



Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:

This is an **author produced version** of a paper published in:

Applied Energy 213 (2018): 179-194

doi: <https://doi.org/10.1016/j.apenergy2018.01.34>

Copyright: © Elsevier 2018

El acceso a la versión del editor puede requerir la suscripción del recurso
Access to the published version may require subscription

Absorption refrigeration cycles based on ionic liquids:

Refrigerant/absorbent selection by thermodynamic and process analysis

Daniel Moreno, Víctor R Ferro, Juan de Riva, Rubén Santiago, Cristian Moya, Marcos Larriba, José Palomar*

Sección de Ingeniería Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain

*Corresponding author: pepe.palomar@uam.es

Keywords: Refrigeration; Absorption; Ionic Liquids; COSMO-RS; Aspen HYSYS

Abstract

A COSMO-based/Aspen HYSYS methodology has been used to perform an extensive thermodynamic evaluation of potential application of ionic liquids (ILs) to absorption refrigeration cycles. By applying this *a priori* methodology, 7200 systems, formed by 900 ILs and 8 refrigerants, representative of available commercial/cation and refrigerant, were evaluated, which would be otherwise unviable due to the lack of experimental data. Firstly, COSMO-RS analysis was carried out for the preliminary selection of suitable ILs as absorbents for each refrigerant, by means of predicted values of Henry's Law constants of refrigerants in ILs. Selected ILs were then introduced in Aspen HYSYS simulator database by using the molecular information by COSMO-RS method. The reliability of COSMO-based/Aspen HYSYS calculations was successfully validated by comparison to available experimental data (>2700 points) of pure and mixture properties of absorbent-refrigerant systems. Then, the performance of selected ILs (and other proposed in the bibliography) in absorption refrigeration cycles was evaluated by process simulations (>230 refrigerant/IL pairs studied at 60 different operating conditions) using COSMO-based/Aspen HYSYS methodology. Cycle efficiency was analyzed in terms of the coefficient of performance (COP), solution circulation ratio (*f* ratio) and the total mass flow pumped from the absorber to the generator, a new parameter proposed to compare the results obtained with different refrigerants. COSMO-based/Aspen HYSYS methodology allowed the selection of adequate refrigerant-absorbent pairs (refrigerant with high cooling capacities and IL with absorption capacity) competitive to conventional systems as H₂O/LiBr or NH₃/H₂O. Furthermore, the analysis of operating condition effects by COSMO-based/Aspen HYSYS methodology allows selecting refrigerant/IL

pairs with maximum efficiency in the cycle for a fixed cooling temperature, revealing additional advantage of the applications of IL in absorption refrigeration technologies.

1. Introduction

Nowadays, cooling systems are an essential technology in the domestic and industrial sectors, such as food preservation, air conditioning, air separation, natural gas liquefaction, ice production, etc. [1]. The two most common refrigeration systems used in domestic and industrial applications are compression and absorption refrigeration systems. In compression cycles, an electrical compressor is used to increase the pressure of the refrigerant. In contrast, in absorption refrigeration systems, the refrigerant is absorbed into another fluid (absorbent) and pumped to the condenser pressure [2]. In the generator (Figure 1), a heating source provides the energy required to vaporize the refrigerant. Because of this, the main energy consumption of an absorption cycle is cheaper than the electric power used in compression cycles. In absorption refrigeration, the use of thermal energy to generate the refrigerant vapor allows the use of residual energy (e.g., combustion gases, low quality steam, etc.) and renewable energy (solar, geothermal) [3, 4]. For this reason, absorption refrigeration cycles are becoming an attractive alternative to compression cycles.

Regarding the fluids involved in absorption refrigeration system, the refrigerant selection is crucial because it determines the operating conditions and cycle performance. [5, 6]. Water is a good refrigerant because it presents high enthalpy of vaporization and low molar mass, consequently water presents high cooling capacity per mass unit of refrigerant. Water is a nontoxic, nonflammable compound; however, it has a high triple point temperature (0°C) and the requirement to operate at pressures below atmospheric due to its low vapor pressure are the main disadvantages of using water as refrigerant [5]. Absorption refrigeration cycles using H_2O as refrigerant and LiBr as absorbent present high performance, due to the high solubility of H_2O in the LiBr mixture and the high-water mass cooling capacity (high vaporization enthalpy). The main disadvantages of H_2O - LiBr systems are the crystallization of the mixture in the rich-absorbent solution at low temperatures, the low-pressure of the system and the impossibility to work at temperatures below 0°C . As alternative refrigerant/absorbent pair, $\text{NH}_3/\text{H}_2\text{O}$ system can work at temperatures below 0°C . In fact, $\text{NH}_3/\text{H}_2\text{O}$ absorption system is used in refrigeration applications at -77°C and NH_3 as refrigerant allows working at pressures

near 4-20 bar [7]. The main problem with this mixture is the small difference in volatility between the compounds, which may imply the use of a rectifier to prevent the presence of absorbent into the evaporator [8]. Other compounds evaluated as refrigerant in absorption cycles are alcohols with short alkyl chains (methanol, ethanol) and fluoroalcohols, which work at low pressures. Examples of fluoroalcohols used as refrigerants are 2,2,2-trifluoroethanol (TFE), 2,2,3,3-tetrafluoropropanol and hexafluoroisopropanol, which are non-corrosive and non-combustible and have appropriate thermal characteristics [6]. On the other hand, hydrofluorocarbons (HFCs) are widely used in compression refrigeration systems since they have good technical properties allowing moderate operating pressures but these compounds contribute to global warming. The selection of the refrigerant can also influence the required operations involved the refrigeration cycle. In fact, using water as refrigerant involves working at temperatures above 0°C and negative system pressure; in addition, water/LiBr crystallization must be prevented. If the selected refrigerant is ammonia, depending on the chosen absorbent a rectifier may be necessary. Regarding the properties of the absorbent, it should be a fluid with a low vapor pressure to prevent its evaporation in the generator, thermally and chemically stable with a low freezing temperature and low viscosity to reduce the transport energy expenses and improve the mass and energy transfer. In addition, the refrigerant must present high solubility in the selected absorbent to minimize the operating and investment costs. In sum, it is well stated that the adequate selection of both the refrigerant and the absorbent are crucial for the suitable performance of the absorption refrigeration system [2, 5, 6, 9].

Consequently, the research in this field is focused on finding more efficient and environmentally friendly absorption refrigeration compounds, searching for alternative refrigerant/absorbent pairs with improved properties [8, 10, 11]. Ionic liquids (ILs) are potential candidates to replace traditional absorbents, due to their high absorption capacity of common refrigerants, very low vapor pressure and good thermal stability [10, 12-14]. The low volatility of ILs allows for a good refrigerant/absorbent separation in the generator, consequently advanced separation equipment is not necessary to achieve the separation of the pure refrigerant [15]. In this regard, Shiflett and Yokozeki patented the application of ILs as absorbents in absorption refrigeration systems [11]. They proposed using Freon, H₂O, NH₃ or CO₂ as refrigerants and ILs, such as H₂O/[emim][BF₄] [16], NH₃/[N_{11H}(EtOH)][MeCOO], as absorbents (see Table S1 for IL nomenclature) [15]. These studies included the evaluation of the thermodynamic performance of the

absorption refrigeration cycles in terms of the solution circulation ratio (f ratio) and the coefficient of performance (COP) as common thermodynamic efficiency parameters of the cycle usually used. The results revealed that the selection of the IL had a significant influence on the performance of the system. Finally, they compared their results with a conventional system and found that the COP was slightly lower than the $\text{H}_2\text{O}/\text{LiBr}$ system, concluding that ILs may be good absorbents for refrigeration systems. Kim et al. [17] evaluated additional refrigerant/IL working pairs for absorption refrigeration cycles and heat pumps, proposing $\text{TFE}/[\text{bmim}][\text{Br}]$ and $\text{TFE}/[\text{bmim}][\text{BF}_4]$ systems as adequate candidates. The analysis of these two systems related their good refrigeration cycle performance to the favorable intermolecular interactions between the refrigerant and absorbent IL. Lately, Wang et al. [18] considered the absorption cycles using TFE as refrigerant and $[\text{bmim}][\text{Br}]$ as absorbent, modeling a parallel double effect absorption cycle. Martin et al. [19] discussed the potential use of ILs with supercritical CO_2 , analyzing the thermodynamic behavior of the absorption refrigeration cycle in terms of COP value related to the phase equilibrium data of the system. However, due to the necessity to operate at a higher circulation ratio, the COP was lower than the conventional $\text{NH}_3/\text{H}_2\text{O}$ system value. Zhang et al. [20] also simulated the thermodynamic performance of a heat pump using $\text{H}_2\text{O}/[\text{emim}][(\text{Me})_2\text{PO}_4]$ and $\text{H}_2\text{O}/[\text{mmim}][(\text{Me})_2\text{PO}_4]$ systems as working pairs, and compared the results with the $\text{H}_2\text{O}/\text{LiBr}$ system. The results indicated that the COP of $\text{H}_2\text{O}/[\text{emim}][(\text{Me})_2\text{PO}_4]$ and $\text{H}_2\text{O}/[\text{mmim}][(\text{Me})_2\text{PO}_4]$ systems were slightly lower than that of the $\text{H}_2\text{O}/\text{LiBr}$ system.

