

# THERMODYNAMIC MODELLING OF THE ABSORPTION OF ACID GAS IN A MIXED SOLVENT BY ELECTROLYTE NRTL EQUATION: NEW EQUIPMENT AND MEASURING

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A new process of gas sweetening based on the absorption of acid gas (CO<sub>2</sub> & H<sub>2</sub>S) by mixing chemical solvents (aqueous diethanolamine) and physical solvents (methanol) is being developed at IFP in partnership with TFE. No literature data in representative temperature range concerning the vapour-liquid equilibrium of these systems can be found. Therefore, we developed a new experimental apparatus to measure the vapour-liquid equilibrium of these systems for pressures up to 100 bar and temperatures up to 120°C. There is no much literature concerning the modelling of these kind of systems therefore this aspect is also treated .

## 1 INTRODUCTION

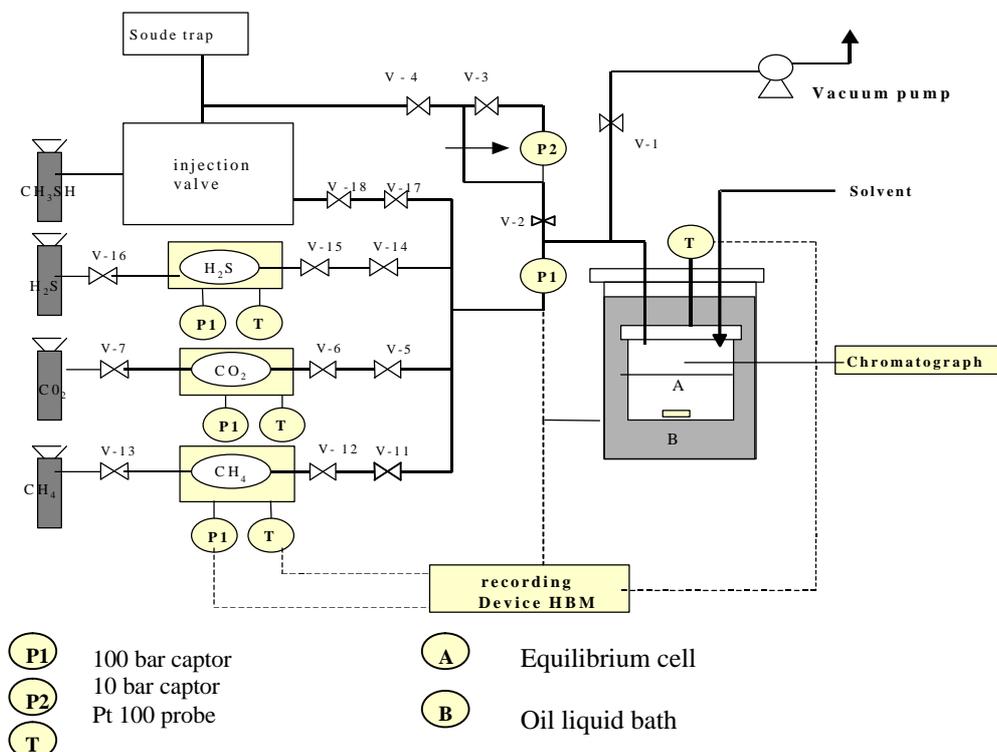
Natural gas issued from well production has to be treated to remove acid gases (CO<sub>2</sub> & H<sub>2</sub>S) in order to meet transport requirements and sale gas specifications. There are two great families of solvents used for this kind of gas treatment; chemical and physical solvents. Chemical solvents are able to reduce the H<sub>2</sub>S and CO<sub>2</sub> content to low levels, resulting in a sharp separation; however the capacity is limited by the stoichiometry of the reaction of the acid gas with alknolamine base. Physical solvents are not limited and their absorption capacities are approximately proportional to the partial pressure of acid gas in the stream to be treated. New solvents such as mixed solvents are an attempt to meld the advantages of chemical and physical solvents.

