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New Experimental Data of CO_2 Solubility in an Amine Solvent

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Carbon Capture, Utilization and Storage (CCUS) is a topic of interest for its relevance in decreasing the emissions to the atmosphere of CO_2, a powerful greenhouse gas, related to the industrial production and power generation by fossil fuels. Aqueous amine solutions can be used as chemical solvents for this aim, though the high energy consumption and the related operating costs, their toxicity and the corrosion issues related to their use do not favor their application on the large scale.
The research on novel solvents for CO_2 removal, that could overcome the disadvantages of the traditional solvents, requires the analysis of phase equilibria of systems for which physical-chemical properties cannot be found in detail in the literature. In particular, the solubility of gases, mainly CO_2, in the mixture to be considered, is fundamental to understand the suitability of a new species as solvent for chemical or physical absorption.
With the aim of overcoming the issues due to the lack of experimental data on novel systems, an experimental unit has been installed at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano aimed at collecting data of solubility and diffusivity of gases into low volatile liquids that could be used as solvents for CO_2 capture. A detailed specific experimental procedure has been defined and the unit has been firstly operated for validation, by collection of solubility data of CO_2 into a 30% wt. MonoEthanolAmine (MEA) solvent, one of the most developed solvents already industrially used. Both the conditions of the absorption section and of the regeneration section, operating at different temperatures, have been considered. Then, the description of the equilibrium attained in the experimental unit has been carried out, taking into account different thermodynamic models and selecting the one best describing the system.

1. Introduction

Carbon Capture, Utilization and Storage (CCUS) is being considered for decreasing the emissions of carbon dioxide in the industrial production (Baker et al., 2018), in power generation (Moioli et al., 2018) and in transports (Tavakoli et al., 2024).
The absorption by aqueous amine solutions is considered suitable for this aim, though the traditionally employed amines are characterized by a high energy consumption and high operating costs, toxicity and corrosiveness. The development of novel solvents aims at overcoming these disadvantages to favor the increase of the number and the size of cost-effective and environmentally friendly CO_2 removal plants. Therefore, research is focusing on solvents that can meet performance criteria as fast absorption rate, high CO_2 loading capacity, low regeneration energy, low degradation rate, low corrosiveness, low environmental impact and low solvent cost (Budzianowski, 2015).
The analysis of phase equilibria (in particular, the solubility of CO_2 in the solvent to be considered) of systems for which characteristics cannot be found in detail in the literature is needed to determine the suitability of a new species as solvent for chemical or physical absorption.
Because of the lack in the literature of experimental data on novel systems, at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano an experimental unit for the collection of data of solubility and diffusivity of gases into low volatile liquids that could be used as solvents has been installed and is in operation. This work focuses on the definition of the specific experimental procedure and on the validation of the unit by the collection of solubility data of CO_2 into a 30% wt. MonoEthanolAmine (MEA) solvent, one of the most industrially used solvents, and their comparison with data already reported in the literature for the same mixture

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and the same operating conditions. Both the conditions of the absorption section, with a temperature of 40°C, and of the regeneration section, with a temperature of 100°C, have been considered.

2. The experimental solubility unit

The Process Thermodynamics laboratory (PT lab) is an experimental laboratory of Politecnico di Milano, that has been created within the “Ingegneria Chimica – Energia (ICE)” collaboration and is located at Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta” (Barbieri et al., 2025; Schiattarella et al., 2024). The PT lab is part of the Process Design and Process Thermodynamics laboratory (PD&PT lab), held by the research group GASP, and is provided with experimental facilities for measuring Vapor-Liquid Equilibrium (VLE), Vapor-Liquid-Liquid Equilibrium (VLLE), Liquid-Liquid Equilibrium (LLE) and solubility and diffusivity of gases in solvents and properties as density and viscosity, useful for the characterization of the system (Moioli and Pellegrini, 2018).
The unit for solubility measurements, reported in Figure 1, has been employed in this work.