The Rovira i Virgili University team led by Prof. Coronas researched the NH_3/ILs refrigeration systems resulting in a doctoral thesis in where different ILs were evaluated (including $[\text{EtOHmim}][\text{BF}_4]$) adjusting experimental measurements to the NRTL thermodynamic model and simulating the refrigeration cycle in Aspen Plus process simulation software to calculate the efficiency parameters [21]. Other authors followed similar methodologies to simulate absorption refrigeration or heat pump cycles with ILs using equation of state (EOS) or activity models such as NRTL [6, 22-30].

Boman et al. [31] made an extensive and remarkable study where they used a large amount of experimental data of several refrigerants with traditional absorbents and ILs to evaluate and discuss the thermodynamics and performance of the systems. Despite the above pioneer studies on the application of ILs to absorption refrigeration cycles, the number of investigated ILs as the potential absorbent is still scarce considering to the increasing number of cation-anion combinations commercially available. In this context,

the application of consistent theoretical methods for the prediction of the thermodynamic properties of refrigerant/IL absorbent systems is of great interest. First, fast and reliable calculations would allow performing systematic studies to evaluate both refrigerant and absorbent effects on the cycle performance as well as to compare the behavior of the refrigerant/IL absorbent pair with traditional systems. Second, predictive methods would provide a preliminary selection of adequate refrigerant/IL absorbent pairs to perform the required experimental studies, minimizing the time and economic costs. In this field, COSMO-based methods, such as COSMO-RS [32-34] and COSMO-SAC [35], have been well established as an affordable approach to predict the thermophysical properties of IL-containing systems, on the basis of quantum chemical calculations. The COSMO-based methods are *a priori* methods that predict thermodynamic properties of fluid mixtures by solely using the molecular surface polarity distributions of the individual compounds. COSMO-RS methodology has been successfully used to study the absorption of various compounds in ILs such as NH_3 [36, 37], CO_2 [38, 39], toluene [40], acetone [41], alkenes [42] and other volatile organic compounds [43]. In fact, several publications have shown the general suitability of the COSMO-RS method to predict the solubilities and Henry's law constants of several gases in ILs [44-47]. An important feature is that the different intermolecular interactions (electrostatic forces, hydrogen bonding and van der Waals forces) between the mixture components can be quantified by COSMO-RS, contributing to the interpretation of gas solubility in ILs from a molecular point of view [36, 43, 48, 49]. In particular, COSMO-based methods have been successfully applied to predict the absorption isotherms and other thermophysical properties of the mixture formed by NH_3 as refrigerant and ILs as absorbent [36, 37, 48]. In these works, a COSMO-RS analysis was successfully used as a guide for driving a rational selection of two task-specific ILs [EtOHmim][BF_4] and [choline][NTf₂] [37], which promote solute-solvent hydrogen bond interactions, correspondingly enhancing the gas solubility in the IL. Kurnia et al. [50] used COSMO-RS to perform a detailed thermodynamic study of water-IL systems, involving several ILs; as a result, they proposed [P₄₄₄₄]₂[Ox] and others di-cationic ILs as absorbents showing strong interactions with water.

On the other hand, nowadays, process simulation plays an important role in the development of new chemical processes. In fact, it has been demonstrated a valuable tool for understanding and evaluating absorption refrigeration systems based on conventional solvents [51-54]. However, the success of process simulation largely relies on the accessibility and accuracy of physicochemical, thermodynamic and kinetic information

for the chemicals involved. Additionally, process simulators could be helpful for selecting and/or designing ILs with optimized properties as refrigerant absorbents, taking into account not only thermodynamics, but also kinetic, technical and economic criteria [37, 55, 56]. Commercial simulators have large databases; however, ILs are not conventionally included in the databases of the commercial process simulators [57]. This is a severe limitation and often hinders progress and effective exploration of unconventional strategies based on ILs [47].

Through the last years, our group has developed a multiscale computational tool, based on the integration of COSMO-based molecular methods and AspenONE professional process simulators, for developing new separation processes based on ILs [37, 55, 56, 58-60]. This approach allows modeling individual units and entire processes at different operating conditions, providing thermodynamic behavior evaluations, kinetic mass transfer, control assessments, energy balances and economic estimations, which introduce new criteria for the best IL selection and allows comparing the performance to conventional technologies. Recently, a free access database (ILUAM01) of 100 common ILs to be used in AspenONE process simulators was published [61, 62]. In a previous work, COSMO-based process simulations using Aspen Plus were successfully applied to evaluate the performance of NH_3 absorption refrigeration cycles with ILs at different operating conditions [37]. It was concluded that ILs with higher NH_3 absorption capacity provide better cycle's performances and allow working with wider NH_3 concentration range in the refrigerant-absorbent solutions [37].

In this paper, the developed multi-scale methodology is used to perform a systematic analysis of the potential applicability of ILs in absorption refrigeration cycles, involving an extensive set of refrigerant-absorbent pairs and establishing relationships between the thermodynamic properties and process performance as well as comparing the process behavior of different refrigerant-absorbent pairs. Firstly, COSMO-RS molecular simulations are performed to evaluate the absorption phenomena and the intermolecular interactions in refrigerant-absorbent systems. For this purpose, Henry's constant is used as key thermodynamic parameter to assess the potential absorption of the refrigerant in the ILs [36, 37, 42, 48, 49], performing COSMO-RS screenings of this property for several refrigerants [water, ammonia, methanol, 2,2,2-trifluoroethanol (TFE), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,2,2-pentafluoroethane (HFC-125), 1,3,3,3-tetrafluoropropene (HFO-1234(ze))] over a wide number of IL (900). This study allows revealing the effect of the cation and the anion on the refrigerant gas solubility, providing

a preliminary selection of ILs with adequate phase behavior as absorbents for each refrigerant. In addition, COSMO-RS method is applied to analyze the refrigerant-absorbent interactions that determine the gas solubility. The advantage of this methodology is that 7200 systems with 900 ionic liquids and 8 refrigerants have been studied, something utterly impossible without a predictive tool. This relevant information, together with the analysis of pure refrigerant properties, allows classifying the properties of the refrigeration cycle systems based on ILs from a thermodynamic perspective, proposing a rational selection of refrigerant-IL samples with favorable properties for further analysis. The second step is focused on modeling the absorption refrigeration cycles for the selected refrigerant-IL absorbent systems. The predictability of COSMO-based/Aspen HYSYS approach was first validated by comparing theoretical and experimental thermodynamic data. In addition, the reliability of the current computational approach is validated by comparing the obtained cycle performance parameters to those previously reported in the literature. Then, the influence of the properties of the refrigerant and the IL on the cycle performance is systematically analyzed by evaluation of COP, f ratio, mass cooling capacity (MCC) and the total mass flow required in the process, which directly affects the cost. Finally, the effect of operating conditions (evaporator and generator temperature) on the thermodynamic cycle behavior is studied for the best refrigerant-IL pairs selection. Thus, an additional contribution of COSMO-based/Aspen HYSYS methodology is the possibility to select and define refrigerant/IL pairs with maximum efficiency in the cycle for different cooling temperatures.

2. Computational details:

2.1. Quantum chemical calculations

The first stage in COSMO-RS calculations was to create the chemical structure of ILs and all the components that are not available in COSMOtherm [63] databases (HFC-134a, HFO-1234(ze), 2,2,2-trifluoroethanol). TURBOMOLE v7.02 (with TmoleX v4.2.1 graphic interface) [64] software was used. Molecular structures of ILs were described by two different molecular models, ion-pair [CA] and independent ions [C+A]. Ion-pair model [CA] optimizes the cation and anion structure as a whole while independent ion model [C+A] optimizes the structure of the cation and the anion individually, where the IL is treated as an equimolar mixture of cation and anion. After that, quantum chemical calculations were carried out to generate a COSMO file. The standard method used in

COSMOtherm is B88-P86 [65, 66] (bp) functional and TZVP basis with RI approximation [67, 68] using COSMO solvation model. As a result of this quantum chemical calculations, a COSMO file was created containing energies, geometries and polarization charge of the σ -surface.

2.2. COSMO-RS calculations

The COSMO-RS method with BP_TZVP_C30_1201 parametrization was used in COSMOtherm software. In this work, COSMO-RS method was applied with two objectives. First, a COSMO-RS analysis was carried out to calculate molecular properties of the pure compounds as the σ -profile/ σ -potential, and mixture properties such as Henry's Law constant (K_H) of refrigerant in ILs; additionally, COSMO-RS allowed to evaluate the different intermolecular interaction contributions to the excess enthalpy [hydrogen bond (HB), misfit (MF) and van der Waals (vdW)] in refrigerant/ILs equimolar mixtures. Based on our previous experience, [C+A] model can be efficiently used to screen Henry's Law constants (and activity coefficients) of different solutes (refrigerants) in a wide number of cation-anion combinations (900 ILs as absorbent) since it allows minimizing the computation time. On the other hand, COSMO-RS information was used to create ILs pseudocomponents into Aspen Properties. Previous studies have shown that the [CA] model of IL describes more accurately the vapor-liquid and liquid-liquid equilibria of different solutes in ILs [38, 56, 69]. COSMOtherm was used to carry out the normal boiling point (NBP), density, σ -profile and COSMO-volume calculations (the last two to use the COSMOSAC model from Aspen Properties). The data exported to the simulator can be found in Table S2 of the supplementary material.

