

The polarity effect upon the methane solubility in ionic liquids: a contribution for the design of ionic liquids for enhanced CO₂/CH₄ and H₂S/CH₄ selectivities†

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Received 2nd May 2011, Accepted 17th August 2011

DOI: 10.1039/c1ee01599k

Aiming at designing ionic liquids for the purification of natural gas, the solubility of methane in ionic liquids is investigated here through the measurement of the solubilities of methane in four ionic liquids (ILs), in a wide range of molar fractions, temperature and pressures. With the exception of the phosphonium-based IL, which behaves as an almost ideal solution, the other ionic liquids show strong positive deviations from ideality, resulting from non-favorable interactions between CH₄ and the ILs. The results indicate that the non-ideality of the solution increases, and the solubility decreases, with the polarity of the ionic liquid. The effect of the ionic liquid polarity on the CO₂/CH₄ and H₂S/CH₄ selectivities is evaluated here. The ionic liquids studied here present the largest CO₂/CH₄ and H₂S/CH₄ selectivities ever reported. The selectivity models previously proposed in the literature are tested against these new experimental data and are shown to fail. Furthermore, it is shown that describing the ILs' polarity using the Kamlet–Taft parameters, the CO₂/CH₄ and H₂S/CH₄ selectivities correlate well with the β -parameter providing a key to the design of ionic liquids with enhanced selectivities.

1. Introduction

Due to energetic and environmental problems, natural gas has been standing out as a clean alternative energy source to coal and oil. Nonetheless, due to natural gas specifications, processing and transportation requirements, the removal of hydrogen sulfide (H₂S), carbon dioxide (CO₂), carbonyl sulfide (COS), organic sulfur compounds, mercury and water is required prior to liquefaction. Apart from some alternative processes, natural gas treatment is processed using solvent absorption that, despite

being simple, cheap and reliable, presents several technological and environmental inconveniences and limitations.¹ Membrane separation, on the other hand, represents the latest approach to methane purification. Polymeric membranes made of silicone rubber,² cellulose acetate,³ polyimide^{4,5} and polyether block amide have been widely tested.⁶ Despite, being effective for CO₂/CH₄ separation, the majority of them cannot be used for gas purification because they are damaged by aggressive gases. Nonetheless, ionic-liquid based liquid membranes, with high fluxes and high selectivities, stand as a promising method for gas separation.^{7,8} A reported “condensing-liquid membrane”⁷ enhanced gas separation by removing unwanted and toxic gases through a continuously refreshed surface with condensed water to avoid contamination of the permselective membrane.⁷ Furthermore, ionic-liquid membrane gas separation seems to be

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† Electronic supplementary information (ESI) available: Bubble point data and CO₂/CH₄ selectivity tables. See DOI: 10.1039/c1ee01599k

Broader context

Aiming at developing innovative separation technologies, the solubility of gases in ionic liquids, in particular the solvation mechanism, has been for the past decade an object of intense study and discussion among the scientific community. Recent works have shown that the physical sorption of most gases, such as CO₂, SO₂, H₂S and NH₃, in ILs is entropically driven, presenting negative deviations from ideality, which limits their solvation in ILs. This work shows that CH₄ solubility in ILs presents instead, strong positive deviations from ideality, resulting from non-favorable interactions between the CH₄ and most ILs. This suggests that the best approach for natural gas purification is the selection of an IL with poor CH₄ solubility, thus with an enhanced selectivity. Furthermore, it is shown that the sour gases/methane selectivities are related to the IL polarity, described by the Kamlet–Taft β -parameter, and that this parameter can be used as the basis for the choice of ILs that maximize the selectivities.

controlled by the gas solubility in the ionic liquid rather than on its diffusivity.^{9,10}

Ionic liquids, due to their outstanding properties, like negligible vapor pressures, high thermal stability, large liquidus range, nonflammability, and high solvation capacity stand out as a viable alternative to replace the solvents commonly used in natural gas treatment. The ILs' aptness for fine-tuning their properties cataloged them as "designer solvents", and this tunable capability, through an endless combination of cations and anions, allows the design of solvents for the development of more efficient and sustainable processes and products. A great deal of work has addressed the use of ionic liquids for CO₂ capture and gas separation purposes,^{11–28} or sulfur containing gases^{20,21,23,29–35} but few authors have addressed CH₄ solubility in ionic liquids.^{11,15,16,19,29,36,37} The understanding and description of the absorption of sour gases in ionic liquids are of importance for the design and operation of processes or the design of new and enhanced sorbents. However, for gas separation processes, more than just the solubility is the selectivity that dictates the choice of an absorbent. The endless combination of cations and anions limits the feasibility of the experimental characterization of all the ILs. Thus, the development of reliable correlations capable of estimating the solubility of methane and sour gases in the ILs stands as a vital key to the pursuit of alternative solvents.