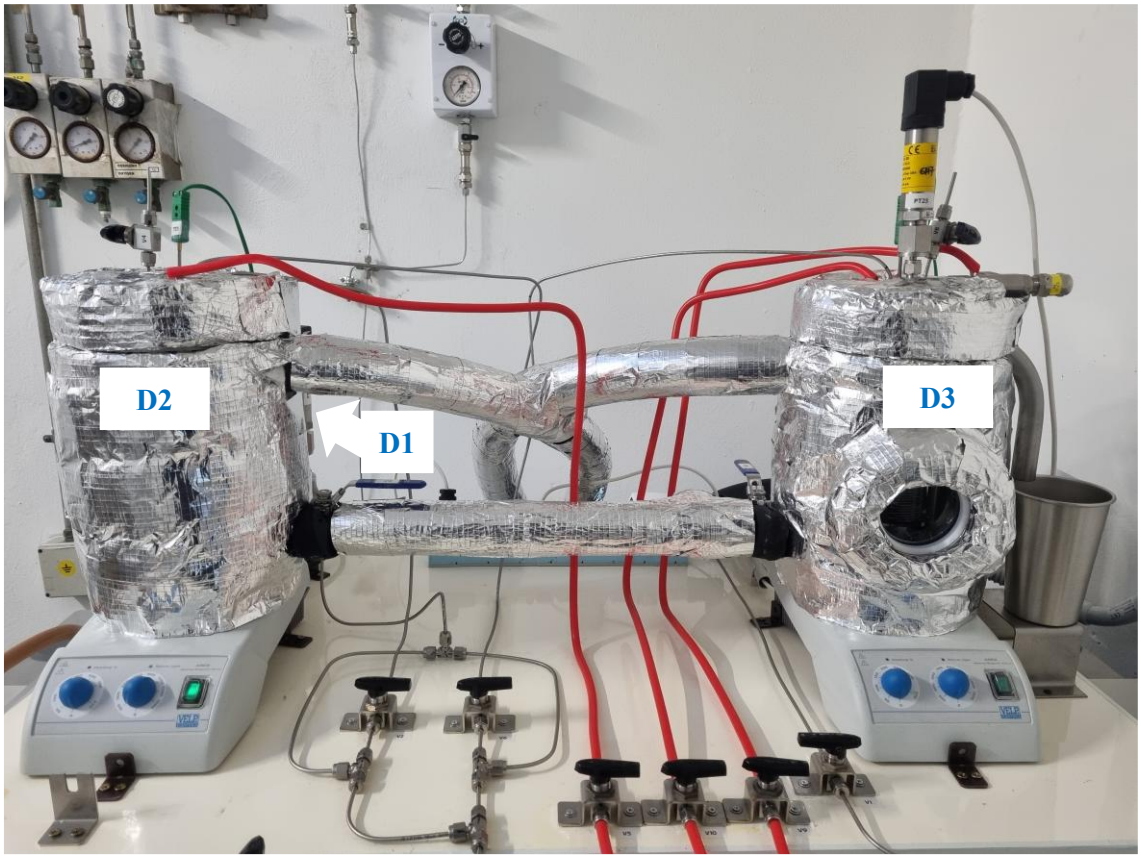


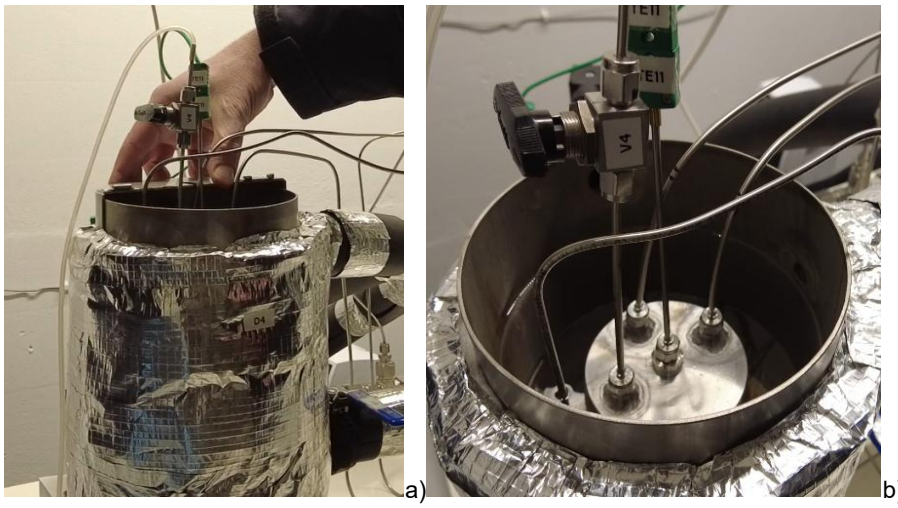
Figure 1: The solubility unit at the PT lab of Politecnico di Milano