2.3. Creating IL property package in the process simulator

To implement ILs into ASPEN HYSYS v9.1 simulator, a property package was created in Aspen Properties v9.1. ILs were defined as pseudocomponents. NBP, density and molecular weight was the required information imported from COSMOtherm needed to create the pseudocomponent. COSMOSAC model was selected as thermodynamic model and gamma method was modified to use COSMOSAC-Mathias modification [70]. In our previous work [37], the liquid-vapor equilibria were adjusted to the experimental data by Henry component specification. In the present work, this approach was not performed because there is not enough available experimental information for the wide number of the refrigerant-IL systems included. Therefore, since the objective of this work

was to systematically analyze the thermodynamic behavior of absorption refrigeration systems using ILs, we have applied a COSMO-based/Aspen HYSYS approach, which does not need from any experimental data to achieve the complete prediction of the mixing properties of the refrigerant-IL system. σ -profile was specified as pure component properties SGPRF1-5 and COSMO-volume as CSACVL component parameter. Property package was generated in Aspen Plus and exported to Aspen HYSYS. More information on this COSMO-based/Aspen HYSYS computational approach was reported in the free access documentation of ILUAM01 database, recently published with information available for 100 common ILs [61, 62].

2.4. Validation of properties and COSMO-based/Aspen HYSYS approach

COSMO-based/Aspen HYSYS predictability was evaluated by two procedures. First, the available vapor-liquid equilibria experimental data of pure refrigerant and refrigerant/IL mixtures were used for validating the current predictive methodology. Second, the refrigeration cycle efficiency parameters (COP and f) available in the bibliography for ILs with refrigerants were compared to the values calculated in this work at the same operating conditions. In all these cases, the relative deviation (mean absolute percentage error) was calculated as eq.1:

$$MAPE = \frac{100}{n} \cdot \sum_i \frac{|x_i^{Calc} - x_i^{Exp}|}{x_i^{Exp}} \quad (\text{eq. 1})$$

2.5. Process simulation

The single-effect absorption refrigeration cycle modeled by Aspen HYSYS process simulator is depicted in Figure 1, containing the main units of a single absorption refrigeration cycle: (i)- condenser, (ii)- expansion valves, (iii)- evaporator, (iv)- absorber, (v)-pump, (vi)- generator and (vii)- heat exchanger to recover energy. The main specifications used in the simulation of the base case were the temperature at the generator (T_G), absorber (T_A), condenser (T_C) and evaporator (T_E): 100°C, 30°C, 40°C and 10°C, respectively. These values were chosen based on previous studies [16, 22, 37] and these temperatures were based on a refrigeration cycle that consumes low-quality heat (100°C) with a moderate cold source (10°C). Pressures at the condenser (P_C) and the evaporator (P_E) correspond to refrigerant saturated pressures at the fixed temperatures. A countercurrent type heat exchanger was modeled to recover the heat from the liquid stream at the generator outlet in order to preheat the input mixture stream to the generator

and to reduce the generator heat duty (Q_G). The heat exchanger effectiveness is the parameter selected to calculate the temperatures of the exchanger output streams (S_2 and S_4). The maximum possible heat transfer is represented as eq. 2.

$$Q_{MAX} = m_3 \cdot C_p \cdot (T_3 - T_1) \quad (\text{eq. 2})$$

The heat exchanged between the currents in each case is calculated as:

$$Q = \varepsilon \cdot Q_{MAX} \quad (\text{eq. 3})$$

Where ε is the effectiveness of the heat exchanger, for which a conservative value of 0.65 [5, 7, 26, 27] was selected in all cases. Streams S_7 and S_9 is refrigerant at saturated conditions, which implies vapor fraction equal to 0 and 1, respectively. The composition of the poor- (streams S_{MIX} to S_2) or rich- (streams S_3 to S_5) IL solutions (x_A and x_G , respectively) was a degree of freedom of the system. x_A was specified for this study as saturated concentration of refrigerant in the IL at absorber conditions (to avoid the possibility of vapor refrigerant in the pump). Additionally, x_A and x_G were associated with the VLE condition at the generator. Lastly, pressure drops in the equipment are ignored, therefore: $P_C = P_G$ and $P_E = P_A$. A screenshot of the simulation in Aspen HYSYS is attached to the supplementary material (Figure S3)

2.6. Absorption thermodynamic and cycle efficiency parameters

As a result of the COSMOtherm screening, Henry's law constants of the different refrigerant in ILs with different cations and anions were represented on a contour map. Henry's Law constant is a typical design parameter of absorption operations because it is related to the volatility of the solute and takes into account the solute-absorbent interactions. Henry's law constant can be defined as the product of the activity coefficient of refrigerant in IL at infinite dilution by the vapor pressure of the pure refrigerant at the temperature of the system (eq. 2).

$$p_i = [\gamma_i^\infty \cdot P_v] \cdot x_i = K_H \cdot x_i \quad (\text{eq. 4})$$

Activity coefficients less than 1 indicate negative deviations from Raoult's Law that favor solute absorption due to attractive molecular interactions. It was intended to find those ILs that have low Henry's law constant since the absorption will be favored.

Within the absorption refrigeration process, thermodynamic efficiency parameters were deducted from the mass and energy balance of the refrigeration cycle. The overall energy balance of the cycle is:

$$Q_G + Q_E + W_p = Q_C + Q_A \quad (\text{eq. 5})$$

Where Q_G , Q_E , Q_C and Q_A were the heat duties of the generator, evaporator, condenser and absorber, respectively and W_P was pump power. The pump powers required as the product of the pressure difference between condenser and evaporator were calculated by the volumetric flow rate of the pump inlet stream. In all the calculations, the power of the pump was negligible with respect to the heat of the generator; therefore, the Coefficient of Performance (COP) was defined as:

$$COP = \frac{Q_E}{Q_G} \quad (\text{eq. 6})$$

In the most unfavorable cases the differences between the COP taking into account the power of the pump is less than 1%.

To evaluate the absorption operation, the Solution Circulation Ratio (f ratio) was used. It is defined as the mass-flow-ratio between the absorber solution (m_S) and the pure refrigerant stream (m_R).

$$f = \frac{m_S}{m_R} \quad (\text{eq. 7})$$

A useful parameter to compare different refrigerants is the mass cooling capacity:

$$MCC = \frac{Q_E}{m_R} \quad (\text{eq. 8})$$

As an alternative efficiency parameter to compare the use of chemicals and the theoretical equipment size for the different refrigerant/absorbent pairs, we defined the total mass flow pumped from the absorber to the generator, that can be derived from the previously defined parameters as:

$$\text{Total mass flow pumped} = m_S = \frac{Q_E}{MCC} \cdot f \quad (\text{eq. 9})$$

3. Results and discussion:

3.1. Molecular simulation analysis

A desirable property in refrigerants is that they have a vapor pressure at the evaporator and condenser conditions as close as possible to atmospheric pressure. The difference in the volatilities of the proposed refrigerants is very significant (Table 1). There are refrigerants like water, methanol or trifluoroethanol that require high vacuum conditions in the cycle to operate. From a strictly technical point of view, this means that special equipment designs will be required to operate with that pressure change with respect to

atmospheric pressure, which leads to higher costs. Refrigerants used and proposed in compression cycles such as ammonia, HFC-125 or HFC-134a and HFO-1234(ze) reverse this problem and work at higher pressures than atmospheric in all parts of the cycle. Finally, pentane has been selected from hydrocarbons as a refrigerant, taking into account their operating pressures which are relatively close to atmospheric pressure, which implies non-excessively high vacuum pressures.

One relevant property in the selection of refrigerants is the enthalpy of vaporization, as it directly affects the mass cooling capacity term and, therefore, the flow requirement in the refrigeration system. Analyzing Table 1, it is evident that the vaporization enthalpy strongly depends on the nature of the refrigerant and its molecular weight. In general, as the molecular weight of refrigerant decreases, the vaporization enthalpy (mass basis) increases. Among the common refrigerants considered, water has the highest enthalpy of vaporization since it establishes intermolecular hydrogen bonds and, also, due to its low molar weight. Ammonia and methanol are also refrigerants characterized by their high enthalpy of vaporization.