Having established in previous works the mechanism of solvation and the limits to the physical sorption of the CO₂²⁸ and other sour gases such as H₂S and SO₂³⁸ in ionic liquids as being entropically driven, it is now clear that the most promising approach to enhance the sour gases/CH₄ selectivities at high pressures is by lowering the methane solubility in ionic liquids and not by increasing the sour gas solubility, that is essentially dependent on the solvent molar volume.^{28,38}

Aiming at exploring the mechanism behind the absorption of methane by ionic liquids and identifying ILs with large sour gases/CH₄ selectivities, the present work investigates the non-ideality of CH₄ in ionic liquids through the measurement of solubilities at high pressure. It will be shown here that, unlike for sour gases, the methane solubility is controlled by the interactions between the methane and the ionic liquids, and that the Kamlet–Taft parameter, β , measuring the solvent hydrogen bonding acceptor character, correlates well with the ILs CO₂/CH₄ and H₂S/CH₄ selectivities and could thus be used to guide the choice of the best ionic liquid for natural gas purification.

2. Experimental section

2.1. Materials

Four ILs, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide (CAS 460092-03-9), [P₆₆₆₁₄][NTf₂], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (CAS 174899-83-3) [C₄mim][NTf₂], 1-butyl-3-methylimidazolium methanesulfonate (CAS 342789-81-5), [C₄mim][CH₃SO₃], and a protic IL, *N*-methyl-2-hydroxyethylammonium propionate, 2mHEAPr, were used in this study. The [C₄mim][NTf₂] and the [C₄mim][CH₃SO₃] were acquired from Io-Li-Tec, with mass fraction purities higher than 99% and the [P₆₆₆₁₄][NTf₂] was an offer from Cytec, with mass fraction purity

higher than 97% and chloride impurity inferior to 0.1%. The 2mHEAPr was supplied by Profs Mattedi and Iglesias from UFBA, Brazil, and the details about the synthesis can be found in Alvarez *et al.*³⁹

Both the [P₆₆₆₁₄][NTf₂] and 2mHEAPr were further purified. The [P₆₆₆₁₄][NTf₂] was washed with ultrapure water followed by drying under high vacuum (1×10^{-4} Pa) and moderate temperature (353 K), for a period of 48 h. The purification process was repeated until no impurities were observed in the IL by NMR analysis. The water used was double-distilled, passed through a reverse osmosis system, and further treated with a MilliQ plus 185 water purification apparatus. It has a resistivity of 18.2 M Ω cm, a TOC smaller than 5 $\mu\text{g L}^{-1}$, and it is free of particles greater than 0.22 μm . The 2mHEAPr was double distilled. Initially, a low vacuum (1 Pa) distillation was carried out and a small fraction of IL, ~ 5 mL, rich in water and other volatile compounds was discarded, while the remaining sample was distilled in high vacuum (1×10^{-4} Pa). The final IL was colorless in contrast to its dark yellow initial color.

The purity of all ionic liquids was checked by ¹H, ¹³C and ¹⁹F NMR and estimated to be better than 99%. Prior to the measurements, all the ionic liquids were dried under high vacuum (1×10^{-4} Pa) and moderate temperatures for at least 24 h. The purification procedure adopted assures that water and volatile compounds are removed and the influence of these impurities on the solubility measurements is minimized.^{40–42} The final IL water content was determined with a Metrohm 831 Karl Fischer coulometer, indicating a water mass fraction of (68, 50, 97 and 250) $\times 10^{-6}$ for [P₆₆₆₁₄][NTf₂], [C₄mim][NTf₂], [C₄mim][CH₃SO₃] and 2mHEAPr, respectively.

Methane (CH₄) was acquired from Air Liquide with a purity $\geq 99.9\%$ and H₂O, O₂, CO₂, C_nH_m, N₂, H₂ and C₂H₆ impurities volume fractions lower than (20, 50, 10, 80, 500, 40 and 400) $\times 10^{-6}$, respectively.

