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Additional Information

Modelling the vapour-liquid equilibria of ionic liquids containing perfume raw materials

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ABSTRACT: In this work, the vapour-liquid equilibria of binary and multinary systems comprising of perfume raw materials and ionic liquids have been computed using two different models: COSMO-RS, a solvation model, and UNIFAC, a group contribution method. For systems already well known in the literature, a comparison with experimental data was performed, and good agreement was observed with both models. Although UNIFAC was not applicable to non-parameterised ionic liquids, COSMO-RS proved very reliable in predicting the vapour-liquid equilibria (VLE) of solutions of perfume raw materials (PRMs) in new-to-the-world ionic liquids. This opens the door for the prediction and modelling of new formulations for novel consumer products, prior to embarking on detailed experimental investigations.

INTRODUCTION

The majority of consumer goods present in the market are characterised by a specific scent. This is an important aspect in the fragrance marketing and companies are constantly improving their products on this basis.¹ Commercial products, and particularly those for use in home care, are complex mixtures of many different ingredients. When a fragrance is added to a product, it must be compatible with all the other ingredients, and even the physical state in which the perfume raw materials (PRMs) are delivered is a function of the choice of molecules and their quantity.²

Physicochemical studies of consumer goods is an essential part of the development of new products. In the case of fragrance release, it is important to study the vapour-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) of the volatile materials.³ In this context, a number of different techniques have been reported for determining the vapour pressure or partial vapour pressure of single or multicomponent systems.⁴⁻⁵ A similar approach has been applied for studying LLE, and a wide variety of cases have been studied.⁶⁻⁷ As thousands of potential perfume raw materials are known,⁸ it is infeasible to study experimentally even a fraction of these in the necessary detail that is required to determine their VLE and LLE properties. In order to garner the necessary information to enable an informed decision to be made for the selection of PRMs for a specific task, it is desirable to develop a computational screening process.

Fragrance formulations have traditionally been based on ethanol as the solvent, but the legal restrictions on volatile organic solvents have prompted the industry to change to other systems.⁹⁻¹⁰ Recently, a new class of perfumes have been reported,¹¹ based on compositions containing at least one ionic liquid and one perfume raw material. Ionic liquids are involatile solvents¹² as they have no measurable vapour pressure at room temperature,¹³ the vapour phase above them is composed only of any solute present in the ionic liquid.

In an ideal case, the solute will obey Raoult's law and there would be a linear relationship between the concentration of the solute in the ionic liquid and the vapour pressure which it exerts. We have recently demonstrated that by controlling the interactions between the solute and the ionic liquid, both positive (*i.e.* repulsive) and negative (*i.e.* attractive) interactions between the liquid phase species induce positive and negative deviation from Raoult's law. Thus, for example, a solute capable of forming strong hydrogen bonds with the anion of the ionic liquid will exhibit strong negative deviation from Raoult's law.^{6,11}

For a given PRM dissolved in an ionic liquid, its vapour-liquid equilibria are a function of at least three general variables: the structure of the cation, the structure of the anion, and the structure of the perfume raw material itself, in addition to the specific variables of temperature, pressure and concentration. It is well established that there are over one million simple ionic liquids accessible,¹⁴ and so, in combination with

thousands of PRMs, there are over one milliard (10^9) possible simple combinations. As an experimental study is clearly infeasible, a computational approach is essential in order to predict the VLE of any specific ionic liquid-PRM combination.

Two predictive approaches are generally reported for representing the phase equilibria relationships in terms of measurable state variables: (a) methods based on the equations-of-state and (b) the activity coefficient methods.¹⁵ In this work, a computational approach based on the latter method was adopted. The target of this study is to evaluate the benefit of using ionic liquids as solvents in the formulation of consumer goods, as opposed to using a conventional volatile organic solvent. This will be achieved by calculating the strength and nature of the interactions between various functionalised cations and anions and PRM solutions.

The **CO**nductor-like **S**creening **MO**del for **R**eal **S**olvents (COSMO-RS)¹⁶⁻¹⁸ was selected, as it had been previously applied to ionic liquid systems with significant success.¹⁹ Here we report the prediction of VLE properties of solutions of PRMs in organic solvents and/or in ionic liquids using COSMO-RS, and compare the predictions with those obtained by using one of the widely used Universal quasichemical Functional group Activity Coefficients (UNIFAC),²⁰ and with experimental data (where available).

PHASE EQUILIBRIA CALCULATIONS

The computation of the thermodynamic properties of multicomponent systems has been widely studied in the literature using various models.²¹ Here, a hierarchical study has been applied starting from binary ethanolic solutions of perfume raw materials, going through multicomponent systems of PRMs, and finally involving new ionic liquid structures. In order to validate the use of the COSMO-RS model in predicting the VLE or LLE of these complex systems, a second independent computational approach was applied, based on the widely used programs, UNIFAC²⁰ and modUNIFAC (modified UNIFAC);²² in the latter approach, temperature dependent parameters are introduced. UNIFAC is a group contribution model for the prediction of the activity coefficients of mixture components. It assumes that molecular interactions in a mixture can be described through those of the functional groups of the solutes and the solvent. The activity coefficient is composed of two terms: combinatorial and residual, depending respectively on the functional group area and volume, and the reciprocal interaction parameters between functional groups. The latter are obtained through the fitting of large experimental datasets (e.g. the Dortmund database).²³⁻²⁴

The use of both models to predict thermodynamic properties, such as VLE, involved multiple calculation steps. For both approaches, the molecular structures had to be calculated in their equilibrium geometry by energy minimisation, here, using density functional theory (DFT) according to Becke's parameterisation with LYP

correlation and a 6-31++G(d) basis set implemented in TurbomoleX.²⁵ The second step for UNIFAC involved the calculation of the residual term, given by the binary interaction parameters, which is related to the interaction energy of molecular pairs. These parameters must be obtained either through experiment, *via* data fitting, or by molecular simulation. In this paper, the former strategy is adopted, but this approach (which is semi-empirical) requires a large set of pre-existing experimental data. UNIFAC is poorly parameterised for ions, and so unable to accurately describe non-additive molecular effects in most ionic liquids.

In COSMO-RS, the second step uses a statistical thermodynamics approach based on the results of a quantum chemical dielectric continuum solvation model, COSMO.²⁶ The link between the microscopic surface interaction energies and the macroscopic thermodynamic properties is provided by statistical thermodynamics. With the COSMOtherm software, here the C30-1401 release with a triple zeta valence polarised basis set, (TZVP) was used, it is possible to predict the activity coefficients of each component in a mixture (including ionic liquids), and process the screening charge density on the surface of molecules. COSMO-RS is a particularly useful model for screening multiple ionic liquids and perfume raw materials, where no experimental data are available. In the open literature, COSMO-RS has been already applied in the study of γ_i^∞ (activity coefficient at infinite dilution), gas solubility, LLE and/or VLE of ionic liquid mixtures, and these have been reviewed elsewhere.²⁷ A recent study on COSMO-RS predictions of γ_i^∞ and LLE has been reported by Wlazło *et al.*,²⁸ who compared predicted and experimental data for twelve ionic liquids and *ca.* sixty organic solutes. They found good qualitative agreement with experiments, including the effects of temperature. Recently, tetraalkylammonium ionic liquids have been reported as solvents for pharmaceutical applications,²⁹ and the solvation process was screened using COSMO-RS.²⁹⁻³⁰

Thus, there have been few meaningful attempts to model the gas phase in equilibrium with ionic liquid solutions of organic molecules, and in particular, there are very few reports of computed VLE data. However, it is extremely important to model volatile species released from consumer goods, particularly in light of recent REACH regulation.³¹

Perfume raw materials in molecular solvents

The simplest perfume raw material systems which have extant experimental data are composed of multinary mixtures of PRMs, both neat, and in ethanolic solution. These have been used as a reference within this study, as they represent widely used formulations in fine fragrance products,³² and have already been computationally parameterised.³³ The VLE data for these systems were computed by Teixeira *et al.*³³ using UNIFAC, and here we will compare (*vide infra*) with results obtained using COSMOtherm.

In addition, PRMs in a non-polar solvent (decane) were examined, as experimental data and UNIFAC predictions

were also available in the literature.³⁴ These data sets were chosen to underline the consistency of the COSMO-RS predictions for solvents with different polarities.

