



Simultaneous Solubilities of CO₂ and H₂S in Diethanolamine Aqueous Solution

E. Blanchon Le Bouhelec-Tribouillois, P. Mougin, A. Barreau, I. Brunella, D. Le Roux, R. Solimando

► To cite this version:

E. Blanchon Le Bouhelec-Tribouillois, P. Mougin, A. Barreau, I. Brunella, D. Le Roux, et al.. Simultaneous Solubilities of CO₂ and H₂S in Diethanolamine Aqueous Solution. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2008, 63 (3), pp.363-372. 10.2516/ogst:2008014 . hal-02002012

HAL Id: hal-02002012

<https://ifp.hal.science/hal-02002012>

Submitted on 31 Jan 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Simultaneous Solubilities of CO₂ and H₂S in Diethanolamine Aqueous Solution

E. Blanchon Le Bouhelec-Tribouillois¹, P. Mougin¹, A. Barreau¹,
I. Brunella¹, D. Le Roux¹ and R. Solimando²

¹ Institut français du pétrole, IFP, Département Thermodynamique et Modélisation Moléculaire,
1-4 avenue de Bois-Préau, 92852 Reuil-Malmaison Cedex - France

² Laboratoire de Thermodynamique des Milieux Polyphasés, Institut National Polytechnique de Lorraine,
École Nationale Supérieure des Industries Chimiques, 1 rue Grandville, 54000 Nancy - France

e-mail: emilie.tribouillois@shell.com - pascal.mougin@ifp.fr - alain.barreau@ifp.fr - isabelle.brunella@ifp.fr
dominique.le-roux@ifp.fr - roland.solimando@ensic.inpl-nancy.fr

Résumé — Solubilités mutuelles de CO₂ et H₂S dans des solutions aqueuses de diéthanolamine —

Dans cet article, nous présentons un équipement expérimental capable de déterminer les solubilités mutuelles du CO₂ et d'H₂S dans des solutions aqueuses de diéthanolamine. Le propos d'un tel équipement est d'étendre les données expérimentales disponibles à propos de tels systèmes. En effet, la littérature est bien documentée en ce qui concerne les solubilités de CO₂ ou d'H₂S mais elle est plus réduite pour les mélanges de gaz acides. L'approche expérimentale employée ici est une méthode semi-synthétique avec échantillonnage de la phase vapeur et détermination du ratio CO₂/H₂S. Nous présentons de nouvelles données à propos du système eau – diéthanolamine – CO₂ – H₂S et nous les comparons à des données de la littérature au travers d'un modèle thermodynamique rigoureux.

Abstract — Simultaneous Solubilities of CO₂ and H₂S in Diethanolamine Aqueous Solution — In this paper, we present a new equipment enable to measure simultaneously solubilities of CO₂ and H₂S in diethanolamine aqueous solution. Its purpose is to increase the number of experimental data about these systems. Indeed, if the literature is relatively well documented on H₂S or CO₂ systems, solubility data concerning both acid gases are relatively scarce. The experimental approach developed in this paper is a semi-synthetic one where the vapour phase is sampled and the H₂S/CO₂ ratio is measured by gas chromatography. New experimental values of partial pressures of CO₂ and H₂S in an aqueous solution of diethanolamine are presented and compared with others from literature through a rigorous thermodynamic model.

NOMENCLATURE

A_ϕ	Debye-Hückel parameter
D	Dielectric constant
d	Molar density
e	Electron charge
G	Parameter of the NRTL model
g	Molar Gibbs energy
I	Ionic strength
k	Boltzmann constant
M	Molecular weight
N	Avogadro's number
NP	Number of experimental data points
n	Mole number
P	Pressure
R	Gas constant
r	Molar ratio between hydrogen sulphide and carbon dioxide in vapour phase
T	Temperature
$\bar{v}$	Partial molar volume
V	Volume
x	Liquid-phase molar fraction
y	Vapour-phase molar fraction
z	Ionic charge
Z	Compressibility factor

Greek Letters

α_{ga}	Acid gas loading
α	NRTL nonrandomness factor
ρ	Closest approach
τ	NRTL binary interaction energy parameter
σ	Deviation

Subscripts

a	Anion
ag	Acid gas
c	Cation
ca	Electrolyte
i, j, k	Any species
m	Molecular species
s	Solvent
w	Water

Superscripts

*	Unsymmetric convention
E	Excess
L	Liquid
bubble	Saturation condition
V	Vapour

Acronyms

DEA	Diethanolamine
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
NRTL	Non Random Two Liquids
PDH	Pitzer Debye-Hückel
RMSD	Root mean Square Deviation

INTRODUCTION

The share of natural gas in the world energy panorama has been appreciably growing for the last 20 years. This trend is expected to increase in the next few decades with the progressive replacement of fuel oil and coal by this relatively environment-friendly source of energy. However, this development will depend on the progress of gas processing technologies to give access to reserves now not exploitable. More than 30% of available gas fields are acid, containing large quantities of CO₂ and H₂S and other sulfur compounds. The technologies generally employed to remove these impurities are often based on their absorption in chemical or/and physical solvents.

Prior to any modelling activity, the precise knowledge of acid gas solubilities in the solvent is essential. For the classic alkanolamine used in the industry (monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA)), if the solubility of a single acid gas (CO₂ or H₂S) is well documented, it is not the case for the mixtures of both acid gases. Table 1 shows the number of experimental data available in the literature since the beginning of 1960 (Sidi-Boumedine, 2003); it can be seen that mixtures of acid gases are the less studied systems. A well defined thermodynamic model should be able to predict not only VLE with one acid gas but also VLE with both acid gases. Therefore, it is useful to consider such data in the development of a model.