It is based on the unit employed by Bientinesi et al. (2016), with some modifications to take into account the different purposes of the equipment installed at PT lab. In particular, it consists in two sections, one related to the collection of experimental data at pressures up to 50 bar (on the left side in Figure 1), similar to the one considered by Bientinesi et al. (2016), and one devoted to the collection of experimental points for systems forming two liquid phases up to 8 bar (on the right side in Figure 1).
Each section operates with two cylindrical vessels:

- the first one (D1), that is common to both the sections, is filled in with the gas to be absorbed into the solvent, *i.e.*, CO_2;
- the second one, one for each section (D2 for the high-pressure tests and D3 for the biphasic solvent tests), is filled in with the solvent and is the unit where the phase equilibrium occurs.

The vessel D1 is equipped with a temperature and a pressure sensor (TE10 and PT20, ranging from 0 to 60 barg) and it is connected directly to the gas feeding line of CO_2 through the valves V15 and V1 and to the N_2 line through the valves V16 and V1. The CO_2 bottle and the N_2 bottle are stored in an external dedicated room.

The vessel D2, detailed in Figure 2, is connected to the vessel D1 through the valve V2. The inlet liquid port is a tube connected to the vessel D2 through the valve V4, that also allows the withdrawal of the gas phase. The tube for discharging the liquid is connected to the bottom of the vessel D2 and to the outside through the valve V5, that allows the discharge at the end of the test. The vessel D2 is provided with a magnetic stirrer to mix the liquid inside the unit and with a temperature sensor (TE11) and two pressure transducers (PT21, ranging from 0 to 10 bara, and PT22, ranging from 0 to 60 barg, with a precision equal to 0.2% of the maximum value), to determine the variation of the operating conditions during time. All the sensor signals are collected and registered in a datalogger and digitally recovered.
The vessel D2 is located in a steel container with a removable lid where the thermostatic oil circulates after opening the valve V12, to keep the temperature at the given value set on the thermostatic bath. A “too full” tank is present so that if the circulation tube gets clogged and oil starts accumulating in the tubes or in the vessel, it can exit without flooding.
In addition, a vacuum pump is installed for decreasing the pressure before and after the charging of the solvent mixture at the beginning of the experimental test.
A N_2 line has been added to improve the efficiency of the discharge procedure (to avoid additional solubility of CO_2 if using this gas for the discharge) and to make the system inert before the beginning of a new experiment.



a) b)

Figure 2: a) The steel tank for the thermostatic oil surrounding the vessel D2 and b) detail of the connections of the vessel D2 of the solubility unit at the PT lab of Politecnico di Milano (Bolis, 2024)

An electronic balance with capacity of 520 g and precision equal to 0.001 g is employed for the weighting. The PT lab is also provided with a section for the preparation of the solvent mixture in nitrogen atmosphere, to not favor the oxidative degradation of the amine.