2.2. Experimental equipment

The high pressure equilibrium cell used in this work is based on a cell designed by Daridon *et al.*^{43–47} by the synthetic method. Both the apparatus and the methodology followed here are fully described in previous works,^{24–27,48} and shown to be adequate to accurately measure the vapor–liquid phase equilibrium in a wide range of pressures and temperatures.

The purity of the IL is checked again by NMR at the end of the study to confirm that no degradation takes place during the measurements.

3. Results and discussion

3.1. Methane solubility

The solubility of methane in the studied ILs, plotted in Fig. 1–4 (detailed results are reported in Tables S1–S4 in the ESI†), was measured for concentrations from 0.04 to 0.8, in the temperature range 293 to 363 K and pressures from 0.1 to 100 MPa.

Initially the solubilities follow the common pattern of gas solubility in ionic liquids decreasing with temperature and increasing with pressure. However, contrary to the CO₂ + IL systems for which the increase in temperature has a large impact on the solubility, for the CH₄ + IL systems this influence is very

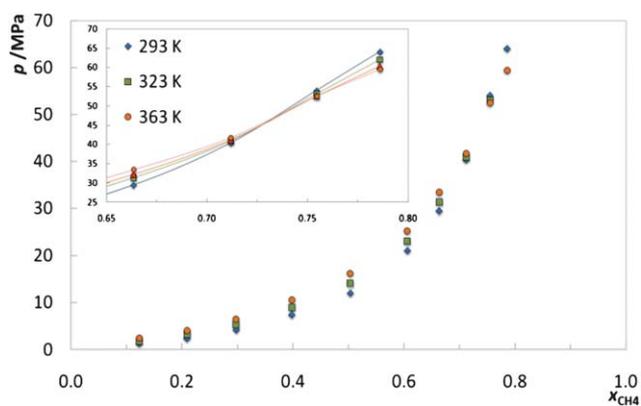


Fig. 1 Pressure–composition diagram of the binary system $[P_{66614}][NTf_2] + CH_4$.

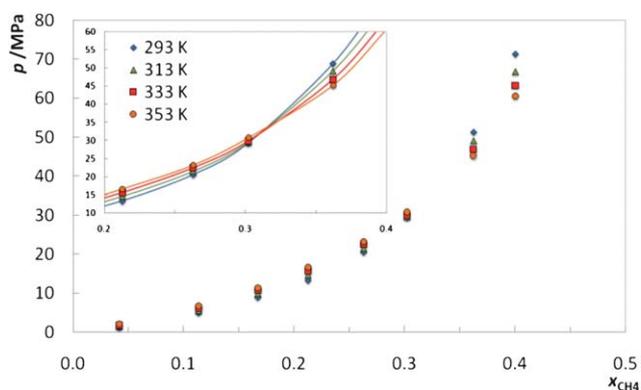


Fig. 2 Pressure–composition diagram of the binary system $[C_4mim][NTf_2] + CH_4$.

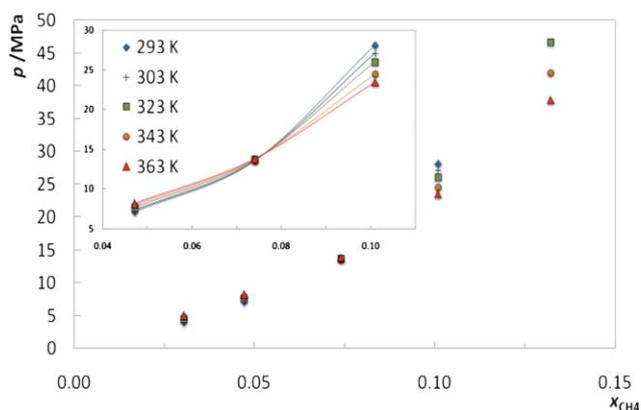


Fig. 3 Pressure–composition diagram of the binary system 2mHEAPr + CH_4 .

small or, in some cases, even negligible. Another peculiar feature of these systems is that for all the studied systems, with the exception of the $[C_4mim][CH_3SO_3] + CH_4$, a crossover is observed above which the temperature dependency of the solubility is reversed and increases with temperature. This type of behavior was previously observed by us, for some high molecular weight ILs (phosphonium-based ILs) + CO_2 ^{27,45} and CH_4 +