Hydrogen bonding in ionic liquids

As discussed in the introduction, ionic liquids have been introduced for application in consumer goods.⁶ To cope with the milliard of potential novel systems, a strategy has been developed to investigate as many formulations as possible, depending on the structure of the ionic liquid and on the components involved. **Hydrogen bonds** play an important rôle in modifying the VLE of the system. Depending on the number and nature of the hydrogen bond donor or acceptor groups present on the PRMs and on the ionic liquid, COSMOtherm allows their parametrisation.

The first data set selected reports vapour pressure for butyltrimethylammonium bis{(trifluoromethyl)sulfonyl}amide, [N_{1,1,4}][NTf₂], mixed with ROH (R = Me, Et or Pr) in the temperature range 298.15-313.15 K.³⁵ Here, COSMOtherm allows a modulation in the hydrogen bond parametrisation.

The second, more complex, system reports vapour pressure data for ternary systems containing protonated mono-, di- or tri-ethanolamine as ionic liquid cation, with [BF₄]⁻ as anion (see Figure 1) and ethanol and water in the temperature range 315-360 K.³⁶

COSMO-therm modelling of ionic liquids in binary mixtures with PRMs

The formulation of consumer goods has to be able to explore the widest range of cations and anions available and registered, and their permutations. This permits the transition from a set of ionic liquids which have been extensively studied and heavily parameterised (*i.e.* imidazolium ionic liquids)³⁷⁻³⁹ but known to be toxicologically unsafe⁴⁰ to structurally new-to-the-world, and toxicologically benign, ionic liquids. These can be screened in complex mixtures, creating a better understanding of the role of the anion and cation used in tuning the VLE of these systems.

As a starting point here, the VLE of a binary mixture of [C₄mim][NTf₂]³⁷ and PRMs (see Figure 1) were calculated using COSMOtherm and UNIFAC. The calculated data is reported as a vapour pressure dependency upon *T*, which was modelled by the Antoine equation, see Equation (1).

$$\log_{10}(P_0) = A - \frac{B}{C+T} \quad (1)$$

where *A*, *B*, *C* coefficients are the Antoine coefficients for a defined *T* range.

An alternative strategy allowed estimation of the VLE for previously unparameterised PRMs or ions pairs (here exemplified by [C₄mim][L-Proinate] with majantol or 2-phenylethanol). In this case, COSMO-therm was used to predict the activity coefficients for organic compounds in binary combinations, providing the parameters to input into UNIFAC.

Insight into the nature of the interactions between binary PRMs and ionic liquids can be gained from Raoult's law,^{4, 41} see Equation (2).

$$P_i = P_i^0 \chi_i \quad (2)$$

where *P_i* is the vapour pressure of the *i*th component in the mixture, *P_i⁰* is the vapour pressure of the pure component at 25 °C, and *χ_i* is its mole fraction in the mixture.

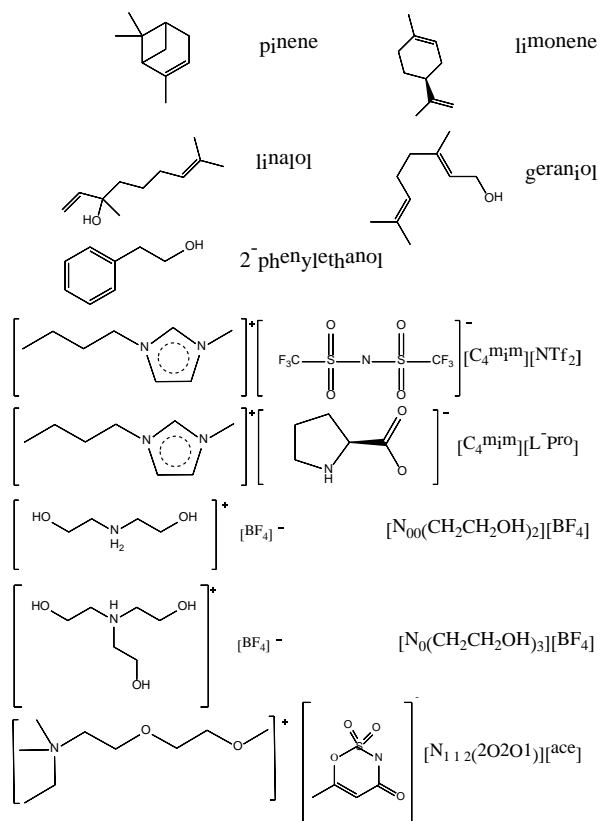


Figure 1. The structure of PRMs and ionic liquids used in this work.

As previously reported, positive or negative deviations from ideality are controlled by the specific interactions between the solutes and the solvent.⁶⁻⁷ As ionic liquids have negligible vapour pressure at room temperature, they have no partial vapour pressure (*i.e.* *P_{IL}⁰* = 0 in Equation (2)). The cations and anions were selected to provide insight into the driving forces of the interactions between anion, cation and PRMs with different functionalities. Here, the strength of the deviation from Raoult's law for a large list of perfume raw materials is calculated using Simpson's integration method⁴² from the area of the deviation curve.

EXPERIMENTAL SECTION

Synthesis of ionic liquids

1-Butyl-3-methylimidazolium chloride ([C₄mim]Cl). A mixture of 1-methylimidazole (70.0 g, 0.853 mol), ethanenitrile (50 cm³) and 1-chlorobutane (102 g, 1.10 mol)

was heated under reflux with vigorous stirring for 48 h. Then, volatile substances were removed in a first step under reduced pressure (*ca.* 50 °C, 20 mbar), and finally, *in vacuo* (*ca.* 80 °C, 0.01 mbar) for 16 h, yielding 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl, 131.8 g, 88.6%) as a pale yellow viscous liquid which crystallised upon cooling to room temperature.

1-Butyl-3-methylimidazolium hydrogensulfate ([C₄mim][HSO₄]). (This preparation was adapted from a published procedure)⁴³ To a solution of 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl, 87.8 g, 0.503 mol) in dichloromethane (50 cm³), concentrated sulfuric acid (96%, 51.4 g, 0.503 mol) was added dropwise, while keeping the mixture refrigerated in an ice/water bath. The resulting solution was then heated under reflux with stirring for 48 h, and volatiles (mostly containing dichloromethane) were then distilled off under reduced pressure (*ca.* 30 °C, 50 mbar), and the hydrogen chloride by-product was similarly removed *in vacuo* (*ca.* 90 °C, 0.01 mbar) during 16 h, yielding 1-butyl-3-methylimidazolium hydrogensulfate ([C₄mim][HSO₄], 118.1 g, 99.4%) as a pale yellow viscous liquid.

Aqueous 1-butyl-3-methylimidazolium hydroxide ([C₄mim][OH]) solution. (This preparation was adapted from a published procedure)⁴⁴ Strontium hydroxide octahydrate (110.14 g, 414.4 mmol) was dissolved in boiling-hot water (*ca.* 1 L). To the resulting cloudy solution, a solution of 1-butyl-3-methylimidazolium hydrogensulfate ([C₄mim][HSO₄], 93.30 g, 394.9 mmol) in boiling-hot water (100 cm³) was added. A white solid immediately precipitated. The mixture was stirred while cooling down to room temperature and then kept at approximately 5 °C overnight (17 h). Then, the white solid was removed by filtration. The resulting clear colourless solution was titrated with standard aqueous HCl solution (0.1 M) to determine the [OH]⁻ concentration (0.27 mol kg⁻¹) in the resulting [C₄mim][OH] solution.

1-Butyl-3-methylimidazolium proline ([C₄mim][L-Pro]). To the aqueous [C₄mim][OH] solution (see above; 1.321 kg, 357.9 mmol [OH]⁻), a solution of L-Proline (41.54 g, 360.8 mmol) in water (100 cm³) was added. The resulting solution was concentrated under reduced pressure in a rotary evaporator (50–60 °C) until most of the water was removed, and then under high vacuum (70 °C) overnight. The resulting yellowish cloudy viscous liquid was mixed with an ethanenitrile/methanol mixture (10:1 by volume, 240 cm³), and allowed to settle in the freezer (*ca.* -20 °C) overnight. The white precipitate was removed by filtration, the resulting solution concentrated in a rotary evaporator (70 °C) until a yellow viscous liquid was obtained, and then dried under high vacuum (70 °C) for 2–3 days. The final ionic liquid ([C₄mim][L-Proline]) was obtained as a yellowish viscous liquid (86.80 g, 95.7%), with a water content of 156 ppm.

