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Assessing Thermodynamic Data of CO₂ capture by Ionic Liquids through Hard and Soft Base Theory

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Abstract

Nowadays ionic liquids (IL) are target of massive research in CO₂ captures technologies, due to its thermic degradation resistance, low vapour pressure and low requirement of power for regeneration. All these properties, including solubility capacity, are known to vary with the nature of the IL cation and anion. The main goal of this study was calculate electronic indicators for ILs that have thermodynamic data available and verify the existence of correlation between them, providing a possible new way to get information of these processes.

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1. Introduction

Nowadays ionic liquids (IL) are target of massive research in CO₂ captures technologies, due to its thermic degradation resistance, low vapour pressure and low requirement of power for regeneration [1]. All these properties, including solubility capacity, are known to vary with the nature of the IL cation and anion [2]. The number of

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combinations between ions to form new substances within this class scales to 10^4 , i.e. it is already well established that trial and error approach for study these material are not feasible [2]. In this context, theoretical methodologies for building predictive models and understand these processes are growing. A class of properties that could give relevant information for carbon capture process is thermodynamic data, such as Henry constant, entropy and enthalpy of dissolution. These are the main properties to represent the gas solubility capacity, molecular ordering during the process, heat required to the sorption and regeneration, and the affinity between the molecules. Also, the knowledge about thermophysical properties is crucial to decide whether a process that employ IL could be extended from laboratory scales to industrial scale [1]. Those data find applications for process modelling proposes too, which appraise wide range of temperatures and pressures [1]. Computational methods are largely employed for building predictive frameworks for this assessment, although the majority of these techniques are time intensive [4,5]. Computational methods are largely employed for building predictive frameworks for this assessment, although the majority of these techniques are time intensive. In this study we employed *ab initio* simulation methods that are more simple and fast. *Ab initio* it is common for frameworks structured for calculating heats of formation and heats of vaporization, and also it is applied to calculate these properties for ILs trough the G3MP2 level of theory [5]. Although, these simpler methods have some limitation due to the approximations made *a priori*, and tends to do not work very well for others properties for compounds with such complexity like ILs. However could be used to calculate others indicators related with electronic density transfer tendency, as the Hard and Soft Base theory, that already was used to create acidity scale to correlate the ability of ILs to solubilize other compounds (6). The HSBA theory was first created to explain reactivity in Lewis acids and latter was a very useful interpretation of parameters of Density Functional Theory equations, providing electronic indicators of reactivity. The main goal of this study was calculate these electronic indicators for ILs that have thermodynamic data available and verify the existence of correlation between then, providing a possible new way to get information of these processes.

2. Material and Methods

Through the mathematical development of Density Functional Theory (DFT) (Eq. 1) some important quantitative indexes of chemical reactivity are derived. The DFT defines the energy of a chemical system in terms of electron density and how it changes with the variation of numbers of electrons and electrical fields. The theorems behind DFT foundations states that everything about a chemical system is defined by the ground state electron density $\rho(\mathbf{r})_0$ [6] Eight Ionic liquids (Table 1) were selected, with thermodynamic data of CO₂ solubility available (Table 2) [7]. The molecular geometry was optimized, firstly with HF/6-31G level of theory and secondly with MP2/6-31G*. Then the energy was calculated with MP2/6-311+G*. The orbital energies was retrieved through the Koopman's theorem and calculated using the HOMO and LUMO orbital energies the following indicators: the chemical electronic potential (Eq. 2), total electrophilicity (the negative of chemical electronic), absolute hardness (Eq. 3), and absolute softness (which is reciprocal to the absolute hardness). These indicators are related with the mechanisms of minimization of the free energy in process of electronic density transfers. The acidity scale we created through the ratio of the square of total electrophilicity to the absolute hardness, representing the tendency to accept electronic density.

Table 1: Ionic liquids names and abbreviations used in this work

Ionic liquid name	Ionic Liquid abbreviation
Tetrafluoroborate 1-3-butylmethylmethyylimidazolium	[bmim][BF4]
bistrifluoromethylsulfonylimides 1-3-butylmethylmethyylimidazolium	[bmim][TFSI]
Hexafluorophosphate 1-3-butylmethylmethyylimidazolium	[bmim][PF6]
bistrifluoromethylsulfonylimides 1-2-3-dimethylbutylimidazolium	[dmbmim][TFSI]
bistrifluoromethylsulfonylimides	[emim][TFSI]
bistrifluoromethylsulfonylimides	[edmi][TFSI]
Bistrifluoromethylsulfonylimides N-methyl-N-butyl-pyrrolidinium	[P14][TFSI]
Hexafluorophosphate 1-2-3-dimethylbutylimidazolium	[dmbmim][PF6]

