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# Enthalpy of Solution and Solubility of Carbon Dioxide in Acetone: Experimental measurements and Modeling

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## **Abstract**

Carbon dioxide and acetone is an attractive mixture for a variety of industrial applications including absorption/desorption processes. To design such processes experimental thermodynamic data such as vapor-liquid equilibria, transport properties and energetic properties are required. These data are essential to develop thermodynamic models aimed at sizing operation units, estimating process parameters and simulating process plants. For (CO<sub>2</sub> + acetone) system, numerous vapor-liquid equilibrium and density data have already been measured over a wide range of temperatures and pressures. However, very little energetic properties are available for that system, only some excess enthalpy data have been reported so far. To the best of our knowledge, experimental enthalpies of solution of gaseous CO<sub>2</sub> and specific heat capacities have never been measured while they are key properties to design absorption/desorption processes and heat exchanger respectively. In this work, the enthalpy of solution of CO<sub>2</sub> in acetone have been determined using a flow calorimetric technique. This technique makes it possible to determine simultaneously the enthalpies of solution and CO<sub>2</sub> solubility limits. A thermodynamic model was used to represent of phase equilibrium and enthalpy of solution. The model parameters were adjusted to fit literature vapor-liquid equilibria data and our enthalpies of solution.

## **Introduction**

The absorption of carbon dioxide (CO<sub>2</sub>) in physical solvents are of interest for many different applications such as natural gas treatment [1], carbon capture and storage [2], absorption refrigeration [3, 4] and compression/absorption or compression/resorption heat pumps [5-17] (these two terms refer to heat pumps working with a refrigerant and a co-fluid). All the industrial processes associated with these applications work with solvents that need to match different criteria including low operating costs, low toxicity, easy regeneration for cycle processes, long term stability and last but not least high solubility of the gas in the solvent. Physical solvents are mainly polar organic compounds, in which CO<sub>2</sub> is absorbed without chemical reactions. Recent studies have shown that the ability of organic solvents to absorb CO<sub>2</sub> is tightly linked to their molecular structure and weight [18] Comparisons of CO<sub>2</sub> solubility in various physical absorbents have highlighted that both carbonyl, ether and ester groups in solvent can enhance CO<sub>2</sub> absorption [19].

Among the potential solvents for CO<sub>2</sub> absorption, acetone has been considered for a variety of applications such as refrigeration, waste heat recovery or extraction. For example, Groll *et al.* [6, 7, 9]

and Mozurkewich *et al.* [10, 11] investigated the performance of (CO<sub>2</sub> + acetone) mixture in compression/absorption cycle for automotive air conditioning. The main interest of using CO<sub>2</sub> with a cofluid is to reduce CO<sub>2</sub> high operating pressure and improve the energy efficiency of a basic CO<sub>2</sub> transcritical cycle [20]. This mixture has also been considered as a working fluid by Dàvila *et al.* [16, 17] and Gómez-Hernández *et al.* [21] for compression/resorption heat pumps. These heat pumps are intended to convert available industrial waste heat into heat with a temperature level appropriate for industrial processes. Hsieh and Vrabec [22] proposed acetone as a co-solvent to be used with supercritical CO<sub>2</sub> in extraction processes.

The experimental thermodynamic properties of (CO<sub>2</sub> + acetone) mixture has then been widely investigated in recent decades. The published papers with experimental vapor-liquid equilibrium (VLE) and density data, were recently were gathered by Ramirez-Ramos *et al.* in tables 1 and 2 of [23]. Our new VLE and density data were collected with the aim to close the knowledge gap in temperature. Our measurements include excess molar enthalpies at 283.15 K and 298.15 K and pressures from 9 MPa to 11 MPa. Zahran *et al.* [24] had measured the heat of mixing of supercritical CO<sub>2</sub> and acetone at temperatures from 313.15 K to 333.15 K and pressures from 9 MPa to 18 MPa. No experimental enthalpy of solution of CO<sub>2</sub> in acetone can be found in the literature, but a value has been derived from a thermodynamic model of phase equilibria [25] at standard condition and 298.15 K ( $\Delta_{\text{sol}}H = -14.3 \text{ kJ}\cdot\text{mol}^{-1} \text{ CO}_2$ ). However, enthalpy of solution together with vapor-liquid equilibrium are crucial properties for the evaluation of the coefficient of performance (COP) of compression/absorption cycle [10, 12].

Experimental heat of mixing CO<sub>2</sub> and acetone have been measured using a flow calorimetry technique previously developed to study acid gas dissolution in aqueous solutions [26]. In the studied conditions of temperature and pressure conditions, CO<sub>2</sub> is at a gas state. The enthalpy of solution as well as the solubility of CO<sub>2</sub> in acetone have been derived from the experimental heat of mixing. A thermodynamic model based on a  $\gamma$ - $\phi$  approach has been used to represent both vapor-liquid equilibrium and enthalpy of solution of (CO<sub>2</sub> + acetone) system. The objective is to get a model that correctly represents both VLE and enthalpy data.

## **Experimental**

### **Materials**

Carbon dioxide (purity  $\geq 99.995\%$ ) was supplied by Air Products and acetone (purity  $\geq 99.9\%$  in mass fraction) by Merck. The chemicals were used without further purification.

### **Apparatus**

Heat of mixing were determined in flow mode, using a BT2.15 calorimeter from Setaram. The overall experimental arrangement and the technical modifications made on the calorimeter to allow measurements at sub-ambient temperatures are described in [23]. Experiments are performed at constant temperature ( $\pm 0.03 \text{ K}$ ) using a Setaram G11 electronic control device. Carbon dioxide and acetone flow to the mixing cell unit located inside the calorimeter, where the heat released by the dissolution process is obtained from thermopile signal. The pure fluids are supplied by two high-pressure syringe pumps (model 260DM from ISCO). These two pumps are regulated at a constant temperature ( $\pm 0.1 \text{ K}$ ) using a thermostatic bath. The two fluids reach the working temperature

before entering the mixing cell using a precooler outside of the calorimeter, and a preheater inside the calorimeter, just above the calorimetric block [23]. The pressure is maintained constant during the experiments using two buffer volumes and a microvalve located at the end of the flow line. The pressure is measured by an electronic Keller pressure gauge placed at the outlets of the mixing cell with an uncertainty of 0.01 MPa.