The experimental apparatus has already been used to study single acid gas (H₂S or CO₂) solubility in aqueous solutions of diethanolamine (Barreau *et al.*, 2006). It has been improved to measure CO₂+H₂S mixtures solubility by adding a sampling loop to analyse the vapour phase.

TABLE 1

Number of experimental points reported by literature in the case of (water + alkanolamine + acid gases) systems

	MEA	DEA	MDEA
CO ₂	478	656	619
H ₂ S	281	528	199
CO ₂ and H ₂ S	141	498	79

First, the equipment is described, focusing our attention on vapour phase sampling and analysing. Then, new measurements on the (water – DEA – CO₂ – H₂S) system are presented. The obtained data are then compared with literature ones by using a consistent thermodynamic model to validate their accuracy.

1 EXPERIMENTAL EQUIPMENT

1.1 Apparatus

The apparatus used in the present study is based on the static method which has already been employed by Kennard and Meisen (1984) to measure the solubility of carbon dioxide in aqueous solutions of diethanolamine and by Maddox and Elizondo (1989) to determine the solubilities of hydrogen

sulfide or carbon dioxide in aqueous solutions of diethanolamine. Details of our equipment are reported in our previous work (Barreau *et al.*, 2006). It has been improved in order to determine the compositions of CO₂ and H₂S in the gaseous phase by adding the sampler ROLSI™ (Guilbot *et al.*, 2000) and a GC analyser. An overall scheme of the apparatus is shown in Figure 1 and a brief description is presented here.

The calibrated equilibrium cell is made of Hastelloy and is designed to operate at pressures up to 10⁴ kPa in a temperature range from 323.15 to 473.15 K. It is equipped with stirring rotors to ensure homogeneity of the liquid and vapour phases. Pressure is measured with a ROLSI™ 20 bar pressure sensor. A Pt 100 probe measures the temperature inside the cell with an accuracy of 0.05 K. It is immersed in a LAUDA liquid bath whose temperature fluctuations do not exceed 0.05 K. The volume of the cell has been calibrated and its value is 253.48 cm³ with an accuracy of 0.19 cm³.

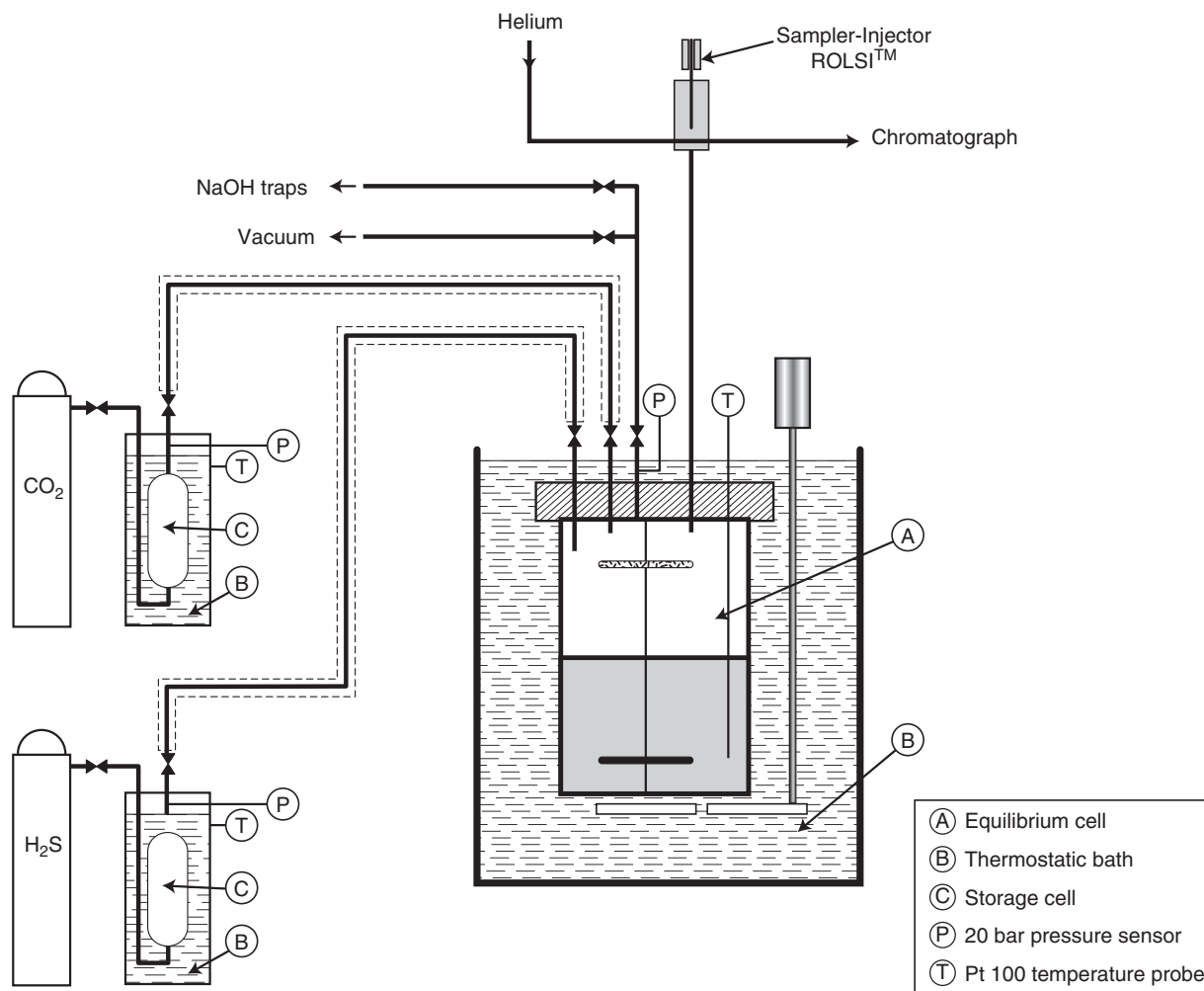


Figure 1

Scheme of the apparatus for acid gas solubility measurements.