Table 2: Ionic Liquids thermodynamic data retrieved from literature

Ionic liquid	Henry constant	Enthalpy (J.mol ⁻¹)	Entropy (J.K ⁻¹ .mol ⁻¹)
[bmim][BF4]	59.0	-13.9	-45.6
[bmim][TFSI]	33.0	-12.5	-41.3
[bmim][PF6]	53.4	-16.1	-53.2
[dmbmim][TFSI]	45.7	-14.5	-47.7
[emim][TFSI]	35.6	-14.2	-46.9
[edmi][TFSI]	39.5	-14.7	-48.7
[P14][NTF2]	38.6	-11.9	-38.7
[dmbmim][PF6]	61.8	-13.0	-42.8

$$dE = \mu dN + \int \rho(r) dv(r) dr \text{ Eq. 1}$$

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_v \text{ Eq. 2}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_v \text{ Eq. 3}$$

$$\text{Acidity} = \chi^2 / \eta \text{ Eq. 4}$$

3. Results and Discussion

Three calculated electronic descriptors were chosen to try correlation with thermodynamic data. Resulted values are in table 3. In Figure 1 the correlation between the calculated Acidity with the enthalpy of carbon dioxide dissolution in the ionic liquids studied, showing that higher acidities (in DFT terms) could indicate higher affinities between the solute and solvent. In Figure 2 the correlation between calculated electrophilicity and Henry constant, which shows that higher electrophilicities could point to lower values of Henry constant, indicating higher sorption capacities. This can lead to interpret the effects of the dissolution as the ability of the solvent to accommodate electronic density of the carbon dioxide.

Table 3: Electronic descriptors resulted from the ab initio calculations

Ionic liquid	Electrophilicity (eV)	Hardness (eV)	Acidity (eV)
[bmim][BF4]	4.815	5.790	2.002
[bmim][TFSI]	4.971	5.832	2.118
[bmim][PF6]	4.768	6.311	1.801
[dmbmim][TFSI]	4.775	5.390	2.115
[emim][TFSI]	5.069	5.620	2.286
[edmi][TFSI]	4.073	4.640	1.788
[P14][NTF2]	5.108	5.757	2.2659
[dmbmim][PF6]	4.398	4.861	1.990

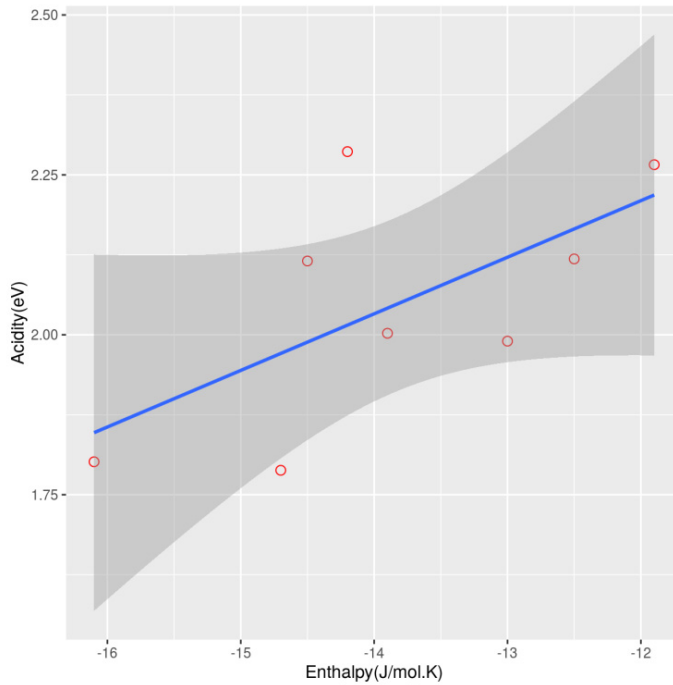


Figure 1: Diagram between calculated acidity (eV) and experimental enthalpy of CO₂ dissolution in the studied Ionic Liquids.

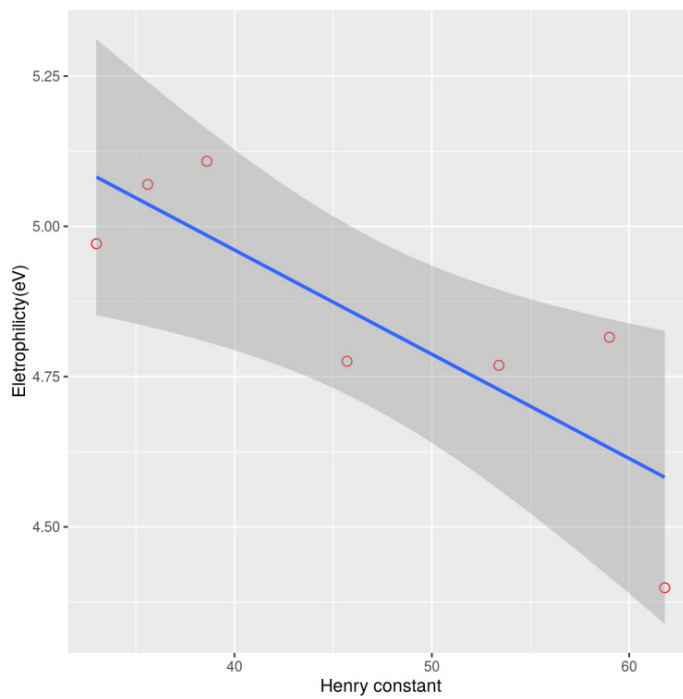


Figure 2: Diagram between calculated Electrophilicity (eV) and experimental Henry constant of CO₂ dissolution in the studied Ionic Liquids.

4. Conclusions

This studied showed that electronic molecular descriptors could be used to interpret the effects of chemical composition in the thermodynamic properties processes. The calculated acidity shows positive correlation with enthalpy of carbon dioxide dissolution in the Ionic liquids studied and the electrophilicity correlates negatively with Henry constant values. This indicates that the best ionic liquids for the CO₂ capture could be those with high capacity to accommodate electronic density.

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