### Operating procedure

The molar enthalpy of mixing  $\Delta_{\text{mix}}H$  is defined as a heat of mixing per mol of mixture (acetone and  $\text{CO}_2$ ). This enthalpy is obtained from the calorimetric signal ( $\Delta\text{signal}$ ), detected by the thermopile surrounding the mixing cell as follows:

$$\Delta_{\text{mix}}H = \frac{\Delta\text{signal}}{K \cdot (\dot{n}_{\text{CO}_2} + \dot{n}_{\text{acetone}})} \quad (\text{eq. 1})$$

where  $\Delta\text{signal}$  is the difference between the electrical signal (mV) recorded during mixing and a baseline. The baseline signal is obtained when only acetone is flowing through the set up.  $K$  is a calibration constant used to convert the calorimetric signal,  $\Delta\text{signal}$  (mV) into heat flux (mW). The calibration constant was determined at each temperature investigated in this study by measuring the heat of mixing of reference systems (see [23]). The molar flow rates  $\dot{n}_{\text{CO}_2}$  and  $\dot{n}_{\text{acetone}}$  are derived from the volume flow rates of the pumps using fluid densities. The densities of acetone and  $\text{CO}_2$  were calculated using NIST equations of state [27, 28]. The experiments are performed at constant temperature and pressure and different gas-solvent flow rate fractions. Considering the uncertainties of fluid flow rates, thermopile calibration and calorimetric signal noises, the relative uncertainty on molar flow rates and molar enthalpies of mixing are less than 1.5% and 5 % respectively.

### Thermodynamic Framework

To develop a thermodynamic model capable of representing both enthalpy and vapor-liquid equilibria data we started from the modeling work of Urukova *et al.* [25] in which the excess Gibbs energy model from Perez-Salado Kamps [29] had been parametrized to represent with a high accuracy the solubility of  $\text{CO}_2$  in acetone. This model, based on a  $\gamma$ - $\phi$  approach, was used in this study to calculate the enthalpy of solution at equilibrium conditions in addition to vapor-liquid equilibria as described in the next two sections.

#### Vapor liquid equilibrium calculation for (CO<sub>2</sub> + acetone) system

The physical equilibria that take place during the dissolution process are expressed as follows:



The vapor-liquid equilibrium of the solvent (eq. 2) is represented via the extended Raoult's law (eq. 4). The asymmetric convention is used for  $\text{CO}_2$  by applying the extended Henry's law (eq. 5). Therefore, the phase equilibrium condition for acetone (A) and the dissolved gas ( $\text{CO}_2$ ) yields:

$$y_A \phi_A p = a_A \phi_A^{\text{sat}} p_A^{\text{sat}} \exp\left(\frac{v_A^{\text{sat}}(p - p_A^{\text{sat}})}{RT}\right) \quad (\text{eq. 4})$$

$$\gamma_{\text{CO}_2} \phi_{\text{CO}_2} p = \gamma_{\text{CO}_2} m_{\text{CO}_2} k_{\text{H,CO}_2,\text{A}}^m(T, p_{\text{A}}^{\text{sat}}) \exp\left(\frac{\bar{v}_{\text{CO}_2,\text{A}}^\infty (p - p_{\text{A}}^{\text{sat}})}{RT}\right) \quad (\text{eq. 5})$$

$p_{\text{A}}^{\text{sat}}$ ,  $v_{\text{A}}^{\text{sat}}$  and  $\phi_{\text{A}}^{\text{sat}}$  are at the saturation, the pressure, the molar liquid volume and the fugacity coefficient of acetone.  $R$ ,  $T$ , and  $p$  refer to the universal gas constant, temperature and pressure respectively.  $a_i$ ,  $y_i$ ,  $\phi_i$ ,  $\gamma_i$  and  $m_i$  stand for the activity, the mole fraction in the vapor phase, the fugacity coefficient in the vapor phase, the activity coefficient in the liquid phase and the molality of component  $i$  (with  $i = \text{A}$  or  $\text{CO}_2$ ).  $k_{\text{H,CO}_2,\text{A}}^m$  and  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$  are Henry's constant of  $\text{CO}_2$  (on the molality scale) in acetone at saturation pressure of the solvent  $p_{\text{A}}^{\text{sat}}$  and the partial molar volume of  $\text{CO}_2$  at infinite dilution in acetone.

The reference sources for the Henry's law constant  $k_{\text{H,CO}_2,\text{A}}$ , on molality scale, for carbon dioxide in pure acetone, the vapor pressure  $p_{\text{A}}^{\text{sat}}$  and molar volume  $v_{\text{A}}$  of pure acetone, are those reported by Urukova *et al.* [25] and Jödecke *et al.* [30]. Since no experimental data was found in the literature to estimate the temperature dependence of  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$ , Urukova *et al.* [25] treated this property as an adjustable parameter using a linear temperature dependence. Nevertheless, the resulting parameters led them to unrealistic values of  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$ . Partial molar volume of  $\text{CO}_2$  at infinite dilution were here obtained from REFPROP9 software at saturation pressure and temperatures from 283.15 K to 383.15 K. The calculated values fitted to a polynomial equation (eq.6):

$$\bar{v}_{\text{CO}_2,\text{A}}^\infty = 75.47 - 0.1122B \cdot T(K) + 3.598 \cdot T(K)^2 \quad (\text{eq.6})$$

The vapor phase fugacity coefficients ( $\phi_{\text{A}}$ ,  $\phi_{\text{CO}_2}$  and  $\phi_{\text{A}}^{\text{sat}}$ ), in eqs 4 and 5, are calculated using a truncated virial equation of state. Pure component second virial coefficients were calculated from the correlation given by Dymond and Smith [31]. Mixed second virial coefficients were obtained with the method proposed by Hayden and O'Connell [32]. Further details were given by Jödecke *et al.* [30].