3. Experimental data in the literature

The solubility unit and the experimental procedure have been tested by comparison with the experimental data of a known solvent already available in the literature. To this aim, the system composed of CO_2+MEA+H_2O has been chosen, for which many papers in the literature from different sources, with different compositions of the solvent and with the solubility data at temperatures characteristic of both the absorption operation and the regeneration operation, can be found. This is due to the fact that the solvent based on an aqueous solution of MEA is employed since the 1930s (Bottoms, 1931) and is considered the benchmark solvent for CO_2 removal from gaseous streams.
In particular, for a concentration of MEA in the solvent equal to 30% wt., Jou et al. (1995) collected experimental data of CO_2 partial pressure at 0°C, 25°C, 40°C, 60°C, 80°C, 100°C, 120°C and 150°C, Ma'mun et al. (2005) at 120°C, Kadiwala et al. (2010) at 40°C, Aronu et al. (2011) at 40°C, 60°C and 80°C, Dugas and Rochelle (2011) at 40°C, 60°C, 80°C and 100°C, Xu and Rochelle (2011) from 100°C to 150°C, Arshad et al. (2014a) and Arshad et al. (2014b) at 40°C, 80°C and 120°C, Idris et al. (2015) at 40°C and Wanderley et al. (2020) at 40°C, 80°C and 120°C. Some of these sources and other sources also focused on other compositions of MEA in water, that are not detailed in this paper for reasons of limited space.

All the references have been firstly compared to check whether the experimental data at the same conditions of temperature, loading and partial pressure of CO_2 obtained from different sources are consistent one each other.

4. Procedure

4.1 Procedure for the collection of the experimental points

The procedure for the collection of the experimental points consists of the following steps:

- the system is flushed with nitrogen to make it inert;
- the thermostatic bath is switched on;
- when the temperature of the thermostatic fluid is equal to the temperature of the set point, the circulation of the fluid is activated;
- the vessel D1 is filled with CO_2, up to a defined pressure;
- the vacuum pump is switched on until the pressure in the vessel D2 is below 0.05 bar;
- a known amount (mass) of the solvent, without CO_2, is added to the vessel D2;
- the vacuum pump is switched on again to remove the atmospheric air fed with the solvent, until the pressure in the vessel D2 is below 0.05 bar;
- part of the CO_2 contained in the vessel D1 is transferred to the vessel D2, up to a defined pressure in the vessel D2;
- time is waited for achieving the phase equilibrium, that is determined on the basis of the trend of the temperature and pressure sensors (even if the temperature of the experiment is set, in case of absorption into a chemical solvent it varies when CO_2 starts to be absorbed because of the exothermicity of the chemical reactions);
- once the equilibrium is achieved, the liquid phase is discharged together with the vapor phase (the pressurization with N_2 is needed to empty the unit);
- the liquid phase is weighted and may be analyzed.

4.2 Procedure for determining the lean loading and the partial pressure of CO_2 in equilibrium

The absorption of CO_2 has been determined both through theoretical calculations and by checking the obtained results with a material balance on the unit.
The theoretical determination of the equilibrium is based on the method described by Park and Sandall (2001), with the calculation of the compressibility factor for the vapor phase, on the basis of the temperature and the pressure values of the two vessels (D1 and D2) before and at the equilibrium condition. These values are experimentally measured by the temperature and pressure sensors of the solubility unit. The detailed calculations are not reported in this paper for reasons of space. The moles of CO_2 that are transferred from the vessel D1 to the vessel D2 and the moles of CO_2 that remain in the vapor phase of the vessel D2 at the equilibrium are evaluated. The difference between these two values provides the moles of CO_2 that are absorbed. The moles of CO_2 in the vapor phase are determined by knowing the volume of the tank and the volume of the solvent. The loading, equal to the ratio of the moles of CO_2 and the moles of MEA, is determined by knowing the amount of MEA that is present in the liquid phase at the equilibrium. Several Equations of State (EoSs) have been considered for the calculation of the compressibility factor Z of CO_2, in particular the Van der Vaals, the Redlich-Kwong (Redlich and Kwong, 1949), the Soave-Redlich-Kwong (Soave, 1972) and the Peng-Robinson (Peng and Robinson, 1976). In addition, Z has been calculated with a function (Bientinesi et al., 2016) interpolating with spline functions the experimental values of Z reported for CO_2 by Perry and Green (1997). The Peng-Robinson EoS has been then selected because, as also reported by Bottcher et al. (2012) and by Hosseini Jenab et al. (2005), it well represents the CO_2 gas phase and it provides the best values of partial pressure of CO_2, in comparison with the other experimental points.
In this work, the losses of the solvent in the vapor phase because of the operation of the vacuum pump and because of the operating temperature have been included in the calculation of the amount of liquid solvent at the equilibrium.
The material balance of the unit is obtained by measuring with the electronic balance the weight of the solvent without CO_2 charged into the D2 vessel and the weight of the solvent rich in CO_2 that is discharged after the equilibrium is reached.

