Oil & Gas Science and Technology – Rev. IFP, Vol. 61 (2006), No. 3, pp. 345-361
Copyright © 2006, Institut français du pétrole

Dossier

Petroleum Industry Applications of Thermodynamics
Applications de la thermodynamique dans l'industrie pétrolière

Absorption of H_2S and CO_2 in Alkanolamine Aqueous Solution:

Experimental Data and Modelling with the Electrolyte-NRTL Model

A. Barreau[1], E. Blanchon le Bouhelec[1], K.N. Habchi Tounsi[2],
P. Mougin[1] and F. Lecomte[1]

1 Institut français du pétrole, 1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
2 Total, DGEP/SCR/ED/ECP, Tour Coupole, La Défense 6, Cedex 45, 92078 Paris La Défense - France
e-mail: alain.barreau@ifp.fr - emilie.blanchon-le-bouhelec@ifp.fr - kenza.habchi-tounsi@total.com
pascal.mougin@ifp.fr - fabrice.lecomte@ifp.fr

Résumé — **Absorption de H_2S et CO_2 dans des solutions aqueuses d'alcanolamine : mesures expérimentales et modélisation avec le modèle NRTL-Electrolyte** — Au cours de ce travail, nous nous sommes intéressés à l'absorption de gaz acides (H_2S et CO_2) dans des solutions aqueuses d'alcanolamine. La première partie de cet article présente l'appareillage expérimental développé pour déterminer la pression partielle en gaz acide en fonction du taux de charge (en phase liquide) en utilisant la méthode synthétique. De nouvelles mesures sur les systèmes Eau + diéthanolamine + CO_2 et Eau + diéthanolamine + H_2S ont été réalisées. La deuxième partie s'intéresse à la modélisation de telles données. Le modèle utilisé couple l'aspect réactions chimiques en phase liquide avec l'aspect équilibre de phases. Nous avons mis en œuvre le modèle NRTL-Electrolyte pour décrire la phase liquide et l'équation d'état de Peng et Robinson pour décrire la phase vapeur. Les paramètres du modèle NRTL-Electrolyte sont déterminés sur les données expérimentales de pression partielle en gaz acide des systèmes étudiés.

Abstract — *Absorption of H_2S and CO_2 in Alkanolamine Aqueous Solution: Experimental Data and Modelling with the Electrolyte-NRTL Model* — In this work, we are interested in acid gas (H_2S and CO_2) removal by aqueous solutions of alkanolamine. The first part of the article deals with the development of the experimental apparatus used to determine the partial acid gas pressure as a function of acid gas loading in the reactive liquid phase with the synthetic method. New measurements on water + diethanolamine + CO_2 and water + diethanolamine + H_2S systems were performed. The second part concerns the modelling of such data. The model used couples the chemical reactions in liquid phase with the phase equilibrium. We use the electrolyte NRTL model for the liquid phase and the Peng and Robinson equation of state to describe the vapour phase. The parameters of the electrolyte NRTL model are determined on experimental acid gas partial pressure data of the studied systems.

NOMENCLATURE

a_{ij}	number of atoms j in the compound i
A_ϕ	Debye-Hückel parameter
b_j	total number of atoms j
D	dielectric constant
d	molar density
e	electron charge
f	fugacity
G	Gibbs energy
g	molar Gibbs energy
$H_{i,j}^{p_j^{sat.}}$	Henry's constant of solute i in solvent j at saturation pressure
I	ionic strength
K_r	equilibrium constant
k	Boltzmann constant
M	molecular weight
N	Avogadro's number
n	mole
P	pressure
R	gas constant
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	acid gas loading
α	NRTL nonrandomness factor
γ	activity coefficient
φ	fugacity coefficient
μ	chemical potential
ν	stoichiometric coefficient
τ	NRTL binary interaction energy parameter
λ	Lagrange multipliers

Subscripts

a	anion
ag	acid gas
c	cation
ca	electrolyte
i, j, k	any species
m	molecular species
s	solvent/solid
w	water

Superscripts

$*$	unsymmetric convention
$\#$	liquid reference state
$\circ$	solid reference state
cal	calculated
E	excess
exp	experimental
L	liquid
sat	saturation condition
V	vapour
∞	infinite dilution

Acronyms

DEA	diethanolamine
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 CO_2 and H_2S and other sulfur compounds. The technologies generally employed to remove these impurities are very often based on their absorption in chemical or/and physical solvents.

The work undertaken at *IFP* over the last few years on hybrid solvents (water-diethanolamine-methanol) (Tabai *et al.,* 1999, Benmansour *et al.,* 2000, Habchi Tounsi, 2003), and more recently on the *TOTAL* amine processes commercialized by *PROSERNAT* has made necessary the development of a competence in thermodynamic centered on reactive solvents, covering both experimental and modelling aspects.

Prior to any modelling activity, the precise knowledge of acid gas solubilities in the solvent is essential. For specific formulations of solvents, which can be encountered when developing new original processes, sufficient data cannot usually be found in the open literature. The apparatus developed at *IFP* to make these measurements uses the synthetic method: the amount of acid compound absorbed in the liquid phase is determined from mass balance equations derived from the known PVT conditions in the cell. Unlike other apparatus based on the analytical method (Lee *et al.,* 1972, Lawson and Garst, 1976, Lal *et al.,* 1985), our equipment

does not require any analysis of the phases which makes it very well adapted for the study of a large panel of solvents.

Beside experimental data acquisition, the availability of robust and relatively predictive models is of prime importance for designing the process units. In the most general case, the system to be modeled 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 and a thermodynamic model is required for the representation of vapour liquid equilibrium.

Two techniques can be employed to solve the chemical equilibrium: the stoichiometric (Barbosa and Doherty, 1987, Ung and Doherty, 1995) and the nonstoichiometric (White *et al.*, 1958, Gautam and Seider, 1979) methods. The model developed by *IFP* is based on the nonstoichiometric method which does not require to set the stoichiometry of the reactions but only the nature of the species present at the equilibrium. This advantage compared to the stoichiometric technique allows the model to be used on various chemical systems, with no need for adaptations that would take into account specific reaction schemes.

Concerning the thermodynamic model, the homogeneous and the heterogeneous approaches can be distinguished. Whereas the first one uses a single equation to determine the properties of both liquid and vapour phases (Fürst and Renon, 1993), the second, also called the "gamma-phi" approach, resides in the use of an activity coefficient model to represent the liquid phase and an equation of state for the vapour. Although some good results have been reported in literature on models of amine systems based on homogeneous approach (Vallée *et al.*, 1999), the heterogeneous option (Electrolyte-NRTL and Peng and Robinson equation of state) was chosen for our model since it is particularly well adapted to the representation of strongly asymmetric systems such as electrolyte solutions in equilibrium with vapour phases.

As already mentioned, this work was first undertaken on acid gas absorption by reactive solvents. It is presented in this paper with the absorption of H_2S and CO_2 in water – alkanolamine solvent.

Obviously, reactive systems are present in many other technical fields studied at IFP, ranging from geochemistry to refining and petrochemistry activities, for which the present work will certainly find a variety of applications.

1 EXPERIMENTAL SECTION

1.1 Materials

DEA was obtained from Aldrich Chemical Co. with a purity of 99%. Water was distilled. CO_2 and H_2S were obtained from Air Liquide with a purity of 99.998% and 99.7%.
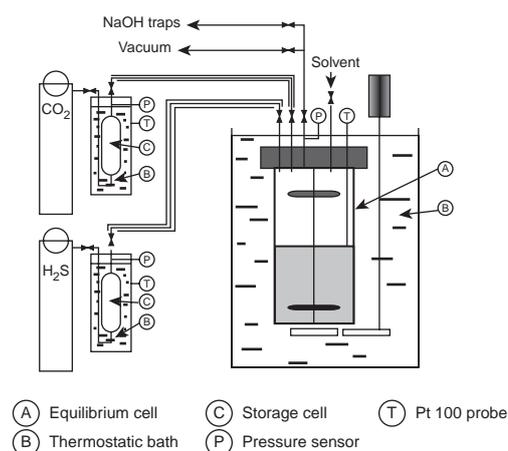

Figure 1

Scheme of the apparatus for acid gas solubility measurements.

1.2 Apparatus and Procedure

The apparatus used in the present study is based on the static method which has already been employed by Kennard and Meisen (1984) for measuring the solubility of carbon dioxide in aqueous solutions of diethanolamine and by Rumpf and Maurer (1992) for determining the solubilities of hydrogen cyanide and sulfur dioxide in water. Figure 1 shows a diagramme of the experimental apparatus.

The equilibrium cell is made of Hastelloy to avoid corrosion problems and its volume is 253.48 cm³. The cell is immersed in a LAUDA® thermostatic oil bath. The cell has been designed to operate at pressures up to 100 bar in a temperature range from 323.15 K to 473.15 K. The cell is equipped with stirring rotors to ensure the homogeneity of the liquid and vapour phases. A Pt 100 probe measures the temperature with accuracy of 0.03 K. The pressure is measured with an HBM® 100 bar pressure sensor with accuracy of 0.015 MPa or an HBM® 20 bar pressure sensor with accuracy of 0.0028 MPa depending on the experimental pressure range.

CO_2 and H_2S are introduced in the equilibrium cell from storage bottles immersed in a thermostatic liquid bath equipped with both a platinum probe to measure the temperature and a pressure sensor. The volumes of the storage bottles were calibrated. All the connecting lines are heated to avoid risks of condensation. The amount of the acid gas introduced in the equilibrium cell is calculated from the temperature and pressure conditions in the storage before and after the injection.

