



## Prediction of CO<sub>2</sub> chemical absorption isotherms for ionic liquid design by DFT/COSMO-RS calculations



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### ABSTRACT

Ionic liquids with an aprotic heterocyclic anion (AHA-ILs) is a promising family of compounds to overcome the challenge of CO<sub>2</sub> capture. In this work, a computational methodology has been developed to predict CO<sub>2</sub> chemical absorption isotherms in AHA-ILs without the need of experimental data. This methodology combines DFT and COSMO-RS calculations allowing the design of new chemical absorbents for CO<sub>2</sub> capture. The CO<sub>2</sub> physical absorption equilibrium constants (Henry's law constants), chemical equilibrium constants and reaction enthalpies were reliably predicted by proposed computational approach, by means of comparison to available experimental data of 9 different AHA-ILs. Finally, 15 newly designed AHA-ILs were evaluated to demonstrate the flexibility of the DFT/COSMO-RS tool by predicting their CO<sub>2</sub> absorption isotherms. The evaluated absorbents compromise very different behaviors: from physical absorption to reactions completely displaced toward products at very low CO<sub>2</sub> partial pressure, emphasizing the extremely tunable character of AHA-ILs. Current results will definitively contribute to link molecular and processes scales in the research of new CO<sub>2</sub> capture technology based on ILs.

### Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the main contributors to the greenhouse effect, whose emissions reached more than 33 Gt in 2019 [1]. For this reason, the development of new technologies able to efficiently remove the CO<sub>2</sub> is a great challenge to the actual society [2–4]. In this field, the use of ionic liquids (ILs) [5,6] and specially those presenting CO<sub>2</sub> chemical capture [7,8] were proposed as a promising technology due to their outstanding properties as solvents, such as their high sorption capacity, and their negligible vapor pressure, among others. Between the numerous families of ILs capable to react with CO<sub>2</sub> molecule, like acetate [9,10] or amino-acid based ILs [11,12], the group of ILs compromising aprotic heterocyclic anions (AHAs) [13] were proved as a competitive option when considering the complete capture process [14].

AHA-ILs present a 1:1 stoichiometric reversible reaction between CO<sub>2</sub> and the heterocyclic nitrogen atom [15]. This reaction is usually displaced to products, being traduced into high absorption capacities at low CO<sub>2</sub> partial pressures [16]. In addition to that high absorption capacity, AHA-ILs present lower enthalpies of reaction with CO<sub>2</sub>

(–35 to –55 kJ/mol) than traditional chemical absorbents such amines (–84 kJ/mol by EDA aqueous solutions [17]), what may mean a reduction of the energy requirements in the solvent regeneration stage. On the other hand, it was found the value of the reaction enthalpy as a critical parameter in the performance of AHA-ILs for CO<sub>2</sub> chemical capture at process scale. More exothermic reaction implies higher CO<sub>2</sub> absorption capacity and, consequently, lower solvent requirements. Besides, it increases the temperature in the absorption column, what improves the mass transfer rate due to the viscosity reduction and, simultaneously, decreases the energy duty required to absorbent regeneration. All these combined effects greatly increase the efficacy in the capture process [14,18,19]. Additional to this, the properties of AHA-ILs and specially their reactivity with CO<sub>2</sub> can be fine-tuned by modification of the substituents of the aromatic ring [13], allowing almost infinite possibilities to design ILs with optimal properties for each particular application.

However, the selection of the optimal IL becomes an inaccessible task by traditional means due to the synthesis and experimental work required to test the vast amount of possible AHA-ILs. Therefore, the use of computational approaches makes possible the evaluation of a great number of possibilities before selecting a few candidates for experimen-

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tal testing. At this regard, our research group has developed over the last years a multiscale research strategy to propose new separation processes based on ILs using a combination of molecular and process simulation [20]. This methodology has been successfully applied to operations of very different nature such as VOC absorption [21], aromatic/aliphatic extraction [22], absorption refrigeration cycles [23] or CO<sub>2</sub> physical absorption [24] among others. This methodology uses DFT and COSMO-RS as *a priori* computational methods to analyze the thermodynamic behavior of IL-CO<sub>2</sub> system, for the preliminary selection of adequate solvent properties. Posterior incorporation of ILs in Aspen Plus commercial process simulator allows introducing technical and economic factors [25] in the selection of ILs for a practical application.

The main advantage of COSMO-based/Aspen methodology is that no experimental data is needed to evaluate the process performance of ILs as CO<sub>2</sub> physical absorbents [26]. However, in the case of chemical absorption of CO<sub>2</sub> in AHA-IL, at the moment, it is required the introduction of experimental reaction enthalpy and equilibrium constants calculated from experimental absorption isotherms for properly data prediction [14,18].

The aim of this work is to develop an *a priori* computational methodology to predict the CO<sub>2</sub> chemical absorption isotherms in AHA-IL systems, to be used in commercial process simulator without any need of experimental work. For this purpose, the Henry's law constants of CO<sub>2</sub> in AHA-IL (physical absorption) and equilibrium constants of CO<sub>2</sub>+AHA-IL reactions (chemical absorption) were calculated by, respectively, COSMO-RS and DFT methods. First DFT calculations using six different computational approaches were tested to obtain the enthalpy and free Gibbs energy of reaction for a series of conventional chemical reactions, in order to predict reliable thermochemical data of CO<sub>2</sub>+AHA-IL reaction. Once validated, the calculated equilibrium constants of physical and chemical absorption were used to predict CO<sub>2</sub> absorption isotherms in AHA-ILs previously reported in bibliography to measure the uncertainty of the method. Finally, several new AHA-ILs were designed by molecular simulation and their correspondent CO<sub>2</sub> absorption isotherms and reaction enthalpies were calculated to demonstrate the ability of this methodology to use the tunability of the AHA-ILs to propose new untested compounds with desired properties for CO<sub>2</sub> capture.