The activity coefficient of  $\text{CO}_2$  in pure acetone,  $\gamma_{\text{CO}_2}$ , is calculated using Pitzer excess Gibbs energy model [33] as modified by Edwards *et al.* [34].

$$\ln \gamma_{\text{CO}_2} = 2m_{\text{CO}_2} \beta_{\text{CO}_2,\text{CO}_2}^0 + 3m_{\text{CO}_2}^2 \tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2} \quad (\text{eq. 7})$$

where,  $\beta_{\text{CO}_2,\text{CO}_2}^0$  and  $\tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$  are the binary and ternary Pitzer interaction parameters respectively which depend on temperature as follows:

$$\beta_{\text{CO}_2,\text{CO}_2}^0 = a_{\text{CO}_2,\text{CO}_2} + b_{\text{CO}_2,\text{CO}_2}/T \quad (\text{eq. 8})$$

$$\tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2} = c_{\text{CO}_2,\text{CO}_2,\text{CO}_2} + d_{\text{CO}_2,\text{CO}_2,\text{CO}_2}/T \quad (\text{eq. 9})$$

$a_{\text{CO}_2,\text{CO}_2}$ ,  $b_{\text{CO}_2,\text{CO}_2}$ ,  $c_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$  and  $d_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$  are adjustable parameters of the model.

The activity of acetone is derived from the Gibbs-Duhem equation:

$$\ln a_{\text{A}} = -M_{\text{A}}(m_{\text{CO}_2}^2 \beta_{\text{CO}_2,\text{CO}_2}^0 + 2m_{\text{CO}_2}^3 \tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2} + m_{\text{CO}_2}) \quad (\text{eq.10})$$

with  $M_{\text{A}}$ , the molecular mass of acetone in  $\text{kg} \cdot \text{mol}^{-1}$ .

The VLE of ( $\text{CO}_2 + \text{acetone}$ ) system are obtained by solving the two equilibrium equations (eqs 4 and 5) with respect to two unknowns using an iterative Newton Raphson method. Here, total pressure of the system and the vapor phase composition are calculated for a given temperature and  $\text{CO}_2$  molality.

### Enthalpy of solution of CO<sub>2</sub> in acetone calculation

The enthalpy of solution of CO<sub>2</sub> in acetone is calculated using Gibbs-Helmholtz equation:

$$\left(\frac{\partial \Delta_{\text{sol}}G/T}{\partial T}\right)_p = -\frac{\Delta_{\text{sol}}H}{T^2} \quad (\text{eq.11})$$

The free enthalpy of solution of CO<sub>2</sub> in acetone (eq 11) is expressed as follows:

$$\Delta_{\text{sol}}G = RT \left[ \ln k_{\text{H,CO}_2,\text{A}}^m(T, p_{\text{A}}^{\text{sat}}) + \ln \left( m_{\text{CO}_2} \gamma_{\text{CO}_2} \exp \left( \frac{v_{\text{CO}_2,\text{A}}^{\infty} (p - p_{\text{A}}^{\text{sat}})}{RT} \right) \right) - \ln (y_{\text{CO}_2} \phi_{\text{CO}_2} p) \right] (\text{eq.12})$$

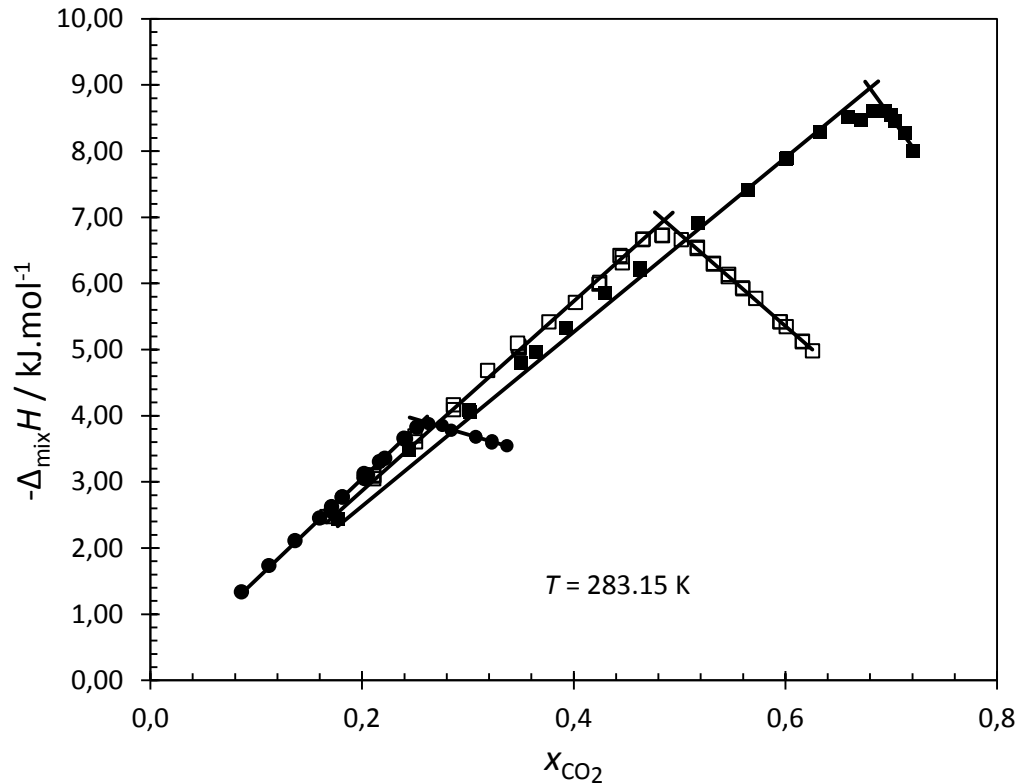
The enthalpy of solution is thus obtained using eq.11 and 12:

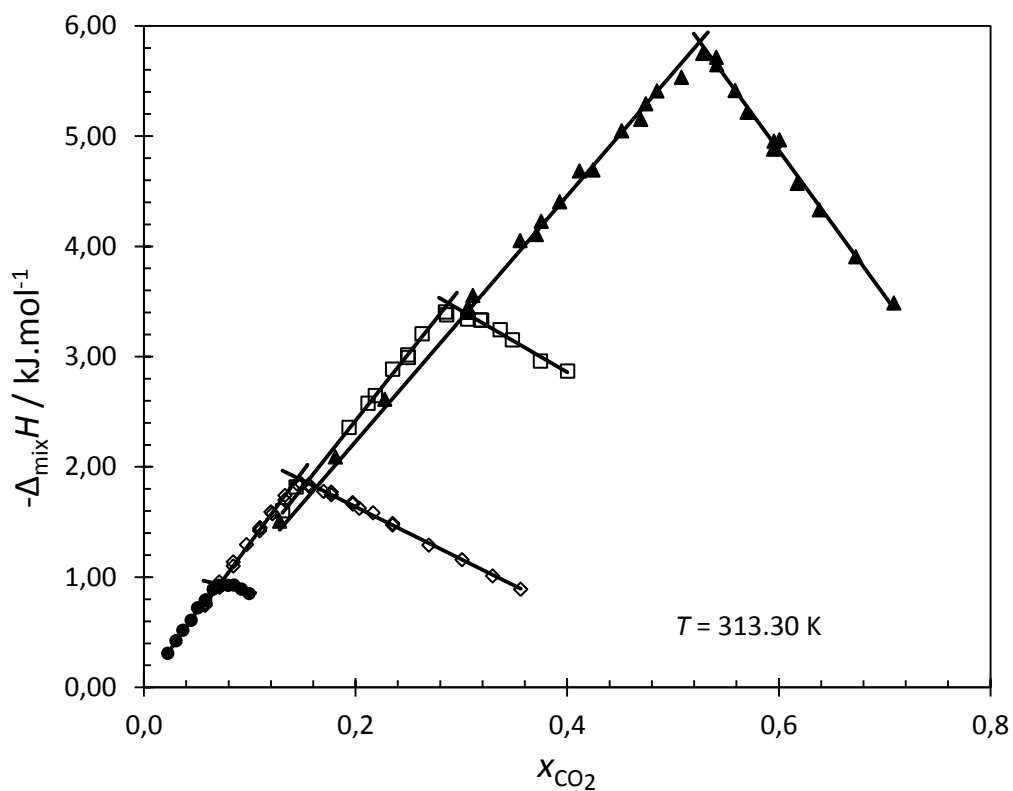
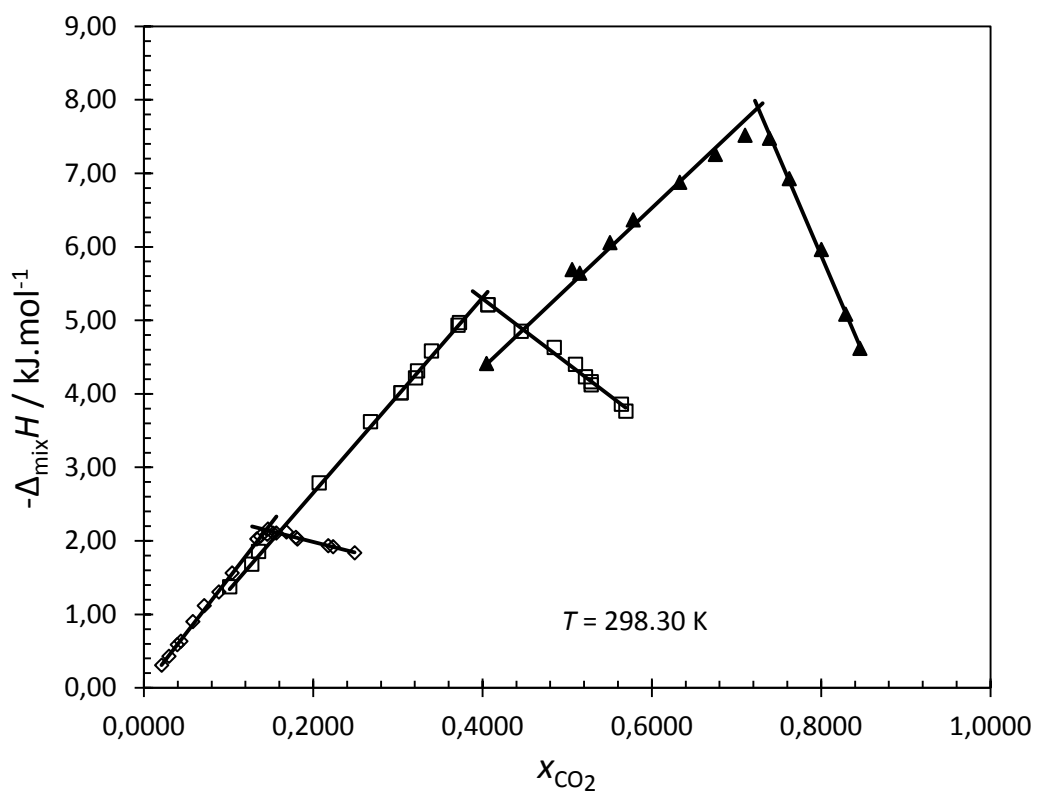
$$\Delta_{\text{sol}}H = -RT^2 \left[ \left( \frac{\partial \ln k_{\text{H,CO}_2,\text{A}}^m(T, p_{\text{A}}^{\text{sat}})}{\partial T} \right)_p + \left( \frac{\partial \ln \gamma_{\text{CO}_2}}{\partial T} \right)_p + \left( \frac{\partial v_{\text{CO}_2,\text{A}}^{\infty} (p - p_{\text{A}}^{\text{sat}})/RT}{\partial T} \right)_p - \left( \frac{\partial \ln \phi_{\text{CO}_2}}{\partial T} \right)_p \right] (\text{eq.13})$$

The enthalpy of solution is calculated at the vapor-liquid equilibrium (eq. 3) at a given temperature and pressure. For that purpose, the composition of the liquid and vapor phase of the system is obtained by solving the two equilibrium equations (eqs 4 and 5) for a given temperature and pressure.

