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CO$_2$ Absorption Hot Paper

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Computer-Aided Design of Ionic Liquids as CO$_2$ Absorbents**

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Abstract: *Ionic liquids (ILs), vary strongly in their interaction with CO$_2$. We suggest simple theoretical approach to predict the CO$_2$ absorption behavior of ILs. Strong interaction of the CO$_2$ with the IL anions corresponds to chemical absorption whereas weak interaction indicates physical absorption. A predictive estimate with a clear distinction between physical and chemical absorption can be simply obtained according to geometries optimized in the presence of a solvation model instead of optimizing it only in gas phase as has been done to date. The resulting Gibbs free energies compare very well with experimental values and the energies were correlated with experimental capacities. Promising anions, for ionic liquids with reversible CO$_2$ absorption properties can be defined by a reaction Gibbs free energy of absorption in the range of -30 to 16 kJ mol^{-1}.*

Ionic liquids (ILs) are promising solvents for CO$_2$ absorption from various waste gases, and this property has been attracting significant scientific and technological attention in the last decade. To achieve maximum efficiency regarding the energy needs of both the transport and the regeneration of the absorbent, the absorption enthalpy must be in a relatively narrow range,[1–3] but it can, of course, deviate from this desired value depending on the aims and the circumstances. Owing to the great variety of ILs (the estimated number of potential IL candidates is ca. 10^{15}), the solubility and absorption enthalpy of CO$_2$ in them can be altered to a great extent, which allows a great deal of flexibility in optimizing these processes. On the other hand, this great variety makes the heuristic design of such solvents highly ineffective, requiring much material and effort.

A possible and desirable way to treat this issue is to establish a simple computational procedure that allows us to estimate the solubility of the gas in the IL in question, so that many candidates can be screened at a time, while by the alternation of the IL structure the different properties can be tuned to the desired value, and finally only the best few substances need to be chosen for experimental inspection. Accordingly, much theoretical data has been published in recent years aiming at an in-depth understanding of CO$_2$–IL interactions, and also to predict the absorption behavior. To this end, gas-phase binding energies were correlated with solubilities,[4,5] and with capacities.[6] Furthermore, gas-phase reaction enthalpies[2] were determined from electronic structure methods to match or even predict experimental values.[3]

Ab initio molecular dynamics simulations[7] revealed that the CO$_2$ molecule shares weak, but numerous dispersion interactions with the IL cation, while with the anion CO$_2$ often has a single,[7–9] but stronger interaction that can be described generally as the formation of a Lewis acid (CO$_2$)/base (anion) pair. Although the two kind of interactions are surmised to be equivalent in total strength in the solution,[7] for the altering of the CO$_2$'s solubility the anion is more often the target,[10] since the strong, and directional interactions are related to many of the anion's properties, such as its basicity.[11]

Herein, we present simple methods based on solvated geometries that provide Gibbs free energies in very good agreement with experimental values and also in excellent correlation with the experimentally observable absorption capacity (mole CO$_2$ per mole IL), in addition the characterization of the interaction is rapidly achieved, helping the further tuning of the related IL absorbent candidates. As a result of this study, we also present several novel ILs that will presumably exhibit excellent absorption characteristics.

The calculated binding energies lie in between 0 and -250 kJ mol^{-1} for the gas-phase geometries and between 0 and -160 kJ mol^{-1} for the solvated geometries. Angles of the CO$_2$ molecule in the complex between 130° and 180° are found in both the gas and solvated geometries (Figure 1). From a chemical reaction that binds CO$_2$, substantial bending of this linear gas molecule can be expected, just as in the extreme example of its interaction with the very basic hydroxide anion, in which case the reaction results in the hydrocarbonate anion with an O-C-O bond angle of approximately 130°. Interestingly, when the CO$_2$'s bond angle in the complexes is plotted against the corresponding binding energies, two clear areas with two different complexes are obtained (boxes in Figure 1). One group of the anions induce less than 10° bending of the CO$_2$, and exhibit rather low binding energies while the other group of the investigated structures show significant bending. These two sorts of complexes can be attributed to physical and chemical absorption, respectively, and therefore this approach can be considered an exact definition for the term "chemical absorption" in the present process. Below we will show that using the solvated geometries leads to a much better agreement to experimental observations while using gas-phase geometries gives erroneous behavior. From these results it is also clear that to find a good absorbent candidate, aiming at chemical absorption would be a good choice, because the larger range of binding energies these anions cover suggests