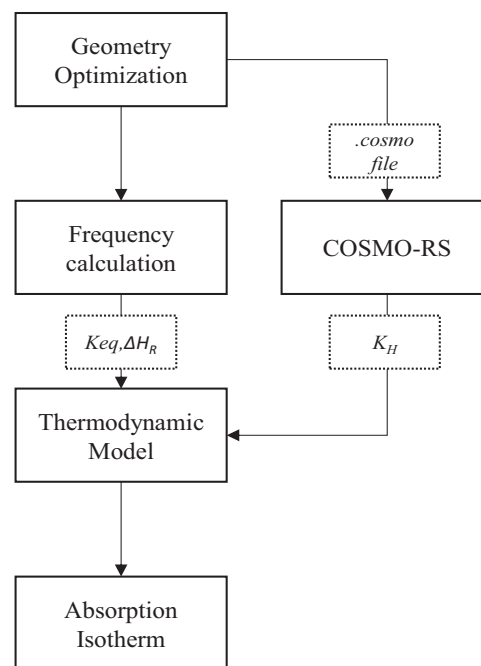
### Computational details

The computational methodology used to obtain absorption isotherms from COSMO-RS and quantum chemistry calculations is depicted in the Scheme 1. As summary, the first step is the optimization of the molecular geometries of the ILs and the reaction products. From these geometries and using COSMO continuum solvation method, ".COSMO" file is obtained to determine Henry's law constants ( $K_H$ ) of CO<sub>2</sub> in the ILs using COSMO-RS theory. The reaction enthalpy ( $\Delta H_R$ ) and equilibrium constant ( $K_{eq}$ ) were determined from the thermodynamic data obtained through vibrational frequency calculations. Finally, all this information is fed into a thermodynamic model that allows obtaining the amount of CO<sub>2</sub> absorbed in IL as a function of CO<sub>2</sub> partial pressure.

#### Molecular geometry optimization

All the components and ILs geometries were calculated by using Turbomole 7.4 software [27]. The geometries were evaluated at six different DFT levels collected in Table 1. Three different functionals were used: (i) B-P86 [28], as a standard used by COSMO-RS software; (ii) B3-LYP [29]; and (iii) M06-2X [30], two of the most wide DFT used functionals. All of them paired with def2-TZVP basis set [31] using DFT-D3 [32] dispersion term, in addition to the use of COSMO solvation for solvent effect [33] was also evaluated. In the case of reaction products of ILs with CO<sub>2</sub>, all the CO<sub>2</sub> binding sites were optimized, and the lowest energy structure was only considered for subsequent steps.

Vibrational frequency calculations were performed to confirm the presence of an electronic energy minimum, in each case. Then, zero-



**Scheme 1.** Methodology for the determination of CO<sub>2</sub> chemical absorption isotherms in AHA-ILs through COSMO-RS and quantum chemical calculations.

point vibrational energy was added to calculations for absolute enthalpies of formation at 0 K, allowing to calculate thermochemical properties to the frequency single-point electronic energy calculation. Thermal corrections using the partition function at 298.15 K were introduced using "freeh" Turbomole module and a scaling factor of 0.95 [34] to calculate absolute enthalpies and entropies of the molecules at working temperature. Finally, thermochemical data for the reactions were calculated as the sum of the individual contributions ( $H_i$ ,  $G_i$ ,  $S_i$ ) multiplied by the correspondent stoichiometric coefficient ( $\nu$ ) (Eq. (1)).

$$\Delta H_R = \sum \nu_i H_i \quad (1)$$

Reaction free Gibbs energy ( $\Delta G_R$ ) and entropy of reaction ( $\Delta S_R$ ) were calculated using an analogous expression to Eq (1). In the case of AHA-ILs only the anion is considered in the reactions, as the available data shares a common cation and the computational expenses of including the cation are not expected to reasonably improve the results [13].

#### COSMO-RS calculations

First, COSMO files for each IL used were generated by using Turbomole 7.4 as independent ions at B-P86/TZVP level. After that, COSMO-RS calculations using COMOSThermX 19 software [35] were carried out to calculate Henry's solubility equilibrium constant of CO<sub>2</sub> in the different AHA-ILs at different temperatures.

**Table 1**  
Different computational approaches used in this work.

Approximation	Functional	Basis Set	COSMO solvation
GAS-B-P86	B-P86	def2-	NO
GAS-B3-LYP	B3-LYP	TZVP	
GAS-M06-2X	M06-2X		
COSMO-B-P86	B-P86	def2-	YES
COSMO-B3-LYP	B3-LYP	TZVP	
COSMO-M06-2X	M06-2X		

### Thermodynamic model for absorption isotherm

CO<sub>2</sub> chemical absorption in AHA-ILs is considered a 1:1 reversible reaction ( $IL + CO_2 \rightleftharpoons IL-CO_2$ ), where 1 molecule of CO<sub>2</sub> binds to the heterocyclic N of the anion to form the reaction product (IL-CO<sub>2</sub>). To describe the full absorption isotherm, a thermodynamic model has been successfully applied in previous works [13, 14, 18]. It combines the physical absorption using Henry's Law with a traditional chemical equilibrium constant (Eq. (2))

$$x_{CO_2} = \frac{P_{CO_2}}{K_H}; K_{eq} = \frac{x_{IL-CO_2}}{x_{IL} \cdot x_{CO_2}} \quad (2)$$

Where  $x_i$  is the molar fraction of the different components,  $P_{CO_2}$  is the partial pressure of CO<sub>2</sub> and  $K_H$  and  $K_{eq}$  are the Henry's and chemical equilibrium constants, respectively. These two expressions can be combined to calculate the amount of CO<sub>2</sub> absorbed as a function of CO<sub>2</sub> partial pressure at it is shown in Eq. (3)

$$z = \frac{P_{CO_2}}{K_H - P_{CO_2}} + \frac{K_{eq} \cdot P_{CO_2} \cdot C}{K_H + K_{eq} \cdot P_{CO_2}} \quad (3)$$