In order to analyze the refrigerant compounds as part of a fluid mixture, the polarized charge density histogram (σ -profile) generated by COSMO-RS is an interesting tool, since it illustrates the polarity of the compound and allows anticipating the behavior of the compound in a liquid mixture environment. The COSMO-RS method also provides the σ -potential of the compounds, which describes the interaction energy with other compounds with a charge density [$\rho^X(\sigma)$] with polarity σ . Figure 2 presents the σ -profile and σ -potential provided by COSMO-RS of representative examples of the refrigerants included in this work.

Regarding the inorganic refrigerants, it can be observed that water presents polarized charge peaks in the high positive polarity region (above the cut off $\sigma_{\text{H-Bond}} > 0.0085 \text{ e/\AA}^2$) and, also, negative polarity region (below the cut off $\sigma_{\text{H-Bond}} < -0.0085 \text{ e/\AA}^2$); *i.e.*, water presents strongly acceptor and donor hydrogen bond (HB) groups. Consequently, its σ -potential indicates that water would promote exothermic mixtures with compounds presenting functional groups with polarized charge in the acceptor and donor HB polar regions. In sum, water is described by COSMO-RS as an amphoteric compound that interacts attractively with polar compounds presenting both HB donors and acceptor groups. Ammonia has a strongly basic behavior, presenting peaks in the σ -profile in the area of $0.02 < \sigma < 0.03$ and a σ -potential showing strong attractive interactions with acidic groups. Regarding the organic refrigerants, the alcohols are distinguished by having the

OH group with a strongly acidic hydrogen and a slightly basic oxygen. As can be seen in the σ -potentials, the strength of interactions with HB donor groups follows the order methanol > water > TFE; whereas interactions with HB acceptor compounds follows the order TFE > water > methanol, since the substitution of hydrogen by fluorine atoms strongly increases the acidic character of TFE. In contrast, the HC (as *n*-pentane), HFC (as HFC-125) and HFO (as HFO-1234(ze)) are mainly non-polar compounds with a distribution of charge around $\sigma = 0$ and repulsive interactions with either basic or acidic polar compounds. However, the high electronegativity of F atoms in HFCs causes a charge defect on the hydrogen atoms, giving the compound more polar character; this effect is more evident in HFC-125, the most F substituted HFC refrigerant among those studied.

Consequently, COSMO-RS analysis indicates that each refrigerant will interact differently with the IL absorbent depending on its nature. This implies that the IL absorbent should be specifically designed for each refrigerant to promote favorable intermolecular interactions and to increase the absorption capacity. The advantage of ILs is that there are a large number of cations and anions with remarkably different structure and, consequently, chemical nature. Figure 3 presents a representative selection of 5 cations and 5 anions to observe the significant differences in their σ -profile and σ -potential.

Thereby, the σ -profile reveals slightly polar cations like $[\text{P}_{2224}]^+$ or very polar like $[\text{EtOHmim}]^+$ whose OH presents an amphoteric character. Consequently, the σ -potential shows that $[\text{P}_{2224}]^+$ presents strong repulsions with polar acidic and basic groups; whereas $[\text{EtOHmim}]^+$ presents strong attraction with HB acceptor groups. Regarding anions, $[\text{NTf}_2]^-$ is described as a low polar specie with weak attractive interactions with HB donor groups; in contrast, $[\text{MeCOO}]^-$ anion presents a peak in the strong HB acceptor zone of the σ -profile and, as a consequence, remarkably strong attractive interaction with HB donor compounds (see its σ -potential in Figure 3). Other anions, as $[\text{MeSO}_4]^-$ or $[\text{BF}_4]^-$, present intermediate behaviors. COSMO-RS analysis reveal, therefore, that ILs present a remarkably versatility as absorbents since the cation and the anion can be selected to selectively absorb each specific refrigerant.

To select and design optimized ILs for a specific solute absorption, COSMO-RS method has been widely applied for predicting the Henry's Law constants (K_H) of the solute in the IL, as thermodynamic parameter of reference for gas solubility [36, 38, 40,

42, 43]. Therefore, COSMO-RS was here applied to calculate the Henry's law constant and activity coefficients at infinite dilution of studied refrigerants in the 900 ILs at 298 K. Figure 4 presents the COSMO-RS screening of Henry's law constants of 4 representative refrigerants in 900 ILs using [C+A] model to perform COSMO-RS calculations (Figure S1 in Supplementary Material collects the corresponding COSMO-RS screening for the rest of refrigerants).

In the case of water (like methanol and TFE), the K_H values are clearly governed by anion effects, increasing the refrigerant solubility with ILs that promote HB interactions between the basic groups of the anion (such as acetate, phosphate or chloride) and the acidic OH group of the refrigerant. Regarding the cation, a low influence in the K_H values is observed, obtaining that less polar cations mean weaker cation-anion interaction and, consequently, stronger refrigerant-anion interactions are allowed. The strong basic character of ammonia makes it strongly interact with acidic protic cations, such as [EtOHmim]⁺ or [choline]⁺. The anion also plays an important role for ammonia refrigerant, being the more favorable cases those anions with low polarity such as [NTf₂]⁻ since it avoids that the HB interaction of cation-anion competes with the refrigerant-cation HB interaction. In fact, anions with strong HB acceptor groups, such as [MeCOO]⁻ generate ILs with low ammonia gas solubility. It should be remarked that the higher Henry's Law constants in ammonia than in water are also related to the higher intrinsic volatility of ammonia (higher vapor pressure in Table 1) attending to K_H definition in eq. 2. Regarding HFCs, the K_H screening of HFC-134a refrigerants reveals a general lower gas solubility in ILs than water and ammonia, where both anion and cation affect the K_H values, increasing the absorption with ILs formed by anions presenting HB acceptor character, due to the slightly acidic character of this refrigerant. Cations with acid groups decrease solubility since they promote competitive cation-anion HB interactions. In contrast, pentane is a totally non-polar compound. Consequently, the refrigerant-IL interactions are not favorable and the calculated K_H values are higher than in previous refrigerants, even when pentane presents a relatively low vapor pressure (see Table 1 and Figure 4). For this refrigerant, the cation plays a major role in gas solubility behavior: ILs formed by non-polar aprotic cations with long alkyl chain presents lower K_H .

In previous studies, COSMO-RS method has also been used to analyze the interactions and solubilities of different gases in ILs in terms of excess enthalpy of solute-solvent mixtures [36, 38, 40, 41, 43]. Figure 5 depicts the excess enthalpy and free energy of equimolar refrigerant-IL mixtures selected by the high refrigerant solubility in IL. The

excess enthalpy is described in terms of the different intermolecular interactions [electrostatic (MF), hydrogen bond (HB) and van der Waals (vdW)] contributing to the calculated values. As can be seen in Figure 5, mixing phenomena generally present an exothermic enthalpy, with the exception of pentane. Clearly, TFE presents an extraordinary thermodynamically-favored mixing behavior with ILs, due to favorable HB and electrostatic interaction between solute and solvent respect to pure compounds, whereas ammonia, HFC-134a, water, HFC-125, methanol and HFO-1234(ze) present intermediate excess enthalpy values between TFE and pentane. From a qualitative point of view, HB interactions are dominant in TFE, ammonia and water, whereas HFC-125, HFC-134a and HFO-1234(ze) present higher contribution of electrostatic (MF) than HB interactions to excess enthalpy. Van der Waals interactions seem to play a minor role in refrigerant-IL mixing behavior. Finally, pentane gives unfavorable interactions with most of the ILs, mainly due to the electrostatic repulsions between the non-polar aliphatic solute and the IL solvent. ILs with better properties as absorbent of pentane are less polar and present long alkyl chains such as attached to phosphonium or ammonium cations paired with anions [FEP] or [NTf₂].

Attending to the results obtained in the above COSMO-RS analysis, a set of ILs were selected as adequate absorbents for each refrigerant, due to their higher absorption capacities (Table 2) to be tested in the simulation of the absorption refrigeration process. As a summary of the thermodynamic properties of selected systems, Table 3 presents Henry's Law constant of each refrigerant-IL pair with the most favorable gas solubility (lowest K_H), described by the terms of eq. 4: activity coefficient at infinite dilution of refrigerant in IL (γ^∞) and the vapor pressure of refrigerant at absorber temperature (283K) calculated by COSMO-RS. As can be seen in this table, the systems using water, methanol and TFE as refrigerant present the lowest K_H , *i.e.*, the higher gas solubility, as a consequence of both low volatility of refrigerant (low P_{VAP} values) and favorable refrigerant-IL intermolecular interactions (low γ^∞). The opposite behavior is found when n-pentane is used as refrigerant, observing a low absorption capacity due to an intermediate volatility but unfavorable refrigerant-absorbent intermolecular interactions. Other cases present an intermediate behavior, such as HFC-125 and ammonia, where the high vapor pressure of the refrigerant is compensated by the high chemical affinity between the refrigerant and absorbent (low γ^∞); or the cases of HFO-1234(ze) and HFC-134a with intermediate vapor pressure and activity coefficient values.