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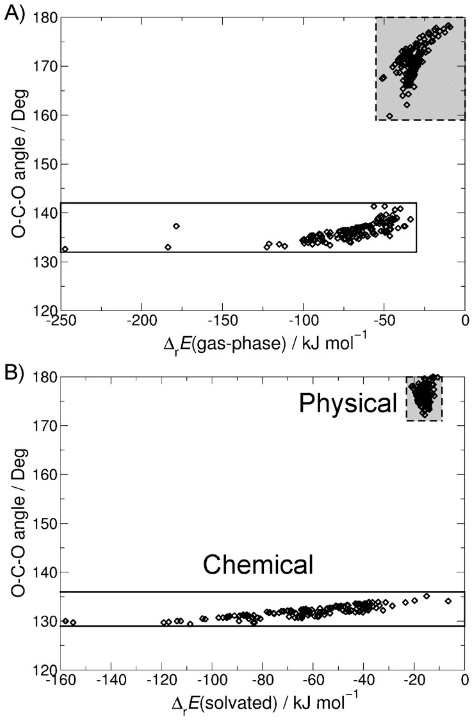

Figure 1. Binding energy versus O-C-O angle for the anion–CO_2 complexes. A) The binding energy is derived from standard optimization in the gas phase (isolated molecule); B) The binding energy is derived from optimization accounting for solvation by a continuum model, see Supporting Information. Comparison of both panels show a much more distinct picture for the solvated geometries.

that tuning the IL to fit the desired process should be more straightforward.

Although the cations (Cat) form many interactions, and thus in total a strong interplay, with the solute gas molecule,[7] according to previous experimental data[9,12,13] the absorption can be altered to a greater extent by changing the anion (An), thus, to estimate the effect of the anion on the CO_2's absorption enthalpy, the enthalpy of the binding reaction [Eq. (1)]

$$An^-(l) + CO_2(g) \rightleftharpoons [An\text{-}CO_2]^-(l) \qquad (1)$$

serves as a measure. Exceptions are when the cation is also performing chemical absorption.[7,17] A value for the equilibrium constant higher than unity indicates a considerable absorption capacity of ILs at the room temperature and moderate pressure,[3] which requires a reaction Gibbs free energy ($\Delta_r G_{exp}$) between -20 and 6 kJ mol^{-1} for the forward reaction. Stronger binding energies will prevent the desorption process. To estimate these values, we employed an approach, which—in contrast to the previous studies[2,3,14,15]—also takes into account the thermal corrections for the relevant species of Equation (1), that is, An^- and $[An\text{-}CO_2]^-$, and the solvation contribution[16] by accounting for [Cat][An] assemblies as ILs (details are given in the Supporting Information).

Table 1: Computed and experimental properties.[a,b]

Anion[c]	$\Delta_r H$	$\Delta_r G_{calcd}$	$\Delta_r G_{exp}$	Abs. cap.[d]
$[Inda]^-$	-63	-26	-16	0.92
$[BnIm]^-$	-67	-23	-13	0.91
$[6\text{-}Br\text{-}BnIm]^-$	-57	-11	-9	0.90
$[2\text{-}CN\text{-}Pyr]^-$	-47	-7	-6	0.88
$[3\text{-}CF_3\text{-}Prz]^-$	-52	-9	-6	0.87
$[1,2,4\text{-}Tri]^-$	-60	-9	-4	0.76
$[2\text{-}SCH_3\text{-}BnIm]^-$	-48	1	-3	0.72
$[3\text{-}Me\text{-}5\text{-}CF_3\text{-}Prz]^-$	-49	3	-2	0.63
$[1,2,3\text{-}Tri]^-$	-53	-1	2	0.25

[a] Computed reaction gas-phase enthalpy ($\Delta_r H$) and solvated Gibbs free energies ($\Delta_r G_{calcd}$) and derived[b] experimental Gibbs free energies ($\Delta_r G_{exp}$) at 298.15 K for the reaction in Equation (1) for the anions in Ref. [3]. Ball-and-stick diagrams to the corresponding abbreviations are depicted in Figure 2A. All energies in kJ mol^{-1}. [b] The experimental equilibrium constants from Ref. [3] were used to calculate $\Delta_r G_{exp}$ at 293 K. [c] Definitions for the abbreviations can be found in the Supporting Information. [d] Absorption capacity in mol CO_2 per mol IL. The data was interpolated to pressure of 0.9 bar from two nearest experimental points of Ref. [1,3].

