair in clusters containing several \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\) pairs; for instance, the mean values calculated for the central dimer in different clusters containing 13 \(\text{C}_4\text{C}_1\text{im}-\text{SCN}\) pairs are +0.804 ± 0.020 and −0.804 ± 0.020 au for the cation and the anion, respectively. The calculated density and enthalpy of vaporization for \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\) are 1082 kg/m\(^3\) and 123.0 kJ/mol, respectively. Very encouraging, these results compare well with the range of experimental results for density and enthalpy of vaporization, i.e., [1070; 1069.8] kg/m\(^3\) [47,49 and 114.5–148 kJ/mol, respectively. The spatial distribution functions (SDF) were calculated using a bin width of 0.05 nm.

## RESULTS AND DISCUSSION

### Excess Volumes (\(V^E\)).

This property describes the deviation of the mixture molar volume from the ideal molar volume. The excess molar volume is estimated from the measured densities as described in eq 1

\[
V^E = \sum x_i M_i \left(\frac{1}{\rho_{\text{mixt}}} - \frac{1}{\rho_i}\right)
\]

where \(x_i\), \(M_i\), and \(\rho_i\) are the molar fraction, molar mass, and density for each component that composes the binary system and \(\rho_{\text{mixt}}\) is the density of the mixture.

\(V^E\) data can be used to obtain information on the strength/type of interactions between components in a given mixture. Negative values of \(V^E\) usually indicate strong and favorable interactions, while positive values of \(V^E\) indicate unfavorable interactions.

Results for the excess molar volumes of the mixtures composed of thiophene with \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) or \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\), within their mutual miscibility range, are presented in Figures 2 and 3, respectively.

Both figures represent data for two temperatures, and independently of the temperature chosen, there is an opposite behavior for mixtures constituted by thiophene and one of the ILs considered. In Figure 2, it is shown that the \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\)-containing system presents large and positive excess molar volumes when mixed with thiophene. This pattern is indeed indicative of nonspecific and unfavorable interactions between the IL ions and thiophene. On the contrary, in the case of the \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\) mixtures with thiophene (Figure 3), negative excess molar volumes are observed in the entire range of compositions. This trend suggests and supports the existence of some sort of specific interaction among the ILs and the molecular species. These findings are in good agreement with the phase diagrams presented in Figure 1.

### Chemical Shift Deviations (\(\Delta\delta\)).

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy are widely used to identify the structure of compounds through differentiation of the atomic neighborhood of protons and carbons, but they may also be a powerful technique to identify favorable or unfavorable interactions among different compounds.\(^{51,52}\) Each type of proton or carbon in a different structural/chemical environment has a characteristic chemical shift (\(\delta\)), represented by the peaks of a NMR spectrum. These peaks are shifted to higher or lower chemical shifts depending on the type of interactions that a given carbon and/or proton suffer in a mixture. The chemical shift deviations (\(\Delta\delta\)) are defined by the following equation

\[
\Delta\delta = \delta_{\text{mixt}} - \delta_{\text{IL}}
\]

where, in this work, \(\delta_{\text{mixt}}\) is the \(^1\text{H}/^{13}\text{C}\) chemical shift of the IL in mixtures with thiophene and \(\delta_{\text{IL}}\) is related to the chemical shift of the pure IL. In general, positive \(\Delta\delta\) identify favorable interactions involving those nuclei, while negative \(\Delta\delta\) values identify atoms with a lower propensity to interact. Finally, protons or carbons with \(\Delta\delta\) values close to zero are not involved in significant and additional interactions.

![Figure 2](image-url) Excess volumes as a function of mole fraction of \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\), at different temperatures. Lines are guides to the eye.

![Figure 3](image-url) Excess volumes as a function of mole fraction of \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\), at different temperatures. Lines are guides to the eye.
Figures 4 and 5 represent the $^1$H and $^{13}$C chemical shift deviations ($\Delta \delta$) for mixtures composed of [C$_4$C$_1$im][SCN] and thiophene, whereas Figures 6 and 7 show the $^1$H and $^{13}$C chemical shift deviations ($\Delta \delta$) for mixtures of [C$_4$C$_1$im][NTf$_2$] and thiophene. Detailed information concerning the individual chemical shifts is presented in Tables S.8−S.15 in the Supporting Information.

For the two evaluated mixtures, only the proton chemical shifts of thiophene present positive chemical shift deviations. Albeit thiophene displays favorable interactions with both ILs, these are particularly strong in the presence of [C$_4$C$_1$im][SCN]. In both ILs, the protons of the cation present negative deviations which suggest that they are not actively interacting with thiophene. Moreover, these unfavorable interactions observed at the $^1$H NMR are more evident with [C$_4$C$_1$im][NTf$_2$]. Therefore, there is clear evidence that the favorable interactions of thiophene occur with the IL anions. This is confirmed by the $^{13}$C chemical shift deviations presented in Figures 5 and 7. Again strong positive chemical shift deviations for the aromatic thiophene carbons are observed with the [C$_4$C$_1$im][SCN]-containing systems, along with strong deviations in the [SCN]$^-$ carbon, both increasing with the content of the other species (with the exception of the carbon atom of the anion, which decreases). Although some favorable interactions are also observed with [NTf$_2$]$^-$ carbon atoms, these seem to be less significant taking into account the magnitude of the chemical shift deviations. Therefore, the NMR data clearly suggest that favorable interactions between thiophene and each
ILs exist, although they are more significant for the [SCN]⁻-based fluid.