### Experimental Results

The enthalpy of mixing of CO<sub>2</sub> in acetone was measured at 283.15 K, 298.3 K and 313.3 K and constant pressures from 0.51 MPa to 4.22 MPa. The numerical results together with their experimental uncertainties are listed in the supplementary information (Tables S1-3). Exothermic effects were observed for all investigated (Figure 1).





**Figure 1.** Enthalpies of mixing of CO<sub>2</sub> in acetone at temperatures 283.15 K, 298.3 K and 313.3 K, and pressures (●) 0.51 MPa (at 313.30 K) and 0.71 MPa (at 298.30 K), (◇) 1 MPa, (□) 2 MPa, (■) 3.01 MPa and (▲) 4 MPa.

These graphs make it possible to distinguish the domains before and after the saturation of acetone by CO<sub>2</sub>. First, the gas is completely absorbed by the solvent and the absolute value of the enthalpy of mixing ( $|\Delta_{\text{mix}}H|$ ) increases linearly with  $x_{\text{CO}_2}$ . Second, after saturation there are two phases, saturated liquid acetone and a rich CO<sub>2</sub> gas phase. The enthalpy of mixing decrease linearly because the enthalpy of mixing is calculated using the total amount of CO<sub>2</sub> delivers by the pump while, after the saturation, only a part of the gas is really absorbed.

The enthalpy of solution  $\Delta_{\text{sol}}H$  (defined as heat per one mole of CO<sub>2</sub>) and the gas solubility are determined simultaneously at each condition of pressure and temperatures from the plots of the enthalpy of mixing versus the gas molar fraction  $x_{\text{CO}_2}$  (Figure 1). For that purpose, a linear regression is used to fit the dependence of  $\Delta_{\text{mix}}H$  on CO<sub>2</sub> molar fraction both in the unsaturated and saturated regions. The intersection point determines the CO<sub>2</sub> solubility limit. The enthalpy of solution is given by the slope of the fitting curve in the unsaturated domain [26]. All the results are given in Tables 2 and 3. The maximum uncertainty on the enthalpy of solution and on the solubility of CO<sub>2</sub>, based on propagation of uncertainty calculations and experimental reproducibility, can be estimated to be 5 and 7%, respectively.

**Table 1.** Experimental and calculated solubility of CO<sub>2</sub> in acetone at 283.15 K, 298.30 K and 313.30 K<sup>a</sup>

$T^a$	$p$	$u(p)$	$x_{\text{CO}_2}^{\text{exp}}$	$u(x_{\text{CO}_2}^{\text{exp}})$	$x_{\text{CO}_2}^{\text{calc b}}$	$x_{\text{CO}_2}^{\text{calc c}}$
K	MPa					
283.15	1.01	0.01	0.257	0.01	0.284	0.270
	2.00	0.01	0.485	0.02	0.527	0.516
	3.01	0.01	0.680	0.05	0.624	0.743
298.30	0.71	0.02	0.144	0.01	0.141	0.139
	2.15	0.03	0.399	0.02	0.423	0.401
	4.22	0.06	0.723	0.04	0.618	0.738
313.18	0.51	0.02	0.068	0.005	0.072	0.073
	1.00	0.01	0.146	0.005	0.149	0.147
	2.00	0.01	0.288	0.015	0.299	0.289
	4.02	0.03	0.525	0.036	0.538	0.548
<b>ARD<sup>d</sup> (%)</b>					6.4	4.0

<sup>a</sup>  $u(T) = 0.03 \text{ K}$

<sup>b</sup> Calculated using model parameters from this work

<sup>c</sup> Calculated using model parameters from Urukova *et al.*

<sup>d</sup> Average relative deviation  $\text{ARD} = 1/N \sum_i^N |x_{\text{CO}_2,i}^{\text{exp}} - x_{\text{CO}_2,i}^{\text{calc}}| / |x_{\text{CO}_2,i}^{\text{exp}}|$

**Table 2.** Experimental and calculated enthalpies of solution CO<sub>2</sub> in acetone at 283.15 K, 298.30 K and 313.30 K<sup>a</sup>

$T^a$	$p$	$u(p)$	$\Delta_{\text{sol}}H^{\text{exp}}$	$u(\Delta_{\text{sol}}H^{\text{exp}})$	$\Delta_{\text{sol}}H^{\text{calc b}}$	$\Delta_{\text{sol}}H^{\text{calc c}}$
K	MPa		kJ.mol <sup>-1</sup> CO <sub>2</sub>			
283.15	1.01	0.01	-15.3	0.7	-14.6	-16.2
	2.00	0.01	-14.3	0.5	-13.7	-17.6
	3.01	0.01	-13.2	0.5	-12.8	-18.5



	0.71	0.02	-14.9	0.7	-13.7	-14.6
298.30	2.15	0.03	-13.3	0.5	-12.9	-15.9
	4.22	0.06	-10.9	0.5	-11.4	-17.5
313.18	0.51	0.02	-13.8	0.6	-12.9	-13.5
	1.00	0.01	-13.1	0.5	-12.7	-13.8
313.30	2.00	0.01	-12.1	0.4	-12.2	-14.4
	4.02	0.03	-11.1	0.4	-10.9	-15.9
<b>ARD<sup>d</sup> (%)</b>					4	22

<sup>a</sup>  $u(T) = 0.03$  K

<sup>b</sup> Calculated using model parameters from this work

<sup>c</sup> Calculated using model parameters from Urukova *et al.* [25]

<sup>d</sup> Average relative deviation  $ARD = 1/N \sum_i^N |\Delta_{sol}H_i^{exp} - \Delta_{sol}H_i^{calc}| / |\Delta_{sol}H_i^{exp}|$

## Modelling Results

First, model parameters determined by Urukova *et al.* [25] have been used to assess the experimental solubilities and enthalpies from this work. Comparisons are given in Tables 1 and 2 and in figure 2. Although their parameters can predict vapor-liquid equilibria data with a good accuracy, they can not correctly represent the pressure dependence of the enthalpy of solution. Indeed, at a given temperature the calculated enthalpies are found to increase with pressure while the opposite variation is observed experimentally (table 2). By analysing carefully, the contribution of each term of eq 13 to the total enthalpy of solution, we have noticed that this resulting wrong pressure dependence was related to the calculation of the temperature derivative of the activity coefficient of CO<sub>2</sub>. Indeed, the temperature dependence of  $\beta_{CO_2,CO_2}^0$  and  $\tau_{CO_2,CO_2,CO_2}$  parameters determined by Urukova *et al.* [25] can not allow a correct representation of the enthalpies.