Where  $z$  is the amount of CO<sub>2</sub> absorbed in mol of CO<sub>2</sub> per mol of IL, and  $C$  is an empirical factor that represents the availability of the IL to react, that is found to be around 0.9 for AHA-ILs [13]. The key parameters that allow the use of these expressions are the physical and chemical absorption equilibrium constants. As we previously described, Henry's constant can be obtained from COSMO-RS calculations, and the reaction equilibrium constant can be obtained from the reaction Gibbs free energy (Eq. (4))

$$\ln K_{eq} = \frac{-\Delta G_R}{RT} \quad (4)$$

#### Temperature effect

It is possible to determine all the parameters required at each temperature of interest. However, some considerations are made in order to facilitate the use of the multiscale computational methodology. In the case of physical absorption, the gas solubility of CO<sub>2</sub> in AHA-IL was calculated at different temperatures and an Arrhenius relationship is used to describe the Henry's law constant (Eq. (5)) dependence with temperature.

$$\ln K_H = A + \frac{B}{T} \quad (5)$$

On the other hand, the free Gibbs energy definition (Eq. (6)) in combination with Eq. (4) is used to achieve Van't Hoff relationship (Eq. (7)) that allows calculating  $K_{eq}$  of CO<sub>2</sub>+AHA-IL reaction at different temperatures (from  $\Delta H_R$  and  $\Delta S_R$  data at 298.15 K).

$$\Delta G_R = \Delta H_R - T \cdot \Delta S_R \quad (6)$$

$$\ln K_{eq} = \frac{\Delta S_R}{R} - \frac{\Delta H_R}{RT} \quad (7)$$

## Results

### Prediction of Henry's equilibrium constants of CO<sub>2</sub> in ILs

The first step to predict the CO<sub>2</sub> chemical absorption isotherm in AHA-ILs is to calculate the amount of CO<sub>2</sub> physically absorbed in the liquid. This is estimated through Henry's equilibrium constant (eq. (2)). This parameter is hard to obtain experimentally in the case of AHA-ILs, since the physical and chemical absorption are coupled, being the amount of CO<sub>2</sub> physically dissolved, especially at low partial pressures, almost undetectable. COSMO-RS method has been proved as an useful tool to estimate the gas solubility in ILs [21, 36]. A validation analysis was done in this work using experimental data found in literature for 18

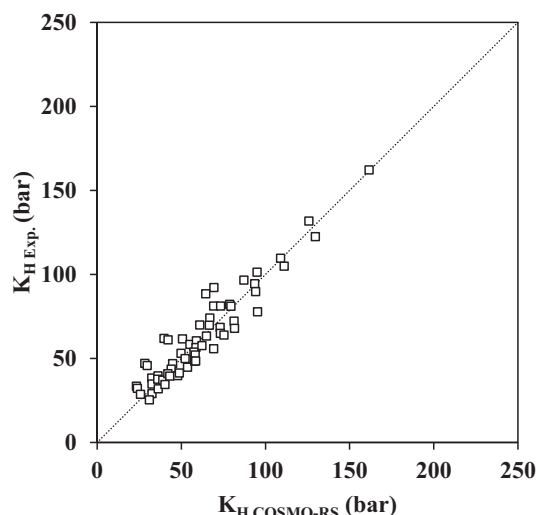


Fig. 1. Experimental Henry's constant values compared to corrected COSMO-RS predictions for several CO<sub>2</sub> physical absorption ILs.

Table 2

Equilibrium Henry's constant at 293.15 K and temperature dependence parameters for eq. (5) of AHA-ILs/CO<sub>2</sub> systems.

AHA-IL	$K_H$ (bar)	A	B
[P <sub>666,14</sub> ][Inda]	33.5	9.92	-1878.7
[P <sub>666,14</sub> ][Bnlm]	33.6	9.95	-1887.6
[P <sub>666,14</sub> ][2-SCH <sub>3</sub> Bnlm]	31.6	10.03	-1928.9
[P <sub>666,14</sub> ][3-CH <sub>3</sub> -5-CF <sub>3</sub> Pyra]	35.5	9.86	-1842.6
[P <sub>666,14</sub> ][3-CF <sub>3</sub> Pyra]	35.2	9.89	-1855.9
[P <sub>666,14</sub> ][6-BrBnlm]	31.7	9.98	-1913.6
[P <sub>666,14</sub> ][2-CNPyra]	32.2	10.05	-1929.0
[P <sub>666,14</sub> ][4-Triaz]	33.6	9.93	-1879.7
[P <sub>666,14</sub> ][3-Triaz]	33.0	9.94	-1888.1

IL-CO<sub>2</sub> systems, only presenting physical absorption at temperatures between 283 and 343 K, (60 data points) (Table S1 in Supplementary Material). Predictions show a linear trend compared to literature ( $R^2=0.9$ ) with a slope of 0.73, meaning that COSMO-RS is systematically underestimating solubility of CO<sub>2</sub> in ILs. In order to increase the accuracy of COSMO-RS predictions, the slope of the fitting is used as correction factor of calculated  $K_H$  values. Fig. 1 presents experimental vs corrected COSMO-RS  $K_H$  values of CO<sub>2</sub> in ILs for total of 60 points. A reasonably good correlation between experimental and predicted data is observed, with an average deviation of 7.2 bar.

A sample of 9 AHA-ILs with available experimental data in literature [13] were selected to test the proposed methodology. All these AHA-ILs shares the trihexyl(tetradecyl)phosphonium cation ([P<sub>666,14</sub>]) and different AHA anions. Henry's equilibrium constants of CO<sub>2</sub> for the AHA-ILs used in this work are calculated using corrected COSMO-RS methodology as explained above. The results in Table 2 shows how physical absorption is favored (relatively low  $K_H$  values; see Fig. 1) due to the bulky phosphonium cation, with nearly none effect by changing the anion. These results agree with previous experimental results for traditional ILs [37,38] and AHA-ILs [39], where the CO<sub>2</sub> solubility is governed by the cation selection and promoted using bulky cations with longer alkyl chains.

### Prediction of thermochemical data of CO<sub>2</sub>+AHA-IL reaction

The published experimental data on standard reaction enthalpies and free energies of ILs with CO<sub>2</sub> is scarce to perform an adequate method

**Table 3**

Statistical parameters derived from fitting experimental to calculated  $\Delta H_R$  values.