For a set of anions, for which also $\Delta_r G_{exp}$ data are available with consistently the same cation (trihexyltetradecylphosphonium; $[P_{6,6,6,14}]^+$), the calculated and experimental[3] data are listed in Table 1. The two $\Delta_r G$ results show very good agreement, both in absolute values and in the trend, with a largest absolute deviation of 10 kJ mol^{-1} which means potential candidates to be considered are in the range of -30 to $+16$ kJ mol^{-1}. This excellent match clearly aids the comparison of experiment and theory, while allowing a more detailed understanding of the IL–CO_2 interactions at the molecular level. Clearly, substitution of the anions with electron-withdrawing ($-$I and $-$M effect) or electron-donating (+I and +M effect) groups changes the capacity and $\Delta_r G$ in a logical way. Attaching a bromide substituent to the anion's ring as in $[6\text{-}Br\text{-}BnIm]^-$ compared to $[BnIm]^-$ decreases the absorbing abilities, hence the slightly smaller capacity. Adding a SCH_3 group between the two nitrogen atoms which exhibit a high steric demand results in $[2\text{-}SCH_3\text{-}BnIm]^-$ being also a worse absorbent than $[6\text{-}Br\text{-}BnIm]^-$. The +I effect provided by the Me group in $[3\text{-}Me\text{-}5\text{-}CF_3\text{-}Prz]^-$ compared to $[3\text{-}CF_3\text{-}Prz]^-$ is non-beneficial because of the steric hindrance which is revealed by the additional structures of the two carboxylate complexes and their rotation profile shown in Figure 2. Note that for the frequently applied $\Delta_r H$ values[2,3,14,15] this agreement is significantly rougher, as these values lack the solvation and entropy contributions.

Figure 1 shows the distinction between physical and chemical absorption is possible based on the knowledge of very simple reaction energies and calculated O-C-O angles. However, care has to be taken to obtain the right geometries as demonstrated in Table 2 in which we list some critical phenolate ILs. Experimental capacities clearly point to chemical absorption[14]—physical absorption under the same conditions does not exceed 0.04 mole CO_2 per mole IL; also, measured FTIR spectra revealed additional peaks at approximately 1600 cm^{-1};[14,17] while the ^{13}C NMR spectrum provided a new band at $\delta = 161$ ppm during the absorption of CO_2, thereby also indicating the formation of carboxylate salts.[14] Gas-phase geometries (O-C-O angles in Table 2) do