A new process of gas sweetening “HYBRISOL” coupling chemical solvent (aqueous solution of Diethanolamine “DEA”) and physical solvent (Methanol “CH<sub>3</sub>OH”) is being developed at IFP in partnership with TFE [1]. The knowledge of acid gases solubility in these liquid solvents is essential for the design of the natural gas treatment units process. That’s why IFP developed a new apparatus permitting the measurement of different liquid-vapour equilibria of mixtures systems (CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>3</sub>SH, CH<sub>4</sub>). In the present paper we will focus our interest over the system H<sub>2</sub>O – DEA – CH<sub>3</sub>OH – CO<sub>2</sub>. The experimental method described in this article is a simple synthetic method. To make sure of the validity of our experimental apparatus and to confirm the experimental procedure, it is necessary to compare our measurements to data reported in the literature. Secondly, we present the modelling of the different under systems water – diethanolamine – methanol, water – diethanolamine – H<sub>2</sub>S and water – methanol – H<sub>2</sub>S which is realized by the mean of the NRTL and Electrolyte NRTL equation.

## 2 MATERIALS AND METHOD

### • Apparatus

The equilibrium measurements were done in the apparatus shown in figure1. This equipment is essentially divided in two main parts. The first one is the equilibrium cell in which we introduce the solvent and the second one is the circuit gas lines connected with the equilibrium cell, constituted from several gas reservoirs.



**Figure 1.** Experimental equipment for liquid-vapour phase equilibrium measurements.

The equilibrium cell is made of Helloy and it is positioned in a LAUDA<sup>®</sup> liquid bath thermostat. The cell has been designed to operate at pressures up to 100 bar and temperatures range between 40 and 200°C. The cell is equipped with an agitation rotor to ensure the homogeneity of the liquid and vapour phase. The temperature is measured by a Pt 100 probe. The pressure is measured with an HBM<sup>®</sup> pressure captor of 10 bar or 100 bar, depending of the pressure range in the cell. The gas circuits consist of three storage bottles (CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S) and an injection valve of CH<sub>3</sub>SH. The storage bottles are plunged in LAUDA<sup>®</sup> liquid bath thermostats, and equipped with a platinum probe to measure the temperature and an HBM<sup>®</sup> 100 bar pressure captor to measure the pressure. All the circuit lines are overheated to avoid risks of condensation. The synthetic method is used for the determination of the acid gas absorbed quantity using the mass balance equation formula based on the knowledge of the system pressure, volume and temperature conditions. Therefore the precise knowledge of the different volumes of the circuit is important ; it is also necessary to calibrate the pressure captors and the temperature probes.

- **Experimental procedures**

We will explain the experimental procedure by using as an example the CO<sub>2</sub>.

The first part of the experimentation consists on the solvent degazification by the cryogenic method. In that purpose the solvent is prepared with desired strength and is introduced in the equilibrium cell which is immersed in a nitrogen liquid bath. The solvent is then crystallised and vacuumed by the way of a pump. The system is then programmed at the experimental conditions, the cell liquid bath and the lines are heated at the desired temperature. When system stabilisation is reached we can read the cell pressure indicated on the recording device; it represents the solvent vapour pressure.

A desired CO<sub>2</sub> amount is introduced in the equilibrium cell. We wait the system stabilisation of the system solvent /CO<sub>2</sub> for about 1 hour. The pressure indicated by the equilibrium cell captor is the total system pressure. This operation of introduction of the acid gas can be repeated in continue, which allow covering a large interval of loading. The loading represents the ratio between the mole number of the absorbed CO<sub>2</sub> and the mole number of diethanolamine. The variables collected in this part are the CO<sub>2</sub> reserve pressure after CO<sub>2</sub> introduction and the total pressure in the equilibrium cell. These different variables allow us to calculate the quantities of carbon dioxide absorbed into the solvent mixture.