Therefore, new parameters have been determined to improve the thermodynamic consistency of the model. For that purpose we combined VLE data used by Urukova [25] in their correlation (Jödecke *et al.* [30] and Adrian and Maurer [35]), with the recent VLE data from Ramirez *et al.* [23] (Table 3) and our enthalpy data (Table 2).

**Table 3.** Selected experimental VLE data from the literature and their comparison with correlation results from the model.

Source	$N^a$	$T$ (K)	$p^{max}$ (MPa)	$m_{CO_2}^{max}$ (mol.kg <sup>-1</sup> )	$\Delta\bar{p}$ (MPa) <sup>b</sup>	$\Delta\bar{p}/p$ (%) <sup>c</sup>
<b>Correlation</b>						
Jödecke <i>et al.</i> [30]	10	313-354	4.56	15.6	0.03	1.4
Adrian and Maurer [35]	9	313-333	3.99	21.1	0.06	1.9
Ramirez <i>et al.</i> [23]	119	283-383	4.75	26.2	0.07	3.1

<sup>a</sup>  $N$  = number of experimental data points within the given ranges.

<sup>b</sup>  $\Delta\bar{p} = 1/N \sum_i^N |p_i^{exp} - p_i^{calc}|$ .

<sup>c</sup>  $\Delta\bar{p}/p = 1/N \sum_i^N |p_i^{exp} - p_i^{calc}| / p_i^{exp}$

The temperature range and the maximum molality for which VLE data have been fitted is from 283.15 K to 383.15 K and  $m_{CO_2}^{max} = 26.2$  mol.kg<sup>-1</sup>. While the ternary Pitzer interaction parameter,  $\tau_{CO_2,CO_2,CO_2}$ , should allow a better representation of the interaction of the system for gas molality above 25 mol.kg<sup>-1</sup>, fits have been restricted to  $m_{CO_2} \leq 27$  mol.kg<sup>-1</sup> to improve our correlation. All the

experimental enthalpies of solution have been included in the regression procedure. The adjustment of the parameters of Pitzer activity coefficient model (eqs. 8 and 9) was performed with Minuit software [36], using Simplex method and the objective function  $F$  as expressed in eq 14:

$$F = w_{VLE} \sum_i^n \left( \frac{p_i^{\text{exp}} - p_i^{\text{calc}}}{p_i^{\text{exp}}} \right)^2 + w_H \sum_i^m \left( \frac{\Delta_{\text{sol}}H_i^{\text{exp}} - \Delta_{\text{sol}}H_i^{\text{calc}}}{\Delta_{\text{sol}}H_i^{\text{exp}}} \right)^2 \quad (\text{eq. 14})$$

where  $p_i^{\text{exp}}$ ,  $p_i^{\text{calc}}$ ,  $\Delta_{\text{sol}}H_i^{\text{exp}}$  and  $\Delta_{\text{sol}}H_i^{\text{calc}}$  are the experimental and calculated pressure and enthalpy of solution of data  $i$ ;  $n$  and  $m$  are the number of experimental vapor liquid equilibria and enthalpy data points respectively and  $w$  denotes weighting factors. As model parameters are much more sensitive to VLE data than to  $\Delta_{\text{sol}}H$  data, weighting factors were initially set to  $w_{VLE} = 1$  and  $w_H = 0.25$  and then, manually adjusted to ensure the best compromise between the reproduction of VLE and  $\Delta_{\text{sol}}H$  data.

The resulting parameters are given in eqs. 15-16.

$$\beta_{\text{CO}_2, \text{CO}_2}^0 = -0.03747 + 1.211/T(\text{K}) \quad (\text{eq. 15})$$

$$\tau_{\text{CO}_2, \text{CO}_2, \text{CO}_2} = 0.3385 \times 10^{-3} - 0.01901/T(\text{K}) \quad (\text{eq. 16})$$