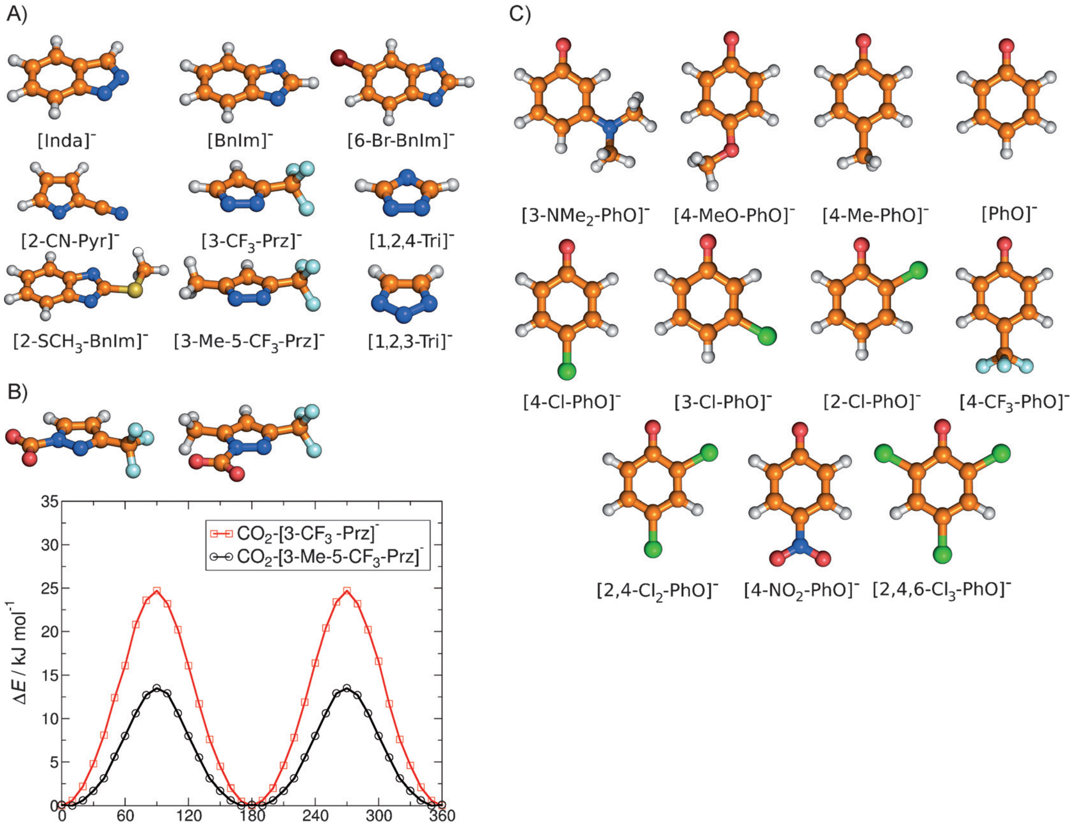

Figure 2. Ball-and-stick picture together with abbreviations of the anion test set chosen from A) Ref. [3] left and C) from Ref. [14]. White H; brown C; blue N; dark red Br and light blue F; yellow S; green Cl. B) Optimized geometries of carboxylates and calculated rotation profile for both of them. Despite the +I effect steric hindrance can decrease the capacity. Note the abbreviations Ph, Pyr etc. are, against the IUPAC recommendations, used to indicate substituted groups, e.g. Ph also indicates C_6H_4 and C_6H_3.

Table 2: O-C-O angles and related properties.[a]

Anion	O-C-O Angles [°] gas	 solv	$\Delta_r G_{calcd}$ [kJ mol^{-1}]	Capacity[b]
[3-NMe$_2$-PhO]$^-$	138	132	−3	0.94
[4-MeO-PhO]$^-$	137	132	−14	0.92
[4-Me-PhO]$^-$	138	132	−9	0.91
[PhO]$^-$	138	132	−7	0.85
[4-Cl-PhO]$^-$	140	132	0	0.82
[3-Cl-PhO]$^-$	141	132	12	0.72
[2-Cl-PhO]$^-$	164	132	11	0.67
[4-CF$_3$-PhO]$^-$	166	133	16	0.61
[2,4-Cl-PhO]$^-$	167	133	19	0.48
[4-NO$_2$-PhO]$^-$	171	134	32	0.30
[2,4,6-Cl-PhO]$^-$	171	134	39	0.07

[a] O-C-O angles, reaction Gibbs free energies ($\Delta_r G_{calcd}$) on solvated geometries, and the experimental CO_2 absorption capacity for trihexyltetradecylphosphonium ILs.[b] Ball-and-stick pictures of the phenolate anions are provided in Figure 2C. [b] The data was taken from Ref. [14]. For the [$P_{6,6,6,14}$][4-NO$_2$-PhO] ionic liquid the CO_2 capacity was determined at 20 °C, whereas for the remaining ILs it was determined at 30 °C.

not reproduce the given tendency, however interestingly the solvated geometries all behave according to experimental trends in that they show angles around 133°.

Having established a simple procedure to indicate chemical absorption, namely the O-C-O angle of solvated carboxylate geometries, we turn now to the further refinement of predicting suitable CO_2 absorbents. To arrive at a predictive tool we correlated all calculated $\Delta_r G_{calcd}$ values based on solvated geometries with the experimental capacities in Figure 3 which demonstrates the applicability. Care has to be taken when dealing with 1,2,3-triazole anions but otherwise the quadratic fit matches the points well enough to provide an estimate and also it confirms the energy range of

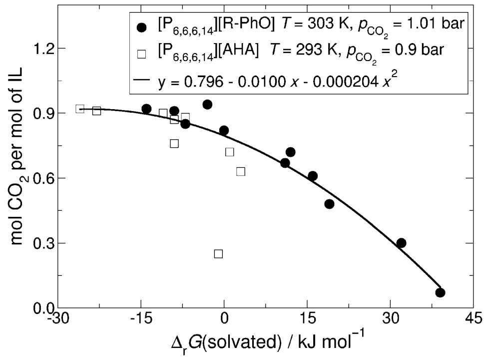

Figure 3. Correlation of calculated $\Delta_r G_{calcd}$ and capacities. [R-PhO] indicates the phenolate anions in Table 2 and Figure 2 right; [AHA] = aprotic heterocyclic anions.