5. Results and Discussion

Figure 3 reports the experimental points collected at the PT lab and the ones reported in different sources in the literature for the solvent composed of water and MEA (30% wt.), for comparison, at 40°C and at 100°C. Because of the characteristics of the unit, for which the pressure is obtained at the equilibrium and cannot be set as a final given point, the exact repetition of the points reported in the literature, at the same partial pressure of CO_2

and loading, cannot be performed. This is a common feature of this type of experimental test and, for this reason, also the points in the literature are not available at the same exact values of P_{CO2} or loading of other sources. For this type of experimental tests, the unit and the procedure are considered validated if the trend of the experimental points is the same, as done for instance by Derks et al. (2010), Ali and Aroua (2004) and Dash et al. (2011) for other amine systems, and no % error can be defined with precision among different sources. In detail, the points collected at the PT lab well represent the trend obtained with the points collected by the other sources. The points by Wanderley et al. (2020) at 40°C have been reported, though they differ from the general trend (Figure 3a)) due to some issues occurred in the measurement of the pressure mentioned by the authors.

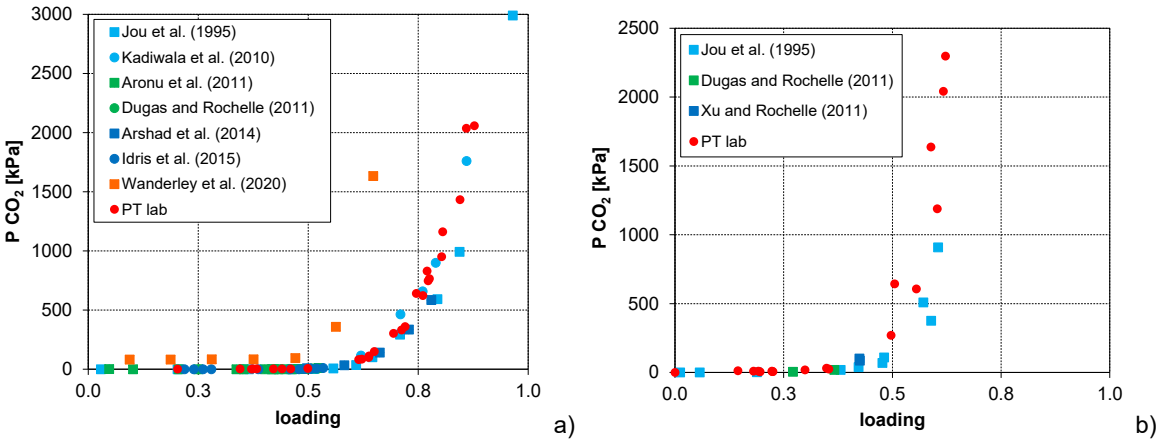


Figure 3: Experimental points of partial pressure of CO_2 reported in the literature (Aronu et al., 2011; Arshad et al., 2014a; Dugas and Rochelle, 2011; Idris et al., 2015; Jou et al., 1995; Kadiwala et al., 2010; Wanderley et al., 2020) and collected at the PT lab of Politecnico di Milano for different CO_2 loadings in the aqueous solution with 30% wt. MEA a) at 40°C and b) at 100°C

6. Conclusions

The solubility of CO_2 in novel solvents is needed to define the suitability of novel solvents for chemical or physical absorption. This work has focused on the validation of the experimental unit installed at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano, aimed at collecting data of solubility and diffusivity of gases into low volatile liquids. The solubility data of CO_2 into a 30% wt. MEA solvent have been experimentally collected and have then been compared to the values already reported in the literature. The analysis of the results confirms the validation of the experimental unit, that can be employed in the future development of this work for the study of new generation solvents.

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