1-Butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([C₄mim][NTf₂]) was prepared as previously described.⁴⁵

Vapour pressure measurements

The vapour pressures of the different liquid mixtures were measured using a purpose-made glass isoteniscope connected to a high vacuum pump and to a pressure gauge (see Figure 2).

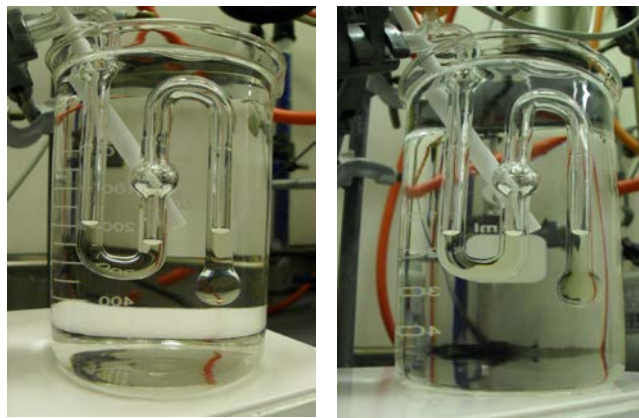


Figure 2. Isoteniscope apparatus.

The liquid sample (*ca.* 3 g) was loaded into the lower reservoir bulb on the end of the isoteniscope, and then the headspace was degassed (minimum pressure $\approx 2 \times 10^{-2}$ mbar) at room temperature. A portion of the sample was then allowed to flow into the U-tube, still keeping some in the reservoir bulb. After increasing the temperature to the desired value by immersing the isoteniscope in a heated oil bath, the pressure was adjusted so that the liquid columns on both sides of the U-tube were levels.

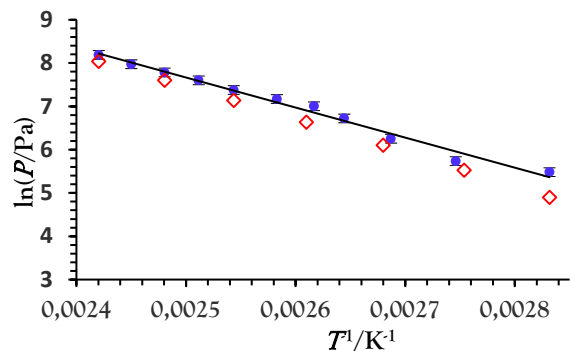


Figure 3 Natural logarithm of the vapour pressure of tetradecane as a function of the temperature. The data points in blue were determined as part of this work; those in red diamonds are from the literature.⁴⁶ The linear fit of the current data is given by $y = -6941x + 25.02$, and has $R^2 = 0.98$. The standard deviation is 0.1, and the slope of the regression line is -6941 ± 326 .

The isoteniscope method was validated in the 80–150 °C temperature range for the vapour pressures of tetradecane, which was chosen as the standard material (amongst the alkanes recommended in the literature for vapour pressure measurements).^{47–49} The data derived are presented in Figure 3 and compared with literature values.^{46, 50} The enthalpy of vaporisation has been calculated in the T, P range reported in Figure 3, and the

experimental value of $\Delta_{\text{vap}}H$ is 57.7 kJ mol^{-1} , which is in reasonable agreement with the literature values,⁴⁶ $57.1\text{--}65.4 \text{ kJ mol}^{-1}$ (360–400 K).⁵⁰

RESULTS AND DISCUSSION

The computed results of the vapour-liquid equilibria for sets of systems ranging from binary to quaternary systems, comprising of PRMs and/or molecular solvents and/or ionic liquids, are reported here. For all of these systems, a comparison is made between the two predictive models, COSMO-RS and UNIFAC, and, where available, the theoretical models were compared with the experimental data.

VLE calculations of PRMs in organic solvent mixtures

The strategy for computing the vapour phase composition of a multinary perfume mixture was to firstly analyse the VLE of a simple binary mixture of PRMs (with no solvent present), and then to introduce either a molecular solvent or an ionic liquid. Here two experimental data sets were analysed: the first (from Teixeira *et al.*)³³ reports the mole fraction in the vapour phase of binary, ternary and quaternary mixtures of PRMs in ethanol at 23°C , and the second (Friberg and Yin)³⁴ reports the vapour pressure of binary and ternary mixtures of limonene (see Figure 4 and 5), 2-phenylethanol and decane at 25°C .

Binary, ternary and quaternary PRM systems in ethanol

These systems are already known in the literature,³⁵ and they have been studied using different UNIFAC models, including the Dortmund variant. Correlation between experimental³³ and our COSMOtherm calculations are plotted for the binary and ternary mixtures of PRMs in Figures 4 and 5. The composition of the gas phases for these systems are reported as the mole fraction in the vapour phase of the individual PRMs, y_i , from the following equation, Equation (4):

$$y_i = \frac{x_i \gamma_i P_i^{\text{SAT}}}{\sum_i x_i \gamma_i P_i^{\text{SAT}}} \quad (4)$$

where x_i , γ_i , P_i^{SAT} are respectively the mole fraction in the liquid phase, the activity coefficient, and the vapour pressure of the pure substance of the i^{th} component of the mixture. The activity coefficient γ_i is estimated via COSMOtherm.

In order to represent the composition of the vapour phase for ternary and multinary systems, the mole fractions are reported in Figure 5 as a surface, and also, in this case, a comparison with experimental data reported in the literature was reported. In all the three data sets reported here, the agreement between experimental and predicted mole fractions in the vapour phase is good. The idea of a Raoult's surface for multinary systems has been already suggested⁴ to depict specific interactions in between the components of liquid mixtures in determining the composition of the vapour phase in equilibria within it.

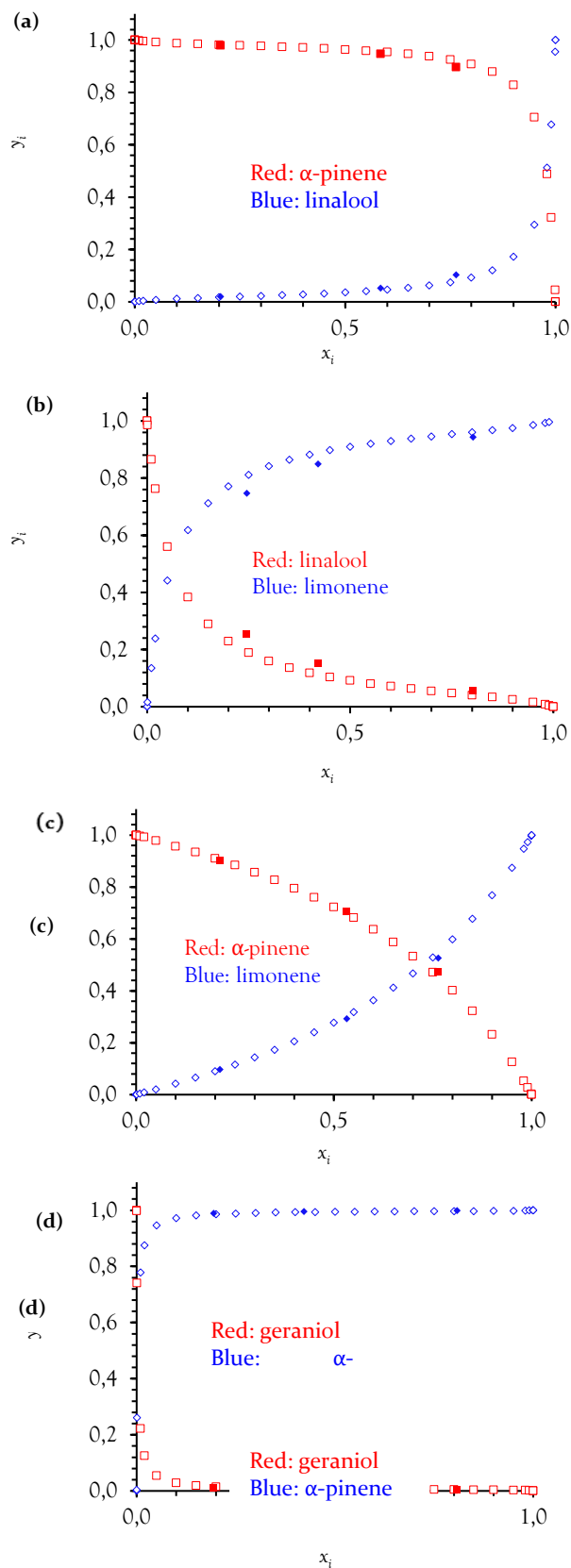


Figure 4. Correlation between experimental (filled squares and diamonds)³⁵ and COSMOtherm predictions (empty squares and diamonds) of the mole fraction of pairs of PRMs (red and blue components) in the vapour phase (y_i), as a function of the liquid phase composition

(x_i).