The solvent mixture prepared by weighing is introduced in the equilibrium cell. Degassing is carried out by a cryogenic method. The cell is then heated at the desired temperature and the bubble pressure of the pure solvent is measured. CO_2 or H_2S are introduced step by step from the storage bottles.

The equilibrium state in the cell is reached after about an hour. After each injection of acid gas, the total pressure is measured.

1.3 Treatment and Results

Using the static method, only overall compositions of the mixture, temperature, pressure and total volume are measured. The compositions of the coexisting phases have to be calculated from raw data. This procedure is quite complex and is described hereafter.

Whereas Kennard and Meisen (1984) and Rumpf and Maurer (1992) calculated the amount of acid gas n_{ag} introduced in the equilibrium cell by weighing, in this work, it is calculated from the temperature and pressure conditions in the storage bottles before and after the injection using a specific equation of state. We have used the IUPAC tables (Angus *et al.,* 1973) for CO_2 and Goodwin (1983) for H_2S. The amount of solvent n_s is exactly known by weighing and the volume of the equilibrium cell V is carefully calibrated.

Once equilibrium is reached, we have two mass balances (the solvent is considered here as a single pseudo component):

$$n_{ag} = n_{ag}^L + n_{ag}^V \qquad (1)$$

$$n_s = n_s^L + n_s^V \qquad (2)$$

and one volume balance:

$$V = V^L + V^V \qquad (3)$$

In these equations, exponents L and V are respectively related to liquid and vapour phase.

The vapour volume is written as:

$$V^V = Z\left(n_s^V + n_{ag}^V\right)\frac{RT}{P} \qquad (4)$$

where P and T are the temperature and the pressure in the equilibrium cell. The liquid volume is given by:

$$V^L = n_s^L \overline{v_s} + n_{ag}^L \overline{v_{ag}} \qquad (5)$$

where $\overline{v_s}$ is the partial molar volume of the solvent and $\overline{v_{ag}}$ is the partial molar volume of the acid gas in the liquid phase.

The following assumptions are made:
– in equation (4), we assume that the compressibility factor of the vapour phase is equal to that of pure acid gas;
– in equation (5), we assume that the partial molar volumes of the solvent and the acid gas only depend on temperature. The solvent volume is determined from Amararène *et al*. (2003) and the acid gas volume is estimated from density measurements of the water + alkanolamine solvent (Rinker *et al*., 2000 Weiland *et al*., 1998) charged with various amounts of acid gas;
– we assume that Raoult's law can be applied on the pseudo binary (solvent + acid gas):

$$\frac{n_s^V P}{n_s^V + n_{ag}^V} = \frac{n_s^L P_s^\sigma}{n_s^L + n_{ag}^L} \qquad (6)$$

where P is the total pressure and P_s^σ is the solvent bubble pressure. This value is measured independently. Using

TABLE 1

CO_2 solubility data in 2 mol.l^{-1} of DEA aqueous solution at 323.15 K

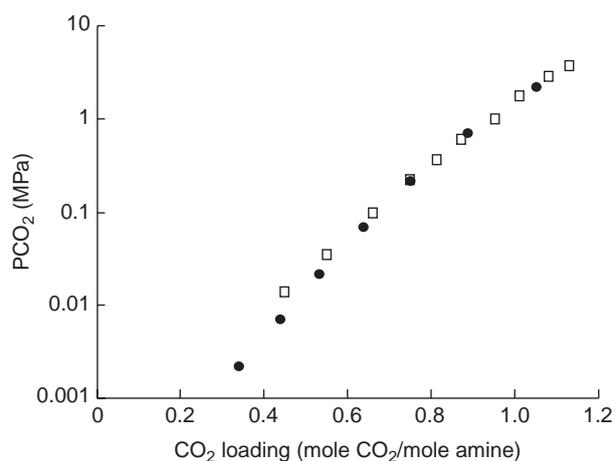| α	P_{CO_2} (MPa)	
(mol CO_2/mol DEA in liquid phase)	This work	Lee *et al*. (1972) smoothed
0.45	0.014	0.007
0.55	0.036	0.028
0.66	0.101	0.089
0.75	0.226	0.212
0.81	0.382	0.376
0.87	0.626	0.617
0.95	1.022	1.099
1.01	1.808	1.647
1.08	2.886	2.587
1.13	3.798	3.370

Figure 2

Solubility of CO_2 in a 2 mole/l aqueous solution of DEA at 323.15 K (●) data of Lee et al.(1972) ; (□) this work.

these assumptions, 6 equations remain to solve the 6 unknowns that are:

$$n_{ag}^L, n_s^L, n_{ag}^V, n_s^V, V^L, V^V$$

We are aware that these assumptions may not be entirely justified. We have therefore tested the sensitivity of the results to each of the assumption.

TABLE 2

CO₂ solubility data in 25.0 wt.% DEA aqueous solution at 338.50 K

α (mol CO_2/mol DEA in liquid phase)	P_{CO_2} (MPa)	
	This work	Lawson and Garst (1976) smoothed
0.098	0.001	
0.199	0.004	
0.288	0.008	
0.378	0.018	
0.464	0.038	0.032
0.565	0.103	0.091
0.659	0.247	0.216
0.738	0.493	0.415
0.799	0.803	0.658

TABLE 3

CO₂ solubility data in 25.0 wt.% DEA aqueous solution at 366.90 K

α (mol CO_2/mol DEA in liquid phase)	P_{CO_2} (MPa)	
	This work	Lawson and Garst (1976) smoothed
0.100	0.0004	
0.224	0.021	
0.283	0.040	
0.400	0.126	0.115
0.497	0.289	0.265
0.581	0.556	0.488
0.650	0.923	0.767

The procedure has been validated by checking results against two literature data systems for CO₂ and one for H₂S. Firstly, the solubility of CO₂ in 2 mol.l⁻¹ of a diethanolamine aqueous solution has been measured at 323.15 K and compared with data obtained by Lee *et al*. (1972). The results are given in Table 1 and plotted in Figure 2. The partial pressure
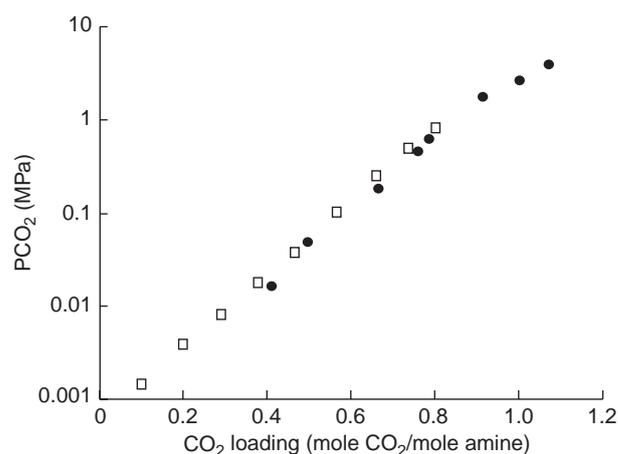

Figure 3

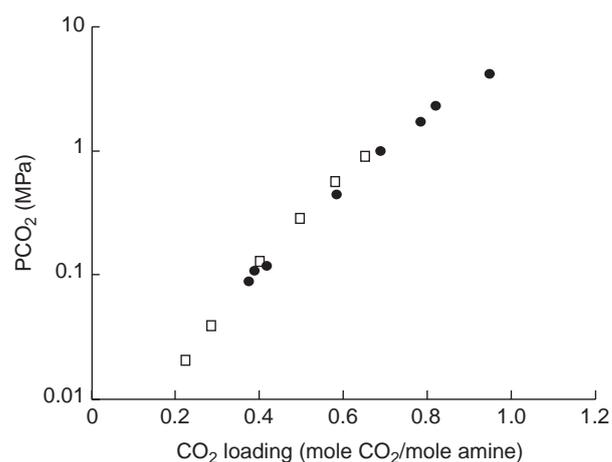Solubility of CO₂ in a 25.0 wt% aqueous solution of DEA at 338.5 K (●) data of Lawson and Garst (1976); (□) this work.

Figure 4

Solubility of CO₂ in a 25.0 wt.% aqueous solution of DEA at 367.0 K (●) data of Lawson and Garst (1976); (□) this work.

of acid gas is reported as a function of the acid gas loading α (mole of acid gas per mole of amine in liquid phase). Figure 2 shows the good agreement between the two data series over three orders of magnitude in partial pressure; the average absolute deviation in partial pressure is about 16%. The procedure was then tested against the data obtained by Lawson and Garst (1976) in a 25.0 wt% DEA aqueous solution at 338.5 K and 367.0 K. The results are given in Table 2 and Table 3 and plotted in Figure 3 and 4. The average deviation in partial pressure is about 12%. These deviations are in agreement with those obtained when we compare experimental data

from many sources. We have also realised repeatability measurement and the deviation between two sets of experimental data is less than 3% in pressure. To compare with the data of Lawson and Garst (1976) for H_2S, we measure the solubility of this acid gas at 339.0 K in a 25.0 wt% DEA aqueous solution. The results are given in Table 4 and plotted in Figure 5. We can notice the good agreement between the two data series as the average absolute deviation in partial pressures is less than 5%.

TABLE 4

H_2S solubility data in 25.0 wt% DEA aqueous solution at 339.0 K

α (mol H_2O/mol DEA in liquid phase)	P_{H_2S} (MPa)	
	This work	Lawson and Garst (1972) smoothed
0.115	0.0034	
0.169	0.0055	0.0039
0.221	0.0077	0.0066
0.285	0.0115	0.0107
0.333	0.0148	0.0145
0.428	0.0234	0.0241
0.482	0.0299	0.0311
0.525	0.0361	0.0376
0.548	0.0401	0.0415
0.626	0.0567	0.0576
0.677	0.0713	0.0715
0.717	0.0857	0.0849
0.752	0.1019	0.0998
0.789	0.1227	0.1191
0.823	0.1471	0.1421
0.893	0.2223	0.2171
0.932	0.2829	0.2862
0.972	0.3650	0.3906

With the aim of developing a new process of gas sweetening coupling chemical solvent and physical solvent, the acid gas solubility has been measured in several mixtures composed by water and alkanolamine and all kinds of physical solvent for a large range of temperature and loading.