Level	B-P86		B3-LYP		M06-2X	
	GAS	COSMO	GAS	COSMO	GAS	COSMO
RAAD* (%)	20.4%	10.3%	14.5%	7.4%	11.5%	6.9%
AAD* (kJ/mol)	88.34	28.24	66.80	13.25	36.40	35.17
Slope	1.126	1.032	1.091	0.999	1.045	0.958
Intersection	15.6	4.7	8.4	-2.0	9.7	-0.9
R <sup>2</sup>	0.9989	0.9996	0.9994	0.9997	0.9997	0.9998

\* RAAD: Relative Average Absolute Deviation; AAD: Average Absolute Deviation.

**Table 4**

Statistical parameters derived from fitting experimental to calculated  $\Delta G_R$  values.

Level	B-P86		B3-LYP		M06-2X	
	GAS	COSMO	GAS	COSMO	GAS	COSMO
RAAD* (%)	26.0%	17.2%	14.8%	18.4%	18.9%	15.8%
AAD* (kJ/mol)	112.84	50.34	91.33	27.18	62.25	17.93
Slope	1.166	1.064	1.129	1.028	1.081	0.986
Intersection	17.1	7.5	9.5	0.5	11.8	2.4
R <sub>2</sub>	0.9991	0.9998	0.9994	0.9999	0.9995	0.9998

\* RAAD: Relative Average Absolute Deviation; AAD: Average Absolute Deviation.

validation. For this reason, a set of 24 conventional chemical reactions (Table S2) with their corresponding standard reaction enthalpies and Gibbs free energies are collected to preliminary select an adequate level of quantum chemistry calculations. These reactions compromise a range between -3000 kJ/mol (for strongly exothermic combustion reactions) up to 242 kJ/mol (for endothermic water dissociation). Then, enthalpy and free Gibbs energy of reaction were calculated by six different computational approaches, using three different functionals (B-P86, B3-LYP and M06-2X) and analyzing the use of COSMO solvation method to describe solvent effects. Table 3 collects some statistical parameters relating the quality of the reaction enthalpy ( $\Delta H_R$ ) predictions. The complete summary of the calculated data can be found in Tables S2 and S3 of Supplementary Material.

All the computational approaches proposed reproduce reasonably well the experimental data, with R<sup>2</sup> values greater than 0.999 in all cases and slopes close to 1. The absolute error of the method ranges

from 13 to 89 kJ/mol. DFT results reveal that using COSMO solvation effect greatly improves the accuracy on the predicted  $\Delta H_R$  values, reducing relative deviations to roughly the half compared to the equivalent method without solvation effect. A comparison between functionals using solvation effect can be found in Fig. 2A. The three proposed functionals predict with reasonable accuracy the experimental  $\Delta H_R$  values, with a relative deviation lower than 10%, being B3-LYP the one that shows better results, showing an absolute deviation of 13.25 kJ/mol (Table 2). The residual analysis in Fig. 2B shows that B-P86 and M06-2X are biased from the experimental trend, while a slope deviated around 4% respect to the unity. A closer look to the interval of -300 – 300 kJ/mol -which is the expected interval of the CO<sub>2</sub>+AHA-IL reactions- shows a more realistic picture of the prediction accuracy of tested computational approaches: low absolute deviations [11.0 kJ/mol (B-P86), 8.1 kJ/mol (B3-LYP) and 7.5 kJ/mol (M06-2X)] are obtained, which lies in the uncertainty typically reported for DFT methods [40].

A similar analysis can be made to the values of free Gibbs energy of reaction. Table 4 collects the parameters resulting from the statistical analysis of the predicted  $\Delta G_R$  data by DFT calculations. As in the previous case, COSMO solvation effect improves quantitatively the obtained results, decreasing the average deviations by a factor of three, reaching an accuracy of 20–30 kJ/mol for B3-LYP and M06-2X.

Data and residual analysis in Fig. 3 indicate that B-P86 and B3-LYP functionals, using COSMO solvent effects, are underestimating free Gibbs energy values, especially for more exothermic reactions, leading to higher error values (Table 4). The highest percentage deviations are originated at  $\Delta G_R$  values close to zero, where a small error is highly penalized.

These deviations at values close to zero are of special interest because it is the range where reversible reactions lie in. Attending to these cases, the uncertainty on the free Gibbs energy values is reduced to around 10 kJ/mol (13.7 kJ/mol for B-P86, 9.7 kJ/mol for B3-LYP and 12.5 kJ/mol for M06-2X).

From these results, B3-LYP and M06-2X methods using COSMO solvation effects are selected to calculate the CO<sub>2</sub>+AHA-ILs thermochemistry. Fig. 4 collects the comparison between experimental and calculated  $\Delta H_R$  values. The experimental values show how the CO<sub>2</sub> chemical absorption process in AHA-ILs is slightly exothermic, with close values between the ILs studied, ranging between -54 and -37 kJ/mol. The comparison between the two different computational approaches used show very similar trend, with M06-2X method systematically overestimating  $\Delta H_R$  by around 15 kJ/mol. Overall, B3-LYP calculations describes much more accurately the reaction enthalpies of CO<sub>2</sub>+AHA-IL, with a mean deviation of 4.9 kJ/mol. For this reason, only B3-LYP is