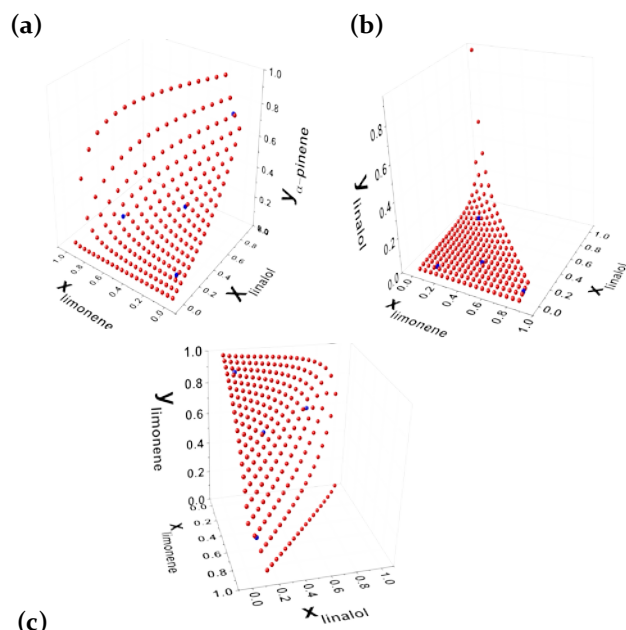


Figure 5. Ternary Raoult's surface plots on the system composed of linalool, α -pinene and limonene, with COSMOtherm calculated data (in red) and experimental data (in blue). The partial vapour pressures of (a) α -pinene, (b) linalool, and (c) limonene are represented.

PRM mixtures in ethanol or decane

The VLE of pure PRM mixtures may be predicted using the COSMO-RS model with high accuracy, but in many practical applications, these organic molecules are dissolved in solvents with different polarity and a change in their activity is expected. For this reason, further data sets have been calculated, introducing ethanol (see Table 1 and Figure 1) or decane as a solvent. The difference between experimental and calculated values is defined by the parameter Δ , see Equation (5)

$$\Delta = y_{EXP}^i - y_{PRED}^i \quad (5)$$

where y_{EXP}^i is the experimental value and y_{PRED}^i is the calculated one.

Table 1. Composition range in the liquid phase for (1) ethanol, (2) limonene, (3) linalool, and (4) geraniol.

Point	x_1	x_2	x_3	x_4
A	0.358	0.141	0.224	0.277
B	0.337	0.138	0.104	0.420
C	0.240	0.182	0.108	0.470
D	0.390	0.153	0.100	0.360
E	0.439	0.206	0.236	0.119
F	0.570	0.060	0.128	0.242
G	0.412	0.191	0.135	0.262
H	0.370	0.360	0.127	0.142

For quaternary mixtures containing ethanol, the mole fraction of the latter dominates the vapour phase (see Table 2). As might be anticipated, there are discrepancies

between the experimental and calculated data, particularly at low partial vapour pressure. This is probably due partially to the error within the experimental method used by Friberg *et al.*,³⁴ and partially to the COSMO-RS parametrisation in the estimation of dispersive and hydrogen-bond interactions for the lower concentrations of PRMs in the ethanol mixtures.

Table 2. Correlation between experimental³⁴ and COSMO-therm predictions of ethanol and PRM mole fractions in the vapour phase for quaternary mixtures. (1) ethanol (2) limonene, (3) linalool, and (4) geraniol.

Point	data	y_1	y_2	y_3	y_4
A	Exp	0.947	0.0477	0.00445	0.00109
	Pred	0.977	0.0213	0.00140	0.00034
B	Δ	-0.030	0.0264	0.00305	0.00075
	Exp	0.946	0.0507	0.00201	0.00173
C	Pred	0.976	0.0232	0.00068	0.00056
	Δ	-0.030	0.0275	0.00133	0.00117
D	Exp	0.918	0.0765	0.00268	0.00259
	Pred	0.963	0.0357	0.00091	0.00084
E	Δ	-0.045	0.0408	0.00177	0.00175
	Exp	0.947	0.0498	0.00189	0.00131
F	Pred	0.976	0.0228	0.00091	0.00084
	Δ	-0.029	0.0270	0.00098	0.00047
G	Exp	0.929	0.0644	0.00605	0.00038
	Pred	0.975	0.0237	0.00115	0.00011
H	Δ	-0.046	0.0407	0.00490	0.00027
	Exp	0.970	0.0268	0.00267	0.00088
A	Pred	0.990	0.0089	0.00060	0.00022
	Δ	-0.020	0.0179	0.00207	0.00066
B	Exp	0.929	0.0671	0.00324	0.00107
	Pred	0.974	0.0248	0.00069	0.00028
C	Δ	-0.045	0.0423	0.00255	0.00079
	Exp	0.905	0.0911	0.00338	0.00051
D	Pred	0.965	0.0341	0.00058	0.00014
	Δ	-0.060	0.0570	0.00280	0.00037

The VLE of a ternary mixture of PRMs in a non-polar solvent (decane) were calculated for the limonene, 2-phenylethanol and decane system. Correlation between experimental and predicted relative vapour pressures, as defined in Equation (6):

$$(p/p_0)_i = x_i \gamma_i \quad (6)$$

where parameters x_i and γ_i were already defined. The results estimated with UNIFAC and COSMOtherm are illustrated in Figures 6-8.

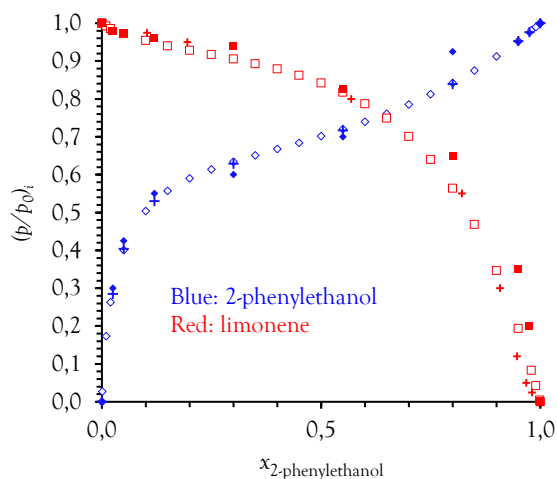


Figure 6. Correlation between experimental (filled squares for limonene and filled diamonds for 2-phenylethanol),³⁵ UNIFAC (plus sign) and COSMOtherm predictions (empty squares for limonene and empty diamonds for 2-phenylethanol) of the mole fraction of pairs of PRMs (red and blue components) in the vapour phase, $(p/p_0)_i$, as a function of the liquid phase composition (x_i).

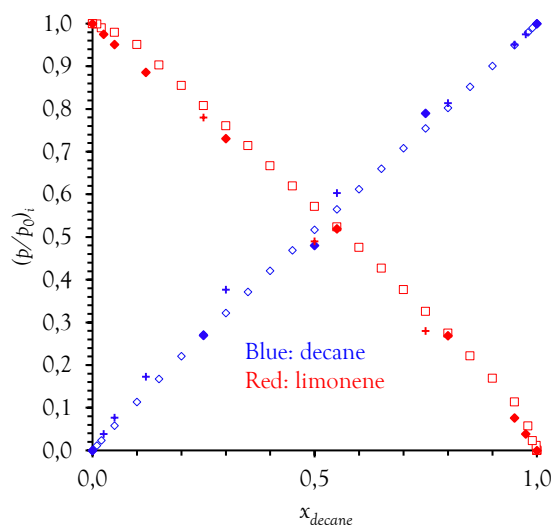


Figure 7. Correlation between experimental (filled squares for limonene and filled diamonds for decane),³⁵ UNIFAC (plus sign) and COSMOtherm predictions (empty squares for limonene and empty diamonds for decane) of the mole fraction of pairs of PRMs (red and blue components) in the vapour phase, $(p/p_0)_i$, as a function of the liquid phase composition (x_i).