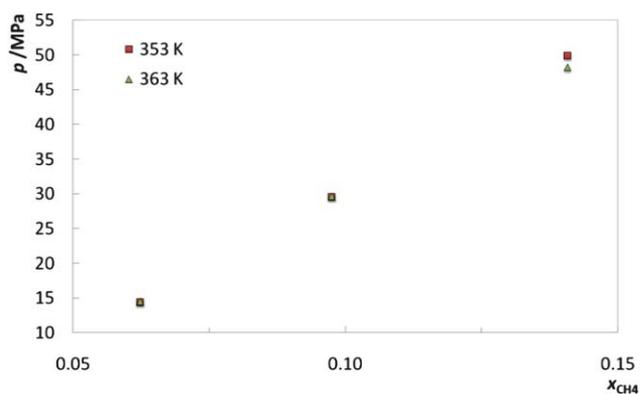


Fig. 4 Pressure–composition diagram of the binary system $[C_4mim][CH_3SO_3] + CH_4$.

heavy alkane systems.^{44,49} Nonetheless, to the best of our knowledge, it is reported here for the first time, for ILs + CH_4 systems. Furthermore, while for the ILs + CO_2 system this behavior seems to be associated with a “liquid–liquid like” type behavior where the CO_2 and ionic liquid have similar densities and an inversion of the phase densities is observed,^{27,45} for ILs + CH_4 systems it seems to be more common and not related to the phases density. The change in temperature dependency of the solubility must thus be related to a change from positive to negative of the enthalpy of solution.

3.2. CO_2/CH_4 and H_2S/CH_4 selectivities

Following the approach used in previous works,^{28,50} the mechanism behind the solubility of CH_4 in ionic liquids is investigated here by analyzing their deviations from ideality in the liquid phase. The system CH_4 + hexane, an athermal, quasi-ideal mixture, with negligible enthalpic interactions and reduced entropic contributions resulting from the differences in size and shape of the species, was adopted to describe the methane ideal behavior. As depicted in Fig. 5, all the studied ionic liquids, with the exception of the $[P_{66614}][NTf_2]$ that presents an almost ideal behavior (though with slightly negative deviations), present strong positive deviations from ideality that result from positive deviations in the residual (enthalpic) term, as shown by the

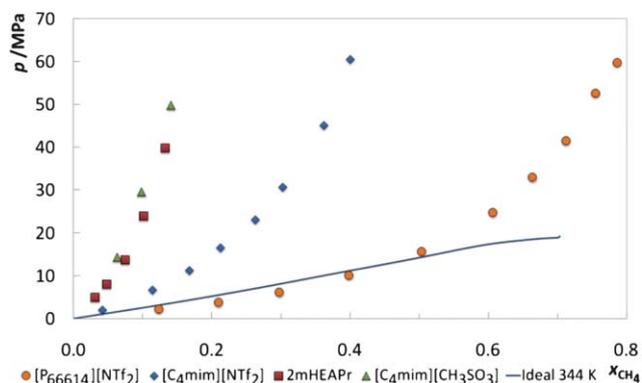


Fig. 5 Pressure–composition diagram of the binary systems: $[P_{66614}][NTf_2]$, $[C_4mim][NTf_2]$, 2mHEAPr and $[C_4mim][CH_3SO_3] + CH_4$ at 353 K and the ideal behavior at 344 K.

deviations from the ideal behavior. These observations do not come as a surprise since the non-ideality of a solution and its impact on the solubility of a given solute depends on a delicate balance between the solute–solute, solvent–solvent and solute–solvent interactions. Thus, the phosphonium-based IL, due to its large cation alkyl chains, would be expected to present similar interactions with the CH₄ and consequently lead to a near ideal behavior, while the other studied ionic liquids would present strong unfavorable solute–solvent interactions. Moreover, the positive deviations from ideality seem to be related to the IL polarity. The higher the IL polarity the larger are the deviations from ideality.

The selection of a solvent for an efficient CO₂/CH₄ separation must focus on the choice of a highly selective solvent. Since, as shown before,²⁸ the CO₂ solubility in ionic liquids is controlled by entropic effects and it is to a large extent independent of the ionic liquid, the maximization of the selectivity must address the minimization of the CH₄ solubility in the ionic liquid. According to the results reported here, the CH₄ solubility being controlled by the enthalpic interactions between the gas and the solvent, the ionic liquid that will maximize the non-ideality of the liquid phase will also minimize the gas solubility and thus maximize the selectivity as will be shown below.