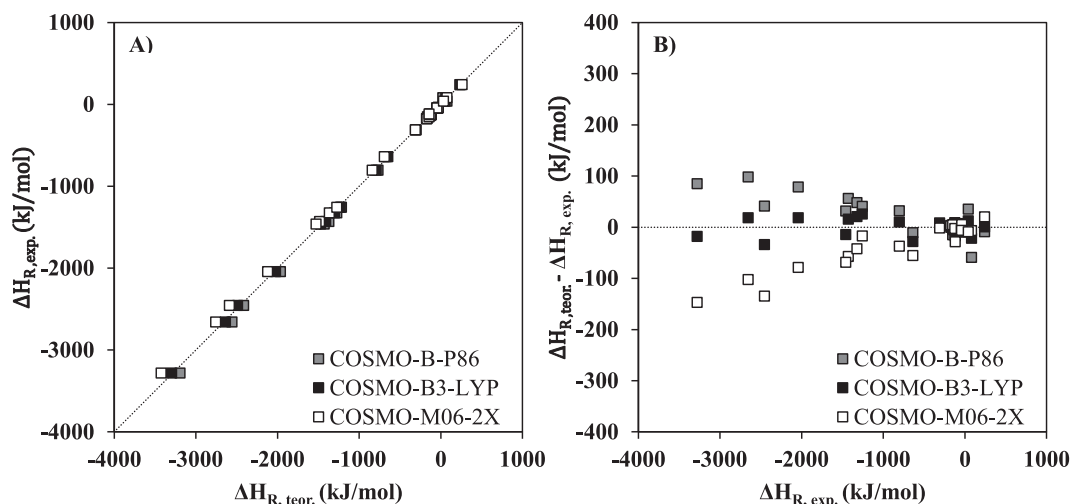


Fig. 2. Experimental vs predicted standard reaction enthalpies (A) and residual plot of the calculated data (B).

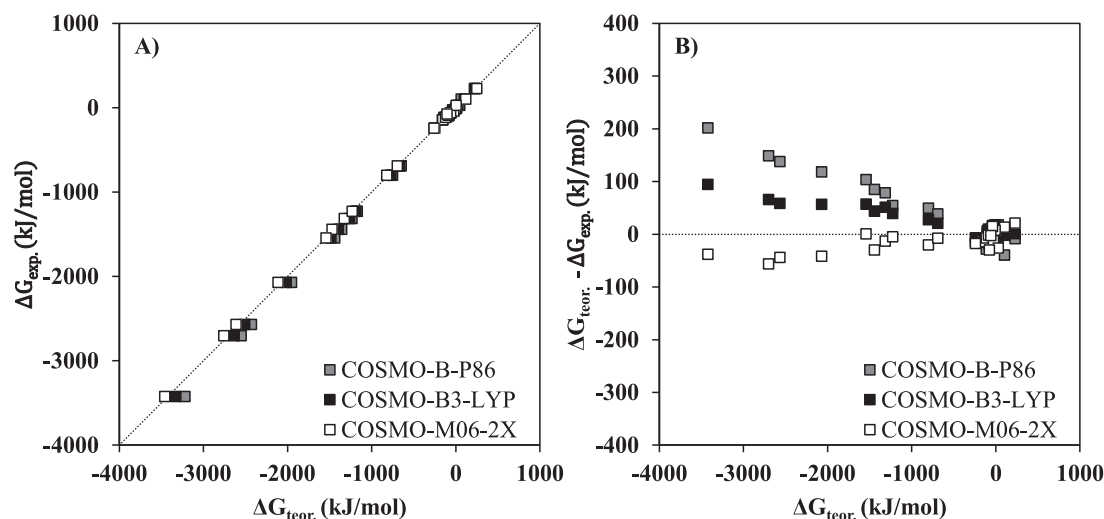


Fig. 3. Experimental vs predicted standard free Gibbs energies (A) and residual plot of the calculated data (B).

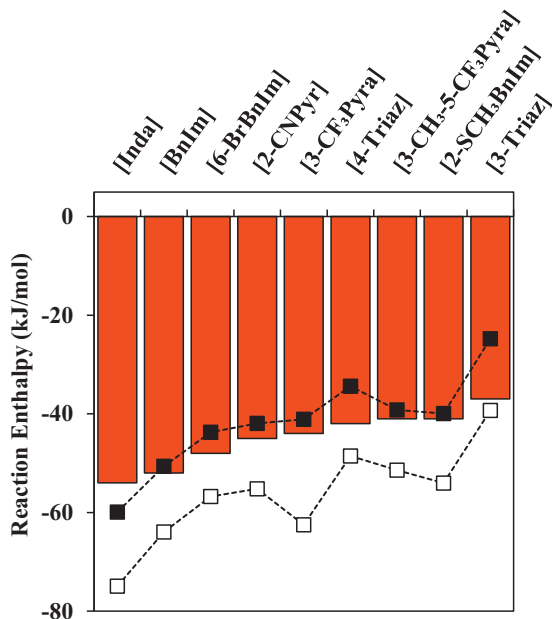


Fig. 4. Calculated  $\Delta H_R$  values using B3-LYP (■) and M06-2X (□) functionals compared to experimental values (bars).

considered in further steps. Table 5 collects the thermochemical data ( $\Delta H_R$ ,  $\Delta S_R$ ,  $\Delta G_R$  and  $K_{eq}$ ) of all  $\text{CO}_2$ +AHA-IL systems calculated using B3-LYP / COSMO approach at 298.15 K.

To compare  $K_{eq}$  values obtained by DFT calculations, the experimental  $K_{eq}$  values are obtained from fitting experimental  $\text{CO}_2$  absorption isotherms in AHA-ILs to the thermodynamic model (eq. (3)) and using Henry's constant values collected in Table 2. Fig. 5A shows the results from this adjustment. It is clear that the proposed thermodynamic model is able to reproduce the shape of the experimental isotherms with great precision, obtaining  $R^2$  values greater than 0.99 in all the cases. The AHA-ILs studied present very different behaviors, from very low  $\text{CO}_2$  chemical absorption for [3-Triaz] anion to the case of [Inda] anion, whose equilibrium is totally displaced to products at very low partial pressures of  $\text{CO}_2$  (Table 5). Fig. 5B compares experimental and

calculated  $K_{eq}$  values, showing the general good predictability of the selected DFT approach, being the mayor deviations found for  $K_{eq}$  values  $\gg 20,000$  or  $\sim 0$  kJ/mol.

#### Prediction of $\text{CO}_2$ +AHA-IL chemical absorption isotherms

The  $\text{CO}_2$  chemical absorption isotherms were calculated for 9 AHA-ILs using Eq. (3) and thermodynamic parameters collected in Table 2 and Table 5. The resulting data were plotted among the experimental data from literature [13] in Fig. 6.