The calculations reported reflect an overall good agreement with both models. They both correctly predict the positive deviation from ideality of the system (limonene + 2-phenylethanol), see Figure 6, the ideal behaviour (limonene + decane), see Figure 7, and the reciprocal insolubility of decane and 2-phenylethanol highlighted by the region for which $(p/p_0)_i > 1$ (see Figure 8; any point above dotted black line).

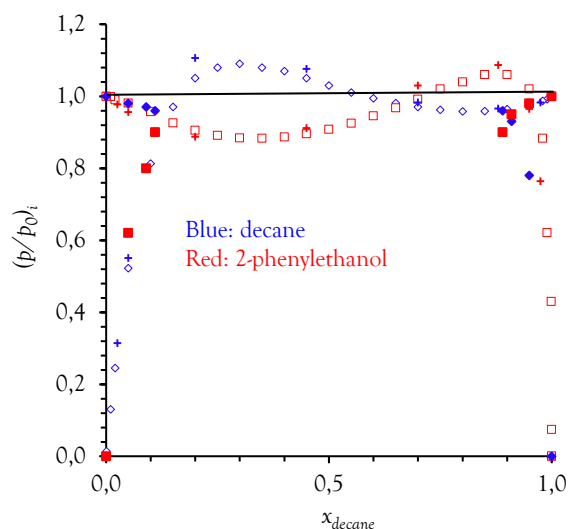


Figure 8. Correlation between experimental (filled squares for 2-phenylethanol and filled diamonds for decane),³⁵ UNIFAC (plus sign) and COSMOtherm predictions (empty squares for 2-phenylethanol and empty diamonds for decane) of the mole fraction of pairs of PRMs (red and blue components) in the vapour phase, $(p/p_0)_i$, as a function of the liquid phase composition (x_i).

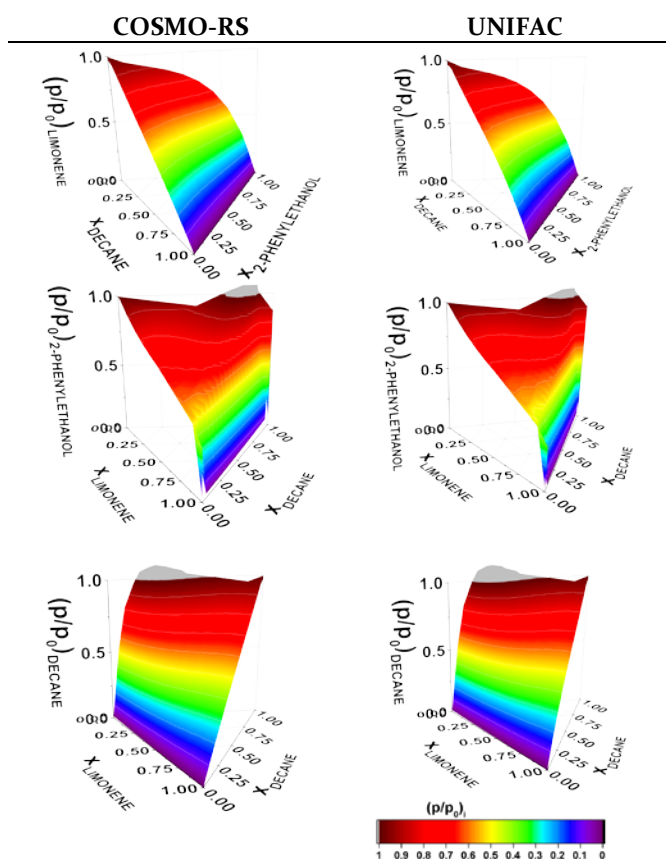


Figure 9. COSMO-RS (left column) and UNIFAC (right column) and predictions (empty squares and empty diamonds) of the mole fraction of pairs of PRMs and decane in the vapour phase, $(p/p_0)_i$, as a function of the liquid phase composition (x_i).

For the ternary mixture (see Figure 9), both models correctly predict the insolubility region at low limonene mole fraction (grey region on the surface), but not further quantitative comparison can be drawn between the experimental and predicted data, since the latter have not been explicitly reported in the literature.

VLE calculation of PRMs in ionic liquids mixtures Ionic liquids systems and hydrogen bond parameterisation

Where the ionic liquid mixtures (i.e. $[N_{1,1,4}][NTf_2]$ + MeOH) involve hydrogen-bonding interactions, the computational approach using COSMO-RS model allows the modulation of the hydrogen bonds parameterisation. This hydrogen bond contribution is added to the misfit energy operator $E(\sigma, \sigma')$, between two different surface potential of the system's components. The hydrogen bonding energy contribution in COSMO-RS is given by:

$$E_{HB}(\sigma, \sigma') = a_{eff} c_{HB} \min(0; \min(0; \sigma_{donor} + \sigma_{HB}) \max(0; \sigma_{acceptor} - \sigma_{HB})) \quad (7)$$

where a_{eff} is the effective contact area; σ_{donor} and $\sigma_{acceptor}$ are surface charge values of hydrogen bonding donor and acceptor sites, respectively, while c_{HB} and σ_{HB} are adjustable parameters. The setting of the c_{HB} coefficient will affect all contributions to the hydrogen bonding energy $E_{HB}(\sigma, \sigma')$.

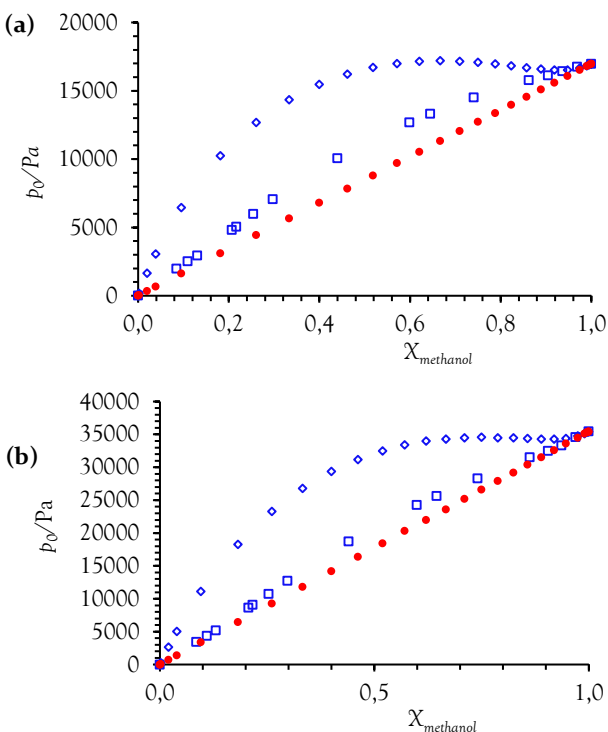


Figure 10. correlation between experimental³⁵ (empty blue squares) and COSMOtherm predicted vapour pressure of the binary systems methanol, in the $[N_{1,1,4}][NTf_2]$ without changing the hydrogen bonding energy settings (empty blue diamonds; $c_{HB}=1$) and with $c_{HB}=0.5$ (red circle) at (a) 25 °C and (b) 40 °C.

COSMOtherm recommends that the adjustable parameter c_{HB} for the hydrogen bonding energy is set to 1.0 which is their default value. However it was found, for the system reported here, that the best agreement between experimental and calculated values was obtained by setting c_{HB} to 0.5 (see Figures 10 and 11).

It is also possible to change the hydrogen bonding energy contribution of specific compounds or differentiate between donors and acceptors. We have however not explored these options.

$[N_{oo}(\text{CH}_2\text{CH}_2\text{OH})_2][\text{BF}_4]$, $[N_o(\text{CH}_2\text{CH}_2\text{OH})_3][\text{BF}_4]$ and ethanol-water ternary systems.