3.2. Process simulation of absorption refrigeration cycles

Firstly, the results of the COSMO-based/Aspen HYSYS approach were compared to experimental data available for refrigerants and ILs. As can be seen in Table 4, the vapor pressures of the refrigerants are well described since they are conventional compounds in the Aspen Properties databases. Pure properties that will be of importance in the simulation of the absorption refrigeration process are refrigerant vapor pressure and ILs properties such as density (ρ) and heat capacity (C_P). Other properties such as viscosity or vapor pressure of the IL (whenever negligible at operating temperatures) present minor effects on this type of thermodynamic calculations. In our recent study [62] COSMO-based/Aspen methodology -used in this work- was extensively validated against experimental data. The estimation of IL density as a function of temperature was obtained with an error lower than 3% due to the high accuracy of the COSMO-RS method in the estimation of density [71]. Regarding the heat capacity, it was verified that the presented methodology provides a reasonable estimation (no experimental data is added) with an average error of less than 15% that decreases with increasing temperature. To confirm this idea, the available experimental data of the ILs implemented in the process simulator for this work were compared with those calculated. Table 5 shows the results of this validation detailed by temperatures (25-100°C) and IL. In general, the mean deviation (MAPE) is less than 10% and a correlation coefficient (R^2) of 0.98 is obtained.

To validate the COSMO-based/Aspen HYSYS methodology for the prediction of solubility values of the different refrigerants in ILs, extensive experimental and calculated equilibrium vapor pressures have been compared at fixed refrigerant composition, using the experimental data available in ILthermo database for a wide number of ILs and refrigerants at different temperatures [72]. Table 6 collects the statistical results of experimental vs calculated VLE data (slope and square correlation of linear regression and MAPE values) for each specific refrigerant, together with the number of data points (> 2500) and different ILs (>50) included in the analysis. No experimental data on pentane/IL mixtures have been found, so a similar compound such as butane (same chemical nature, same interactions and similar number of atoms) has been selected to verify the description of the COSMO-based/Aspen HYSYS methodology. As illustrative cases, Figure 6 presents experimental vs calculated VLE values for H₂O-IL and methanol-IL systems (the results for other refrigerant are available in Figure S2 of Supplementary Material). As can be seen in those figures, reasonable predictions of absorption

equilibrium values are obtained for the case of highly soluble compounds in IL, like water and alcohols (see Table 6: slope close to 1 and $R^2 > 0,97$; MAPE < 20 % and absolute deviation of equilibrium pressure < 5 kPa). In the case of fluorocarbons and hydrocarbons, experimental and calculated VLE data also present reasonable linear relationship (see Table 5: slope close to 1 and $R^2 > 0,95$) with the exception of HFO-1234(ze)), where the prediction error is larger (MAPE > 30 % and absolute deviation of equilibrium pressure > 100 kPa), generally ascribable to the overestimation of the low gas solubility of non-polar solutes in ILs by the ion-pair molecular model (CA) used to describe the ILs in the COSMO-based/Aspen HYSYS approach. Ammonia-IL systems present a worse description of VLE data by this computational approach, which may be related to the dispersion of experimental data, generally centered on high hygroscopic ILs, which –depending of the preliminary purification stage- may present different water content, affecting ammonia absorption capacity. In summary, the COSMO-based/Aspen HYSYS methodology has been revealed to be a suitable computational approach to predict VLE data from refrigerant/IL systems, at least with the required accuracy for the initial stages of the conceptual design of chemical processes and for the purpose to distinguish the role of the cation and anion in the selection of appropriate absorbent for refrigerants of different chemical nature as in other previous works published by our group [37, 40, 55, 56, 58-60, 69].

To further validate the proposed COSMO-based/Aspen HYSYS methodology, the absorption refrigeration systems were modeled using the ILs and operating conditions reported in the bibliography. Then, the COP and f efficiency parameters of absorption refrigeration cycles for 22 refrigerant-IL systems were estimated and compared in Figure 7 to those values available in previous studies [6] (data collected in Table S3 of Supplementary Material). It is important to mention that most of the available COP and f values from the literature are not directly obtained from experimental results, but they are also results of thermodynamic calculations or simulations. As can be seen in Figure 7, the COSMO-based/Aspen HYSYS approach provides COP values very close to those reported for a wide number of refrigerant-IL systems. The quality of the estimate of f ratio values is also reasonable, with the exception of mixtures with ammonia, since the methodology overestimates the solubility of this compound in the ILs (Figure S2 of Supplementary Material). In sum, current results indicated that the COSMO-based/Aspen HYSYS methodology provides predictions with the accuracy required for the conceptual design of chemical process and with good qualitative results, making this computational

approach suitable to compare the performance of different refrigerant-IL systems in absorption refrigeration cycles, which is the objective of this work.

Once the methodology was validated, the absorption refrigeration cycle was modeled using the same operating conditions in all cases, corresponding to the base case: T_A : 30°C; T_G =100°C; T_C =40°C; T_E =10°C for a wide set of ILs that include those studied previously in bibliography and those selected as favorable using COSMO-RS analysis (Table 2) by their high absorption capacity values. The COP results of the systems are compared to the solubility of the refrigerant in the IL at the operating conditions of the absorber in Figure 8. Since ILs generally have a high molecular weight, the mass solubility of low molecular weight refrigerants (water, methanol and ammonia) can be considerably lower than the molar solubility due to the difference in molecular weights, for this reason high IL-solute mass ratios may be required [60]. As can be seen in this figure, COP energy efficiency parameter is successfully related to the absorption capacity of the refrigerant-absorbent pair, observing higher cycle yields when increasing the mass solubility of the refrigerant in the IL, since it means lower mass flows of refrigerant and IL and, therefore, lower heats requirements in the generator to separate the mixture. It can also be observed how a maximum COP value is reached for each refrigerant. This maximum COP is a function of the nature of the refrigerant and its properties such as heat capacity and vaporization enthalpy. The refrigerant with the highest maximum COP is water, with a value near 0.8 in the H₂O-[mmim][Cl] mixture. In addition, TFE and ammonia present maximum COP higher than 0.6. In contrast, refrigerant-IL systems based on fluorocarbons HFO-1234(ze), HFC-134a and HFC-125) show significantly lower maximum COP, near to 0.4. These two different performances may be related to the vaporization enthalpy of the refrigerants: higher vaporization enthalpy causes lower refrigerant mass flows required in the evaporator to obtain the same cooling power in the evaporator. Therefore, the flow of refrigerant/IL in the generator is higher and consequently, requires more energy input to separate them. Finally, hydrocarbons such as pentane have a very low maximum COP due to the combination of two effects: a relatively low vaporization enthalpy (although higher than the fluorocarbons) and a low mass solubility of aliphatic compounds in the IL. The low solubility causes very high flow rates of absorbent required which increases energy costs (Figure 8).

To further examine the idea of COP dependence with the refrigerant properties, Figure 9 compares the calculated COP to the Mass Cooling Capacity (MCC) of refrigerants. It is observed that maximum values of COP generally increase with the mass cooling

capacity of the refrigerant except for NH_3 and pentane. In the case of the hydrocarbon, this is due to the low solubility of the compound in the ILs. In the case of NH_3 it is quite possible that the description of solubility with the methodology is of lower quality than in the rest of compounds (as can be seen in Table 6). It is also clearly visible how the proper selection of the absorbent significantly affects the performance of the cycle. ILs with higher solubilities are the most energy-efficient systems.

In addition to COP, f ratio is generally proposed as a reference parameter for the selection of a refrigerant-absorbent pair. It is necessary to remind that the f ratio simply indicates the amount of absorbent required per mass unit of refrigerant (eq. 7), but it is not a reference to the absolute flow rate, and hence to the mass and energy requirements associated with the pumping of that flow rate. Figure 10 compares the total mass flow of refrigerant/absorbent mixtures in the pump feed (streams S_1 and S_2 of Figure 1) to the f ratio calculated for the different systems studied. A linear relationship is observed between the f values and the flow of refrigerant/IL comparing various refrigerants, decreasing the f ratio when increasing the absorption capacity of IL for each specific refrigerant (this effect can be confirmed by observing eq. 7). On the other hand, the slope of this linear relationship is determined by the nature of the refrigerant, decreasing in the order water < methanol ~ ammonia < TFE < pentane < HFC-134a ~ HFO-1234(ze) < HFC-125, since greater MCC minimizes the required flow in the cycle as we evidenced above. According to Figure 10, it can be concluded that f ratio is not an adequate efficiency parameter to evaluate the refrigeration cycle performance when different refrigerants are compared. For this reason, to compare systems, we consider more useful to evaluate the total mass flow (refrigerant+IL) that circulate in the absorber-pump-generator area as defined in the eq. 9. The required refrigerant flow in the cycle is a function of the power of the evaporator (Q_E) and the properties of the selected refrigerant (MCC). Figure 11 shows how the flow rate in the pumping stage for all systems varies according to the refrigerant MCC. It shows that the flow rates required at this stage vary significantly between the different ILs because lower solubilities will imply higher IL flow rates and higher recirculation flow rates at the generator outlet. On the other hand, when comparing refrigerants, it is exposed that higher cooling capacities require lower flow rates. The systems formed by each refrigerant with its best absorbent have the lowest flow rates but this minimum flow rate decreases as the MCC of the refrigerant increases.