The second part of the equipment is made of CO₂ and H₂S calibrated storage bottles. Both are equipped with an HBM® 100 bar pressure sensors and a Pt 100 probe. They are immersed in a LAUDA liquid baths to keep them at a given temperature. Each reservoir is directly connected to the cell and several valves allow the isolation of the equilibrium cell from the storage bottles. NaOH traps are installed in order to catch H₂S while cleaning between two series of measurements.

The analytical loop consists of the sampler ROLSI™ connected to the equilibrium cell through a Monel capillary (i.d.: 0.1 mm, e.d.: 1 mm and length: 1 m). It can be operated in wide ranges of pressure (200–600 × 10² kPa) and temperature (up to 673.15 K). It is crossed by the carrier gas (Helium) which sweeps the sample to be analysed to the injector of the gas chromatograph. The sampler is pneumatically controlled and different sizes of the withdrawn samples can be obtained by varying the depressurising time. Due to the small volume of gas sampled, successive samplings can be withdrawn without modifying the overall composition in the cell. All the circuit lines in Figure 1, the capillary and ROLSI™ are overheated to avoid condensation risks. All pressure sensors were calibrated by comparison with a reference gauge (DPI 605 Druck). The estimated experimental uncertainties are:

$$\text{and } \sigma_{P_{20 \text{ bar}}} = 0.2 \text{ kPa} + 0.0002 P$$

$$\sigma_{P_{100 \text{ bar}}} = 0.5 \text{ kPa} + 0.0006 P$$

Pt 100 probes were also calibrated by comparison with a standard probe in a calibrating HART oven: $\sigma_T = 0.05 \text{ K}$.

A 3800 Varian Gas Chromatograph equipped with a TCD analyser was used for the vapour phase analysis. A 50 m long, 0.53 mm diameter CP-Porabond Q column from Varian operated isothermally at 313.15 K was used for the separation. Rates between H₂S and CO₂ in the vapour phase are on interest. Therefore, TCD was comparatively calibrated with three H₂S/CO₂ mixtures prepared by Air Liquide. The mixtures are 19.96, 50.4 and 84.45 mol% H₂S respectively, so that the full range of acid gases concentrations can be investigated. The estimated experimental deviation on these concentrations is lower than 1%.

At equilibrium, samples are withdrawn. Their size can be easily adjusted so that equilibrium is not perturbed when total pressure increases. Once characteristic chromatographic areas of each acid gas are constant, the areas ratio yields to the concentration ratio r through the calibrated curve.

1.2 Procedure of a Measurement

The experimental procedure to study the solubility of a single acid gas is fully detailed in our previous work (Barreau *et al.*, 2006). The solvent (water + diethanolamine) is prepared by weighing and degassed by a cryogenic method. The cell is then heated at the desired temperature and the bubble pressure of

the solvent is measured. Single acid gas is then introduced step by step from the storage bottles. Once the equilibrium state is reached, total pressure is measured. To measure CO₂ + H₂S mixtures solubility one acid gas is first introduced. When equilibrium is reached, the second acid gas is introduced. This procedure allows controlling the loadings of each acid gas introduced. At equilibrium, samples of the vapour phase are withdrawn if total pressure is higher than 200 kPa.

2 EXPLOITATION OF MEASUREMENTS

Using a semi-synthetic method, the composition of the coexisting phases are calculated from overall liquid compositions in the cell, temperature, pressure and the H₂S/CO₂ ratio of the vapour phase at equilibrium state. In a previous work, we detailed the procedure in the case of a single acid gas (Barreau *et al.*, 2006); the extension of this method for a mixture of acid gases is described hereafter.

The amount of acid gas n_{ag} introduced in the equilibrium cell can be determined from the temperature and pressure conditions in the storage bottles before and after injection. The amount of solvent n_s is exactly known by weighing and the volume of the equilibrium cell V is carefully calibrated.

Once the equilibrium is reached, three mass balances for each acid gas and for the solvent (which can be considered as a single pseudo component) and one volume balance can be written:

$$n_{\text{H}_2\text{S}} = n_{\text{H}_2\text{S}}^L + n_{\text{H}_2\text{S}}^V \quad (1)$$

$$n_{\text{CO}_2} = n_{\text{CO}_2}^L + n_{\text{CO}_2}^V \quad (2)$$

$$n_s = n_s^L + n_s^V \quad (3)$$

$$V = V^L + V^V \quad (4)$$

In these equations, exponents L and V are respectively related to liquid and vapour phase. For the liquid phase, acid gases are treated as apparent species *i.e.* the subscripts “H₂S” and “CO₂” represent all molecular and ionic species derived from chemical reactions involving acid gases (see hereafter). The same approach is also employed in the case of amine.

The chromatographic analysis gives the following ratio r in the vapour phase:

$$r = \frac{P_{\text{H}_2\text{S}}}{P_{\text{CO}_2}} \quad (5)$$

The vapour volume is written as:

$$V^V = Z \left(n_s^V + n_{\text{H}_2\text{S}}^V + n_{\text{CO}_2}^V \right) \frac{RT}{P} \quad (6)$$

where P , T and Z are respectively temperature, pressure in the equilibrium cell and compressibility factor of vapour phase. The liquid volume is given by:

$$V^L = n_s^L \bar{v}_s + n_{H_2S}^L \bar{v}_{H_2S} + n_{CO_2}^L \bar{v}_{CO_2} \quad (7)$$

where $\bar{v}_s$ is the partial molar volume of the solvent and $\bar{v}_{CO_2}$ and $\bar{v}_{H_2S}$ are the apparent partial molar volume of the acid gases in the liquid phase.