The following section looks at a system which can not be empirically realised, as the tetrafluoroborate ion hydrolyses in water to release toxic hydrogen fluoride. Nevertheless, as an exercise in computational prediction, it has some value. In particular, the influence of hydrogen bond parameterisation has been studied for more complex ionic liquid systems composed by $[N_{oo}(\text{CH}_2\text{CH}_2\text{OH})_2][\text{BF}_4]$ or $[N_o(\text{CH}_2\text{CH}_2\text{OH})_3][\text{BF}_4]$ with ethanol and water with experimental vapour pressure provided by Shen and coworkers, despite the potential inaccuracies.^{36, 51} Also, for these data sets, the impact of the c_{HB} coefficient is compared here by setting it to values of 0.5 and 1 (see Figure 11). As reported by Shen and coworkers, the vapour pressure for the ternary system is calculated as:

$$p_0 = \sum_i x_i \gamma_i P_i^{SAT} \quad (8)$$

where x_i , γ_i , P_i^{SAT} are the mole fraction, the activity coefficient and the vapour pressure of the pure i^{th} component and the summation is extended to ethanol and water. As shown below, the agreement between experimental and COSMOtherm predicted vapour pressure either with $c_{HB}=1$ or $c_{HB}=0.5$ is very good. The use of $c_{HB}=0.5$ slightly improves the vapour pressure prediction also in this case.

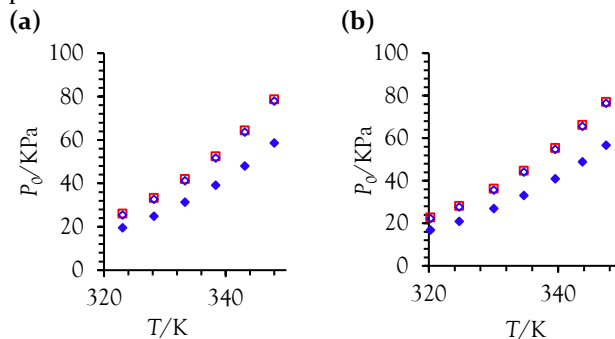


Figure 11. Correlation between experimental (full blue diamond)³⁶ and COSMO-therm predicted vapour pressure either with $c_{HB}=1$ (red squares) or $c_{HB}=0.5$ (blue empty diamonds) for the ternary systems: $N_{oo}(\text{CH}_2\text{CH}_2\text{OH})_2$ (a), $N_o(\text{CH}_2\text{CH}_2\text{OH})_3$ (b) $[\text{BF}_4]$, ethanol with $x_{ethanol}=0.0852$ (a), with $x_{ethanol}=0.0859$ (b) and water.

The insensitivity of the system to c_{HB} would suggest there is very little hydrogen-bonding interaction between ethanol or water and the protonic cations.

Modelling the designed ionic liquid anion-PRM interaction

In order to classify the nature of the interaction between ionic liquids and PRMs here, Raoult's plots have been illustrated as a direct representation of the VLE data. The systems computationally and experimentally studied are imidazolium ionic liquids in binary mixtures with PRMs and a graphical representation of experimental and predicted vapour pressure is reported (see Figure 12).

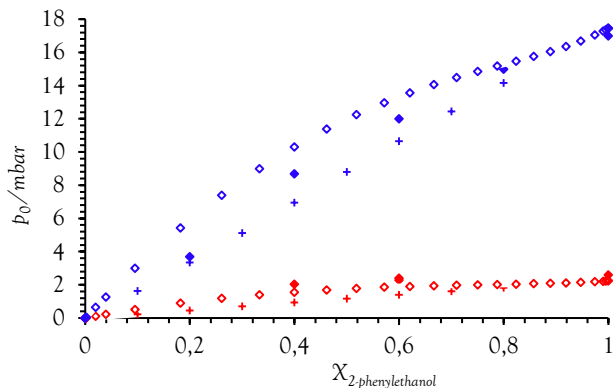


Figure 12. Correlation between experimental (filled diamonds),³⁵ UNIFAC (plus sign) and COSMOtherm predictions (empty diamonds) of the mole fraction of 2-phenylethanol in [C₄mim][NTf₂] (at 100 °C for the blue data set and 60 °C for the red dataset.) in the vapour phase, as a function of the liquid phase composition (x_i).

The data obtained using a computational (COSMOtherm and UNIFAC models) or the experimental approach (VLE measurements) are in a good agreement for the two datasets here recorded at two temperatures. The nature and the strength of the interaction between the PRM and the bistriflamide ionic liquid illustrate, as proof of principle, that repulsion of the solute by the ionic liquid result in positive deviation from Raoult's law.⁵

Having considered a fragrance release technology based on the design of the cation,⁷ here a similar approach is reported for the anion with an extension in terms of theoretical modelling of the system. In particular, an L-Proinate anion was introduced in order to see the effect of the anion structure on the vapour pressure of the PRMs. The data reported in Table 3 and Figure 13 exhibit the cosmotropic effect of the proinate anion on the 2-phenylethanol dissolved in [C₄mim][L-Pro], and the corresponding chaotropic effect of the bistriflamide anion with the same PRM.

These two type of interactions, as previously reported, can be used in fragrance release technology and it is fundamental to be able to model these systems in order to predict the correct response for any given PRM-ionic liquid pair. For this reason, an extended study on a wider range of temperature for the VLE data is reported in Table 4 with a comparison of UNIFAC and COSMO-RS vapour pressure prediction (as $P = P_0 x \gamma$) with experimental data³⁷ across a broad range of PRM mole fractions and temperature.

Table 3. Vapour pressure data for binary mixtures of 2-phenylethanol and either [C₄mim][NTf₂] or [C₄mim][L-Pro] at 100 °C recorded using the isoteniscope apparatus, described in the experimental section.

X_{PRM}	[C ₄ mim][NTf ₂]			[C ₄ mim][L-Pro]		
	$P/mbar$	P/P_0	$\Delta P/\%$	$P/mbar$	P/P_0	$\Delta P/\%$
1	15.9	1.00	-	15.9	1.00	-
0.8	15.0	0.95	-5.32	10.0	0.63	37.02
0.6	11.6	0.73	-26.97	4.0	0.25	-74.81
0.4	8.3	0.53	-47.45	1.8	0.11	-88.66
0.2	4.4	0.28	-72.29	0.9	0.06	-94.40
0	0.0	0.00	-	0.0	0.00	-

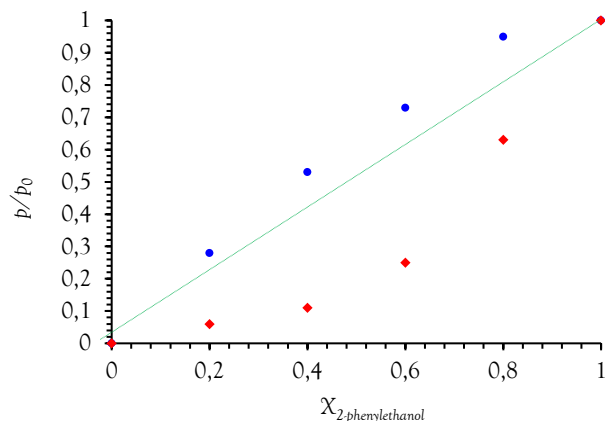


Figure 13. Experimental VLE data, recorded using the isoteniscope apparatus described in the experimental section at 100 °C for 2-phenylethanol in [C₄mim][NTf₂] (filled blue circles), [C₄mim][L-Pro] (filled red diamonds). The straight green line represents the ideal Raoult's law at 100 °C.

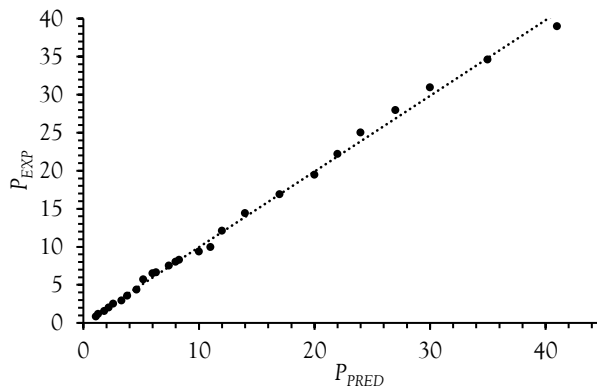


Figure 14. Comparison of experimental (recorded using the isoteniscope apparatus described in the experimental section) and calculated (UNIFAC) vapour pressure data for the system melonal-[C₄mim][NTf₂] mixture (see Table 4). Linear regression has the equation $y = 0.995x - 0.006$, $R^2 = 0.997$.