- **Determination of the absorbed CO<sub>2</sub> quantity in the mixed solvent**

The synthetic method consists in determining the CO<sub>2</sub> quantity absorbed in the liquid phase by the knowledge of the introduced quantity of CO<sub>2</sub> and the quantity of CO<sub>2</sub> in the vapour phase. We can calculate the acid gas mole number introduced in the equilibrium cell, by using a specific equation of state and the knowledge of the reserves volume, the pressure and the temperature of the system before and after the acid gas introduction in the equilibrium cell. In order to determine the absorbed quantity of acid gas in the solvent, we write the mass conservation equation (for the present demonstration the acid gas used is CO<sub>2</sub>). The quantity of carbon dioxide introduced in the cell is divided into two part : a quantity of CO<sub>2</sub> in the vapour phase and another quantity of carbon dioxide absorbed by the solvent.

$$n_{CO_2 \text{ Introduced}} = \frac{P_{1CO_2 \text{ reserve}} V_{circuitCO_2}}{Z_{CO_2} RT_{1 \text{ reserve}}} - \frac{P_{2CO_2 \text{ reserve}} V_{circuitCO_2}}{Z_{CO_2} RT_{2 \text{ reserve}}} = n_{CO_2 \text{ cell}} = n_{CO_2 \text{ Liquid}} + n_{CO_2 \text{ vapour}} \quad (1)$$

where:

$n_{CO_2 \text{ Vapour}}$  : CO<sub>2</sub> mole number in the vapour phase.

$n_{CO_2 \text{ Liquid}}$  : CO<sub>2</sub> mole number absorbed by the solvent.

$P_{1CO_2 \text{ reserve}}$  is the CO<sub>2</sub> pressure in the reservoir before introduction,  $P_{2CO_2 \text{ reserve}}$  represents the CO<sub>2</sub> pressure in the reservoir after introduction,  $T_{1 \text{ reserve}}$  is the CO<sub>2</sub> temperature in the reserve before introduction,  $T_{2 \text{ reserve}}$  is the CO<sub>2</sub> temperature in the reserve after introduction of CO<sub>2</sub>,  $V_{circuit CO_2}$  is the volume of the CO<sub>2</sub> circuit, R is the gas perfect constant and  $Z_{CO_2}$  is the CO<sub>2</sub> compressibility factor. The CO<sub>2</sub> compressibility factor is a function of the temperature and the pressure and is determined from the IUPAC tables [2]

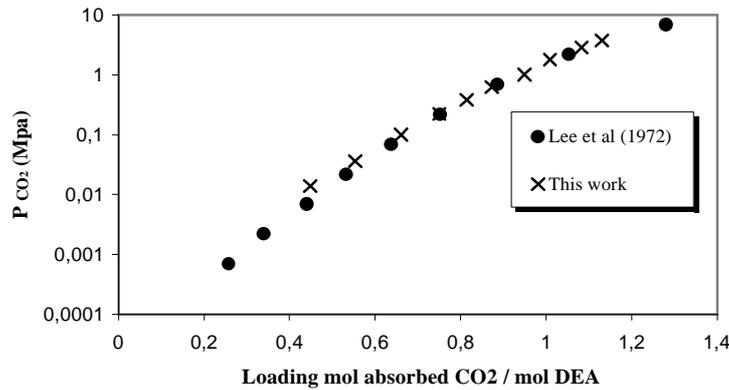
All the details concerning this method are presented by Habchi Tounsi *et al.* [3].