2 WATER- ALKANOLAMINE - ACID GAS SYSTEMS MODELLING

The model developed to predict simultaneously chemical and physical equilibrium of water – alkanolamine – acid gas systems is based on the nonstoichiometric method with the heterogeneous approach (Electrolyte-NRTL and Peng and Robinson equation of state).
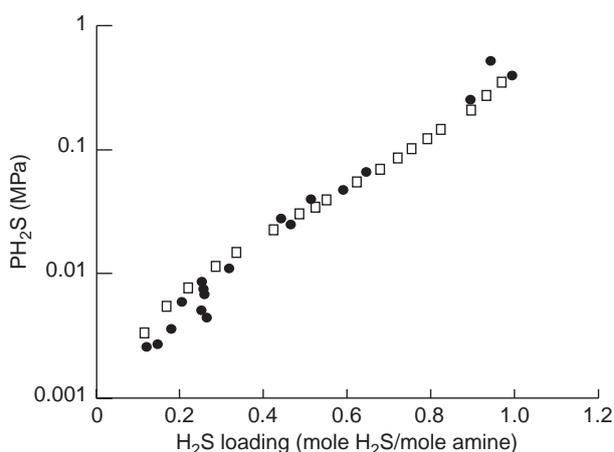
Figure 5

Solubility of H_2S in a 25.0 wt.% aqueous solution of DEA at 339.0 K (●) data of Lawson and Garst (1976); (□) this work.

2.1 Gibbs Energy Minimisation

This method is based on the definition of compounds that may be present at the steady state. For the following discussion, we can define the following types of compounds:
- solids, which allows for the formation of pure solid states;
- molecular compounds present in the liquid and vapour phases;
- ionic species in an aqueous liquid phase.

For each compound, we require the expression of the chemical potential as a function of temperature, pressure and composition of the phase. This information allows us to calculate the Gibbs energy of the system in order to determine the fraction of each compound which minimises the total energy of the system.

For the solid compounds, we may assume that the chemical potential is independent of the pressure and that the solid phase is only composed by one compound; its chemical potential is then given by the following relationship:

$$\mu(T,P) = \mu^\circ(s,T) \qquad (7)$$

where $\mu^\circ(s, T)$ is the standard chemical potential of the pure solid compound at the temperature T and a pressure of 0.1 MPa.

For the others compounds, which are present in the liquid and vapour phases, the chemical potential is written introducing their fugacity, f_i. If we use the ideal gas as the reference state, the chemical potential is then given by the following relationship:

$$\mu_i = \mu_i^\circ(T) + RT \ln \frac{f_i}{f_i^\circ} = \mu_i^\circ(T) + RT \ln \frac{\varphi_i n_i P}{n} \qquad (8)$$

In this relation, $\mu_i^{\circ}(T)$ is the chemical potential of the ideal gas at the temperature T; n_i is the number of moles of compound i in the considered phase, n is the total number of moles of this phase. φ_i is the fugacity coefficient of the compound in the mixture given by an equation of state and P is the pressure. We could also use another choice such as a liquid state as reference $\mu_i^{\#}(T)$; then, the excess term is written introducing the activity coefficient. The chemical potential is expressed by:

$$\mu_i = \mu_i^{\#}(T) + RT \ln \frac{\gamma_i n_i}{n} \qquad (9)$$

For the present calculation, we consider two types of phases: the solid compounds and the fluid phases with all species included molecular and ionic. The Gibbs energy of the whole system is given by the sum of the Gibbs energy of each phase (solid phases and fluid phases ϕ):

$$G = \sum_{j=1}^{S} \mu_j n_j^S + \sum_{j=S+1}^{C} \sum_{\alpha=1}^{\phi} \mu_j^{\alpha} n_j^{\alpha} \qquad (10)$$

We consider that the S first compounds form solid phases. The compounds between $S + 1$ and C are the molecular and ionic species. n_j^S is the number of moles of solid j which forms the S phases, n_j^{α} is the number of moles of compound i in the α phase and n^{α} is the total number of moles in the phase α. Writing this relation in dimensionless form (G/RT) and introducing the chemical potential, the Gibbs energy of the system is given by the following relationship:

$$\frac{G}{RT} = \sum_{j=1}^{S} d_j n_j^S + \sum_{j=S+1}^{C} \sum_{\alpha=1}^{\phi} n_j^{\alpha} \left(c_j + \ln \left(\frac{\varphi_j^{\alpha} n_i^{\alpha}}{n^{\alpha}} \right) \right) \qquad (11)$$

In this relation, we have introduced the following notations:

$$d_j = \frac{\mu_j^S}{RT} = \frac{\mu_j^{\circ}(s,T)}{RT}$$

$$c_j = \frac{\mu_j^{\circ}}{RT} + \ln(P) \qquad (12)$$

If the liquid reference state is adopted, the excess term is written with activity coefficient instead of fugacity coefficient and c_j becomes:

$$c_j = \frac{\mu_j^{\#}}{RT} \qquad (13)$$

The numbers of moles are constrained by the three relationships or constraints:
– The first relations are the mass balances and in this approach they are written in atomic terms:

$$\sum_{k=1}^{S} a_{jk} n_k^S + \sum_{k=S+1}^{C} \sum_{\alpha=1}^{\phi} a_{jk} n_k^{\alpha} = b_j \qquad (14)$$

where a_{jk} is the number of atoms j in the compound k

b_j is the total number of atoms j in the system.

There are p relations which correspond to the p types of atom considered in the system.
– The second relation is related to the ionic species. This is the electroneutrality constraint:

$$\sum_{j=S+1}^{C} \sum_{\alpha=1}^{\phi} z_j n_j^{\alpha} = 0 \qquad (15)$$

where z_j is the charge of species i. The total charge of molecular species equals zero.
– The last relations are the positive restraints: the numbers of moles presented in each phase should be positive.

$$n_i^S \geq 0$$
$$n_i^{\alpha} \geq 0 \qquad (16)$$

The nonstoichiometric method searches the number of moles of each compound (solids and fluids phases) which minimizes the total Gibbs energy with the restraints given by the last three kinds of relations. There are many numerical approaches proposed in the literature to solve this problem. Indeed, the choice of the thermodynamic model leads to different forms of function to optimise and each case demands a particular method to be sure that the real minimum is reached. Some of these methods use mathematical properties of the objective function in specific cases. For example Mc Donald and Floudas (1995) developed an algorithm which gives the true optimum if the thermodynamic model used is a classical activity model such as NRTL, UNIQUAC, Wilson and ASOG.

A second approach comes from the work of White *et al*. (1958), who first applied such a method to chemical systems. The method uses the Lagrange multipliers to realise the minimisation with restraints. In its first utilisation, the method was applied to ideal gas systems. Then, the method was modified and extended by many authors: generalised to multiphase systems by Boynton (1960) and Dayhoff *et al*. (1964, 1967) and with introduction of the ionic species by Gautam and Seider (1979). The method of Lagrange multipliers allows the equality restraints to be taken into account. Yet, to take into account the inequality restraints on the positive values of the number of moles, it is better to introduce the method of Kuhn-Tucker (Gupta *et al.,* 1991). George *et al*. (1976) modified the Lagrange's parameters to introduce the inequality restraints. In this work, we limit ourselves to use the RAND method with the Lagrange multipliers.

In our particular case, we want to calculate the composition at the steady state in the liquid phase when all reactions have occurred. Thus, we search the minimum of the Gibbs

energy in the liquid phase with the restraints on mass and electroneutrality balances. This leads to choosing the liquid phase as reference term for the chemical potential. The use of Lagrange multipliers allows us to write a new function which takes the restraints directly into account and in this situation, the objective function becomes unconstrained. This new simplified relation is the following:

$$Q = G\!\!\Big/\!\!{RT} + \sum_{l=1}^{p} \lambda_l \left(b_l - \sum_{k=1}^{C} a_{lk} x_k \right) + \lambda_e \sum_{j=1}^{C} z_j x_j \qquad (17)$$

The λ parameters are the Lagrange multipliers. There are p+1 values of Lagrange multipliers. The p first ones are related to the atomic mass balances and the last one is related to the electroneutrality. The numbers of moles which minimise the *(G/RT)* function and verify the restraints are ones which minimise *Q*. They are therefore obtained solving the following relationship:

$$\frac{\partial Q}{\partial n_j} = \frac{\partial Q}{\partial \lambda_j} = \frac{\partial Q}{\partial \lambda_e} = 0 \qquad (18)$$

As the Gibbs energy is not a linear function, the derivations lead to solving a set of non-linear equations. To realise the optimisation, we substitute a quadratic Taylor Series for the Gibbs energy. Let *O* be a vector of mole numbers close to the vector solution *N*. The Gibbs energy should be written as:

$$G(N) = G(O) + \left[G'(O) \right]^t [\Delta] + \frac{1}{2} [\Delta]^t \left[G''(O) \right] [\Delta] \qquad (19)$$

$$\frac{G(N)}{RT} = \frac{G(O)}{RT} + \left[\left(\frac{G}{RT} \right)' (O) \right]^t [\Delta] + \frac{1}{2} [\Delta]^t \left[\left(\frac{G}{RT} \right)'' (O) \right] [\Delta] \qquad (20)$$

where:

$\left(\dfrac{G}{RT} \right)'$ is the vector of the first derivatives of vector $\dfrac{G}{RT}(O)$

with respect to number of moles and $\left(\dfrac{G}{RT} \right)''$ is the matrix of the

second derivatives of vector $\dfrac{G}{RT}(O)$ with respect to number of moles.