As a summary, Figure 12 presents the total mass flow of refrigerant and absorbent per evaporator power and the estimated COP values for the best refrigerant-IL pairs (Table

2) and the systems traditionally used like the $\text{H}_2\text{O}/\text{LiBr}$ and the $\text{NH}_3/\text{H}_2\text{O}$ (the data have been taken from the references [16] and [22] respectively). It is concluded that, at the operating condition of refrigeration cycle base case, water (compound with the highest enthalpy of vaporization in Table 2) is the refrigerant that provides best results, since: i) it requires the lowest flow of refrigerant/IL and, therefore, the energy consumed in the pumping, the size of the installation and the amount and IL consumption is the minimal; ii) the COP of the water-IL system is the highest among the systems selected, which means that the energy costs to carry out the separation of the compounds in the generator is minimal; and iii) presents a relatively low f ratio, indicating the favorable absorbent used due to the high capacity of selected ILs to absorb water. Regarding other cases, methanol, TFE and ammonia constitute a group of high-performance refrigerants based on the results of Figure 12. Methanol provides similar cycle performance than water but its lower enthalpy of vaporization leads to lower yields. Ammonia has a relatively high vaporization enthalpy similar to methanol. The results of the systems using ammonia as a refrigerant indicate lower performance than methanol systems because of the lower solubility of the refrigerant in the IL. TFE has good mixing properties due to the strong interactions with ILs; however, it has a substantially lower vaporization enthalpy. HFCs are compounds that have a lower enthalpy of vaporization and, consequently, the required flow rates in the absorber are higher. Furthermore, these refrigerants have lower COP values, so it can be concluded that these compounds are not appropriate to be used in absorption refrigeration cycles under these conditions, although they may be of interest in hybrid compression-absorption systems [6]. Finally, current results indicate that hydrocarbons are not suitable to be used as refrigerants in refrigeration cycles absorption, obtaining clearly unfavorable cycle efficiency parameters, due to the relatively low mass cooling capacity and the very low solubility in ILs. When we compare the results of the ILs-based systems with traditional refrigerant/absorbent mixtures, we found that the $\text{H}_2\text{O}/\text{LiBr}$ and $\text{H}_2\text{O}/[\text{mmim}][\text{Cl}]$ result in very similar COP, as when comparing the $\text{NH}_3/\text{H}_2\text{O}$ system with $\text{NH}_3/[\text{EtOHmim}][\text{BF}_4]$. However, since the mass solubility is lower in the case of IL absorbents (the IL molecular weights are higher than traditional absorbers such as LiBr, H_2O or LiNO_3), systems based on ionic liquids require greater mass flow (f ratios are higher). However, it must be reminded that the main advantage of ILs in this process is to avoid the technical problems associated with traditional absorbents such as crystallization, loss of absorbent or the requirement of a rectifier.

Next, the influence of the operating conditions in absorption refrigeration cycles is evaluated for the optimized refrigerant-IL pairs selected in Table 2. The variables to be studied are the generator temperature, since it is important to know the efficiency and the capacities when using heat sources of different temperatures and qualities, and the evaporator temperature, which is the temperature of the desired refrigeration application.

Generator temperature: The behavior of the variables of the refrigeration cycle has been studied by modifying the temperatures of the heat source. We have chosen generator temperatures between 60°C and 150°C since these are typical temperatures of residual heats in the process, as hot waters or low quality vapors. All the other variables of the absorption refrigeration cycle remain constant with the same specifications as in the base case analysis. Regarding the COP (Figure 13), an initial increase of the COP can be observed for all the refrigerants with the increase of the temperature of the generator, to later stabilize and decrease slightly. Except for pentane, the other systems have maximum COP around 70-90°C, while in the case of pentane it is around 100°C.

Figure 14A shows that increasing the temperature decreases the f ratio, since higher temperatures favor the separation between compounds and minimize the amount of required refrigerant/IL. For the same reason, if the refrigerant-IL mass flow pumped is compared (Figure 14B), a decrease in the mass flow pumped is observed as the generator temperature increases. For some mixtures as water and methanol, temperatures around 80°C involve working at maximum COPs and low mass flow; for others, such as the TFE or ammonia, the refrigerant/absorbent mass flow trends reach the minimum at around 105°C. A different behavior is observed in the mixtures with the HFC and HFO, where - due to their lower enthalpy of vaporization- the mass flows are always higher than in the cases presented previously; in addition, the generator temperatures that make the minimum refrigerant/IL mass flow required are quite different from the temperatures at which the COP is maximum.

Evaporator temperature: The study of the evaporator temperature is fundamental because it is the cooling application temperature of the system. Cooling temperatures between -20°C and 15°C have been chosen to cover the operations ranges such as freezing and food preservation, refrigeration and conditioning of environments and the obtaining of refrigerated water, among others. All other variables remain constant as in the base case analysis. The effect of the evaporator temperature on the energy requirements is depicted in Figure 15A, observing that calculated COP value decreases with lower evaporator temperature. It should be remembered that a diminution of the evaporator

temperature implies decreasing the evaporator and absorber pressure (Figure 15B) which results in a lower absorption capacity of the refrigerant in the IL. The lower solubility of the refrigerant at lower evaporator temperatures implied the necessity of increasing the flow of IL to absorb the same amount of refrigerant, resulting in higher flows of refrigerant/IL fed to the generator and an increase of the energy duties.

Figure 16 presents the calculated f ratio (A) and the total refrigerant/IL mass flow pumped (B) with respect to the variation of the evaporator temperature. When the cooling temperature decreases, the mass flow needed in the system increases exponentially. Comparing refrigerants, the pentane undergoes a very significant variation of f ratio and total mass flow pumped due to its limited absorption in the IL. The opposite behavior is observed for refrigerants with high molar weight such as TFE and HFO-1234(ze).

It should be reminded that water-based systems cannot operate at temperatures below 0 °C because of the triple point. Water is precisely the refrigerant with the lowest total flows required between 5°C and 15°C and it presents the highest COP. Therefore, it is particularly interesting to compare the systems below 0°C. In such temperature range, methanol (due to its high refrigerating capacity, as mentioned above) requires lower flows compared to other refrigerants. TFE requires lower mass flow than methanol at temperatures below -5°C, mainly due to the decreasing pressures in the evaporator that appreciably decreases the absorption capacity of methanol in the IL. These results indicate that, at temperatures below -10 °C, TFE has better performance (higher COP and lower mass flows required) than methanol as refrigerant. For temperatures below -10°C, COP are relatively low. Refrigerants that have better performance (both COP and low mass flow) at these low temperatures are HFO-1234(ze) and HFC-125.

In view of these results, it can be argued that, for refrigeration applications using IL as absorbents, the refrigerants should be selected depending on the desired refrigeration temperatures. For evaporator temperatures higher than 0 °C, the optimum refrigerant is water, since it requires the lowest flow rates in the system and promotes the highest energy yields. For temperatures between -5 and 5 °C, methanol is a coolant with good performance that can compete with TFE. For lower temperatures, the use of TFE gives higher yields due to its higher solubility at lower operating pressures; however, the operating pressures are quite low which implies higher capital costs with better airtight insulation to prevent air ingress. Ammonia has operating pressures above atmospheric pressure and COP and yields slightly lower than TFE, which may be a technical

alternative for absorption refrigeration cycles based on ILs. Finally, the HFC and HFO compounds are competitive at lower temperatures.

4. Conclusions

The successful integration of molecular (COSMO-RS) and process (AspenONE) simulations tools has allowed performing a systematic thermodynamic analysis of a wide sample of commercial refrigerant/IL liquid systems and evaluating the performance in absorption refrigeration cycles. By applying this *a priori* methodology, it has been possible to study the efficiency of refrigeration cycles with a large variety of 7200 system formed by 900 ILs and 8 refrigerants at 60 different operating conditions, which would be otherwise unviable due to the lack of experimental data. An extensive validation of the COSMO-based/Aspen HYSYS approach has been carried out comparing the predictions of relevant properties of pure compounds and mixtures to the available experimental data, obtaining accuracy at the level required in the conceptual design of chemical processes and with the correct qualitative description of IL effects on refrigerant absorption extent. In addition, calculated cycle efficiency parameters were compared to those previously reported in the bibliography for several refrigerant-IL systems, demonstrating an adequate level of accuracy for the conceptual design of industrial processes.

Molecular simulations illustrate that refrigerant/IL phase behavior is determined by the intrinsic volatility of the refrigerant and the chemical nature of both refrigerant and absorbent. Therefore, the selection of an adequate IL absorbent for each refrigerant was successfully conducted to enhance the absorption capacity by promoting favorable solute-solvent intermolecular interactions. As a result, a sample of refrigerant-IL systems was proposed as potential good candidates for absorption refrigeration cycles, which cover a wide range of mass cooling capacities, mixing properties and gas solubilities.