The following assumptions can be made:

- in Equation (6) we assume that the compressibility factor of the vapour phase is only due to both acid gases. Pure CO₂ compressibility factor is calculated from the IUPAC tables (Angus *et al.*, 1976) and pure H₂S compressibility factor is calculated from Goodwin equation of state (Goodwin, 1983):
- $$Z = y_{CO_2} Z_{CO_2} + y_{H_2S} Z_{H_2S} = \frac{1}{1+r} (Z_{CO_2} + r Z_{H_2S}) \quad (8)$$
- in Equation (7), we assume that the partial molar volumes of the solvent and of the acid gas only depend on temperature. The solvent partial molar volume is determined from Amararène *et al.* (2003). The acid gas partial molar volumes are estimated from density measurements of the water + alkanolamine solvent (Rinker *et al.*, 2000; Weiland *et al.*, 1998) charged with various amounts of single acid gas;
 - we assume that Raoult's law can be applied on the (solvent + acid gases) system:

$$P_s = \frac{n_s}{n_s + n_{CO_2}^L + n_{H_2S}^L} P_s^{\text{bubble}}(T) \quad (9)$$

where P is the total pressure and P_s^{bubble} is the solvent vapour pressure measured independently. Equation (9) is based on ideal state; including real behaviour needs the introduction of activity coefficients and so some empirical parameters. Despite this apparent limitation, we will see later that all this assumption is perfectly justified.

Assuming that the total pressure is the sum of acid gas partial pressures and solvent pressure, the partial acid gases pressure should be calculated as follows:

$$P_{CO_2} = \frac{1}{1+r} \left(P - \frac{n_s}{n_s + n_{CO_2}^L + n_{H_2S}^L} P_s^{\text{bubble}}(T) \right) \quad (10)$$

$$P_{H_2S} = r P_{CO_2}$$

Equations 1 to 10 can be transformed into a system of 2 non linear equations containing $n_{CO_2}^L$ and $n_{H_2S}^L$, the amount of acid gases in liquid phase, as unknown variables. The values of $n_{CO_2}^L$ and $n_{H_2S}^L$ can be determined by solving

iteratively (Newton-Raphson method) the system of equations. It is thus possible to determine partial pressures of acid gases with respect to gas loading in the liquid phase:

$$\alpha_{ga} (= n_{ga} / n_{\text{alkanolamine}})$$

The loading is defined as the ratio between the apparent acid gas mole and the apparent alkanolamine mole in the liquid phase.

The procedure described above is based on an "apparent components" approach to describe the liquid phase composition and under the assumption of liquid phase ideality (Equation 9) for the calculation of vapour pressure of solvent. The precision of present assumptions is sufficient and the use of such simplified approach can lead to correct experimental results as it has been described in our previous paper in the case of (water + DEA + H₂S) system.

In this paper, we have compared our measurement to the literature one with another experimental set-up. A good agreement between literature data and our measured values (a 5% absolute average deviation in partial pressure of acid gas) shows that these assumptions are justified in the case of our temperature, composition and pressure conditions. Some tests of reproducibility have shown an absolute standard deviation in partial pressures of 7%.

3 EXPERIMENTAL MEASUREMENT

Phase equilibrium measurements between aqueous solutions of diethanolamine (DEA) and mixtures of carbon dioxide and hydrogen sulphide have been performed. The origin and the purity of DEA and acid gases are given in Table 2. We studied an aqueous solution of 25% weight of DEA at a temperature of 339.1 K and the results are presented in Table 3.

The influence of each acid gas can be studied with the help of these experimental values. It can be observed from Figure 2 that the introduction of carbon dioxide at constant loading of hydrogen sulphide increases the partial pressure of hydrogen sulphide. In the same time, the partial pressure of carbon dioxide is increasing too. The same behaviour is observed if the loading of carbon dioxide is fixed and hydrogen sulphide loading increases (Fig. 3). The lines on these two figures are produced by a thermodynamic model described in the next section.

TABLE 2
Origin and purity of the compounds

Compound	Origin	Purity (%)
Diethanolamine	Aldrich®	99
Carbon dioxide	Air Liquide®	99.998
Hydrogen sulphide	Air Liquide®	99.7

TABLE 3

Solubilities of carbon dioxide and hydrogen sulphide in an aqueous solution of 25% weight of DEA at 339.1 K

CO ₂ loading	P_{CO_2} (kPa)	H ₂ S loading	$P_{\text{H}_2\text{S}}$ (kPa)	P (kPa)
0.421	156	0.294	46	226
0.419	185	0.359	114	323
0.525	461	0.350	205	689
0.511	604	0.425	323	951
0.490	163	0.198	29	215
0.482	245	0.302	108	375
0.546	423	0.297	152	598
0.534	540	0.363	234	797

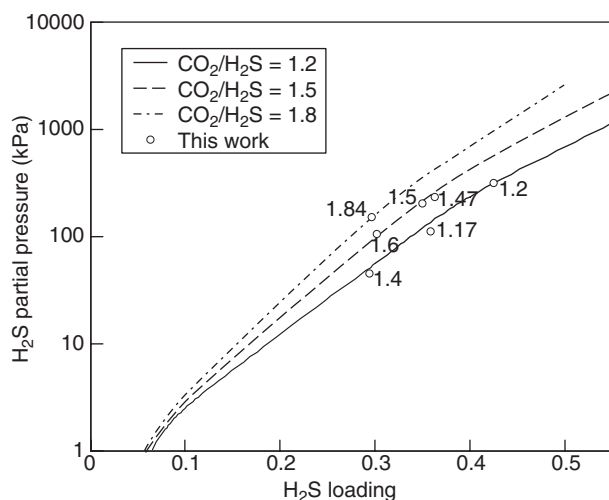


Figure 2

Partial pressures of H₂S at different H₂S loadings and for different $n_{\text{CO}_2}/n_{\text{H}_2\text{S}}$ ratio at $T = 339.1$ K (this work).