$[\Delta]$ is the vector of *N - O*.

Here, we suppose the main assumption of the developed method: the expressions of first and second derivation of *G* require the differentiation of the activity coefficient with respect to the number of moles and these expressions are specific to the thermodynamic model used. Here, we have chosen the Electrolyte-NRTL model (Chen *et al*., 1986). To simplify the development of this approach, we assume that the variations of the activity coefficient are small at each iteration and we

can ignore the variation of the activity coefficient. In this case, the derivatives of the Gibbs energy become the following:

$$\frac{\partial G\!\!\Big/\!\!{RT}}{\partial n_i} = c_i + \ln \frac{n_i \gamma_i}{n} \qquad (21)$$

$$\frac{\partial^2 G\!\!\Big/\!\!{RT}}{\partial n_i^{\,2}} = \frac{1}{n_i} - \frac{1}{n} \qquad (22)$$

$$\frac{\partial^2 \left(G\!\!\Big/\!\!{RT} \right)}{\partial n_i \partial n_j} = -\frac{1}{n} \qquad (23)$$

Including these relations into the expression of the Taylor series of the Gibbs energy, we obtain:

$$\frac{G(n)}{RT} = \frac{G(O)}{RT} + \sum_{j=1}^{C} \left(c_j + \ln \frac{o_j \gamma_j}{o} \right) (n_j - o_j)$$
$$+ \frac{1}{2} \left(\sum_{j=1}^{C} \frac{n_j - o_j}{o_j} - \frac{\bar n - \bar o}{\bar o} \right) \qquad (24)$$

This relation is then introduced into the Q function and the minimisation process is realised using equation (18):

$$\frac{\partial Q}{\partial n_j} = \frac{\partial Q}{\partial \lambda_j} = \frac{\partial Q}{\partial \lambda_e} = 0 \qquad (25)$$

After some manipulations, we obtain the expressions for the mole numbers in the liquid phase of the next iteration as a function of the previous values, of the chemical potential and of the Lagrange multipliers:

$$n_i = -g_i + u\, o_i + \left(\sum_{j=1}^{p} \lambda_j a_{ji} \right) o_i + \lambda_e z_i o_i \qquad (26)$$

with :

$$g_i = o_i \left(c_i + \ln \frac{\gamma_i o_i}{o} \right) \qquad (27)$$

These relations introduce a new variable *u*(= *n/o*). The set of parameters of these equations (λ, u) are obtained from the following set of linear equations:

$$\begin{pmatrix} r_{11} & \cdots & r_{1p} & N_1 & s_1 \\ \vdots & r_{ij} & \vdots & \vdots & \vdots \\ r_{p1} & \cdots & r_{pp} & N_p & s_p \\ N_1 & N_l & N_p & 0 & 0 \\ s_1 & s_l & s_p & 0 & t \end{pmatrix} \begin{pmatrix} \lambda_1 \\ \vdots \\ \lambda_p \\ u \\ \lambda_e \end{pmatrix} = \begin{pmatrix} b_1 + \sum_{k=1}^{C} a_{k1} g_k \\ \vdots \\ b_p + \sum_{k=1}^{C} a_{kp} g_k \\ \sum_{k=1}^{C} g_k \\ \sum_{k=1}^{C} g_k z_k \end{pmatrix} \qquad (28)$$

where

$$r_{ij} = r_{ji} = \sum_{k=1}^{C} a_{jk} a_{ik} o_k \qquad s_l = \sum_{k=1}^{C} a_{lk} o_k z_k \qquad (29)$$

$$N_l = \sum_{j=1}^{C} a_{lj} o_j \qquad t = \sum_{j=1}^{C} z_j^2 o_j \qquad (30)$$

The variables N_l are equal to the atoms number in the liquid phase, s_l and t are related to electroneutrality.

In summary, the optimisation method is an iterative process. Starting from an initialisation which verifies the mass and electroneutrality balances, a linear set of equations is solved to give some intermediary parameters such as the Lagrange multipliers. Then the number of moles of each compound in the liquid phase is estimated and the process is continued until convergence criteria on mole numbers are reached. We could notice that the size of the linear equations is a function of the number of atoms considered. As the latter is lower than the number of compounds, it is possible to consider a large amount of compounds without increasing the computer time.

2.2 Thermodynamic Framework

The thermodynamic framework used in the model presented here is based of two types of equilibrium: chemical and vapour-liquid phase equilibria.

2.2.1 Chemical Equilibrium

The chemical equilibrium governs the distribution in the liquid phase between free molecular species and ionic forms. It is solved by the Gibbs energy minimisation presented above. To enhance this method, numerical values of the chemical potential of the species i are required. In the following, we describe how these parameters are evaluated.

In aqueous solutions, H_2S and CO_2 react in an acid-base buffer mechanism with alkanolamines. The species considered in our system are:
- molecular species: H_2O, CO_2, H_2S, $R_1R_2R_3N$
- ionic species (non-volatile): OH^-, H_3O^+, HS^-, S^{2-}, HCO_3^-, CO_3^{2-}, $R_1R_2R_3NH^+$, $R_1R_2NCOO^-$.

In these formulae, $R_1R_2R_3N$ is the chemical formula of the alkanolamine. R represents an alkyl group, alkanol group or hydrogen. Here, the alkanolamine is the diethanolamine (DEA): $R1 = H$ and $R_2 = R_3 = CH_2\text{-}CH_2\text{-}OH$ forming a secondary alkanolamine.
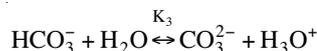
The concentration of each species depends through acid-base equilibrium reactions written as chemical dissociations:

- Ionization of water: $2H_2O \overset{K_1}{\leftrightarrow} HO^- + H_3O^+$

- Dissociation of carbon dioxide:

$$CO_2 + 2H_2O \overset{K_2}{\leftrightarrow} HCO_3^- + H_3O^+$$
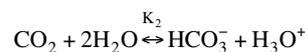
- Dissociation of bicarbonate:

$$HCO_3^- + H_2O \overset{K_3}{\leftrightarrow} CO_3^{2-} + H_3O^+$$

- Dissociation of hydrogen sulphide:

$$H_2S + H_2O \overset{K_4}{\leftrightarrow} HS^- + H_3O^+$$
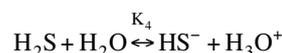
- Dissociation of disulphide: $HS^- + H_2O \overset{K_5}{\leftrightarrow} S^{2-} + H_3O^+$

- Dissociation of protonated alkanolamine:

$$R_1R_2R_3NH^+ + H_2O \overset{K_6}{\leftrightarrow} R_1R_2R_3N + H_3O^+$$
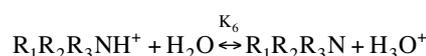
- Carbamate reversion to bicarbonate (occurs only with primary and secondary amines):

$$R_1R_2NCOO^- + H_2O \overset{K_7}{\leftrightarrow} R_1R_2NH + HCO_3^-$$
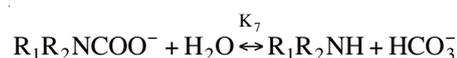
In this work, water is treated as the solvent. The standard state associated is the pure liquid at the system temperature and pressure. The standard state for ionic and the other molecular solutes (CO_2, H_2S and DEA) is the ideal, infinitely dilute aqueous solution at the system temperature and pressure. This leads to the following unsymmetric convention for normalisation of activity coefficients (indicated by *): for water (solvent), $\gamma_w \to 1$ as $x_w \to 1$; for ionic and molecular solutes, $\gamma_i^* \to 1$ as $x_i \to 0$.

The reference terms of the chemical potential are calculated from literature (Barner and Scheurman, 1978) when they are available and by considering the mass balance laws for the other cases:

$$RT \ln K_r = -\sum_i \nu_{i,r} u_i^{\#} \qquad (31)$$

Equilibrium constants are based on the mole fraction scale. They are available in the literature but are expressed on the molality concentration scale *(Table 5)*. It was then necessary to convert these equilibrium constants from a molality basis to a mole fraction basis. This linear system of seven equations and twelve unknowns can be solved if four chemical potentials are fixed at literature values. Then, the other chemical potentials can be determined.

The activity coefficient of the species *i* is required to evaluate its excess chemical potential term. It is calculated from the Electrolyte-NRTL equation (Chen and Evans, 1986) which 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 (Renon and Prausnitz, 1968) is adopted to account for the local contribution.