Table 4. Comparison of UNIFAC and COSMO-RS in vapour pressure calculations

PRM	Ionic Liquid	N ^a	T/°C	UNIFAC model		COSMO-RS model	
				Slope	R ²	Slope	R ²
Phenyl ethyl alcohol	[C ₄ mim][NTf ₂]	103	50-150	1.13	0.96	1.54	0.94
	[C ₄ mim][L-Proline]	29	81-120	0.90 ^b	0.90 ^b	0.94	0.90
Melonal	[C ₄ mim][NTf ₂]	28	15-90	0.99	0.99	0.90	0.95
Manzanate	[C ₄ mim][NTf ₂]	45	20-70	-	-	0.92	0.95
Majantol	[C ₄ mim][L-Proline]	29	81-120	0.95 ^b	0.94 ^b	1.01	0.97
	[C ₄ mim][L-Proline]	27	86-125	-	-	1.00	0.96

^aN represent the number of experimental points in the dataset ^bReciprocal interaction parameters for L-Proline with the functional groups of the PRM were calculated from the activity coefficients of butane, ethanol, benzene and toluene in [C₄mim][L-Proline],

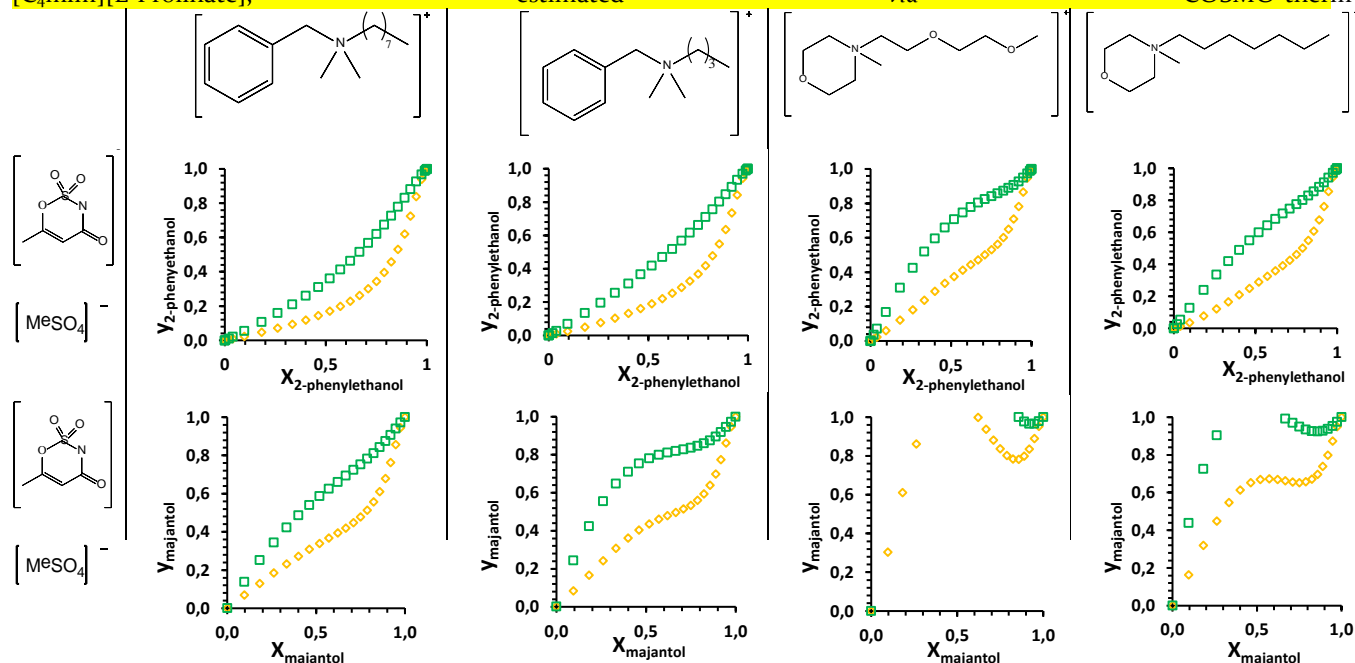


Figure 15. COSMO-therm screening of new-to-the-world ionic liquids at 25°C. Data for acesulfamates are represented in green squares; data for methyl sulfates anion are represented in yellow diamonds; data for 2-phenylethanol are in the upper row and for majantol in the lower row.

Also, in this case, both theoretical models provide a good prediction of the vapour pressure of the PRMs in the two reference ionic liquids. For ionic liquids for which UNIFAC parameters are available³⁷ both models can be applied and predictions compared, see the correlation plot Figure 14 and Table 4). As for the cases of 2-phenylethanol or majantol in [C₄mim][L-Proline], it is also possible to use COSMO-therm prediction of the activity coefficients of simple organic compounds in a binary mixture with the ionic liquid to calculate the unknown parameters in UNIFAC. For ionic liquids not parameterised in UNIFAC, COSMO-therm can provide an *ab-initio* estimate of the activity coefficients and partial vapour pressure of the PRMs dissolved in new-to-the-world ionic liquids

COSMO-therm prediction of the partial vapour pressure of PRMs dissolved in new-to-the-world ionic liquids

The analysis of theoretical and experimental VLE data for binary and multinary systems clarify that COSMO-RS is able to indicate the nature and the strength of the interaction between the ion pairs and the PRMs. Imidazolium and ammonium cations have been reported and analysed using both computational and experimental approaches, but in defining the target system different functionalities can be used, either in the cation and or the anion. The interaction of the ions of the ionic liquids with the PRM can be optimised by using the principles of supramolecular chemistry and molecular recognition.⁵²

Cosmotropic and chaotropic effects are obtained either using hydrophobic and/or hydrophilic ion pairs. In this scenario, the predicted vapour pressures of different PRMs in some of the target ammonium and morpholinium ionic liquids are reported in Figure 15 and