The label near each data is the $n_{\text{CO}_2}/n_{\text{H}_2\text{S}}$ ratio.

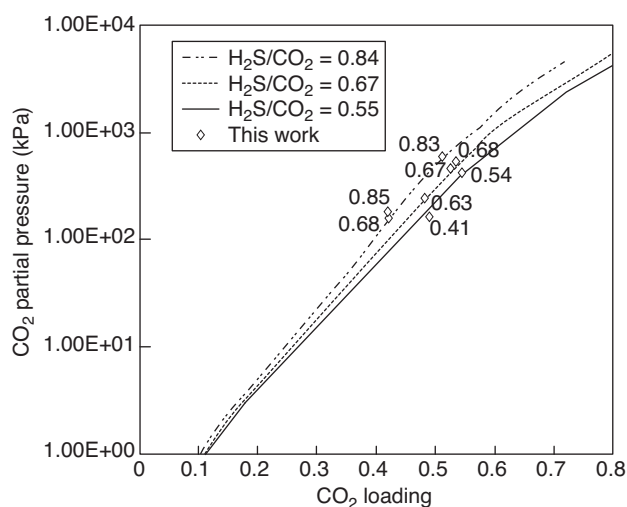


Figure 3

Partial pressures of CO₂ at different CO₂ loadings and for different $n_{\text{H}_2\text{S}}/n_{\text{CO}_2}$ ratio at $T = 339.1$ K (this work)

The label near each data is the $n_{\text{H}_2\text{S}}/n_{\text{CO}_2}$ ratio.

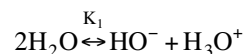
Experimental data of quaternary system (water + DEA + CO₂ + H₂S) reported in the open literature shows various conditions of temperature, loadings, solvent's properties and acid gas partial pressures (Lee *et al.*, 1974; Lawson and Garst, 1976; Lal *et al.*, 1985; Ho and Eguren, 1988; Jane and Li, 1997; Rogers *et al.*, 1997). A direct comparison of our experimental values with literature ones is thus not possible due to the lack of similar data in the same range of acid gas loadings. A consistent thermodynamic model was used to validate data presented in this work as explained in the next section.

4 VALIDATION WITH A THERMODYNAMIC MODEL

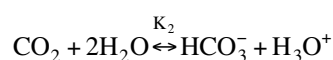
In the most general case, the system to be modelled is composed of a vapour phase made of molecular species and a reactive liquid phase containing molecular and ionic species. To establish the compositions of the species at equilibrium, a

reactive flash algorithm is needed for determining the chemical equilibrium in the liquid phase and a thermodynamic model is required for the representation of vapour liquid equilibrium. In this work, we have used a classical “ γ - ϕ ” approach with an activity coefficient model for the liquid phase and a classical equation of state for the vapour phase. The modelling of the system and the set of adjusted parameters have been described in our previous work (Barreau *et al.*, 2006). Here we briefly resume it. The reactive flash is calculated by the nonstoichiometric (White *et al.*, 1958; Gautam and Seider, 1979) method taking into account the classical chemical reactions of the water – alkanolamine – acid gases system:

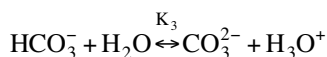
– Ionization of water:



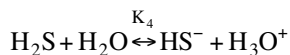
– Dissociation of carbon dioxide:



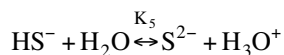
- Dissociation of bicarbonate:



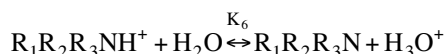
- Dissociation of hydrogen sulphide:



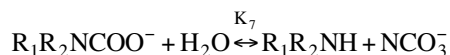
- Dissociation of disulphide:



- Dissociation of protonated alkanolamine:



- Carbamate reversion to bicarbonate (occurs only with primary and secondary amines):



The thermodynamic model employs the heterogeneous approach where the activity coefficient model used to represent the liquid phase is the Electrolyte-NRTL model developed by Chen and Evans (1986). The equation of state of Peng and Robinson (1976) is applied for the vapour phase.

The Electrolyte-NRTL equation is a generalised excess Gibbs energy model that accounts for molecular/ionic interactions between all liquid-phase species. The model postulates the excess Gibbs energy to be the sum of two contributions, one related to the short-range or local interactions between all the species and the other related to the long-range electrostatic interactions between ions. The Non Random Two Liquids (NRTL) theory is adopted to account for the local contribution (Renon and Prausnitz, 1968). The Pitzer-Debye-Hückel formula (Pitzer, 1980) is used to represent the long-range interaction contribution.

$$\frac{g_{PDH}^E}{RT} = - \left(\sum_k x_k \right) \sqrt{\frac{1000}{M_w}} \left(\frac{4A_\phi I_x}{\rho} \right) \ln(1 + \rho \sqrt{I_x}) \quad (11)$$

where A_ϕ is the usual Debye-Hückel parameter, function of the solvent (= water) dielectric constant (D_w) and density (d_w):

$$A_\phi = \frac{1}{3} \sqrt{\frac{\pi 2 d_w N}{1000}} \left(\frac{e^2}{D_w k T} \right)^{\frac{3}{2}} \quad (12)$$

I_x is the ionic strength defined on a mole fraction basis:

$$I_x = \frac{1}{2} \sum_i x_i z_i^2$$

ρ is the “closest approach” parameter set to 14.9 Å and M_w is the solvent molecular weight.