### 3 EXPERIMENTAL RESULTS

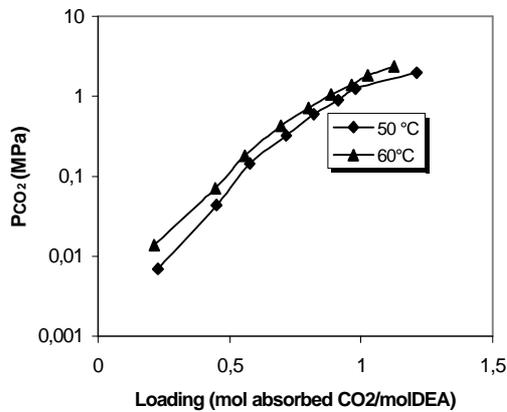
In order to test our equipment, we have compared the solubilities of CO<sub>2</sub> in 2 mole/l of a diethanolamine aqueous solution measured at 50°C with the data obtained by Lee *et al* [4].

This comparison is shown in figure 2. As we can see, there is a good agreement between the two data series.

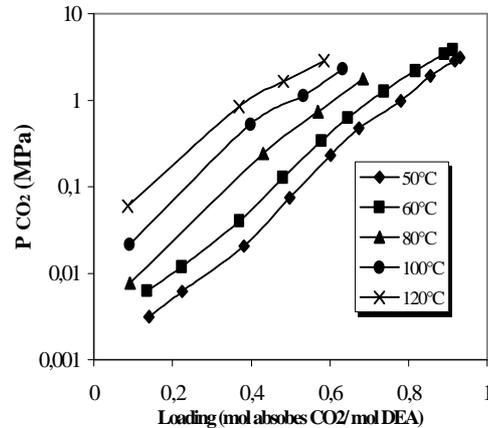
After this validation, we focused our interest over new equilibrium data for the CO<sub>2</sub> in mixed solvent. CO<sub>2</sub> solubilities were measured in mixed solutions over two massic compositions 40% H<sub>2</sub>O-40% DEA-20% -CH<sub>3</sub>OH and 40% H<sub>2</sub>O-20% DEA-40% CH<sub>3</sub>OH, at temperatures from 50°C to 120°C over a range of CO<sub>2</sub> partial pressures from 0.02 to 36 bar. The results are plotted in figures 3 and 4.



**Figure 2.** Solubility of CO<sub>2</sub> in 2 mole/l aqueous solution of DEA at 50°C : (●) data of Lee *et al* (1972) ; (×) this study.



**Figure 3.** CO<sub>2</sub> solubility in a 40% H<sub>2</sub>O 20% DEA 40% CH<sub>3</sub>OH



**Figure 4.** CO<sub>2</sub> solubility in a 40% H<sub>2</sub>O 40% DEA 20% CH<sub>3</sub>OH

#### 4 MODELLING

In this second part our aim is the modelling of the system Water – diethanolamine – methanol – H<sub>2</sub>S by the use of electrolyte – NRTL model to represents activity coefficient behaviour. To represent this system we have to regress the parameters related to the different sub systems.

- Water – Diethanolamine – Methanol
- Water – Méthanol – H<sub>2</sub>S
- Water – diethanolamine – H<sub>2</sub>S

The electrolyte – NRTL is an excess Gibbs energy model with long range interactions from

Debye – Hückel theory, local interactions from the NRTL model and a Born correction term for mixed solvent effects on ionic activity coefficients.

$$\frac{g_{ex}^*}{RT} = \frac{g_{exPDH}^*}{RT} + \frac{g_{exBorn}^*}{RT} + \frac{g_{NRTL}^*}{RT} \quad (2)$$

Gas phase nonidealities are accounted for by using the Peng Robinson equation of state. Details of the model can be found in the works of Chen *et al* [5] and in Austgen *et al* [6]. Parameters regressed in this work are from the NRTL local interaction form term and are represented by the Greek letter  $\tau_{ij}$  where “i” and “j” are chemical species. The tau parameters has the following temperature dependence,  $\tau_{ij} = a_{ij} + b_{ij}/T$ . The nonrandomness parameters were assumed to be symmetric as  $\alpha_{ij} = \alpha_{ji}$ . When no ionic species are present this model reduces to the NRTL form.