**Molecular Dynamics Simulations.** In this type of computer simulations involving a large number of atoms, the radial distribution function, $g(r)$ or RDF, can be employed to describe the structural organization of a system. This function gives the probability of finding a particle at the distance $r$, from another particle (considered as the reference particle) and will be used here to aid the interpretation of the experimental results. The $g(r)$ values provide a quantitative description of enhancement (values larger than 1) or depletion (values smaller than 1) of densities of atoms or groups of atoms around a selected moiety with respect to bulk values. The calculated radial distribution functions are depicted in Figures 8–11, while peak maxima are given in Tables S.16–S.19 (Supporting Information).

**Cation−Thiophene Interactions.** For the cation of [C₄C₁im][SCN], there is a higher intensity peak for the atom C10, the carbon at the alkyl chain extremity, especially when considering the atom of sulfur of thiocyanate (Figure 8). However, the atoms at the ring of the imidazolium cation (except the C2) as well as the carbon C6 from the methyl group show also significant interactions with thiophene. Since both ILs are composed by the same cation, it is not surprising to see that, in the case of [C₄C₁im][NTf₂], Figure 9, the radial distribution functions are similar to those calculated for [C₄C₁im][SCN]; i.e., the interactions involve the same atoms. However, in the case of [C₄C₁im][NTf₂], the intensities of the S−C(cation) peaks are higher than those observed with [C₄C₁im][SCN]. Thus, these intensities suggest that the cation interactions with thiophene are dominant in the former IL.

**Anion−Thiophene Interactions.** The RDFs calculated for the interactions involving the [SCN]⁻ and [NTf₂]⁻ anions and thiophene are displayed in Figures 10 and 11, respectively. Figure 10 shows that the sulfur atom of thiocyanate has a higher probability to surround the carbon atoms of thiophene (the CS and CC carbons) than to surround the sulfur atom, with peak intensity maxima of 1.26 for CS and 1.08/1.11 double peak corresponding to CC atoms. The RDFs calculated for the C and N atoms of [SCN]⁻ do not present visible peak intensity maxima (Figure S.2 in the Supporting Information), suggesting that S atoms are pointing toward the thiophene carbon atoms while the former atoms are rotating in a conical shape oriented outward from the thiophene ring. For systems composed of [C₄C₁im][NTf₂] and thiophene, the RDFs calculated for atoms of [NTf₂]⁻ and thiophene show peaks...
that occur at large distances, with $g(x)$ values being close to or lower than unity (Figures 11 and S.3 in the Supporting Information). Nevertheless, in the case of the carbon from the anion (note that the anion [NTf$_2$]$^-$ is here considered to be a symmetric structure, similar to thiophene), in Figure 11, there is significant interaction between this atom and thiophene constituting atoms which is represented by a double peak (with very similar RDF shapes for the three different atomic species of thiophene). In summary, the RDFs show a more specific orientation of the anion [SCN]$^-$ around the thiophene moiety, with a preferable orientation toward CS and CC atoms of thiophene, suggesting more favorable interactions with the latter atoms than with the sulfur atom of thiophene. These specific orientations are not evident in the case of the [NTf$_2$]$^-$ anion for which similar RDFs were obtained for all the interactions with thiophene.

**Final Remarks.** In summary, negative values of $V^E$ and positive $^{13}$C chemical shift deviations revealed the presence of favorable and stronger interactions of thiophene with the [SCN]$^-$ anion. MD simulations provided a reinforcement to the results obtained experimentally, since it was possible to identify a specific interaction between [SCN]$^-$ and thiophene through a well-defined spatial orientation which is thus responsible for the LCST behavior. For the system composed of [C$_4$C$_1$im][SCN] and thiophene, the common UCST behavior is observed—behavior typical of systems with weaker and/or nonfavorable interactions. The positive values of $V^E$ and the dispersion forces acting between the thiophene and the terminal groups of the alkyl chains of the cations are in good agreement with this type of phase diagram.

The results here reported confirm the suggestion of Revelli et al. which posed that a specific interaction is present in the binary system [C$_4$C$_1$im][SCN]–thiophene; however, the molecular picture gathered from this work is completely different from that initially proposed. They suggested that four thiophene molecules in a pseudo-tetrahedron spatial orientation were surrounding the [SCN]$^-$ anion with its sulfur atom.
were used to understand the molecular basis of the phenomena observed.

Negative values of $V^d$, as well as strong positive chemical shift deviations for the carbon atom from the anion $[\text{SCN}]^-$ obtained for the $[\text{C}_4\text{C}_1\text{im}] [\text{SCN}]$ systems, showed the presence of strong and specific interactions between the ionic liquid anion and the thiophene protons. The molecular dynamics simulations further supported this view. For $[\text{C}_4\text{C}_1\text{im}] [\text{SCN}]$, it was possible to identify a specific spatial orientation of the sulfur atom of the anion with the thiophene protons which is suggested to be responsible for the LCST behavior. The interactions of thiophene with other ionic liquids, here represented by the $[\text{C}_4\text{C}_1\text{im}] [\text{NTf}_2]$, are of a different nature, being weak and of a dispersive type between the cation alkyl chains and the thiophene, leading to the more common UCST type of liquid–liquid phase diagram.

**ASSOCIATED CONTENT**

Supporting Information

Lists of CHelpG atomic charges and Lennard-Jones parameters for the species considered; $^1$H and $^{13}$C NMR chemical shift deviations for the different systems considered; position and intensities of RDF peak maxima; additional RDFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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