For most of the AHA-ILs the theoretical data match the experimental trend, specially for the most favourable cases such as [Inda] or [BnIm] anions, demonstrating the reliability of the selected DFT/COSMO-RS approach to predict the  $\text{CO}_2$  chemical absorption isotherm in AHA-ILs. Regarding the ILs based on [3-Triaz] and [4-Triaz] anions, it seems that  $\text{CO}_2$  solubility in these AHA-ILs were a bit underestimated, due to the observed small deviations in  $\Delta H_R$  values in Fig. 4.

Finally, the effect of temperature on the  $\text{CO}_2$  absorption is analyzed for the particular case of [P<sub>666,14</sub>][2-CNPyrr]. Having complete absorption isotherms at different operating temperatures is the especial interest for process design of new  $\text{CO}_2$  capture applications. Regeneration of IL occurs normally by a combination of rising the temperature of the solvent and lowering partial pressure of  $\text{CO}_2$ , reverting chemical reaction [14]. For this purpose, Eq. (5) and 7 were used to calculate  $K_{eq}$  and  $K_H$  for [P<sub>666,14</sub>][2-CNPyrr] at a wide range of temperatures, being the resulting absorption isotherms shown in Fig. 7.

The predicted isotherms represent adequately the expected behavior of the  $\text{CO}_2$  absorption phenomena in IL [41], decreasing the amount of captured  $\text{CO}_2$  as temperature rises. This is produced by the combined effect of reducing  $K_{eq}$ , displacing the chemical equilibria to reactants, and increasing Henry's constant due to the decreased gas solubility at higher temperatures, consequently diminishing the overall amount of dissolved  $\text{CO}_2$  in the liquid phase.

#### Design of new AHA-ILs for $\text{CO}_2$ chemical capture

One of the main advantages of AHA anions is the ability to fine-tuning their thermodynamic behavior in the  $\text{CO}_2$  chemical reaction by ring functionalization [13,42]. Being able to tune these properties and predicting the resulting  $\text{CO}_2$  absorption isotherms, this methodology opens the doors to propose and test new AHA-IL absorbents at process scale using COSMO-based/Aspen approach [14], without the need of the high time demanding task of synthesizing and experimental testing

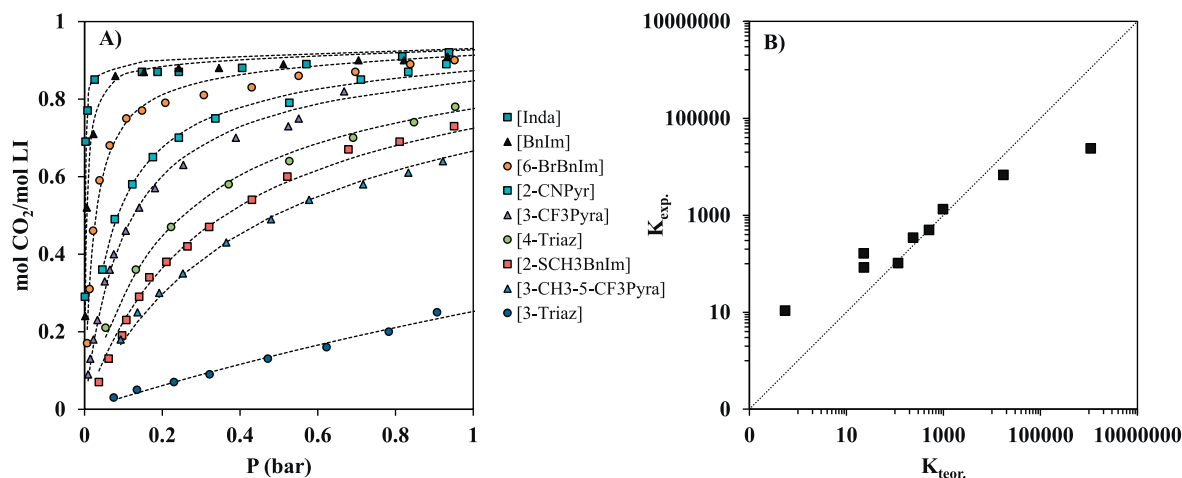


Fig. 5. (A) CO<sub>2</sub> absorption isotherms in AHA-ILs at 292 K (adapted from [13]) and fitting from Eq. (3) (dotted-lines); (B) Calculated  $K_{eq}$  values using COSMO-B3-LYP approach compared to experimental adjusted data.

Table 5

Thermochemical properties of the AHA-IL reactions with CO<sub>2</sub> calculated with B3-LYP functional using COSMO solvation method at 298.15 K.

AHA Anion	Structure	$\Delta H_R$ (kJ/mol)	$\Delta G_R$ (kJ/mol)	$\Delta S_R$ (J/mol•K)	$K_{eq}$
[Inda]		-59.9	-33.9	-87.4	1,090,447
[BnIm]		-50.6	-23.8	-90.1	17,297
[6-BrBnIm]		-43.7	-16.8	-90.4	982.1
[2-CNPyr]		-41.9	-15.2	-89.8	504.6
[3-CF <sub>3</sub> Pyra]		-41.1	-13.3	-93.2	235.7
[4-Triaz]		-34.4	-7.6	-89.9	22.8
[3-CH <sub>3</sub> -5-CF <sub>3</sub> Pyra]		-39.2	-7.6	-106.0	22.8
[2-SCH <sub>3</sub> BnIm]		-39.9	-11.6	-95.1	115.9
[3-Triaz]		-24.8	1.5	-88.0	0.5

of ILs for screening purpose. This approach has been proved useful in the case of CO<sub>2</sub> physical absorption by ILs using COSMO-RS approximation in ASPEN process simulations [43]. Therefore, the theoretical methodology developed in this work can be used to extend the current scarce knowledge of CO<sub>2</sub> chemical absorption in AHA-IL [14], allowing massive screening to find an optimized absorbent for certain CO<sub>2</sub> capture process configuration. For example, several AHA anion struc-

tures are tested to see the capabilities of this methodology, being the enthalpies of reaction with CO<sub>2</sub> and absorption isotherms predicted. First, the effect of using different heterocyclic ring of AHA anions with common cyano (-CN) substituent is analyzed in Fig. 8A (structures of all the compounds can be found in Table S4 of Supplementary Material). For the different AHA anions studied the values of reaction enthalpy from strongly exothermic -60 kJ/mol for [6-CN-Bnpyr] to endothermic re-