<div align="center">

TABLE 5

Temperature dependence of the equilibrium constants for chemical dissociations (see text for formulae)

</div>

Chemical dissociation	Temp range, K	Source
1	273.15 – 573.15	Olofsson and Hepler, 1975
2	273.15 – 498.15	Edwards *et al.*, 1978
3	273.15 – 323.15	Peiper and Pitzer, 1982
4	273.15 – 573.1	Millero, 1986
5	298.15 – 423.15	Kryukov *et al.*, 1974
6	298.15 – 423.15	Oscarson *et al.*, 1989
7	298.15 – 358.15	Internal source

The Pitzer-Debye-Hückel formula (Pitzer, 1980) is used to represent the long-range interaction contribution:

$$\frac{g_{PDH}^{E*}}{RT} = -\left(\sum_k x_k\right)\sqrt{\frac{1000}{M_w}}\left(\frac{4A_\phi I_x}{\rho}\right)\ln\left(1+\rho\sqrt{I_x}\right) \quad (32)$$

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

$$A_\phi = \frac{1}{3}\sqrt{\frac{\pi 2 d_w N}{1000}}\left(\frac{e^2}{D_w kT}\right)^{\frac{3}{2}} \quad (33)$$

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

$$I_x = \frac{1}{2}\sum_i x_i z_i^2 \quad (34)$$

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 (Chen and Evans, 1986). 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:

$$\frac{g_{NRTL}^{E}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}}$$
$$+\sum_c X_c \sum_{a'} \frac{X_{a'}\sum_j G_{jc,a'c}\tau_{jc,a'c}}{\left(\sum_{a''} X_{a''}\right)\left(\sum_k X_k G_{kc,a'c}\right)} \quad (35)$$
$$+\sum_a X_a \sum_{c'} \frac{X_{c'}\sum_j G_{ja,c'a}\tau_{ja,c'a}}{\left(\sum_{c''} X_{c''}\right)\left(\sum_k X_k G_{ka,c'a}\right)}$$

with :

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \qquad G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \quad (36)$$

$$\alpha_{mc} = \alpha_{cm} = \frac{\sum_a X_a \alpha_{m,ca}}{\sum_{a'} X_{a'}} \qquad \alpha_{am} = \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}} \quad (37)$$

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:

$$G_{jc,a'c} = \exp\left(-\alpha_{jc,a'c}\tau_{jc,a'c}\right) \quad G_{ja,c'a} = \exp\left(-\alpha_{ja,c'a}\tau_{ja,c'a}\right)$$
$$G_{ca,m} = \exp\left(-\alpha_{ca,m}\tau_{ca,m}\right) \qquad G_{im} = \exp\left(-\alpha_{im}\tau_{im}\right) \quad (38)$$
$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca} \quad \tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca}$$

For ionic and molecular solutes, the Gibbs energy must be normalised to reflect the unsymmetric reference states adopted:

$$\frac{g_{NRTL}^{E*}}{RT} = \frac{g_{NRTL}^{E}}{RT} - \sum_{m\neq w} x_m \ln \gamma_m^\infty - \sum_c x_c \ln \gamma_c^\infty - \sum_a x_a \ln \gamma_a^\infty \quad (39)$$

The Electrolyte-NRTL equation defined in the unsymmetric convention is then expressed by:

$$\frac{g^{E*}}{RT} = \frac{g_{PDH}^{E*}}{RT} + \frac{g_{NRTL}^{E*}}{RT} \quad (40)$$

The activity coefficient for any species is derived from the partial derivative of the excess Gibbs energy with respect to mole number:

$$\ln \gamma_i^* = \left[\frac{\partial\left(ng^{E*}/RT\right)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \quad (41)$$

2.2.2 Vapour-Liquid Phase Equilibrium

Phase equilibrium governs the distribution of molecular species between the vapour and liquid phases. The vapour molar fractions of volatile species are determined from a bubble point calculation. The condition of phase equilibrium is given by: $f_i^L = f_i^V$.

For the molecular solutes, Henry's constants at the saturation pressure of water represent liquid reference state fugacities:

$$\varphi_i^V \cdot y_i \cdot P = x_i \cdot \gamma_i^* \cdot H_{i,w}^{P_w^{sat.}}(T) \cdot \exp\left[\overline{v_i}^{-\infty} \frac{\left(P - P_w^{sat.}(T)\right)}{RT}\right] \quad (42)$$

where $H_{i,w}^{P_w^{sat.}}$ and $\overline{v}^{-\infty}$ are the Henry's constant and partial molar volume at infinite dilution for molecular solute i in pure water at the system temperature and at the vapour pressure of water. The partial molar volumes of H_2S, CO_2 and DEA at infinite dilution in water are given by:

$$\overline{v_i}^{-\infty}\left(cm^3 \cdot mol^{-1}\right) = A_{vol}T^2 + B_{vol}T + C_{vol} \quad (43)$$

Coefficients A_{vol}, B_{vol} and C_{vol} are summarised in Table 6. Henry's constants have units of Pascal and the temperature dependence is given by :

$$\ln H_{i,w}^{P_w^{sat.}} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \quad (44)$$

Coefficients C_1 to C_4 are given in Table 7.

TABLE 6

Temperature dependence parameters of the partial molar volume at infinite dilution in water

Solute	A_{vol}	B_{vol}	C_{vol}	Temp range, K
H_2S	0.0006	-0.325	78.702	273.15 – 423.15
CO_2	0.00057	-0.309	74.315	273.15 – 423.15
DEA	0.0	0.0	173.6	273.15 – 423.15

TABLE 7

Temperature dependence parameters of Henry's constant for H_2S, CO_2 and DEA

Solute	C_1	C_2	C_3	C_4	Temp range, K
H_2S	358.138	-13236.8	-55.0551	0.059565	273.15 – 423.15
CO_2	170.7126	-8477.711	-21.9574	0.005781	273.15 – 373.15
DEA	344.46	-23865.0	-49.452	0.04175	273.15 – 423.15

For water, vapour-liquid equilibrium is given by:

$$\varphi_w^V \cdot y_w \cdot P = x_w \cdot \gamma_w \cdot P_w^{sat.}(T) \cdot \varphi_w^\circ \cdot \exp\left[\overline{v_w} \frac{\left(P - P_w^{sat.}(T)\right)}{RT}\right] \quad (45)$$

where $\overline{v_w}$ is the molar volume of pure liquid water at the system temperature and saturation pressure. The vapour fugacity coefficients are calculated by using the well-known Peng-Robinson equation of state (1976) with the classical Van der Waals mixing rules.

2.3 Data Regression: Determining Interaction Parameters

The adjustable parameters of the Electrolyte-NRTL model consist of three types of short-range binary interaction parameters: molecule-molecule, $\tau_{mm'}$ and $\tau_{m'm}$; molecule-ion pair, $\tau_{m,ca}$ and $\tau_{ca,m}$; and ion pair-ion pair (with common cation or anion) $\tau_{ca,ca'}$ and $\tau_{ca',ca}$ or $\tau_{ca,c'a}$ and $\tau_{c'a,ca}$. Best values of these binary parameters were determined by data regression using binary and ternary VLE system data.

Acid gas-water interaction parameters were fitted in the earlier work of Chen and Evans (1986) and are set to these values. DEA-water binary parameters were fitted on the experimental data of Abendinzadegan Abdi and Meisen (1999) and Horstmann *et al.* (2002). Because of the lack of experimental data, DEA-acid gas binary parameters are fixed to zero without affecting the representation. Concerning the ion pair-ion pair parameters, Chen and Evans (1986) suggested setting them to zero without significantly affecting representation of VLE data. Molecule-ion pair parameters are chosen to be determined on ternary systems experimental data. Many species are present in the liquid phase at low or negligible concentration so that parameters associated with them do not affect representation of VLE. There are set to default values: $\tau_{water-ion\ pair} = 8.0$, $\tau_{ion\ pair-water} = -4.0$, $\tau_{DEA-ion\ pair} = \tau_{acid\ gas-ion\ pair} = 15.0$ and $\tau_{ion\ pair-DEA} = \tau_{ion\ pair-acid\ gas} = -8.0$. Following Chen and Evans (1986), the nonrandomness factor are fixed at 0.2 for molecule-molecule interactions and for water-ion pair interactions except for the binary water-DEA which are set to 0.47. Nonrandomness factors for DEA-ion pair and acid gas-ion pair interactions are fixed at 0.1 as suggested by Mock *et al.* (1986).

After determining molecule-molecule binary parameters, ternary systems are studied to fit the molecule-ion pair and ion pair-molecule interaction parameters adopted:

for the DEA-H_2S-H_2O system:

$\tau_{water-DEAH^+,HS^-}$, τ_{DEAH^+,HS^--DEA} and $\tau_{DEAH^+,HS^--water}$.

for the DEA-CO_2-H_2O system:

$\tau_{water-DEAH^+,HCO_3^-}$, $\tau_{water-DEAH^+,DEACOO^-}$, $\tau_{DEAH^+,HCO_3^--DEA}$, $\tau_{DEAH^+,HCO_3^--water}$, $\tau_{DEAH^+,DEACOO^--water}$

and $\tau_{DEAH^+,DEACOO^--DEA}$.

These parameters are temperature dependent as follows:

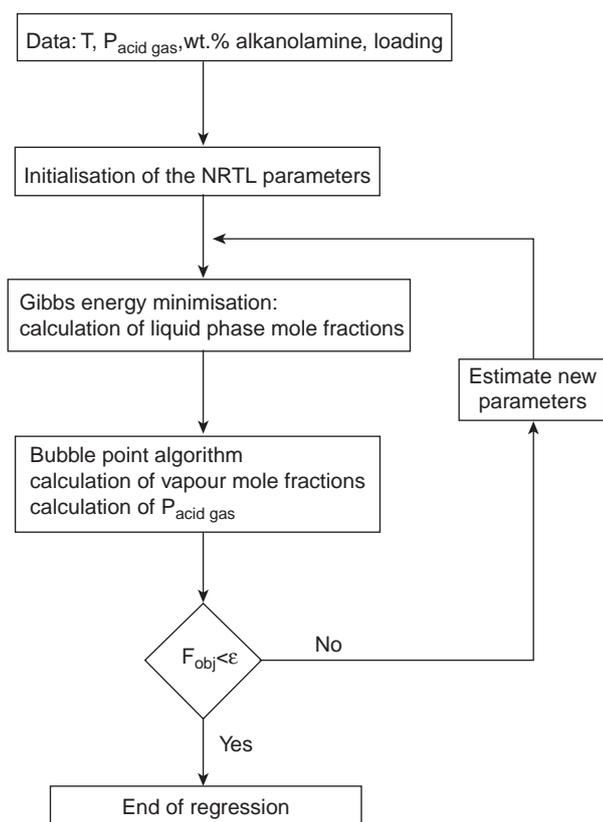$$\tau_{kl} = \tau_{kl}^0 + \frac{\tau_{kl}^1}{T} \quad (46)$$

Figure 6

Optimisation algorithm.