The local interaction contribution to the excess Gibbs energy is derived from the local composition concept of the NRTL hypothesis and the assumptions of like-ion repulsion and local electroneutrality. The first of these assumptions stipulates that in the immediate neighbourhood of a cation (anion) the local composition of all other cations (anions) is zero. Local electroneutrality requires that in the immediate neighbourhood of a molecule, the composition of cations and anions is such that the local electric charge is zero. The NRTL contribution to the Electrolyte-NRTL equation is reproduced here:

$$\begin{aligned} \frac{g_{NRTL}^E}{RT} = & \sum_m X_m \frac{j}{\sum_k X_k G_{km}} \sum_j X_j G_{jm} \tau_{jm} \\ & + \sum_c X_c \sum_{a'} \frac{X_{a'} \sum_j G_{jc,a'c} \tau_{jc,a'c}}{\left(\sum_{a''} X_{a''} \right) \left(\sum_k X_k G_{kc,a'c} \right)} \\ & + \sum_a X_a \sum_{c'} \frac{X_{c'} \sum_j G_{ja,c'a} \tau_{ja,c'a}}{\left(\sum_{c''} X_{c''} \right) \left(\sum_k X_k G_{ka,c'a} \right)} \end{aligned} \quad (13)$$

with :

$$G_{cm} = \frac{\sum_{a'} X_a G_{ca,m}}{\sum_{a'} X_{a'}} \quad G_{am} = \frac{\sum_{c'} X_c G_{ca,m}}{\sum_{c'} X_{c'}} \quad (14)$$

$$a_{mc} = a_{cm} = \frac{\sum_{a'} X_a a_{m,ca}}{\sum_{a'} X_{a'}} \quad G_{am} = \frac{\sum_{c'} X_c G_{ca,m}}{\sum_{c'} X_{c'}} \quad (15)$$

where $X_j = x_j Z_j$ with $C_j = Z_j$ for ions and $C_j = 1$ for molecules. α is the nonrandomness parameter, τ is the binary energy interaction parameter,

$$\begin{aligned} G_{jc,a'c} &= \exp(-\alpha_{jc,a'c} \tau_{jc,a'c}) & G_{ja,c'a} &= \exp(-\alpha_{ja,c'a} \tau_{ja,c'a}) \\ G_{ca,m} &= \exp(-\alpha_{ca,m} \tau_{ca,m}) & G_{im} &= \exp(-\alpha_{im} \tau_{im}) \\ \tau_{ma,ca} &= \tau_{am} - \tau_{ca,m} + \tau_{m,ca} & \tau_{mc,ac} &= \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \end{aligned} \quad (16)$$

More details about the developed thermodynamic model should be found in our previous work. The adjustable parameters of the Electrolyte-NRTL are binary interaction energy parameters, τ_{ij} .

Three types of parameter can be defined: molecule-molecule, molecule-ion pair, ion pair-molecule and ion pair-ion pair with common cation or anion. When data is available,

molecule-molecule parameters were fitted on binary molecular systems. All ion pair-ion pair parameters are set to zero. Following the approach already adopted, nonrandomness factors are set to given values and are supposed to be symmetric. The only adjustable parameters are molecule-ion pair and ion pair-molecule parameters ($\tau_{\text{molecule-ion pair}}$ and $\tau_{\text{ion pair-molecule}}$). They are assumed to be temperature dependent:

$$\tau_{ij} = \tau_{ij}^0 + \frac{\tau_{ij}^1}{T}$$

and are fitted on acid gases partial pressures in ternary (water-DEA-acid gas) and quaternary (water-DEA-CO₂-H₂S) systems in order to minimize the Root Mean Square Deviations (RMSD):

$$\text{RMSD (\%)} = \frac{100}{\text{NP}} \cdot \sqrt{\sum_{i=1}^{\text{NP}} \left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right)^2} \quad (17)$$

Table 4 shows the data base used for the fitting procedure. Figures 4 and 5 show the comparison between the experimental pressures and the calculated values for the water + diethanolamine system at 339 K. We have reported our experimental data and those from Lawson and Garst (1976) (same system at the same temperature and the same solvent

properties). These figures show that our measurements are in relatively good agreement with the model. The high deviations between our data and the model are obtained for the lower loadings. We can also observe that the model underestimates experimental carbon dioxide pressures whereas it over estimates hydrogen sulphide partial pressures. There are no evident reasons to explain this behaviour. RMSD between our data and the model is about 17.8% and the deviation between the data of Lawson and Garst and the model is about 24.3%: both deviations are in the same order of magnitude. We can conclude that our measurements are in agreement with those from literature and that the simplified procedure we used to treat our raw data (paragraph 2) is adequate and leads to experimental points having sufficient accuracy.