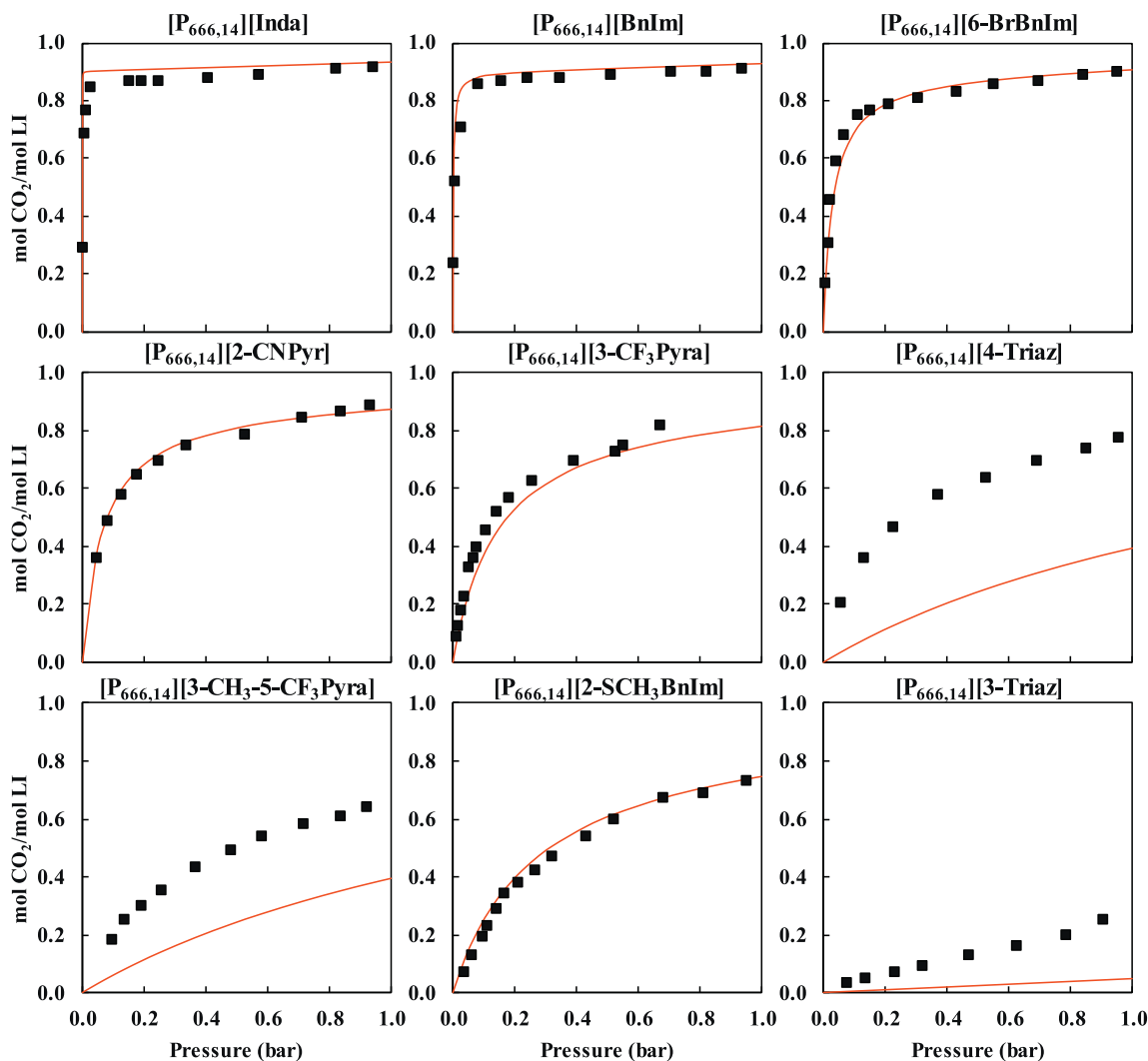


Fig. 6. CO<sub>2</sub> chemical absorption isotherms derived from quantum chemical calculations (lines) compared to experimental data [13] (■).

actions in the case of [3-Triaz]. In addition, the effect of using different substituents on common pyrrolide anion (H substituent) is illustrated in Fig. 8B. The nature of the substituent greatly affects the behavior of the AHA-IL as CO<sub>2</sub> chemical absorbent, from barely no effects in  $\Delta H_R$  values (like the methyl group) to complete inhibition of the reaction with CO<sub>2</sub> in the case of nitro group. These results are related with the steric hindrance effect and the modification of the electronic density in the aromatic ring, lowering the heterocyclic N ability to make the nucleophilic attack on CO<sub>2</sub> molecule.

The different values of enthalpies imply a wide spectrum of CO<sub>2</sub> absorption isotherms in AHA-IL. Fig. 9A collects all the isotherms calculated in this work for the different AHA-ILs at 298 K for comparison purposes. In addition, Fig. 9B relates the values of reaction enthalpy and equilibrium constant of CO<sub>2</sub>+AHA-IL systems. Due to the low scattering in  $\Delta S_R$  values all the ILs are placed in the same linear trend, being possible to directly correlate the values of  $K_{eq}$  and  $\Delta H_R$ .