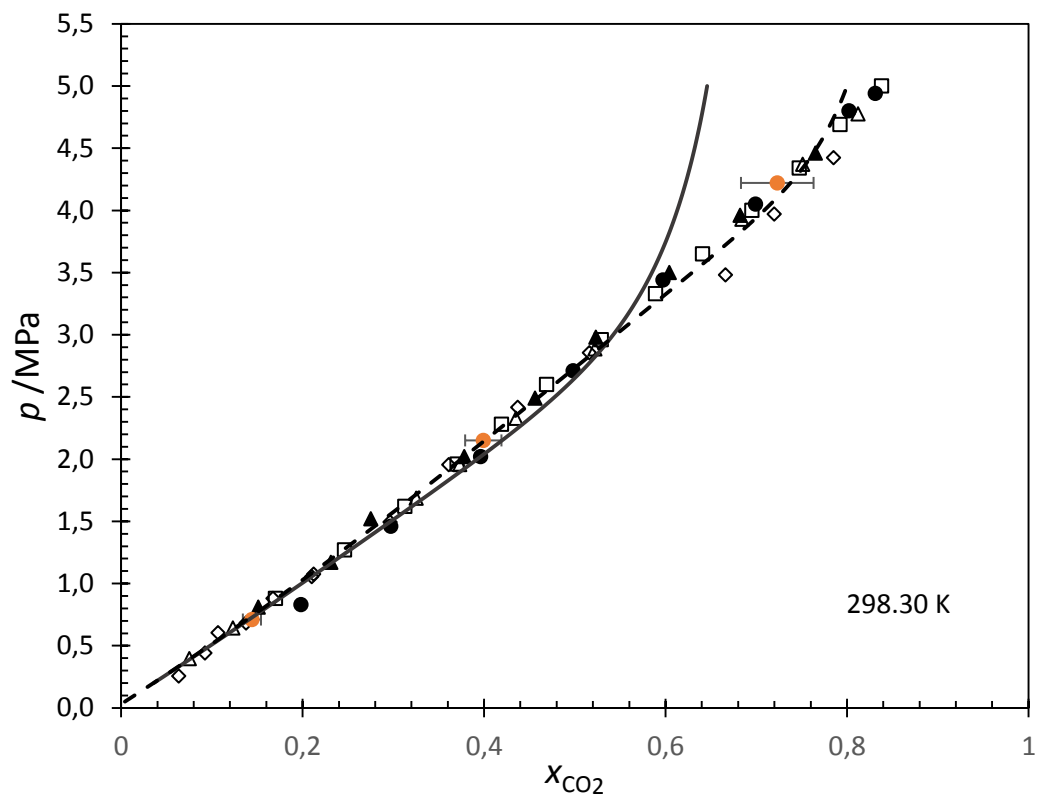
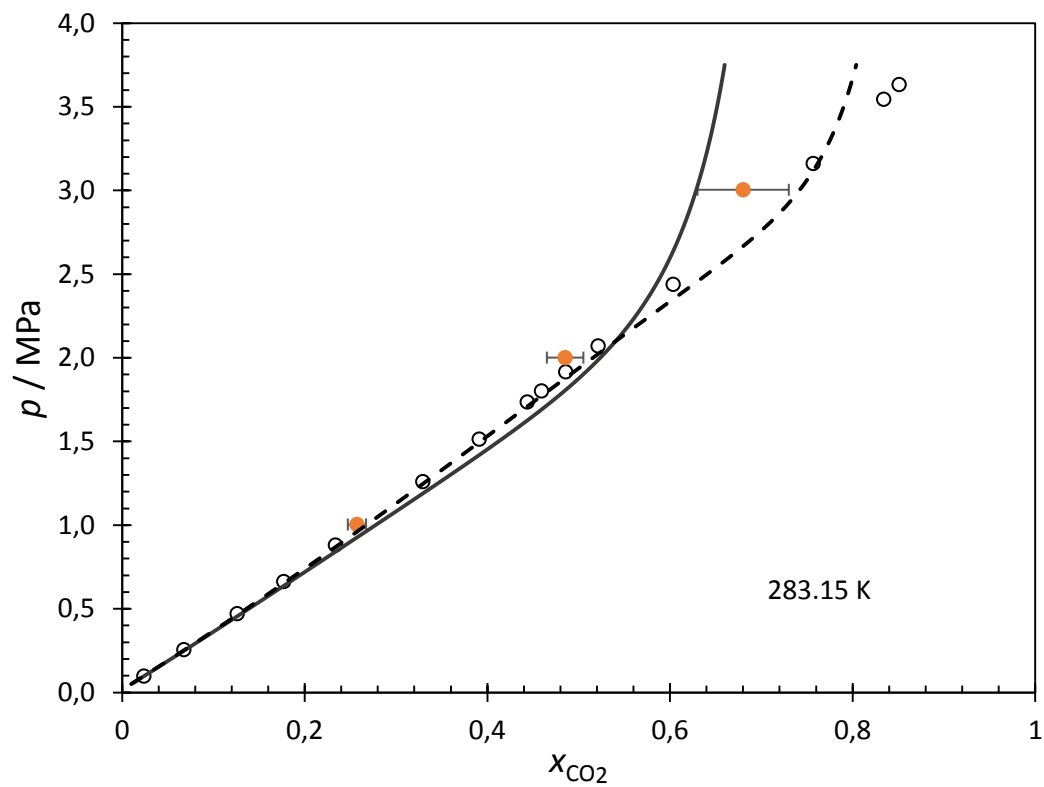
The average relative deviations of the regression are given in Table 2 and Table 3 for the enthalpies and the vapor-liquid equilibria data respectively.