If we consider global deviations on the whole data base, RMSD values for ternary and quaternary systems are respectively equal to 25% (278 data point) and 32% (142 data point). We have also used the data of Lal *et al.* (1985) and of Ho and Eguren (1988) in order to estimate the RMSD for quaternary systems not taken into the regress dataset and we have obtained a value of 38.2%. Deviation obtained in this work for the ternary systems is in the same order of magnitude than this obtained in our previous work. For the quaternary systems, the deviations seem rather important. The degradation of the results observed in this case could have

TABLE 4
Database used in the fitting procedure

Authors	Temperature range (K)	Partial pressure range (kPa)	DEA %Weight
water-DEA-CO ₂			
Lawson and Garst, 1976	310.93-394.26	2-4186	25
Lal <i>et al.</i> , 1985	313.15	(9.8 × 10 ⁻³)-1.13	20.55
Maddox <i>et al.</i> , 1987	298.15	8.4-2012	5.24-20.55
Rogers <i>et al.</i> , 1997	323	(3.4 × 10 ⁻⁴)-0.5515	20.2
Sidi-Boumedine, 2003	298.13-348.07	0.4-4651.8	41.78
Blanchon Le Bouhelec, 2006	338.45-366.84	8.1-922.7	25
Water-DEA-H ₂ S			
Lawson and Garst, 1976	310.93-422.04	(9.34 × 10 ⁻⁴)-351	25
Lal <i>et al.</i> , 1985	313.15-373.15	(1.1 × 10 ⁻²)-3.18	20.55
Sidi-Boumedine, 2003	313.17-373.01	1.2-1332.2	41.78
Blanchon Le Bouhelec, 2006	339.01	7.7-365.0	25
water-DEA-CO ₂ -H ₂ S			
Lee <i>et al.</i> , 1974	323.15	CO ₂ : 0.552-5765 H ₂ S: 3.85-600	20.55
Lawson and Garst, 1976	310.93-394	CO ₂ : 1.46-5135 H ₂ S: 2.13-2186	25
Rogers <i>et al.</i> , 1997	313.2-323	CO ₂ : (3.4 × 10 ⁻⁴)-0.89 H ₂ S: (2.8 × 10 ⁻³)-9.477	20.2-20.3
This work	339	CO ₂ : 156-604 H ₂ S: 29.2-323	25

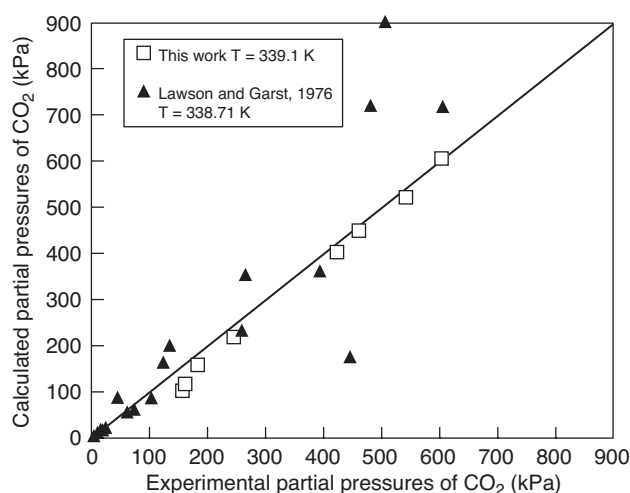


Figure 4

Comparison between carbon dioxide experimental pressures and calculated ones in the (water + DEA + CO₂ + H₂S) system.

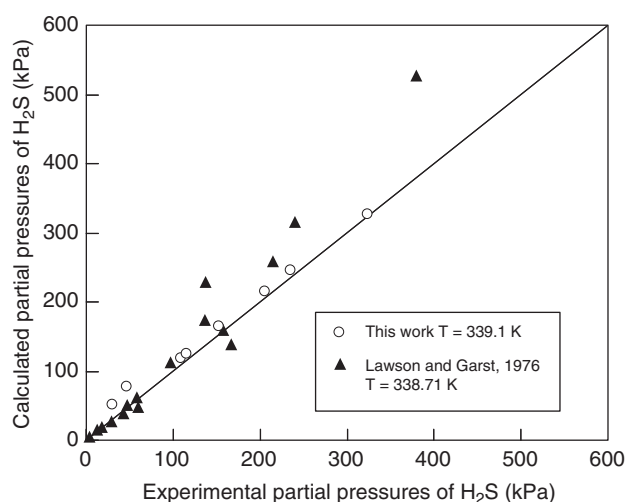


Figure 5

Comparison between hydrogen sulphide experimental pressures and calculated ones in the (water + DEA + CO₂ + H₂S) system.

different explanations. Firstly, the scattering of experimental data in quaternary systems, as it is evident from observation of Table 4, is very difficult to represent with a unique set of parameters. Secondly, from theoretical point of view, interaction between the 2 acid gases in the liquid were not considered in our approach because we have not adjusted “cross parameters” (*i.e.* acid gas 1 - ion pair from acid gas 2 parameter). It is thus evident that such type of interactions should be considered in our quaternary systems to obtain more precise results. Here our purpose is only to validate the experimental measurement.

CONCLUSION

In this work, we are interested in acid gases (H₂S and CO₂) removal by an aqueous solution of alkanolamine. We performed measurements of simultaneous hydrogen sulphide and carbon dioxide solubilities in an aqueous solution of diethanolamine. We showed that it is possible to use a semi-synthetic method in order to realize such measurements. The apparatus and the treatment of the experimental data are detailed.

It is not possible to compare rigorously our experimental data with those from literature (it is difficult to have exactly the same experimental acid gases’ loadings). The validation of the new data is thus obtained through a thermodynamic model.

We employed a model which couples chemical reactions in liquid phase and phase equilibrium between vapour and liquid. The liquid phase is modelled by the electrolyte NRTL activity coefficient and the vapour phase is described by the

classical Peng and Robinson equation of state. The adjustable parameters of the model have been determined on experimental acid gas partial pressure data of the studied systems (water + diethanolamine + CO₂, water + diethanolamine + H₂S and water + diethanolamine + CO₂ + H₂S). We compared our measurements with the prediction of the model. We obtained a deviation close to 18% and this result was in agreement with the deviation obtained for identical systems from literature. This result shows that it is possible to use a semi-synthetic method to perform such measurements.