The set of 26 predicted gas-liquid isotherms can be fundamentally placed in three groups, represented in different colors at the image. First group (blue) consists of ILs with no chemical absorption. It comprises all the ILs with  $\Delta H_R$  lower than  $-30$  kJ/mol, in these cases  $K_{eq} < 1$ , where only physical absorption takes place. At the other side (red), there are AHA-ILs that have reached saturation at very low CO<sub>2</sub> partial pressures, corresponding to  $\Delta H_R$  values higher than  $-50$  kJ/mol, as the cases of [Pyr] or [2-CH<sub>3</sub>-Pyr]. These high values make the desorption process

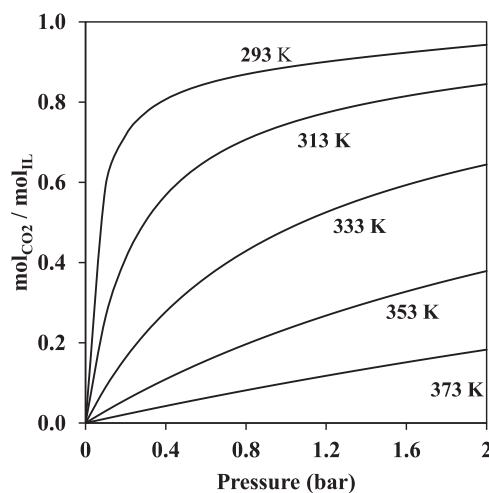


Fig. 7. Calculated CO<sub>2</sub> absorption isotherms in [P<sub>666,14</sub>][2-CNPyra] at different temperatures using Eq. (5) and 7 and calculated equilibrium constants.

a more energy demanding step. Finally, last group corresponds to AHA-ILs with intermediate behavior (yellow), with enthalpies of reaction between  $-30$  and  $-50$  kJ/mol. This narrow range of 20 kJ/mol covers up

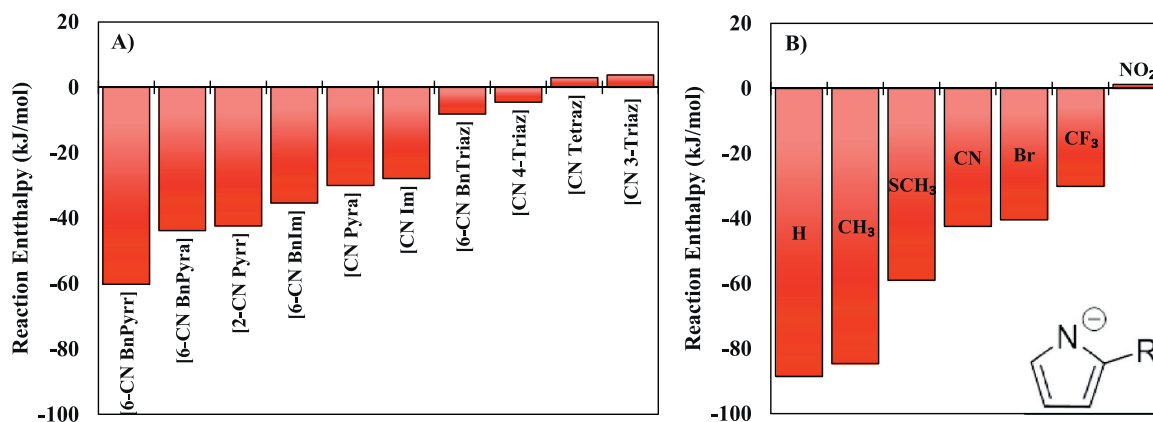


Fig. 8. Calculated  $\Delta H_R$  for CO<sub>2</sub> reaction with different cyano- substituted AHA anions (A) and pyrrol anion using various substituents (B).

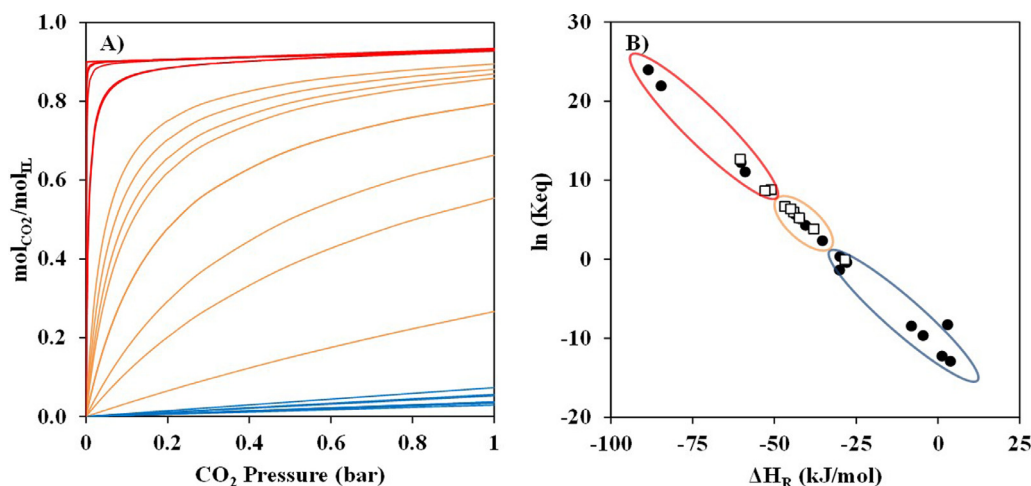


Fig. 9. CO<sub>2</sub> chemical absorption isotherms calculated in this work (A) and corresponding  $\Delta H_R$  and  $K_{eq}$  (B) for published AHA ILs (□) and new AHA ILs (●).

most of the possible CO<sub>2</sub> absorption isotherms. However, only a few of the new AHA-ILs are included in this interesting group.

## Conclusions

In this work, a methodology based on DFT calculations and COSMO-RS theory have been successfully applied to the prediction of CO<sub>2</sub> chemical absorption isotherms in AHA-ILs and their corresponding enthalpies of reaction. The results indicate that the use of B3-LYP functional among COSMO continuum solvation method provides an accurate description of CO<sub>2</sub> absorption isotherms in AHA-ILs. After properly validation with 9 previously published AHA-ILs, a set of new 15 systems were computed, obtaining a wide range of different CO<sub>2</sub> absorbent behaviors that proves the flexibility of the tool. It demonstrates the usefulness of this computational methodology to design new AHA-ILs with optimized CO<sub>2</sub> absorbent properties, since it allows screening among hundreds of compounds to give promising candidates to be evaluated in CO<sub>2</sub> capture by process simulation for, finally, moving into the synthesis and experimental tests at laboratory and pilot plant scales.

## Declaration of Competing Interest

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

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cej.2020.100038](https://doi.org/10.1016/j.cej.2020.100038).

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