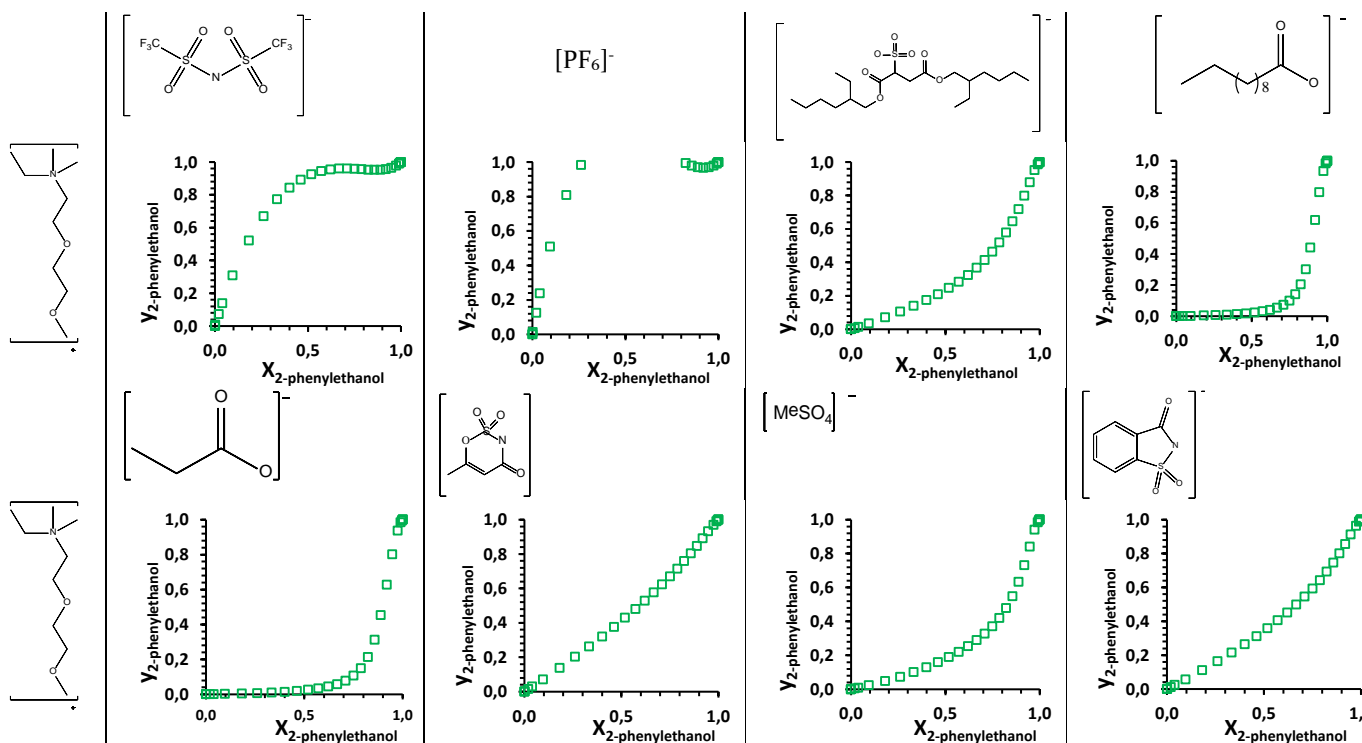


Figure 16. COSMO-therm screening of eight new-to-the-world ionic liquids at 25°C.

The Raoult's plots are illustrated for a defined cation, coupled with either acesulfame or methyl sulfate.

Ethyl sulfate, ethanoate and docusate are able to attract the 2-phenylethanol and hence reduce its vapour pressure. This effect has been reported elsewhere for multi-etherated alkylammonium ionic liquids.⁷ Nicotinate and acesulfamate tend to follow an ideal Raoult's law trend, bis{(trifluoromethyl)sulfonyl}amide and hexafluorophosphate tend to repel the 2-phenylethanol.

As a screening tool, COSMOtherm can be used to select the best combination of PRM and ionic liquids in order to design the most suitable perfume based on the final application. The nature and strength of the interaction is given by the sign and the area of the deviation, A_d , from Raoult's law. Table 5 details this deviation parameters for the most common PRMs.

Table 5. The area of deviation from Raoult's law (A_d) calculated using a Simpson integration method.⁴² The data were reported in the first column for the perfume raw materials listed here with the ionic liquid $[N_{1,1,2}(2O_2O_1)][ace]$.

Perfume Raw Material	A_d/U
Adoxal	0.8530
Ambercore	0.5765
Ambrinol	0.3306
Ambrocenide	1.1502
Amyl cinnamate	0.3374
Amyl cinnamic aldehyde	0.7548

Apritone	0.5555
Azurone	0.1105
Benzyl benzoate	-0.0468
Benzyl cinnamate	0.1199
Benzyl iso eugenol	0.2254
Benzyl salicylate	0.1476
Bornafix	0.2023
Boronal	0.4655
Brahmanol	0.1053
Carnaline	-0.7691
Cashmeran	0.3987
Cedac	0.2717
Cedrolcrude	0.4258
Cis-3-exenyl benzoate	0.4032
Citronitril.	0.0481
Citrawnil B	0.0969
Corps racine VS	0.1952
Coumarin	-0.0950
Cyclabute	0.1671
Cycloxadecenone	0.8400
Cyclohexyl salicylate	0.4499
Delta muscenone	1.1562
Dihydro iso jasmonate	0.1802
Dimethylbenzylcarbinybutyrate	0.4982
Dulcynil	-0.0517

Dupical	0.4510	Methyl betanaphtyl ketone	0.1389
Ebanol	0.2233	Methyldihydrojasmonate	0.1388
Ethylmaltol	-0.1225	Methyljasmonate	0.07887
Ethylenebrassylate	0.0410	Mevantral	0.3081
Ethylphenylglycidate	-0.0845	Muscenone	0.8285
Ethylvanillin	-0.7567	Muscogene	0.8214
Exaltenone	0.5812	Musk RI	0.0529
Exaltolide R	0.2920	Muskone	1.0338
Firsantol	0.1900	Myrrhone	0.2117
Fixolide	0.6010	Nectaryl	0.6969
Fleuranyl	0.1825	Nerolidol	0.7748
Florex	0.4921	Nootkatone	0.1676
Fructalate	-0.0945	Norlimbanol	0.9244
Frutene	0.6676	Octalynol	0.2165
Galaxolide	1.0336	Okoumal R	1.0356
Gammaundecalactone R	0.1785	Oxalone R	-0.0592
Geranyl phenylacetate	0.4651	Oxyoctaline formate	0.4860
Geranyl butyrate	0.2154	Para anisyl phenylacetate	-0.0744
Geranyl tiglate	0.8610	Para cresyl phenylacetate	0.1105
Glycolierral	0.6394	Peonile	0.2247
Healingwood	0.4216	Pharone	0.5403
Helional	-0.0433	Phenyl ethyl salicylate	0.0242
HelvetolideR	0.3920	Phenyl ethylphenylacetate	0.1248
Hexalon	0.6453	Phenyl benzoate	0.0662
Hexyl salicylate	-0.6918	Phenylethyl benzoate	0.0059
Hexylcinnamic aldehyde	0.5940	Pivacyclene	0.3473
Hindinol	-0.0249	Polysantol	0.3551
Hydroxyambran	0.1245	Prenyl salicylate	-0.7341
Hydroxyol	-0.0189	Raspberry ketone	-0.7310
Iso-E-Super R	0.7554	Romandolide	0.3555
Iso bornyl cycloexanol	0.4234	Sandalore	0.5037
Iso ambrettolide	0.2756	Silvanone Ci	0.4221
Javanol R	0.1362	Spiro[5.5]undec-8-en-1-one, 2,2,7,9-tetramethyl-	0.8872
Karanal	2.6522	Spirogalbanone	0.5093
Kephalis	0.2798	Sulfurol	-0.1164
Khusimol	0.0524	Tabanone coeur	0.0979
Khusinil	0.1623	Timberol	0.9220
Labienoxime	0.0627	Transluzone	0.0462
Laevo trisandol	0.0486	Trifone DPG	-0.1156
Linalyl cinnamate	0.6386	Trimofix O	0.6562
Lyra IR	0.0183	Vanillin isobutyrate	-0.0075
Magnolan	0.1776	Z-ambrettolide	0.8492
Majantol	-0.0122	Zenolide	-0.0233
Maltol	-0.6543	Butylundecilenate ₁	1.4086
Maltol isobutyrate	-0.1064	Cascalonetzvp	0.0459
Methyl ionone	0.5613	Cis-3-esyl salicylate	-0.7010
Methyl lavender ketone	-0.0467		

Trans-hedione	0.0446
Vanillin	-0.7649
Veramoss	-0.7492
Vertofix	0.7509

CAS numbers and IUPAC references are available.^{11, 52}

Except for aromatic PRMs bearing an hydroxyl functionality (e.g. 2-phenylethanol), all the other compounds (see Table 5) are predicted to have a positive deviation from Raoult's law (positive area values, see Table 5) due to the chaotropic effect of the [N₁₁₂(2O₂O₁)] [ace] on the PRM solution. In tetraalkylammonium ionic liquids (see Figure 15 and 16), most of the PRMs with a pronounced positive deviation from ideality, can be solubilised at 0.15 mole fraction or above, which would correspond to the likely highest concentration in a real formulation. Morpholinium cations show lower solubilisation of the PRMs, though when used in combination with acesulfame, they are the only ones predicted to induce a positive deviation from ideality for 2-phenylethanol or majantol (see Figure 15).

CONCLUSIONS

It has been demonstrated here that COSMO-RS provide an excellent theoretical framework to model the VLE behaviour of solutions of volatile organic compounds in ionic liquids. Moreover, it is also successful at modelling multicomponent systems with more than one organic solute and/or more than one ionic liquid. However, the real strength of the approach is the ability to model ionic liquids which have not been synthesised with a vast range of perfume raw materials, obviating the need for extensive empirical studies until optimal systems have been identified. Additionally, UNIFAC has also been applied to a set of known ionic liquids. Although it is successful for parameterised systems, its weakness is its inability to predict non-parameterised one.

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