The objective function chosen, which is minimised by the Levenberg-Marquadt method, is the following:

$$F = \sum_{i} \left(\frac{P_i^{exp,acid\ gas} - P_i^{cal,acid\ gas}}{P_i^{exp,acid\ gas}} \right)^2 \qquad (47)$$

Figure 6 describes our fitting algorithm and the experimental data are summarised in Table 8.

2.4 Results of Model Fitting

In this section, results of the model fitting on the ternary systems and predictive calculations on quaternary systems (sour gas mixtures) are presented.

2.4.1 Ternary Systems: Comparison with Experimental Data

Fitting was carried out over 220 experimental data points for the DEA-CO_2-H_2O system and over 250 experimental data points for the DEA-H_2S-H_2O system. The results are given in terms of RMSD (Root Mean square deviation):

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

RMSD (DEA-CO_2-H_2O) = 22.32%
RMSD (DEA-H_2S-H_2O) = 23.95%

Figure 7 compares the CO_2 experimental partial pressure over a 25.0 wt% DEA solution with the partial pressure calculated by our model with fitted Electrolyte-NRTL parameters (solid line) versus loading. Figure 8 gives the equivalent information for the DEA-H_2S-H_2O system. As these figures show, the NRTL-Electrolyte model gives satisfactory results. It is noticeable however that when temperature increases, our model tends to overestimate the experimental partial pressure of CO_2. For the DEA-H_2S-H_2O system, this trend is not so important (cf. *Fig. 8*).

The model presented here successfully represents experimental acid gas solubility data. Moreover, the model gives the distribution of any species in the liquid phase at the thermodynamic equilibrium. Figures 9 to 12 are speciation plots for the DEA-H_2S-H_2O and DEA-CO_2-H_2O systems at different temperatures or DEA concentrations. They illustrate how our VLE model can be used to determine liquid-phase equilibrium composition. They also illustrate trends of the ionic and molecular species compositions at equilibrium as a function of temperature and as a function of acid gas loading.

TABLE 8

Summary of literature sources of experimental VLE data used for adjusting binary interaction parameters

| Source	Amine concn	Temp range, K	Acid gas loading range
	DEA-H_2S-H_2O		
Lee *et al*. (1973)	2.0, 3.5, 5.0 M	298.15 – 393.15	0.04 – 1.76
Lawson and Garst (1976)	25.0 wt %	310.93 – 380.37	0.0038 – 1.582
Huang and Ng (1995)	30.0, 50.0 wt%	313.15 – 393.15	0.0034 – 1.28
	DEA-CO_2-H_2O		
Lee *et al*. (1972)	0.5, 2.0, 3.5, 5.0 M	298.15 – 393.15	0.084 – 2.695
Lawson and Garst (1976)	25.0 wt%	310.93 – 394.26	0.321 – 1.167
Maddox *et al*. (1987)	0.5, 2.0 M	298.15	0.582 – 2.012
Maddox and Elizondo (1989)	20.0, 35.0, 50.0 wt%	299.82	0.1033 – 0.5622
Lal *et al*. (1985)	2.0	313.15	0.042 – 0.367
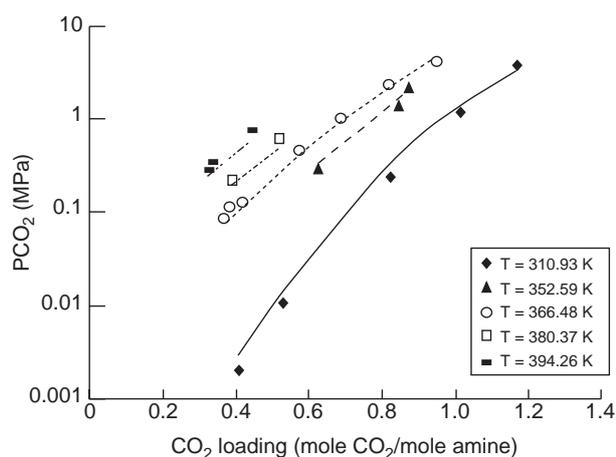
Figure 7

Comparison of estimated curves and experimental points of CO$_2$ equilibrium partial pressure over a 25.0 wt.% DEA solution from Lawson and Garst (1976).
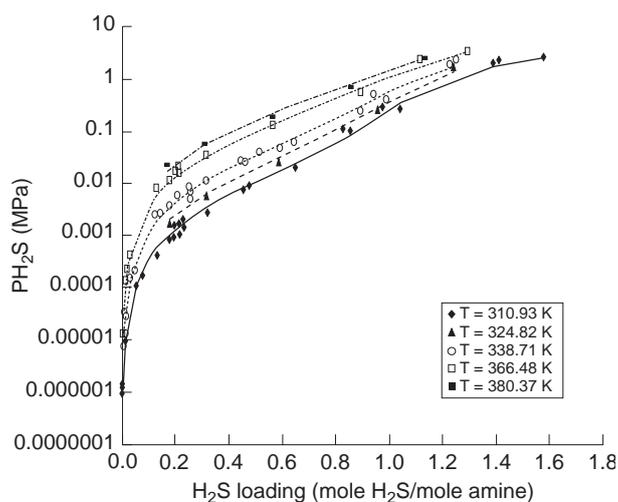

Figure 8

Comparison of estimated curves and experimental points of H$_2$S equilibrium partial pressure over a 25.0 wt.% DEA solution from Lawson and Garst (1976).
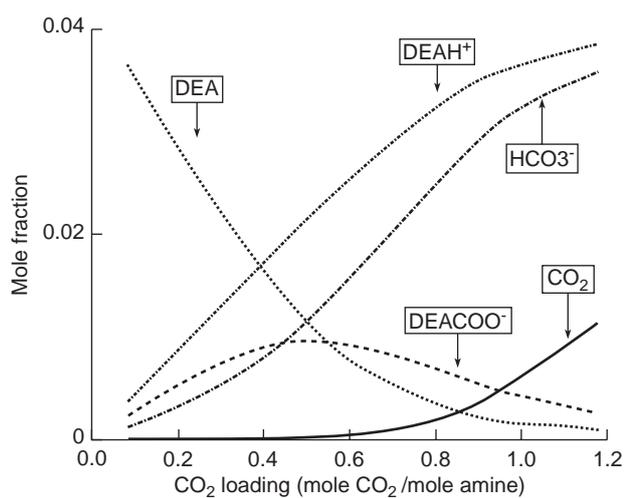

Figure 9

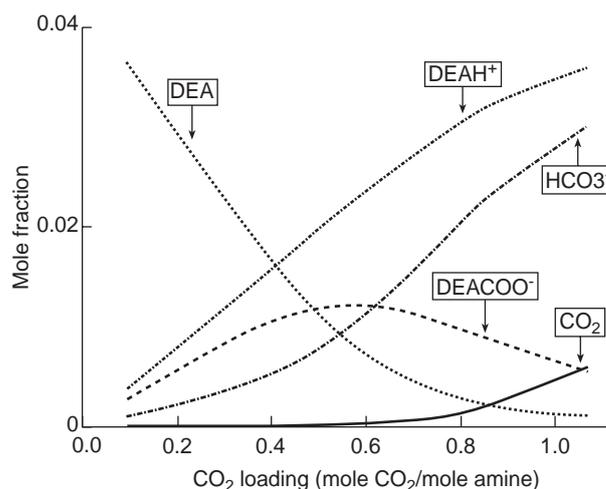Liquid-phase composition of a 2.0 M DEA solution loaded with CO$_2$ at 348.15 K. Compositions were calculated by using the VLE model.

Figure 10

Liquid-phase composition of a 3.5 M DEA solution loaded with CO$_2$ at 348.15 K. Compositions were calculated by using the VLE model.

Equilibrium weight percentages of CO$_2$ and DEACOO$^-$ in the liquid phase were measured by Sidi-Boumedine (2003). We can thus compare these data with calculated values. In Figure 13 and 14, measured data with a precision of 15% are plotted for one temperature and two concentrations of DEA. There is relatively good agreement between experimental data and calculated values (note that there is no comparison for such experimental data in the open literature and that the quantity measured and calculated are very small).