Process simulations of the absorption refrigeration system using several refrigerant-IL pairs (more than 230 refrigerant/IL pairs studied selected in this work as a result of the COSMO-RS analysis or proposed previously in the bibliography at 60 different operating conditions) demonstrated that the selection of the refrigerants is key to reaching high refrigeration capacities with low costs associated to pumping, equipment size and operating cost among others. In addition, the selection of the adequate IL to promote high absorption capacity for each refrigerant has a drastic impact on cycle performance. It was found that higher cycle energy efficiency (described in terms of COP parameter) is

determined by both higher mass cooling capacity of refrigerant and higher absorption capacity of the selected IL. The amount of IL needed (described in terms of total mass flow pumped per evaporator power) was also decreased when increasing the gas solubility of refrigerant in IL and the refrigerant mass cooling capacity. Remarkably, the analysis of operating condition effects on cycle performance revealed that the variation of the evaporator temperature represents a meaningful change in the refrigerant absorption capacity of the IL. In fact, this means that optimum refrigerant-absorbent pairs should be selected depending on the cooling temperature. Water has been shown to have excellent thermodynamic characteristics to be used as refrigerant in absorption refrigeration cycles based on ILs, because of its high enthalpy of vaporization as well as its affinity for ILs. Since their applicability is limited to temperatures above 0°C, methanol and ammonia have proved to be good refrigerants for cooling temperatures between -5°C and 5°C, whereas TFE based systems have better properties at lower temperatures. Hydrocarbon and fluorocarbon refrigerants demonstrated to present less favorable properties to be used in absorption refrigeration cycles, mainly due to their low mass cooling capacity which results in a decrease in energy yield and high flow rates of refrigerant/IL compared to the others systems unless working at very low application temperatures, which means relatively low yields. The group of alkanes (*n*-pentane) has the lowest yields of all systems, which is ascribable to the unfavorable intermolecular interactions with the ILs because of their low polarity.

Acknowledgments

The authors are grateful to Comunidad Autónoma de Madrid for the Project S2013/MAE-2800 and to Ministerio de Economía y Competitividad (MINECO) of Spain for financial support of Project CTQ2017-89441-R. We are very grateful to Centro de Computación Científica de la Universidad Autónoma de Madrid for computational facilities. Marcos Larriba also thanks MINECO for awarding him a Juan de la Cierva-Formación Contract (Reference FJCI-2015-25343).

References

- [1] Stoecker WF JJ. Refrigeration and air conditioning. McGraw-Hill. 1986.
- [2] Moran M.J SHN. Fundamentos de Termodinámica técnica. Editorial Reverte. 2004.
- [3] Balaras CA, Grossman G, Henning HM, Ferreira CAI, Podesser E, Wang L, et al. Solar air conditioning in Europe - an overview. Renewable & Sustainable Energy Reviews. 2007;11:299-314.

- [4] Zhang J, Zhang HH, He YL, Tao WQ. A comprehensive review on advances and applications of industrial heat pumps based on the practices in China. *Appl Energy*. 2016;178:800-25.
- [5] Torrella Alcaraz E. La Producción de frío. Universitat Politècnica de València. 1996.
- [6] Zheng D, Dong L, Huang W, Wu X, Nie N. A review of imidazolium ionic liquids research and development towards working pair of absorption cycle. *Renewable and Sustainable Energy Reviews*. 2014;37:47-68.
- [7] Herold K, Radermacher R, Klein S. *Absorption Chillers and Heat Pumps*, Second Edition: CRC Press; 2016.
- [8] Srihirin P, Aphornratana S, Chungpaibulpatana S. A review of absorption refrigeration technologies. *Renewable & Sustainable Energy Reviews*. 2001;5:343-72.
- [9] Kim YJ, Kim S, Joshi YK, Fedorov AG, Kohl PA. Thermodynamic analysis of an absorption refrigeration system with ionic-liquid/refrigerant mixture as a working fluid. *Energy*. 2012;44:1005-16.
- [10] Khamooshi M, Parham K, Atikol U. Overview of Ionic Liquids Used as Working Fluids in Absorption Cycles. *Adv Mech Eng*. 2013;2013:1-7.
- [11] Shiflett M.B YA. Absorption cycle utilizing ionic liquids as working fluid. WO 2006/08426 A1;2006.
- [12] Seddon KR. Ionic liquids: A taste of the future. *Nat Mater*. 2003;2:363-5.
- [13] Werner S, Haumann M, Wasserscheid P. Ionic Liquids in Chemical Engineering. In: Prausnitz JM, Doherty MF, Segalman RA, editors. *Annual Review of Chemical and Biomolecular Engineering*, Vol 1. Palo Alto: Annual Reviews; 2010. p. 203-30.
- [14] Abumandour E-S, Mutelet F, Alonso D. Are Ionic Liquids Suitable as New Components in Working Mixtures for Absorption Heat Transformers? In: Handy S, editor. *Progress and Developments in Ionic Liquids*. Rijeka: InTech; 2017. p. Ch. 01.
- [15] Yokozeki A, Shiflett MB. Ammonia solubilities in room-temperature ionic liquids. *Ind Eng Chem Res*. 2007;46:1605-10.
- [16] Yokozeki A, Shiflett MB. Water Solubility in Ionic Liquids and Application to Absorption Cycles. *Ind Eng Chem Res*. 2010;49:9496-503.
- [17] Kim KS, Shin BK, Lee H, Ziegler F. Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate, and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide plus trifluoroethanol and 1-butyl-3-methylimidazolium tetrafluoroborate plus trifluoroethanol. *Fluid Phase Equilib*. 2004;218:215-20.
- [18] Wang JZ, Zheng DX. Performance analysis of absorption cooling cycle utilizing TFE-[BMIm] [Br] as working fluid. Kung Cheng Je Wu Li Hsueh Pao/Journal of Engineering Thermophysics. 2008;29:1813-6.
- [19] Martin A, Bermejo MD. Thermodynamic analysis of absorption refrigeration cycles using ionic liquid plus supercritical CO₂ pairs. *J Supercrit Fluids*. 2010;55:852-9.
- [20] Zhang XD, Hu DP. Performance simulation of the absorption chiller using water and ionic liquid 1-ethyl-3-methylimidazolium dimethylphosphate as the working pair. *Appl Therm Eng*. 2011;31:3316-21.
- [21] Ariyadi HM. *Thermodynamic Study on Absorption Refrigeration Systems Using Ammonia/ionic Liquid Working Pairs*: Universitat Rovira i Virgili; 2016.
- [22] Yokozeki A, Shiflett MB. Vapor-liquid equilibria of ammonia plus ionic liquid mixtures. *Appl Energy*. 2007;84:1258-73.

- [23] Dong L, Zheng D, Nie N, Li Y. Performance prediction of absorption refrigeration cycle based on the measurements of vapor pressure and heat capacity of H₂O+[DMIM]DMP system. *Appl Energy*. 2012;98:326-32.
- [24] Yoon Jo K, Kim S, Joshi YK, Fedorov AG, Kohl PA. Thermodynamic analysis of an absorption refrigeration system with ionic-liquid/refrigerant mixture as a working fluid. *Energy*. 2012;44:1005-16.
- [25] Kim S, Kohl PA. Theoretical and Experimental Investigation of an Absorption Refrigeration System Using R134a/[bmim][PF₆] Working Fluid. *Ind Eng Chem Res*. 2013;52:13459-65.
- [26] Kim S, Kohl PA. Analysis of [hmim][PF₆] and [hmim][Tf₂N] ionic liquids as absorbents for an absorption refrigeration system. *International Journal of Refrigeration*. 2014;48:105-13.
- [27] Kim S, Patel N, Kohl PA. Performance Simulation of Ionic Liquid and Hydrofluorocarbon Working Fluids for an Absorption Refrigeration System. *Ind Eng Chem Res*. 2013;52:6329-35.
- [28] Kim YJ, Gonzalez M. Exergy analysis of an ionic-liquid absorption refrigeration system utilizing waste-heat from datacenters. *International Journal of Refrigeration*. 2014;48:26-37.
- [29] Wang M, Infante Ferreira CA. Absorption heat pump cycles with NH₃ – ionic liquid working pairs. *Appl Energy*. 2017;204:819-30.
- [30] Ayoub DS, Currás MR, Salavera D, García J, Bruno JC, Coronas A. Performance analysis of absorption heat transformer cycles using ionic liquids based on imidazolium cation as absorbents with 2,2,2-trifluoroethanol as refrigerant. *Energy Conversion and Management*. 2014;84:512-23.
- [31] Boman DB, Hoysall DC, Staedter MA, Goyal A, Ponkala MJ, Garimella S. A method for comparison of absorption heat pump working pairs. *International Journal of Refrigeration*. 2017;77:149-75.
- [32] Klamt A. Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. *The Journal of Physical Chemistry*. 1995;99:2224-35.
- [33] Klamt A. COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design: Elsevier; 2005.
- [34] Klamt A, Eckert F, Arlt W. COSMO-RS: An Alternative to Simulation for Calculating Thermodynamic Properties of Liquid Mixtures. *Annual Review of Chemical and Biomolecular Engineering*. 2010;1:101-22.
- [35] Lin ST, Sandler SI. A priori phase equilibrium prediction from a segment contribution solvation model. *Ind Eng Chem Res*. 2002;41:899-913.
- [36] Palomar J, Gonzalez-Miquel M, Bedia J, Rodriguez F, Rodriguez JJ. Task-specific ionic liquids for efficient ammonia absorption. *Sep Purif Technol*. 2011;82:43-52.
- [37] Ruiz E, Ferro VR, de Riva J, Moreno D, Palomar J. Evaluation of ionic liquids as absorbents for ammonia absorption refrigeration cycles using COSMO-based process simulations. *Appl Energy*. 2014;123:281-91.
- [38] Palomar J, Gonzalez-Miquel M, Polo A, Rodriguez F. Understanding the Physical Absorption of CO₂ in Ionic Liquids Using the COSMO-RS Method. *Ind Eng Chem Res*. 2011;50:3452-63.