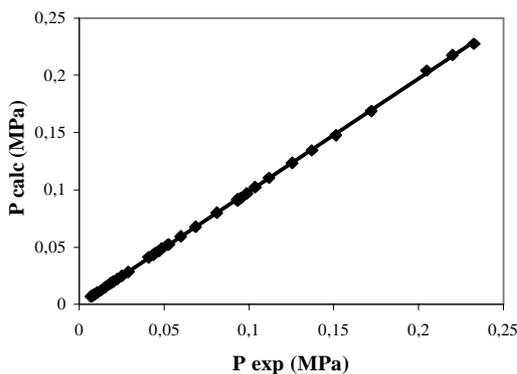
### • Reference States

In this work, different reference states are used depending on whether the species in consideration is solvent or solute. The reference state of solvent is the pure solvent at the system temperature and pressure. Solutes are considered to be at their reference state at infinite dilution in the solvent. Expressions of the Henry’s law constants for the solutes in pure water are given in the works of Posey *et al* [7], Teja *et al* [8] and Edwards *et al* [9] for DEA, methanol and H<sub>2</sub>S respectively.

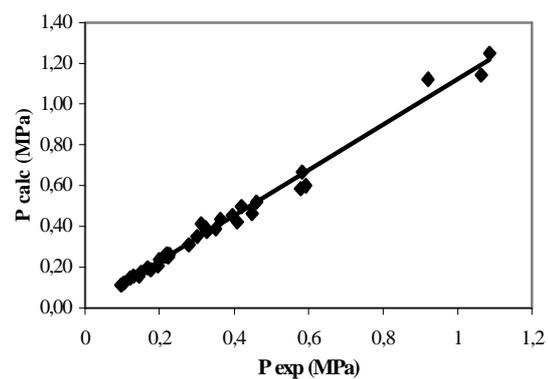
Data regression : Determining Interaction parameters

There are three types of binary interaction parameters in the NRTL contribution to the excess Gibbs energy or activity coefficient: molecule – molecule, molecule - ion and ion - ion. These parameters have been fitting on total pressure data. As parameters are about binary interactions, we fit the parameters on sub systems:

- Water – diethanolamine – methanol;
- Water - methanol - H<sub>2</sub>S;
- Water - methanol - H<sub>2</sub>S.



**Figure 5.** Comparison of the experimental total pressure and calculated model values for the H<sub>2</sub>O – DEA –methanol system.



**Figure 6.** Comparison of the experimental total pressure and calculated model values for the H<sub>2</sub>O– methanol – H<sub>2</sub>S system.

The data used in these regressions come from references [10, 11, 12, 13]. For the two first sub - systems, we have only molecular species and in the third one, we fit the molecule - ion

parameters. In this work, we have only regressed the interaction between water and two ionic species  $\text{HS}^-$  and  $\text{DEAH}^+$ , the others ionic parameters come from the work of Austgen et al. [6]. The results are shown in figure 5 and 6.

The standard deviation obtained for each system is recapitulated in the table 4.

**Table1.** The obtained standard deviation for each system

Systems	Average standard deviation (%)
Water – diethanolamine – methanol	1.36
Water – methanol – $\text{H}_2\text{S}$	14.1
Water – diethanolamine – $\text{H}_2\text{S}$	22.1

## 1 CONCLUSION

The ultimate goal of our work is the design of a new gas treatment process using mixed solvent (an aqueous diethanolamine solution and methanol). One of the aims of the present work is to present a new experimental equipment and liquid vapour measurements procedure for the  $\text{H}_2\text{O}$ -DEA- $\text{CH}_3\text{OH}$ - $\text{CO}_2$  systems. We present the validation results of this new apparatus by comparing our results with those of Lee *et al.* The second aim of this paper is the modelling of the system mixed solvent – acid gases. In the present work we have obtained a good representation of the different sub systems by the NRTL and NRTL electrolyte equation and by considering the infinite dilution reference state for diethanolamine, methanol and  $\text{H}_2\text{S}$ .

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