To evaluate the CO₂/CH₄ selectivities the carbon dioxide solubilities in these ionic liquids were estimated using the correlation developed, by us, in a previous work.²⁸ To evaluate the CH₄/H₂S selectivities the hydrogen sulfide solubilities in these ionic liquids were estimated using the γ – ϕ approach based on the Flory–Huggins model described in a recent work.³⁸ It is shown in Fig. 6 that the studied ionic liquids present a wide range of CO₂/CH₄ and H₂S/CH₄ selectivities, following the order: [P₆₆₆₁₄][NTf₂] < [C₄mim][NTf₂] < [2mHEAPr] < [C₄mim][CH₃SO₃].

Here the low CH₄ solubilities (and high selectivities) do not seem to be directly related to the solvents' molecular weight, as in the case of the carbon dioxide,²⁸ but instead to the higher or lower polarity of the ionic liquid. To evaluate this relationship the ionic liquids' polarity scale adopted was the multidimensional Kamlet–Taft based on three parameters: β , the hydrogen bond accepting ability; α , the hydrogen bond donating ability; and π^* , a measure of non-specific interactions (polarizability, dipole–dipole interactions, and dipole–induced dipole interactions). The α and β parameters are compared with the

selectivities in Fig. 6. The Kamlet–Taft parameters were obtained from the literature.^{51–54} Since no data were available for the 2mHEAPr, the Kamlet–Taft parameters for the 2-hydroxyethylammonium formate were used assuming that they are a good approximation to the protic IL parameters.⁵⁴ It can be observed that the ILs CH₄/CO₂ and H₂S/CH₄ selectivities present a similar trend to the Kamlet–Taft β parameter indicating that, as expected from the non-ideality analysis carried out above, the solubility of methane in the ILs is related to the ionic liquids' polarity, in particular to their hydrogen bond accepting ability. A similar observation has been recently reported for acetylene + ionic liquid systems by Palgunadi *et al.*⁵⁵ Unfortunately both methane and hydrogen sulfide solubility data and the Kamlet–Taft parameters are still scarce and more data are required for a more comprehensive analysis to be carried out and a correlation proposed.

3.3. Ionic liquids CO₂/CH₄ selectivity models

Several authors^{56–59} have proposed correlations for gas solubilities in ionic liquids. Camper *et al.*⁵⁶ developed a model for alkyl methyl imidazolium-based-ionic liquids based on the assumption that single-gas solubility in ILs was primarily a function of molar volume of the IL. Furthermore, Camper's model stated that the smaller the IL's molar volume the better the selectivity and as the IL molar volume increases the amount of gas absorbed per volume of fluid initially increases and then starts to decrease. Kilaru *et al.*^{58,59} developed a couple of two parameter models, similar to those of Camper's, where the viscosity and surface tension of the IL have an important role on the solubilities. Later, Scovazzo,⁵⁷ from a multivariable linear regression of a wider set of experimental data, developed a model (the so-called "Universal model"), covering an extended set of IL families, in which the dependence of viscosity on the permeability/selectivity has a minimal influence on the solubility. All the authors, nonetheless, agree that the CO₂–anion interaction is not the dominant factor that determines the relative CO₂ solubility between ILs. This corroborates a recent work²⁸ where we have developed a model, valid for pressures up to 5 MPa, for temperatures ranging from room temperature up to 363 K and molalities up to 3 mol kg⁻¹, showing that when the molecular weight effect is removed from the analysis by comparing the solubilities in molalities, instead of molar fractions, the CO₂ solubilities in various systems (ILs, alkanes, methyl esters, fatty acids, PEGs, *etc.*) are identical and the solubility of CO₂ in nonvolatile solvents is essentially solvent independent.

With the exception of Scovazzo's work⁵⁷ none of the other authors extended these models to CH₄ solubilities and selectivities in ionic liquids. Scovazzo's work,⁵⁷ despite presenting several IL families like imidazolium, ammonium and phosphonium, focuses essentially on ionic liquids based on the bis(trifluoromethylsulfonyl)imide anion. Therefore, given the similar polarities of the ionic liquids, one would expect similar deviations from ideality, and consequently a well-behaved selectivity vs. IL. In fact, for the set of ionic liquids studied Scovazzo proposed a "Universal correlation"⁵⁷ that provides a good fit to the experimental data used. However, when new ionic liquids, with different polarities than those used in the model regression, are compared against it, the correlation fails to describe their