This new device can be also easily used to measure simultaneous CO₂ and H₂S solubilities in (water + alkanolamine) containing a physical solvent such as methanol. This type of mixed solvent constitutes an interesting alternative for acid gas absorption when classical chemical aqueous solvent (water + alkanolamine) is not enough efficient.

REFERENCES

- Amararène F., Balz P., Bouallou C., Cadours R., Lecomte F., Mougin P., Richon D. (2003) Densities of hybrid solvents: diethanolamine + water + methanol and N-methyl-diethanolamine + water + methanol at temperature ranging 283.15 to 353.15 K, *J. Chem. Eng. Data* **48**, 1565-1570.
- Angus S., Reuck K.M., Armstrong B. (1973) *International Thermodynamic Tables of the fluid state-6 Carbon dioxide*, Pergamon Press.
- Barreau A., Blanchon Le Bouhelec E., Hachi-Tounsi K., Mougin P., Lecomte F. (2006) Absorption of H₂S and CO₂ in alkanolamine aqueous solution: Experimental data and modelling with the Electrolyte-NRTL model, *Oil Gas Sci. Technol. – Rev. IFP* **61**, 3, 345-361.
- Blanchon Le Bouhelec E. (2006) Contribution à la thermodynamique de l’absorption des gaz acides H₂S et CO₂ dans les

solvants eau – alcanolamine – méthanol : Mesures expérimentales et modélisation, *Thèse de l'Institut National Polytechnique de Lorraine*, France.

Chen C.C., Evans L.B. (1986) A local composition model for the excess Gibbs energy of aqueous electrolyte systems, *AIChE J.* **32**, 3, 444-454.

Gautam R., Seider W. (1979) Computation of phase and chemical equilibrium, *AIChE J.* **25**, 6, 991-1015.

Goodwin R.D. (1983) *Hydrogen Sulfide Provisional Thermophysical Properties from 188 to 700 K at Pressures to 75 MPa*, NBSIR 83-1694, National Bureau of Standards.

Guilbot P., Valtz A., Legendre H., Richon D. (2000) Rapid on-line sampler-injector: a reliable tool for HT-HP sampling and on-line GC analysis, *Analyst* **28**, 426-431.

Ho B.S., Eguren R.R. (1988) Solubility of acidic gases in aqueous DEA and MDEA solutions, *AIChE Spring National Meeting*.

Jane I.S., Li M.H. (1997) Solubilities of mixtures of carbon dioxide and hydrogen sulfide in water + diethanolamine + 2-amino-2-methyl-1-propanol, *J. Chem. Eng. Data* **42**, 98-105.

Kennard M.L., Meisen A. (1984) Solubility of carbon dioxide in aqueous diethanolamine solutions at elevated temperatures and pressures, *J. Chem. Eng. Data* **29**, 309-312.

Lal D., Otto F.D., Mather A.E. (1985) The solubility of H₂S and CO₂ in a diethanolamine solution at low partial pressures, *Can. J. Eng. Data* **63**, 681-685.

Lawson J.D., Garst A.W. (1976) Gas sweetening data: equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous monoethanolamine and aqueous diethanolamine solutions, *J. Chem. Eng. Data* **21**, 20-30.

Lee J.I., Otto F.D., Mather A.E. (1974) The solubility of mixtures of carbon dioxide and hydrogen sulfide in aqueous diethanolamine solutions, *Can. J. Eng. Data* **52**, 125-127.

Maddox R.N., Bhairi A.H., Diers J.R., Thomas P.A. (1987) Equilibrium solubility of carbon dioxide or hydrogen sulfide in

aqueous solutions of monoethanolamine, diglycolamine, diethanolamine and methyldiethanolamine, GPA Project 841, *Gas Processors Association Report No. 104*.

Maddox R.N., Elizondo E.M. (1989) Equilibrium solubility of carbon dioxide or hydrogen sulfide in aqueous solutions of diethanolamine at low partial pressures, GPA Project 841, *Gas Processors Association Report No. 124*.

Peng D.-Y., Robinson D.B. (1976) A new two-constant equation of state, *Ind. Eng. Chem. Fundam.* **15**, 59-64.

Pitzer K.S. (1980) Electrolytes. From dilute solutions to fused salts, *J. Am. Chem. Soc.* **102**, 9, 2902-2906.

Renon H., Prausnitz J.M. (1968) Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE J.* **14**, 135-144.

Rogers W.J., Bullin J.A., Davison R.R., Frazier R.E., Marsch K.N. (1997) FTIR method for VLE measurements of acid gas – alkanolamine systems, *AIChE J.* **43**, 3223-3231.

Rinker E.B., Colussi A.T., McKnight N.L., Sandall O.C. (2000) Effect of hydrogen sulfide loading on the density and viscosity of aqueous solutions of methyldiethanolamine, *J. Chem. Eng. Data* **45**, 254-256.

Sidi-Boumedine R. (2003) Étude des systèmes gaz acide/alcanolamine/eau: mesures couplées de composition de la phase liguide et de solubilité, *PhD Thesis*, École des Mines de Paris, Paris.

Weiland R.H., Dingman J.C., Cronin D.B., Browning G.J. (1998) Density and viscosity of some partially carbonated aqueous alkanolamine solutions and their blends, *J. Chem. Eng. Data* **43**, 378-382.

White W.B., Johnson S.M., Dantzic G.B. (1958) Chemical equilibrium in complex mixtures, *J. Chem. Phys.* **28**, 5, 751-755.

Final manuscript received in February 2008

Published online in May 2008