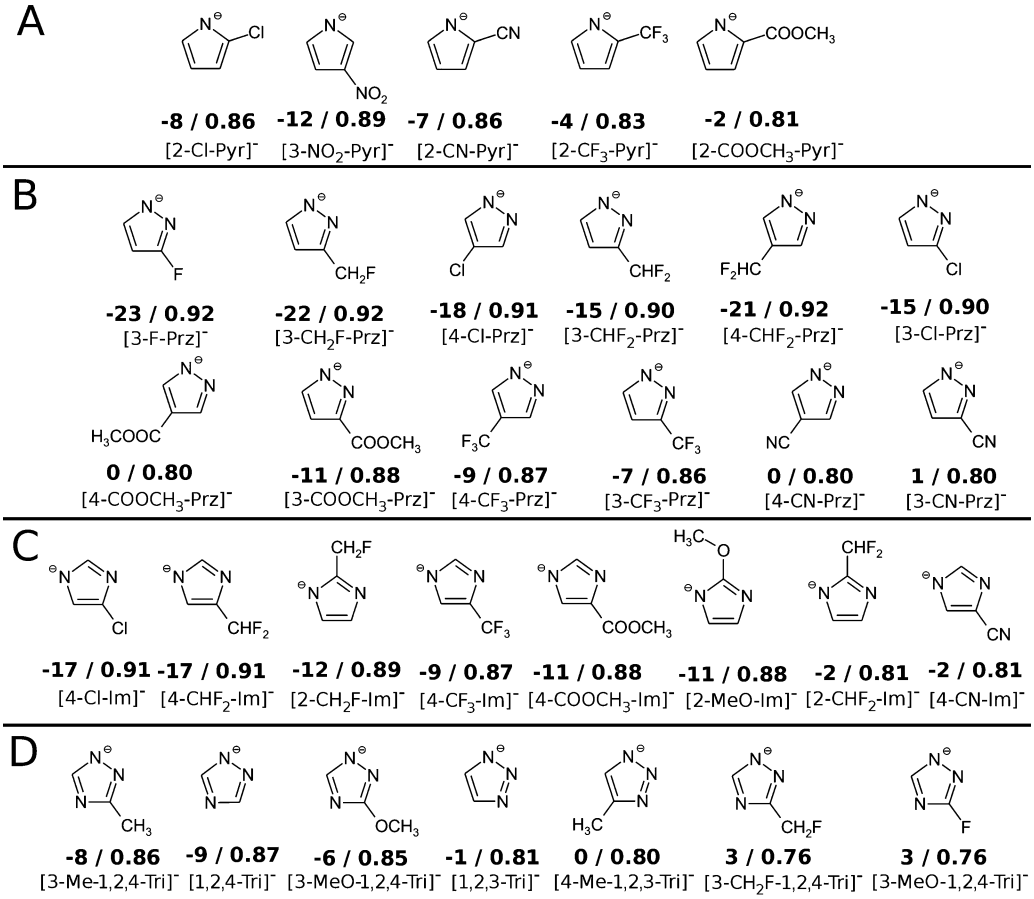

Figure 4. List of the anions suitable for the chemical absorption of CO_2. A) contains pyrolide-based anions, B) pyrazolide-based anions, C) imidazolide-based anions, and D) triazolide-based anions. The values of the $\Delta_r G_\mathrm{calcd}$ and calculated capacity from the quadratic fit in Figure 3 are given under each Lewis structure.

16 to $-30\,\mathrm{kJ\,mol^{-1}}$; note the convergence behavior around $-30\,\mathrm{kJ\,mol^{-1}}$.

We used the optimized geometries and the known $\Delta_r G_\mathrm{calcd}$ range to establish possible azalide candidates[11,18] which are given in Figure 4 together with their energies and estimated capacities. Owing to the deviating behavior shown in Figure 3, the results for 1,2,3-triazole anions should be treated with special care. While the pyrrole anions show a weak trend with substitution and good capacities in the range of 0.81–0.89 (at the energy range of -2 and $-8\,\mathrm{kJ\,mol^{-1}}$), the pyrazole anions achieve higher capacities especially when substituted in the α-position with electronegative atoms. While imidazole anions can exhibit superior capacities (0.91 at $\Delta_r G_\mathrm{calcd} = -17\,\mathrm{kJ\,mol^{-1}}$) the triazole anions only show moderate (0.76) to good (0.86) capacities.

In Conclusion, we can say that when calculated solvated carboxylate geometries exhibit angles smaller than 140° a chemical absorption is very probably. Based on this, calculated $\Delta_r G_\mathrm{calcd}$ values and correlated capacities—if $\Delta_r G_\mathrm{calcd}$ lies between $16\,\mathrm{kJ\,mol^{-1}}$ and $-30\,\mathrm{kJ\,mol^{-1}}$—indicate possible candidates for good to excellent chemical absorption. We provided several examples of possible candidates which might be tested experimentally.

Keywords: absorption · carbon dioxide · computer chemistry · ionic liquids

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