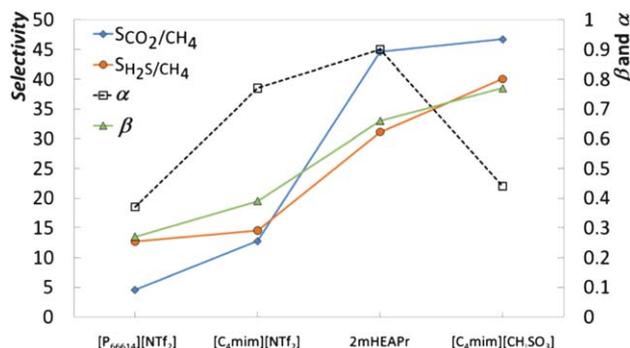


Fig. 6 Selectivities, the Kamlet–Taft α and β parameters for the studied ILs at 353 K.^{51–54}

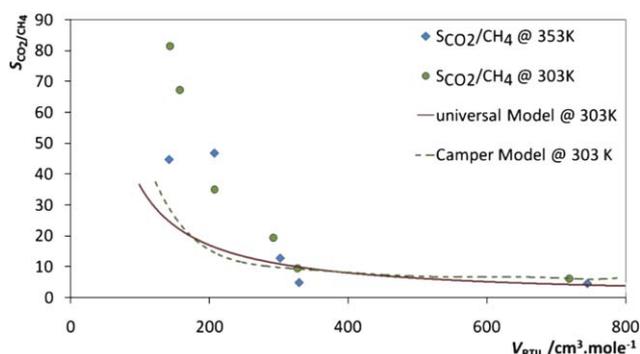


Fig. 7 Experimental and fitted (Universal⁵⁷ and Camper's model⁵⁶) CO₂/CH₄ selectivity vs. ILs' molar volume at 303 and 353 K, Table S5†.

selectivities, as shown in Fig. 7. These results show that the Scovazzo correlation is limited by the nature of the ionic liquids used in its derivation and that a single parameter such as the IL molar volume is not able to describe the CH₄/CO₂ selectivities, as would be expected from their dependency on the CH₄/ionic liquid interactions.

Although we demonstrate in this work that the ionic liquid polarity is an essential feature in the design of ionic liquids with large CH₄/CO₂ selectivities, the limited amount of data available precludes the development of a reliable correlation for CH₄ solubilities of selectivities at present. The development of reliable correlations capable of estimating the solubilities/selectivities of methane in ILs, needs to take into account the high diversity of molecular interactions inherent to the ionic liquids, and they are a vital key to the design of alternative solvents for more sustainable and efficient processes.

4. Conclusions

Gas solubilities of methane in four ionic liquids, namely trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium methanesulfonate and *N*-methyl-2-hydroxyethylammonium propionate were presented for molar compositions of 0.04 to 0.8, in the temperature range 293 to 363 K and pressures up to 100 MPa.

With the exception of the [P₆₆₆₁₄][NTf₂] that presents slightly negative deviations from ideality, showing that methane solubility in these ionic liquids is dominated by entropic factors, all the remaining ionic liquids present large positive deviations from ideality denoting the strong unfavorable interactions between CH₄ and the ILs.

Adopting the description of the compound's polarity as a multidimensional variable defined by the Kamlet–Taft parameters we have shown that the models available in the literature are only able to describe a narrow set of ionic liquids, with similar polarities, but fail to describe the selectivities/solubilities in ionic liquids that fall out of this polarity range.

Furthermore, for the studied systems the Kamlet–Taft β parameter provides a good correlation for the ILs CO₂/CH₄ and H₂S/CH₄ selectivities, indicating that the higher or lower solubility of methane in the ILs is related to the ionic liquids' polarity, and not only with the solvent molecular weight as

observed for the carbon dioxide or the molar volume as proposed by some authors. The Kamlet–Taft β parameter can thus be used as the basis for the choice of ionic liquids that maximize the selectivities of sour gases/CH₄.

Acknowledgements

The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project PTDC/EQU-FTT/102166/2008) and PhD grant (SFRH/BD/41562/2007) of Pedro J. Carvalho. The authors would like to acknowledge Dr Silvana Mattedi and Dr Víctor H. Alvarez, from Escola Politécnica da Universidade Federal da Bahia (UFBA) and Faculdade de Engenharia Química da Universidade Estadual de Campinas (UNICAMP), respectively, for the synthesis of the *N*-methyl-2-hydroxyethylammonium propionate IL.

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