- [39] Gonzalez-Miquel M, Bedia J, Abrusci C, Palomar J, Rodriguez F. Anion Effects on Kinetics and Thermodynamics of CO₂ Absorption in Ionic Liquids. *J Phys Chem B*. 2013;117:3398-406.
- [40] Bedia J, Ruiz E, de Riva J, Ferro VR, Palomar J, Rodriguez JJ. Optimized Ionic Liquids for Toluene Absorption. *Aiche J*. 2013;59:1648-56.
- [41] Ruiz E, Ferro VR, Palomar J, Ortega J, Rodriguez JJ. Interactions of Ionic Liquids and Acetone: Thermodynamic Properties, Quantum-Chemical Calculations, and NMR Analysis. *J Phys Chem B*. 2013;117:7388-98.
- [42] Fallanza M, Gonzalez-Miquel M, Ruiz E, Ortiz A, Gorri D, Palomar J, et al. Screening of RTILs for propane/propylene separation using COSMO-RS methodology. *Chem Eng J*. 2013;220:284-93.
- [43] Gonzalez-Miquel M, Palomar J, Rodriguez F. Selection of Ionic Liquids for Enhancing the Gas Solubility of Volatile Organic Compounds. *J Phys Chem B*. 2013;117:296-306.
- [44] Babiker OE, Mahadzi S, Mutalib MIA. Molecular Simulation for Piperazinium based ILs: Effects of Alkyl Chain, Concentration and Anions on Henry's constants. In: Ahmed I, editor. *Process and Advanced Materials Engineering*. Stafa-Zurich: Trans Tech Publications Ltd; 2014. p. 448-53.
- [45] Zhao X, Yang Q, Xu D, Bao Z, Zhang Y, Su B, et al. Design and screening of ionic liquids for C₂H₂/C₂H₄ separation by COSMO-RS and experiments. *Aiche J*. 2015;61:2016-27.
- [46] Liu XY, Huang Y, Zhao YS, Gani R, Zhang XP, Zhang SJ. Ionic Liquid Design and Process Simulation for Decarbonization of Shale Gas. *Ind Eng Chem Res*. 2016;55:5931-44.
- [47] Dong K, Liu X, Dong H, Zhang X, Zhang S. Multiscale Studies on Ionic Liquids. *Chemical Reviews*. 2017;117:6636-95.
- [48] Bedia J, Palomar J, Gonzalez-Miquel M, Rodriguez F, Rodriguez JJ. Screening ionic liquids as suitable ammonia absorbents on the basis of thermodynamic and kinetic analysis. *Sep Purif Technol*. 2012;95:188-95.
- [49] Gonzalez-Miquel M, Talreja M, Ethier AL, Flack K, Switzer JR, Biddinger EJ, et al. COSMO-RS Studies: Structure-Property Relationships for CO₂ Capture by Reversible Ionic Liquids. *Ind Eng Chem Res*. 2012;51:16066-73.
- [50] Kurnia KA, Pinho SP, Coutinho JAP. Designing ionic liquids for absorptive cooling. *Green Chemistry*. 2014;16:3741-5.
- [51] Balamuru VG, Ibrahim OM, Barnett SM. Simulation of ternary ammonia-water-salt absorption refrigeration cycles. *Int J Refrig-Rev Int Froid*. 2000;23:31-42.
- [52] Yokozeki A. Theoretical performances of various refrigerant-absorbent pairs in a vapor-absorption refrigeration cycle by the use of equations of state. *Appl Energy*. 2005;80:383-99.
- [53] Darwish NA, Al-Hashimi SH, Al-Mansoori AS. Performance analysis and evaluation of a commercial absorption-refrigeration water-ammonia (ARWA) system. *Int J Refrig-Rev Int Froid*. 2008;31:1214-23.
- [54] Somers C, Mortazavi A, Hwang Y, Radermacher R, Rodgers P, Al-Hashimi S. Modeling water/lithium bromide absorption chillers in ASPEN Plus. *Appl Energy*. 2011;88:4197-205.
- [55] Ferro VR, Ruiz E, de Riva J, Palomar J. Introducing process simulation in ionic liquids design/selection for separation processes based on operational and economic criteria through the example of their regeneration. *Sep Purif Technol*. 2012;97:195-204.
- [56] de Riva J, Ferro VR, Moreno D, Diaz I, Palomar J. Aspen Plus supported conceptual design of the aromatic-aliphatic separation from low aromatic content naphtha using 4-

methyl-N-butylpyridinium tetrafluoroborate ionic liquid. *Fuel Process Technol.* 2016;146:29-38.

[57] Ferro VR, Ruiz E, Tobajas M, Palomar JF. Integration of COSMO-based methodologies into commercial process simulators: Separation and purification of reuterin. *Aiche J.* 2012;58:3404-15.

[58] Ferro VR, de Riva J, Sanchez D, Ruiz E, Palomar J. Conceptual design of unit operations to separate aromatic hydrocarbons from naphtha using ionic liquids. COSMO-based process simulations with multi-component "real" mixture feed. *Chem Eng Res Des.* 2015;94:632-47.

[59] Díaz I, Palomar J, Rodríguez M, de Riva J, Ferro V, González EJ. Ionic liquids as entrainers for the separation of aromatic–aliphatic hydrocarbon mixtures by extractive distillation. *Chemical Engineering Research and Design.* 2016;115, Part B:382-93.

[60] de Riva J, Suarez-Reyes J, Moreno D, Díaz I, Ferro V, Palomar J. Ionic liquids for post-combustion CO₂ capture by physical absorption: Thermodynamic, kinetic and process analysis. *International Journal of Greenhouse Gas Control.* 2017;61:61-70.

[61] V. R. Ferro, C. Moya, D. Moreno, R. Santiago, J. de Riva, G. Pedrosa, et al. Ionic Liquid database for AspenONE simulators (ILUAM).

[62] Ferro VR, Moya C, Moreno D, Santiago R, de Riva J, Pedrosa G, et al. Enterprise ionic liquids database (ILUAM) for its use in Aspen ONE® programs suite with COSMO-based property methods. *Ind Eng Chem Res.* 2018: DOI: 10.1021/acs.iecr.7b04031.

[63] Eckert F, Klamt A. COSMOtherm, Version C3.0, Release 16.01;. COSMOlogic GmbH & Co KG, Leverkusen, Germany. 2015.

[64] TURBOMOLE GmbH G, 2016. Turbomole V 7.1 2016.

[65] Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical review A, General physics.* 1988;38:3098-100.

[66] Perdew JP, Yue W. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Physical review B, Condensed matter.* 1986;33:8800-2.

[67] Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R. Auxiliary basis sets to approximate Coulomb potentials (*Chem. Phys. Letters* 240 (1995) 283-290). *Chem Phys Lett.* 1995;242:652-60.

[68] Eichkorn K, Weigend F, Treutler O, Ahlrichs R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theor Chem Acc.* 1997;97:119-24.

[69] Larriba M, de Riva J, Navarro P, Moreno D, Delgado-Mellado N, García J, et al. COSMO-based/Aspen Plus process simulation of the aromatic extraction from pyrolysis gasoline using the {[4empy][NTf2] + [emim][DCA]} ionic liquid mixture. *Sep Purif Technol.* 2018;190:211-27.

[70] Lin ST, Mathias PM, Song Y, Chen CC, Si. S. Improvements of Phase-Equilibrium Predictions for Hydrogen-Bonding Systems from a New Expression for COSMO Solvation Models. *AIChE Annual Meeting.* Indianapolis 2002.

[71] Palomar J, Ferro VR, Torrecilla JS, Rodriguez F. Density and molar volume predictions using COSMO-RS for ionic liquids. An approach to solvent design. *Ind Eng Chem Res.* 2007;46:6041-8.

[72] Kazakov A, Magee JW, Chirico RD, Paulechka E, Diky V, Muzny CD, et al. NIST Standard Reference Database 147: NIST Ionic Liquids Database - (ILThermo)", Version 2.0. National Institute of Standards and Technology, Gaithersburg MD, 20899.