2.4.2 Quaternary System: Comparaison with Experimental Data

For the quaternary system, no new parameters are adjusted so that the model is used in a predictive manner to evaluate representation of experimental quaternary system composed of mixed acid gases; the data sources are summarised in Table 9. Figures 15 and 16 show the calculated acid gas partial pressure versus the experimental one for carbon dioxide and hydrogen sulphide respectively. The pressure range of these
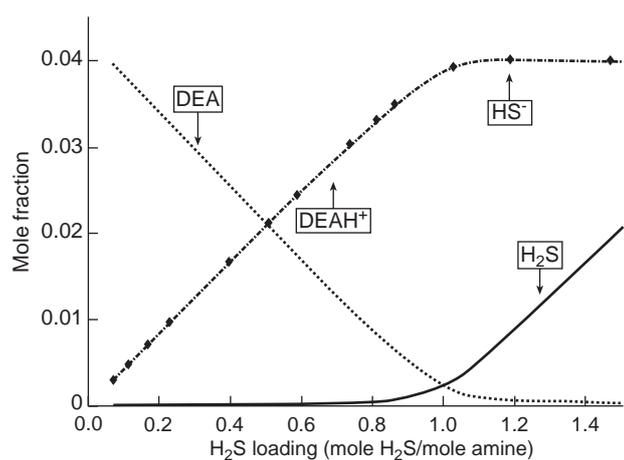
Figure 11

Liquid-phase composition of a 2.0 M DEA solution loaded with H_2S at 298.15 K. Compositions were calculated with the VLE model.
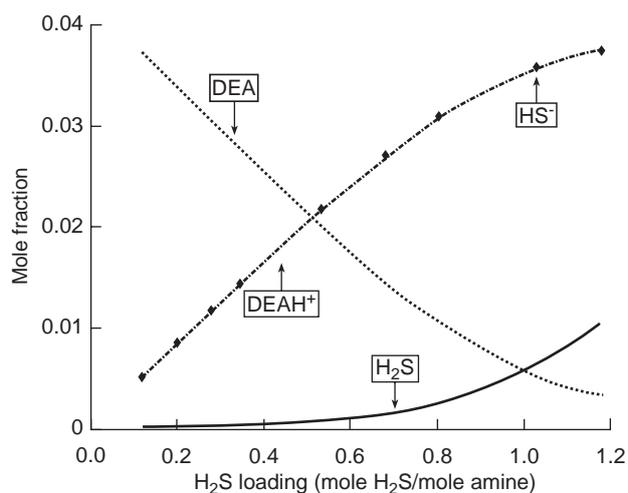

Figure 12

Liquid-phase composition of a 2.0 M DEA solution loaded with H_2S at 373.15 K. Compositions were calculated with the VLE model.
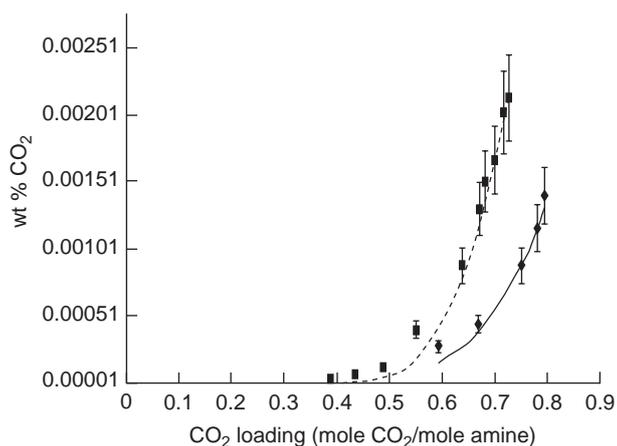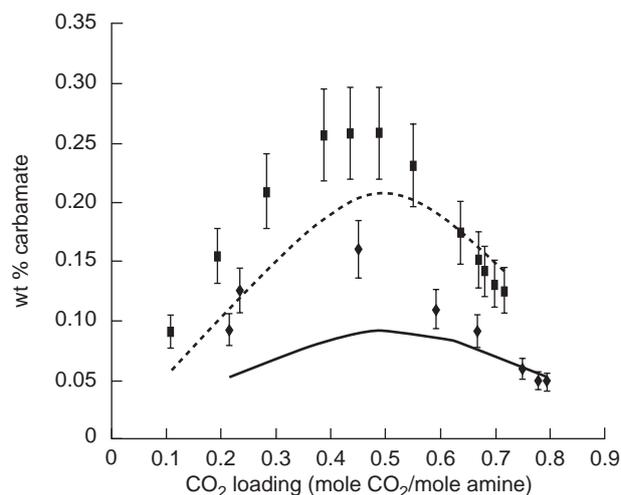

Figure 13

Comparison of Electrolyte-NRTL results (solid lines) with experimental data for CO_2 wt.% at 298.15 K ($\blacksquare$,— — —) 41.77 wt.% ; ($\blacklozenge$,———) 20.7 wt.%.

Figure 14

Comparison of Electrolyte-NRTL results (solid lines) with experimental data for carbamate wt.% at 298.15 K ($\blacksquare$,— — —) 41.77 wt.% ; ($\blacklozenge$,———) 20.7 wt.%.

TABLE 9

Summary of literature sources of experimental VLE data for the quaternary system DEA-H_2S-CO_2-H_2O

| Source	Amine concn (wt. %)	CO_2 partial pressure range (MPa)	H_2S partial pressure range (MPa)
Lawson and Garst (1976)	25.0	$3.066 \ 10^{-3} - 2.293$	$8.39 \ 10^{-3} - 2.199$
Lee *et al.* (1974)	20.55	$3.075 \ 10^{-4} - 5.764$	$1.57 \ 10^{-3} - 1.506$
Ho and Eguren (1988)	50.0, 35, 5.3	$2.66 \ 10^{-2} - 0.958$	$5.0 \ 10^{-3} - 1.183$
Jane and Li (1997)	0.3	$1.7 \ 10^{-3} - 0.101$	$1.35 \ 10^{-2} - 0.123$
Rogers *et al.* (1997)	20.2, 20.3	$3.46 \ 10^{-7} - 8.91 \ 10^{-4}$	$6.30 \ 10{-6} - 9.467 \ 10^{-3}$
Lal *et al.* (1985)	20.55	$4.1 \ 10^{-5} - 5.49 \ 10^{-4}$	$1.27 \ 10{-4} - 3.392 \ 10^{-3}$
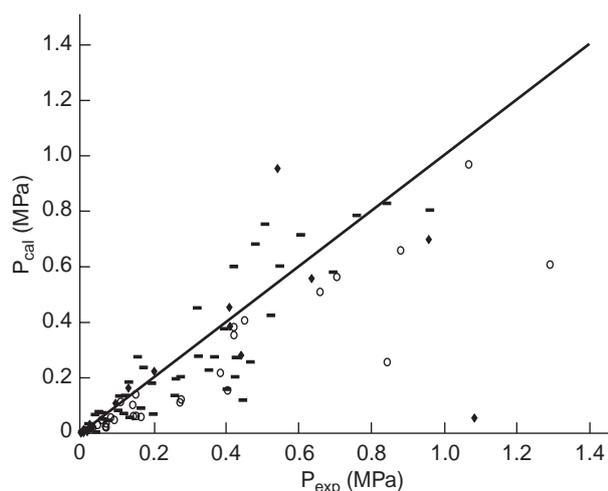
Figure 15

Calculated CO_2 equilibrium partial pressure versus experimental CO_2 equilibrium partial pressure. (◆) Ho and Eguren (1988). (-) Lawson and Garst (1976) (○) Lee *et al*. (1974). (solid line = bisecting line).
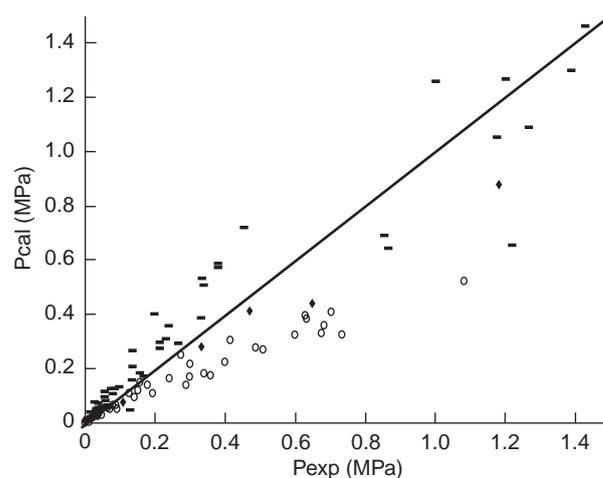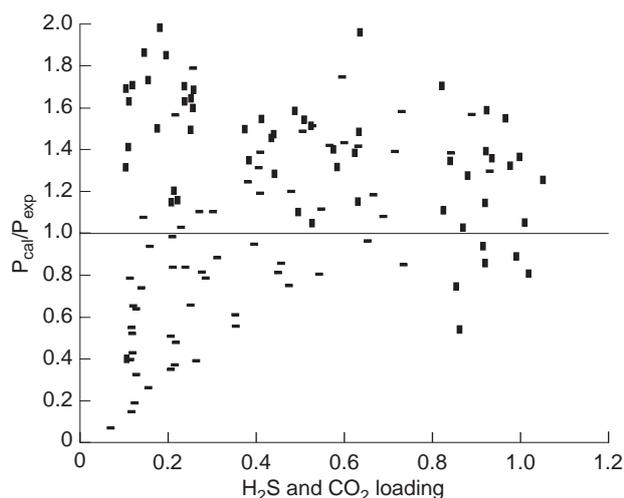

Figure 16

Calculated H_2S equilibrium partial pressure versus experimental H_2S equilibrium partial pressure. (◆) Ho and Eguren (1988). (-) Lawson and Garst (1976) (○) Lee *et al*. (1974). (solid line = bisecting line).

Figure 17

Ratio of calculated to experimental values of H_2S and CO_2 equilibrium partial pressure over a 25.0 wt.% DEA solution. Lawson et Garst (1976) : (■) H_2S ; (-)CO_2.
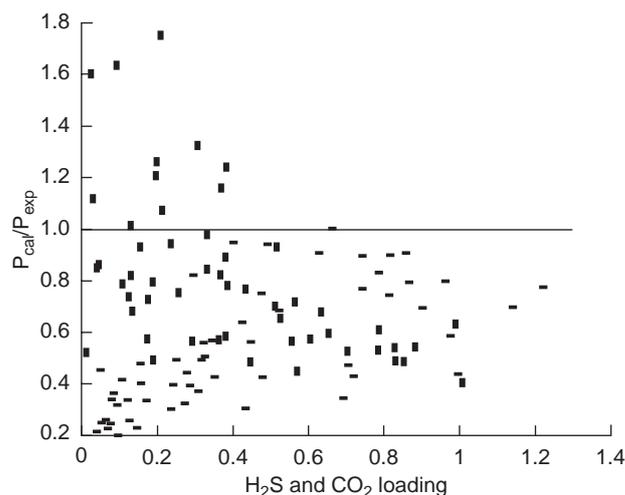

Figure 18

Ratio of calculated to experimental values of H_2S and CO_2 equilibrium partial pressure over a 20.55 wt.% DEA solution. Lee *et al*. (1974): (■) H_2S; (-) CO_2.

data is large and here we show only the range between 0 – 1.5 MPa. CO_2 partial pressures are better estimated than those of H_2S. Moreover, for CO_2 there is an underestimation for all authors whereas for H_2S, it depends on the data source: Lawson and Garst (1976) data are overestimated and Lee *et al*. (1974) and Ho and Eguren (1988) are underestimated. The root mean square deviations are 42% and 49% for carbon dioxide and hydrogen sulphide respectively.