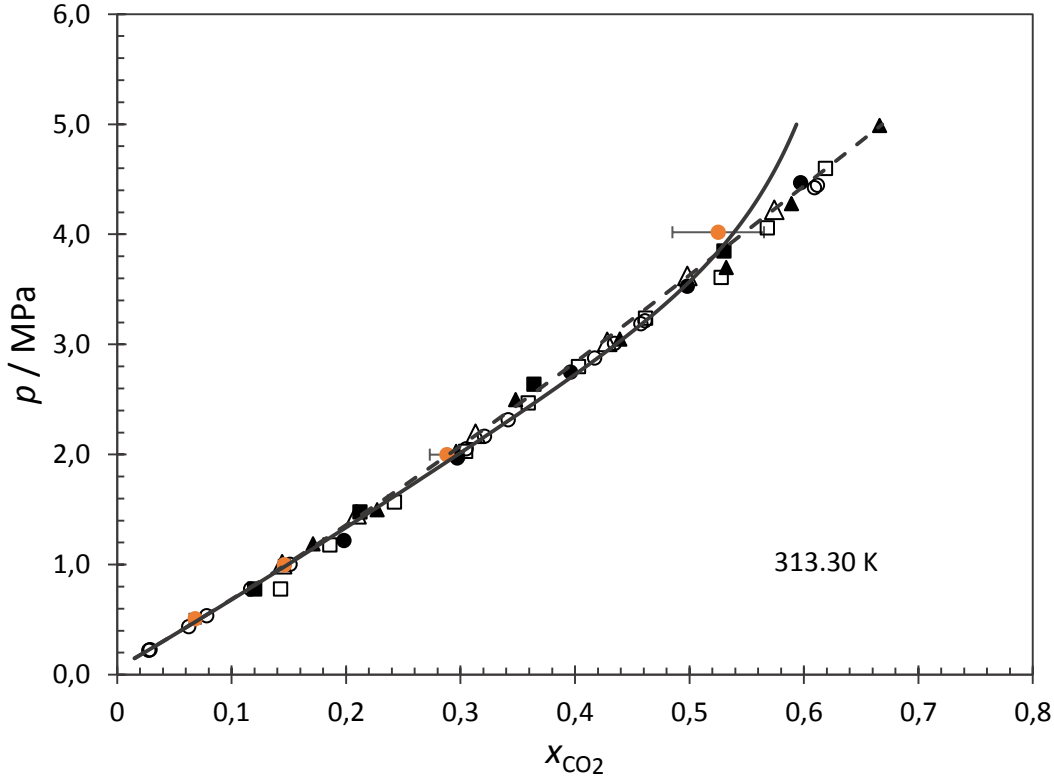
## **Discussion**

### **CO<sub>2</sub> solubility in acetone**

The solubility of CO<sub>2</sub> in acetone at temperatures from 283.15 K to 313.3 K and pressures from 0.51 to 4.22 MPa were compared with experimental literature data in Figure 2. At 298.3 K and 313.3 K, a good agreement within the experimental uncertainties is observed. At 283.15 K and 3.01 MPa, experimental solubility data exhibits a slight discrepancy with the values from Ramirez-Ramos *et al.* [23]. It should be noted that experimental determination of CO<sub>2</sub> solubility limit is usually based on direct vapor-liquid equilibria measurements using static synthetic or analytic methods [37]. Values obtained indirectly in this study from calorimetric measurements exhibit thus a larger uncertainty compared to literature data.

In figure 2, calculated solubility using both model parameters from Urukova *et al.* [25] and those from this work are represented. A good agreement is observed between calculated and experimental value using Urukova *et al.* [25] model parameters except for pressures above 3.5 MPa and 5.0 MPa at 283.15 K and 298.3 K respectively. The parameters obtained in this work can not correlate the solubility with the same accuracy, calculated equilibrium data diverge much more quickly from  $x_{\text{CO}_2} > 0.55$  ( $m_{\text{CO}_2} \approx 21 \text{ mol.kg}^{-1}$ ).





**Figure 2.** Comparison of our experimental solubility of CO<sub>2</sub> in acetone measurements with literature data. (●), this work ; (○), [23]; (●), [38]; (□), [39]; (■), [40]; (△), [41]; (▲), [42]; (◇), [37]. Lines and dotted lines are calculated using model parameters from this work and Urukova *et al.* [25] respectively.

### Enthalpy of solution

The enthalpy of solution  $\Delta_{\text{sol}}H$  (in Joule per mole of dissolved CO<sub>2</sub>) at constant temperature and pressure determined from the composition dependence of  $\Delta_{\text{mix}}H$  (Figure 1) are resumed in Table 2. The enthalpy of solution of carbon dioxide in acetone is exothermic in the range of temperature and pressure investigated. At a constant temperature, it is observed that the absolute value  $|\Delta_{\text{sol}}H|$  decreases with increasing pressure. At a constant pressure, absolute value  $|\Delta_{\text{sol}}H|$  decreases with increasing temperature which agrees with the temperature dependence of solubility measurements.

The agreement between calculated enthalpies and experimental results (Table 2) is within experimental uncertainty (5%). At each temperature the model parameters determined in this work allow a correct representation of the pressure dependence of the enthalpy of solution. The accuracy on the calculated enthalpy depends mainly on the accuracy of temperature dependence of model parameters such as the Henry's constant of CO<sub>2</sub> in acetone ( $k_{\text{H},\text{CO}_2,\text{A}}^m$ ), the partial molar volume of CO<sub>2</sub> at infinite dilution in acetone ( $\bar{v}_{\text{CO}_2,\text{A}}^\infty$ ), the fugacity ( $\phi_{\text{CO}_2}$ ) and the activity coefficient of CO<sub>2</sub> ( $\gamma_{\text{CO}_2}$ ). Among them, Henry's constant of CO<sub>2</sub> in acetone ( $k_{\text{H},\text{CO}_2,\text{A}}^m$ ) has been carefully determined by Jödecke *et al.* [30]. Likewise, the fugacity coefficient of CO<sub>2</sub> is calculated using a virial equation of state for which the temperature dependence of the pure component and mixed second virial coefficient is well estimated (Jödecke *et al.* [30]). Only  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$  and  $\gamma_{\text{CO}_2}$  ( $\beta_{\text{CO}_2,\text{CO}_2}^0$  and  $\tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$ ) remain to be determined. As pointed out by Urukova *et al.* [25], there are many combination of the three parameters,  $\beta_{\text{CO}_2,\text{CO}_2}^0$ ,  $\tau_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$ , and  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$  which may results in a good correlation of the experimental solubility data. Since no volumetric data are available to estimate  $\bar{v}_{\text{CO}_2,\text{A}}^\infty$ , its temperature dependence has been approximated using REFPROP9. It allows thus to limit the number

of parameters to adjust and give a more realistic estimation of this data. Finally, by using enthalpies of solution data in the regression and setting  $\bar{v}_{\text{CO}_2, \text{A}}^\infty$  temperature dependence, the number of combinations has been reduced and provide a more consistent representation of (CO<sub>2</sub> + acetone) system.

## Conclusion

CO<sub>2</sub> absorption in acetone was investigated using a thermodynamic approach. Experimental enthalpies of solution and gas solubility data were determined as a function of temperature (283.15 K, 298.30 K and 313.30 K) and pressure (from 0.51 to 4.22 MPa). To our knowledge, these are the first experimental enthalpies of solution of CO<sub>2</sub> in acetone to be reported in the literature. A thermodynamic model based on a  $\gamma$ - $\phi$  approach was used to describe CO<sub>2</sub> dissolution. New binary and ternary interaction parameters were determined to represent the non-ideality of the liquid phase using Pitzer excess Gibbs energy model. These parameters can be used for process simulation to estimate the enthalpy of solution of CO<sub>2</sub> in acetone in a large range of temperature (283 K < T < 383 K) and vapor-liquid equilibrium data for  $m_{\text{CO}_2} < 21 \text{ mol.kg}^{-1}$ .

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