Figures 17 and 18 illustrate for two different DEA concentrations the ratios of the calculated to the experimental equilibrium CO_2 and H_2S partial pressures versus the acid gas loading: larger deviations are observed at lower loadings. However, when the loading increases, this trend becomes less important.

CONCLUSION

In this work, we are interested in acid gases (H_2S and CO_2) removal by an aqueous solution of alkanolamine. This work

is divided into two main sections: the experimental one where the apparatus and the treatment of experimental data are developed and the modelling with application of electrolyte –NRTL activity coefficient model on such data.

The experimental apparatus was developed to determine the partial acid gas pressure as a function of acid gas loading in the reactive liquid phase using the synthetic method. The treatment of the experimental data are detailed. The apparatus was satisfactorily checked on literature data on aqueous solutions of diethanolamine loaded with CO_2 and H_2S. In order to develop of a new process of gas sweetening, acid gas solubility has been measured in several mixtures composed by water and alkanolamine and all kinds of physical solvent for a large range of temperature and loading.

The modelling of these data must couple 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 decribed by the classical Peng and Robinson equation of state. The nonstoichiometric method is used to solve the chemical equilibrium in the liquid phase. This approach allows us to model any kind of acid gas systems with the same algorithm. The adjustable parameters of the electrolyte NRTL model were determined on experimental acid gas partial pressure data of the studied systems (water + diethanolamine + CO_2 and water + diethanolamine + H_2S). The resulting model compares well to those from the literature.

ACKNOWLEDGMENT

REFERENCES

Abedinzadegan Abdi, M., Meisen, A. (1999) A novel process for diethanolamine recovery from partially degraded solutions. Process description and phase equilibria of the DEA-BHEP-THEED-Hexadecane system, *Ind. Eng. Chem. Res.*, **38**, 8, 3096 - 3104.

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., Amstrong, B. (1973) *International Thermodynamic Tables of the fluid state-6 Carbon dioxide*, Pergamon Press.

Austgen, D.M. (1989) A model of vapor-liquid equilibria for acid gaz-alkanolamine-water systems, *PhD Dissertation,* University of Texas, Austin, USA.

Barbosa, D., Doherty, M.F. (1987) A new set of composition variables for the representations for two-phase reactive systems, *Proc. R. Soc. Lond.*, A413, 459.

Barner, H.E., Scheuerman, R.V. (1978) *Handbook of thermochemical data for compounds and aqueous species*, John Wiley & Sons, New York, USA.

Benmansour, S., Barreau, A., Mougin, P. (2000) Modélisation thermodynamique des équilibres liquide - vapeur gaz acides - solvants complexes, *Rapport IFP 54 383.*

Boynton, F.P. (1960) Chemical equilibrium in multicomponent polyphase systems, *The Journal of Chemical Physics*, **32**, 1880-1881.

Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B. (1982) Local composition model for excess Gibbs energy of electrolyte systems, *AIChE J.*, **28**, 4, 588-596.

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.

Dayhoff, M.O., Lippincott, E.R., Eck, R.V. and Nagarajan, G. (1967) *Thermodynamic equilibrium in prebiological atmospheres of C, H, O, N, P, S and Cl.* Nasa Report. Wahsington D.C.

Dayhoff, M.O., Lippincott, E.R., Eck, R.V. (1964) Thermodynamic equilibrium in prebiological atmospheres, *Science*, **146**, 1461-1464.

Edwards, T.J., Maurer, G., Newman, J.M., Prausnitz, J.M. (1978) Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes, *AIChE J.*, **24**, 6, 966-976.

Fürst, W., Renon, H. (1993) Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State, *AIChE J.*, **39**, 990.

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

George, B., Brown, L.P., Farmer, C.W., Buthod, P., Manning, P.S. (1976) Computation of Multicomponent, multiphase equilibrium, *Ind. Eng. Chem. Process Des Devl.*, **15**, 3, 372-377.

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

Gupta, A., Bishnoi, P., Kalogerakis, N. (1991) A method for the simultaneous phase equilibria and styability calculations for multiphase reacting and non-reacting systems, *Fluid Phase Equilib.*, **63**, 65-89.

Habchi Tounsi, K.N. (2003) Modélisation thermodynamique de l'absorption des gaz acides dans un solvant mixte (eau-diéthanolamine-méthanol), *Thèse,* université d'Aix Marseille II.

Ho, B., Eguren, R. (1988) Solubility of acidic gases in aqueous DEA and MDEA solutions, *presented at the 1988 AIChE Spring National Meeting*, March 6-10.

Horstmann, S., Mougin, P., Fischer, K., Gmelhing, J., Lecomte, F. (2002) Phase equilibrium and excess enthalpy data for the system methanol + 2,2' diethanolamine + water, *J. Chem. Eng. Data*, **47**, 6, 1496-1501.

Huang, S.H., Ng, H.-J. (1995) Solubility of H_2S and CO_2 in alkanolamines, *Research Report RR-155*, Gas Processors Association.

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.

Kryukov, P.A., Starostina, L.I., Tarasenko, S.Y., Primanchuk, M.P. (1974) Second ionization constant of hydrogen sulfide at temperatures up to 150°C, *Geochemistry International*, **11**, 4, 688-698.

Lal, D., Otto, F.D., Mather, A.E. (1985) The solubility of H_2S and CO_2 in a diethanolamine solution at low partial pressures, *Čan. J. Chem. 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**, 1, 20-30.

Lee, J.I, Otto, F.D., Mather, A.E. (1972) Solubility of carbon dioxide in aqueous diethanolamine solutions at high pressures, *J. Chem. Eng. Data*, **17**, 4, 465-468.

Lee, J.I. Otto, F.D., Mather, A.E. (1973) Partial pressures of hydrogen sulfide over aqueous diethanolamine solutions, *J. Chem. Eng. Data*, **18**, 4, 420.

Lee, J.I., Otto, F.D., Mather, A.E. (1973) Solubility of hydrogen sulfide in aqueous diethanolamine solutions at high pressures, *J. Chem. Eng. Data*, **18**, 1, 71-73.

Lee, J.I., Otto, F.D., Mather, A.E. (1974) The solubility of mixture of carbon dioxide and hydrogen sulfide in aqueous diethanolamine solution, *J. Chem. 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 methydiethanolamine, *Research Report RR-104*, Gas Processors Association.

Maddox, R.N., Elizondo, E.M. (1989) Equilibrium solubility of carbon dioxide in aqueous solutions of diethanolamines al low partial pressures, *Research Report RR-124*, Gas Processors Association.

McDonald C., Floudas C. (1995) Global optimisation for the phase and chemical equilibrium problem: application, to the NRTL equation, *Computers Chem. Engng*, **19**, 11, 1111-1139.

Millero, F.J. (1986) The thermodynamics and kinetics of the hydrogen sulfide system in natural waters, *Marine Chemistry*, **18**, 121-147.

Mock, B.L., Evans, L.B., Chen, C.C. (1986) Thermodynamic representation of phase equilibria of mixed-solvent electrolyte system, *AIChE J.*, **32**, 1655.

Olofsson, G., Hepler, L.G. (1975) Thermodynamic of ionization of water over wide ranges of temperature and pressure, *J. Sol. Chem.*, **4**, 2, 127-143.

Oscarson, J.L., Wu, G., Faux, P.W., Izatt, R.M., Christensen, J.J. (1989) Thermodynamics of protonation of alkanolamines in aqueous solutions to 325°C, *Thermochimica Acta*, **154**, 119-127.

Peiper, J.C., Pitzer, K.S. (1982) Thermodynamics of aqueous carbonate solutions including mixtures of sodium carbonate, bicarbonate and chloride, *J. Chem. Therm.*, **14,** 613-638.

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**, 1, 135-144.

Rogers, W.J., Bullin, J.A., Davison, R.R., Frazier, R.E., Marsh, K.N. (1997) FTIR method ofr VLE measurements of acid gas-alkanolamine systems, *AIChE J.*, **43**, 12, 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.

Rumpf, B., Maurer, G. (1992) Solubilities of hydrogen cyanide and sulfur dioxide in water at temperatures from 293.15 to 413.15 K and pressures up to 2.5 Mpa, *Fluid Phase Equilibria*, **81**, 241-260.

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

Tabai, S., Cadours, R., Mougin, P. (1999) Désacidification du gaz naturel par solvant mixte – aspect enthalpique et équilibre entre phases, *Rapport IFP 45 738*.

Ung, S., Doherty, M. (1995) Vapor-Liquid phase equilibrium in systems with multiple chemical reactions, *Chem. Eng. Sci.*, **50**, 1, 23.

Vallée, G., Mougin, P., Jullian, S., Fürst, W. (1999) Representation of CO₂ and H₂S absorption by aqueous solutions of diethanolamine using an electrolyte equation of state, *Ing. Eng. Chem. Res.*, **38**, 3473-3840.

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

White, W.,B., Johnson, S., M. and Dantzig, G., B. (1958) Chemical equilibrium in complex mixtures, *The Journal of Chemical Physics*, **28**, 5 , 751-755.